THE UNIVERSITY OF MICHIGAN
COLLEGE OF ENGINEERING
Department of Chemical and Metallurgical Engineering

Technical Report

THE EFFECT OF SURFACE TENSION OF A LIQUID METAL ENVIRONMENT ON THE FRACTURE STRENGTH OF SOLID METALS

D. A. Kraai
S. Floreen
C. A. Stickles
D. V. Ragone

E. E. Hucke
Principal Investigator

UMRI Project 2782

under contract with:

DIRECTORATE OF SOLID STATE SCIENCES
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
AIR RESEARCH AND DEVELOPMENT COMMAND
CONTRACT NO. AF 49(638)-422
WASHINGTON, D.C.

administered by:

THE UNIVERSITY OF MICHIGAN RESEARCH INSTITUTE ANN ARBOR

July 1960

Parts I and II of this report have also been submitted as dissertations in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The University of Michigan, 1960.

PREFACE

This report is divided into three sections. Each section covers a specific aspect of the relationship of surface and environments and their effects on the mechanical properties of solids. This separation of topics necessarily involves some repetition such as in the literature reviews. However, in the interest of clarity and emphasis the different aspects were presented separately. Each section exists as a complete report in itself and contains its own introduction, body, conclusions, references, and pagination.

The conclusions of this technical report are the summation of the conclusions of each section.

Following are the titles of each section:

1) Effects of Some Liquid Metal Environments on the Fracture of Copper.

2) The Effect of Strain on the Surface Energy of Solids.

3) The Effect of Tensile Stress on Dihedral Angles in Leaded Copper.

Part I - EFFECTS OF SOME LIQUID METAL ENVIRONMENTS ON THE FRACTURE OF COPPER

PREFACE

The author wishes to express appreciation to Professor Edward E. Hucke for his interest, guidance, and generous contribution of his time and suggestions throughout the period of this investigation.

The advice and contributions of the other members of the doctoral committee are also gratefully acknowledged.

The author also wishes to acknowledge Mr. John Verhoeven and Mr. Frank Drogosz for their aid and advice on the design and construction of the equipment.

A fellowship grant from the Universal Cyclopes Steel Corporation over a period of two years was sincerely appreciated.

The author wishes tc acknowledge the financial support of the Air Force through their Contract No. AF 49(638)-422.

TABLE OF CONTENTS

	Page
PREFACE	ii
LIST OF TABLES	iv
LIST OF FIGURES	v
ABSTRACT	ix
INTRODUCTION	1
LITERATURE REVIEW	3
The General Features of Liquid Metal Embrittlement	4
Theories of Liquid Metal Embrittlement	15
EXPERIMENTAL PROGRAM	30
EQUIPMENT AND EXPERIMENTAL PROCEDURE	32
EXPERIMENTAL RESULTS AND DISCUSSION	38
CONCLUSIONS	55
REFERENCES	57

LIST OF TABLES

1. Summary of Fracture Strength Data. 62

2. Strengths of Copper in Liquid Lead-Bismuth Alloy Environments. 63

3. Strengths of Copper in Liquid Thallium-Bismuth Alloy Environments. 65

4. Strengths of Copper in Liquid Cadmium-Bismuth Alloy Environments. 66

5. Strengths of Copper in Liquid Zinc-Bismuth Alloy Environments. 67

6. Strengths of Copper in Liquid Antimony-Bismuth Alloy Environments. 68

7. Published Strengths of Copper in Liquid Lead-Bismuth Environments; Grain Size = 0.025 mm. 69

8. Published Strengths of Copper in Liquid Lead-Bismuth Environments; Grain Size = 0.050 mm. 70

9. Equilibrium Grain Boundary Dihedral Angles in Cu-Pb-Bi Alloys. 71

10. Data Used for Figure 13. 72

11. Published Interfacial Free Energies of the Solid Copper Liquid Lead-Bismuth System. 73

12. Data Used for Figure 15. 74

LIST OF FIGURES

		Page
1.	Internal Liquid Phase Dihedral Angle.	75
2.	Liquid Drop on a Metal Grain Boundary.	75
3.	Equilibrium State of Surface Forces.	75
4.	Vacuum Furnace.	76
5.	Vacuum Furnace, Section A-A.	77
6.	Wire Specimen and Liquid Metal Reservoir.	78
7.	Copper Strength vs. Time of Immersion in Bismuth.	79
8.	Average Strengths of Copper vs. Ratio Pb/Pb + Bi.	80
9.	Strength of Copper vs. Ratio Pb/Pb + Bi. Grain Size = 0.025 mm. Morgan's Table XXI. (1)	81
10.	Strength of Copper vs. Ratio Pb/Pb + Bi. Grain Size = 0.050 mm. Morgan's Table XXII. (1)	82
11.	Comparison of Ultimate Strengths of Copper Obtained by Morgan and Present Investigation.	83
12.	Equilibrium Grain Boundary Dihedral Angles vs Ratio Pb/Pb + Bi.	84
13.	Fracture Strength of Copper vs Interfacial Free Energies.	85
14.	Solid Copper, Liquid Lead-Bismuth Interfacial Free Energies.	86
15.	Fracture Strength of Copper vs Morgan's Interfacial Energy Value.	87
16.	Fracture Strength of Copper vs Time of Immersion in 10%Cd-90%Bi Environments.	88
17.	Ultimate Strength of Copper Fractured in Liquid Alloys of Bismuth and Small Amounts of Other Elements.	89
18.	Average Ultimate Strength of Copper Fractured in Liquid-Bismuth-Antimony Alloy Environments (wt%).	90

Page

19. Average Ultimate Strength of Copper Fractured in Liquid Bismuth-Zinc Alloy Environments (wt%). 91

20. Average Ultimate Strength of Copper Fractured in Liquid Bismuth-Cadmium Alloy Environments (wt%). 92

21. Average Ultimate Strength of Copper Fractured in Liquid Bismuth-Thallium Alloy Environments (wt%). 93

22. Ultimate Strength of Copper Fractured in Liquid Alloys of Bismuth and Small Amounts of the Other Elements (atom%). 94

23. Average Ultimate Strength of Copper Fractured in Liquid Bismuth-Antimony Alloy Environments (atom%). 95

24. Average Ultimate Strength of Copper Fractured in Liquid Bismuth-Zinc Alloy Environments (atom%). 96

25. Average Ultimate Strength of Copper Fractured in Liquid Bismuth-Cadmium Alloy Environments (atom%). 97

26. Average Ultimate Strength of Copper Fractured in Liquid Bismuth-Thallium Alloy Environments (atom%). 98

27. Copper Specimen Fractured at 650°F With No Environment Present;100X. 99

28. Microstructure of Copper Prior to Fracture; 100X. 99

29. Sketch Showing Possible Behavior of Fracture Strength as a Function of the Solid - Liquid Interfacial Energy. 100

30. Schematic Frequency Distribution of Observed Internal Angles of Liquid Phase in Microsection. 100

31. Schematic Frequency Distribution of Observed External Angles of Liquid Phase in Microsection. 100

32. Copper Specimen Fractured at 650°F in 100% Lead Environment;100X. 101

33. Copper Specimen Fractured at 650°F in 100% Bismuth Environment;50X. 101

34. Copper Specimen Fractured at 650°F in 100% Bismuth Environment;500X. 102

35. Copper Specimen Fractured at 650°F in 100% Bismuth Environment;13X. 102

Page

36. Copper Specimen Fractured at 650°F in 100% Bismuth Environment;20X. 103

37. Copper Specimen Fractured at 650°F in 80%Bi-20%Pb Environment;20X. 103

38. Copper Specimen Fractured at 650°F in 60%Bi-40%Pb Environment;20X. 104

39. Copper Specimen Fractured at 650°F in 60%Bi-40%Pb Environment;20X. 104

40. Copper Specimen Fractured at 650°F in 40%Bi-60%Pb Environment;13X. 105

41. Copper Specimen Fractured at 650°F in 20%Bi-80%Pb Environment;13X. 105

42. Copper Specimen Fractured at 650°F with No Environment Present;20X. 105

43. Copper Specimen Fractured at 650°F in 60%Bi-40%Pb Environment;13X. 106

44. Copper Specimen Fractured at 650°F in 60%Bi-40%Pb Environment;20X. 106

ABSTRACT

The variation of fracture strength of solid copper wire was investigated as a function of the interfacial free energy between the specimen and its liquid metal environment.

Numerous reports in the literature indicate that non-corrosive environments can have a significant effect on the tensile fracture strength of materials. The general effect of liquid metals is to reduce both strength and ductility. The more deleterious environments sharply reduce the level of normal fracture stress. The literature further indicates that changes in fracture strength due to changing environmental conditions might be explained on the basis of interfacial free energies. That interfacial energies are associated with fracture seems logical not only because free surfaces are formed, but also because the environments are non-corrosive, they do not form compounds with the solid metals, and their mutual solubilities are essentially zero in many cases. Such an effect must then act at the surface. A measure of such surface effects would be the interfacial energy, a physical property, between the solid metal and its environment.

From considerations of the energy required to propagate a crack in a brittle material previous investigators have shown that the fracture stress

can be approximately represented by the following equation:

$$\sigma_f = K\left(\frac{E\gamma}{d}\right)^{\frac{1}{2}} .$$

Where σ_f is the fracture stress, E is Youngs modulus, d is the grain size, γ is the total surface free energy expended in exposing unit area of the crack faces and K is a dimensionless coefficient of the order of 5.

The experimental part of this work dealt with establishing; 1) the existence of an effect of environment on fracture strength; 2) the relative magnitude of the effect; 3) the approximate validity of the expression given above.

These aims were realized by fracturing copper wires partially wet by external liquid lead-bismuth environments systematically varied in composition. Changing the composition of the environment varied the interfacial free energy. It was found that the tensile fracture stress of a copper wire was reduced by the successive addition of bismuth to a lead-bismuth environment. At 650°F for instance, an environment of liquid lead gave little reduction in strength while an environment of liquid bismuth reduced the fracture strength to 7,200 psi from 45,000 psi for liquid lead. Copper failed in an intergranular brittle manner when fractured in bismuth with no significant reduction in area. Copper failed in lead after considerable elongation and showed approximately 60% reduction in area. The change in fracture stress with changing interfacial energy corresponded to that predicted by the above expression for the higher bismuth region of lead-bismuth environments. The value of K obtained in the investigation is about 15 or 3 times the value theoretically indicated.

It was found that reliable and reproducible values for the fracture strength of a solid metal in a liquid metal environment depend on the following: 1) obtaining intimate contact between the solid and liquid metals; 2) having a supply of liquid metal present for the continued propagation of a failure crack.

The strength of copper in lead-bismuth environments is not affected by the length of time of immersion of the copper in a stress free condition prior to fracture at the temperature and times of immersion used in this investigation.

Small additions of zinc, cadmium, thallium, and antimony were added to bismuth in place of lead to determine the effect that they have on the fracture strength of copper. The effect was beneficial relative to 100% bismuth in all cases with antimony being the most effective.

INTRODUCTION

There are numerous reports in the literature indicating that non-corrosive environments play a considerable role in the fracture of materials. References show that the environments having this effect may be thin solid films, organic liquids, aqueous liquids, liquid metals, and gases including air. An environmental effect is evident not only in ordinary tensile tests, but in creep and fatigue tests as well. A non-corrosive environment is considered to be one which has no electrochemical reaction with the solid material that is insoluble in the solid and shows negligible solubility for the solid.

The effects of environment on fracture takes on an added importance since the effect is usually detrimental, causing materials to fail in a brittle manner at very low applied stresses. The problem is not that such materials fail in a brittle manner, but that failure occurs under applied stresses where the material would normally behave in a ductile manner. It thus appears evident that the strength of a material can not be specified or understood simply in terms of such metallurgical variables as stress, strain, yield points and elastic constants, but that the properties of the surrounding medium are also involved even though the environment may be of a so called "non-corrosive-nature".

Other variables such as size, time, and stress conditions are also intimately involved with fracture. Different strength values are also obtained depending on the method of testing such as tensile creep, and fatigue tests. These other factors may also have some relationship with environment.

The purpose of this work was an attempt at clarifying the effect of liquid metal environments on fracture. This was experimentally performed by fracturing copper wires partially wet by external liquid metal environments systematically varied in composition.

The isolation of the fundamental characteristics of the effect of liquid metal environments on fracture behavior will be of practical value to the metallurgist in the selection of a metal, alloy or other material for many applications. One obvious advantage of such information would be in the design and construction of equipment for use in atomic power plants where liquid metals are used as heat transfer media. Other areas where a knowledge of this effect might be applied are in the brazing and welding of metals, in the study of hot shortness, and the study of hot tearing of castings. The effect of environments on fracture will also be of theoretical importance in clarifying, understanding, and adding to the theory of fracture.

The following section will be devoted to an analysis and summary of the salient features of liquid metal embrittlement as previously published in the technical literature. The theories of liquid metal embrittlement are also reviewed.

LITERATURE REVIEW

A large number of reports exist in the literature which indicate that liquid metal environments play a considerable role in the mechanical behavior of materials. A review of the literature presents a somewhat perplexing problem as most of these studies while concerned with the effect of environments on the mechanical properties, particularly fracture, have been made quite independent of each other and have not followed a consistent pattern of development. The Russian literature has reported the effects of environment since about 1930. Although some of their earlier work was concerned with individual systems their studies are now primarily directed to an evaluation of the cause of the effect in a rather consistent fashion. Probably the reason for this is that from 1930 until the present their studies have been primarily under the direction of a single person, Rebinder. The Russian work has, however, until quite recently remained quite divorced from the rest of the world. Work other than the Russian on the effect of environments has been devoted to specific systems and has been primarily concerned with the general aspects of embrittlement. It has remained quite independent of the Russian work in this area. There exists then, two general schools of thought on the effect of environment on failure, the Russian school and the so-called English school.

In 1954 Morgan (1) studied liquid metal embrittlement as well as reviewed the general aspects of liquid metal embrittlement as previously reported with the exception of the Russian School. Morgan (2) extended his review in another publication in 1959. However, he made little mention of

the Russian work on embrittlement. To aid in the discussion of the literature it is useful to consider separately the general features of liquid metal embrittlement. This will be done similar to a scheme used by Morgan (2) and will consider the following factors and their relationship to liquid metal embrittlement as published in the literature: 1) the surface conditions, 2) the grain size and microstructure of the solid metal; 3) the stress level and pattern, 4) the strain rate, 5) temperature, 6) time of immersion in the liquid metal, 7) size effect or surface to volume ratio, 8) composition of the solid; and 9) composition of the molten metal. Following the review of the above factors, the theories of liquid metal embrittlement will be reviewed.

The General Features of Liquid Metal Embrittlement

The general effect of liquid metals is to reduce fracture strength and ductility. The more deleterious environments sharply reduce the level of normal fracture stresses under conditions of a constant rate of deformation. A considerable reduction of ductility (value of deformation before rupture) is associated with this reduction in strength. A detrimental environment causes failure at some earlier point on the characteristic stress-strain curve of a solid. No significant changes have been reported in the remaining stress-strain characteristics of the solid metal as it is deformed. However, under conditions of creep, when a constant stress acting on the metal is lower than the stress of brittle fracture, a plasticizing effect is reported in the presence of liquid metals as well as other liquid media.

The evidence supporting this is somewhat contradictory and will be discussed in some detail later in this report.

1. Surface Condition.

One of the prime requisites for embrittlement noted in all publications is that the liquid metal should come into intimate contact or "wet" the solid metal surface (2). Any method of surface preparation that presents a clean solid metal surface to a liquid metal environment should initiate failure in a suitable system (2). In 1935 van Ewijk (3) reported that he used a zinc chloride flux to obtain wetting of steels by molten solder, lead, tin, zinc, cadmium or Lipowitz alloy. Embrittlement was not observed with specimens on which the flux had not been used or with specimens on which zinc chloride alone was used. Van Ewijk also tried other fluxes such as ammonium chloride which he described as, "giving slower wetting and thus slower fracture". He found that rosin, glycerine, palm oil, borax, sulfur and stearine did not give adequate wetting. Patterman (4) in a discussion to van Ewijk's paper said that in studies similar to those of van Ewijk he also used zinc chloride and described the effect of zinc chloride as "only a mediating one, making the surface fit for wetting by liquid metals". Goodrich (5) used "Coraline" as a flux and also found that it had no significant effect by itself. In 1951 Jepson (6) in a study of the effect of surface conditions on embrittlement found that steel plated with nickel did not fail in molten solder. He also found that an oxide film had some beneficial effect and a copper-plated specimen had very little. Grassi, Bainbridge and Elliot (7) in a study of the stress rupture properties of low alloy and stainless steels in lead-bismuth

alloys found that pre-coating of the steel was necessary. In a later study of the molybdenum and niobium at 1600 and 1800°F in lead and bismuth no pre-coating procedures were used since it was found that intimate contact developed of its own accord at these temperatures (8). Oxide films which are not soluble in the liquid metal and which will not be reduced by the liquid metal might be protective, however, at very high deformations the oxide film may crack and thus expose clean unoxidized surfaces to the molten metal (2). Morgan (1) considered that since the free energies of lead and bismuth oxides were more stable than copper oxide, copper oxide would be reduced and contact between the solid and liquid metals would be obtained without the use of a wetting agent or flux.

2. Grain Size and Microstructure.

There is almost unanimous agreement in the literature that the larger the grain size the more deleterious is the effect of liquid metals on causing embrittlement. Genders (9) reported in 1935 that coarse grained materials are more susceptible than fine grained. Goodrich has also reported that the resistance to embrittlement varied inversely as the grain size (5). He found that quenched and tempered structures gave better results than normalized or annealed structures. Goodrich found no correlation between temper brittleness and liquid metal embrittlement. He also reported that the effect of grain size was more pronounced at lower temperatures than at higher temperatures. Van Ewijk, in a discussion to Goodrich's paper also reported that embrittlement was increased with a coarsening of the grain size (10). Desch (11,12) considered that grain shape as well as grain size is important. Austin (13,14)

found that for a number of engineering materials in molten solder an increase in hardness and secondary grain size was deleterious. He also found that the temper embrittled state did not increase embrittlement. Edmunds (15) reported that "as-rolled" mercury coated brass tensile specimens possessed better resistance to penetration than recrystallized test-pieces. He attributed the decreased strength of recrystallized materials to increased grain size and showed a general decrease of strength in grain-size did not seem to have a marked deleterious effect on the room temperature properties of copper after immersion in bismuth although the strength had decreased with a very large grained specimen. Morgan did, however, report a decrease in strength of copper tested in liquid bismuth at 350°C with an increase in grain size. Genders (16) showed that the degree to which a metal had been cold-worked and the shape of the grain boundaries influenced intercrystalline embrittlement by liquid metals.

Likhtman (17) noted that in general the effect of a medium is more pronounced if the sample has greater strength and hardness. He did not mention any grain size influence as such. This general decrease of strength with increasing grain size has been qualitatively explained by stating that "crack propagation is easier if the direction of the boundary does not change with short distances" (2) and in another instance that "the larger grain size and consequently shorter path of fracture along the grain boundary should result in greater susceptibility" (15). It is difficult to generalize on the effect of cold work and hardness. Such a generalization needs to consider grain size, grain shape, and the type and magnitude of residual stresses present. Another question which remains unanswered is whether or not the effect of grain size is more or less pronounced with varying section size.

Another aspect of the relationship of microstructure to embrittlement is the presence of different phases. Dickenson (18) reported that α brasses are more resistant to penetration by molten solders than $\alpha\beta$ brasses which are more resistant than β brasses. Edmunds (15) also showed this to be the case with mercury embrittlement of brass. Goodrich (5) showed that the presence of free ferrite in steels decreased their liability for embrittlement in the presence of solders. Steels in which the ferrite formed a complete network had the best resistance to embrittlement.

The effect of environment or single crystals and bi-crystals has also been investigated. Single and bi-crystals may be considered as a special case of the effect of grain size variations on liquid metal embrittlement. Edmunds (15) showed that a single crystal of brass failed in a completely ductile manner and showed no deleterious effects when tested with mercury. Morgan (1) found that a bi-crystal possessing a boundary of high orientation difference failed in a brittle manner. A low orientation difference bi-crystal was ductile. A number of works are reported in the Russian literature on the effects of liquid metals on single crystals. They are generally agreed that with the proper system the strength and plasticity of single crystals can be considerably reduced (17). They are quite emphatic, however, in reporting that their results "indicate directly the important fact that the action of surface-active liquid metal is not associated with the presence of boundaries between the grains of a high melting metal". They showed that the action of low melting metals on single crystals may attain considerable magnitude under favorable temperature conditions. They do not, however, postulate that the

grain boundaries in a polycrystalline metal play no role at all in the action of liquid metals. They assert that grain boundaries may play a significant role, and in some cases a decisive role (17).

3. The Stress Level and Pattern.

The general consensus of reported studies is that an embrittling agent does not produce any effect under the action of compressive stresses and produces a large effect under the action of tensile stresses. If a compressive stress is applied the strength of material in liquid metals is comparable to that in air (13,18). Several reports indicated that the rate of embrittlement is slow below a critical stress, that there is usually a certain minimum tensile stress necessary to produce any effect, and that no embrittlement occurs in the absence of stress (19,20,21,22). Some reports indicated that embrittlement does not occur unless the elastic limit is exceeded (23) while others indicated that embrittlement can occur in both the elastic and the plastic region (3,24). The level of stress at which brass coated with mercury forms intercrystalline cracks has been shown to depend on the amount of free mercury and the time available for penetration(22). Hartley found that the stress required to fracture a test piece was time dependent and the stress-rupture curves were of parabolic form (19). Radeker (25) made stress-rupture tests on steel specimens immersed in molten zinc. He found that the relationship between stress and time to failure yielded a straight line on a double log plot. Internal or residual stresses also produce intergranular cracking and failure of high melting point metals

in the presence of liquid metals. This effect is often associated with season-cracking (2). The effect has often been used to detect the presence of internal stresses in materials (22,26,27,28,29,30).

4. Strain Rate.

Likhtman reported that the effectiveness of a liquid metal environment in reducing the strength of a solid metal increased as the rate of loading or the rate of deformation of the sample is decreased (17). This is also reported by Moore, Beckinsole and Mallinson (22). Goodrich reported that a number of steels coated with lead and lead-tin solders show a gradual decrease in the yield and maximum loads with slower rates of loading (5). This view is supported by Wang who showed that an increased rate of application of load decreased the tendency of molten brazing alloys to penetrate steel (23). Greenwood found that an increase of strain rate decreased the degree of embrittlement of copper in mercury and that the greatest decrease was shown in the elongation values (31). The stress-rupture tests of Hartley and Radeker support the view that lower strain rates give decreased fracture strengths (19,25).

5. Temperature.

Likhtman indicated that the effectiveness of an embrittling agent increases appreciably as the temperature of the experiment is increased (17). Goodrich reported that for steels coated with lead-tin solders and a bearing metal an increase of temperature brought about a more rapid decrease of the maximum load (5). Wang indicated that intercrystalline attack of steels by low melting point metals did not occur above about 400°C, and that the

penetration of steels by brazing alloys was diminished above 950°C (23). Dickenson (18) showed that the maximum strength and deflection of a solid metal tested in bending when coated with a molten metal was decreased by an increase in temperature. He did not note if the degree of embrittlement increased with temperature faster for the coated or the uncoated specimens. Goodrich (5) and Genders (16) indicated that the effect of grain size, in lowering the properties of a solid metal in a liquid metal, was greater at low temperatures than at high temperatures. This is contrary to findings as reported above. Rozhanskii et.al. reported that with an increase in temperature from 120°F to 160°F brittleness of zinc single crystals coated with mercury is eliminated and that plasticity and strength are restored (32). As these pronounced temperature effects were fully reversible they did not associate the effect with removal of the mercury by evaporation. Their report clearly shows an increase in ductility with temperature, however, the mentioned increase in strength is not clearly indicated. It appears that the effect of temperature depends on the materials involved and is a function of the rate of change of surface energies, the migration of the liquid metal, and the change in yield point, if any, of the solid metal. In any analysis it is important to separate the true effect of a temperature increase on embrittlement of a solid by a liquid metal apart from better contact between the liquid metal and the solid resulting from dissolution or breakdown of any surface film.

6. Time of Immersion in Liquid Metal.

The length of time that a specimen is immersed in a liquid metal in a stress free condition prior to testing could have an effect on the degree of

embrittlement. Such an effect could result from two distinct causes, the breakdown of any surface barrier such as an oxide film, or from any other effect of the liquid metal in direct contact with the solid.

Likhtman (17) indicated that the effectiveness of a liquid metal environment increased as the time of contact between the sample and the liquid metal increased before the experiment. Likhtman also reported that if a single crystal of zinc covered by a film of liquid tin is maintained for a sufficiently long time without stress at 400°C and is then placed into liquid lead for a sufficiently long time, embrittlement disappears completely and the normal strength of single crystals of zinc is re-established. He further postulated that this experiment indicates that no appreciable role is played by the normal diffusion of tin into zinc. Likhtman did not clearly indicate the times involved. Moore, Bechinsale and Mallinson found that a very brittle deleterious effect was brought about by immersion of brass in mercury followed by testing after removal of the liquid (22). In one experiment Morgan immersed copper specimens in lead-bismuth alloys at constant temperature for increasing lengths of time and then evaluated their room temperature properties (1). The results showed that the effect of the time of immersion in lead was negligible and no embrittlement was observed. Test pieces immersed in bismuth showed a progressive decrease in the room temperature mechanical properties with an increase in the time of immersion. Morgan also found that an increase in the time of immersion at the testing temperature prior to the test reduced the fracture stress of copper in bismuth but that the effect was not very marked (1). The elongation was not appreciably altered. Van Ewijk (3)

found that the effect of liquid solders on steels was practically instantaneous with rupture occuring after a time of contact of only a few seconds. The few seconds before rupture might be attributed to the time required for the liquid to wet the solid.

7. Size Effect.

Edmunds reported that large section test specimens possessed better resistance to penetration than small-section test pieces (15). Morgan showed that the relative effect of an embrittling environment was greater on small diameter specimens than on large diameter (1). As mentioned earlier in a discussion of the effect of grain size, any appraisal of embrittlement relative to specimen size will also need to involve the ratio of grain size to specimen size.

Small diameter single crystals, for example whiskers, have been shown to have increased strength as the diameter decreases. Whether or not this relationship holds, and to what extent if it does, when liquid metal environments are present has not yet been studied, although Brenner (33) indicated that the strength of vacuum heated whiskers appeared to be somewhat higher and that impurities and surface films contribute to the fracture strength of whiskers.

8. Composition of the Solid.

Treated under this title will be small systematic variations of the solid composition as apart from entirely different solids or materials. Moore, Beckinsale and Mallinson reported results which showed that while copper was not embrittled by mercury the susceptibility to failure increased

with the zinc content (22). Edmunds confirmed this finding in the range of 10-40% zinc (15). Schottky, Schiehtel and Stolle showed that for steels with the carbon content in the range of 0.1-0.5% there was no effect on the resistance to penetration (34). A number of authors have examined the effect of small amounts of alloying elements to brasses on embrittlement in mercury. In all the cases the authors concluded that none of the elements added, accelerated failure and that the beneficial effect, if any, was small (36,37, 38). Morgan reported that there is no appreciable difference in the mechanical properties of copper of different degrees of purity when tested at room temperature after immersion in molten bismuth (1).

9. The Effect of Composition of the Molten Metal.

Likhtman (17) reported that it is the opinion of many authors that liquid metals which form solid solutions or intermetallic compounds with the basic solid metal are more effective in decreasing the properties of the solid metal than of liquid metals which have no interaction with the solid. He gave no evidence to support this view. Likhtman also reported that the strength of zinc single crystals tested in lead-tin alloys is progressively lowered as the amount of tin is increased, however, zinc is considerably more soluble in tin than in lead and this factor is not considered apart from the true degree of embrittlement resulting from changes in the liquid alloy composition (17). Hartly showed that the tin content of solders had an effect on the embrittlement of brasses. Increasing the tin content gave more rapid failure (19). Morgan showed that successively increasing the amounts of bismuth to lead progressively lowered the properties of solid copper (1). Morgan's work will be discussed in more detail later in this work.

Theories of Liquid Metal Embrittlement.

The general features of liquid metal embrittlement have been reviewed. It is now of interest to review several of the theories of liquid metal embrittlement. Results obtained by investigators on materials other than metals will also be mentioned when pertinent.

In 1928 Joffe reported that the tensile strength of rock salt could be increased from 750 to 230,000 psi by pulling under water or immediately after removing it from the water (39). He attributed the increase in strength to the removal of cracks by surface dissolution. Joffe reached his conclusions on the basis of earlier work of Griffith. Griffith assumed that the discrepancy between the theoretically estimated and the observed values of the tensile strength was due to the presence of very small cracks or other flaws around which a strong stress concentration arose when the solid was stressed(40). According to Griffith such a crack of flaw will propagate if the free energy of the system is reduced. He considered two types of energy, the surface energy of the crack, and the stored elastic energy. He calculated that the fracture stress should be given by the following expression:

$$(1) \qquad \sigma_f = \left[\frac{2E\gamma}{(1-\nu^2)\pi c}\right]^{\frac{1}{2}} \cong \left[\frac{2E\gamma}{\pi c}\right]^{\frac{1}{2}}$$

σ_f = Fracture stress

E = Youngs Modulus

γ = Total surface free energy expended in exposing unit area of the crack faces

ν = Poissons Ratio

2c = Internal microcrack length

This idea has been extended to different geometries and different shaped cracks but the results differ only by small numerical factors. For instance, Sack has obtained the following expression for a 3-dimensional analysis (41):

$$(2) \qquad \sigma_f = \left[\frac{\pi E \gamma}{2(1-\nu^2)c}\right]^{\frac{1}{2}}$$

Note that it is only a factor $\pi/2$ greater than that obtained by Griffith.

Classen-Nekludova also indicated that premature failure of rock salt crystals was due to surface defects (42). He considered the existence of two types of surface defects; primary defects or distortions such as cracks on the surface of the specimen, and secondary defects on distortions which arise on the surface of the specimen during the process of plastic deformation. He claimed that the removal or dissolution of these two sorts of surface defects of the specimen or rock salt which is insured by carrying out the process of deformation under water resulted in an increase in strength and in the degree of elongation of these crystals (43). He also claimed that if only the primary defects are removed by preliminary dissolution of the surface and subsequent extension of the crystal in air, an increase in the strength and elongation are observed but not to the extent as in the case when the entire process of deformation takes place in a solvent.

To determine if this view of fracture also is true in the case of metallic crystals, as well as rock salt Classen-Nekludova studied the deformation of single crystals of bismuth and zinc in nitric and sulphuric acids with the supposition that the acids would remove the surface defects by dissolution. He found that dissolution of the specimen surfaces with acids

during the process of deformation caused an increase in the strength of single crystals of bismuth (up to 270%) and in the degree of plastic deformation. Preliminary dissolution with subsequent extension in air did not cause any appreciable change in the mechanical properties of single crystals of bismuth. This indicated to him that primary defects (cracks on the surface) do not, of themselves, have a considerable influence on the behavior of single crystals of bismuth. No significant increase in the mechanical behavior of single crystals of zinc tested in acids was noted.

Classen-Nekludova also reported on the following unpublished works (43). In 1926-1927 B. J. Pines made a study of the influence of dissolution on the strength of zinc crystals with negative results. In 1930-31 S. N. Shurkov attempted to cause an increase in the strength of thin aluminum wires by dissolving them with acids during the process of elongation. However, the strength of aluminum was reduced under these conditions and disintegration of the inter-crystalline layers was observed.

In 1956 Aerts and Dekeyser studied the effect of gases in Rocksalt and the Joffe effect (44). They found that gases can affect in a considerably way the mechanical properties of crystals. They showed that the dissolving or healing of cracks as put forth by Joffe was not that which causes rocksalt to be ductile, but they indicated that crystals such as rocksalt are inherently ductile and that brittleness results when adsorbed gases pin down the dislocations and prevent their movement. The resulting pile up of dislocation produces surface cracks. Gorem et. al. also investigated the effect of surface conditions on ionic crystals (45). It was found that face-centered cubic and body-centered cubic ionic materials can exhibit a considerable amount of

ductility under controlled surface conditions. Gorem suggested that dislocation-pile-up at the surface results when certain gases, especially O_2 and N_2 are adsorbed. Contrary to this view, Machlin and Murray found that molecular O_2 and N_2 have no effect on the ductility of rock salt single crystals (46). They concluded that oxygen will embrittle rock salt if it is provided as atomic oxygen, O, O_3 or NO. They considered it likely that atomic oxygen combines with the NaCl to form $NaClO_3$ which acts as a barrier to the outward motion of dislocations.

The mechanical properties of glasses also depend to a considerable extent on the environment in which the tests are performed. Orowan has suggested, particularly in the cases of glass, silica, and mica, that adsorption from the atmosphere, possibly moisture, diminishes the surface energy and thus, according to the Griffith equation, equation 1 reduces the strength (47,48). Gurney has proposed a mechanism which involves corrosion at particular locations such as the root of a microcrack on the surface of the specimens (49). Both mechanisms may operate together and whether one plays a major role or not probably depends on the systems involved. Floreen (5 has recently reviewed the effects of environment on the failure of glass.

Benedick and Ruben reported in 1945 on experiments carried out on the change in the breaking strength of solids due to wetting (51). Since then the effect has experimentally been studied by Benedick and his co-workers on several materials. They concluded that the breaking strength of solids should be affected by the surrounding medium (52-55).

As for the origin of the weakening effect, Benedick proposed a theory of lines of force (51,55). According to him, some lines of force emanating

from atoms on the solid surfaces are bound between the atoms along the solid surface and will decrease if the solid is wetted by the liquid.

Benedick found a definite change in the strength of glass and quenched steel, and a particularly strong effect of zinc wetted by zinc saturated mercury (51). For a quenched carbon steel Benedick found that the bending tensile strength changed when fractured in a surrounding medium of water and kerosene by -21 and +28 percent respectively (52).

Sato has also discussed the weakening caused by liquids on solid bodies (56,57). He assumes that the work done by the breaking all goes into new surfaces as an interfacial tension between the solid and the wetting liquid and shows that the breaking stress of a given solid can be expressed as a function of the surface tension of the wetting liquid and the angle of contact. He shows that his relationship holds with data obtained by measuring the fracture strength of Almond Oilstone in various organic and aqueous solutions processing different surface tensions.

In 1948 Smith (68) published an account of the effect of interfacial energies on the equilibrium form of a microstructure. Smith suggested that the shape and distribution of micro-constituents were determined by the free energies of grain boundaries and interphase boundaries in metals. Smith postulated that if the included angle (dihedral angle), θ, of a liquid phase at a grain boundary is less than 60° but more than 0°, the liquid phase will spread as prisms along the grain edges. Figure 1 illustrates a dihedral angle. If the angle is reduced to 0°, however, the liquid phase would spread across the faces of the grains. If the dihedral angle is greater than 60° the liquid would remain as discreet globules. Smith tried to explain the

embrittlement of copper-bismuth alloys by this concept. He suggested that since the dihedral angle of bismuth should penetrate between the crystals completely wetting the grain faces and disintegrating the solid. Lead would not have the same deleterious effect since the dihedral angle on copper was much greater than zero.

Morgan considered the application of Smith's ideas in the study of liquid metal embrittlement (1). Morgan found no evidence of penetration of copper by bismuth and yet the copper was brittle. He concluded therefore some other mechanism was responsible for embrittlement. He considered that diffusion cracking which preceded penetration.

Eborall and Gregory considered liquid metal embrittlement and showed that it would be expected that a liquid phase with an included angle of more than 60° can also cause serious embrittlement, differing merely in degree from that caused by liquid phases with lower included angles (59). They based this idea on the Griffith equation (ew. 1) which showed that the applied stress required to make a thin crack grow, in an elastic material, was proportional to the square root of the surface energy of the new surfaces formed. The dihedral angle is under some conditions merely a relative measure of the interfacial free energies which vary continuously with composition.

In 1928 Rebinder first initiated the idea that adsorption from the environment can have a strong effect on the strength of a solid (60).

In later papers the idea of adsorption was expanded not only with respect to fracture, but with respect to grinding, hardness, drilling, ductility, scratching, fatigue and creep (61-70). The Russian literature

generally considers that adsorption of various surface active organic materials affects the fracture strength, plasticizes metallic crystals and lowers their yield point, that that the effect has a maximum for definite temperatures and deformation rates. The very general aspects of adsorptive strength reduction with corresponding interfacial energy reduction has been studied in detail for metals which had adsorbed organic surface active substances under various conditions (64,69,71,72,73).

In 1937 Rebinder and Venstrom showed that the plastic flow of usual polycrystalline wires and plates of lead, tin or copper is rendered much easier, if, without changing the tensile stresses, very small quantities of surface active substances are added to a nonpolar hydrocarbon liquid in which the deformation of the metal is taking place (63). This effect, when studied with reference to the concentration of the surface active substances, was found to be an absorption phenomenon, with a distinct maximum at the point when the adsorption layer reached saturation. This effect consisted in increasing the rate of the plastic flow so that rupture started earlier. The specimens on which this was observed, were all of considerable cross-section, the wires, eg. measuring 0.5 to 1.0 mm across. It was supposed that behind the phenomenon might lie a deep penetration of the adsorption layers inside the specimen. In 1941 Rebinder hypothesized that should such penetration proceed along intercrystalline boundaries then in the case of single metallic crystals the effect was likely to be less distinct, if there would be any such effect at all (61). To determine the validity of this hypothesis he studied the effect of different surface active media on highly pure single crystals of tin and zinc. He found that deformation was facilitated to a very great extent when the surface active

substance was present. He then concluded that at the base of the adsorption effect lies the penetration of thin films of the active medium deep into the volume of the single crystal. According to Likhtman and Rebinder (74) these films push far inside through microcracks which develop in the process of deformation (which may be small) along glide planes having their outlets to the surface worked out by etching.

In 1958 Labzin and Likhtman studied creep of metal single crystals in strongly surface active media, low melting metals (75). The creep of zinc single crystals was investigated at a constant strain rate in lead and tin as well as alloys of these metals in different proportions. They found a considerable increase in the steady-state creep rate of zinc single crystals coated with a thin film of tin. A lead film reduced the steady-state creep rate.

Contrary to the above, Schulman and Nanis (93) have found no significant difference in the creep data between uncoated and coated copper wires. The wires they used were carefully prepared and coated with oleic acid in paraffin oil. They did not indicate if they would obtain the same results using liquid metals.

Since some low melting metals influence the mechanical properties of polycrystalline high melting metals, Rebinder, et.al., decided to study the effect on metal single crystals (65). They showed that single crystals of zinc coated with a very thin film of molten tin have reduced the strength as well as plasticity. They also showed that these effects are quite reversible and should not therefore, necessarily be connected with the action of the molten metal on the grain boundaries (65,76).

The above work of Rebinder was performed at high temperatures, that is above the melting point of the low-melting metal. Rozhanskii studied the effect of a surface active metallic coating on the strength of single crystals of zinc, tin, cadmium and lead at room temperature (62). The surface active substance was mercury which was deposited as a thin film. They assumed that the extremely small amount of mercury and the relatively low solubility of the metals in mercury prevented any appreciable corrosive effect by the mercury. It was found that the strength of zinc and tin when coated with mercury is several times less than that of unamalgamated specimens. This sharp reduction of the strength was associated with considerable lowering of the interfacial free energy at the metal-mercury boundary and by the reduced energy required to form a new surface crack leading to breaking. It was also suggested that the development of cracks in a slip plane is apparently aided by surface migration of mercury along developing lattice defects. Zinc crystals showed that cracks were formed both in the body and on the surface of the crystals. The formation of body cracks was associated with considerable diffusion of the mercury into the zinc at room temperature, followed by reduced interfacial energies on the internal surfaces of separation. This indicated to Rozhanskii that crack nucleation is not the critical step in the process of fracture, but that fracture is controlled by crack growth. On raising the temperature to 160°C(340°F) the brittleness of zinc single crystals was eliminated, thus completely restoring the strength and plasticity. In the transition range from brittle to ductile behavior (120-160°C) "partial embrittlement" was observed. These pronounced temperature effects were fully reversible and thus were not associated with the removal of mercury by evaporation. A

reduced deformation rate produced effects analogous to raising of the temperature. Similar experiments with amalgamated single crystals of cadmium and lead did not reveal such a great reduction of strength.

Since molten metals cause a considerable reduction in strength and plasticity of higher melting metals, so that the latter assume the brittle state, Likhtman, et. al considered that a comparative study of the relations governing the deformation and fracture of metals in strongly surface active melts with the analogous relations for the same metals in the brittle state but an inactive media would be informative (77). A study of mercury on zinc and N_2 (inactive brittling agent) on zinc was made. It was found that as a surface active substance mercury produces a brittle state in single crystals of zinc which is characterized by the same relationship of deformation and fracture as the brittleness produced by low temperature in the absence of a surface active substance. The pronounced drop in the normal fracture stress in the presence of mercury was considered due to a considerable drop in the interphase surface tension at the boundary between the saturated solution of zinc in mercury and zinc. Structural defects, microcracks were considered to be formed in the deformation process and rapidly filled with mercury by a mechanism of two-dimensional migration, which considerably facilitated their further growth up to brittle fracture under the action of even very small stresses. The high mobility of the mercury atoms, enabling them to penetrate fairly rapidly into the interior of the microcracks during their formation, was considered a pre-requisite for observing a reduction in strength and plasticity. At low temperatures, when the mercury atoms were deprived of their mobility, an increase was observed in the brittle strength of single

crystals of zinc coated with a mercury film. Likhtman considered this due either to the alloying of zinc with the mercury or the resistance to shear and fracture introduced by the film itself.

Several other papers by Russians have also appeared recently on the effects of surface active median on other mechanical properties. Fracture was mentioned in some of them but only in a minor fashion. These papers dealt with such things as surface hardening of metals (78), work hardening of metals (79), dislocation mechanism of crack formation in plastically deformed crystals (80), crack formation in zinc single crystals (81) and the effect of wetting the surfaces of ionic crystals on the development of one of the equivalent dodecahedral glide systems during linear deformation(82). Most of the results previously obtained on fracture in different media are now being explained by the relation between these conditions and the dislocations theory of plastic flow and brittle fractures. This idea has for its foundation the ideas as set forth by Zener, Mott, Stroh, Cottrell and Petch based on the dislocation clustering mechanism of crack formation. Rozhanskii was the first of the Russian school to consider the relationship between a dislocation mechanism of fracture and adsorptive strength reduction (62). This has subsequently been expanded by others of the Russian school (17,80,81,83).

The idea of dislocations and brittle fracture has received considerable attention lately. There exist several different treatments and while they differ in details the main points are the same. All the approaches arrive at the same general type of equation. All the equations resemble Griffith's

equation (eq. 1) except instead of the crack size, C, a term equivalent to the grain size is involved. The general form of such equations is the following:

$$(2) \quad \sigma_f = K \left(\frac{E\gamma}{d}\right)^{\frac{1}{2}}$$

where d = grain size.

Petch (84) has obtained the following:

$$(3) \quad \sigma_f = \sigma_o + 4 \left(\frac{3\ E\gamma}{2\pi(1-\nu^2)L}\right)^{\frac{1}{2}}$$

where ν = Poissons ratio and L = the length of a dislocation array. Petch showed that $L \alpha d$, the grain size, and suggests that $L = d/2$. Equation 3 then becomes:

$$(4) \quad \sigma_f = \sigma_o + 4 \left(\frac{3\ E\ \gamma}{\pi(1-\nu^2)d}\right)^{\frac{1}{2}} \approx \sigma_o + 4 \left(\frac{E\gamma}{d}\right)^{\frac{1}{2}}$$

Cottrell (85) has obtained the following:

$$(5) \quad \sigma_f = \left(\frac{2\beta\ E\gamma}{(1+\nu)L}\right)^{\frac{1}{2}} = \left(\frac{4\beta E\gamma}{d}\right)^{\frac{1}{2}} \approx 2 \left(\frac{\gamma E}{d}\right)^{\frac{1}{2}}$$

where β = constant of the order of 1, and $L = d/2$.

Sarrak has obtained the following (86):

$$(6) \quad \sigma_f = \sigma_o + \left(\frac{3\pi\gamma\ E}{(1-\nu^2)L}\right)^{\frac{1}{2}}$$

He however assumed L = d. If for comparison with the above we again set $L = d/2$ we obtain

$$(7) \quad \sigma_f = \sigma_o + \left(\frac{6\pi\ E\ \gamma}{(1-\nu^2)d}\right)^{\frac{1}{2}} \approx \sigma_o + 5 \left(\frac{E\ \gamma}{d}\right)^{\frac{1}{2}}$$

Likhtman and Shchukin while concerned primarily with single crystals also obtain equations of the above form (17).

Rozhanskii et.al., have recently reported at a Russian conference on the mechanical behavior of non-metallic substances "that the decrease in interfacial energy due to adsorption of surface-active substances has a substantial influence on the emergence of dislocations at the surface of the crystal, and on the formation and development of cracks. One of the manifestations of this effect involves the appearance of brittleness due to the action of melted metallic coatings" (87).

Some experimental confirmation of the relationship between σ_f and $\gamma^{\frac{1}{2}}$ was found by Petch in the adsorption of hydrogen by steel and its resulting brittle failure (84).

It may be noticed above that where the fracture stress is calculated on the basis of dislocations equations result with the fracture stress σ_f, inversely proportional to the square root of the grain size. That this is essentially the case has been experimentally verified in a number of instances. This implies that there may be substantial validity to their results.

Recently a considerable amount of distussion has centered around what the surface energy term in equations such as those developed by Petch and Cottrell should involve. Orowan (88) originally suggested a modification of Griffith treatment where γ would include not only the interfacial free energy associated with the crack but also a plastic work term, p, for plastic deformation which occurs together with fracture. The relative size of p with respect to γ depends to a considerable extent on whether or not plastic deformation occurs during or after fracture.

More recently Gilman (89) has quite thoroughly discussed the processes absorbing energy upon fracture of real materials. In addition to the creation of new surfaces these processes include plastic deformation, an elastic effect, electrical effects, and the formation of cleavage steps.

Low has emphasized the importance of distinguishing between transcrystalline and intercrystalline fracture (90). He also points out that intercrystalline brittle fractures constitute a special class. First, because the energy absorbed in crack propagation appears to be very low compared to transcrystalline fracture, and second, because such fractures cannot be expected to be influenced by the structural changes within the grains which might improve the resistance to the transcrystalline brittle fracture.

Allen also qualitatively discussed the surface energy term in relation to intercrystalline fracture (91). He states that if the energy absorbed during the passage of a brittle crack through a specimen having embrittled grain boundaries is measured it is many times less than the energy absorbed during the fracture of a corresponding less-brittle specimen, and it is many times larger than the simple surface energy required to separate the fracture faces. Allen states that surface energy is never in itself the total energy consumed in grain boundary fracture, but, its value evidently strongly influences this total energy (91).

In summary, the literature review indicates that a considerable amount of information is known about the effect of environments on fracture and indicates that changes in fracture stress due to environments might be explained on the basis of interfacial energies. That interfacial energies are associated

with fracture seems logical not only because free surfaces are formed, but also because the environments are non-corrosive, they do not form compounds with the solid metals, and their mutual solubilities are essentially zero in many cases. Such an effect must then act at the surface. A measure of such surface effects would be the interfacial energy, a physical property of the material and its environment.

EXPERIMENTAL PROGRAM

In order to establish more definitely the role of environments in fracture the experimental part of this work dealt with establishing; 1) the existence of an effect of environments on the fracture strength; 2) the relative magnitude of the effect; 3) possible explanations of the effect and the approximate validity of the expressions given in the literature review.

It was intended that these aims could be realized by measuring the stress at which a material fractures when in a non-corrosive environment which is systematically varied. The materials considered for study were solid copper with a liquid environment of lead-bismuth alloys. These materials were chosen as considerable information exists concerning the interfacial energies of these materials. Small additions of elements other than lead were also added to the bismuth to determine what effect they may have on the fracture strength of copper.

Although the interfacial energy is a variable with which this work is concerned, the interfacial energies of solids are in general not known or are very difficult to obtain. The following, based on Smith's work (58), is a way of obtaining some relative value of the energy of the new formed surfaces of a brittle intercrystalline fracture. Figure 2 represents a liquid drop on the boundary of a metal. Figure 3 represents the equilibrium state of the surface forces. From the geometry

$$(8) \qquad \frac{\gamma_{LS}}{\gamma_B} = \frac{1}{2}\sec\frac{\theta}{2}$$

γ_B = grain boundary energy
γ_{LS} = solid-liquid interfacial energy
θ = dihedral angle or included angle of a boundary

From the above expression it can be seen that the interfacial and grain boundary energy ratio is proportional to the grain boundary dihedral angle. The dihedral angle is a function of temperature and of the material and its environment. The dihedral angle is a measurable quantity and some values have been obtained for the copper-lead-bismuth system.

Now if a value is assumed for γ_B and γ_B is assumed to be constant with change in external environment, the value of γ_{LS} can be calculated and the general form of the fracture equation, equation 2, can be checked. From equation 2

$$(9) \quad \sigma_f^2 = K^2 \frac{E}{d} \gamma .$$

γ which equals the total surface free energy expended in exposing unit area of the crack faces equals $\gamma_{LS} - \frac{\gamma_B}{2}$. Equation (9) then becomes:

$$(10) \quad \sigma_f^2 = \frac{K^2 E \gamma_{SL}}{d} - \frac{K^2 E \gamma_B}{2d}$$

Since γ_B is assumed to be constant $\frac{K^2 E \gamma_B}{2d}$ can be designated as σ_o^2 and the following is obtained:

$$(11) \quad \sigma_f^2 = \frac{K^2 E}{d} \gamma_{SL} - \sigma_o^2$$

A plot of σ_f^2 vs. the interfacial energy γ_{SL} should yield a straight line if the analysis is correct. The slope of this line would be $\frac{K^2 E}{d}$ and the intercept of the line at zero strength should be the assumed value of γ_B. Approximate values of E and d could be used and a value of K obtained. As noted in the literature review the expected value of K based on theory should be about 5.

The following section will be devoted to a discussion of the experimental equipment and procedure.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

A. Furnace and Vacuum System

A furnace was constructed for tensile testing wire samples in liquid metal environments in a vacuum. A vacuum furnace was necessary to eliminate oxidation of both the specimen and the metal environment.

The furnace is illustrated in figures 4 and 5. Conex glands with neoprene sealants were used as friction vacuum seals. Such glands permitted the transmission of a force form outside the furnace to the specimen inside the furnace while maintaining the specimen under vacuum. The wire sample when placed in the furnace was secured by means of a set screw in the bottom yoke of the furnace as shown in figure 4. This prevented movement through the bottom conex gland. As the wire elongated under an applied load it moved through the top conex gland. The resultant friction force of the top conex gland was measured for each test by continuing the pulling of the wire through the gland after fracture had occurred. This fraction force was then subtracted from the total load for each test to give the net applied load acting on the wire. The seal had a resisting force of only 0.2 to 0.7 pounds in most cases relative to fracturing loads of 23 to 80 pounds. The friction force therefore represented only about 1% of the fracture load. It was assumed that the resultant friction force remained constant during a given test.

To prevent deterioration of the neoprene sealant in the glands by the furnace heat, cooling coils were fixed to the top and bottom of the furnace.

The furnace was heated by resistance heating elements which were coiled and cemented in place between two ceramic tubes. The temperature was regulated

by means of a temperature controller which held the temperature to $\pm$ 2°F. To measure the temperature of the liquid metal environment an adjustable thermocouple was originally built into the furnace such that it could be partially immersed by the liquid metal. The controller also used this thermocouple to regulate the temperature. The thermocouple was made from calibrated chromel-alumel wires insulated by means of a two hole ceramic tube surrounded by a stainless steel tube 2 mm. O.D. The thermocouple was spot welded to the end of the steel tube for accurate and rapid response. It was found that this thermocouple arrangement interferred with the results. Zinc chloride which was used as a flux (discussed later) evaporated to some extent at 650°F and condensed on the wire specimen and the thermocouple at a cooler location in the furnace and bonded the two together. The thermocouple also bent or interferred with the wire specimens in some cases and this could not be prevented with this arrangement. To avoid this problem the thermocouple was immersed in the liquid with a specimen in place while another thermocouple used by the controller was imbedded in the windings as shown in figure 4. By this means the temperature and controller were calibrated with a specimen in place and eliminated the need for the immersion thermocouple in tests.

During fracture of the copperwire a vacuum of about 1 micron was maintained. No oxidation was evident on the copper wire or the alloy environment if they were cooled while under a vacuum. Any oxidation, if present took place when the furnace chamber was opened while the specimen was still hot.

The specimens were in the furnace for 1 hour prior to testing. Although several tests were performed after shorter time this was found to be the minimum time required to equilibrate the temperature and obtain a reasonably good vacuum.

B. Specimen Preparation

The specimens were prepared from 14 gauge electrolytic commercial copper wire. The wire was removed from the spool and cold straightened. Pyrex tubing, 7 mm. O.D. was affixed to the copper wires with a Savereisen* cement. This was found to be a satisfactory means of securing some type of reservoir around the copper wire. Previous to cementing the reservoir to the specimen a considerable amount of effort was expended in obtaining a direct glass to metal seal by heating and drawing the pyrex around the wire. This worked in some cases however the seal was readily broken. If the seal broke while the alloy was molten the liquid metal would drop to the bottom of the furnace and solidify. This required that the furnace be dismantled to clear the passage for other specimens. Previous to cementing the pyrex tubes to the copper wire the pyrex tubes were constricted near the bottom end, such that the wire would just pass through. Figure 6 illustrates the specimen and the reservoir. The constriction served two purposes; 1) provided a convenient centering device for the copper wire and; 2) provided a stop for the Sauereisen cement. The cement holding the pyrex to the copper wires was allowed to set 24 hours in air. After the cement had set, the wires were heated in a vacuum from room temperature to 900°F over a $2\frac{1}{2}$ hour period. This heating procedure annealed the copper, hardened the cement and drove off any volitile gases from the cement. The wire was bright and metallic looking after annealing and showed no indication of oxidation after this procedure. In no case was any reaction between the cement and the liquid metal noted after any of the tests.

* Trade name of a Sauereisen Cement Company product.

Pieces of the environmental alloy in which the fracture was to be made were placed into the reservoir. The reservoir was positioned so that the alloy would be in the hottest part of the furnace.

C. Alloy Preparation

The alloys which were used in these tests were prepared from analytical reagent elements. The individual elements required to make up the desired alloy composition could not be added separately to the wire specimen reservoir. If the elements required for a given composition were separately added to the alloy reservoir, instances arose in which the bismuth would adhere to and wet the copper above the main body of the liquid alloy. This procedure lead to erratic results.

The alloys were prepared by sealing appropriate amounts of the desired elements in evacuated vycor capsules. These were then placed in a furnace at a temperature either higher than the highest melting element or 750°F whichever was higher and held for 3 hours. They were then furnace cooled to 750°F and quenched in water. The alloy when removed from the vycor was ready to be placed into the specimen reservoir. Chemical analysis of portions of an alloy originally prepared to be 80% bismuth yielded the following results 80.3, 79.3 and 79.2%. These are all within 1% of the desired composition. The alloys were therefore assumed to be the composition as made up.

D. Testing Procedure

All of the specimens were pulled with an "Instron" tensile machine. The furnace was mounted onto the tensile machine by placing the yoke at the

bottom of the furnace (see figure 6) into the lower jaws. The lower jaws were fixed onto the lower crosshead of the tensile machine. The top jaws of the Instron were connected to a cell from which the applied load is automatically recorded.

The furnace was readily loaded by removing the top of the furnace and inserting the specimen with the desired alloy together with zinc chloride flux in the reservoir, down into the furnace. Zinc chloride was first placed into the reservoir, then the desired alloy followed by more zinc chloride. This insured wetting of the copper. The wire specimen was then positioned so that the liquid metal would be at the hottest part of the furnace. The top of the furnace was placed in position with the wire going through the top conex friction gland and was then sealed. The top and bottom conex glands were then tightened to give a good vacuum seal. The start of time for which the copper and environment were in contact was determined as the time at which the furnace temperature reached 620°F.

If the furnace was left open for an appreciable length of time a blank wire was placed into the furnace. The furnace was then heated and the vacuum pumps turned on until a suitable vacuum could be obtained. This was done because the ceramic in the furnace adsorbed a considerable amount of gas and the time required to reach a suitable vacuum was more than one hour.

Before a fractured specimen was removed from the furnace helium was admitted to the vacuum chamber and furnace. This considerably reduced the time required in succeeding tests to obtain a suitable vacuum in the furnace.

The specimens were all fractured at a constant cross head speed of 1 inch per minute.

E. Grain Boundary Measurements

The measurement of grain boundary dihedral angles was done in a manner similar to that used by Smith (58). All the alloys were melted in a graphite crucible and cast into round ingots 2" long 3/4" diameter.

The alloys were made up of 98% copper with the remainder being lead and bismuth. The samples were melted and solidified under a helium atmosphere followed by air cooling. They were then cold rolled, annealed in vacuum at 1150°F for 1 1/2 hours, cold rolled again and annealed in vacuum at the desired temperature for 24 hours. The equilibrium grain boundary dihedral angle was taken to be the median of 75 angle measurements for each specimen. The 24 hour anneal was done at 649°F, 920°F, and 1260°F. Eight samples each of different composition were annealed at each temperature.

After the 24 hour anneal the ingots were cut into pieces which were mounted and carefully prepared metallographically. The angles were measured at a magnification of 2,000 X. The appropriate angles were measured by rotation of the stage of a Bausch and Lomb metallograph to align the appropriate boundaries successively with a cross-hair in a micrometer eyepiece. The angles were read to 0.1°, although as Ikeuye (92) mentions, the accuracy is probably not above 3° because of uncertainty in setting the cross-hair tangent to the sometimes curved boundary. The angles were successively read down the center of each specimen.

EXPERIMENTAL RESULTS AND DISCUSSION

One of the major problems in this work was to obtain results which were reasonably reproducible. After a considerable amount of preliminary testing it was found that reproducible values for the fracture strength of copper wet by an external environment depend on several conditions. There must be good contact between the copper and the liquid metal environment, a supply of liquid metal must be present to continue a brittle failure crack and the copper must have a small grain size.

Various methods were tried before finally settling on a suitable method of insuring contact between the liquid and the copper. Originally the desired alloy was merely added to the reservoir. This yielded values that varied by at least 100%. Apparently even though the free energies are such that lead and bismuth oxides are more stable the kinetics are so slow at 650°F that a protecting oxide film between the copper and the liquid alloys prevented wetting or contact between the copper and the liquid alloy. Since the wires were very metallic in appearance and no oxidation was indicated any film present must have been quite thin. In the study of the effect of the immersion time in the liquid metal before the test it is very important to know not only that wetting takes place, but also at what time. It was in such time studies that a large variation in strength was noted. One attempt to promote better wetting was to pre-stress the specimens a given amount such that the copper would deform but not fracture. The idea of this was to break the oxide film. Somewhat better results were obtained but there still was considerable scatter.

After this an attempt was made to do away with the reservoir technique altogether and pre-wet the copper with the liquid alloy by other means. It was intended that once the metal wet the copper it would form a bead on the wire and stay in contact with the copper while in the test chamber. Several different techniques were employed to obtain good contact between the liquid metal and the copper. Ultrasonic soldering, reducing flames, fluxes, and cleaning the copper by ion bombardment or cathodic etching were tried. While these methods probably achieved good contact between the copper and the liquid metal another problem presented itself. When these specimens were placed in the furnace and heated the liquid metal would no longer remain as a bead on melting, but would run down or fall off from the wire in many cases. In some cases, however, a thin film of metal would remain and when such specimens were loaded a crack would start propagating but would not lead to complete failure. Ductile failure would then occur at a higher load. In most cases it was not possible to determine from the recorded stress-strain curve when such non-propagating cracks appeard although in some cases this was readily apparent. Some of the specimens exhibited numerous such non-propagating cracks circumferencially around the specimen as observed after the specimen had been removed from the furnace. Since the above indicated that a supply of liquid must be present to maintain the growth of a propagating crack the reservoir technique was again employed.

To assure that intimate contact existed between the liquid metal and the copper, zinc chloride was added to the reservoir along with the alloy to act as flux or wetting agent. Zinc chloride was used as a flux because it has a suitable melting point and is stable in the presence of the other

elements. As mentioned in the literature review, zinc chloride has frequently been used as a flux or wetting agent.

That a supply of liquid metal is required to maintain a propagating crack was also evident in other tests. Some specimens fractured above the main body of the liquid alloy in the reservoir. It appeared that as some metal in contact with the copper melted it would adhere to the copper above the main bath of liquid after melt-down. Since such adhering metal was near the main supply it would be at the same temperature and thus act similar to the bath and allow failure to occur above the main supply of liquid alloy. Upon examination of the specimens after failure several of the fracture surfaces indicated that a sufficient supply of liquid was not present to give a completely brittle failure although complete failure resulted. Part of the fracture surface was indicative of brittle failure and another of ductile failure.

Another experiment was performed which indicated that a supply of liquid metal is necessary for embrittlement. Two specimens having a 100% bismuth environment were placed into the furnace and run similar to the other tests except that they were removed from the furnace without having been loaded or fractured. One was in the furnace 1 hour the other was left in the furnace for 9 hours at temperature. After they were removed from the furnace the bismuth was removed from the wire so that no bismuth could be seen adhering to the wires when viewed at 15X. Most of the bismuth was readily removed from the specimen while it was still liquid. Any remaining bismuth was removed by slight scraping and the use of 00 emergy paper. The

specimen that had been in the liquid bismuth for 9 hours showed a slight amount of dissolution attack. The attack was quite uniform, however, the depth of attack was not enough to be measured. After the bismuth was removed the wires were again run as they ordinarily would have been except with no bismuth or zinc chloride environment present. They were both heated for 1 hour and then fractured. The specimen that had previously been immersed for 1 hour in bismuth fractured with an ultimate strength of 22,100 psi. The specimen previously immersed for 9 hours failed at an ultimate strength of 21,400 pis. Both these strengths are above the average value obtained for specimens fractured in a zinc chloride environment, but were about 2000 psi lower than the average for the specimens fractured with no environment except vacuum (see table 2). The discrepancy could be accounted for from possible damage to the surface of the wires that resulted when the bismuth was removed. These results clearly demonstrate that copper if in the presence of bismuth need not be permanently damaged. The strength was restored to its original value by removing the external liquid metal environment.

Other results of the tests of lead-bismuth alloys are listed in table 2. To facilitate further discussion an environment of for example 0.40 Pb/Pb + Bi ratio in composition will be called a 40% lead environment. This assumes that the solubility of copper in the alloy is of negligible amount which is approximately true at 650°F. The ultimate strengths listed in table 2 are calculated on the basis of the maximum load and the original cross sectional area of $3.225 \times 10^{-3} in^2$. With alloys of 40% or more lead the final areas of the test specimen were measured. Specimens fractured in environments of less than

40% did not show significant reduction in area. For these, fracture strengths were assumed equal to the ultimate strengths. For the specimens that failed with considerable reduction in area the fracture strength was calculated on the basis of the final cross-sectional area and the ultimate load. The ultimate load was equal to the fracture load in all the tests.

When the values of the ultimate strength of 100% bismuth are plotted as a function of the length of time of immersion (see figure 7) no trend of either decreasing or increasing strength is indicated. Some 1 hour immersion time strengths are greater than those of longer times and some are of lower strength. This behavior was also true of all the other alloy environments as well. It was found that if all the results for a given alloy composition were averaged together, independent of time, the strengths after both short and long times of immersion would sometimes be higher and sometimes lower than the average. It was therefore assumed that a length of immersion time up to as much as 20 hours for some specimens prior to testing had no effect on the strength of copper. Table 1 which lists the average strength values of copper in each alloy environment also gives the percent average deviation of the ultimate strengths. Although the average deviation is 9.8% for 60% Pb it is only about 3% in most cases. Table 2 lists the average strengths $\pm$ the average deviation in psi. An alloy of 10% cadmium in bismuth was an exception to the above and will be discussed later.

Table 2 also lists values of the ultimate strengths of copper under various conditions, such as without any liquid metal or flux, flux only and lead only.

It is now of interest to compare representative microstructures and photographs of several specimens. Figure 27 is a photomicrograph of a specimen that was fractured with no metal environment or zinc chloride flux present. It underwent considerable deformation and grain elongation that is indicative of ductile failure. While copper fractured with no liquid metal or flux environment had only a slightly higher ultimate strength than if it was fractured in lead, figure 32 indicates that lead embrittled copper to a considerable extent. Figure 32 shows much less reduction in area than figure 27. Figure 33 is a photomicrograph of a specimen fractured in a bismuth environment and shows practically no reduction in area. The right side of figure 33 indicates a crack that has opened to some extent, but did not continue propagating. Another crack along the side of the same specimen is shown in figure 34 at a higher magnification (500x). Cracks such as that shown in figure 34 were quite prevalent on a number of specimens. The crack appears to have progressed to a boundary that tended to run parallel to the tensile stresses. The normal stresses on the crack were thus considerably reduced and the crack could no longer propagate.

Figures 35 through 44 are photographs of several specimens after they had been fractured in different alloy environments. It is readily apparent from these photographs that the reduction of area increases as the amount of bismuth in the environment decreases. Besides showing the brittle type of fracture that occurs in 100% bismuth alloys, figure 35 illustrates another interesting feature. It shows some bismuth adhering to copper above the fracture. As discussed earlier, fractures would sometimes start at such

locations, but would not continue to propagate to complete failure. This is indicated quite clearly in figures 43 and 44. They are photographs on different sides of the same specimen.

Finally, figure 42 again clearly indicates the ductile type of fracture that results when no liquid metal or flux is present.

The experimental results of this work clearly demonstrate that a change in environment affects fracture strength. It is of interest to compare the fracture strengths as found in this investigation with similar data obtained by Morgan (2). Tables 7 and 8 list the values that he obtained. In comparing the values that Morgan obtained with those of the present investigation it is important to consider the following similarities and differences between the two sets of data. Morgan used 0.178" diameter machined specimens compared to 0.064" (14 gage) diameter wire specimens used in this investigation. His specimens were held at temperature for one hour, the same as this investigation, but were fractured at 662°F while in the present investigation the wires were fractured at 650°F. Morgan's samples were annealed under different conditions. The specimens listed in table 7 were annealed 4 hours at 932°F and he indicates that the grain size was 0.025 mm. The specimens referred to in table 8 were annealed 2 hours at 1380°F and Morgan indicates a grain size of 0.050 mm. The specimens that were used in this investigation were annealed by heating from room temperature to 900°F over a $2\frac{1}{2}$ hour period. After reaching 900°F they were removed from the furnace and left to cool under vacuum. The grain size of these specimens is about 0.050 mm (see figure 28) although the grain size is somewhat irregular. In the present investigation zinc chloride was used as a flux but Morgan assumed that he obtained good wetting without a wetting agent or flux.

The values in tables 7 and 8 are plotted in figures 9 and 10. There exists considerable scatter in his data and it is rather difficult to draw a "best" curve through the points. This is especially true of the points for both the ultimate and fracture strengths as given in figure 9. Morgan did not indicate the reporducibility of his data or did he indicate what he would use as the "best" curve for his data. Approximate curves were drawn through his data points. The ultimate strength curves are replotted together with the ultimate strength data obtained in this investigation in figure 11. Considering the different testing conditions there is fair agreement between the results of this investigation and Morgan's especially at the end compositions. At the 50% lead composition Morgan's data is, however, about 20% higher than that found in this investigation. There is no obvious reason why the curves of Morgans data for different grain size should cross at 30% lead as they are drawn in figure 11.

Another characteristic of Morgan's data worth disucssing is the shape of the fracture strength curves as given in figures 9 and 10. Again there is no obvious reason for the large difference in the two curves as shown. Not only are the fracture values considerably different in the high lead region, but there is also a considerable difference in the shapes of the two curves. The shape of the curve as drawn in figure 9 is similar to the type of data that was obtained in the early part of this work. The data was taken before the importance of having a good contact between the copper and the liquid environment was realized as being a problem and the data showed very poor reproducibility. The fracture strength as determined in this investigation is considerably higher than that determined by Morgan in the high lead region. Although the present tests were done at 650°F and Morgan's

tests were done at 662°F it would not be expected that such a great difference should exist between the two sets of data. The difference might also be due to the type and size of specimen fractured. Morgan used 0.178 inch diameter tensile specimens while in this investigation 0.064 inch diameter wire was used. Another difference between the two sets of data is the strain rate and this could also account for the difference in the values of the fracture strengths. Morgan tested his specimens at a strain rate of 0.016 inches per inch per minute which is considerably lower than the rate used in this investigation. The samples fractured in this study were fractured by moving the crosshead at a constant rate of speed of one inch per minute. The entire specimen length was about 15" or this would correspond to a strain rate of 0.067" per inch per minute. In the present investigation however there existed a temperature gradient in the wire. This would considerably increase the actual strain rate in the hottest zone of the wire. The temperature at the hottest part of the wire was constant over about a one inch length and if it is considered that the entire crosshead motion resulted in straining primarily this region the strain rate would amount to 1" per minute. Both Morgan's and the present data indicate that appreciable amounts of plastic deformation starts to occur when the lead content of the liquid environment becomes about 30%.

Equilibrium grain boundary dihedral angles were taken to be the median of 75 angle measurements. The results are given in Table 9 and plotted as a function of the ratio Pb/Bi + Pb in figure 12. The results for 649°F are not as consistent as those for 1260 and 920°F.

There really was no reason to draw the smooth curve for 649°F in figure 28 considering the scatter or variation of the data. The curve was drawn as a smooth curve since this is indicated for 940 and 1260°F and the dihedral angles should be somewhat larger as the temperature is lowered. A curve of this nature has also been determined for copper-bismuth-lead alloys by Smith (71). His values of the dihedral angles start at about the same value as those indicated in this work, but he extrapolates his curve to a zero dihedral angle at about a 0.90 Bi/Bi + Pb ratio.

In the literature review several relationships relating fracture strength and interfacial energies were given. Values of the interfacial energy have been calculated using values from the curve drawn for 649°F in figure 12 and assuming a constant grain boundary energy of 550 ergs/cm^2. These are listed in table 10. The value of 550 ergs/cm^2 is the value that Morgan (1) used after a careful consideration of several values existing in the literature. If a value other than 550 ergs/cm^2 is used the functional relationship between fracture strength and interfacial energy is not altered greatly. Also in table 10 are values of the fracture strength as taken from figure 8. In figure 13 the fracture strength is plotted as a function of the interfacial energy. A smooth curve is drawn through the data, however, the data could be approximately represented by two straight lines of different slope corresponding to two different values of K as given by equation 2. It is of interest to note that the slope in the curve starts increasing at 40-60% lead, the region where a significant reduction in area occurs. Calculations of K from the curve of smallest slope using a grain size of 0.05mm and a Young's modulus of 10 x 10^6 psi give a value of approximately 15. This is about

3 times the value that is predicted by several theories. If a value of 5 is assumed for K the corresponding value of γ_{SL} is increased by a factor of about 10 or to about 3000 ergs/cm^2. A value of 3000 ergs/cm^2 is conceivable on the basis of a report by Floreen (50). He showed that the interfacial energy of a solid is a function of the elastic strain. An equation of the following form was obtained:

$$(12) \quad \gamma_{SL} = \gamma_o + L\epsilon^2$$

where ϵ is the elastic strain, γ_o is the strain free interfacial energy and L is a coefficient on the order of 10^9ergs/cm^2. According to equation 12, a stress of about 16,000 psi would give a value of γ_{SL} = 3000 ergs/cm^2. The value given for L was determined at room temperature and it probably decreases with temperature. At 650°F its value would, therefore, be less than 10^9. The portion of the curve in figure 13 having the greater slope yields a value of about 240 for the value of K. This is far greater than expected and is indicative of possibly some other type of fracture. The fracture is still somewaht intergranular in this region, however, a considerable reduction in area has occurred.

The vertical portion of the curve in figure 13 must change slope near 100% lead value as lead has very little effect on the strength of the copper. Table 2 shows that the ultimate strength of copper is 18,300 psi when fractured in a lead media and is 24,300 psi with no flux or metal present. The slope must therefore become approximately zero and the strength will be relatively independent of the surface energy of the environment for higher values of surface energy. This type of curve is schematically indicated in figure 29. This curve is representative of the energy-transition curve obtained as a function

of temperatures in impact tests. The transition on such a curve represents the transition from ductile to brittle failure and the corresponding drop in energy consumption as the temperature is lowered.

Morgan also studied the change of interfacial energies with changes in liquid composition by measuring and statistically analyzing dihedral angles. He did not, however, measure internal angles but external ones formed where a grain boundary came to the surface (see figure 2). These angles are similar to those formed on a solid surface by thermal etching. Morgan measured a large number of such angles for each alloy and took the most frequent angle as being the equilibrium true dihedral angle. The values he obtained are given in table 11 and plotted in figure 14. His values are approximately the same as those obtained in this investigation in the high bismuth region. In the high lead region however, he gets about 90° for 100% lead while in this investigation a value of 65° was obtained. The values obtained in this investigation agree quite well with those obtained by Smith (58). Smith considered internal angles and obtained values 60° and 70° for copper-lead at 600°C, 55° for 25% bismuth, 75% Pb, 40° for 50% Bi - 50% Pb and 30° for 75% Bi - 25% Pb at 650°C (58). Iheyne and Smith showed that at these temperatures the dihedral angle is quite insensitive to temperature (92).

The values of the interfacial energies obtained by Morgan are also questionable in that he assumed that the method used by Smith of taking the most frequently measured angle as the true dihedral angle would also apply in the case of external angles. A basic assumption in either method is that there exists a unique dihedral angle corresponding to the solid and liquid of

given composition and temperature or correspondingly, there exists a unique value of the interfacial energy of a given system. There are, however, variations of grain boundary energies corresponding to different crystallographic planes and orientation of adjacent grains. It has previously been assumed that such variations are negligible. Morgan, however, obtains a distribution curve for the angles measured by his method similar to that shown in figure 30. He took the most frequent angle as corresponding to the unique interfacial energy of the given system. Ideally, however, he should have obtained a curve as shown in figure 31 where the most frequent angle would be the smallest angle measured, the cut off angle as shown. Should there be any small variations in interfacial energies in the system the smallest angle measured would correspond to a region having the lowest interfacial energies and would be the probable location of the start of a brittle failure. If there were large variations in the interfacial or grain boundary energies a distribution of the type obtained by Morgan would be obtained. Another factor that might affect the frequency distribution curve is a very small grain size. If the grain size was so small that in a plane section dihedral angles were frequently obtained that were affected by grains immediately below, but not apparent, a non-ideal distribution would result. This, however, would also be true for included dihedral angles.

The values obtained by Morgan are used with fracture strength values obtained in this investigation and are listed in table 12 and plotted in figure 15. The same shaped curve is again obtained as was obtained by using the interfacial angles obtained in this investigation except that the more vertically sloped portion is displaced toward higher interfacial energy values.

The use of the values obtained by Morgan are somewhat questionable as discussed above and if the frequency distribution curve that he obtained resulted from the existance of a large variation in interfacial and grain boundary energies the values obtained using internal angles would also suffer from the same fault. This throws serious doubt on any dihedral angle measurements especially if they are used to give quantitative data. The interfacial energy values so obtained were used to correlate the fracture strengths because unfortunately, they are the only means of getting at some value of the interfacial energies of solids.

The effect of small amounts of elements other than lead in bismuth were also investigated. One of the elements, thallium, is similar to lead and bismuth in its reaction with copper in that it is immisible with copper and has a very limited solubility for copper at 650°F. Thallium concentrations of 5 and 10% in bismuth were investigated. The data is given in table 3 and shown graphically in figure 21. Other elements investigated were zinc, cadmium and antimony. The length of time of immersion in several zinc-bismuth alloys was also investigated and the results were found to be independent of the time of immersion. This was not the case with the 10% cadmium alloy. Appreciable amounts of cadmium were vaporized at 650°F in the longer immersion time tests to change the actual liquid alloy composition. For this alloy the values were extrapolated to zero time of immersion to obtain the copper strength on the basis of 10% cadmium. The 10% cadmium data are plotted in figure 16. The values of the ultimate strengths of copper when these elements were present as small percentages in bismuth are given in table 4, 5, 6, and shown graphically in figures 18, 19,20. In figure 17 all of the results using the different

elements are shown. This graph shows the relative effect of the elements in changing the ultimate strength of copper. Figures 22-26 show the above results plotted on the basis of atomic ratio. The relative effect of the various elements appears different depending on whether the effects are compared on the basis of atomic ratio or weight ratio. There was little reduction in area of the specimens fractured in these alloys and the fracture strengths are approximately equal to the ultimate strengths.

In table 1 the average values of the ultimate and fracture strengths are summarized. The average deviations for each alloy are also given. The average deviation is generally about 3 to 4%.

As would be expected, the effect of small amounts of thallium in bismuth is similar to that of lead in bismuth. This is to be expected because the elements thallium, lead and bismuth are next to each other in the periodic table, they all have very limited solubility of copper at 650°F and they do not form intermetallic compounds with copper. The other elements studied, antimony, zinc and cadmium all tend to form intermetallic compounds with copper and small additions of these elements all increase the strength of copper when present as small amounts in bismuth. Antimony has an appreciable effect even when present in amounts as small as 1/4% in bismuth. The effect which small amounts of elements alloyed with bismuth have on the fracture strength of copper can be summarized by saying that they all tend to increase the fracture strength. Elements that form intermetallic compounds with copper raise the strength of copper greater than those that are immisible with copper. Probably the most significant portion of the curves in figures 17 and 26 are the

initial slopes, especially of the alloys with zinc, cadmium and antimony additions. Enough thermodynamic data was available for the zinc-copper-bismuth system to calculate that about 3/4 wt% or 2.3 at.% zinc in bismuth corresponded to the formation of copper-zinc β phase. This composition also approximately corresponds to the point in the curve in figure 23 where there is a significant change in slope. Below this composition the curve has a greater slope than above this composition. Above 2.3 at.% the curve is relatively straight and corresponds to the liquid phase of varying composition in equilibrium with the copper surface whose surface composition corresponds to β brass. Antimony and cadmium in bismuth also exhibit a behavior similar to that of zinc except more pronounced. The greater initial slopes of the antimony and cadmium curves may result because of the greater tendency for compound formation of these elements with copper. Both the cadmium and the antimony curve remain approximately parallel to the lead and thallium curves after the initial rapid increase in strength while the zinc curve tends to increase somewhat faster. A possible explanation for this is that the antimony and cadmium intermetallic compounds have very limited solubilities while the β brass has a considerable solid solubility range.

Smith (58) showed that the dihedral angle in the Cu-Pb-Zn system progressively increases as the amount of zinc increased. He did not indicate if this relationship also held for the Cu-Bi-Zn system.

No other consistent correlation could be made relating the fracture strengths of copper to the addition of small amounts of elements to bismuth. The correlations tried were element melting points, liquid surface energies, atomic number and density. It could be argued that the increased strength

of copper could be due to an alloying effect of the material itself other than a general change in surface composition at the copper-liquid alloy interface. The facts, however do not support this conclusion, since some alloys, bismuth-lead for example, do cause a considerable change in the strength of copper depending on the alloy composition even though there is very limited solubility of either element in copper and they do not form intermetallic compounds with copper. If the change in strength were due to alloying it would be expected that the fracture strength would be a function of the time of immersion which is not the case. Calculations also indicated that the amount of diffusion of these elements into copper is insignificant after only one hour at 650°F.

Finally, although the idea that interfacial free energy is never in itself the total energy consumed in grain boundary failure and would limit a quantitative analysis, this work has shown that the value of the interfacial free energy evidently strongly influences intergranular fracture strength.

CONCLUSIONS

The following conclusions can be made on the basis of the present investigation:

1) The ultimate and fracture strengths of copper are a function of the liquid metal environment. Major changes in the strength can result when copper is fractured in liquid alloys. At 650°F an environment of liquid lead gave little reduction in strength while an environment of liquid bismuth reduced the fracture strength to 7,200 psi from 45,000 psi for liquid lead.

2) Brittle intergranular fractures result when copper is fractured in a liquid media giving low strengths. With no deleterious liquid alloy present ductile fracture results with considerable elongation and reduction in area. At 650°F copper fractured in bismuth with no significant reduction in area. Copper failed in lead after considerable elongation and showed approximately 60% reduction in area.

3) Reproducible and meaningful values for the ultimate strength of copper wire in different liquid metal environments can be obtained only when good contact exists between the copper and its environment. In the present investigation a zinc chloride flux produced the best results.

4) A supply of liquid metal is required to maintain the continued propagation of a failure crack.

5) The ultimate and fracture strengths of copper in lead-bismuth environments are not affected by the length of time of immersion of the copper in a stress free condition prior to fracture at the temperature and times of immersion used in this investigation.

6) The fracture strength of copper can be represented as a function of copper-liquid metal interfacial energy by the following function. $\sigma^2 = \frac{KE\gamma_{SL}}{d} - \sigma_o^2$ in the brittle fracture region. In the region where there exists a considerable ductility the value of K increases considerably.

7) Liquid metals immisible with copper tend to lower the strength of copper greater than elements forming compounds with copper. Small percentages of elements in bismuth raise the strength of copper relative to 100% bismuth in the following order: Pb, Tl, Zn, Cd, Sb. 10% of Pb in Bi will increase the strength of copper 11% compared to 100% bismuth while 1/4% Sb in bismuth raises the strength of copper 60% compared to bismuth with no antimony present.

REFERENCES

1. W. A. Morgan, The Effect of Stress on the Interactions Between Solid and Liquid Metal and Alloys, Ph.D. thesis, Cambridge Univ. 1954.

2. W. A. Morgan, Metal Treatment and Drop Forging, 6, 333, 1959.

3. L. van Ewijk, J. Inst. Met. 56, 241, 1935.

4. O. Patterman, J. Inst. Met., 56, 254, 1935.

5. W. E. Goodrich, J. Iron St. Inst., 132, 43, 1935.

6. M. D. Jepson, Metallurgia, 4, 62, 1951.

7. R. C. Grassi, D. W. Bainbridge, R. O. Elliott, Univ. of Calif. Engr. Res. Ser. 15, Issue 1, Sept. 1950.

8. R. C. Grassi, D. W. Bainbridge, J. W. Harmon, AECU 2201, July 1952.

9. R. Genders, J. Inst. Metals, 56, 249, 1935.

10. L. van Ewijk, J. Iron, St. Inst., 132, 65, 1935.

11. C. H. Desch, J. Inst. Metals, 22, 247, 1919.

12. C. H. Desch, J. Inst. Metals, 56, 249, 1935.

13. G. W. Austin, J. Inst. Metals, 56, 248, 1935.

14. G. W. Austin, J. Inst. Met., 58, 173, 1936.

15. G. Edmunds, Symposium on Stress Corrosion Cracking of Metals, A.S.T.M. and A.I.M.E. 69, 1944.

16. R. Genders, J. Inst. Metals, 37, 215, 1927.

17. V. I. Likhtman and E. D. Shchukin, Soviet Physics Uspekii , 66, 91, 1958.

18. J. H. S. Dickenson, J. Inst. Metals, 24, 315, 1920.

19. H. J. Hartley, J. Inst. Metals, 37, 193, 1927.

20. D. S. Anderson and G. E. Pool, J. Inst. of Metals, 37, 237, 1927.

21. H. J. Miller, J. Inst. Met. 37, 183, 1927.

22. H. Moore, S. Beckinsale, and C. Mallinson, J. Inst. Met., 25, 35, 1921.

23. M. S. Wang, The Intercrystalline Penetration of Molten Alloys into Steel, Thesis, Leeds University, June 1943.

24. R. Genders, J. Inst. Metals, 58, 187, 1936.

25. W. Radeker, Stahl. u. Eisen., 73, 10, 1953.

26. E. Heyn, J. Inst. Metals, 12, 3, 1914.

27. H. S. Rawdon, Proc. Amer. Soc. Testing Materials, 18, 2, 1918.

28. A. K. Huntington, J. Inst. Metals, 12, 3, 1914.

29. H. Moore and S. Beckinsale, J. Inst. Metals, 23, 225, 1920.

30. ASTM Standards, Pt. 2, Philadelphia, 409, 1952.

31. J. N. Greenwood, J. Inst. Metals, 81, 177, 1953.

32. V. N. Rozhanskii, N. V. Pertsov, E. D. Shchukin and P. A. Rebinder, Doklady Acad. Nauk SSSR, 116, 769, 1957.

33. S. S. Brenner, J. of App. Phy., 27, 1484, 1956.

34. H. Schottky, K. Schichtel and R. Stolle, Arch. Eisenhuttenwessen, 4, 541, 1931.

35. H. Schottky, K. Schichtel and R. Stolle, Iron Steel Ind., 4, 322, 1931.

36. W. Lynes, A.S.T.M. 41, 859, 1941.

37. W. H. Bassett, A.S.T.M. 18, 2, 1918.

38. T. C. Wilson, G. Edmunds, E. A. Anderson, and W. M. Peirce, Symposium on Stress Corrosion Cracking of Metals, A.S.T.M. and A.I.M.E., 173, 1944.

39. A. Joffe, The Physics of Crystals, McGraw-Hill, New York, 1928.

40. A. A. Griffith, Phil. Trans. Roy. Soc., (A), 221, 163, 1920.

41. A. R. Sack, Proc. Phy. Soc., 58, 729, 1946.

42. M. V. Classen-Nekludova, Jr. Exp. and Theo. Phy., 6, 584, 1936.

43. M. Classen-Nekludova, Tech. Phy. of the USSR. 5, 827, 1938.

44. E. Aerts and W. Dekeyser, Acta Met., 4, 557, 1956.

45. A. E. Gorum, E. R. Parker, and J. A. Pask; J. Am. Ceram. Soc., 41, 161, 1958

46. E. S. Machlin and G. T. Murray, J. App. Phy., 30, 1731, 1959.

47. E. Orowan, Z. Phys., 86, 195, 1933.

48. E. Orowan, Nature, Lond., 154, 341, 1944.

49. C. Gurney, Proc. Phy. Soc., 59, 169, 1947.

50. S. Floreen, The Effect of Strain on the Surface Energy of Solids, Ph.D. Thesis, Univ. of Mich. 1960.

51. C. Benedick and G. Ruben, Jernk. Ann., 129, 37, 1945.

52. C. Benedick and R. Harden, Arkiv For Fysik, 3-4, 407, 1951-2.

53. C. Benedick, Comptes Rendus, 232, 24, 1951

54. C. Benedick, Ibid., 233, 409, 1951.

55. C. Benedick, Intern. Symp. React. Solids, Gothenburg, 477, 1952.

56. M. Sato, Arkiv För Fysik, 10, 37, 1956.

57. M. Sato, Arkiv För Fysik, 10, 45, 1956.

58. C. S. Smith, Trans. A.I.M.E., 175, 15, 1948.

59. R. Eborall and P. Gregory, J. Inst. Metals, 84, 88, 1955-56.

60. P. A. Rebinder, Doklady n a VI syezda fizekov M., 1928.

61. P. A. Rebinder, V. I. Likhtman and V. M. Maslenikov, Comptes Rendus (Doklady) de l' Academic des Sciences de' USSR, 32, 125, 1951.

62. V. N. Rozhanskii, N. V. Pertov, E. D. Shuhukin and P. A. Rebinder, Dokl. Akad. Nauk SSSR, 116, 769, 1957, or Soviet Phy. Doklady, 2, 460, 1957.

63. P. Rebinder and E. K. Venstrom, Bull. Acad. Sci., URSS., No. 4/5, 531, 1937.

64. P. A. Rebinder, Izd. An SSSR. 1, 123, 1947.

65. P. A. Rebinder, V. I. Likhtman and L. A. Kochanova, Doklady, Akad. Nauk SSSR. 111, No. 6, 1278, 1956.

66. P. A. Rebinder, Z. Physik., 72, 191, 1931.

67. V. I. Likhtman, P. A. Rebinder and G. V. Karpenko, The Influence of a Surface Active Substance on Metal Deformation, (in Russian), 1947.

68. P. A. Rebinder, N. A. Kalinovskaya, Zhur. Tekh. Fiz., 2, 726-754, 1932.

69. V. I. Likhtman, P. A. Rebinder and G. I. Karpenko, Effect of a Surface Active Medium on the Deformation of Metals, (in Russian), 1954.

70. V. D. Kuznetsov, Surface Energy of Solids, (in Russian), 1953.

71. W. Klinkenberg, K. Lucke and G. Masing, Z. für Metallkunde, 44, 362, 1953.

72. V. N. Rozhanskii and P. A. Rebinder, Dok. Akad. Nauk. SSSR, 91, 129, 1953.

73. A. Pfutzeureter and G. Masing, Z. Metal, 42, 361, 1951.

74. V. I. Likhtman and P. A. Rebinder, Comptes Rendus, Acad. Sci. USSR, 32, 130, 1941.

75. V. A. Labzin and V. I. Likhtman, Doklady Akad. Nauk. SSSR, 121, 443, 1958.

76. L. S. Bryukhanova, L. A. Kochanova and V. I. Likhtman, Soviet Physics, Solid State, 1, 1329, 1960.

77. V. I. Likhtman, L. A. Kochanova and L. S. Briukhanova, Soviet Physics, Doklady 120, 757, 1958.

78. G. I. Epifanov, N. I. Glagolev and P. A. Rebinder, Dok. Akad. Nauk. SSSR, 123, 663, 1958.

79. V. D. Kuznetsov, A. I. Loskutov and S. N. Pavlova, Doklady Akad. Nauk, SSSR., 123, 272, 1958.

80. V. N. Rozhanskii, Dok. Akad. Nauk SSSR, 123, 648, 1958.

81. E. D. Shchukin and V. I. Likhtman, Dok. Akad. Nauk, SSSR, 124, 111, 1959.

82. V. P. Bobrikov, Sov. Physics—Tech. Phys., 2, 758, 1957.

83. E. D. Shchukin, Dok. Akad. Nauk, SSSR, 118, 1105, 1958.

84. N. J. Petch, London Phil. Mag., 1, 331, 1956.

85. A. H. Cottrell, Trans. A.I.M.E., 212, 192, 1958.

86. V. I. Sarrak, Sov. Phy. Uspekii, 67, 150, 1959.

87. V. N. Rozhanskii, Yu. V. Goryunov, E. D. Shchukin and P. V. Pertsov, Ibid. 175.

88. E. Orowan, Reports Prog. Phy., 12, 85, 1949.

89. J. J. Gilman, Fracture, J. Wiley, N. Y. p. 193, 1959.

90. J. R. Low, Fracture, J. Wiley, N. Y., p. 68, 1959.

91. N. P. Allen, Fracture, J. Wiley, N. Y., p. 123, 1959.

92. K. K. Ikeuye and C. S. Smith; Metals Transactions, 185, 762, 1949.

93. J. H. Schulman and L. Nanis, NONR 266(64), Columbia University, 1959.

TABLE 1

SUMMARY OF FRACTURE STRENGTH DATA

Average strengths of 14 gage copper in liquid metal environments at 650°F, $ZnCl_2$ used a wetting agent.

Liquid Alloy	Weight Ratio	Average Ultimate Strength psi	Average Deviation (%)	Average Fracture Strength psi
Pb/Pb+Bi	0.000	7,220	3.0	7,220
"	0.111	8,020	3.0	8,020
"	0.200	8,810	0.8	8,810
"	0.400	10,700	5.2	13,300
"	0.600	13,300	9.8	18,600
"	0.800	16,000	3.6	31,100
"	1.000	18,300	1.9	44,900
Tl/Tl+Bi	0.050	8,400	6.7	
"	0.100	8,330	5.4	
Cd/Cd+Bi	0.0025	8,180	5.5	
"	0.0075	7,870	2.9	
"	0.050	8,710	0.3	
"	0.100	9,550		
Zn/Zn+Bi	0.0025	8,240	5.6	
"	0.0075	7,700	6.5	
"	0.020	8,250	2.9	
"	0.045	10,800	4.9	
"	0.073	10,200	8.0	
Sb/Sb+Bi	0.0025	11,500	4.8	
"	0.0050	12,800	3.1	
"	0.0075	11,800	3.9	
"	0.050	12,100	1.9	
"	0.100	12,600	5.5	

TABLE 2

STRENGTHS OF COPPER IN LIQUID LEAD-BISMUTH ALLOY ENVIRONMENTS.

14 gage copper wire tested at 650°F in lead-bismuth environments. $ZnCl_2$ used as wetting agent.

Pb/Pb+Bi (wt.)	Time of Immersion (hrs.)	Ultimate Load (lbs.)	Ultimate Strength (psi)	Reduction Area (%)	Fracture Strength (psi)	Avg. Ult. Strength (psi)	Avg. Fract. Strength (psi)
0.00	1	22.2	6,880		6,880		
"	1	22.9	7,100		7,100		
"	1	21.9	6,780		6,780		
"	1	23.9	7,410		7,410		
"	1	23.4	7,260		7,260	7,220±215	7,220±215
"	1½	23.3	7,220		7,220		
"	2	24.8	7,680		7,680		
"	2	24.2	7,500		7,500		
"	6	22.8	7,070		7,070		
"	12	23.7	7,350		7,350		
0.11	1	25.0	7,750		7,750		
"	1	25.3	7,840		7,840		
"	1	25.8	8,000		8,000	8,020±240	8,020±240
"	6	27.7	8,590		8,590		
"	16 2/3	25.6	7,940		7,940		
0.20	1	28.1	8,720		8,720		
"	2	28.8	8,930		8,930	8,810±70	8,810±70
"	11½	28.4	8,810		8,810		
0.40	1	36.8	11,400	15.3%	13,500		
"	2	33.7	10,450	25.2%	14,000		
"	7 2/3	36.0	11,150	20.9%	14,100	10,700±560	13,300±800
"	20	31.8	9,860	16.6%	11,800		
0.60	1	45.0	14,000	35.8%	21,800		
"	2	51.0	15,800	30.0%	22,600		
"	2	37.0	11,500	28.0%	16,000	13,300±1300	18,600±2920
"	10	38.7	12,000	20.5%	15,100		
"	19	42.2	13,100	24.4%	17,300		

TABLE 2 (cont.)

Pb/Pb+Bi (wt.)	Time of Immersion (hrs.)	Ultimate Load (lbs.)	Ultimate Strength (psi)	Reduction Area (%)	Fracture Strength (psi)	Avg. Ult. Strength (psi)	Avg. Fract. Strength (psi)
0.80	1	48.8	15,100	37.0%	24,000		
"	1	50.9	15,800	47.8%	30,300		
"	1	53.6	16,600	42.8%	29,000	16,000±580	31,100±4000
"	3	55.0	17,000	54.1%	37,000		
"	18	52.3	16,200	53.8%	35,200		
1.00	1	57.7	17,900	60.7%	45,600	18,300±350	44,900±700
"	1	60.0	18,600	57.9%	44,200		
*1.00	1	60.1	18,600			19,300±650	
"	1	64.1	19,900				
$ZnCl_2$ Flux only	1	69.1	21,400				
	1	54.9	17,000				
	1	64.5	20,000			20,900±1720	
	1	74.5	23,100				
	1	74.8	23,200				
	$9\frac{1}{2}$	65.9	20,400				
No flux or liq. metal	1	80.7	25,000				
	1	78.2	24,300			24,300±400	
	$5\frac{1}{4}$	76.6	23,800				

* Lead only - No flux

TABLE 3

STRENGTHS OF COPPER IN LIQUID THALLIUM-BISMUTH ALLOY ENVIRONMENTS

14 gage Cu wire tested at 650°F in thallium-bismuth environments. $ZnCl_2$ used as wetting agent.

Tl/Tl+Bi (wt.)	Tl/Tl+Bi (At.)	Immersion Time(hrs.)	Ultimate Load(lbs)	Ultimate Strength(psi)	Avg. Ult. Strength psi.
0.050	0.0511	1	29.8	9,240	
"	"	1	24.4	7,560	8,400±560
"	"	1	28.0	8,680	
"	"	1	26.2	8,130	
0.100	0.102	1	27.2	8,420	
"	"	1	28.8	8,930	8,330±450
"	"	1	24.7	7,660	

TABLE 4

STRENGTHS OF COPPER IN LIQUID CADMIUM-BISMUTH ALLOY ENVIRONMENTS

14 gauge copper wire tested at 650°F in bismuth-cadmium environments. $ZnCl_2$ used as wetting agent.

Bi/Cd+Bi (wt.)	Bi/Cd+Bi (at.)	Immersion Time (hrs)	Ultimate Load (lbs)	Ultimate Strength (psi)	Avg. Ult. Strength	
0.0025	0.0049	1	27.8	8,620	8,180±450	
"	"	1	24.9	7,730		
0.0075	0.0139	1	26.5	8,220		
"	"	1	24.4	7,570	7,870±230	
"	"	1	25.3	7,830		
0.050	0.0890	1	28.0	8,680	8,710±30	
"	"	1	28.2	8,740		
0.100	0.171	1	29.1	9,030		
"	"	2	29.1	9,030		
"	"	6	25.3	7,850	extrapolate to 30.8 at 0 immersion	
"	"	12 2/3	26.8	8,320	time or = 9,550 psi (see Fig. 16)	
"	"	42 1/2	23.5	7,290		

TABLE 5

STRENGTHS OF COPPER IN LIQUID ZINC-BISMUTH ALLOY ENVIRONMENTS

14 gauge copper wire tested at 650°F in zinc-bismuth environments. $ZnCl_2$ used as wetting agent.

Zn/Zn+Bi (wt.)	Zn/Zn+Bi (at.)	(hr's) Immersion Time	(lbs) Ultimate Load	(psi) Ultimate Strength	Average Ultimate Strength (psi)
0.0025	0.0079	1	25.1	7,780	8,240±460
"	"	1	28.1	8,700	
0.0075	0.0235	1	27.3	8,460	
"	"	1	25.2	7,810	
"	"	6	22.1	6,850	
"	"	11	25.2	7,810	7,700±500
"	"	12 1/2	26.5	8,220	
"	"	23 1/2	22.7	7,030	
0.020	0.0622	1	26.5	7,900	
"	"	1	26.8	8,310	8,250±240
"	"	3 2/3	27.6	8,550	
0.045	0.1310	1	31.1	9,640	10,800±530
"	"	1	36.5	11,300	
*0.073	0.20	1	30.2	9,360	10,200±820
		1	35.4	11,000	

* Approximate solubility limit.

TABLE 6

STRENGTHS OF COPPER IN LIQUID ANTIMONY-BISMUTH ALLOY ENVIRONMENTS

14 gauge copper wire tested at 650°F in antimony-bismuth environments. $ZnCl_2$ used as wetting agent.

Sb/Sb+Bi (wt.)	Sb/Sb+Bi (at.)	Length of Immersion (hrs.)	Ultimate Load (lbs.)	Ultimate Strength (psi)	Average Ultimate Strength
0.0025	0.0043	1	35.1	10,900	11,500±550
"	"	1	38.7	12,000	
0.0050	0.0085	1	43.4	13,500	
"	"	1	41.6	12,900	
"	"	1	41.6	12,900	12,800±400
"	"	1	39.0	12,100	
"	"	1	40.0	12,400	
0.0075	0.0128	1	36.5	11,300	
"	"	1	40.9	12,700	11,800±460
"	"	1	36.9	11,400	
0.050	0.083	1	38.6	12,000	
"	"	1	40.3	12,500	12,100±230
"	"	1	38.2	11,900	
*0.10	0.16	1	43.0	13,300	12,600±700
"	"	1	38.4	11,900	

* Approximate Solubility Limit.

TABLE 7

PUBLISHED STRENGTHS OF COPPER IN LIQUID LEAD-BISMUTH ENVIRONMENTS
GRAIN SIZE=0.025mm

H.C.Copper 0.178" diameter, 1" gauge length. Annealed 4 hours at 500°C. Held at temperature 1 hour before testing. Tested to fracture at 350°C(662°F). Strain rate 0.016"/in/min.
From Morgan (1) Table XXI.

Molten Metal		Ton/in^2				psi (where 1 ton = 2240 lb.)			
% Lead	% Bismuth	Mc	Mt	Fc	Ft	Mc	Mt	Fc	Ft
Air		7.8	10.4	6.8	10.5	17,500	23,300	15,200	23,500
100	0	6.8	9.2	6.0	9.9	15,200	20,600	13,400	22,200
99	1	6.9	9.3	4.8	7.3	15,500	20,800	10,750	16,350
90	10	7.1	9.3	4.8	7.0	15,900	20,800	10,750	15,700
80	20	7.2	9.0	4.6	7.0	16,100	20,150	10,300	15,700
70	30	6.8	8.8	5.2	7.2	15,200	19,700	11,650	16,100
60	40	6.7	8.4	5.5	7.7	15,000	18,800	12,300	17,250
50	50	7.2	7.7	6.6	7.9	16,100	17,250	14,800	17,700
45	55	6.8	7.3	6.6	7.5	15,200	16,350	14,800	16,800
40	60	6.4	7.0	6.4	7.2	14,300	15,700	14,300	16,100
30	70	5.0	6.1	5.0	6.1	11,200	13,700	11,200	13,700
25	75	4.7	5.6	4.7	5.6	10,500	12,550	10,500	12,550
20	80	4.4	5.0	4.4	5.0	9,850	11,200	9,850	11,200
10	90	4.1	4.1	4.1	4.1	9,200	9,200	9,200	9,200
5	95	4.0	4.0	4.0	4.0	8,950	8,950	8,950	8,950
0	100	4.0	4.0	4.0	4.0	8,950	8,950	8,950	8,950

Mc = Maximum Stress, Conventional
Mt = Maximum Stress, True
Fc = Fracture Stress, Conventional
Ft = Fracture Stress, True

TABLE 8

PUBLISHED STRENGTHS OF COPPER IN LIQUID LEAD-BISMUTH ENVIRONMENTS
GRAIN SIZE=0.050mm.

H.C. copper. 0.178" dia., 1" gauge length. Annealed 2 hr. at 750°C. Grain size 0.05mm. Held at temp. 1. Hour before testing. Tested to fracture at 350°C. Strain rate 0.016"/in/min. From Morgan (1) Table XXII.

Environment		ton/in^2				psi(ton=2240 lb)			
%Pb	%Bi	Mc	Mt	Fc	Ft	Mc	Mt	Fc	Ft
Air		8.0	10.5	6.5	11.0	17,900	23,500	14,600	24,600
100	0	8.0	10.0	7.0	11.4	17,900	22,400	15,700	25,550
99	1	8.4	10.4	7.3	11.6	18,800	23,300	16,350	26,000
90	10	7.8	10.0	6.1	11.0	17,500	22,400	13,700	24,600
80	20	8.2	10.2	6.1	10.7	18,400	22,800	13,700	24,000
70	30	7.6	9.2	6.6	10.1	17,050	20,600	14,800	22,600
60	40	7.2	8.4	6.8	9.6	16,100	18,800	15,250	21,500
50	50	6.6	7.8	6.1	8.0	14,800	17,500	13,700	17,900
45	55	5.6	6.3	5.6	6.3	12,550	14,200	12,550	14,200
40	60	6.0	6.0	6.0	6.0	13,450	13,450	13,450	13,450
30	70	4.7	4.7	4.7	4.7	10,500	10,500	10,500	10,500
25	75	4.5	4.5	4.5	4.5	10,100	10,100	10,100	10,100
20	80	4.7	4.7	4.7	4.7	10,500	10,500	10,500	10,500
10	90	4.0	4.0	4.0	4.0	8,950	8,950	8,950	8,950
5	95	4.0	4.0	4.0	4.0	8,950	8,950	8,950	8,950
0	100	3.5	3.5	3.5	3.5	7,840	7,840	7,840	7,840

TABLE 9

EQUILIBRIUM GRAIN BOUNDARY DIHEDRAL ANGLES OF Cu - Pb - Bi ALLOYS

Pb/Bi + Pb	1260°F	920°F	649°F
0.0	56.8°	60.4	64.5
0.2	56.6	59.5	51.1
0.4	41.0	51.4	44.4
0.6	31.1	42.3	44.7
0.8	25.8	31.9	40.9
0.9	21.9	28.4	41.9
0.95	15.4	24.4	28.3
1.0	14.3	20.4	30.1

TABLE 10

DATA USED FOR FIGURE 13

Dihedral angles-from figure 12; fracture strengths-from figure 8.

Pb/Bi+Pb	Dihedral Angle, θ	Interfacial* free energy ergs/cm^2	$\left(\text{Fracture Strength}\right)^2$ psi^{2}x10^{-7}
1.00	64.5	325	203
.90	62.0	321	145
.80	59.5	317	99.5
.70	57.0	311	61.7
.60	53.5	308	36.5
.50	50.0	303	24.1
.40	46.5	299	16.9
.30	42.5	295	10.1
.20	38.5	291	7.7
.10	34.0	287	6.1
.00	30.0	284	5.2

* Based on $\gamma_{SL} = \gamma_B \frac{1}{2} \sec \frac{\theta}{2}$; $\gamma_B = 550$ ergs/cm^2

TABLE 11

PUBLISHED INTERFACIAL FREE ENERGIES OF SOLID COPPER LIQUID-LEAD-BISMUTH SYSTEM

H.C. Cooper Annealed 4 hrs. 500°C Immersed 10 hrs. at 350°C.
From Morgan (1) Table VIII

Composition of Molten Metal		Dihedral Angle	Ratio of Interfacial Energies	Interfacial Energies, γ_{SL} Taking γ_B=550 ergs/cm^2.
% Lead	% Bismuth	θ	γ_{SL}/γ_B	
100	0	90.0	0.71	390.5
99	1	88.0	0.70	385.0
90	10	88.0	0.70	385.0
80	20	87.0	0.69	379.5
70	30	87.0	0.69	379.5
60	40	62.0	0.59	324.5
50	50	40.0	0.54	297.0
45	55	35.0	0.53	291.5
40	60	33.0	0.53	291.5
30	70	30.0	0.52	286.0
25	75	35.0	0.53	291.5
20	80	28.0	0.52	286.0
10	90	20.0	0.51	280.5
0	100	20.0	0.51	280.5

TABLE 12

DATA USED FOR FIGURE 15

Fracture strengths from figure 8; Interfacial Energies from Figure 14.

Pb/Pb+Bi	Fracture Strength (psi)	$\left(\text{Fracture Strength}\right)^2$ $psi^2 \times 10^{-7}$	Interfacial Energies, $ergs/cm^2$
1.00	45,000	203	388
0.90	38,000	145	384
0.80	31,500	99.5	378
0.70	24,800	61.7	362
0.60	19,100	36.5	325
0.50	15,500	24.1	302
0.40	13,000	16.9	292
0.30	10,500	10.1	288
0.20	8,750	7.7	285
0.10	7,800	6.1	282
0.0	7,200	5.2	280

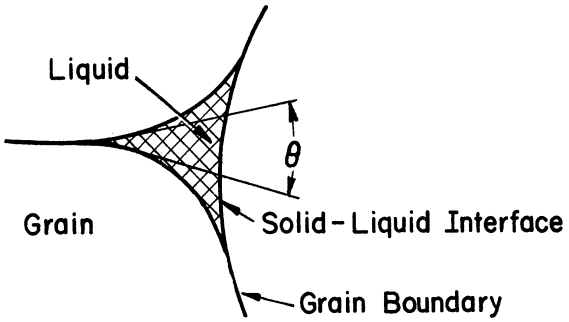


FIGURE 1. Internal Liquid Phase Dihedral Angle

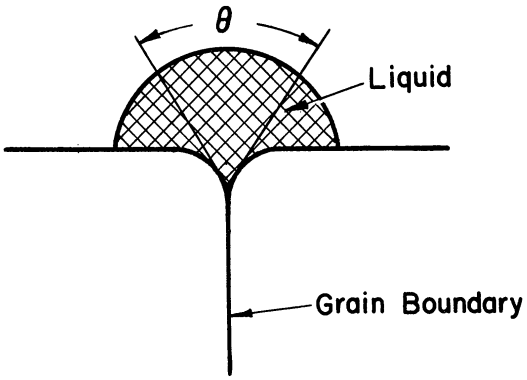
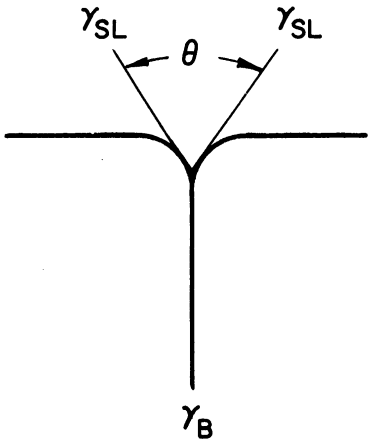


FIGURE 2. Liquid Drop on a Metal Grain Boundary, Representative of External Dihedral Angle



$$\gamma_{SL} = \gamma_{\frac{1}{B_2}} \text{SEC} \frac{\theta}{2}$$

FIGURE 3. Equilibrium State of Surface Forces

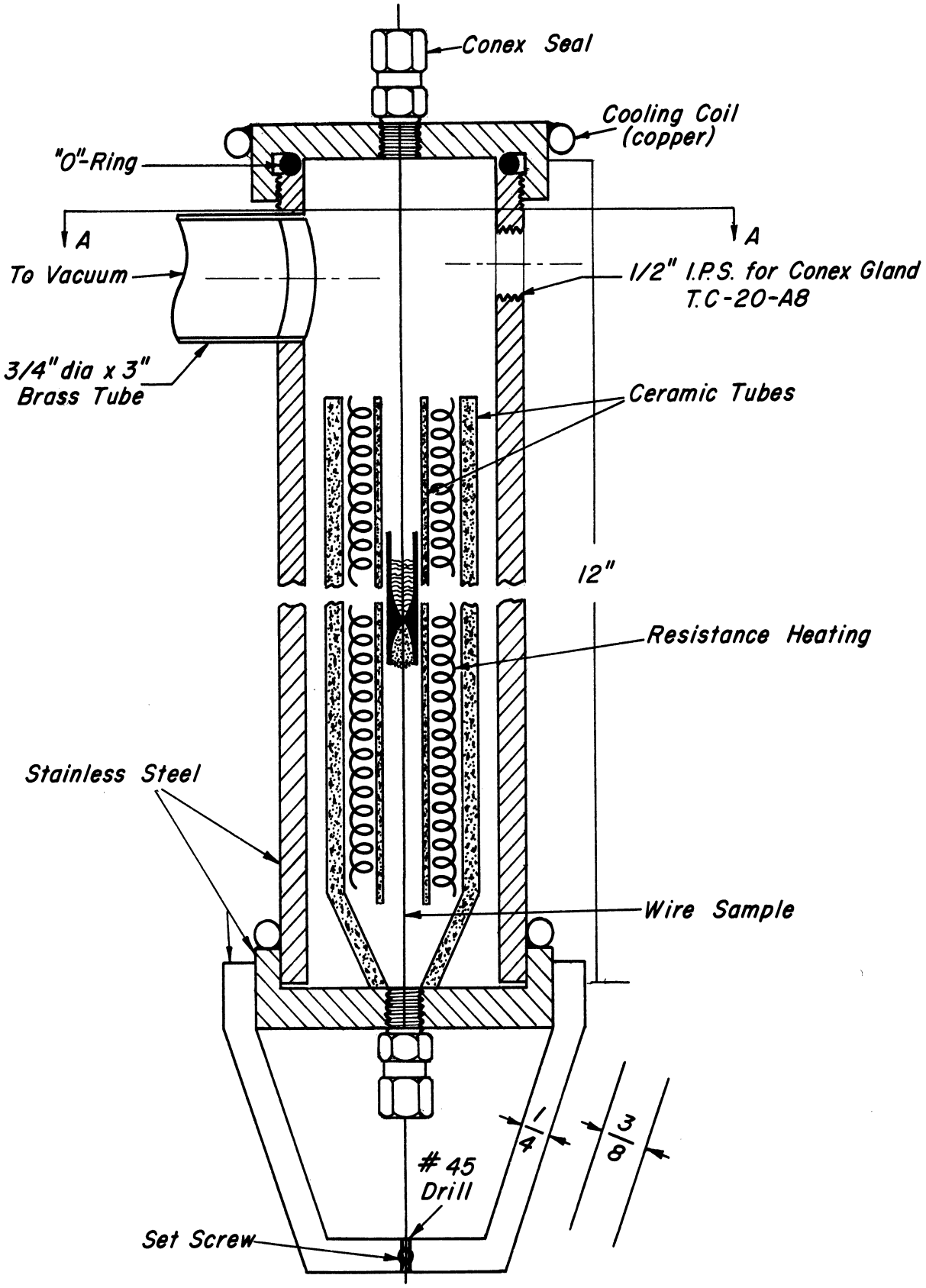


FIGURE 4. Vacuum Furnace

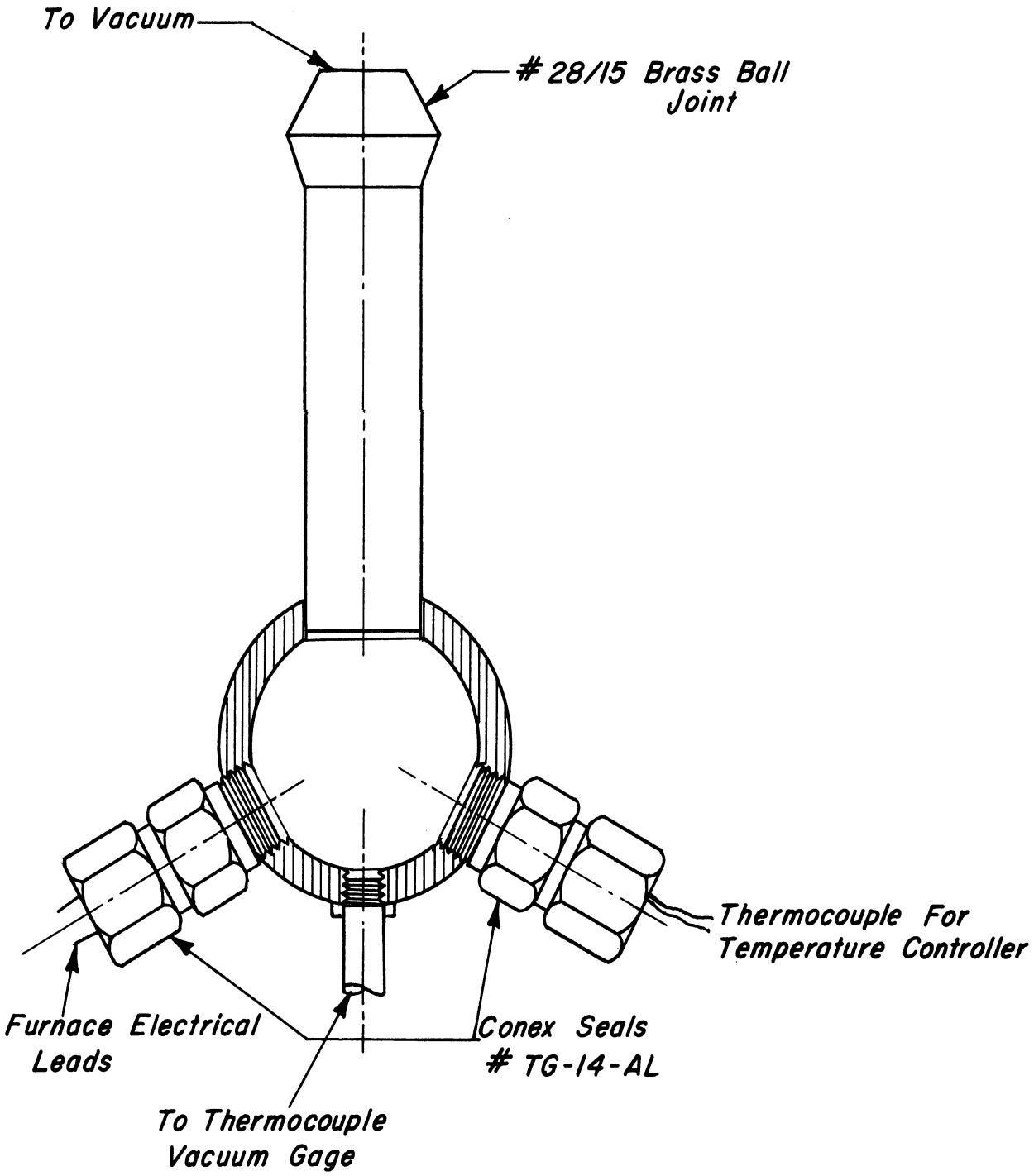


FIGURE 5. Vacuum Furnace; Section-A - A

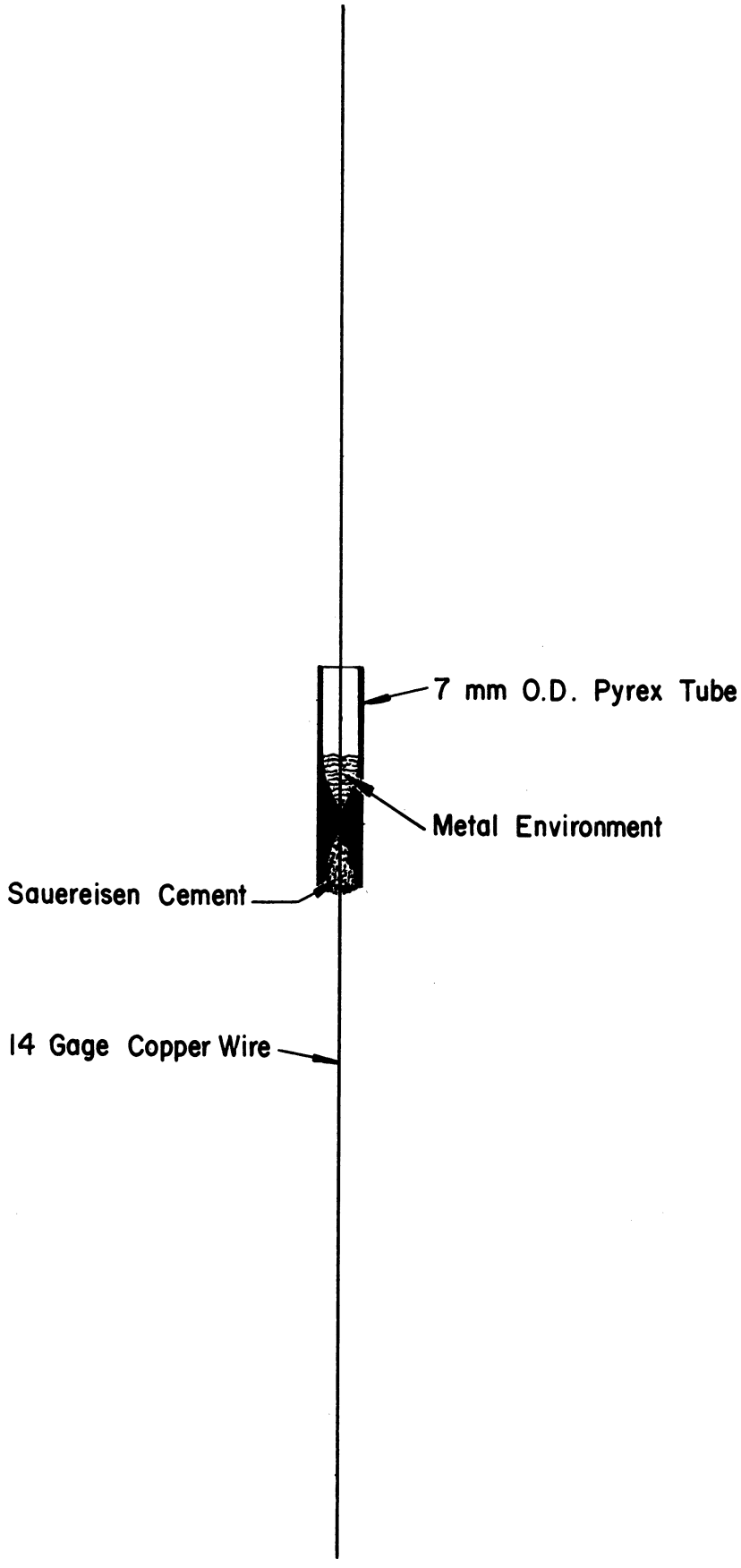


FIGURE 6. Wire Specimen and Liquid Metal Reservoir

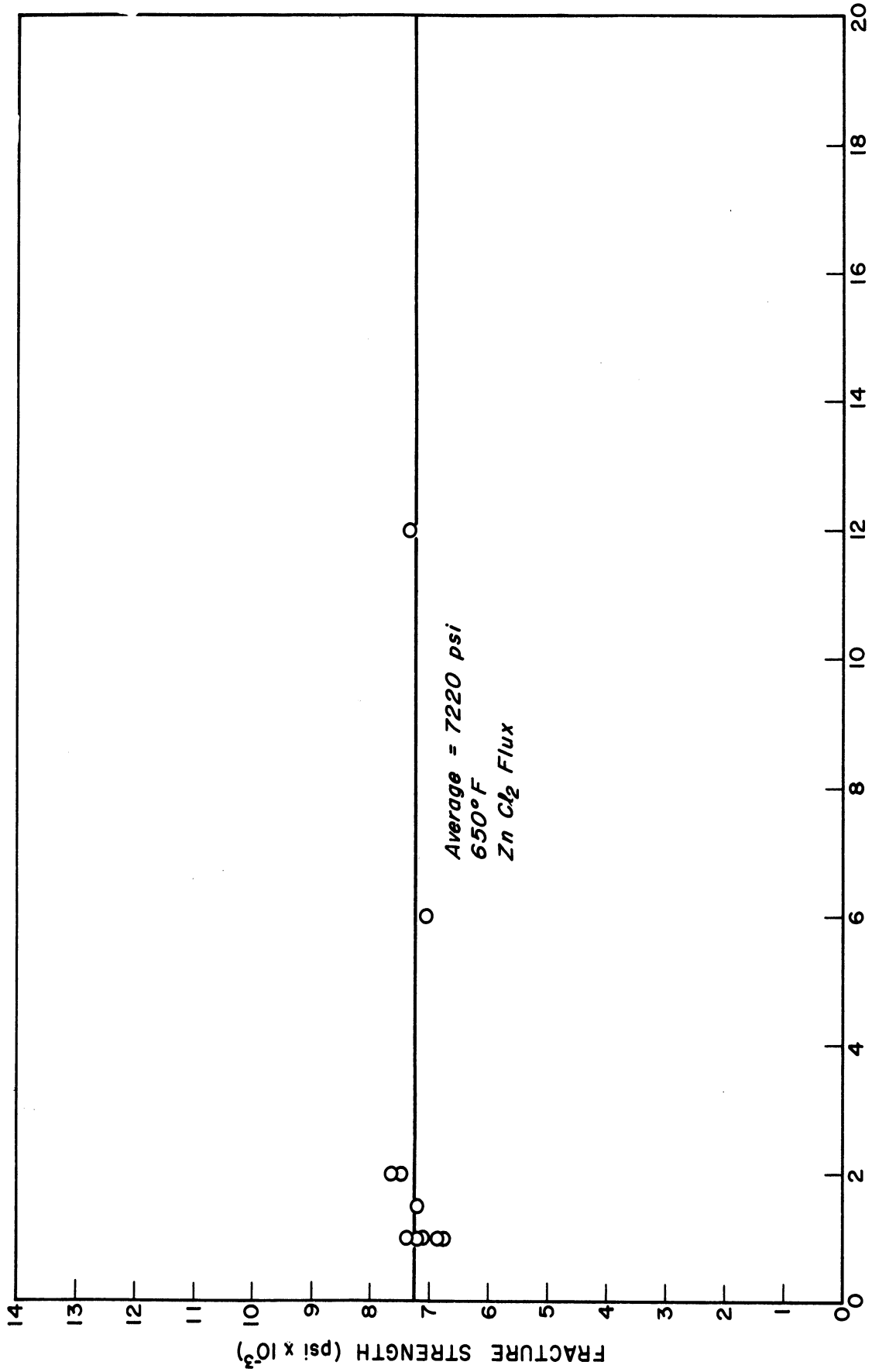


FIGURE 7. Copper Strength vs. Time of Immersion in Bismuth

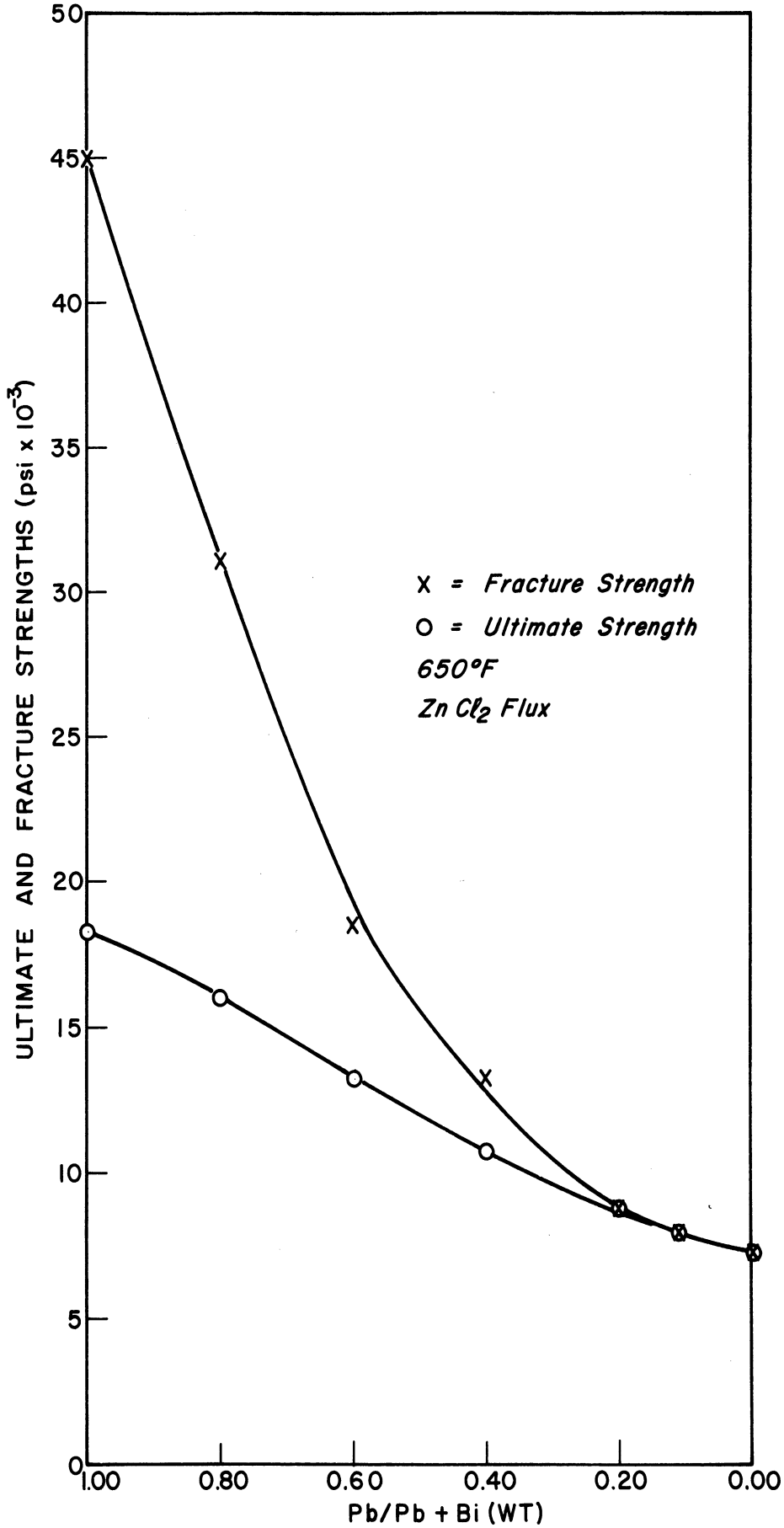


FIGURE 8. Average Strength of Copper vs. Ratio Pb/Pb + Bi

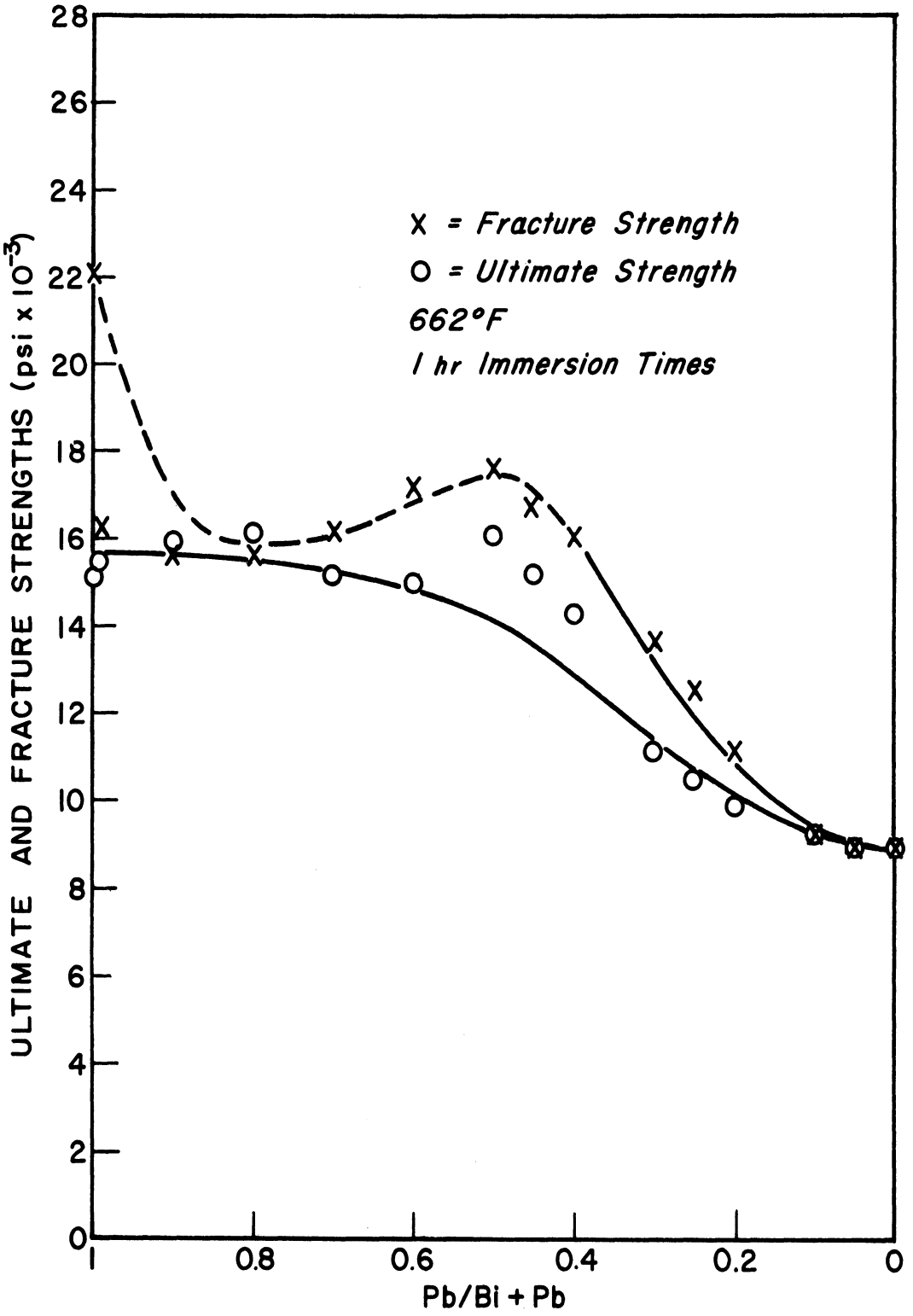


FIGURE 9. Strength of Copper vs. Ratio Pb/Pb + Bi; Grain Size = 0.025 mm; Morgan's Table XXI, (1)

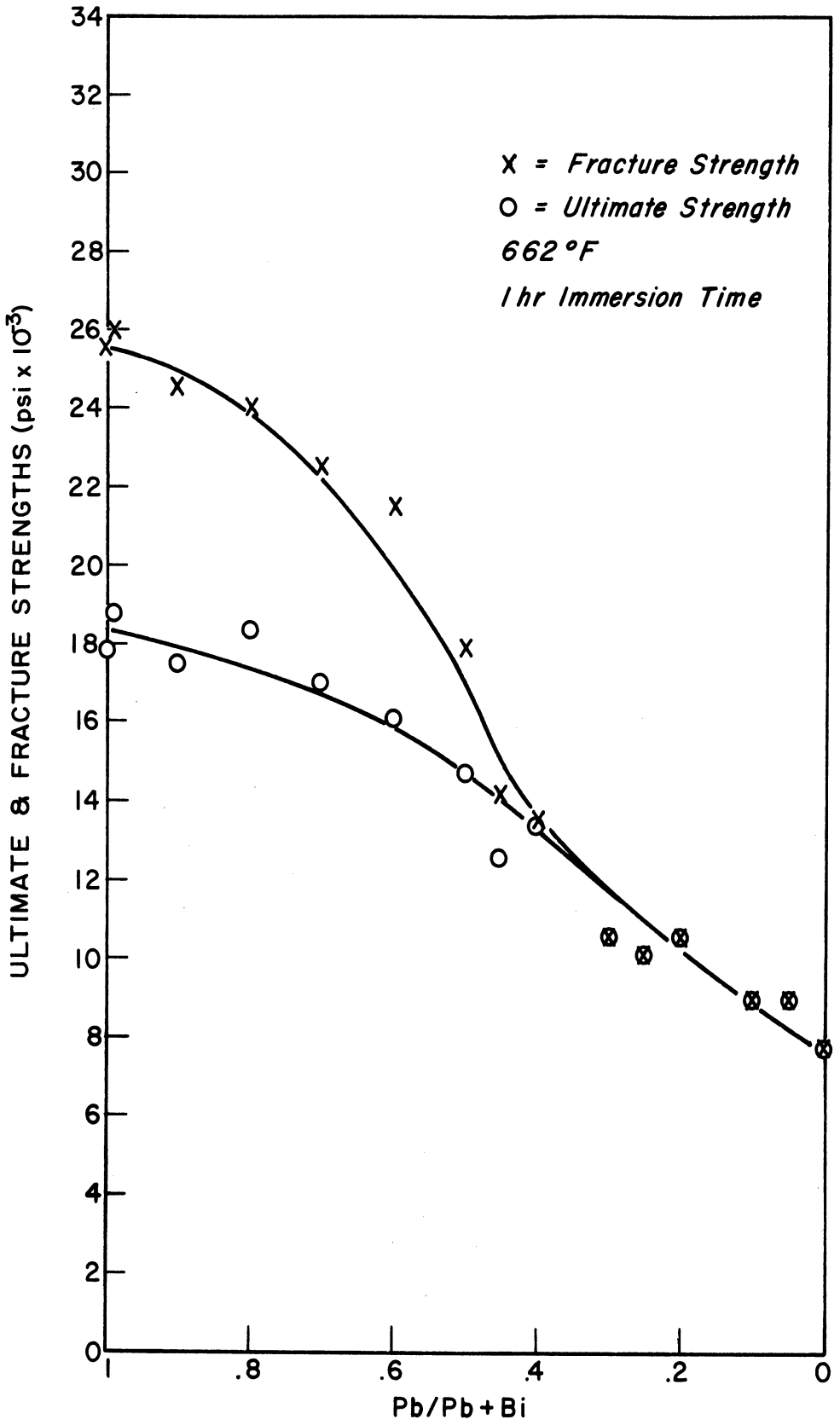


FIGURE 10. Strength of Copper vs. Ratio Pb/Pb + Bi; Grain Size = 0.050 mm; Morgan's Table XXII, (1)

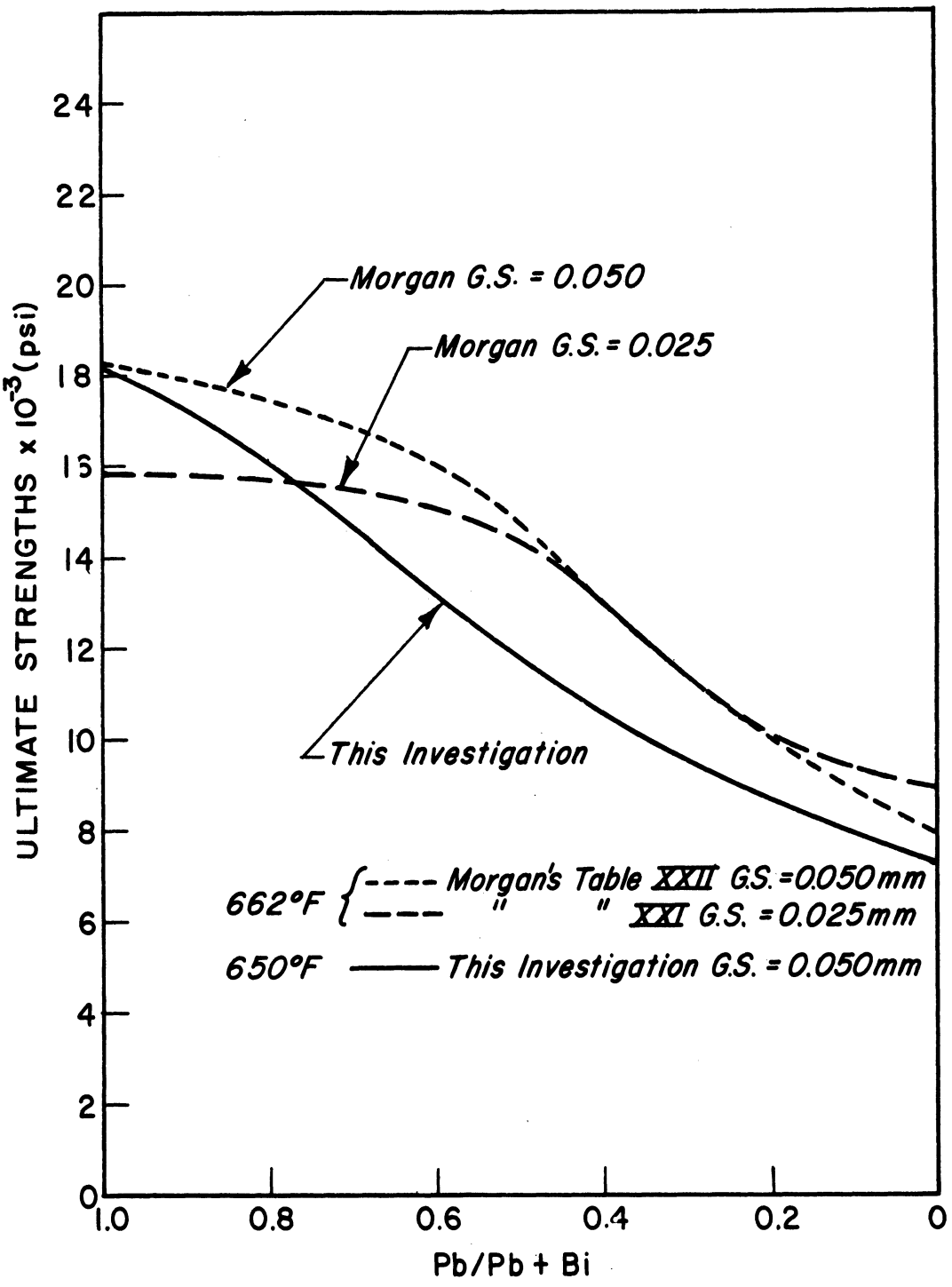


FIGURE 11. Comparison of Ultimate Strengths of Copper Obtained by Morgan and Present Investigation

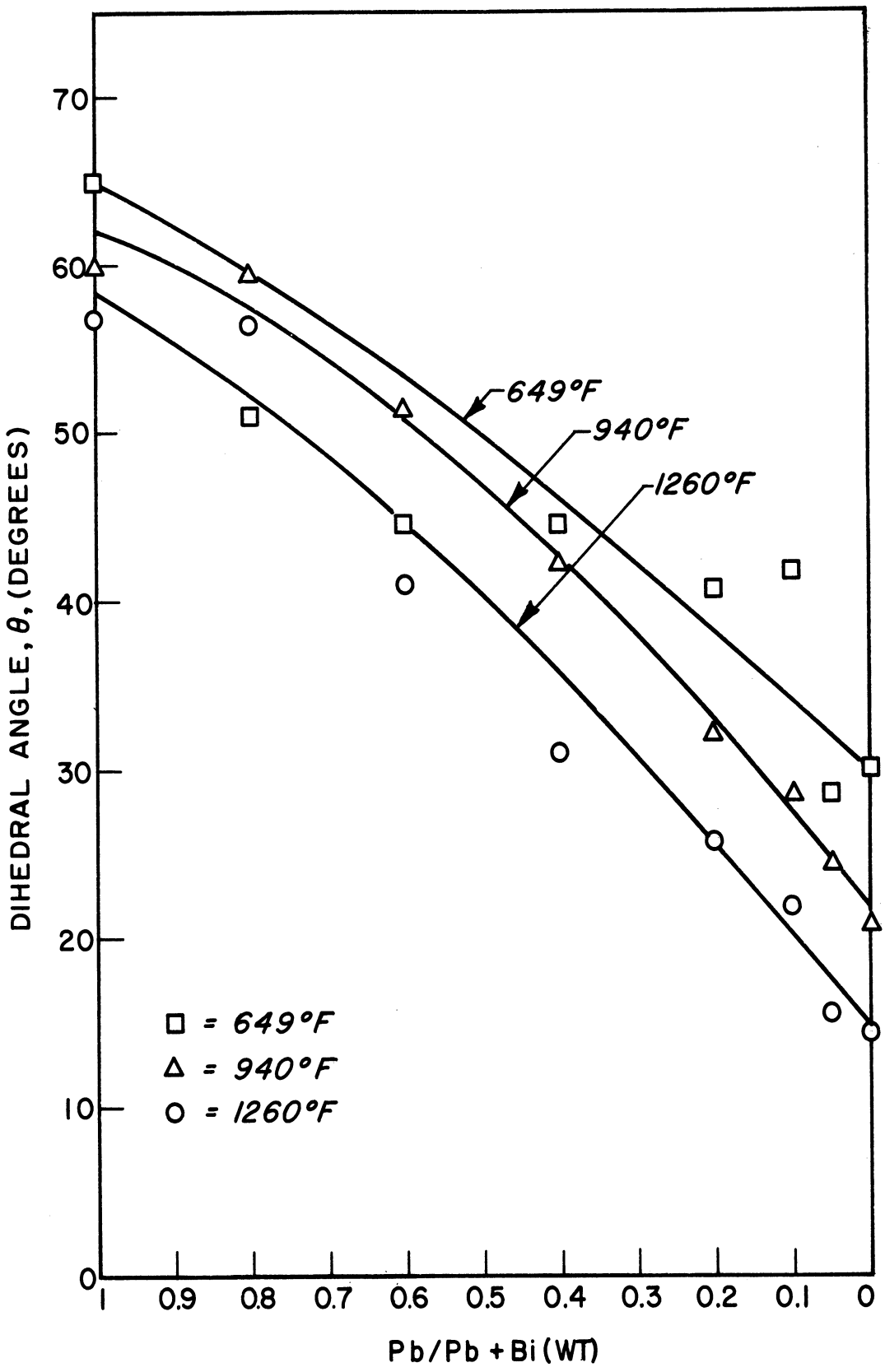


FIGURE 12. Equilibrium Grain Boundary Dihedral Angles vs. Ratio Pb/Pb + Bi

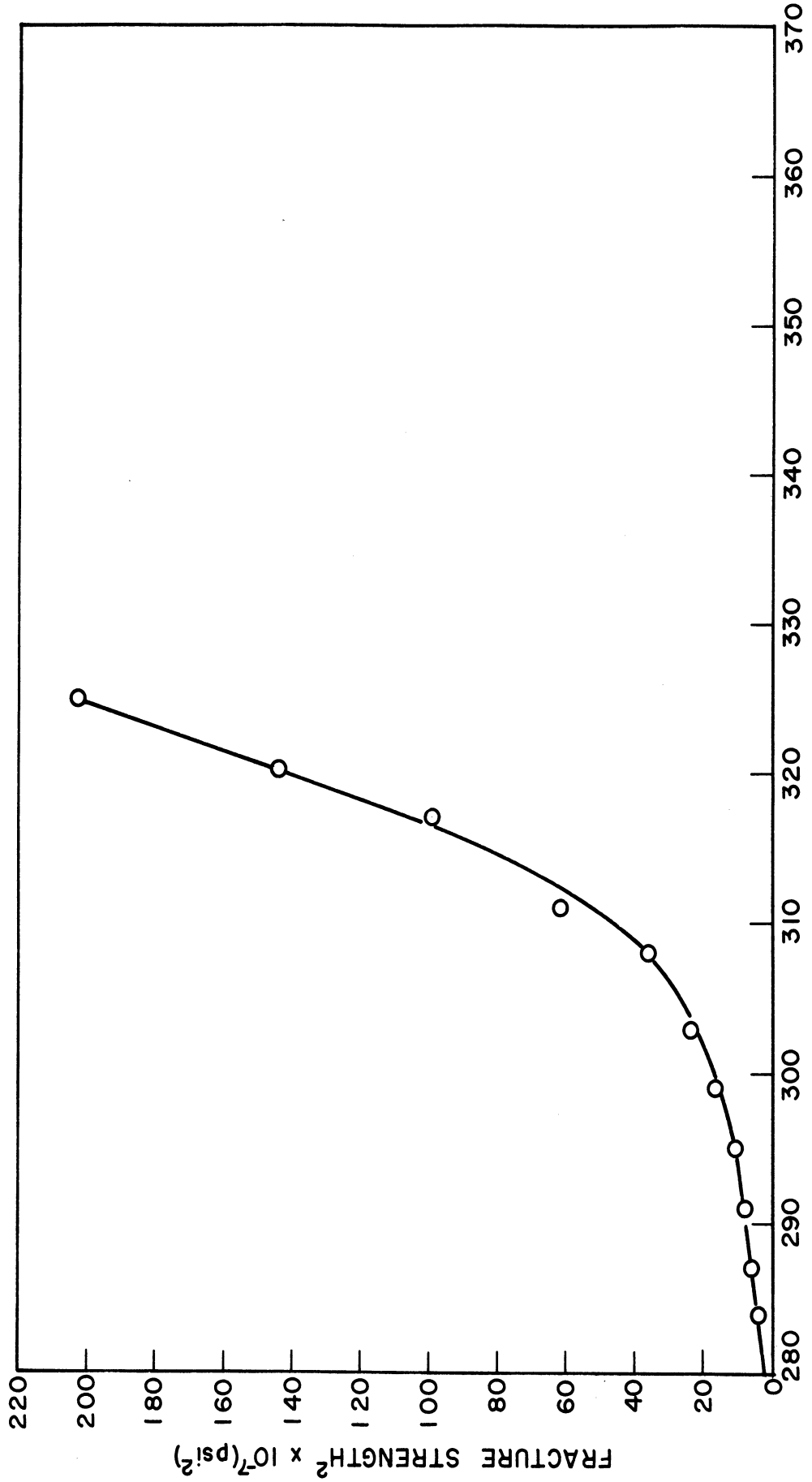


FIGURE 13. Fracture Strength of Copper vs. Interfacial Free Energies

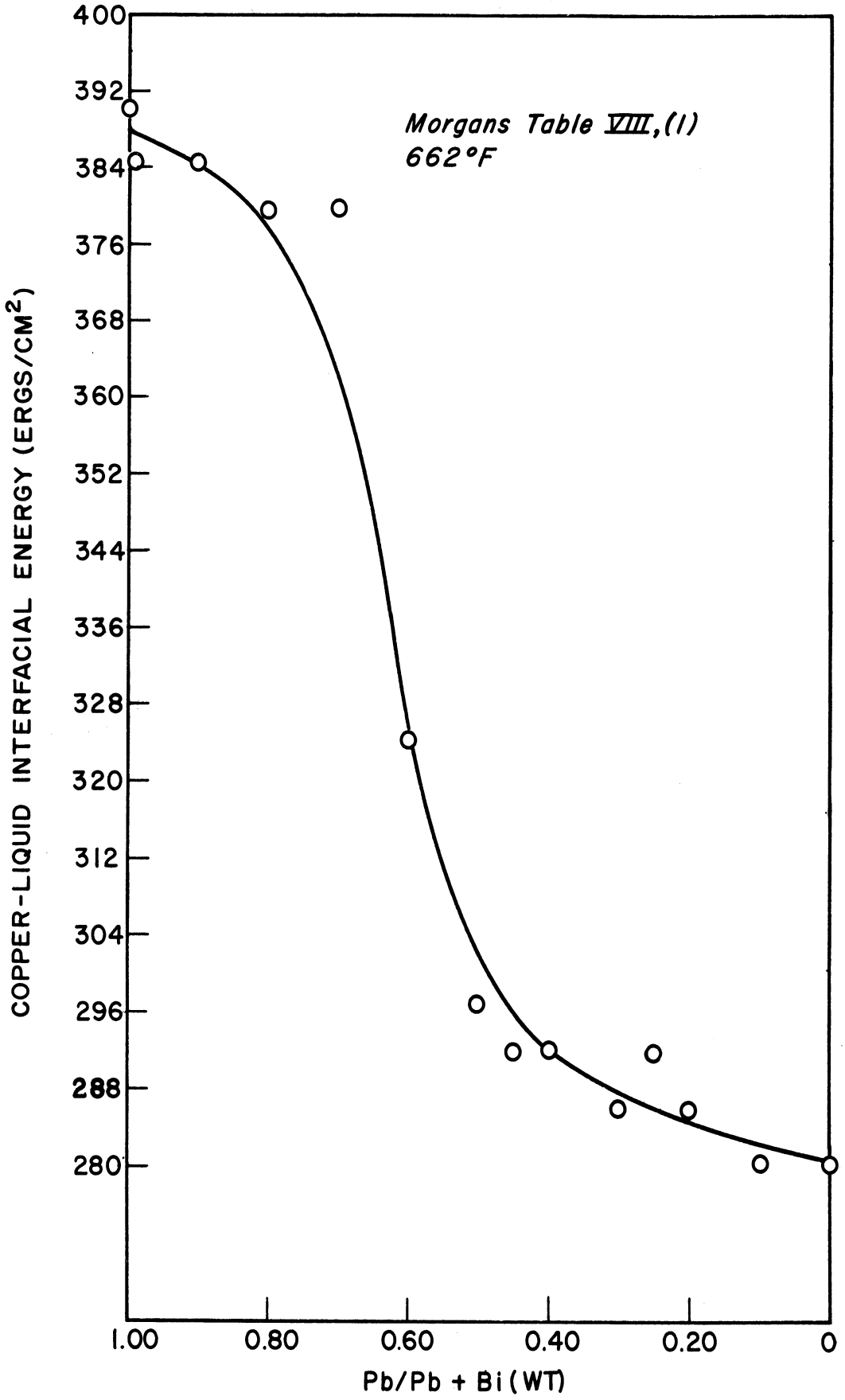


FIGURE 14. Solid Copper, Liquid Lead - Bismuth Interfacial Free Energies

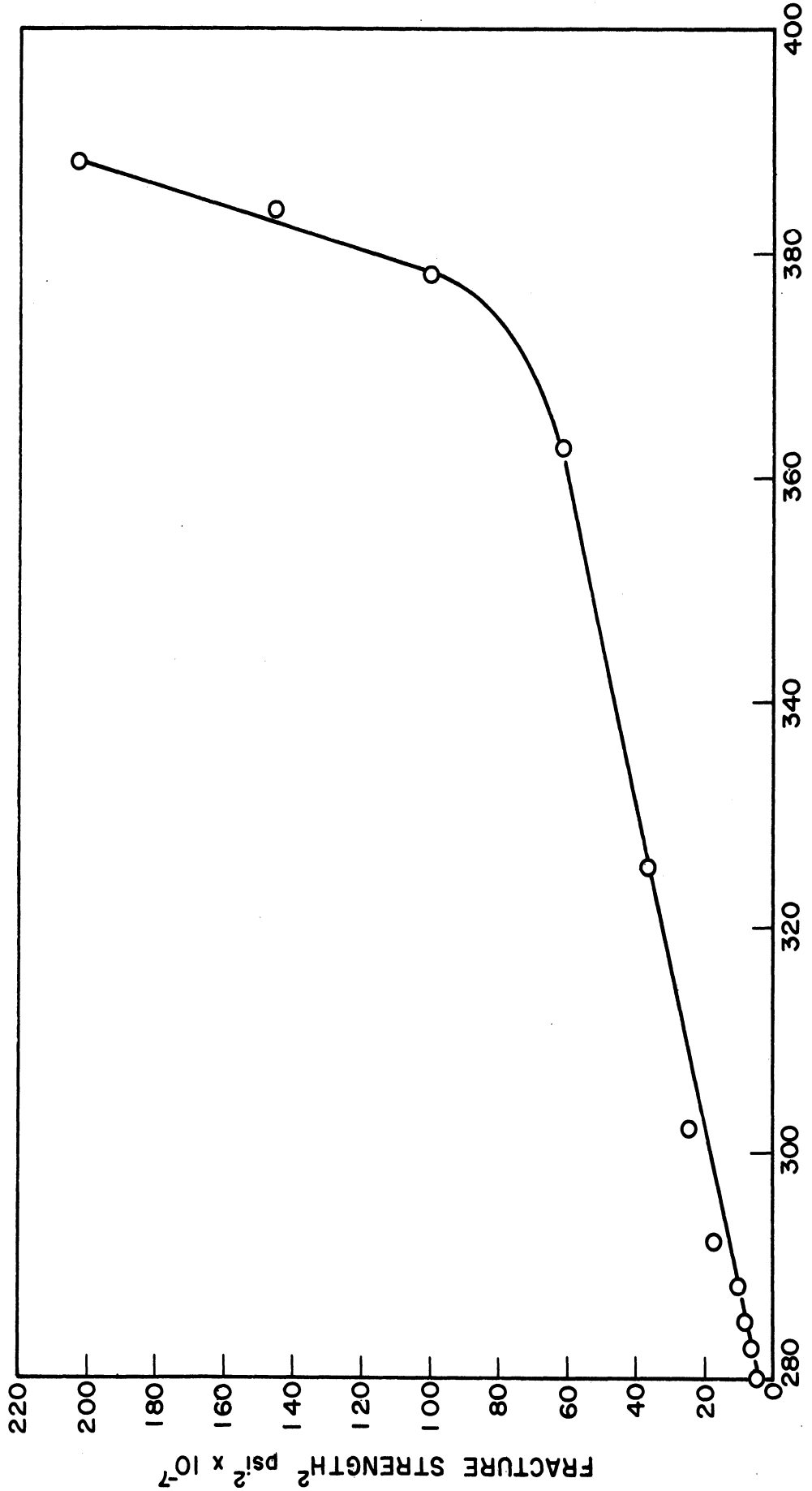


FIGURE 15. Fracture Strength of Copper vs. Morgan's Interfacial Energy Values

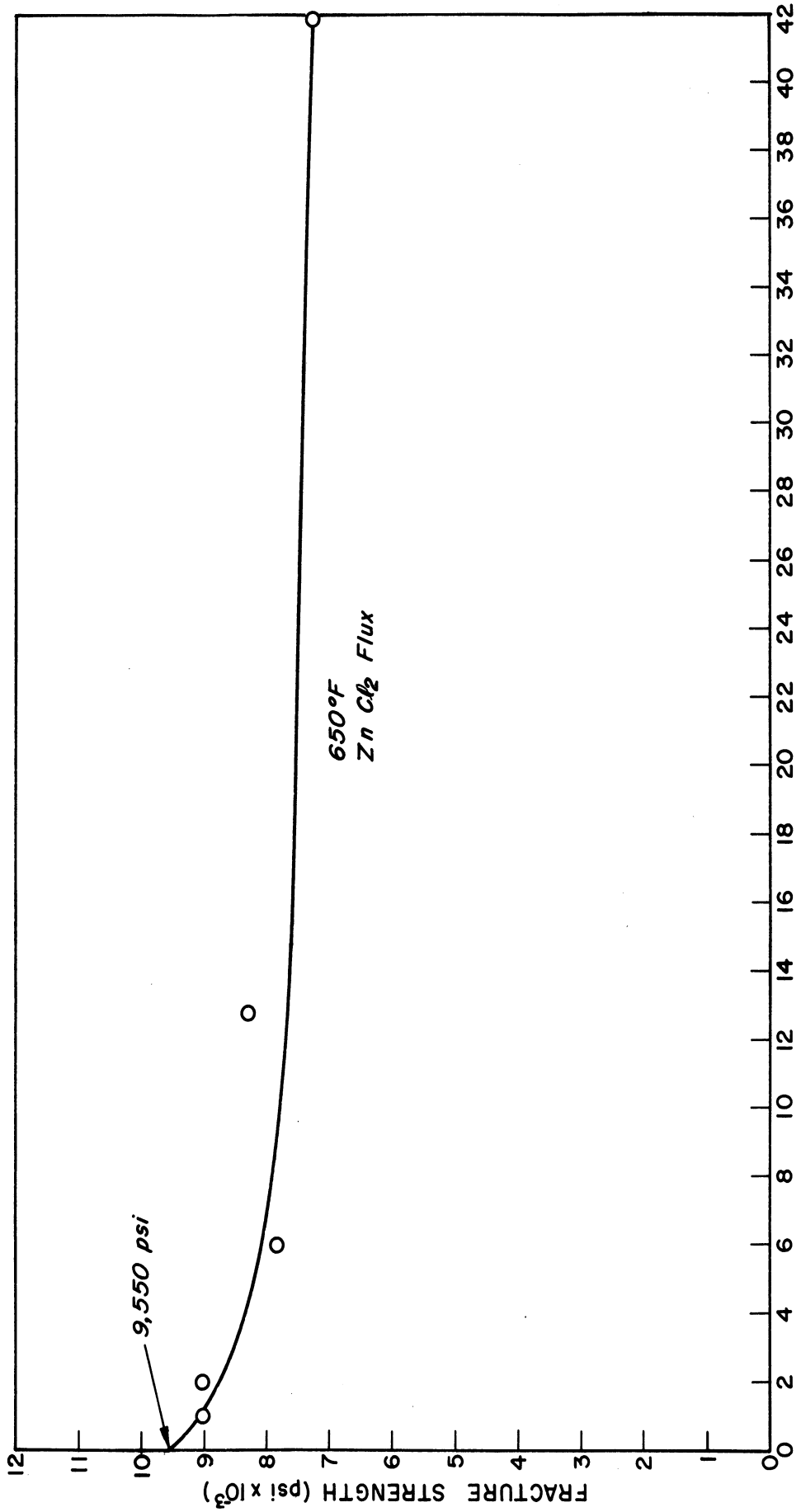


FIGURE 16. Fracture Strength of Copper vs. Time of Immersion in 10% Cd - 90% Bi Environments

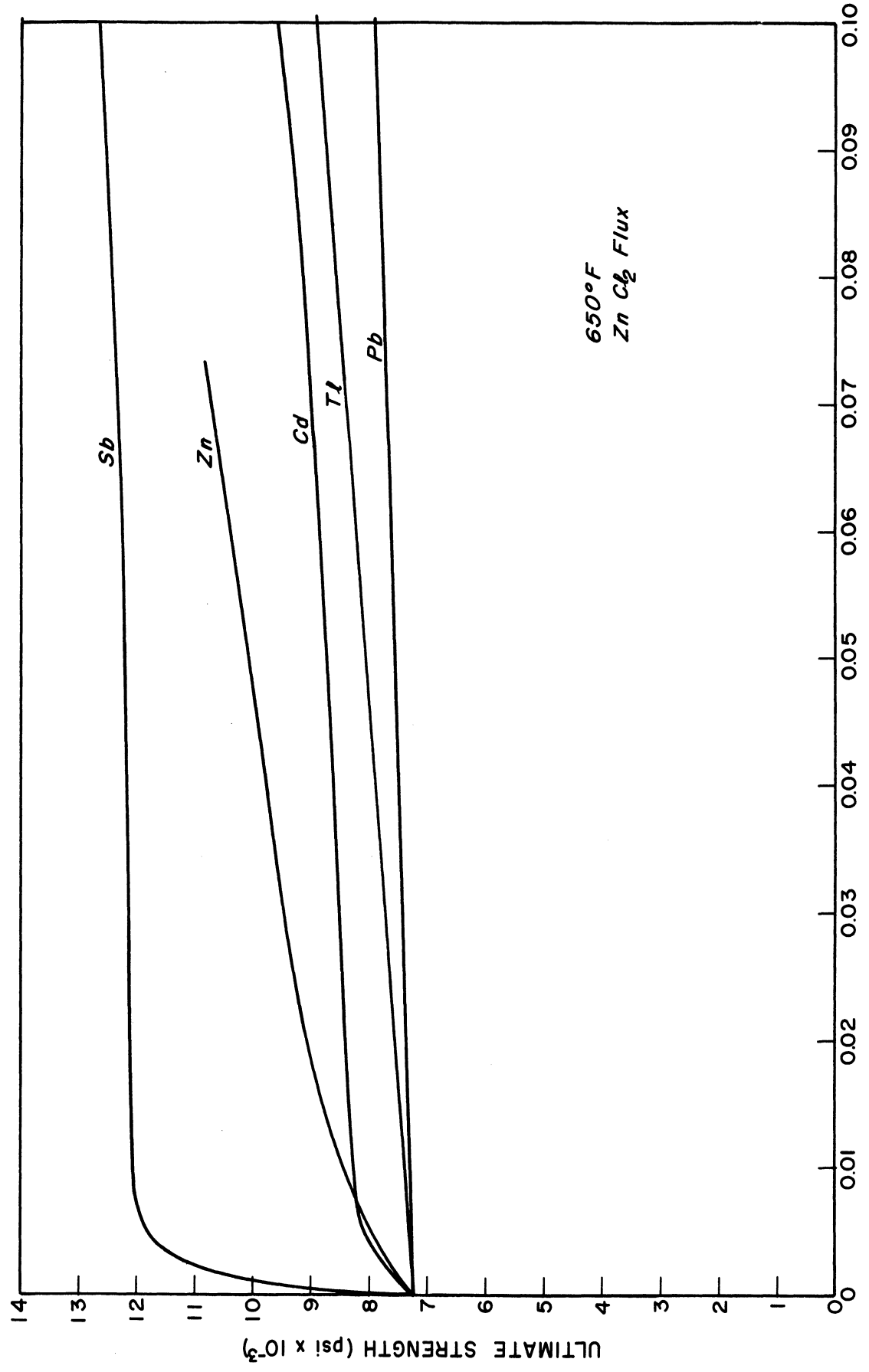


FIGURE 17. Ultimate Strength of Copper Fractures in Liquid Alloys of Bismuth and Small Amounts of Other Elements

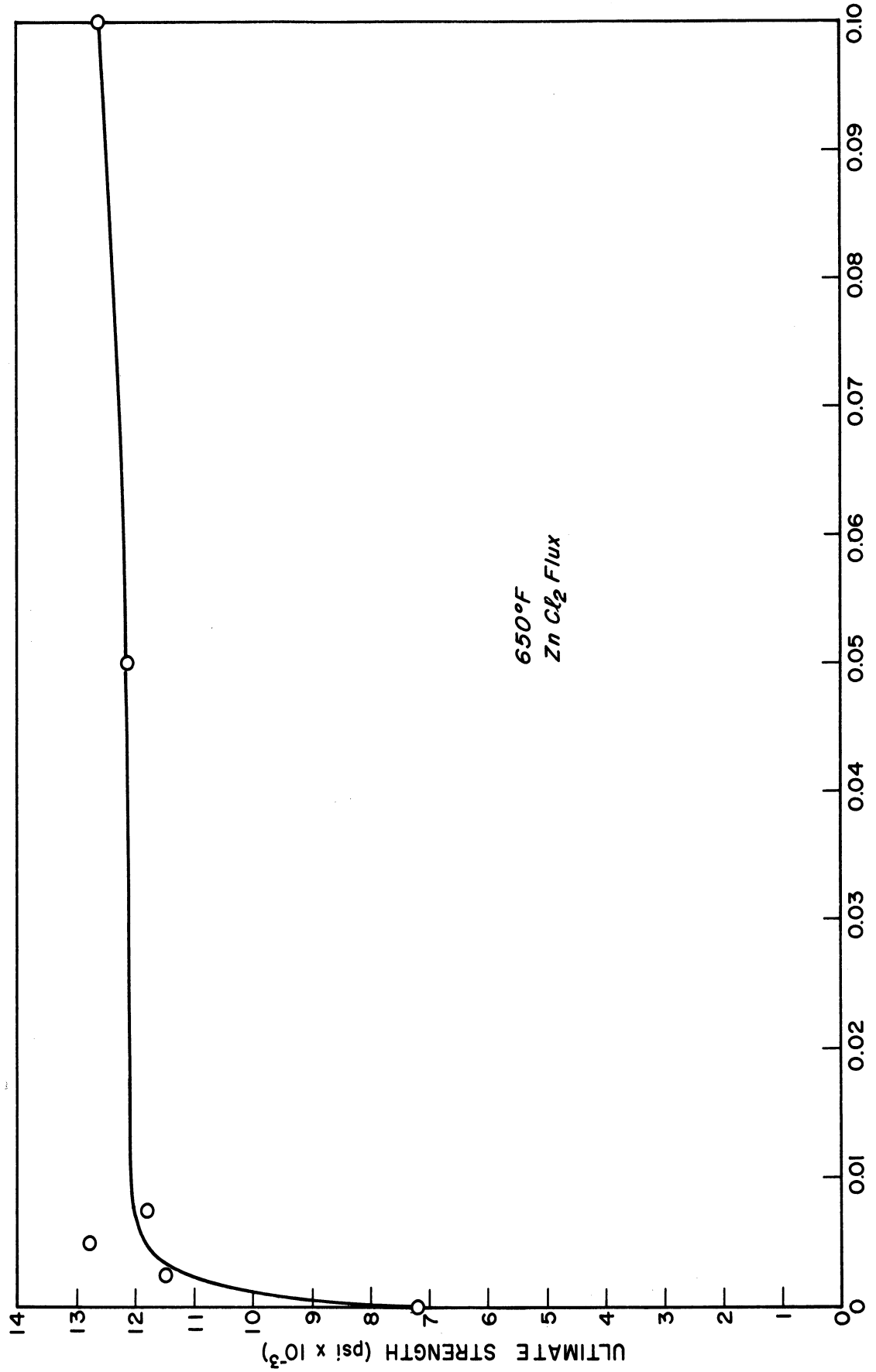


FIGURE 18. Average Ultimate Strength of Copper Fractured in Liquid Bismuth - Antimony Alloy Environments (wt. %)

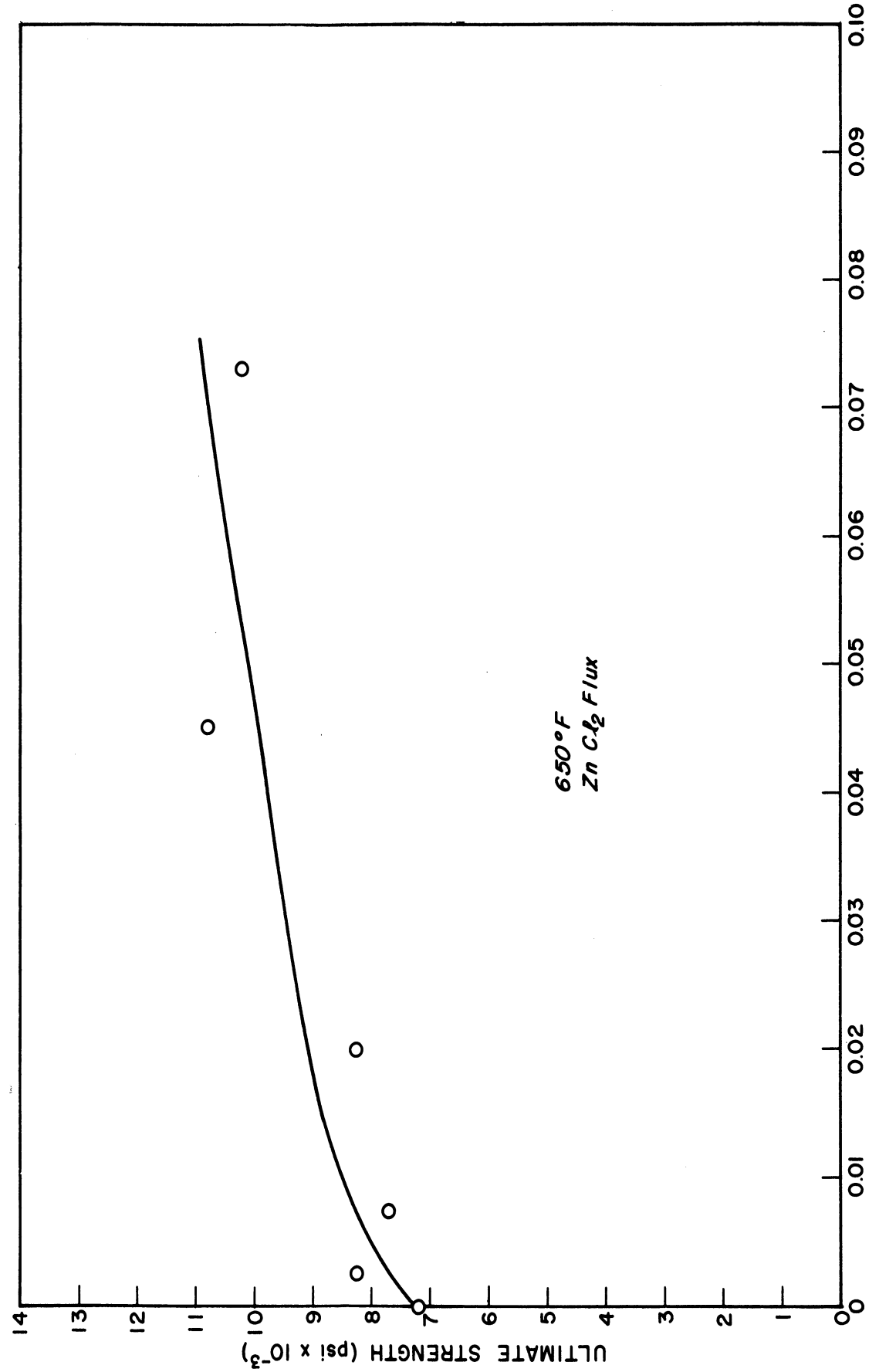


FIGURE 19. Average Ultimate Strength of Copper Fractures in Liquid Bismuth - Zinc Alloy Environments (wt. %)

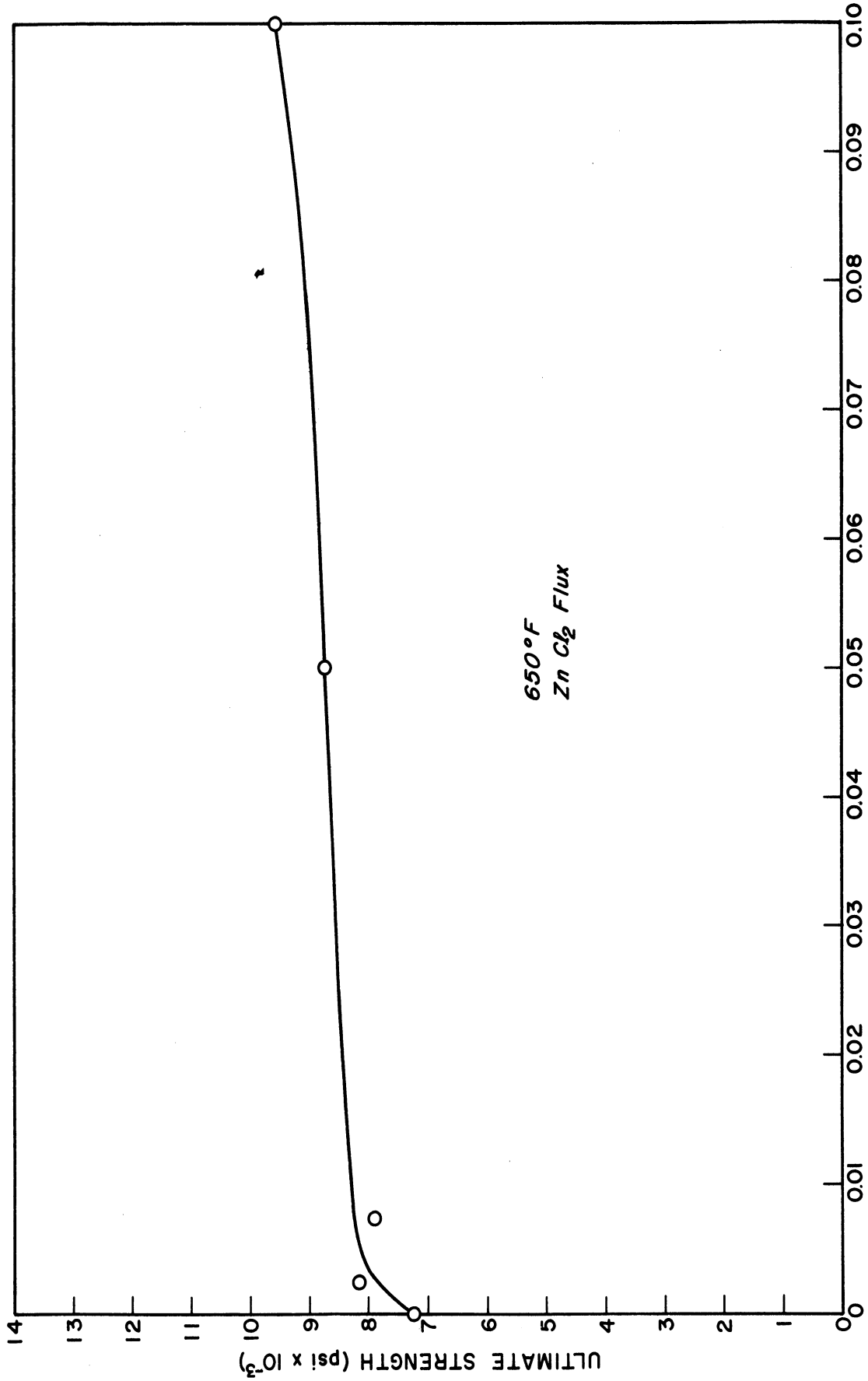


FIGURE 20. Average Ultimate Strength of Copper Fractured in Liquid Bismuth - Cadmium Alloy Environments (wt. %)

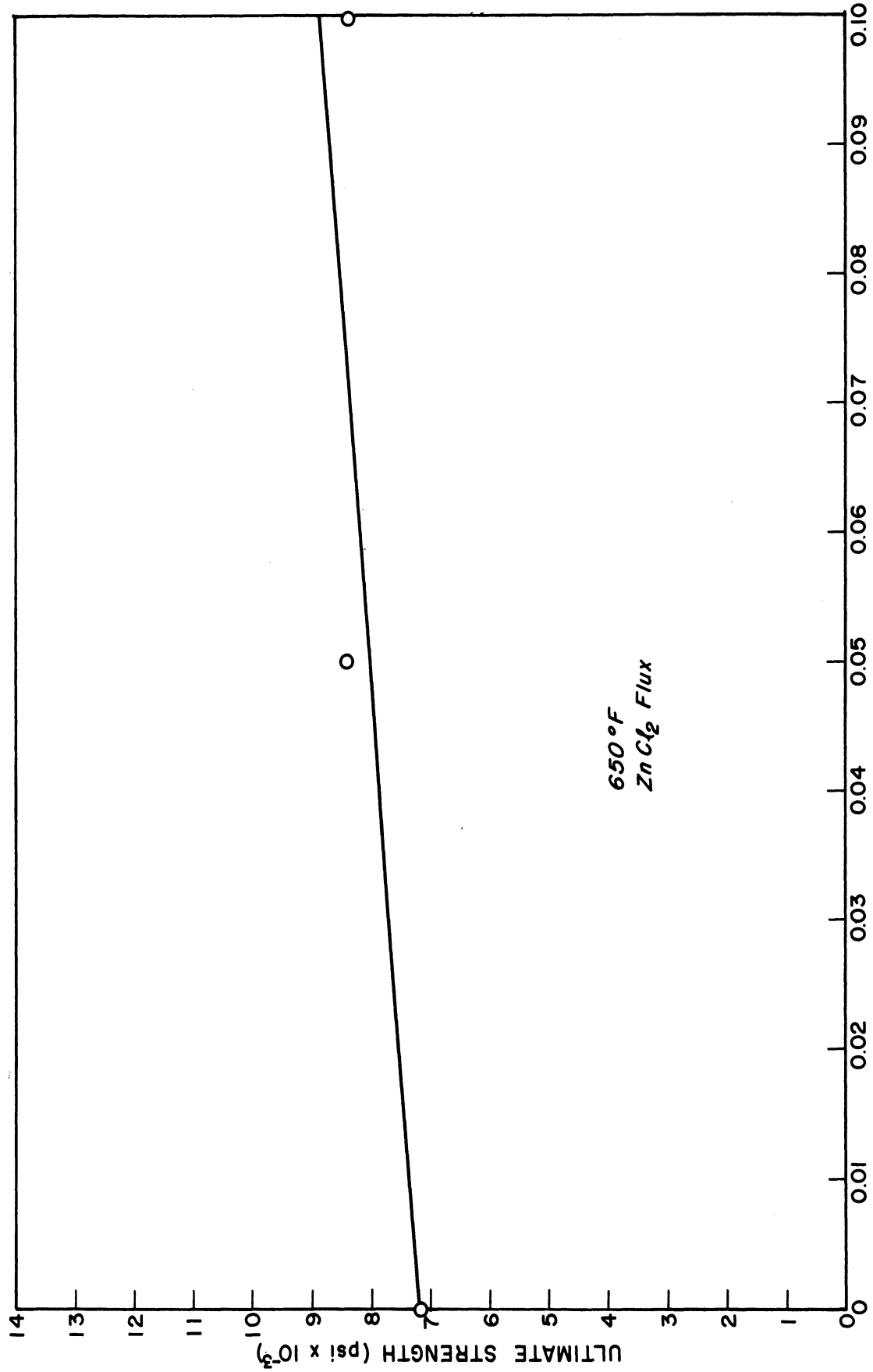


FIGURE 21. Average Ultimate Strength of Copper Fractured in Liquid Bismuth - Thallium Alloy Environments (wt. %).

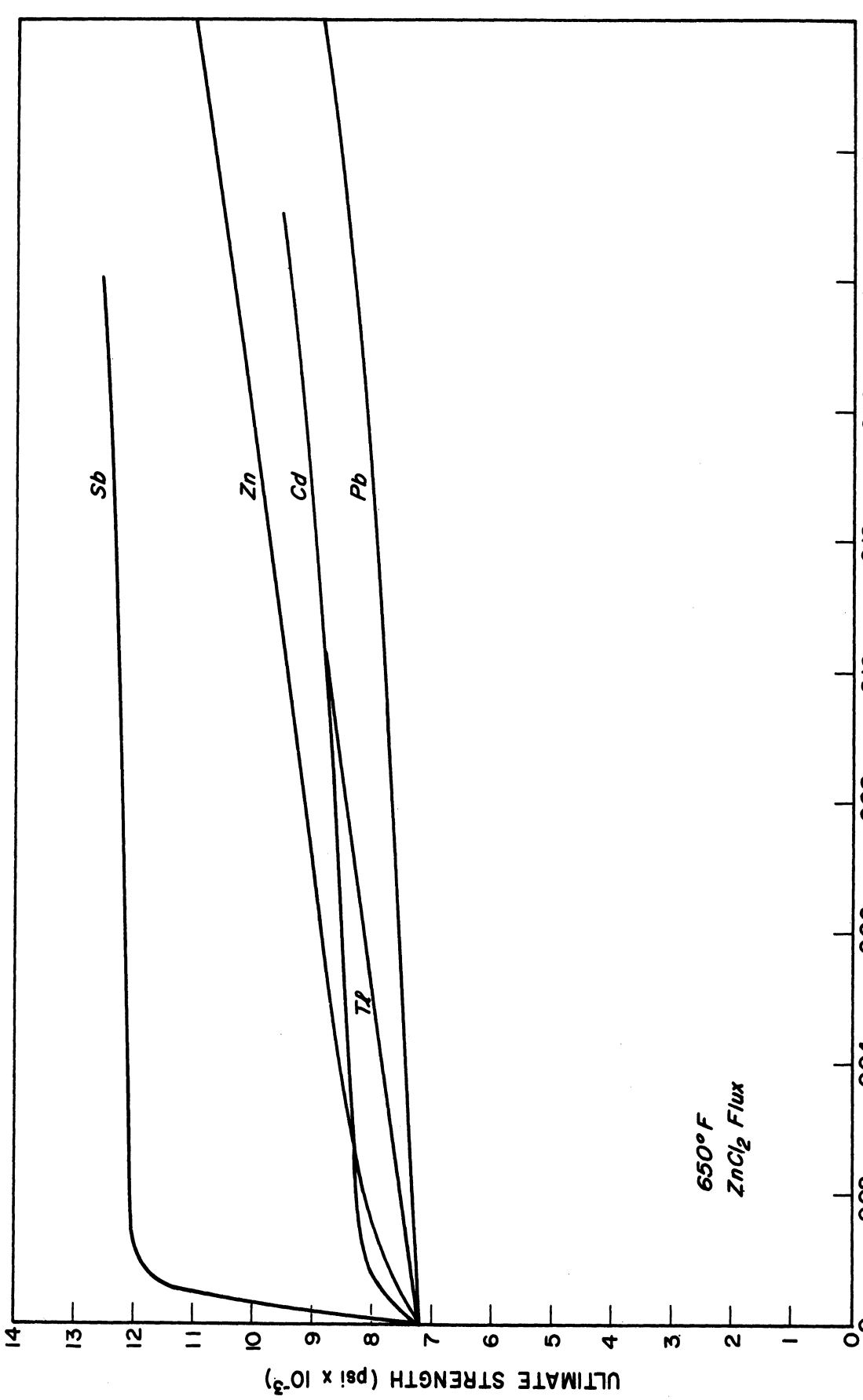


FIGURE 22. Ultimate Strength of Copper Fractured in Liquid Alloys of Bismuth and Small Amounts of Other Elements (atom %)

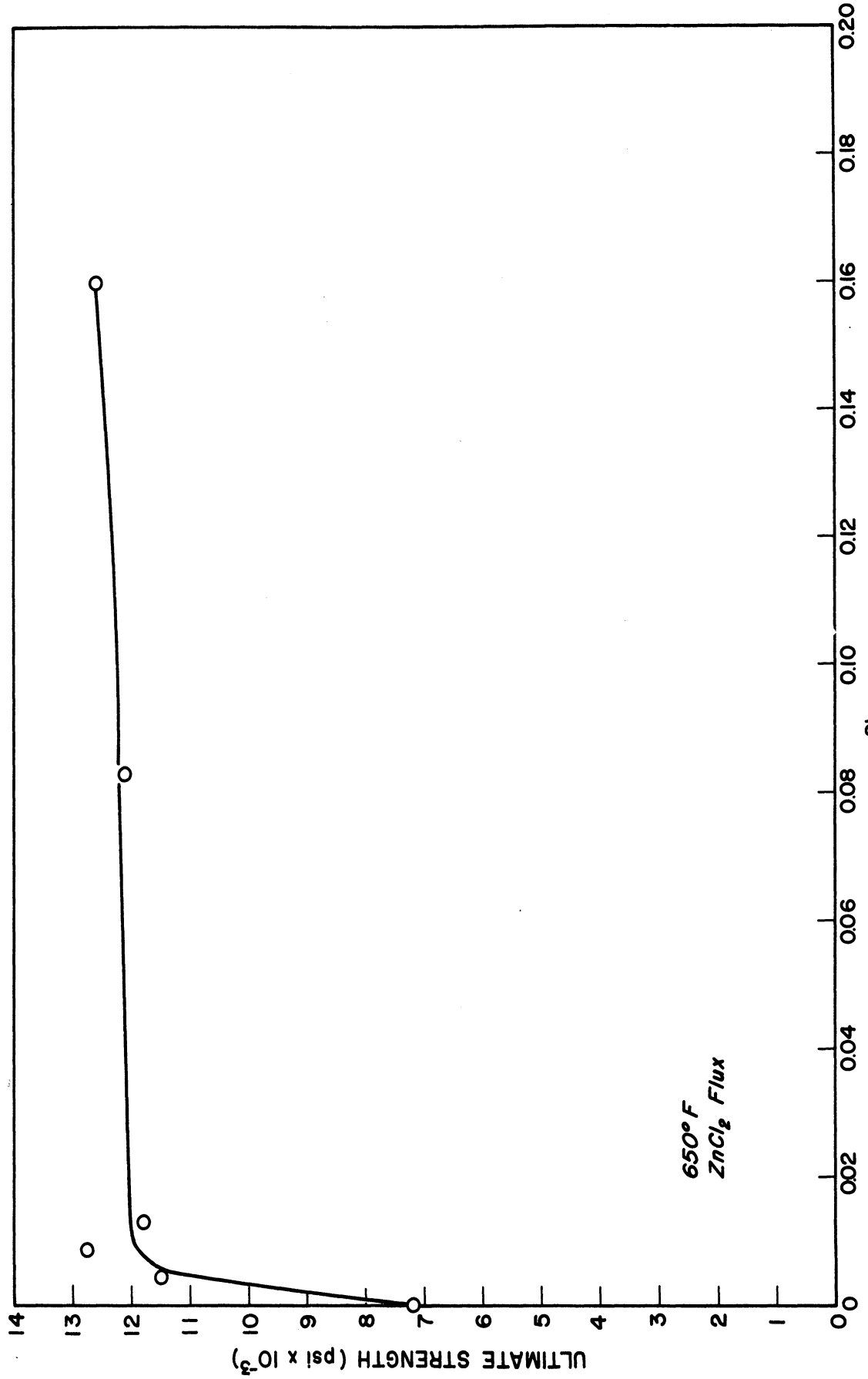


FIGURE 23. Average Ultimate Strength of Copper Fractured in Liquid Bismuth - Antimony Alloy Environments (atom %)

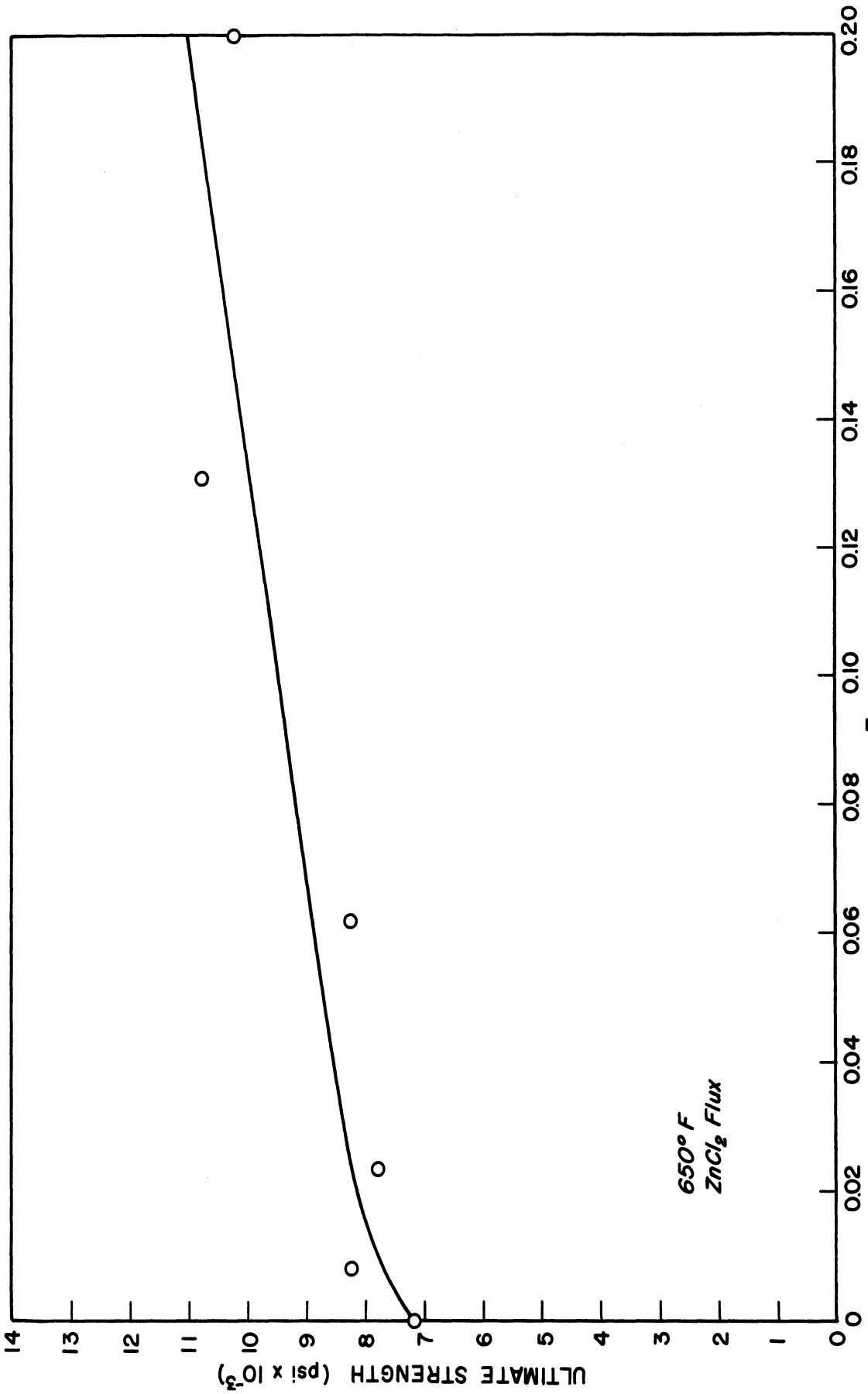


FIGURE 24. Average Ultimate Strength of Copper Fractured in Liquid Bismuth Alloy Environments (atom %)

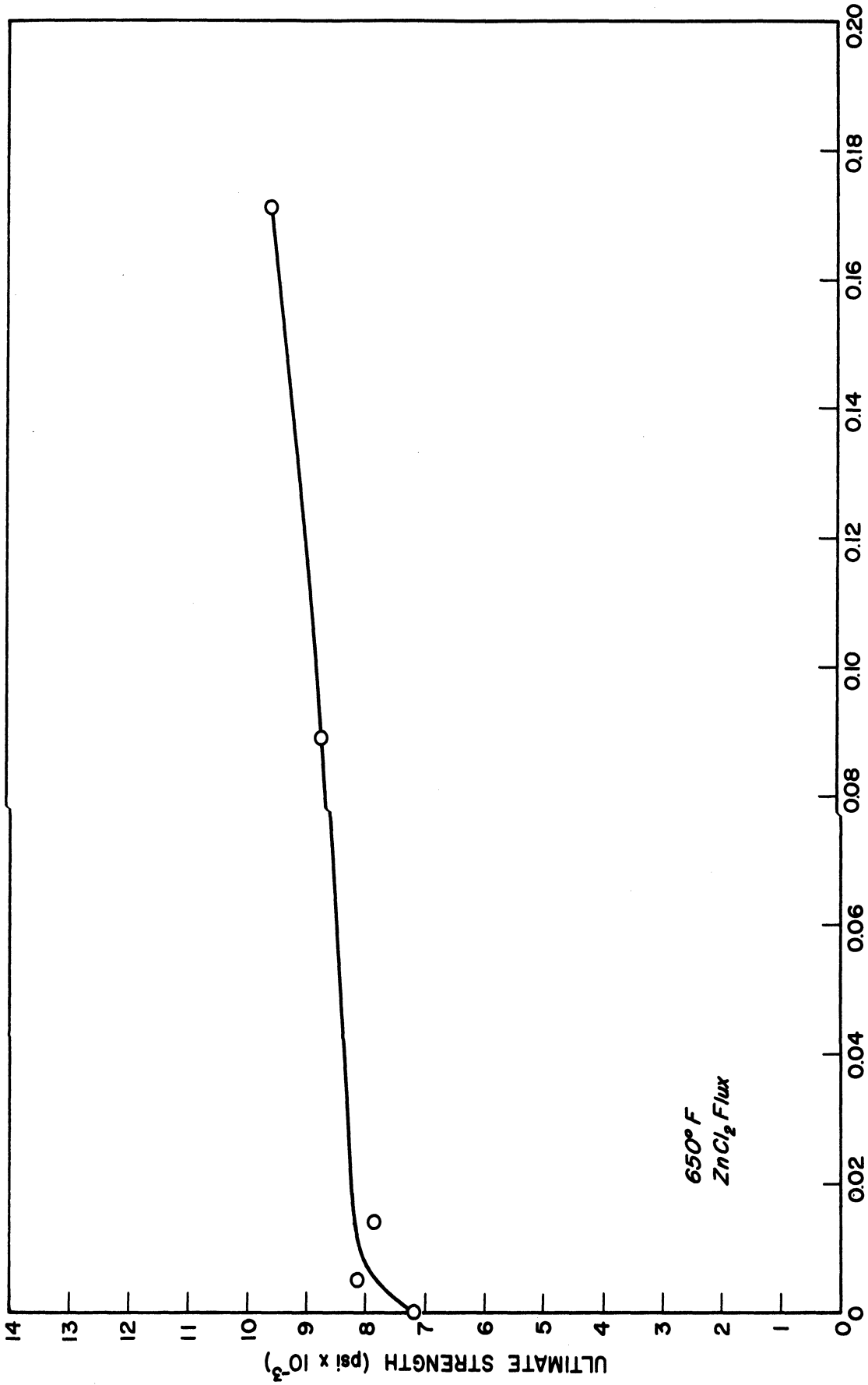


FIGURE 25. Average Ultimate Strength of Copper Fractured in Liquid Bismuth - Cadmium Alloy Environments (atom %)

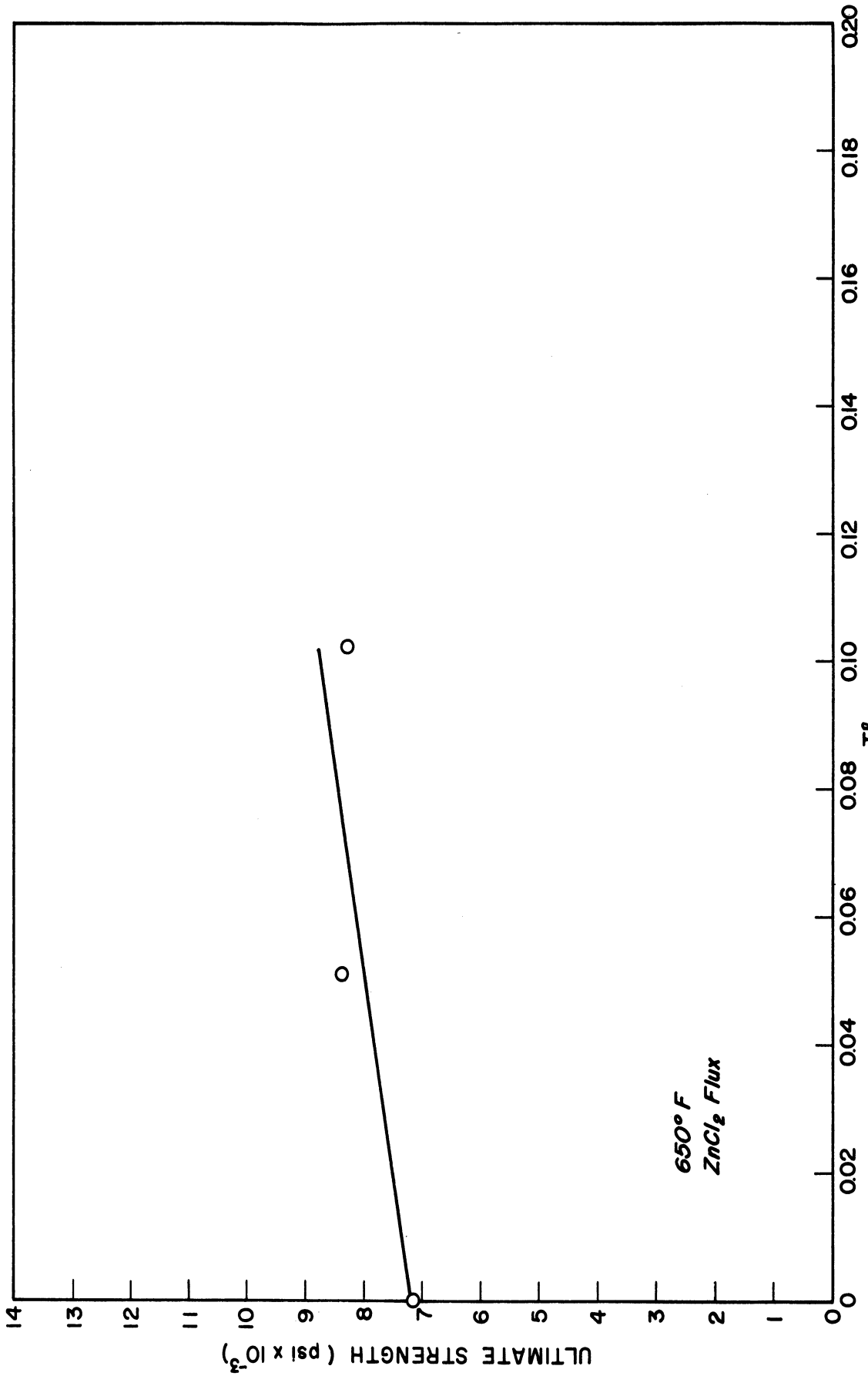


FIGURE 26. Average Ultimate Strength of Copper Fractured in Liquid Bismuth - Thallium Alloy Environments (atom %)

Fig. 27. Copper specimen fractured at 650°F with no environment present. 100X

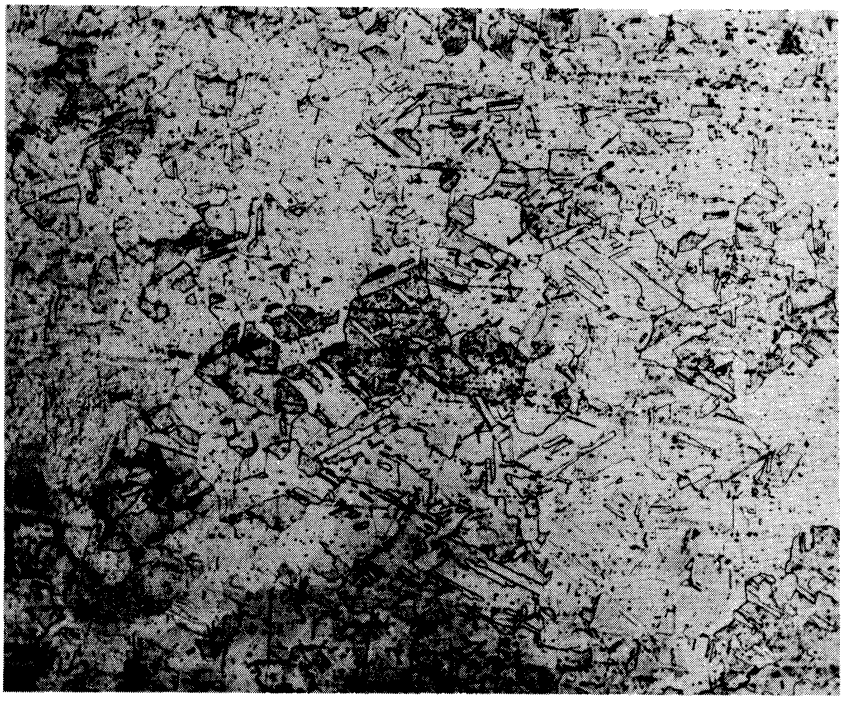


Fig. 28. Microstructure of copper prior to fracture. 100X

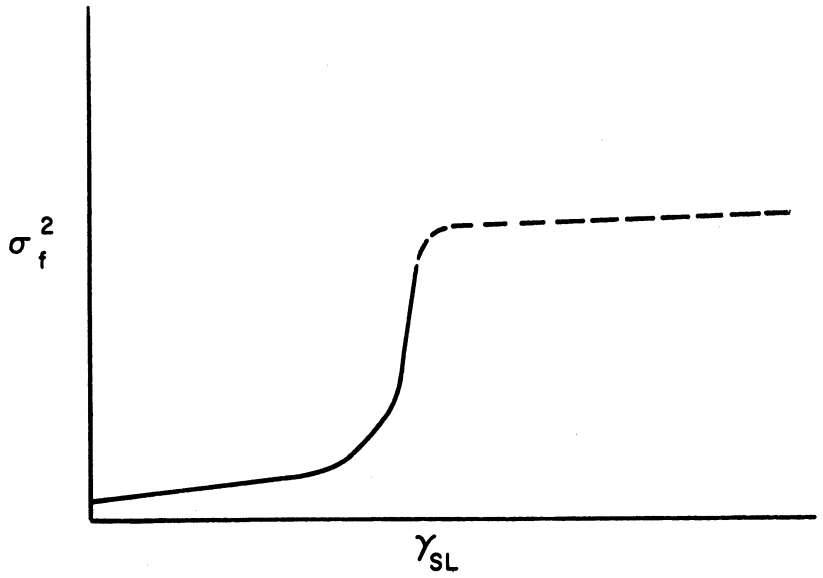


FIGURE 29. Sketch Showing Possible Behavior of Fracture Strength as a Function of the Solid - Liquid Interfacial Energy

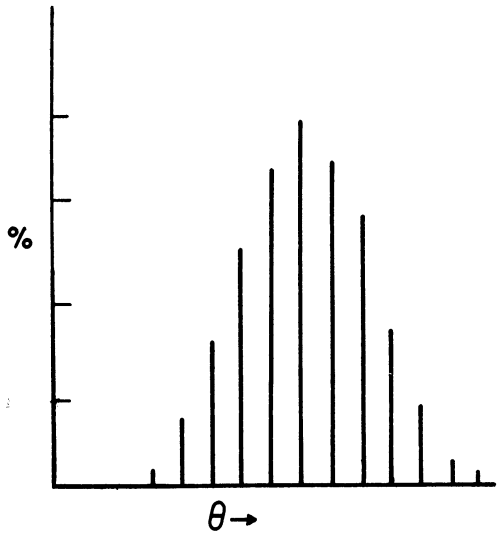


FIGURE 30. Schematic Frequency Distribution of Observed Internal Angles of Liquid Phase in Microsection

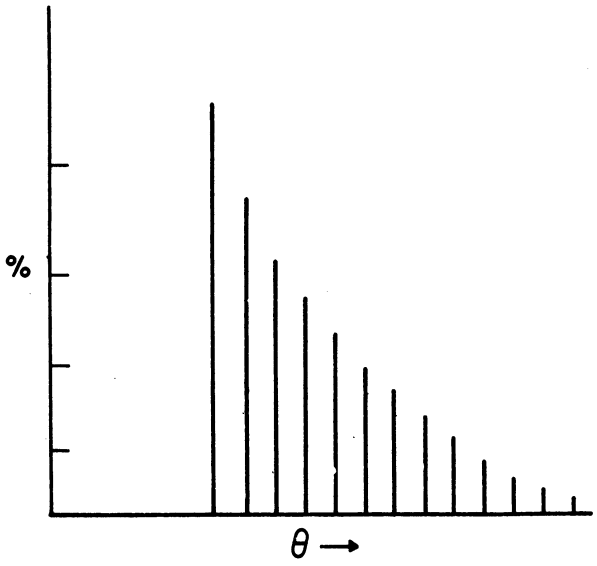


FIGURE 31. Schematic Frequency Distribution of Observed Internal Angles of Liquid Phase in Microsection

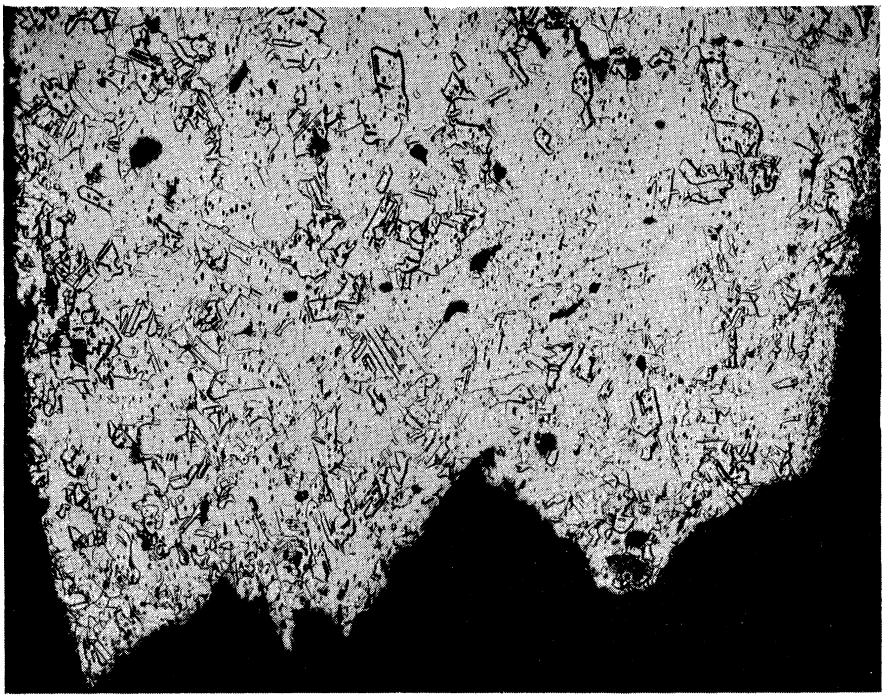


Fig. 32. Copper specimen fractured at 650°F in 100% lead environment. 100X

Fig. 33. Copper specimen fractured at 650°F in 100% bismuth environment. 50X

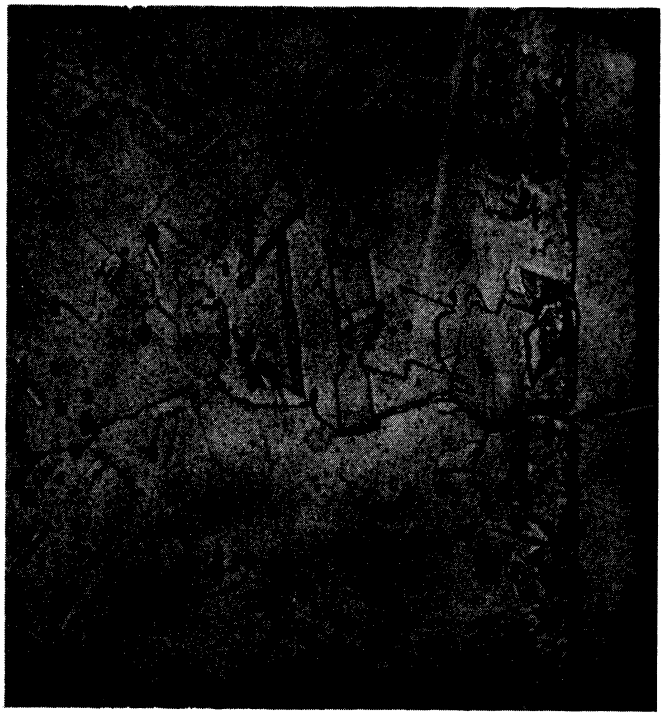


Fig. 34. Copper specimen fractured at 650°F in 100% bismuth environment. 500X

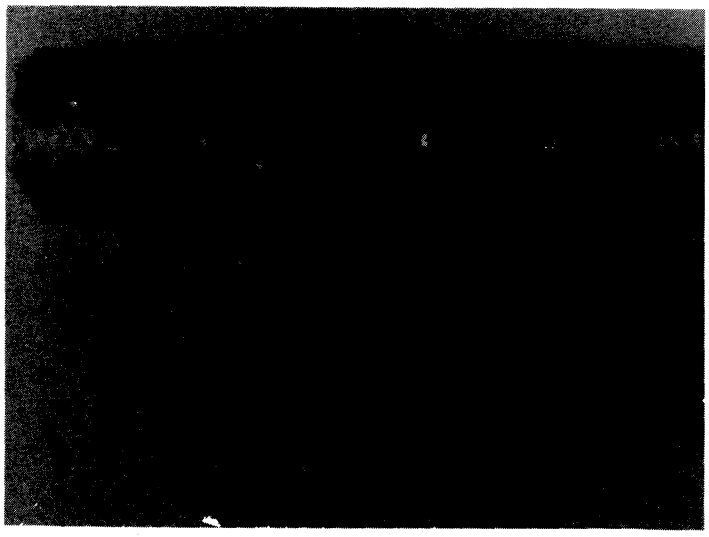


Fig. 35. Copper specimen fractured at 650°F in 100% bismuth environment. 13X

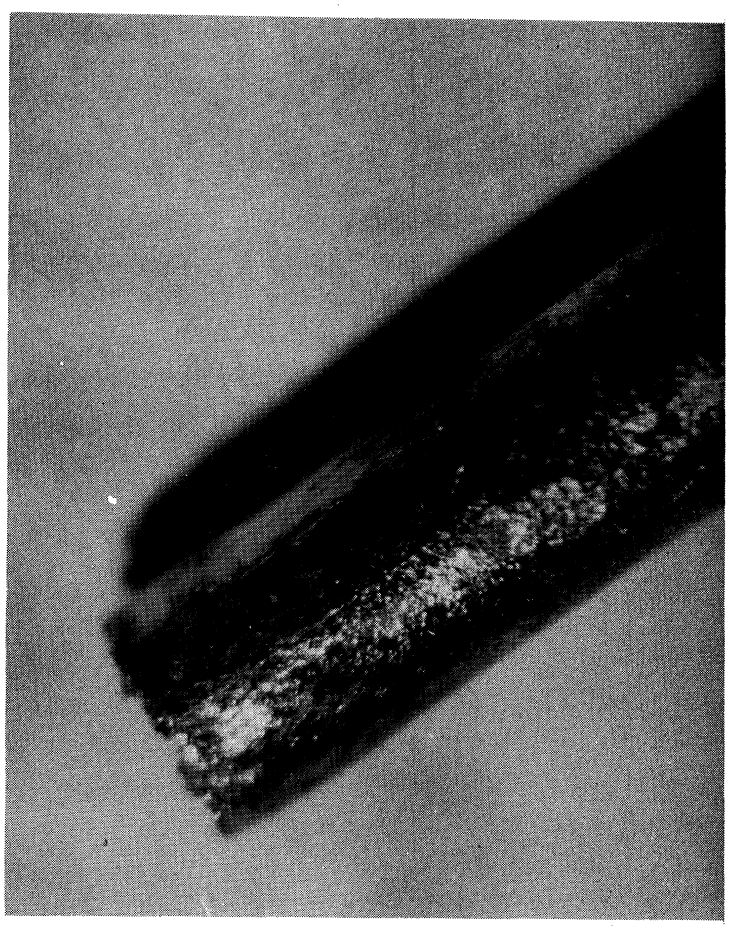


Fig. 36. Copper specimen fractured at 650°F in 100% bismuth environment. 20X

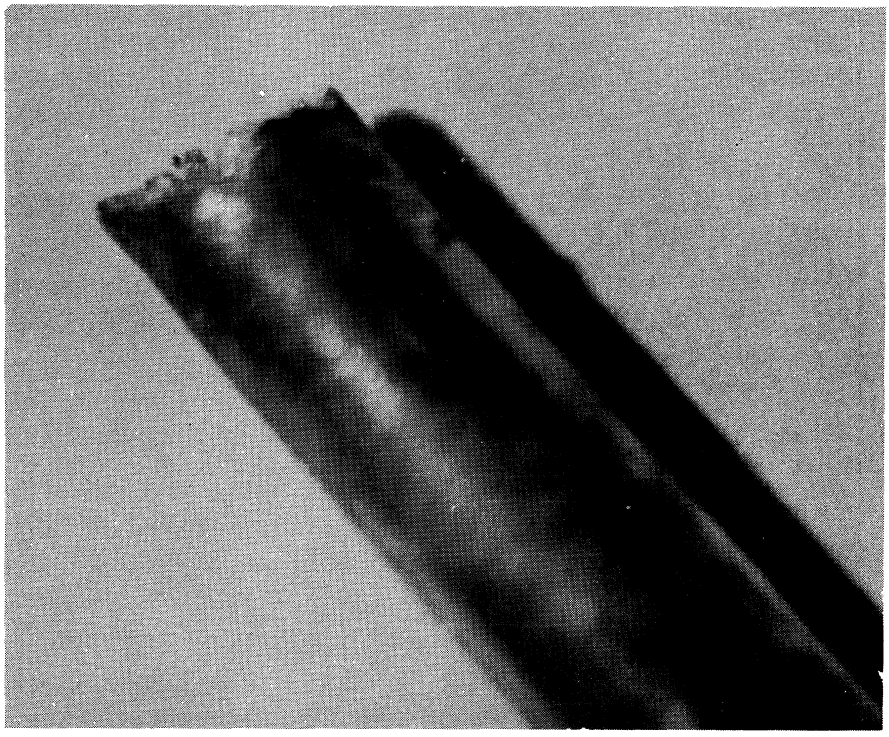


Fig. 37. Copper specimen fractured at 650°F in 80% Bi - 20% Pb environment. 20X

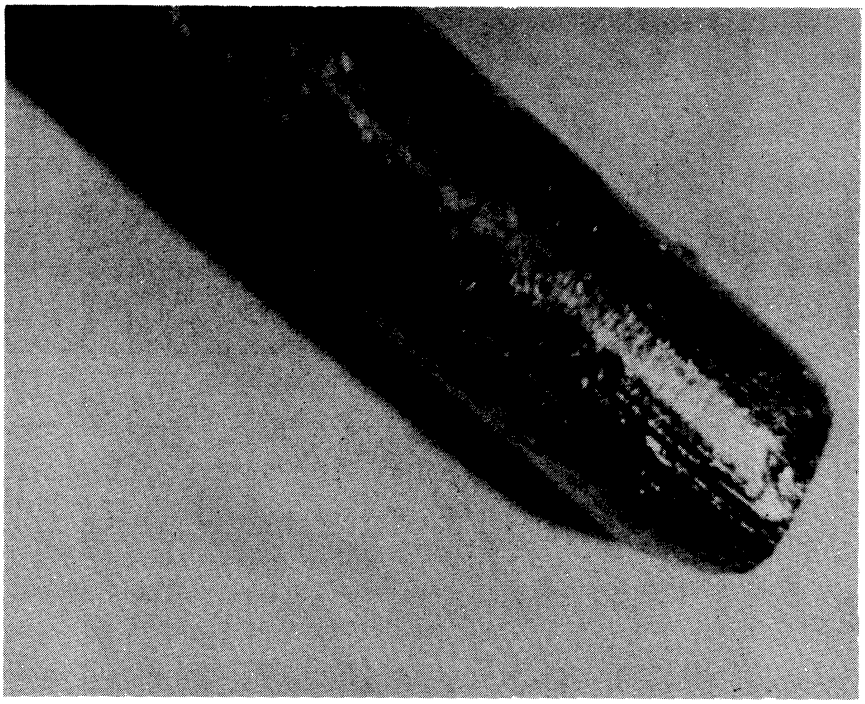


Fig. 38. Copper specimen fractured at 650°F in 60% Bi - 40% Pb environment. 20X

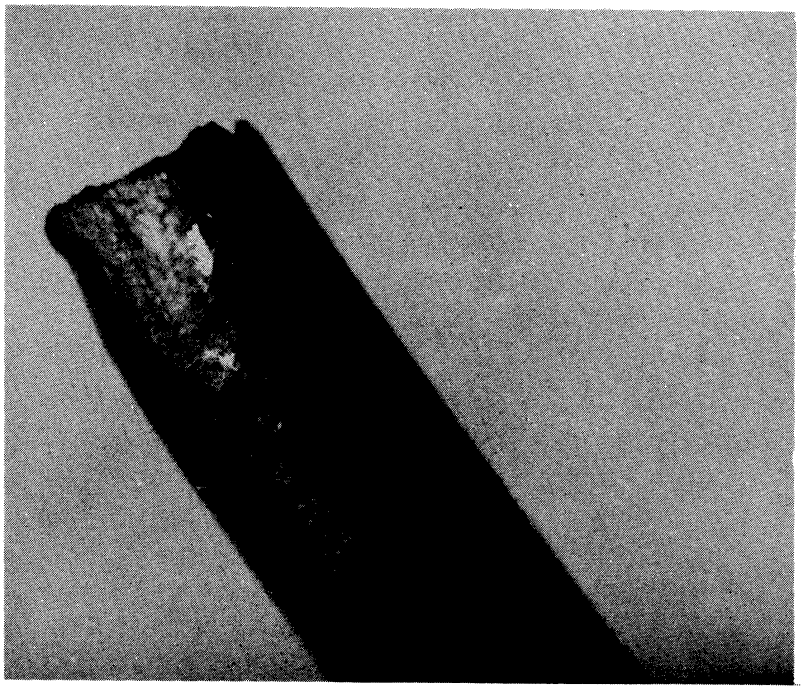


Fig. 39. Copper specimen fractured at 650°F in 60% Bi - 40% Pb environment. 20X

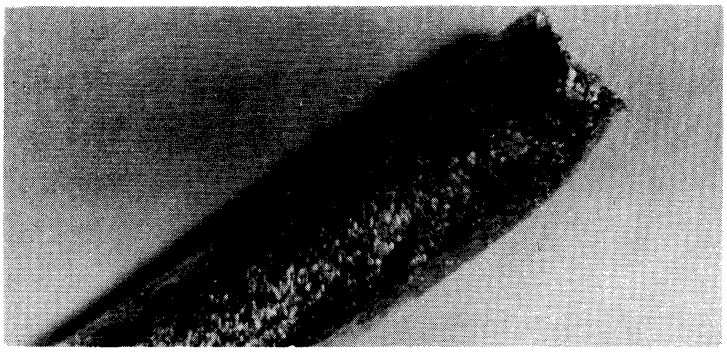


Fig. 40. Copper specimen fractured at 650°F in 40% Bi - 60% Pb environment. 13X

Fig. 41. Copper specimen fractured at 650°F in 20% Bi - 80% Pb environment. 13X

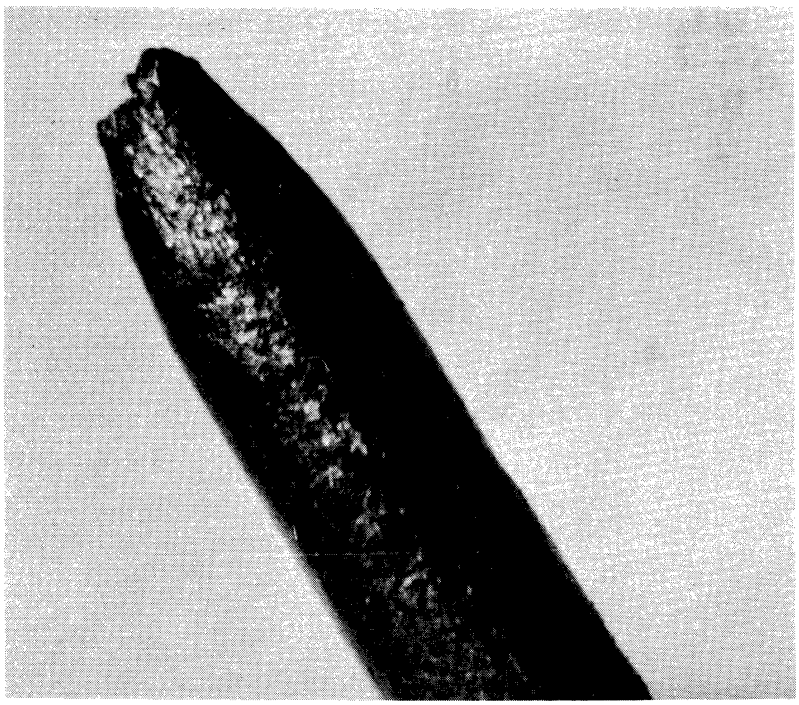


Fig. 42. Copper specimen fractured at 650°F with no environment present. 20X

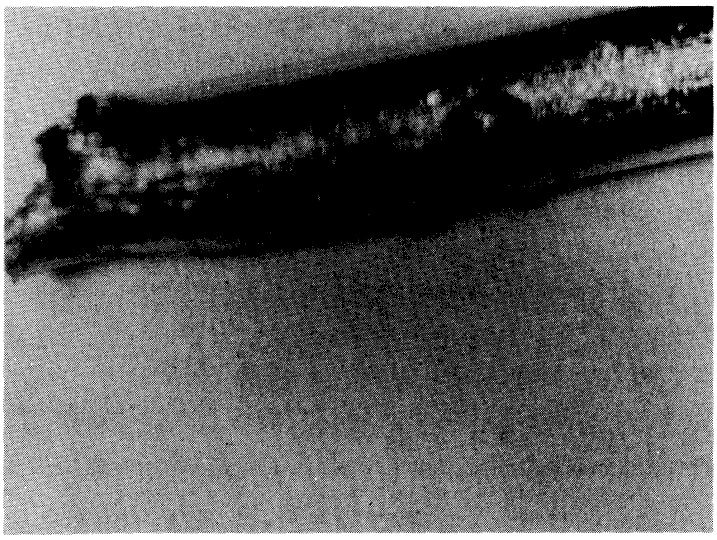


Fig. 43. Copper specimen fractured at 650°F in 60% Bi - 40% Pb environment. 13X

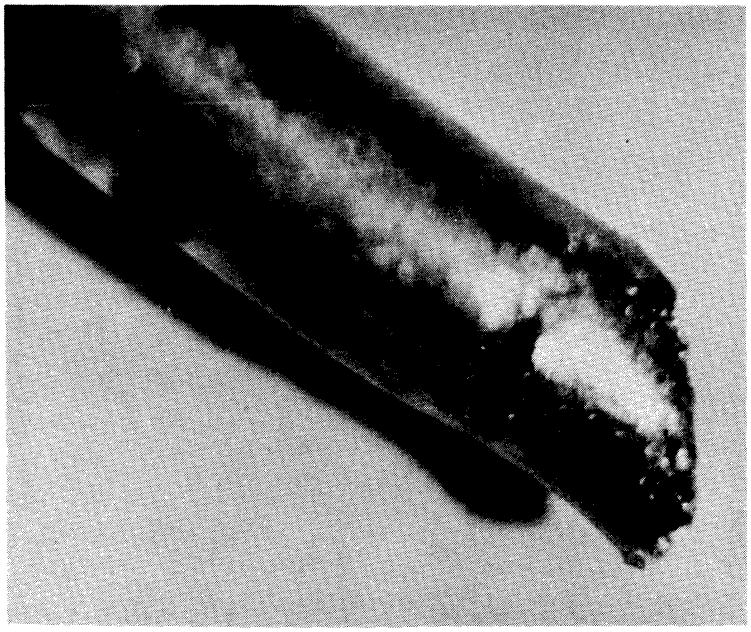


Fig. 44. Copper specimen fractured at 650°F in 60% Bi - 40% Pb environment. 20X

Part II - THE EFFECT OF STRAIN ON THE SURFACE ENERGY OF SOLIDS

PREFACE

It is a pleasure to adknowledge the help of the many people who contributed to this work. In particular the author would like to thank the members of his doctoral committee for their advice and assistance. In addition he would like to thank Professor Wilbur C. Bigelow for assistance in developing the ion bombardment cleaning apparatus, and Professors David V. Ragone and Joseph J. Martin for their help and advice on the thermodynamic development. Finally the author owes a great debt of gratitude to Professor Edward E. Hucke for his advice, assistance, and encouragement throughout the course of the investigation.

This research was supported by the United States Air Force through the Air Force Office of Scientific Research (ARDC).

TABLE OF CONTENTS

	Page
LIST OF TABLES	iv
LIST OF FIGURES	v
ABSTRACT	vii
INTRODUCTION	1
Literature Review	6
Summary of Literature Review	44
THEORETICAL CONSIDERATIONS	46
EXPERIMENTAL PROCEDURE	57
Preliminary Tests on Wire Specimens	57
Tests on Sheet Specimens	65
Specimen Preparation and Design	65
Cleaning Technique	69
Testing Technique	74
RESULTS	79
Tests with Changing A_o/V	93
Tests on Other Environments	94
Fracture Tests	101
DISCUSSION	103
Summary	123
CONCLUSIONS	125
REFERENCES	127

LIST OF TABLES

		Page
I.	Changes in E' with Environment from Data Reported in the Literature	56
II.	Tests on .010 inch Metal Wires in Various Environments. Observed values of E'	60
III.	Maximum and Minimum Differences in the Values of k in ergs/cm^2 Corresponding to E' Values in Table II	61
IV.	Observed Values of E' for Platinum and Tungsten Wires of Various Diameters	64
V.	Observed values of E' for Copper Sheet Tensile Specimens in Various Environments	80
VI.	Values of k and j corresponding to E' values in Table V	91
VII.	Values of E' for Specimens Coated with Mercury	98
VIII.	Values of E' for Specimens Tested in Distilled Water Saturated with Stearic Acid Without Prior Ion Bombardment Cleaning	99
IX.	Fracture Strengths and Reductions in Area for Specimens Tested in Air and After Wetting with Mercury	102

LIST OF FIGURES

		Page
1A.	Schematic View Showing Excess Bonding Energy Available at Surface.	2
1B.	Schematic View Showing Adsorption and Excess Bonding Between Surface Atoms.	2
2.	Sketch Showing Relative Positions of Binding Energy Curves for Interior and Surface Atoms.	4
3.	Schematic View of Apparatus for Testing Wires in Liquid Environments.	59
4.	E' Versus 1/diameter for Platinum Wires in Air and Water.	62
5.	E' Versus 1/diameter for Tungsten Wires in Air and Water.	63
6.	Sheet Tensile Specimen.	68
7.	Ion Bombardment Cleaning Apparatus.	71
8.	Photograph of Ion Bombardment Cleaning Apparatus.	72
9.	Gripping Arrangement for Testing Sheet Specimens.	77
10.	E' versus A_o/V Air Environment.	83
11.	E' versus A_o/V Water Environment.	84
12.	E' versus A_o/V Water Saturated with Stearic Acid Environment.	85
13.	E' versus A_o/V Strain Gage Environment.	86
14.	E' versus a_o/V Air Environment.	87
15.	E' versus a_o/V Water Environment.	88
16.	E' versus a_o/V Water Saturated with Stearic Acid Environment.	89
17.	E' versus a_o/V Strain Gage Environment.	90
18.	E' versus A_o/V for Specimens Annealed at 600°F Showing Effect of Changing A_o/V.	95
19.	E' versus A_o/V for Specimens Annealed at 1200°F in Three Liquid Environments.	97
20.	Change in Surface Free Energy with Plasic Strain.	116
21.	Relief of Surface Energy by Introduction of an Array of Edge Dislocations.	119

ABSTRACT

A thermodynamic relationship has been developed to show that the surface free energy and grain boundary energy of a solid change with elastic strain in the following manner:

$$f^S = f_o^S + k\epsilon^2$$

$$f^B = f_o^B + j\epsilon^2$$

where f^S and f^B are the average surface energy and grain boundary energy at strain ϵ, f_o^S and f_o^B are the respective energies at zero strain, and j and k are constants. The development also shows that the surface tension of a solid should vary with strain in the same manner as the surface energy, but that the surface energy and surface tension are not necessarily equal.

It is also shown that the slope of the stress curve in the elastic region E', may be expressed in the following form

$$E' = E + 2k \frac{A_o}{V} + 2j \frac{a_o}{V}$$

where E is the elastic modulus of the solid, A_o the surface area, V the volume, and a_o the grain boundary area.

A series of preliminary tests were made to measure the values of E' of various wire specimens in different environments. These tests showed that there were small but distinct changes in E' with changing environment around the wires, and with changing size.

A further series of tests were made using copper sheet tensile specimens of different thicknesses and grain boundary areas. The specimens were machined from a large copper plate so as to minimize any changes in orientation or microstructure between specimens of varying thickness. The specimens were cleaned by ion bombardment, exposed directly to the testing environment, and the values of E' then measured in the environment.

The results showed that E' varied linearly with A_o/V and a_o/V in the various environments. It was also found that the intersections of the E' versus A_o/V curves with the E' axis corresponded reasonably well with the value of the elastic modulus E of the copper. On the basis of these results the value of k is on the order of 10^9 ergs/cm^2 and the value of j is on the order of 10^8 ergs/cm^2.

A review was made of the literature concerning the effects of environment on the mechanical properties of solids. It was concluded that many of the various environment effects that have been observed could be accounted for by surface energy considerations.

INTRODUCTION

The purpose of this investigation was to study the changes in surface free energy of a solid as the solid is strained. Herring (1) and Shuttleworth (2) have pointed out that there should be some change in the surface energy of a solid with strain but did not attempt to formulate this change. Most current applications of the concept of surface energy however, do not consider the possibility that the surface energy might change. It might be worthwhile therefore to show why one might expect a variation in the surface energy with strain.

The surface energy may be thought of as an excess energy that exists because a surface has been created. One rather simple way of visualizing this excess energy has been suggested by Benedicks (3) and is shown schematically in figure 1. As the figure shows, the bulk of the solid may be considered as a regular array of atoms which are bonded to each other by a certain bonding energy represented by the connecting lines between the atoms. At the surface there is an excess bonding energy because the lattice has been discontinued and there are no atoms on one side of the surface to take up the bonding energy that is available (Fig. 1A). Some of this excess bonding energy will be used by foreign atoms that become adsorbed on the surface, but the remaining excess energy becomes an increased bonding energy between the solid atoms at the surface (Fig. 1B). Surface energy might be pictured as the excess bonding energy between the surface atoms.

This model of course is a crude one because, for example, it pictures all the surface energy as being concentrated in the single row of surface atoms whereas in general this energy spreads beneath the surface to a depth of 100 atoms or more. In addition it suggests that surface forces would be tensile

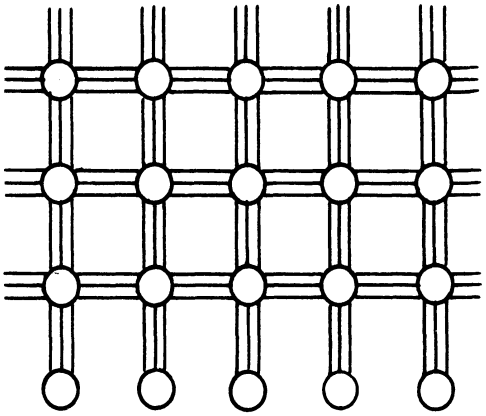


FIGURE 1A - SCHEMATIC VIEW SHOWING EXCESS BONDING ENERGY AVAILABLE AT SURFACE

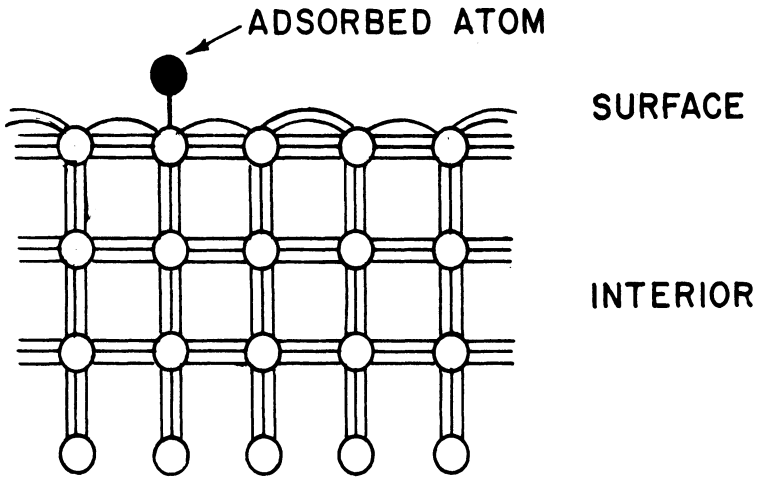


FIGURE 1B - SCHEMATIC VIEW SHOWING ADSORPTION AND EXCESS BONDING BETWEEN SURFACE ATOMS

only, which may not always be the case. The model does furnish however, a means of visualizing surface energy.

Now consider what happens when the solid is acted upon by a tensile stress acting parallel to the surface. With an applied stress the atoms become displaced somewhat from their equilibrium positions, causing a change in their potential energy. At the surface this displacement of the atoms will cause some change in the excess bonding energy and therefore cause a change in the surface energy.

This effect can be illustrated by use of the binding energy-atomic distance curve. A typical curve is shown in figure 2. At equilibrium the atoms within the lattice rest at the energy minimum at r_o. With an applied stress the atoms become displaced from this minimum energy position and the energy increases. The increase in energy with elastic displacement is of course related to the elastic modulus of the solid, and the modulus can be derived from the energy-position curve.

The surface atoms will have a different energy-position curve than that of the atoms within the bulk because of the excess bonding energy between these atoms. This curve will be displaced downward and somewhat to the left of the bulk curve (figure 2). Now since the surface energy is equivalent to the excess bonding energy, and since this energy increases with displacement of the atoms from the equilibrium positions, one can see why some change in the surface energy should be expected with strain.

It should be noted that while one expects a change in surface energy with strain for a solid the same would not be true for a liquid. In a liquid the surface atoms are sufficiently mobile so that after a displacement the atoms

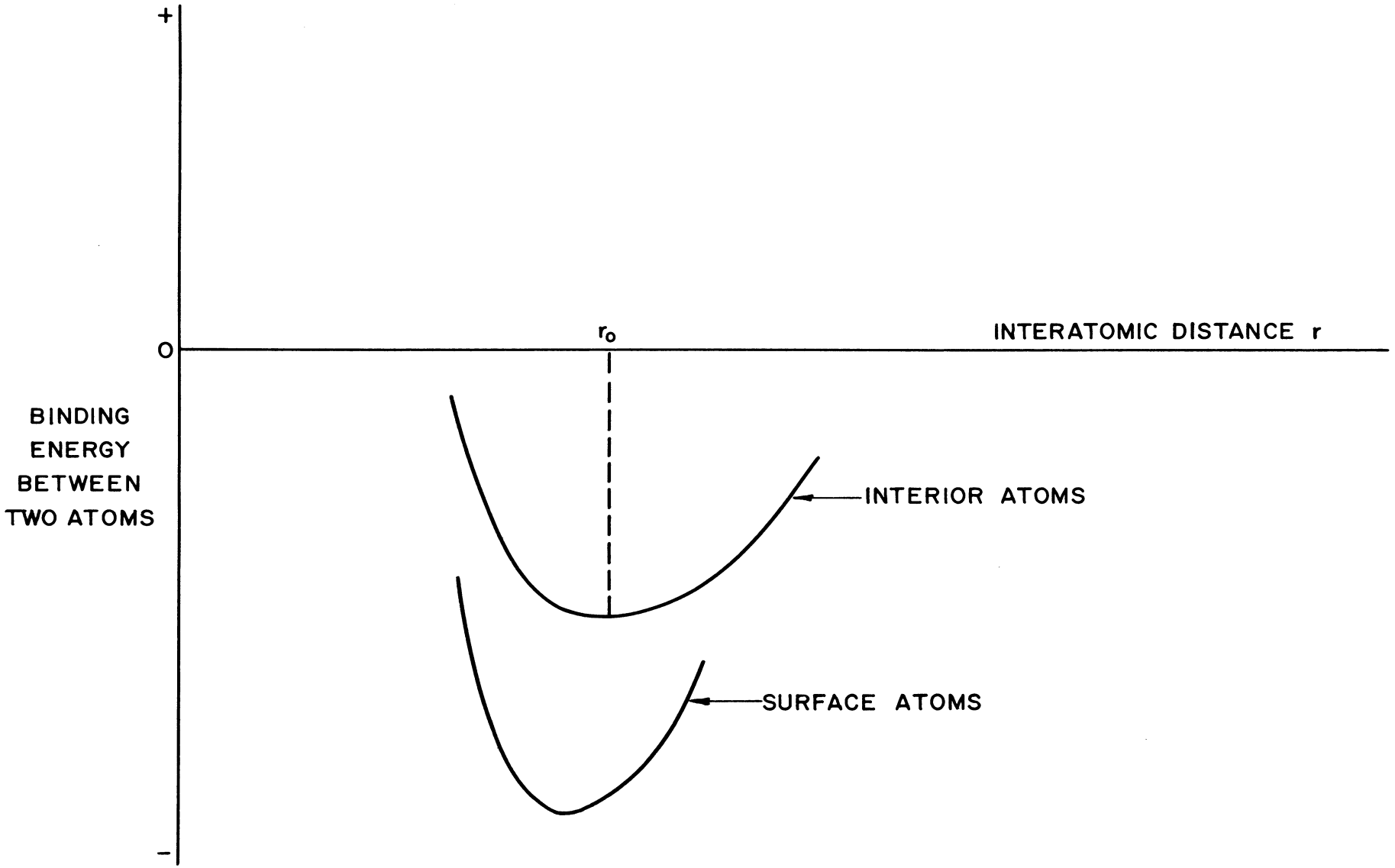


FIGURE 2 - SKETCH SHOWING RELATIVE POSITIONS OF BINDING ENERGY CURVES FOR INTERIOR AND SURFACE ATOMS

can immediately return to their original equilibrium positions. In a solid the atoms are more rigidly held in position and cannot migrate back to their lower energy sites when the solid is strained. There are of course intermediate situations, such as liquids with high viscosities or solids at high temperatures, in which readjustment of the surface atoms after straining will not take place instantaneously but may take place in some finite time period. In cases such as these the surface energy would depend not only on the strain but also on time. Benson, Balk, and White (4) have recently calculated changes in surface energy of alkali halide crystals on the order of several hundred ergs/cm^2 with relaxation in the surface region. These estimates show that local atomic rearrangements can cause significant changes in the surface energy.

Considerations such as those just given indicate that there should be some change in surface energy with strain. Before beginning a detailed treatment of this change however, some attention must be given to the intended application of the present work.

One of the primary reasons for this investigation was to try to develop some means of accounting for the effects of environment on the mechanical properties of solids. Of particular interest are the environment effects in which corrosion does not play a dominant role. A considerable amount of work has been done in this field, and a number of interesting theories have been put forward. To date however, no general mechanism has been developed which successfully accounts for the various diverse effects that have been observed. Thus there is clearly a need for work in this field.

In order to achieve some perspective and to prepare the way for future discussions it seems essential to study the work that has been done to date. For this reason a literature review of this work is now presented.

Literature Review of the Effects of Environment on Mechanical Properties.

An immediate consequence of any attempt to review the influence of environment is that the effect of specimen size must also be taken into account. The reason for this is that if the surface is a place of greater strength or weakness then the overall strength of the specimen must be a function of the surface to volume ratio. Thus changes in size must also be considered in studying environment effects.

This requirement can sometimes lead to erroneous conclusions, for it may happen that changes in mechanical properties with size occur independently of surface effects. Examples of this type of change are whiskers of certain metals. In these cases the increases in strength have been attributed to lower dislocation densities, and not to any surface effect. One must be careful in dealing with size effects therefore, to make certain that only the size and not some intrinsic variable of the solid has been altered.

The review itself has been rather arbitrarily divided into three classes of solids. The first is glasses, including SiO_2 in various forms and commercial grades of glass. The second class, called ceramics for want of a better title, includes other oxides, alkali halides, and various miscellaneous inorganic compounds. The final class deals with metals. For each class of solids the review is further subdivided into effects observed with changing size and effects with changing environment.

In most cases the effects that are described are independent of stress-corrosion. The major exception to this are the studies on glass. Glass suffers from stress-corrosion in air, and therefore most of the work in glass strictly belongs in the field of stress-corrosion. It was felt worthwhile to include

glass in the review however because the results are interesting in themselves and also because some of the results are related to those of other classes of solids.

With regards to the other materials, a certain amount of stress-corrosion may have occurred in some of the investigations described. In view of the large number of investigations that have been made, and the wide variety of solid-environment combinations studied, this is almost inevitable. For the most part however, corrosion is probably not a serious effect in these studies.

One important environmental effect that has not been included in the review is some of the changes in elastic properties with environment or size. These changes are directly related to the method to be used in this investigation for determining the changes in surface energy with strain, and it was felt that they would better be discussed at that time.

GLASS

Size Effects.

The first systematic investigation of the variation in the strength of glass with size was made by Griffith in connection with his microcrack theory (5,6). Griffith found that the strength of glass fibers varied inversely with the diameter of the fibers, and that at very small fiber diameters the strength approached the theoretical strength. Griffith attributed the high strength of the small fibers to the decreasing number of microcracks or imperfections on the surface of the fibers. Thus the strength was related to the size in that with decreasing sizes there was less and less probability of finding a crack which would cause fracture.

The relationship of fracture strength to microcrack size developed by Griffith is given by the well-known equation;

$$\sigma = K\sqrt{\frac{f^s E}{c}} \qquad (1)$$

where σ is the fracture strength, K a constant on the order of unity, E is Youngs modulus, c the micro-crack length and f^s the surface energy. Griffith's treatment has been modified by subsequent investigators but remains essentially in this form.

Griffith's work called attention to the important role that pre-existing small defects, the microcracks, play in the fracture properties of solids. His idea has been extended to cover the general phenomena of brittle fracture in solids and the basic idea remains one of the keystones of fracture theory. The idea is of special interest in glass, since the strength of glass in general is very sensitive to, if not controlled by microcracks.

A number of subsequent investigators confirmed Griffith's result that the strength of glass fibers was inversely proportional to the diameter of the fiber (7-17).

The strength of the fibers has also been shown to vary with the length. Reinkober took a long fiber, broke it, and then tested the two halves of the broken fiber. By repeating this process over and over for each of the fractured segments Reinkober found a steady increase in strength from generation to generation (13).

The yield properties of SiO_2 whiskers have been reported by Brenner (18). He found a maximum yield strain of 5.2% measured in tension, which is much higher than that of bulk silica.

That microcracks actually exist on the surface of glass fibers and influence the strength has been shown by several experiments. Griffith noted that when a freshly-drawn fiber was brought in contact with a hard surface or even another fiber there was a marked decrease in the strength of the fiber. Several investigators have delineated cracks on the surface of glass specimens by decoration and observed that on standing in air there was an increasing number of cracks (19-21). Levengood found that the number of flaws decreased rapidly with decreasing fiber diameter, and that the strength was inversely proportional to the number of these flaws (22). He also noted that the strength variation with size depended on the type of flaws present at the surface. For small flaws the strength was inversely proportional to the square root of the fiber diameter. For a larger flaw that was deliberatly cut on the surface, the strength was inversely proportional to the diameter (23). Holland and Turner have also noted significant effects on the strength from scratching the surface (24). Orowan found that the strength of mica increased ten fold with a gripping arrangement that minimized the stresses on the edges of the mica specimens (25). Several investigators have noted that there is some increase in the strength of glass specimens when tested at slightly elevated temperatures, presumably because surface diffusion allows some crack healing (26,27). It is also recognized that annealing and quenching glass specimens in such a way as to introduce compressive stresses in the surface region increases the strength (28,29). Such a treatment would of course minimize the influence of surface cracks. Finally Gurney (30) has shown that the compressive fracture load is on the order of eight times the tensile load, which strongly suggests the presence of cracks.

At one time it was considered that the increasing strengths at smaller sizes might be due to orientation changes in the Griffith flaws at the surface. This has been disproved by Otto and Preston, who showed that fiber strengths in tension and in torsion were about equal, and thus that the strengths were about equal parallel to and at 45° to the tension axis (31). The equal strengths in the two directions ruled out any orientation effect of the flaws. It was also considered that the strength increase might be due to a preferred orientation effect inside of the fibers with decreasing size (32,33). No oriented structure has been found within glass fibers, however (34,35).

Most of the early work with glass was interpreted by the theory that with decreasing specimen size there was a corresponding decrease in the probability of finding a micro-crack which would cause low strength. Thus the strength might be expressed by the statistical probability of the specimen containing microcracks of a certain size. A number of attempts have been made to develop such a statistical approach to fracture, but without much success (36-45). As Orowan has pointed out, many of these attempts are more interesting mathematically than correct physically (46). Among the difficulties encountered in such treatments is the choice of the distribution function for expressing the number of cracks per volume or per surface. Other problems may also arise. For example, as Epstein points out, one crack on the surface of a specimen may lower the strength considerably while a number of cracks have little effect (43). The mathematical treatment of such physical effects can be extremely difficult.

By far the biggest shortcoming of the various statistical approaches is that they neglect the fabrication history of the specimen. In recent years it has become apparent that the size effect depends markedly upon the fabrication

history. Slayter found little change in fracture stress between .002" and .0002" fibers when they had been drawn from the molten glass to give the same cooling rate (441). Otto found that fiber strength was a function of the temperatures of the glass when it was drawn into a fiber. By drawing at the same temperature and drawing rate he produced fibers whose fracture stress was independent of thickness (442). Thomas made fibers by drawing glass out of a crucible and turning it around a drum. He then tested the portion of the fiber between the drum and the crucible. He found the fracture stress was independent of the diameter of the fiber, temperature of the crucible, and the speed of drawing (443). Bartenev and Tsepkov produced fibers whose fracture stress was independent of size by keeping the amount of plastic strain constant during drawing. They also found a constant fracture stress in glass plates of various sizes when the smaller plates were made by grinding down one side of a larger plate (47). Finally, several investigators have shown that the strength of larger size glass pieces may be considerably increased by careful polishing of the surface (48, 49).

These results are somewhat contradictory in themselves, but clearly demonstrate that glass strength is very sensitive to the fabrication history.

It has also been proposed that the size effect may not be due to microcracks but to a difference in bulk structure between fine fibers and massive glass (50-52). Because of the large surface to volume ratio of fibers they have a very high cooling rate when drawn from hot glass. This increasing cooling rate would tend to freeze into the glass more of the disordered structure from the high temperature and thus change the strength.

Several points argue against this theory. The first is the many results which clearly show that micro-cracks are present on the surface and have a marked influence on the mechanical properties. The second is that no one has ever been able to detect any significant change in structure between bulk glass and fibers. Bateson (48) found only a slight decrease in density and refractive index with decreasing fiber size, which indicates there is no significant change in structure.

Another interesting experiment along this line was made by Powell and Preston (53). They measured the cracking force of small areas on the surface of a large glass plate as various size steel balls were pressed into the plate. They found that the stress at which cracking began in the plate increased with decreasing ball size. They concluded that strength is therefore a function of size tested and not to differences in structure.

Environment Effects.

The primary concern of many of the environment experiments with glass has been to study stress-corrosion in air.

The effect of air on strength is perhaps best shown by the static fatigue experiments (54-62). In these experiments a glass fiber is loaded to some point below the fracture stress and left standing under constant load. After a certain time period the fiber will fracture. The time to fracture of the fiber depends on the load, testing temperature and the environment surrounding the fiber.

Two general mechanisms to account for the effect of environment on strength have been suggested, one by Gurney (63) and one by Orowan (64). The

Gurney mechanism involves corrosion at particular locations such as the root of a microcrack on the surface of the specimen. At such places the stress will be higher because of the stress concentration. Consequently corrosion will be accelerated at these sites, and the cracks will increase in depth until a crack reaches the critical size and fracture occurs (62). The effect of environment thus depends upon the degree of corrosion it causes.

Orowan's mechanism relates changes in strength to changes in surface energy. The Griffith equation shows that the strength is proportional to the square root of the surface energy. Changing the environment changes the surface energy and consequently causes a change in strength. Orowan has shown that the fracture strengths of mica in vacuum and in air are proportional to the square roots of the surface energies in the two environments, as the Griffith equation predicts (65).

It would seem that both of these mechanisms could be operative at the same time, and that the time to failure in an environment could be due to a combination of corrosion (Gurney's mechanism) and surface energy change (Orowan's mechanism).

The static fatigue experiments also show that the strength of glass in commercial usage can be time dependent. This may be of some consequence because glass equipment may thus fail with standing. Of practical significance are the results of Silverman and Gearing showing that atmosphere can cause whiskey bottles to fail (66). Shand has found that glass may be permanently weakened by a temporary stress that does not cause failure (67).

An interesting point is that the fatigue life of glass in cyclic fatigue, with an oscillating load, was found to be the same as in static fatigue (68). This would indicate that surface flaws are also the controlling influence in cyclic fatigue testing of glass.

Glass does not have to be under stress for air to produce deleterious effects. A number of investigators have noted that there is a marked decrease in the strength of freshly drawn glass on standing in air or other environments (69-73). Thus the time between glass drawing and testing can be a significant variable in strength measurements, and current researchers usually take some pains to either test glass immediately after drawing or to protect the specimens from corrosive environments.

With longer time exposure to air glass may show some increase in strength. This effect has been attributed to a rounding off of the microcracks with prolonged exposure (49). Pulliam has suggested that the effect of environment might be due to a precipitation in the roots of the microcracks (74). Other investigators have noted that etching glass fibers prior to testing may increase the strength by a factor or three or more (14,16). A light etch is generally most effective, and further etching does not produce a corresponding further increase in strength. This last result may be taken to indicate that surface flaws are the most damaging and that once they are minimized the effect of further etching is not as great.

A number of more or less random environment effects have also been found. Benedicks and co-workers noted that the fracture strength could be either increased or decreased by testing under various liquids (75,76). Milligan noted that coating the surface with dry paraffin raised the breaking stress about 20% (77).

Schurkow found a progressive increase in strength for fibers tested in water, alcohol, and in vacuum (17). Florenski found the strength of mica to depend upon the testing media (78). Orowan's explanation for the effect of environment has already been noted in connection with these results on mica. Obriemoff noted that when mica was partially cleaned under a vacuum the time until the final depth of the cut was reached depended upon the partial pressure of the atmosphere surrounding the mica (79). Levengood and Johnson found that slow fracture strengths vary when different gases surrounded the glass. They also found that internal gas composition, produced by bubbling gas through the glass when it was molten, influenced the strength (80). They showed that the fracture rate depended upon the rate or arrival of the internal gas at the microcracks. Holloway has shown that vacuum drawing and testing of glass increases the strength markedly (81). Various other experimenters have also shown the influence of environment on tensile or hardness properties (82-85).

These environment effects can generally be explained by either the corrosive (Gurney mechanism) or surface energy (Orowan mechanism) changes, or a combination of the two. Both of these mechanisms involve changes in composition at the surface. A third mechanism, involving penetration of the external environment into the volume of the body, has been proposed by Rebinder (86). He suggests, with reference to the deformation of mica, that the environment penetrates into small, wedge-shaped cracks which are formed during deformation and run to a considerable depth into the volume of the mica. Rebinder's theory was developed primarily in connection with metals, and will be discussed in more detail in that section. As far as glasses are concerned, Rebinder's mechanism may be considered as interesting but unsupported.

CERAMICS

Size Effects.

The changes in plastic deformation and fracture strength of ceramics with size have received only scant attention. Muller (87) noted that the tensile strength of rock salt increased as the cross-section was diminished. In a more complete investigation, Jenkel prepared small specimens of rock salt by etching down larger crystals (88). He found the yield and fracture stress of the specimens was inversely proportional to the diameter. Recently Iad et al have shown that the ductility of MgO increased with decreasing size (89).

Smekal observed that slip in thin pieces of rock salt did not occur in the plane or direction corresponding to the maximum resolved shear stress. Instead slip was favored in directions corresponding to shorter slip paths through the crystal (90).

Webb and Forgeng (91) have studied the properties of very small crystals of Al_2O_3, Cr_3O_4, Fe_3C and other such compounds that were extracted from two phase alloys. They noted that the crystals had very high strengths. Several investigators have studied whisker specimens of various ceramics (18,92-94). They have noted very high maximum elastic yield stresses, and yield strains on the order of 1%. These yield strains are several orders of magnitude greater than those found in bulk specimens. Gordon (95) has shown that the elastic limit of Na Cl and KCl varies inversely to the diameter.

The fracture strengths of Na Cl whiskers have been measured by several investigators (95-97). Gyulai (96) found a gradual increase in strength down to about five microns diameter, and then a very large increase in strength for smaller specimens. The scatter in strength at the smaller diameters was very large. For

whiskers 2 microns in diameter the strengths ranged from 10 to 110 Kg/mm^2. Gordon found somewhat smaller breaking strengths than Gyulai, which may be due to the different growth conditions he used (95).

It may be noted that these results with whiskers are similar to those observed with metal whiskers. Whisker properties are somewhat complicated, and several different theories have been put forth to explain them. Some discussion of these theories will be included in the section on metals.

Environment Effects.

The influence of surface environment on plasticity and strength has been more widely investigated. An early investigation by Voight and Sella (98) showed that the strength of rock salt changed with the crystallographic plane of the external surface. In 1914 Kleinhanns noted that rock salt crystals bent under liquids which dissolved NaCl showed high ductility, whereas in liquids in which there was no solution of NaCl the ductility was nil (99).

The modern phase of these studies began with the work of Joffe on the strength of rock salt in water (100,101). Joffe noted that by testing rock salt in water the strength could be raised over 100 fold. He also found that crystals that were wetted in H_2O and then stored in vacuum could be readily deformed (102). Joffe attributed the effect of water to the removal of micro-cracks from the surface of the specimens.

Schmid and Vaupel (103) did not find an effect as great as Joffe's but did note a 25 fold increase in strength for NaCl in water. Polanyi and Ewald (104,105) also noted that the plasticity increased when the surface was wet, which they attributed to a lowering of the elastic limit. The results of Sperling (106)

and Domerich (107) however, showed that the critical shear stress of NaCl was the same in air and water.

Recently Aerts and Dekeyser (108) found that freshly cleaned rock salt specimens could be bent as easilly in paraffin or ether as in water. They further showed that the stress-strain curve of rock salt was very sensitive to adsorption or desorption of gases from the surface of the rock salt. Thus, with reference to the earlier work, the effect of water would seem to consist in polishing the surface and in preventing subsequent gas adsorption on the surface. The water does not have any healing action during deformation.

The effect of gas adsorption was further demonstrated by Parker and others (109-111). They showed that a number of oxides and halides were ductile when freshly cleaved from bulk crystals, but that they became brittle on standing in air or other gas environments. Recently Machlin and Murray found that the brittleness of rock salt appears to be a function of the ozone or NO content, and not the O_2 or neon content of the air (112).

Machlin also found that the application of either anodic or cathodic polarization to the surface of brittle rock salt specimens increased the ductility of the specimens to a marked degree. When the polarization was applied to clean, ductile specimens however, the effect on ductility was negligible (113).

Iad (114) has studied the effect of aging on the formation of surface cracks on rock salt. He found that aging in air, a drybox, or in vacuum all produced small cracks on the crystal faces at certain preferred crystallographic angles. Iad also observed crack formation under stress. He found that small surface cracks form at stresses much lower than the fracture stress, and that

the angular distribution of these cracks was the same as was observed in the aged specimens. In connection with this last point it is interesting to note that Al_2O_3 has been found to fail by static fatigue (115,116).

A subsequent investigation of cracking with aging was made by Metz and Lad (117). They found that microcracks were formed by a thermally activated process of 100 Kcal activation energy on an originally crack-free, water polished surface. Crack formation was very slow at room temperature, requiring several months, but could be accelerated by heating, X-ray irradiation or the application of low stresses.

The effect of X-ray irradiation on crack formation was studied in some detail by Leider, Girafalco, and Lad (118). They found that the surface area of powdered rocksalt increased with increasing time of irradiation. At the same time the heat of adsorption of nitrogen on the surface decreased with irradiation time. The explanation offered for these effects was that grinding introduced residual stresses in the powder. Irradiation then supplied enough activation energy to allow the residual stresses to be released by cracking of the particles, with a consequent increase in area and decrease in heat of adsorption.

Lad et al (119) points out that the low rate of cracking of rock salt surfaces at room temperature and the atmosphere effects raise some question as to whether micro-cracks are the main cause of brittle behavior. A second explanation might be that the surface adsorption causes a dislocation barrier effect. This type of effect has been widely discussed in connection with surface effects in metals. The theory consists essentially in the idea that on the specimen surface there is a layer of oxide or some other corrosion product which resists

the passage of dislocations through the surface from the interior of the specimen, and consequently changes the strength properties.

Several investigations have shown that the mode of preparation of the test specimens has a significant influence on the properties. Suzuki (120) found that polished and unpolished KCl crystals had different stress-strain curves and that the critical shear stress was raised by polishing. Similar effects with LiF were noted by Gilman and Johnson (121). Suzuki attributed the difference between polished and unpolished pieces to the fact that a Frank-Read source in plastic flow operates easiest from the surface, and changing the surface condition will therefore affect these sources. This type of mechanism is another attempt to resolve surface effects with dislocation theory. Several investigators (89, 120-122) have pointed out that cleavage introduces a large number of dislocations into the surface region of the specimen. Thus the properties of a specimen prepared by cleaving it from a bulk crystal, as is commonly done, will be somewhat sensitive to the cleaving operation itself. Finally Gordon (95) and Webb (97) noted that alkali halide whiskers showed no embrittlement after prolonged exposure to air. In view of Lad's work this last result may be explainable by the apparent slowness of the embrittlement reaction.

Thus far two general mechanisms have been proposed to account for the surface effects. The first is that microcracks are present or become developed on the surface, with similar effects to those in glass. The second is that the surface acts either as a barrier to dislocations or as a source of dislocations. Several additional investigations have been made which tend to support one mechanism or the other.

In favor of the dislocation theories, Bobrikov (123) noted that certain glide planes in NaCl and KCl crystals could be activated by wetting faces of the crystals. Pratt (124) and Bassett (125) have observed that slip in dry NaCl came up to the surface but did not break through it. When the crystal was tested in water however, slip came through the formed slip steps on the surface.

On the other hand, Bowden (126) noted that dry NaCl , which is normally brittle in tension, can be deformed to large strains in compression. This effect is readily explainable by the microcrack theory, but is difficult to explain in terms of dislocation effects.

A third mechanism, to account for the action of water on the strength of rock salt type crystals was originally suggested by Smekal (127, 128), and elaborated on by subsequent investigators (129). This mechanism is that the water penetrates into the volume of the crystal and increases the plasticity. This type of effect is similar to Rebinder's proposal (86), but in the present case some experimental data has been gathered to support it.

Quittner and Smekal showed that exposing rock salt to water produced marked changes in the conductivity (130). Barnes measured the amount of absorbed water inside rock salt crystals after exposure to water. He found that the ductility varied with the amount of water inside the crystal; and that high ductility was associated with the presence of water in the crystal (131,132). More recently Gunther and Erdman-Jeznitzer (133,134) studied the compression and Vickers hardness of rock salt in various media. They found that wetting the crystal also influenced the deformation under compressive loadings, and that there was a certain time period after the application of the environment before

it reached full effectiveness. They believed that the changes in plasticity were due to penetration of the liquid into the crystals.

One other interesting example of penetration is the fragmentation of Mg_2Sn crystals in water. Robertson and Uhlig found that as-grown Mg_2Sn crystals in water break up into small pieces, presumably because water enters the (111) planes of the parent crystal (135,136).

Kuznetsov has recently summarized a number of Russian investigations on the influence of environment on the communition of alkali halides (137). He showed that the grinding, scratching, drilling, etc. properties of this class of solids may be considerably influenced by the environment, presumably because of surface energy effects. With respect to mechanical working of brittle solids, he argues that the medium, especially if it is surface active, may penetrate to a considerable depth beneath the surface of the solid and alter the strength. Benedicks has also put forth the theory that penetration of a liquid into cracks can either increase or decrease the strength of solids (138).

One important fact that does emerge from these various results is that ceramic materials, which are normally thought of as being very brittle, can have an appreciable amount of ductility with proper surface treatment. The reason for this, as indicated, is not at all clear.

METALS

Size Effects.

Probably the outstanding examples of the change in mechanical properties with size belong to the group of small metal crystals known as whiskers. In 1952 Herring and Galt showed that small filaments of tin on the order of two microns

in diameter had strengths approaching theoretically predicted strengths (139). Since that time whiskers of a number of different metals have been studied. These investigations have shown that not only the mechanical properties, but also the electrical, magnetic, corrosion, etc. properties of whiskers may be significantly different from the properties of bulk metals. A considerable body of data has been collected on whiskers, and only a very brief description of some of these results can be given here. For a more complete description of these results reference should be made to some of the reviews that have been written on the subject.

The outstanding mechanical property of whiskers is their very high elastic strains at the yield point. In all cases this strain is several orders magnitude greater than that found in bulk crystals (140).

When a whisker is strained to the yield point one of three things has been found to happen. The whiskers may break with a brittle, cleavage-type fracture, it may deform plastically, or it may creep (140).

The fracture strengths of whiskers are generally much greater than those of bulk specimens. Usually however, there is a considerable scatter in the strengths for whiskers of any one size, and only a small percentage of the whiskers reach the extremely high strengths that are sometimes quoted to show their outstanding properties. For iron and copper whiskers, the strength has been found to be inversely proportional to the diameter of the whiskers (141). In other metals, this trend has not been observed or has been masked by scatter in the data.

If a whisker deforms plastically it generally does so at a stress level much lower than the yield stress. The amount of plastic flow in whiskers of some

metals may be considerable, and during this deformation there may be only a very slight increase in the flow stress up to very large strains. It is believed that this type of deformation is due primarily to Luder's band propogation and not easy glide. In some metals the plastic deformation takes place by creep (140).

Bending tests have shown that when the elastic limit is exceeded the whisker kinks. If the kinked whisker is then annealled at an elevated temperature it frequently unkinks and assumes its original shape. Copper and iron whiskers however, that were strained beyond their yield point in either tension or compression and then annealed showed no return of the yield point. Recovery has been observed in silicon whiskers.

Several investigators have studied creep in whiskers prior to yielding. Cabrera found that room temperature creep in Cu and Zn whiskers depended upon the diameter of the whiskers and caused a two-fold increase in the yield strength (142). Brenner, however, was unable to duplicate Cabrera's results (140).

Although the foregoing are only brief examples of some of the effects that have been observed in whiskers, they should be sufficient to demonstrate that whiskers have mechanical properties that may be significantly different from those of bulk metals. The reason, or reasons, for these differences is uncertain. It was originally thought that whiskers, because of their mode of growth, contained a very low density of dislocations and therefore were proportionately more difficult to deform. This explanation may still be true for some whiskers. More recent work has shown however, that whiskers may have fairly high dislocation densities and still exhibit high strengths. Furthermore, as will be discussed in more detail, whisker-sized specimens obtained from bulk crystals also show strengths comparable to whiskers. Thus the strength of whiskers may

not be solely due to low dislocation densities. It has been suggested that whiskers or other small size specimens may be too small to contain a three dimensional dislocation network which could serve as a source of dislocations during deformation (143).

It has also been suggested that the strength may be influenced by surface or volume defects in the whiskers such as pits, corrosion products, occasional grain boundaries, and so on (140). Such defects have been shown to be important in a few cases. Bulk silicon, for example, exhibits strengths on the order of whisker strengths if the surface imperfections are carefully etched away (144). Brenner found, in a manner similar to that of glass fibers, that the strength of a copper whisker increased progressively as the broken halves of the whisker were tested (141). Thus, as in glass, the strength may be dependent upon the probability of finding a defect of suitable size. Whether this explanation is valid in general for metals remains to be seen.

It has been suggested by Cabrera and Price that strengthening of small specimens might be attributable to a dislocation barrier at the surface of the specimen (145). If the surface acted as a barrier to dislocation flow, then with decreasing size there would be relatively more barrier per volume and the strength properties should increase. It does not seem possible to relate the properties of whiskers solely to a surface barrier effect, although some of the results obtained in small specimens have been explained this way.

Finally, Gilman (146) has noted that there is an intrinsic size effect which becomes important in bending when the specimen size is less than one micron. This effect is due to the fact that slip must take place by a dislocation movement of a finite distance, and that this movement becomes a significant displacement in a small enough specimen.

These latter theories imply that strength is a consequence of size alone and does not necessarily depend on a low dislocation density or some other major change in the volume of the specimen. It is too early to tell whether or not size per se controls the strength, but there is an increasing amount of evidence that suggests that this may well be so. This evidence is in the form of a wide variety of investigations showing changes in plastic behavior and fracture strength with size.

The changes in plastic properties with size are best examplified by the variations in yield stress and glide behavior. Andrade has reported that the critical shear stress of a cadmium single crystal increased 14 times as the diameter of the crystal was decreased from 500 to 25 microns (147). Suzuki and co-workers (148) noted an increase in critical shear stress for copper and brass single crystals with decreasing size, but over a much narrower size difference. Similar effects have been noted for the yield stress of aluminum, cadmium, and tin (149-151).

The extent of easy glide in single crystals is also dependent on the size of the crystals. A number of investigators have shown that the easy glide range in copper and in aluminum increases with decreasing crystal size (148,149, 152-154). Wu and Smoluchowski found that slip did not occur in the plane or direction of the maximum resolved shear stress in thin aluminum crystals. Instead slip was favored in directions corresponding to short slip paths through the crystals (155). Gilman noted that the plastic deformation of zinc single crystals that caused the greatest increase in surface area required higher stresses (156). Andrade and Kennedy found that the coefficient of β creep in lead varied with diameter (157).

The most popular explanation for the increase in yield stress with smaller sizes is that the surface restricts the emergence of dislocations. The other investigators who were more concerned with easy glide maintain that glide is easier in smaller specimens because the dislocations can emerge more easily from smaller crystals and not be stopped within them. These two explanations are somewhat contradictory. The yield stress explanation requires that it is more difficult to move a dislocation through the surface barrier than through the crystal, while the easy glide explanation requires just the opposite. One possible way to reconcile this difference is that yielding destroys part of the surface barrier to dislocations, and that subsequent dislocations arriving during easy glide can therefore emerge relatively easily. The work of Mukai (158) and of Evans and Schwartzenberger (159) indicate that slip will take place preferentially in regions where the surface film has been broken.

Changes in fracture strength with specimen size have been widely investigated. In 1858 Karmarsch noted that the fracture strength of metal wires became inversely proportional to the diameter for very small wires (160). Taylor in 1924 prepared thin metal filaments by drawing out glass tubes containing molten metal and then etching away the glass. Taylor found the filaments were very pliable and had much higher strengths than ordinary size wires. The strength of a 30 micron antimony wire, for example, was about 30 times greater than the strength of bulk antimony (161). Schlichta prepared copper wires by Taylor's method and found increasing strengths with smaller sizes. He also prepared small specimens by electropolishing down larger diameter copper wires. One wire electropolished from 81 microns to 4 microns had a fracture stress of over 225,000 psi (162). Schlichta also noted that there was a decreasing amount of

plastic deformation with size until with the smallest specimens there was no plastic yielding prior to fracture (162). Pearson, Read and Feldman found that small specimens of silicon cut from a bulk crystal had strengths comparable to silicon whisker (163). Ono found a strength increase with decreasing diameter for aluminum single crystals (164). Backer, Marshall, and Shaw have shown an increase in shear strength of steel particles with decreasing size of sheared particles (165). Several investigators have found that thin metal films, on the order of several hundred angstroms in thickness, have strengths considerably higher than bulk specimens (166-171).

Most of the foregoing size effects were obtained with specimens that were a good deal smaller than the conventional specimens used for engineering tests. There is also some information that suggests that there are small but noticeable size effects in larger size specimens (172-179). In particular, a number of studies have been made of the variation in impact strength of notched specimens of steel of varying sizes but geometrically similar shapes (180-190). These tests showed a marked increase in impact strength with decreasing size for notched specimens. Un-notched specimens however, showed little or no size effect. Yukawa (191) has recently found that the effect of size becomes more pronounced with sharper notches and with higher transition temperatures of steel. He has explained the size effect by assuming that the fracture stress may be expressed by a form of the Griffith equation in which the fracture propagation from the notch is the same as from a microcrack.

Environment Effects.

The amount of published work showing the effects of environment on mechanical strength is enormous. Much of this literature is concerned with work that can be only mentioned briefly in passing. Included in this category are such topics as plating and other types of surface finishing, irradiation effects, and so on. Even neglecting these subjects there is still a large amount of information showing the effects of surface environment.

At the present time there exist two schools of thought concerning the effects of environment. These schools, for want of better titles, might be labeled the Russian school and the Western school. Each of these schools has developed its own generalized concepts and theories, and each has done extensive work to support its views. In some instances the theories and results of these respective schools are in sharp contrast to each other. At the moment however, neither school can claim to have solved all the problems that have arisen.

The Russian school originated with the investigations of Rebinder and his co-workers in the 1930's (192-200). Rebinder tested a number of different metals and other solids in various environments. He found that when the materials were tested in surface-active environments, i.e. environments readily adsorbed on the solid surfaces and which lowered the interfacial energy, that there was a marked increase in the extent of plastic flow in the solid. Rebinder also measured the resistivity of metal specimens during deformation. He found the resistivity increased on the order of 5 times when the deformation was performed in a surface active environment. He also found that when the load was released the resistivity tended to return to its original unloaded value.

These findings led Rebinder to conclude that during deformation small microcracks formed in the solid which were filled by the external environment. This penetration of the surface-active environment caused a decrease in the surface energy of the solid, thereby lessening the stress required to deform the solid and increasing the plastic flow. On releasing the load the microcracks closed up and the metal returned to its normal state, except that some of the surface active material might remain entrapped within the metal in the places where the microcracks had been formed.

Following Rebinder's original work there has been a number of articles by various Russian investigators on the influence of environment.

These investigations have been made with both single crystal and polycrystalline metals. Surface-active environments used include various organic liquids and low melting liquid metals. In general it was found that surface active environments produced greater plastic flow and lowered the fracture stress (86, 201-233). A number of investigations also showed that metal shaping, cutting, and other surface deforming operations are influenced by the environment (234-249).

At the present time there appears to be some controversy over these results. One explanation for these effects is still essentially Rebinders theory, with some modifications of the micro-crack concept. The more recent ideas suggest that the environment may diffuse into the bulk metal to pre-existing discontinuities such as grain boundaries, cavities or voids. It has also been suggested that micro-cracks may form internally during deformation and become wetted by the environment. The resultant change in mechanical properties in either case is then due to the lowering of the surface energy of the metal(250-252).

Other Russian writters however, have become more inclined to interpret the results in terms of dislocation theory, and are more in accord with the Western school (253-257).

There is little doubt that one would find a significant decrease in fracture strength if microcracks having a low interfacial energy were formed inside a metal. The important point is whether or not such microcracks form. It is becoming evident that microcracks may form within a metal during deformation, and much of the recent work in fracture theory is concerned with the nucleation and propagation of these cracks. What is questionable is whether an external environment diffuses to these cracks prior to fracture and lowers their surface energy.

A second point is the question of whether or not merely lowering the surface energy should promote plastic deformation to the extent that has been found. Using nominal values for the surface energies, the changes in total energy required to deform a metal in air and in a surface-active environment are negligibly small. Yet very marked differences in deformation behavior have been observed. Masing (258-260) and also Likhtman and Shchukin (253) have attempted to show that the surface energy change can produce the observed effects by including the change in surface energy as part of the change in activation energy for slip. Such an approach may account for changes in the kinetics of deformation, i.e. the changes in deformation rate under a constant load. It does not seem possible however, to account for all the changes in plastic behavior that have been observed by this means.

In contrast to the Russian school is the work of the Western school. This work was begun by Roscoe in 1936 (261). Roscoe took clean cadmium single

crystals and exposed them to various environments. He found that exposure to N_2, CO, and H_2O produced no change in critical shear stress of the crystals. Exposure to oxygen however formed a oxide film on the cadmium surface and markedly increased the critical shear stress with increasing film thickness. The increase in shear stress was remarkable, 50% for a 20 atom thick oxide film. When the crystals were treated with acid that destroyed the films the effects were removed.

Subsequent investigators found that the critical shear stress (262,263) yield stress, (264-266) tensile deformation, (267-274) twinning, (275-277) and creep (278-284) of a variety of different metal single crystals could be markedly changed by a surface film. A wide variety of films were found to be effective, including oxides, hydroxides, sulfides, other metals, and even synthetic plastics.

Several investigations have been made to attempt to duplicate Rebinders effects with surface active liquids. It was found that the liquid had a significant effect only when there was an oxide layer on the surface of the specimen. When the surface was clean the liquid had only a minor effect (263,267). Harper and Cottrell (263) suggested that liquid environments have a secondary effect by action on the oxide film, and that if the film is thin enough there is no effect. They found the response of the specimen to a liquid was not instantaneous, but varied linearly with the viscosity of the environment. Harper and Cottrell concluded that the liquid permeated the oxide and cracked it, weakening the adherence and altering the hardening effect.

Three separate investigations have been made to attempt or find the changes in resistivity found by Rebinder during deformation in surface active liquids (260,262,270). None of these investigations found resistively changes of the order of magnitude found by Rebinder.

Other investigations to show the nature of the surface coating effect have taken a variety of forms. Shapiro and Read (285) studied the internal friction of oxide covered single crystals and cleaned single crystals of cadmium. They found the internal friction had a much more rapid raise versus the vibration amplitude in the oxide coated crystals. They concluded that the oxide film effect cannot be simply an inhibiting effect on surface dislocation formation.

Barrett and others (286-289) have studied the relaxation of twisted wires. They found that when the surface film on the wires was removed during the relaxation there was a marked change in the relaxation behavior. The effect was found to vary with the environment used to remove the film and also with the type of film on the metal surface. Gilman (273) found by x-ray studies that there was an interaction between the film and the metal during deformation. Brame and Evans (290) studied the deformation of various metallic films on single crystals of silver and platinum. They found the deformation decreased with increasing difference in lattice parameters between the film and the substrate. They also found that the greater the elastic modulus of the film over that of the substrate the greater was the inhibition of flow.

In all of the studies the thicknesses of the films were very small, usually several hundred angstroms or less. Thus the changes in properties are not easily attributed to the load carrying properties of the film, because this would require that the films have strengths of an order of magnitude or so greater than normal. The recent results which show that metal films may have much higher strengths however, suggests that in some instances the strengths of the film may indeed be a significant variable (280,283,291).

A number of different explanations have been offered to account for the effects of surface films. The most popular one, and the one that is probably most consistent with the variety of results that have been reported, is that the film acts as a dislocation barrier. Although this concept is easy to visualize qualitatively, little of a quantitative nature involving dislocation theory has been done. The work of Brame and Evans suggests some means of approach. One problem is explaining the numerous and sometimes contradictory results that have been found. For example, in some cases the strengthening effect has been found to increase with film thickness, where in others it is independent of thickness. The crystallographic orientation and strain rate have also been found to have unexplained effects. Part of this difficulty may be due to the wide variety of materials, testing techniques, etc., that have been employed.

In addition to these studies on plastic deformation there have been several investigations which show that the fracture strength may be affected by surface films. The fracture strength of zinc single crystals was significantly altered by various metallic, oxide, and sulfide films (292-294). In this case the effect appears to be due to changes in the twinning behavior with orientation. In other tests Nanis and Shulman have found that oleic acid reacted with surface oxides on copper during creep and produced a 3 to 5 fold decrease in rupture life (295).

While there is certainly enough evidence to show that surface films have a considerable effect on mechanical properties there is also some evidence that equally strong effects may be produced without necessarily forming a surface film. Masing has found that adding surface active agents to the environment

surrounding a gold wire increased the speed of elongation (259-260). Since gold does not normally have an oxide layer on its surface this result indicates that interaction with a surface film is not necessary for an effect. Masing also applied both anodic and cathodic polarization to the surface of gold wires. In both cases he found an increase in the elongation rate, which may be taken for further evidence against a surface layer effect. It is interesting to note that electrochemical theory predicts that both anodic and cathodic polorization should decrease the surface energy. Thus Masing's results agree with Rebinder's view that the surface energy is the controlling mechanism. There is also some evidence that surface films do not influence the strength of whiskers. Several investigators noted that films had little effect (141,163). Also gold films and whiskers have been found to be considerably stronger than bulk gold (166, 167,170,296). Other investigators however have found a change in properties with a metallic coating on whiskers(297). There is also some data that suggests that fracture of bulk crystals may not depend on films. Weiner fractured zinc crystals in a number of different environments (298). He claimed that when there was no film present the strength was constant in different environments. His strength data, however, show differences in strength on the order of 20% in the environments where there was no film formation.

In addition to these investigations which were intended to show the effects of films there have been a number of engineering studies of the changes in mechanical properties in various environments. Benedicks and co-workers have shown that the strength properties of various metals may be increased or decreased considerably by testing in environments such as water, glycerine, methanol, etc. (138,299). Benedicks believes the effect of environment to be

due to the surface energy changes. In this respect one wonders about the relative effect of surface films on fracture strength. If the film significantly changed the mode of deformation, as has been found in zinc, then one would expect a major change in fracture strength. In the more general case however, where the metal being tested probably already contains some surface film which is not affected very much by the changes in environments, it would be difficult to see how a film effect could account for the strength difference. Various other investigators have also noted changes in strength which are more in agreement with the idea that the change in surface energy is the predominant effect (300-302).

Of some interest are the rather spectacular increases in strength found in less ductile metals with suitable surface conditions. These results are reminiscent of those found in ceramics for they indicate that considerable gains in strength may be achieved by proper surface conditions. Mention has already been made of the fact that bulk silicon exhibits very high strengths if the surface is carefully polished (144,163). M. Classen-Neckludova (303) found that preliminary etching of bismuth single crystals in acid produced no effect, but that when the crystals were tested in acid they were much more ductile and stronger than in air. Zinc single crystals, on the other hand, were about equally strong in acid and in air, and surface scratching had no effect on the strength. Briedt, Hobstetter and Ellis (304) found the fracture stress of germanium increased from 7Kg/mm^2 to 48Kg/mm^2 when the specimens were tested in acid. If specimens were removed from the acid the strength in air persisted for a short time and then fell off with increasing time. Johnston, Stokes, and Li found the strength of germanium in a "CP 4" etching solution to be 300 Kg/mm^2, which is about 3 times the strength of germanium whiskers (305). These results show that less ductile metals are especially sensitive to surface conditions.

Changes in fatigue properties with surface conditions have been widely studied. It is well recognized that thin metallic coatings can have a profound influence on fatigue strength. These effects on strength may be due to mechanical effects, such as cracks in the coating, residual stresses and so on (306). A number of different investigations have also been made of fatigue in various environments (203-207,209,217,231-233,307-313). Liquid metals, especially mercury, have been found to be very damaging to fatigue life. Tests in gaseous environments indicate that oxygen and/or water vapor tend to lower the fatigue life. Wadsworth and Hutchings (314) have found that small surface cracks tended to form on copper and aluminum specimens early during the fatigue tests. These cracks formed in both air and in vacuum at about the same time. In air however, the cracks propagated much faster. They also found the fatigue varied with the air pressure. They concluded that there were two effects which could cause the changes in life; stress-corrosion in the crack (Gurney's mechanism) or oxidation of the sides of the crack to prevent rehealing of the cracks. It would seem that if fatigue life is controlled by crack propagation that Orowan's mechanism should also be important.

The creep of metals and metal alloys in gas environments has been studied by a number of different workers (315-325). In some cases it was found that creep strength was greater in air than in vacuum or inert gases, while in other cases the reverse was true. These contradictory results probably reflect the different testing conditions that were employed by the various investigators. Shahinan and Achter found with Nickel (325) and Nichrome (324) that at higher temperatures and lower stresses the materials were stronger in air than in vacuum. With low temperatures and high stresses the materials were stronger in vacuum.

They suggested that these effects were due to two competing mechanisms, oxidation film strengthening at lower stresses and cracking due to lower interfacial energies at higher stresses. Thus, as pointed out by Achter and Fox, there should be a critical oxygen content to saturate the surface at the rate dictated by the creep rate of the specimen (326).

One final point that might be mentioned in connection with external environment is the effect of alpha particle bombardment on the surface during deformation. Alpha particles penetrate only a very short distance beneath metallic surfaces, and thus the influence of alpha bombardment during deformation should be due primarily to the surface changes produced. Three different investigators have studied the effect of alpha bombardment during deformation. The results are completely out of accord with each other. One investigator found an increase in the speed of deformation (327), one found no effect (328), and one found a decrease in the rate of deformation (329).

Internal Surfaces.

Thus far only the effects of changes in the environment at the external surface have been considered. There is also the possibility, as suggested by Rebinder, that there may be significant effects due to the penetration of the environment into the bulk of the metal during testing. It seems worthwhile to review some of the evidence concerning this possibility.

There are several situations that have been studied where penetration appears to have taken place. One of these is the grain boundary penetration by liquid metal into a solid metal. When a solid metal is deformed in the presence of a liquid metal a number of different effects have been observed,

including dissolution of the solid metal, intermetallic compound formation, erosion, mass transfer, etc. (330). With certain combinations of solid and liquid metals, however, the major effect seems to be one of the liquid metal penetrating and wetting the grain boundaries of the solid metal. This last possibility offers some chance to study penetration by an external environment.

The energy criteria for spontaneous grain boundary wetting is given by the equation:

$$f^S \leqslant \tfrac{1}{2} f^B \qquad (2)$$

where f^S, f^B are the solid-liquid and grain boundary interfacial energies respectively. Several examples of systems where spontaneous wetting takes place are Cu-Liquid Bi, austenite-liquid FeS, and WC-liquid Co (331). Another interesting example is Al-liquid Ga. Elbaum (332) found when Ga was placed on a sheet of polycrystalline aluminum that within a short time the liquid wetted the grain boundaries and destroyed the cohesion between the grains. The individual grains could then be separated in the same way as the pieces in a jig-saw puzzle.

It should be noted that grain boundary wetting of this type is not a corrosion reaction in the general sense of the word. No compound is formed, and there does not appear to be any change in valence of the respective metals. What seems to be involved is a replacement of the solid metal atoms by the liquid metal.

It is clear that if a solid metal were deformed in a liquid metal in which equation (2) were obeyed that there would be a noticeable drop in strength and considerable boundary penetration. Combinations of solid and liquid metals that have such interfacial energies are not the general case however. In most cases the liquid-solid interfacial energy is not low enough to product spontaneous wetting. It appears however, that in many of these latter cases wetting

may be promoted by the application of a tensile stress to the solid. Numerous investigations of this effect have been made (333-365,444). The most common systems studied are copper alloys and steels in low melting metals such as lead, mercury, and solders of various compositions.

From these investigations several pertinent facts have emerged. The first is that at equilibrium, with no stress applied to the solid, there is negligible penetration of the liquid phase. It also appears that there is no significant change in the stress-strain characteristics of the solid metal as it is deformed. That is, the load-elongation curve of a metal in a liquid metal follows essentially the same curve as the metal in air (346,350,362,366,367). However when the solid metal is tested in the liquid, fracture takes place at a much lower stress. Thus the effect of the liquid metal does not seem to be one of a film effect because there is no noticeable change in the plastic deformation characteristics of the solid.

In addition, a tensile stress seems necessary to show any marked decrease in strength. If a compressive stress is applied the strength in liquid metals is comparable to that in air (338,349,361). Furthermore, there is usually a certain minimum tensile stress necessary to produce any effect, and if this stress is not reached during testing the solid is unaffected by the deformation (341,344,345,348,358). A residual tensile stress will also produce surface cracking. In fact one of the methods for determining the presence of residual stresses in brass is to emerse the brass in a mercurous nitrate solution and then inspect it for surface cracks (368).

There has been an additional set of investigations on the effect of an internal liquid phase on the mechanical properties. In these investigations a

metal with a low melting second phase is generally used, such as a leaded brass or steel. For example Eboral and Gregory (369) noted that the effect of an internal lead phase on the strength of brass above the melting point of the lead. They found that when the brass was heated above the melting point of the lead with no stress that the lead remained as discreet globules. When the brass was fractured however, the lead was found to have wet the boundaries of the brass. A number of other investigators have noted sharp fall-offs in strength with various two phase alloys when the testing temperature exceeded the solidus temperature of the low melting phase (370-375).

These results are of great importance in a number of metallurgical problems. Weld cracking, hot tearing, and hot shortness, for example, are all associated with cracking or fracture promoted by a lower melting point liquid in contact with a solid metal. William, Rieppel, and Voldrich have reviewed over 1400 papers dealing with weld cracking and hot cracking (376). They concluded that cracking is intergranular and associated with the segregation of low melting constituents to the grain boundaries. Cracking is also controlled by the stresses imposed upon the solid during cooling. Later work supports this idea, and suggests that low melting point eutectics at the grain boundaries together with a stress on the solid metal are the causes of cracking (377,378).

Although it is clear that low melting liquids are deleterious to the strength, it is not certain whether penetration of the liquid into the solid grain boundaries is the sole cause of this effect. Petch has pointed out that a soft phase inside a hard matrix would act as a notch and reduce the strength of the matrix (379). Thus there is the possibility that the effect of an internal liquid is only that it has low strength and introduces notches in

the bulk metal. There is also the possibility that an external liquid may produce notch effects. If the external liquid wetted the boundaries to a limited extent, this wetting might be sufficient to produce notches at the grain boundaries and a consequent decrease in strength.

Other explanations are also possible. By Orowan's mechanism the lowering of the surface energy may be sufficient to explain many of the general effects that have been noted. The most prevelant opinion seems to be however, that there is some penetration of the liquid metal into the grain boundary ahead of fracture (338,343,346,347,364,365,380,381). It has been noted, for example, that the fracture may be time and temperature dependent (340-342,349). This would suggest a diffusion of the external environment into the grain boundaries. Most of the other commonly observed results with liquid metals are in agreement with the idea that wetting takes place prior to fracture.

Why should wetting take place? One reason is that the adsorption of foreign atoms at a grain boundary would tend to lower the grain boundary energy (382-384). Thus a liquid metal that did not cause complete wetting might still be partially adsorbed at the grain boundary. This lowering of the grain boundary energy thus provides the driving force necessary for the penetration of the environment. The problem then becomes the one of kinetics, that of diffusion of the external atoms into the grain boundary.

Other, and perhaps better evidence of penetration is furnished by studies of gaseous environments on solid metals. A well-known phenomena during creep, for example, is the development of voids or cracks at the grain boundaries. The occurrence of these defects has been found to be fairly sensitive to the external environment (385-388). Various interpretations have been made for these

results. The point however, is that changes in the external environment produce a change in the internal deformation. In this case the only reasonable way this could happen is that the external environment penetrated into the grain boundaries.

Another well-known example is hydrogen embrittlement of steel. If a steel contains a sufficient amount of hydrogen it will become brittle. Also if the steel is held under stress in an atmosphere containing hydrogen, there is a pronounced tendency for embrittlement of the steel (389-402). The question is then, does the external hydrogen diffuse into the steel and promote fracture by the same mechanism as the internal hydrogen, or does the external hydrogen act by some equally serious but different mechanism at the surface. It seems more reasonable to assume that the hydrogen diffused into the steel and that the embrittling mechanism is the same in both cases.

With respect to the hydrogen embrittlement mechanism, it is interesting to note that more recent opinions hold that the embrittlement is due to the formation of low-interfacial-energy cracks (403-407). This mechanism of course, is the one originally postulated by Rebinder to account for the influence of surface-active agents.

Other examples might also be given. The foregoing should be sufficient however, to show that under certain conditions the external environment may penetrate into the bulk of the metal. Whether this is always the case during deformation in surface active environments, as claimed by the Russian school, remains to be seen. There is certainly reason to doubt however, that penetration is such a general phenomena.

Summary of Literature Review.

There appears to be no doubt that environments which have only a limited reaction with solids may produce major changes in mechanical properties. A number of proposals have been made to explain these effects. These various theories can probably be classified into four different mechanisms.

1) The microcrack mechanism.

This mechanism predicts the strength to be controlled by the microcracks or defects on the solid surface. A mechanism of this type appears well suited for more brittle materials such as glasses or ceramics. The manner in which the microcracks are formed, and how they may be modified by the environment is not fully understood. There is little doubt however, that microcracks are the most important single mechanism in accounting for the strength of the brittle solids.

2) The surface energy mechanism.

The effect of changes in environment on brittle fracture strength may be explained in general by Orowan's mechanism. Unfortunately, accurate interfacial energy data is available for only a few scattered systems and thus quantitative confirmation of Orowan's mechanism is not possible. Also, Orowan's mechanism does not show how ductile deformation is affected by surface energy changes.

3) The penetration mechanism.

This mechanism is really a modification of Orowan's mechanism. It predicts that the environment penetrates into the solid and forms low surface energy interfaces. The major objection to this mechanism is that it has not been shown that penetration occurs except in a few special cases. A second objection is that the changes in ductile deformation are difficult to account for by this mechanism.

4) The dislocation barrier machanism.

This mechanism predicts that surface films block the exit of dislocations. There is a good deal of evidence that suggests that this is true, but again only qualitative confirmation has been obtained.

These four machanisms, if one is free to choose the proper one at the proper time, can probably account for most of the results that have been obtained. The problem is, what dictates whether one mechanism or another becomes the most important. In some cases this decision is fairly obvious; in others it is not. For example, ceramic solids seem to react in some cases by the microcrack mechanism and in others to a dislocation barrier one. The reason why this should be so is not clear.

There seems to be two possible ways to resolve this difficulty. The first is to perform a number of suitable investigations which show the dividing boundaries where one mechanism loses predominance and another takes over.

A second, and seemingly more attractive possibility, is to try to develop a general theory which would account for all the various results. It would seem that surface energy might be a basic quantity that could be used as a common denominator to explain the results. Some of the uses and shortcomings of surface energy approches have been pointed out. If there were significant changes in surface energy with strain however, a much more general usage of surface energy might be possible.

With these considerations in mind the immediate problem of the nature and extent of these changes should now be dealt with. There are several possible ways that might be used to relate surface energy changes with strain. Since surface energy is basically a thermodynamic quantity however, the problem seems best approached by a thermodynamic treatment. This treatment is presented in the following section.

THEORETICAL CONSIDERATIONS

For two phases in equilibrium the surface free energy of the interface between the phases is defined as:

$$f = \frac{F^T - F^1 - F^2}{A} \tag{3}$$

where f = the surface free energy.

F^T = the total Helmholtz free energy of the system.

F^1 = the Helmholtz free energy of phase one.

F^2 = the Helmholtz free energy of the second phase.

A = the interfacial area between the two phases.

Now let us consider a system consisting of a polycrystalline solid surrounded by an external environment. The total free energy of this system may then be taken as the sum of the free energies of the solid and the environment phases, plus the surface free energies of the grain boundaries and external surface of the solid. That is

$$F^T = F^V + F^E + f^B a + f^S A \tag{4}$$

where F^V = the volume free energy of the solid, which equals the sum of the free energies of the individual grains within the solid.

F^E = the free energy of the external environment surrounding the solid.

f^B = the average grain boundary free energy of the solid.

a = the total grain boundary area of the solid.

f^S = the average surface free energy of the solid.

A = the total area of the external surface of the solid.

Now let us deform the solid elastically and isothermally by the application of a uniaxial tensile force to some strain ϵ. Then at strain ϵ

$$F_\epsilon^T = F_\epsilon^V + F_\epsilon^E + f_\epsilon^B a_\epsilon + f_\epsilon^S A_\epsilon \qquad (5)$$

where the subscript ϵ refers to the strained condition. The change in free energy going from zero strain to strain ϵ is:

$$F_\epsilon^T - F_o^T = (F_\epsilon^V - F_o^V) + (F_\epsilon^E - F_o^E) + (f_\epsilon^B a_\epsilon - f_o^B a_o) + (f_\epsilon^S A_\epsilon - f_o^S A_o) \qquad (6)$$

where the o subscript refers to the unstrained condition.

If the system is deformed by applying a load to the solid, then the change in free energy of the surrounding environment is negligible. That is $F_\epsilon^E - F_o^E = 0$. (7)

The change in the total free energy of the solid when it elastically and isothermally strained is equal to the reversible work. So

$$F_\epsilon^T - F_o^T = \text{work rev.} = \int F dl \qquad (8)$$

where F = applied force.

l = length.

For uniaxial elastic deformation the change in length is proportional to the applied force. Thus for small strains the change in the total free energy of the solid may be reduced to

$$F_\epsilon^T - F_o^T = \frac{V}{2} E' \epsilon^2 \qquad (9)$$

where V = the volume of the solid

ϵ = axial strain

E' = the slope of the stress-strain curve

The change in the volume free energy of the solid is given by

$$F_\epsilon^V - F_o^V = \frac{V}{2} E \epsilon^2 \qquad (10)$$

where E is the elastic modulus of the solid. It is important to note that in general, E does not equal E'. The elastic modulus E is related to the bonding

energy of the atoms within the solid and for example, may be related to the speed of sound in the solid. The slope of the stress-strain curve E', is related to the total reversible work in deforming the solid. Several investigators have shown, as will be discussed more fully later, that changing the external environment causes a change in E'. It is difficult to see how these changes in environment could cause a change in the bond strength of the atoms in the bulk of the solid and thus cause a change in the modulus E. Since it is possible to change E' without changing E, the two are not necessarily equal. E' is a measure of energy required to deform the bulk solid and the interface, while E measures on the energy required to deform the bulk.

Equation (6) becomes:

$$\frac{V}{2}\left[E' - E\right]\epsilon^2 = \left[f^B_\epsilon a_\epsilon - f^B_o a_o\right] + \left[f^s_\epsilon A_\epsilon - f^s_o A_o\right] \qquad (11)$$

Now consider the change in external area A. A simplification may be made by noting that

$$A_\epsilon = A_o + \Delta A = A_o + A_o\,(1 - \nu)\epsilon \qquad (12)$$

where ν = Poissons ratio

or

$$A_\epsilon = A_o\,(\,1 + (1 - \nu)\epsilon) \qquad (13)$$

For elastic strains $\epsilon \ll 1$ so to a good approximation $A_\epsilon = A_o$ (14)

In the same manner the changes in grain boundary area are also negligible with small strains so that

$$a_\epsilon = a_o \qquad (15)$$

and so

$$\frac{V}{2}(E' - E)\epsilon^2 = (f_\epsilon^B - f_o^B)\, a_o + (f_\epsilon^s - f_o^s)A_o \tag{16}$$

is a good approximation of Equation (7) for very small values of ϵ.

Rearranging this last equation gives:

$$\frac{V}{2A_o}\,(E' - E) = \frac{1}{\epsilon^2}\left[(f_\epsilon^s - f_o^s) + \frac{a_o}{A_o}\,(f_\epsilon^B - f_o^B)\right] \tag{17}$$

Now let us perform two mental experiments. Let us take some solid measure V, A_o, a_o, E' and E and strain it to a strain ϵ in some environment. Equation (17) then becomes

$$C_1 = \frac{1}{\epsilon^2}\left[(f_\epsilon^s - f_o^s) + C_2\,(f_\epsilon^B - f_o^B)\right] \tag{18}$$

where C_1 and C_2 are constants depending upon the measured values.

Now let us take the solid, change V and A_o somewhat, and again strain the solid to the same strain in the same environment. Then we may write

$$C_3 = \frac{1}{\epsilon^2}\left[(f_\epsilon^s - f_o^s) + C_4\,(f_\epsilon^B - f_o^B)\right] \tag{19}$$

where C_3 and C_4 are new constants. Then substracting equation (19) from equation (18)

$$C_1 - C_3 = \frac{1}{\epsilon^2}\,(C_2 - C_4)\,(f_\epsilon^B - f_o^B) \tag{20}$$

or

$$f_\epsilon^B - f_o^B = \frac{C_1 - C_3}{C_2 - C_4}\,\epsilon^2 = j\epsilon^2 \tag{21}$$

where j is a constant. In the same manner it can be shown that

$$f_\epsilon^s - f_o^s = k\epsilon^2 \tag{22}$$

where k is another constant.

Equations (21) and (22) are the important results of this derivation for they show that the surface and grain boundary free energies should vary as the second power of strain. It may also be shown that these results indicate that the surface tension changes in the same fashion as the surface free energy.

First, substituting (21) and (22) into equation (17) gives

$$\frac{V}{2}\left[E' - E\right] = kA_o + ja_o \tag{23}$$

The surface tension may be defined by the equation

$$\gamma = \left[\frac{\partial F^T}{\partial A}\right]_{T,V,n_i} \tag{24}$$

where γ = surface tension

T = temperature

n_i = number of moles of component i.

From Equation (9)

$$F_\epsilon^T = F_o^T + \frac{V}{2} E' \epsilon^2 \tag{25}$$

so

$$\gamma_\epsilon = \frac{\partial F_o^T}{\partial A} + \frac{\partial}{\partial A}\left[\frac{V}{2} E' \epsilon^2\right] \tag{26}$$

At strain ϵ, V and ϵ are constant so that

$$\gamma_\epsilon = \frac{\partial F_o^T}{\partial A} + \frac{V}{2} \epsilon^2 \frac{\partial E'}{\partial A} \tag{27}$$

but

$$\left[\frac{\partial F_o^T}{\partial A}\right]_{T,V,n_i} = \gamma_o \tag{28}$$

and from (23)

$$\frac{\partial E'}{\partial A} = \frac{2k}{V} \tag{29}$$

so that

$$\gamma_\epsilon = \gamma_o + k\epsilon^2 \tag{30}$$

where the constant k is the same constant as found for the surface free energy change with strain. The surface energy and surface tension in general are not equal unless one arbitrarily selects a convention for locating the dividing surface which makes them equal. The present result shows however, that both the surface energy and the surface tension change in the same manner with elastic strain.

It should be emphasized that these relationships are approximate ones and not rigorous ones. The approximations involved are that the changes in surface area and volume are negligible. It is also assumed that E' is constant over the range of strains that are being considered. Since the elastic strains are quite small these approximations are justified.

It should also be noted that the grain boundary and surface energies and the surface tension are average values of these quantities. There will of course, be local variations in these quantities because of local variations in crystallographic orientation. The changes in f^B, f^S, and γ with orientation are usually fairly small however, and so it is reasonable to use average values.

Equations (21), (22) and (30) indicate that f^B, f^S, and γ should vary with strain. The important point therefore, is the magnitude of the constants j and k. If these constants are relatively small, then the changes would be negligible. If they are large however, then these changes could be significant.

Unfortunately, measurements of the grain boundary and surface energies or surface tension are difficult to perform, and such measurements have been made on only a few systems. To the author's knowledge, no one has measured f^B, f^S or γ as a function of the strain. With the use of the foregoing analysis however, it is possible to arrive at values of j and k by measuring E'. Equation (23) shows that

$$\frac{V}{2}\left[E' - E\right] = kA_o + ja_o \qquad (23)$$

Therefore, it should be possible to arrive at estimates of k by studying the variations in E' with size or environment. There are a number of such changes in E' that have been reported in the literature.

Many investigators have noted an increase in E' in glass or "quartz" fibers with decreasing fiber diameter. Perhaps the most systematic study has been a series of investigations by Reinkober on "quartz" fibers (13-15,408). Reinkober found that the stress-strain slope increased inversely to the diameter of the fiber, and approached a very large value at small diameters. A number of other investigators have noticed the same trend in quartz or glass (7,409-414).

On the other hand, Jurkow (16) found little variation in E' with size in this size range, but all his values of E' were much higher than nominal values for bulk quartz. Bateson and Murgatroyd noticed decreases in E' in glass fibers in this range (48,415). Murgatroyd's results were obtained from bend tests, however. The variations in surface energy with bending have not been considered, but the effect should be different because part of the surface is strained in tension and part in compression.

Variations in E' of glass with environment have been noted in both fibers (17) and bulk specimens (416).

With regards to other non-metallic solids, several investigators have noted large changes in E' from nominal values with changes in size or environment in materials such as MgO (119) and graphite (417).

Changes in E' with size in metal specimens have received surprisingly little attention. Several investigations of metal whiskers or thin films have noted E' measurements more or less in passing. The results themselves are contradictory. In one case the values of E' were larger than normal (170), while in others the results indicated a decrease in E' (171,418). Small sized silicon samples showed E' values consistent with bulk values, but these measurements were made by bend tests (163).

Changes in E' with environment in bulk metal specimens have been shown by Sato (419). He found E' for a 1.5% C steel changed up to 20% from the values in air when the specimens were tested in various liquid environments. Russian investigators have also noted that there should be changes in E' with environment (227).

In addition to direct measurements of E' there is another group of investigations which also indicate that there are changes in E' with environment. These investigations have shown that solids will undergo small changes in length with changes in the adsorbed atoms on the surface. In many cases these changes in length were found to be reversible.

Since the solid supports its own weight it is under some stress, and a change in length over a fixed length is equivalent to a strain. Therefore, some finite strain has occurred under constant stress, which would certainly

indicate that some change in E' has taken place with absorption.

Changes in length of this type have been found by Bangham (420,421) Yates (422-424), and others (425,426) for porous materials such as coal and charcoal and also for glass. Benedicks found similar changes in length in quartz and platinum fibers that were held under constant load and alternately emmersed in air and distilled water (3). Finally, McBains and Sessions noted that "quartz" springs changed in length on exposure to various gaseous environments (427).

Although all these various results are not conclusive, they clearly show that there are changes in E' with environment or specimen size. In a few cases, the data is sufficient to allow an estimate of the value of k.

For a cylindrical specimen or radius r, and assuming "quartz" fibers have no grain boundaries, equation (23) then becomes

$$E' = E + \frac{4k}{r} \tag{31}$$

Reinkober (15) found empirically that E' for "quartz" fibers could be expressed by an equation

$$E' (kg/mm^2) = 4500 + \frac{36000}{d} \tag{32}$$

where d is the diameter of the fibers in microns. The data of the other investigators agrees fairly well with this result. Converting to cgs units Reinkober's constant of 36000 gives a value of k of 1.76×10^8 ergs/cm^2.

It is also possible to derive some estimate of k by measuring the difference in E' when the solid is tested in two different environments. Thus if

$$E_1' = E + \frac{4k_1}{r} \tag{33}$$

for environment (1) and

$$E_2' = E + \frac{4k_2}{r} \tag{34}$$

for environment (2), then subtracting,

$$E_1' - E_2' = \frac{4}{r}\left[k_1 - k_2\right] \tag{35}$$

If the indices are chosen such that $E_1' > E_2'$, then $k_1 - k_2$ is positive. Assuming both k_1 and k_2 are positive, then

$$k_1 = k_2 + \left[E_1' - E_2'\right] \frac{r}{4} \tag{36}$$

and experimental determination of E_1' and E_2' determine the minimum value of k_1.

Measurements of E' in different environments made by several different investigators are tabulated in Table I. In general, they indicate that $k_1 - k_2$ to be on the order of 10^8 to 10^9 ergs/cm^2. Therefore, the values for k seem to be this order of magnitude or greater.

It should also be possible to evaluate the magnitude of j by the change in E' with the grain boundary area to volume ratio or with changes in boundary composition. A number of investigations have been made (428-434) of the variations in E' with grain size, but these results do not lend themselves to accurate measurements of j. The reason for this is due to the way in which these grain size changes were achieved. In these investigations, the materials were cold worked and then annealed at different temperatures to produce the varying grain sizes. This method changes not only the grain size but also the orientation of the grains. Thus the resultant variations in E' would be due not only to the grain boundary to volume ratio in itself but also to the

changes in crystallographic texture which could change E'. For this reason, these results cannot be used to give any estimate of j. In the same manner, changes in E' with grain boundary composition are of no use because other variations within the specimen make it impossible to single out the composition effects alone.

TABLE I

Changes in E' with Environment from Data Reported in the Literature

Solid	Environment	E' dynes/cm^2	Reference
glass	air	5.22×10^{11}	416
	methanol	4.56×10^{11}	
	glycerine	3.65×10^{11}	
	distilled H_2O	3.46×10^{11}	
quartz	air	11.2×10^{11}	3
	distilled H_2O	7.41×10^{11}	
platinum	air	8.35×10^{10}	3
	distilled H_2O	3.59×10^{10}	
steel	air	23.9×10^{11}	419
	methanol	22.4×10^{11}	
	glycerine	19.4×10^{11}	
	distilled H_2O	19.1×10^{11}	

EXPERIMENTAL PROCEDURE

Preliminary Tests on Wire Specimens.

In order to confirm the reported variations in E' with environment a series of preliminary tests were made to determine if such changes could indeed be observed.

These tests were conducted using metal wires. The materials investigated were copper, platinum, tungsten, and coin silver. All four were purchased in the form of .010" diameter wire. Whenever possible the specimens of each material were taken from one continuous length of wire in order to minimize any variations in size, composition, microstructure,etc. between the specimens of one material. This procedure was possible for all specimens except those of coin silver. In this case the wire was supplied in 12" lengths. All of these specimens were taken from one small shipment of wire.

Tensile tests on these wires were conducted on an Instron Testing Machine. In order to insure that the wires were not pulled through the gripping jaws of the machine during testing the following procedure was used. The bottom half of the "C" load cell universal of the Instron was removed and a .020" diameter hole was drilled through the universal pin. In each test the wire was placed through this hole and then a ball of solder was applied to the upper portion of the wire. Another ball of solder was applied to the lower portion of the wire which was then held by the lower jaws of the machine. By this method a firm grip could be obtained on the wire, and also some of the slack normally present was eliminated.

The environment was placed around the specimen by holding it in a glass tube that was sealed near the bottom of the wire by cement. The weight

of the environment was accounted for by balancing of the Instron recorder. A schematic view of the experimental arrangement is shown in figure 3.

Prior to testing, the wires were cleaned to remove any grease on the surface. No attempt was made to produce a chemically-clean surface. It was later found that some wires that had not been cleaned but were tested in the as-received condition gave no appreciable difference in measured properties from the degreased ones. Thus the superficial surface cleaning does not seem to be significant in the present results.

Four different environments were used, air, distilled water, distilled water saturated with stearic acid, and benzene. The tests were conducted at a strain rate of .02" per minute. The stress-strain slopes were measured by cylcing the applied load between two stresses at which no relaxation was detectable. No hysteresis loop was observed in the stress-strain curves. Some additional tests at higher strain-rates showed that there was no detectable change in the values of E' for strain rates up to 0.5 inches per minute. Most of the E' measurements were conducted at stresses ranging from 7000 to 10,000 psi. Tests at lower stresses did not show any detectable variations in the values of E'. Thus the assumption that E' is a constant is valid within the experimental accuracy of these measurements.

The measured values of E' for the four materials in the various environments are listed in Table II. Each value listed in the table represents an average of four or more separate tests.

It is apparent from Table II that there are distinct changes in E' for each material as the environment is changed. Furthermore, in view of the relatively small scatter in the data in most cases, it does not seem possible

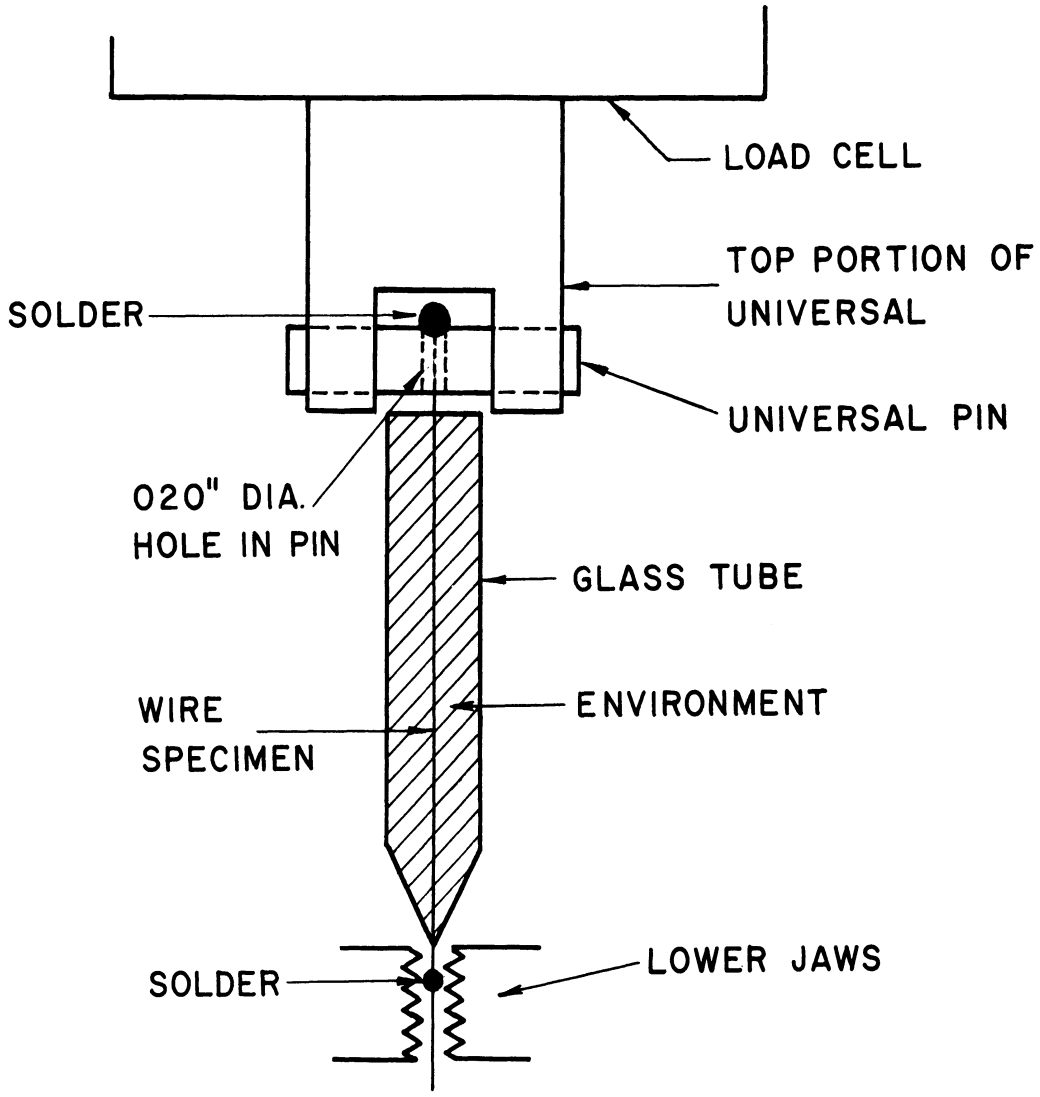


FIGURE 3 - SCHEMATIC VIEW OF APPARATUS FOR TESTING WIRES IN LIQUID ENVIRONMENTS

to attribute the difference to an overall variation in E' of each material. It is questionable whether it is significant to include the second decimal point in measuring the stress-strain slope, but rounding off the values to the nearest tenth still shows distinct differences in E' in most cases.

TABLE II

Tests on .010 inch metal wires in various environments.
Observed values of E' (psi x 10^6)

	Material			
Environment	Copper	Platinum	Tungsten	Coin Silver
Air	13.49 ± .18	25.6 ± .2	45.9 ± .4	9.94 ± .04
Dist. H_2O	12.09 ± .01	24.8 ± .1	46.6 ± .2	9.79 ± .11
Dist. H_2O plus stearic acid	12.80 ± .12	24.7 ± .1	43.9 ± .5	9.68 ± .16
Benzene	13.17 ± .01	24.9 ± .6	43.4 ± .7	9.58 ± .03

conversion factor: 1 psi = 6.89 x 10^4 dynes/cm^2.
± values are mean deviations

The values in Table II are somewhat lower than the nominal modulus values for these materials. Probably the slack in the testing arrangement is responsible for part of this effect. Since only differences in modulus are important however, the individual values are not critical because the same method was employed throughout.

The maximum difference in k's and also the minimum differences in k's for each material corresponding to the changes in E' are listed in Table III. In all cases the differences in k's are on the order of 10^8 ergs/cm^2. Therefore these tests agree fairly well with the reported results which indicate that k is on the order of at least 10^8 ergs/cm^2.

TABLE III

Maximum and Minimum Differences in the Values of k in ergs/cm^2 Corresponding to E′ Values in Table II.

	Copper	Platinum	Tungsten	Coin Silver
MAX Δk	6.12×10^8	3.94×10^8	1.40×10^9	1.58×10^8
MIN Δk	1.40×10^8	0.44×10^8	2.18×10^8	0.44×10^8

In addition to changing the environment a series of tests were run to determine if variations in E′ could be observed with changing wire diameter. Platinum wires of .005" and .003" diameter and tungsten wires of .006", .004" and .001" diameter were investigated. Two environments were used, air and distilled water. The method of measuring E′ was the same as that used for the .010" wires.

The results of these tests are listed in Table IV. The results show that E′ increases with decreasing wire diameter as would be expected from equation 23. On the basis this equation, E′ should vary linearly with the reciprocal of the wire diameter, and the slope of this line should be proportional to k. Plots of E′ versus the reciprocal diameter for the two materials in the two environments are given in figures 4 and 5. Measurements of E′ for the .001" tungsten wire in water were abandoned because of difficulty in testing the wire.

Figures 4 and 5 show that while E′ does increase with the reciprocal of the diameter the variations are not linear. However if one fits straight lines to each set of three points for the platinum values the corresponding values of k are approximately 0.7×10^8 ergs/cm^2, which is in general agreement

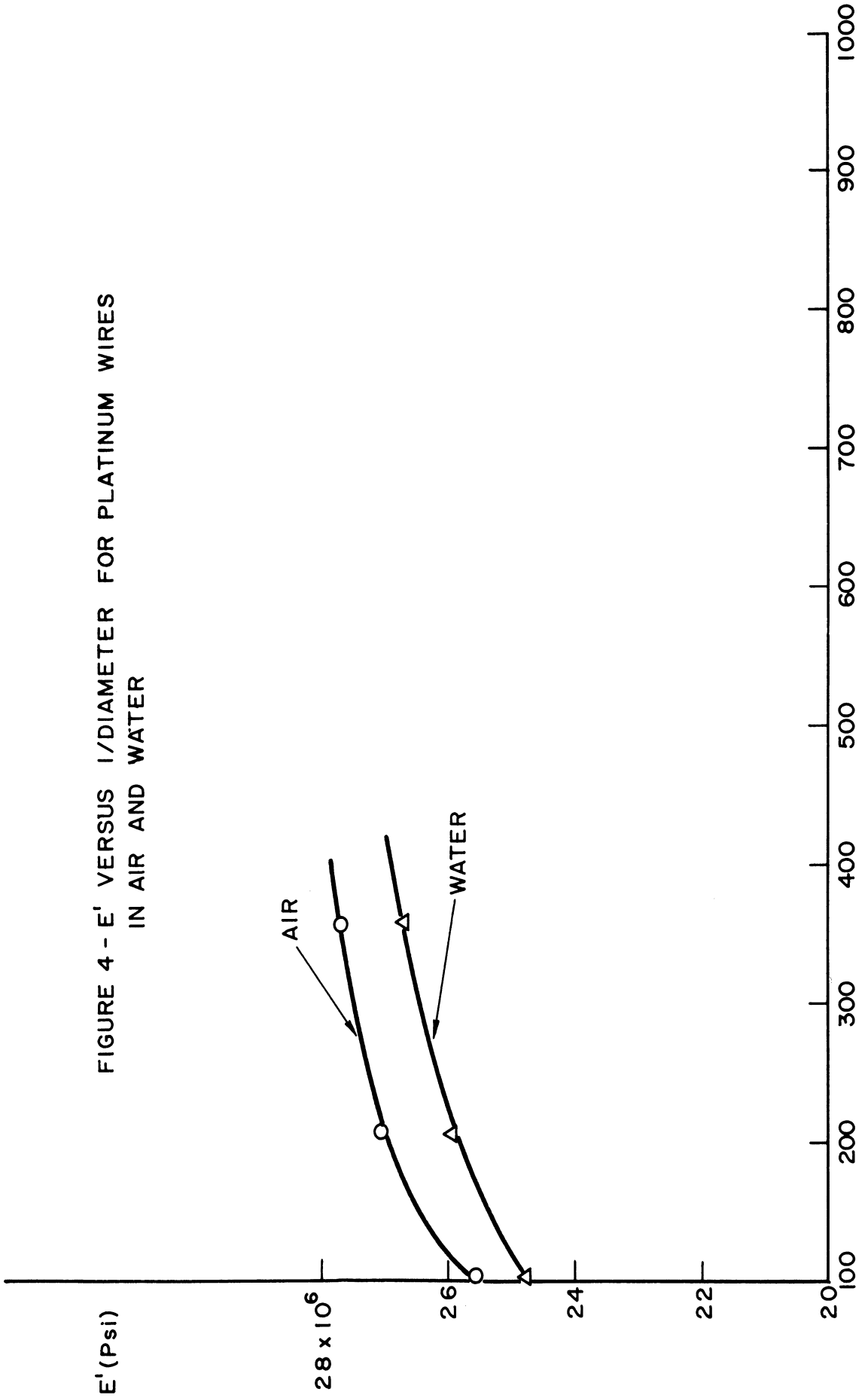


FIGURE 4 - E' VERSUS 1/DIAMETER FOR PLATINUM WIRES IN AIR AND WATER

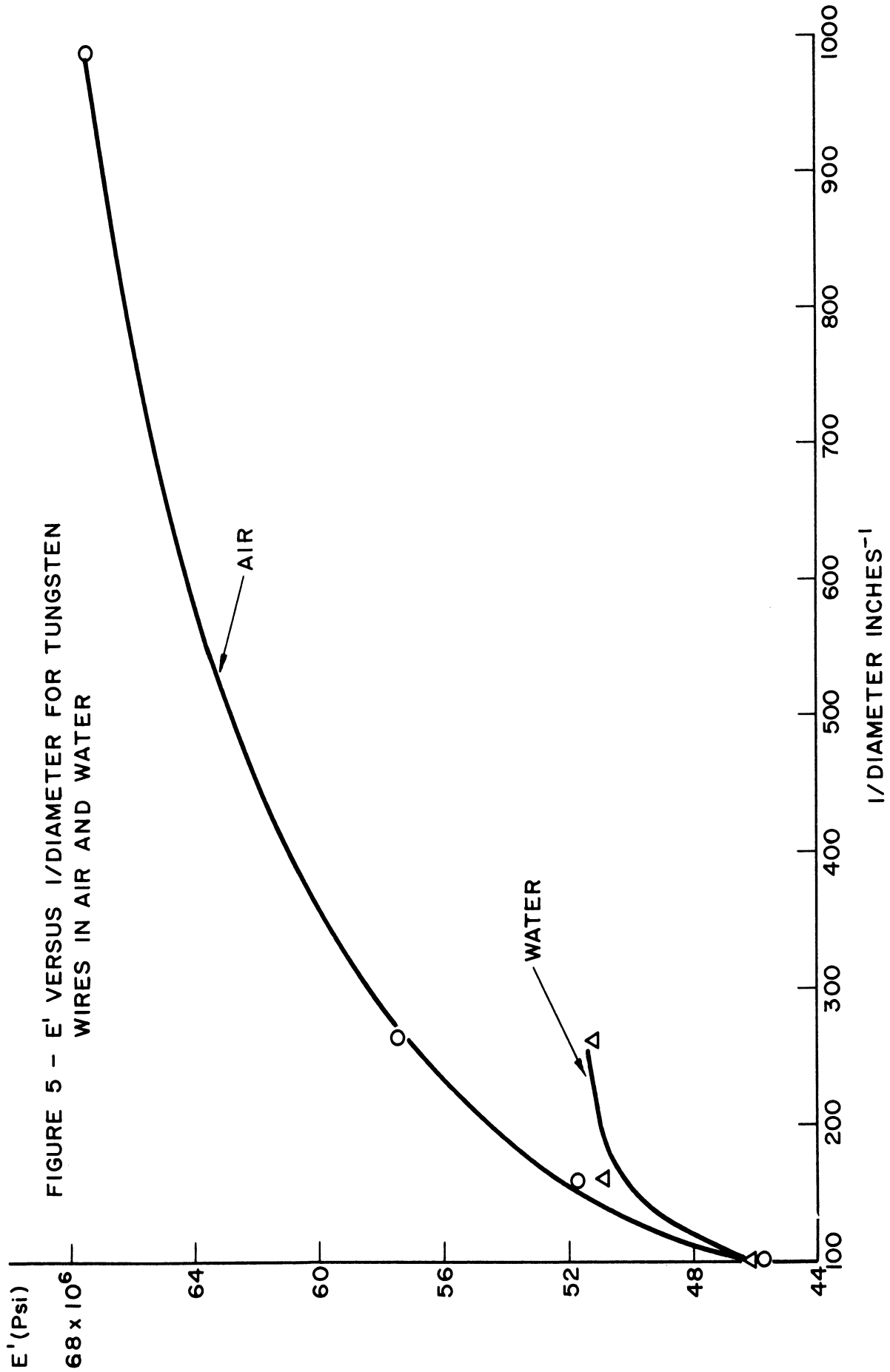


FIGURE 5 – E' VERSUS 1/DIAMETER FOR TUNGSTEN WIRES IN AIR AND WATER

with the previous results. The tungsten data shows a much greater departure from linearity and are not easily approximated by straight lines.

TABLE IV

Observed values of E' for platinum and tungsten wires of various diameters.

Material	Diameter	Environment	E' (psi) x 10^{-6}
platinum	.010	air	25.6 ± .2
platinum	.005	air	27.1 ± .2
platinum	.003	air	27.7 ± .3
platinum	.010	dist. H_2O	24.8 ± .1
platinum	.005	dist. H_2O	26.0 ± .2
platinum	.003	dist. H_2O	26.7 ± .3
tungsten	.010	air	45.9 ± .4
tungsten	.006	air	51.8 ± .6
tungsten	.004	air	57.7 ± .6
tungsten	.001	air	67.5 ± .9
tungsten	.010	dist. H_2O	46.6 ± .2
tungsten	.006	dist. H_2O	51.0 ± .6
tungsten	.004	dist. H_2O	51.2 ± .5

conversion factor 1 psi = 6.89×10^4 dynes/cm^2.

± values are mean deviations

These results are not conclusive however, because of the possible variations in structure between wires of different diameter. That is, it is possible that there are differences in crystallographic orientation between different sized wires of the same material. Differences such as this could be the cause of the variations in E'. Thus even if these results had shown a linear dependence of E' on the reciprocal diameter the results would not be conclusive because of the intrinsic variations possible within the wires might be the cause of changes in E'. Thus the real value of these latter tests is only that they are consistent with the predicted trend.

It should be pointed out that these objections with regard to variations in metal wires with size are not applicable to glass fibers. Thus the results of Reinkober and others who found variations in E' with size in glass fibers are still valid. This is so because there are no significant changes in structure or orientation in glass fibers with changing amounts of reduction. In the case of metal whiskers or films however, there may be significant variations in structure from those of bulk metals. Thus there may be changes in E' in these specimens because of intrinsic differences within the specimens.

Tests on Sheet Specimens.

The preliminary tests on the wires confirmed the reported changes in E' with environment and size and also that the values of k were on the order of $10^8 ergs/cm^2$ or larger. These results were not sufficient however, to fully show the possible variations in E', and did not furnish accurate estimates of the actual values of k and j. Therefore a second series of tests were conducted to more fully explore these points. These tests were conducted on a series of copper sheet tensile specimens.

Specimen Preparation and Design.

On the basis of equation 23 there are two possible ways to arrive at the values of k and j. The first way is to take two specimens of different sizes, that is of two values of A_o and V, and determine E, E' and a_o for each specimen. One would obtain two equations of the form:

$$C_1(k) + C_2(j) = C_3 \qquad (37)$$

$$C_4(k) + C_5(j) = C_6 \qquad (38)$$

where the constants depend upon the particular values that were found. One would then have two equations, and could solve for the unknowns, k and j.

The major objection to this method is that it is limited by the accuracy of the measurements of the modulus E. In practice determinations of E, by measuring the speed of sound for example, are accurate to about 2%. Large specimens would be necessary in order to measure E, however, and the variations in E' would only be on the order of several per cent. Thus the accuracy of this method would be quite limited.

The second way to determine k and j, and the one that was used, is to determine the slopes of plots of E' versus A_o/V and a_o/V. On the basis of equation 23 these slopes should be proportional to k and j. Furthermore, the intersections of the E' vs A_o/V curve with the E' axis should equal to $(E+2ja_o/V)$. Thus the consistancy of the plots can be checked by measuring E, but the values of k and j can be obtained without the necessity of using the value of E.

As was previously pointed out however, it is necessary when using this method to minimize any variations in the internal structure of specimens of different sizes. To attain this end the following method of specimen preparation was used. A large sheet of commercial purity copper of 3/8" thickness was purchased in the cold-rolled condition. One inch by six inch strips were cut from the sheet normal to the rolling direction. These strips were then recrystallized by annealing them for one-half hour at 600°F. After annealing the strips were divided into three equal batches. The first batch was not annealed further. The second batch was additionally annealed for $\frac{1}{2}$ hour at 1200°F. The third batch was annealed for $\frac{1}{2}$ hour at 1500°F.

These heat treatments were employed in order to vary the grain size of the specimens. In order to measure j it is necessary to measure the change in E' with changing a_o/V, or thus measure E' with changing grain size. By giving all of the specimens the same original annealing treatment at 600°F a recrystallized, fine grained structure with the same texture was produced in all three groups of specimens. The secondary anneals were then employed to increase the grain size. By this treatment three different grain sizes could be obtained while minimizing the difference in the texture between the specimens.

After these heat treatments tensile specimens of three different thicknesses were machined from the bars in order to provide changes in A_o/V. A total of nine specimens was thus produced, consisting of three different thicknesses for each of the three grain sizes. The thicknesses of the finished specimens were .040, .069, and .250 inches. These three thicknesses correspond to values of A_o/V of 58, 37, and 16 inches^{-1} respectively. A sketch showing the finished specimens is given in figure 6. The machining of the specimens was done so that each specimen was cut from the center portion of the strip. After machining, 1/8" thick cold rolled steel plates were bonded to the shoulders of the specimens with epoxy resin in order to provide additional load-carrying support. A $\frac{1}{4}$" hole was then drilled through each shoulder. During testing the specimen was held by steel dowel pins running through these holes. Finally the specimens were given a stress-relief anneal of $\frac{1}{2}$ hour at 350°F in order to minimize any residual stresses from the machining operations.

Duplicate strips were given the same annealing procedures in order to provide specimens for a sonic measurement of E and for metallographic examination to determine a_o/V.

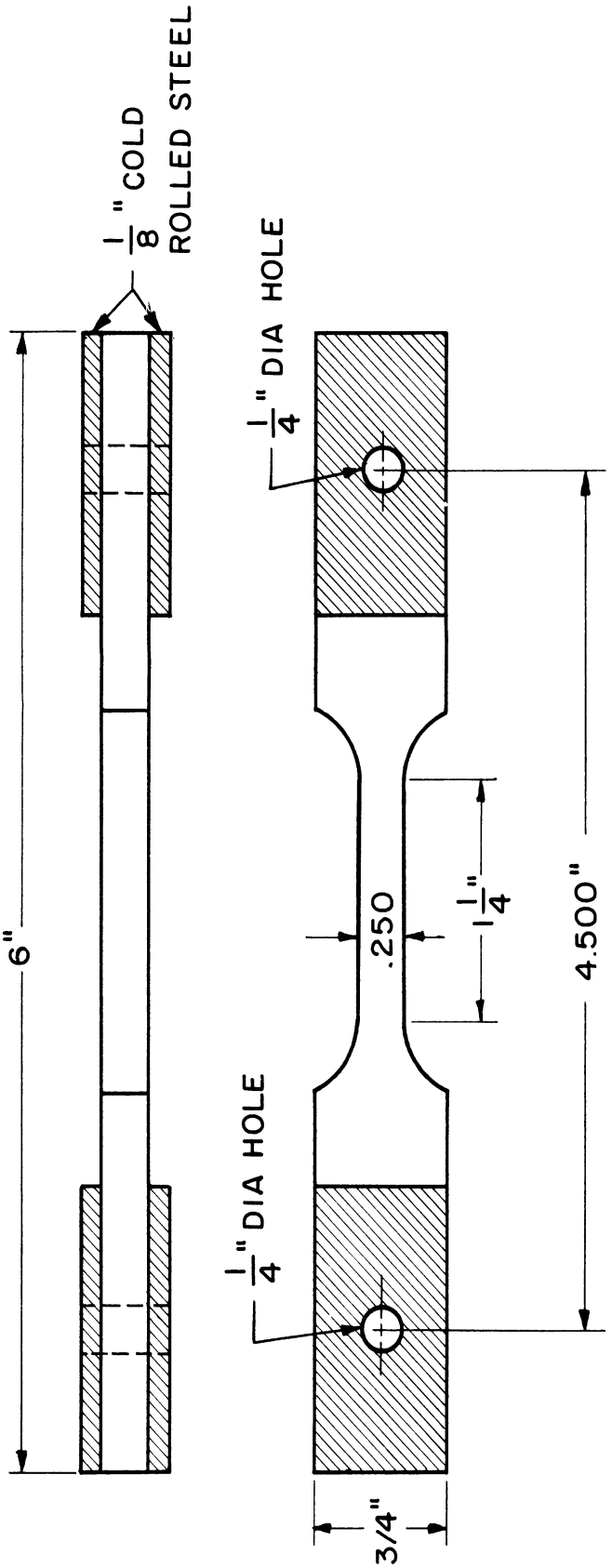


FIGURE 6 SHEET TENSILE SPECIMEN

By the above procedure it was possible to obtain specimens of varying a_o/V and A_o/V while minimizing the differences in orientation, composition, and cold work between the specimens.

Cleaning Technique.

If E' is affected by the environment surrounding the specimen it is logical to assume that the better the contact of the environment with the solid the more pronounced will be the changes in E'. For this reason it was felt desirable to thoroughly clean the surface of the specimens and then expose the cleaned surface directly to the testing environment before re-contamination in the atmosphere could take place.

Unfortunately most of the standard cleaning procedures act only to remove the excess surface grease or tarnish and, in many cases, replace the original contamination by some different type of surface layer. At the other extreme, it is very difficult to produce a chemically clean surface. Therefore some method of cleaning was required which would be effective in cleaning but which would not require overly lengthy or difficult procedures.

The method selected was cleaning by ion bombardment. Ion bombardment or cathodic etching has been developed in the past few years primarily as a method for etching metallographic specimens, and has proved of some value with materials that are not readily etched by conventional techniques. Several studies have also shown that ion bombardment is very effective in cleaning the surface (435-438).

The experimental arrangement for ion bombardment is quite straightforward. The sample is placed in a chamber together with a second metal plate that is located parallel to the surface to be cleaned and about 6 inches away

from it. The chamber is evacuated and a small amount of a slightly ionized gas, usually argon or krypton, is introduced into the chamber. An electric potential on the order of several kilovolts is then applied to the two pieces of metal such that the surface to be cleaned is cathodic and the second metal is anodic. This potential causes a coulomb attraction of the gas ions, which accelerate toward the cathode surface and strike it with high velocities. It is this bombardment by the gas ions, which physically knock off the surface atoms, that procedures cleaning and subsequent etching of the surface of the cathode.

The experimental arrangement used in the present investigation is shown in figure 7. A photograph showing the cleaning chamber is given in figure 8. The arrangement consisted of a vacuum system leading into the cleaning chamber. The chamber itself was essentially a thick walled glass cylinder with various inlets. The specimen to be cleaned was placed in the middle of the chamber and was connected by a copper rod running through the stopper to the voltage source. The aluminum plates at each end of the chamber were grounded and served as anodes during ion bombardment. Two anodes were used so that both the top and bottom surfaces of the specimen were bombarded. Small glass plates were placed on the steel shoulder supports of the specimen to serve as shields and concentrate the bombardment in the central portion of the specimen.

In operation the chamber was evacuated and flushed with argon several times. It was then evacuated and a small amount of argon bled in until a pressure of 10 to 20 microns was reached. A potential of about two kilovolts was then applied. When the potential was applied there was a marked increase in pressure indicating that material was being knocked off the surface of the specimen. The

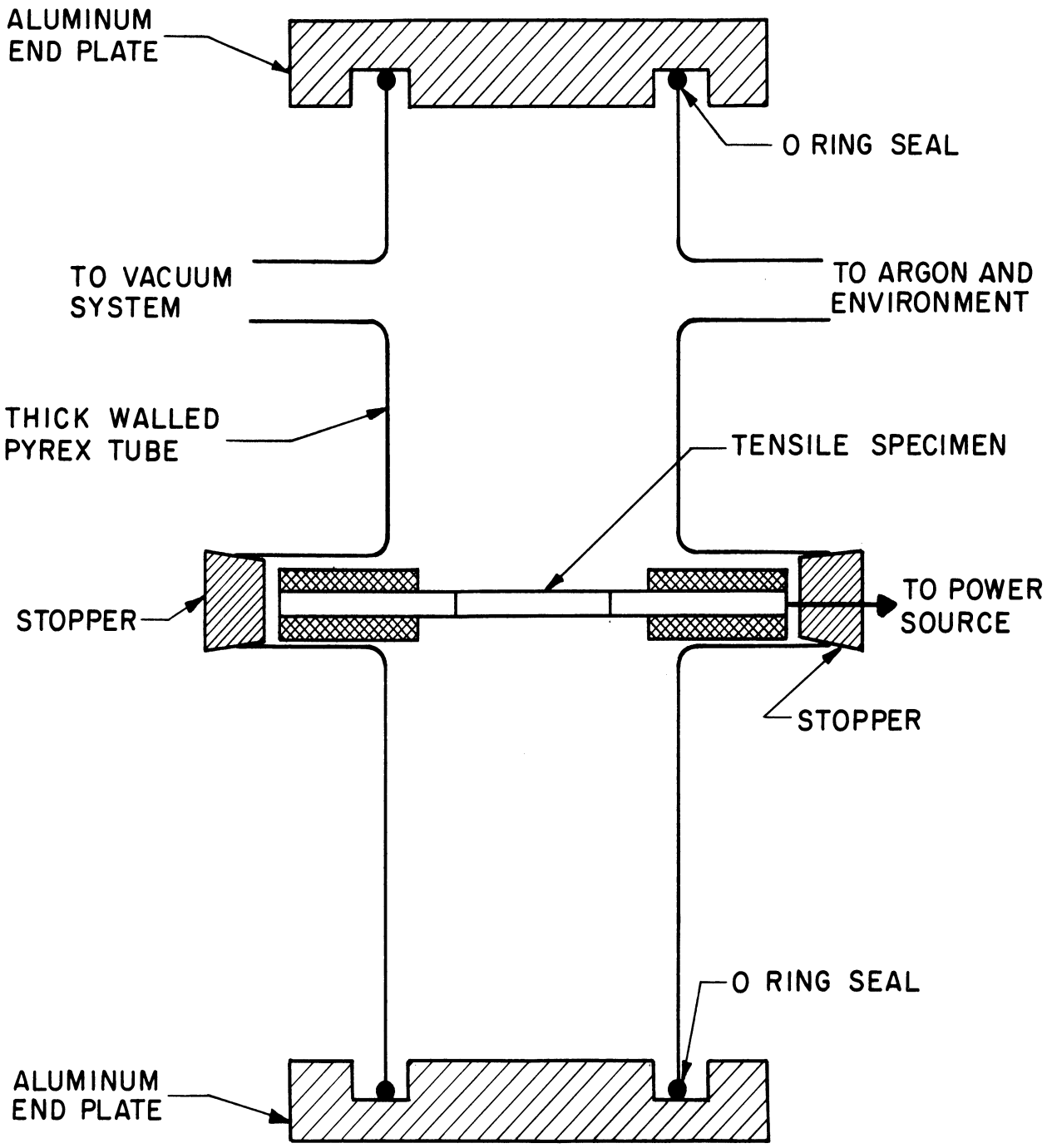


FIGURE 7 ION BOMBARDMENT CLEANING APPARATUS

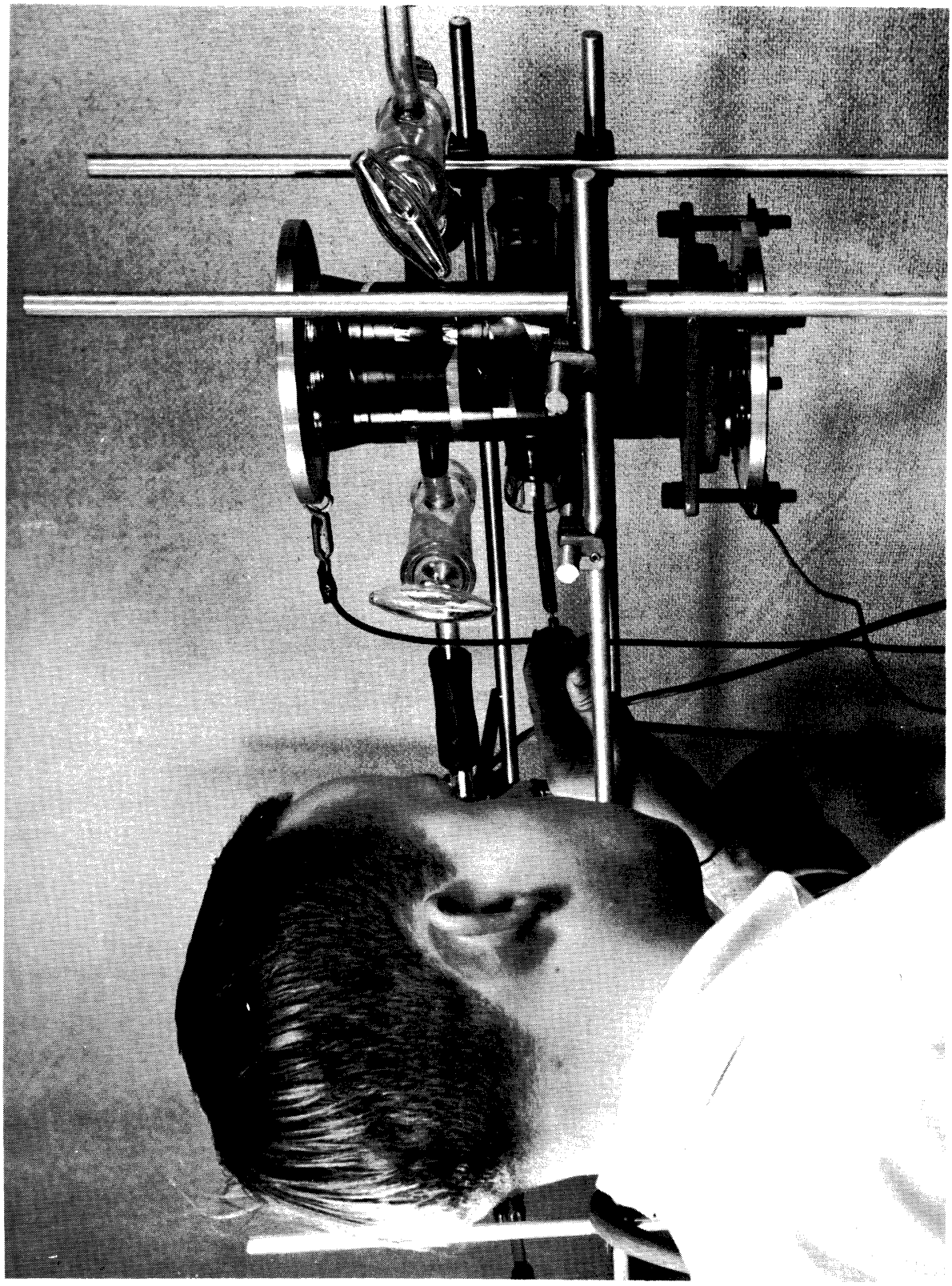


Fig. 8. Photograph of ion bombardment cleaning apparatus.

potential was then turned down until the pressure again dropped below 20 microns. The potential was then reapplied. The second application of potential usually produced a much smaller increase in pressure. This procedure was repeated several times, with more argon bled in periodically, until a 20 micron pressure was maintained with a potential of 3 kilovolts. At this point the potential and the vacuum source were turned off and the evacuated chamber opened directly to the testing environment. The specimen was removed from the flooded chamber and stored in the environment until testing.

After ion bombardment the specimens appeared quite clean. Copper specimens that originally were tarnished to the color of an old penny appeared very bright after bombardment. Wettability tests also indicated the surfaces were clean. A drop of water placed on the copper surface for example, approached a zero contact angle. The surface is quite likely not chemically clean, but is probably much cleaner than conventional cleaning operations produce.

Metallographic examination of some cleaned surfaces did not reveal any signs of etching. After cleaning about five or six specimens however, the inner walls of the cleaning chamber became covered by a visible film of copper indicating that some copper as well as surface impurities were knocked off by the ion bombardment. If the film within the chamber were allowed to accumulate the pumping efficiency of the vacuum system was markedly impaired, probably because the film adsorbed additional impurities which had to be removed by the vacuum system. This difficulty was overcome by periodically removing the film by scouring the inside of the chamber with a light abrasive.

The length of time, or the number of potential-pumping cycles before cleaning was complete depended to some extent on the elapsed time between cleaning

operations. That is, a specimen that was cleaned and tested on the previous day was generally much easier to clean again than one that had been sitting in air for a week. This difference of course merely reflects the increased degree of surface oxidation and contamination on standing in air. It was also noted that there was some difference in the ease of cleaning with differences in the environment to which surface had been previously exposed. Specimens exposed to the liquid environments were easier to reclean than those that were exposed to air.

Testing Technique.

In order to determine E' two independent measurements are necessary, the applied force and the strain. Force measurements are usually quite straightforward, requiring only a measure of the load applied to the specimen. Strain measurements on the other hand, are usually more difficult since they normally entail the use of some type of transducer which converts the strain in a fixed length of the specimen into some type of electrical or mechanical signal. Commonly these transducers are bonded to the specimen surface in some manner, such as an electrical strain gage which is glued to the surface or an extensometer arrangement which is mechanically clamped to the surface.

In the present case however, the problem was to study the effect of the surface itself. Thus the surface had to be kept free, and could not be covered by a transducer because then a new environment, the transducer environment, would replace the environment whose effects were to be studied. For this reason conventional strain measurement techniques could not be used in this investigation.

The method used was to calibrate the recorder of the Instron machine so that the recorder could be used to measure the actual values of E'. As was pointed out in connection with the tests on wires, the components of the Instron apparatus, the jaws, universal, load cell, and so on, will deflect to a certain extent under a given load. Thus the Instron chart measures not only the deflection in the specimen but also that of the machine itself. Fortunately however, it was found experimentally that the Instron deflection was linear over a fairly large load range. Thus by measuring the actual value of E' of a specimen with some transducer on the surface and noting the corresponding value of E' on the Instron recorder, the recorder could be calibrated so that subsequent E' values could be read from the recorder. It was then possible to test the specimens in the various environments without any transducers on their surfaces, and obtain the values of E' from the recorder.

To measure E' of the specimens SR-4 strain gages were bonded to the surfaces with Duco cement and then painted with neoprene to protect against aging of the cement. Gages were placed on opposite surfaces of each specimen in order to correct for strain variations due to bending. Strains were measured on a Baldwin strain indicator with a supplemental potentiometer to allow strain readings to the nearest micro-inch per inch. Stresses were applied by means of adding weights to a load pan hung by a dowel pin through the lower $\frac{1}{4}$" hole in the specimen shoulder. A series of weights were added and removed from the weight pan and the corresponding strains measured until approximately 20 separate load-strain readings were obtained. The strain in the specimens during loading never exceeded 10^{-3}.

The specimens were then tested in the Instron machine and the corresponding E' of the recorder determined with the SR-4 gages still in place. The specimens were held by steel dowel pins through the shoulder holes. The pins rested on specially machined "V" blocks which were inserted in the load cell "D" grips of the Instron. This gripping arrangement is shown schematically in figure 9. The reason for using this type of arrangement was to minimize the variation in gripping between tests. It had been found that to some extent the deflection of the Instron depended upon the gripping of the specimen by the jaws. This variation obviously had to be minimized to obtain reproducible slopes on the recorder, and so the present arrangement was used.

Measurements of E' were then made in three different environments, air, distilled water, and distilled water saturated with stearic acid. The specimens were cleaned by ion bombardment, exposed to these environments, and then tested in the Instron using the calibration results to determine E'. For each specimen an average of five separate cleaning and testing operations were employed with each environment. During each test in the Instron the measured slope was taken as the average of at least 6 individual slopes on the recorder chart. Thus the value of E' for each specimen in each environment represents an average of approximately 30 separate slopes.

The testing procedure was similar to that used on the wire specimens. The slopes were measured between two stresses where there was no visible relaxation. All tests were conducted in the elastic region, generally between strains of 10^{-4} and 10^{-3}. The strain rate was .02 inches per minute. Subsidiary tests showed that there was no changes in the values of E' measured at lower stresses or with increases in strain rate up to 0.1 inches per minute.

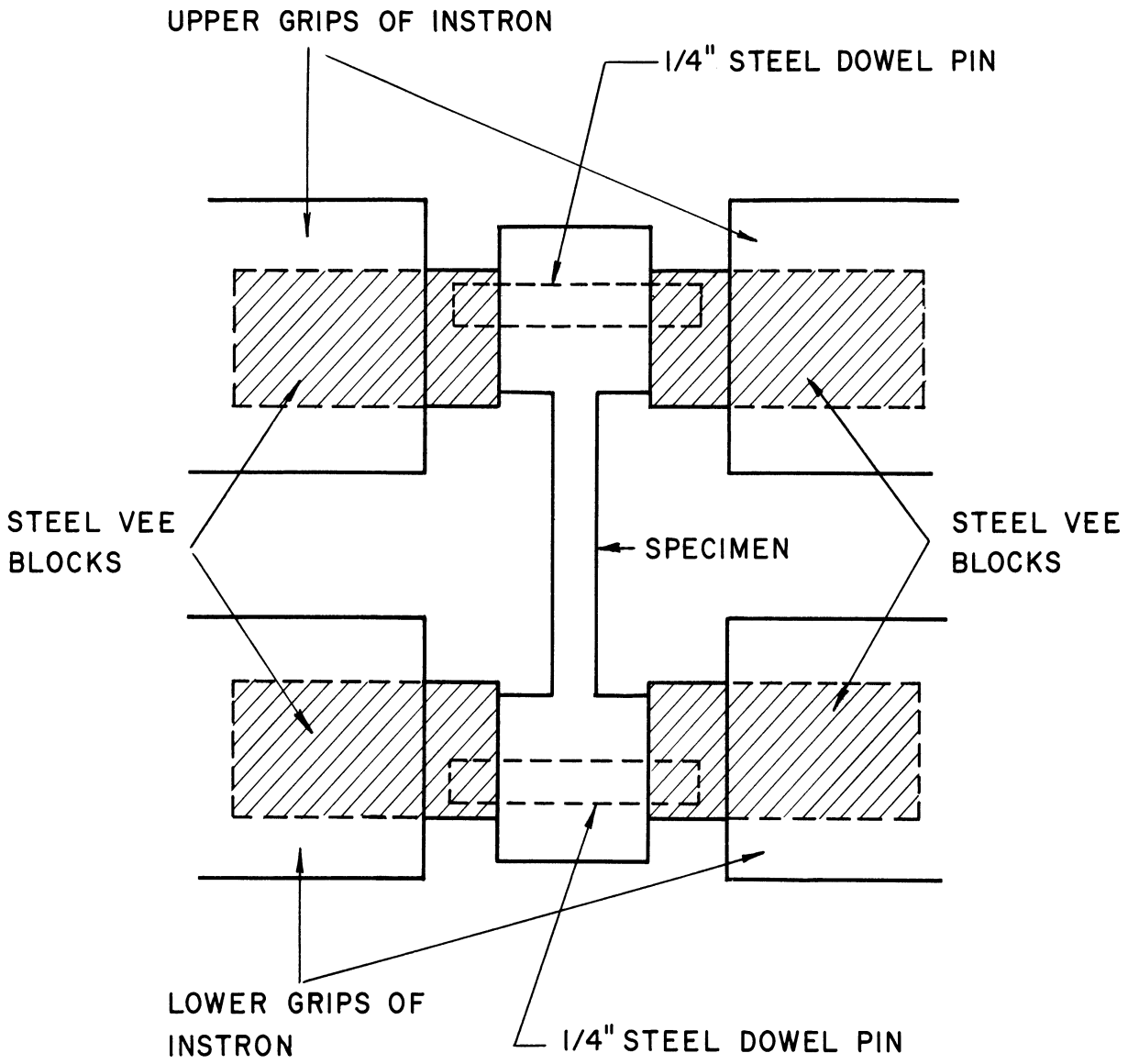


FIGURE 9 - GRIPPING ARRANGEMENT FOR TESTING SHEET SPECIMENS

For tests in liquids the environment was held around the specimen during testing by means of a small piece of thin walled rubber tubing. The tubing proved flexible enough to form a water-tight seal around the lower shoulder of the specimen with the aid of a small clamp, and was still strong enough to support the weight of the liquid around the test section of the specimen without any external support.

In addition to the three above-mentioned environments several tests were conducted in other environments. Some other complementary tests were also conducted. These latter tests will be described in the section on Results.

RESULTS

The results of the E' measurements with the strain gages on the specimens and in the three environments are listed in Table V. In the table the numbers 6, 12, and 15 refer to the three grain sizes produced by the 600°F, 1200°F and 1500°F anneals.

For the air and liquid environments each mean deviation listed in Table V is the deviation from the average value of five separate tests. This deviation is due to the variance within an individual test and also to the variance from the average values of the separate tests. The variance within a single test is due to the differences in slopes on the Instron chart during the test. The approximate value of this variance is about .075. The variance from the average values of the single tests is approximately 7.5. An analysis of variance by a statistical "F test" shows that the differences between the average values from the separate tests are the major cause of the deviations listed in Table V.

Further analysis shows that the variance in E' values between separate specimens to be approximately 7.5, while the variance in the average E' value of a single specimen is about 0.25. Analysis of variance shows that to a 99 per cent confidence level the differences in the E' values are due to changes in E' with changing size of environment, and not to any overall scatter in data.

It is difficult to determine just what are the chief causes of the variance from test to test in the air and liquid environments. No doubt some variance is due to variations in the Instron recorder between tests. It is

TABLE V

Observed values of E' (in psi x 10^6) for copper sheet tensile specimens in various environments.

Specimen thickness(in)	heat treatment	air	dist.H_2O	dist.H_2O+ stearic acid	strain gage
.250	6	18.94±.06	18.49±.38	18.16±.15	18.33±.09
.250	12	18.50±.15	18.25±.20	17.81±.35	17.99±.04
.250	15	18.19±.19	18.06±.28	17.64±.22	17.84±.12
.069	6	19.80±.19	19.28±.07	19.01±.14	19.02±.08
.069	12	19.54±.15	19.04±.08	18.52±.30	18.75±.09
.069	15	19.16±.05	18.71±.12	18.36±.18	18.60±.13
.040	6	21.08±.22	19.92±.28	19.66±.23	19.69±.08
.040	12	20.68±.25	19.48±.17	19.44±.13	19.33±.15
.040	15	20.32±.10	19.31±.35	19.31±.14	19.24±.05

Heat treatment numbers refer to the following heat treatments.

6 = $\frac{1}{2}$ hour at 600°F.

12 = $\frac{1}{2}$ hour at 600°F plus $\frac{1}{2}$ hour at 1200°F.

15 = $\frac{1}{2}$ hour at 600°F plus $\frac{1}{2}$ hour at 1500°F.

conversion factor 1 psi = 6.89 x 10^4 dynes/cm^2

± values are mean deviations

necessary when using the Instron to balance the recroder at zero load and also against some known dead weight hanging from the upper grips. Any errors in this balancing will of course result in some error in the observed slope. In addition the recorder has a tendency to drift somewhat from the balanced readings with time. The effect of this drift was minimized by checking the zero and deal weight readings prior to every test and making suitable corrections whenever necessary. In addition to the variations within the recorder itself there may also be some variation due to mechanical effects, such as slight changes in gripping.

Another cause of scatter may be due to variations in the surface environment between tests. These variations could be due to differences in the degree of cleaning achieved by the ion bombardment, or to variations in the chemical composition of the environment.

This latter possibility is supported by the fact that the scatter in the two liquid environments was generally greater than that in air. If the scatter were due solely to variations in the recorder or mechanical system of the Instron, or to the ion bombardment, then one would expect about the same scatter in all three environments because the specimens were cleaned and tested in the same way. To some extent this greater scatter with the liquid environments is not too surprising because it is probably easier to achieve a more uniform air environment than uniform liquid environments. In the case of the liquids all normal precautions were taken to try to minimize any contamination, but it is possible that there were some local variations in composition from test to test.

Despite this scatter in the individual values, the average values of E' are reasonably close to being linear with A_o/V and a_o/V. Plots of the average values of E' versus A_o/V in the various environments are shown in figures (10-13). The corresponding plots of E' versus a_o/V are shown in figures (14-17). The values of a_o/V were determined by the linear intercept method of C. S. Smith (439,440). It is interesting to note that the calibration tests with the strain gages on the specimens gave very consistent results. Apparently the cement-neoprene combination provided a uniform environment, which has been entitled to the strain-gage environment.

As may be seen in the figures, the results are closer to linearity the less the scatter in the E' data. That is, the strain gage data showed the smallest scatter, and the E' plots for the strain gage environment show the smallest variations from linearity. The air data showed somewhat greater scatter and greater variations from linearity. Finally the two liquids showed the greatest scatter and also the greatest departures from linearity. Thus one is tempted by inverse reasoning to ascribe the departures from linearity to the scatter in the E' data. Whether this is actually so however, cannot be proved.

It is interesting to note that in most of the figures the sets of nine points give three lines which are close to being parallel to each other. This result agrees with the theory because on each plot the value of k or j should be constant and thus the lines should have the same slope.

The values of k and j corresponding to these slopes are listed in Table VI. The results indicate that the values of k are on the order of 10^9 ergs/cm^2 and those of j on the order of 10^8 ergs/cm^2.

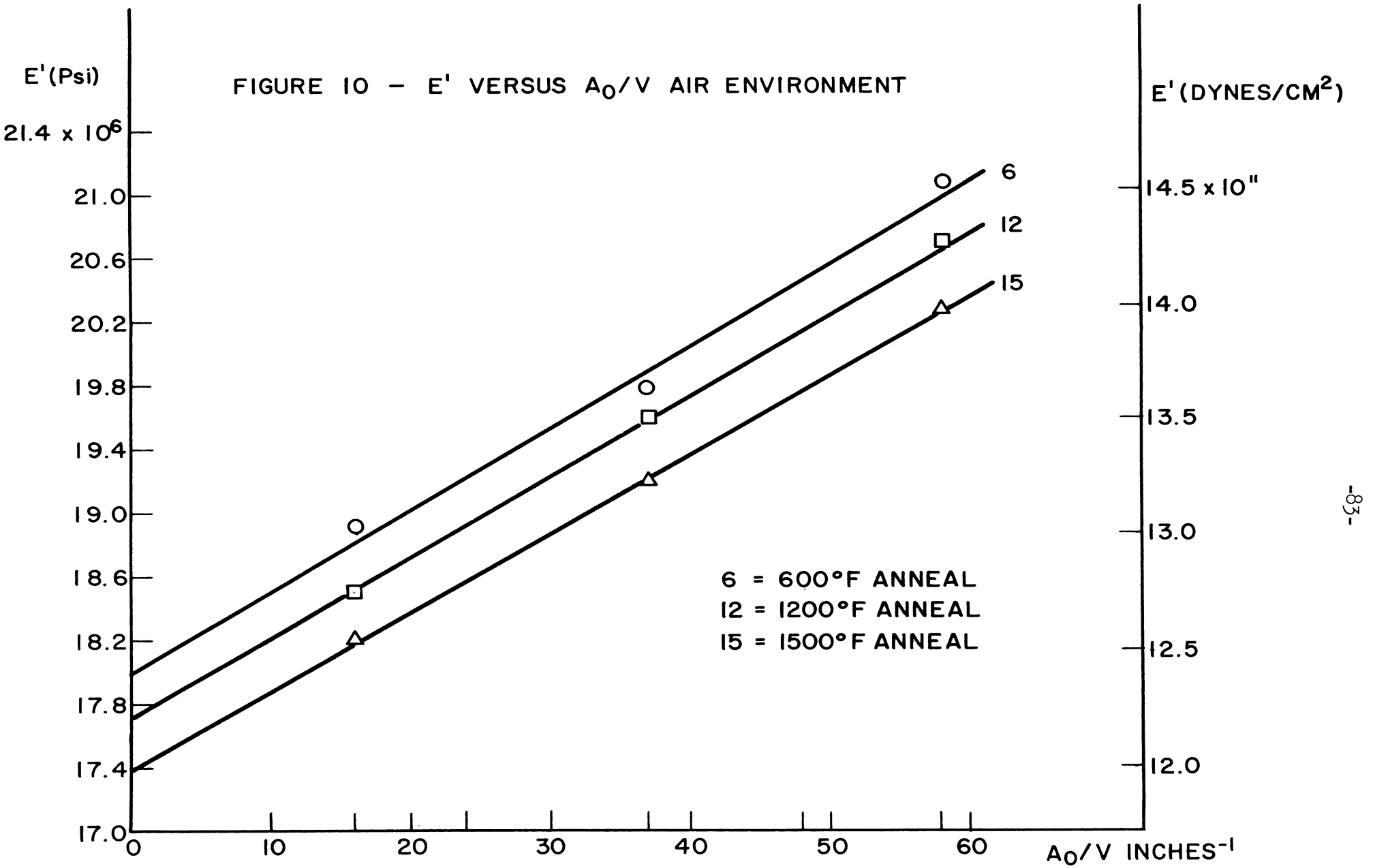
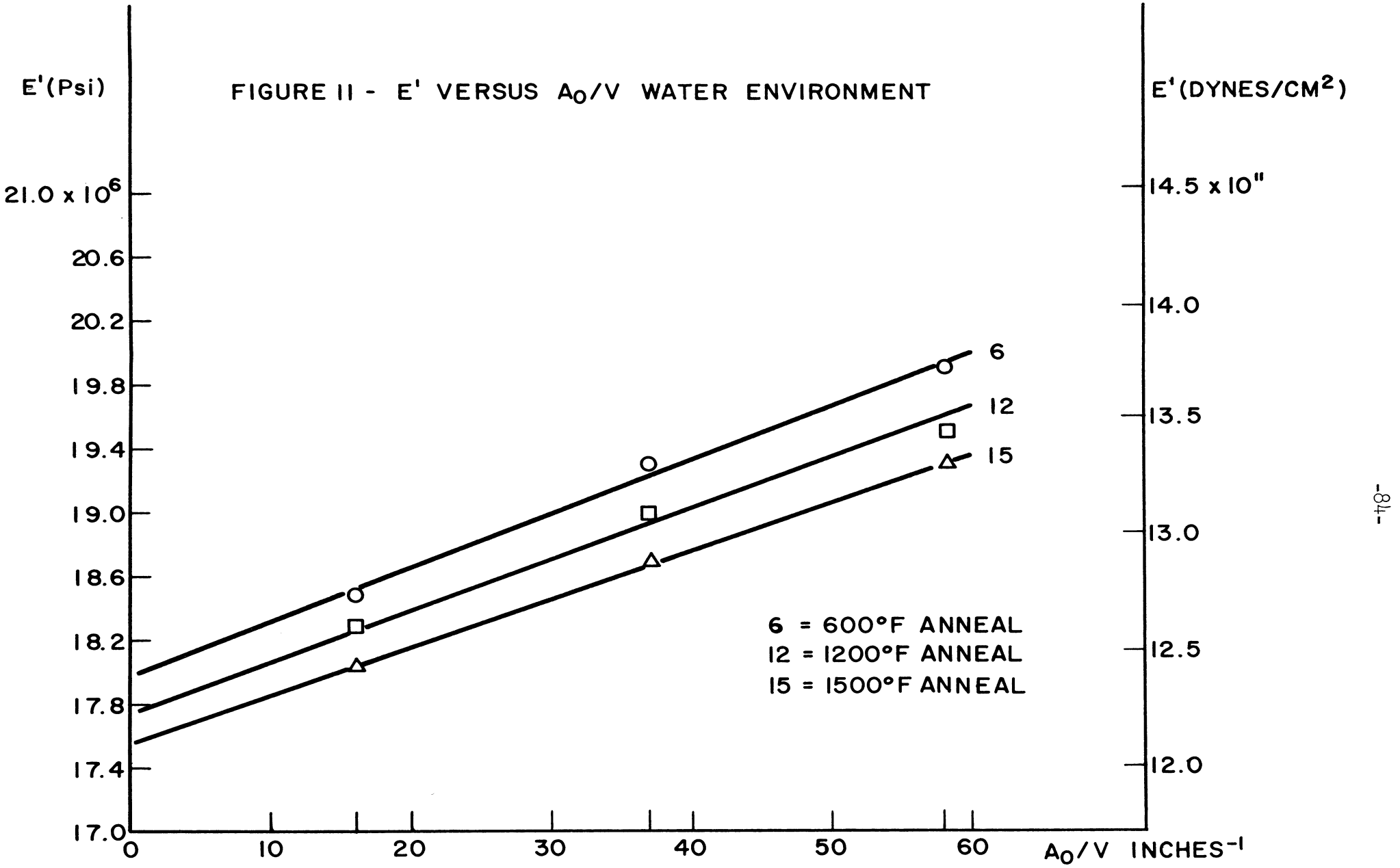


FIGURE 10 – E' VERSUS A_0/V AIR ENVIRONMENT
E'(Psi)
21.4 x 10^6
21.0
20.6
20.2
19.8
19.4
19.0
18.6
18.2
17.8
17.4
17.0
0
10
20
30
40
50
60
A_0/V INCHES^-1
E'(DYNES/CM^2)
14.5 x 10^11
14.0
13.5
13.0
12.5
12.0
6
12
15
6 = 600°F ANNEAL
12 = 1200°F ANNEAL
15 = 1500°F ANNEAL


E'(Psi)
FIGURE 11 - E' VERSUS A_O/V WATER ENVIRONMENT
E'(DYNES/CM^2)
21.0 x 10^6
20.6
20.2
19.8
19.4
19.0
18.6
18.2
17.8
17.4
17.0
14.5 x 10"
14.0
13.5
13.0
12.5
12.0
0
10
20
30
40
50
60
A_O/V INCHES^{-1}
6
12
15
6 = 600°F ANNEAL
12 = 1200°F ANNEAL
15 = 1500°F ANNEAL

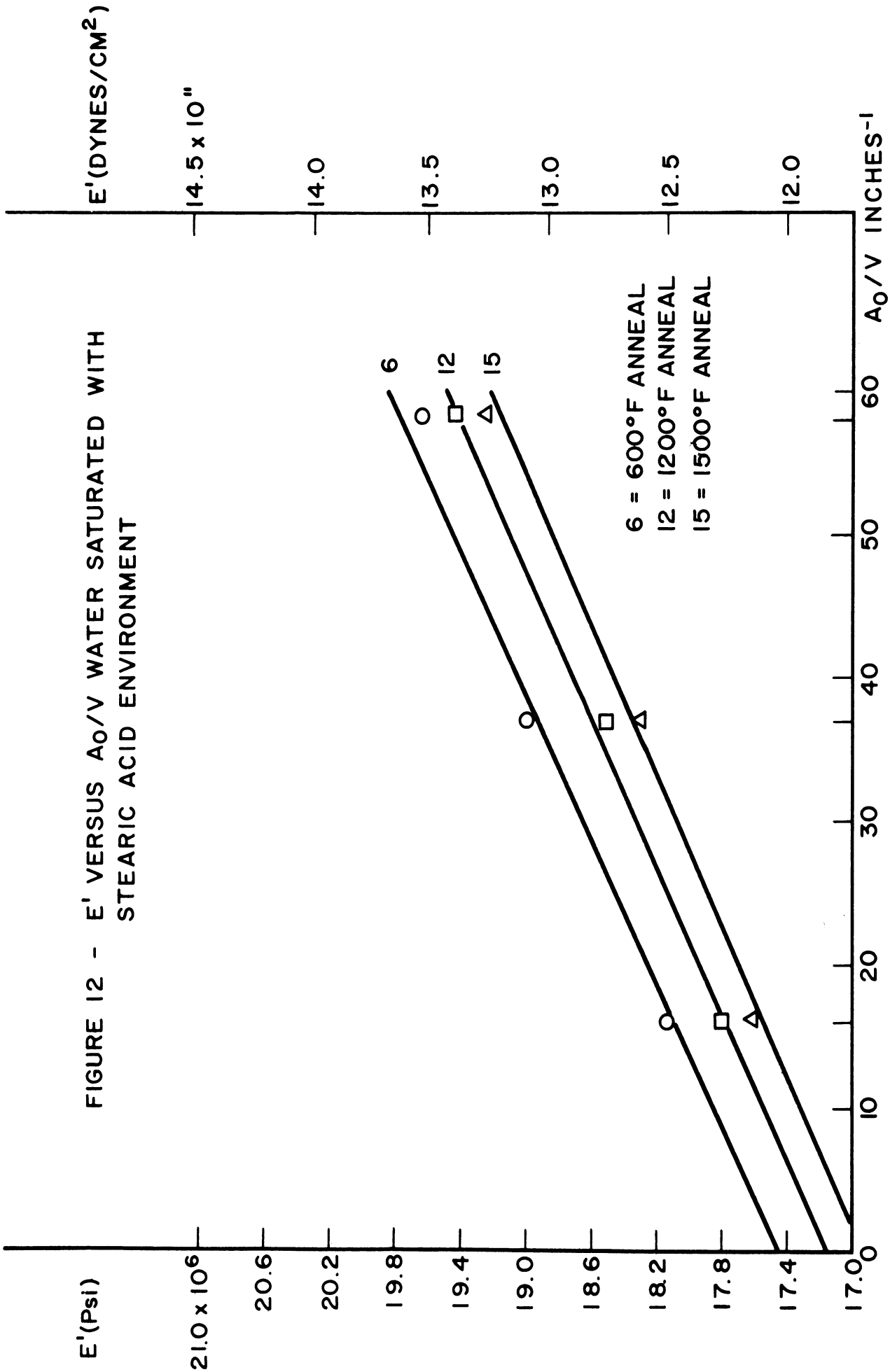
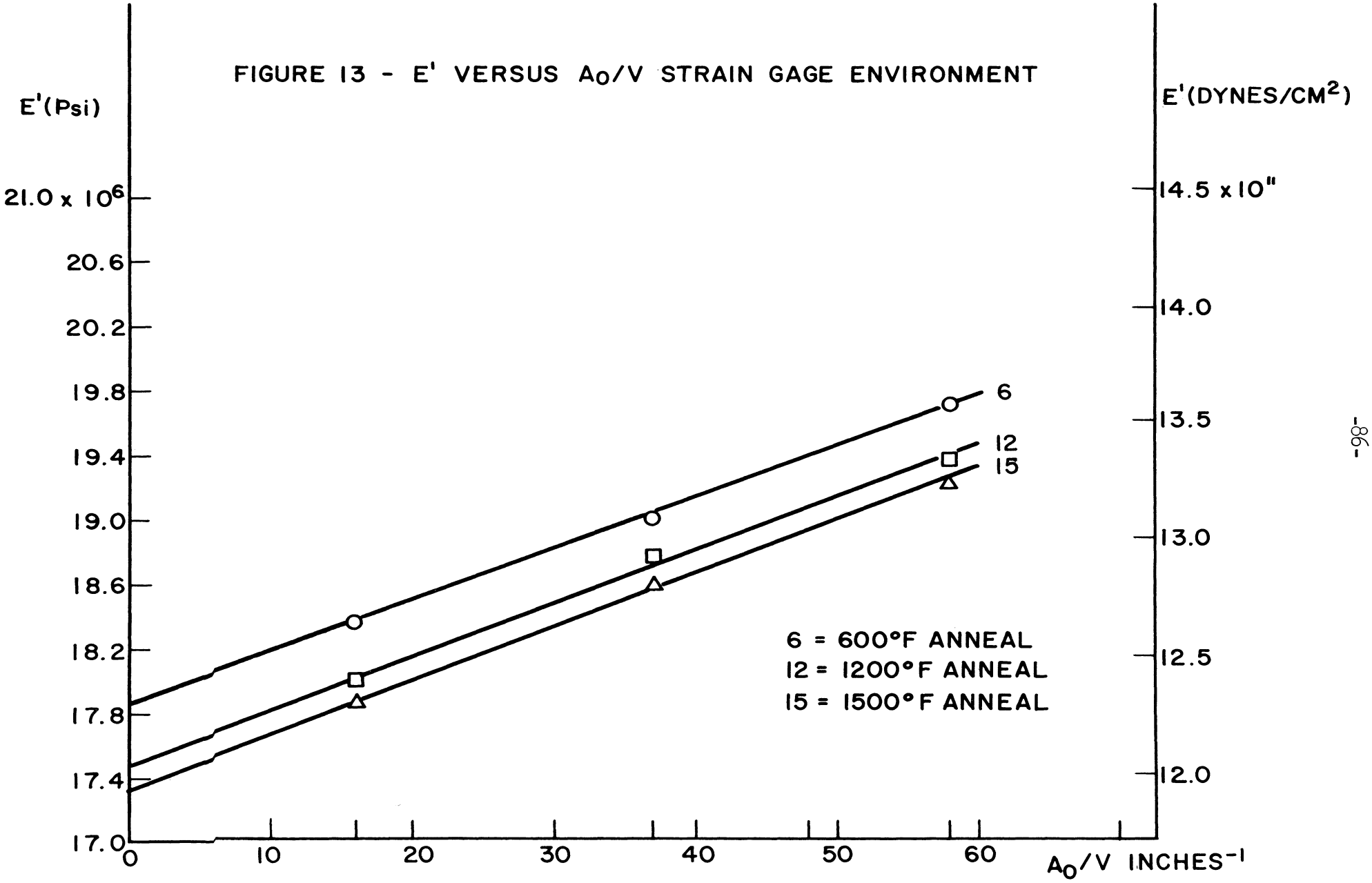


FIGURE 12 - E' VERSUS A_0/V WATER SATURATED WITH STEARIC ACID ENVIRONMENT

FIGURE 13 - E' VERSUS A_o/V STRAIN GAGE ENVIRONMENT



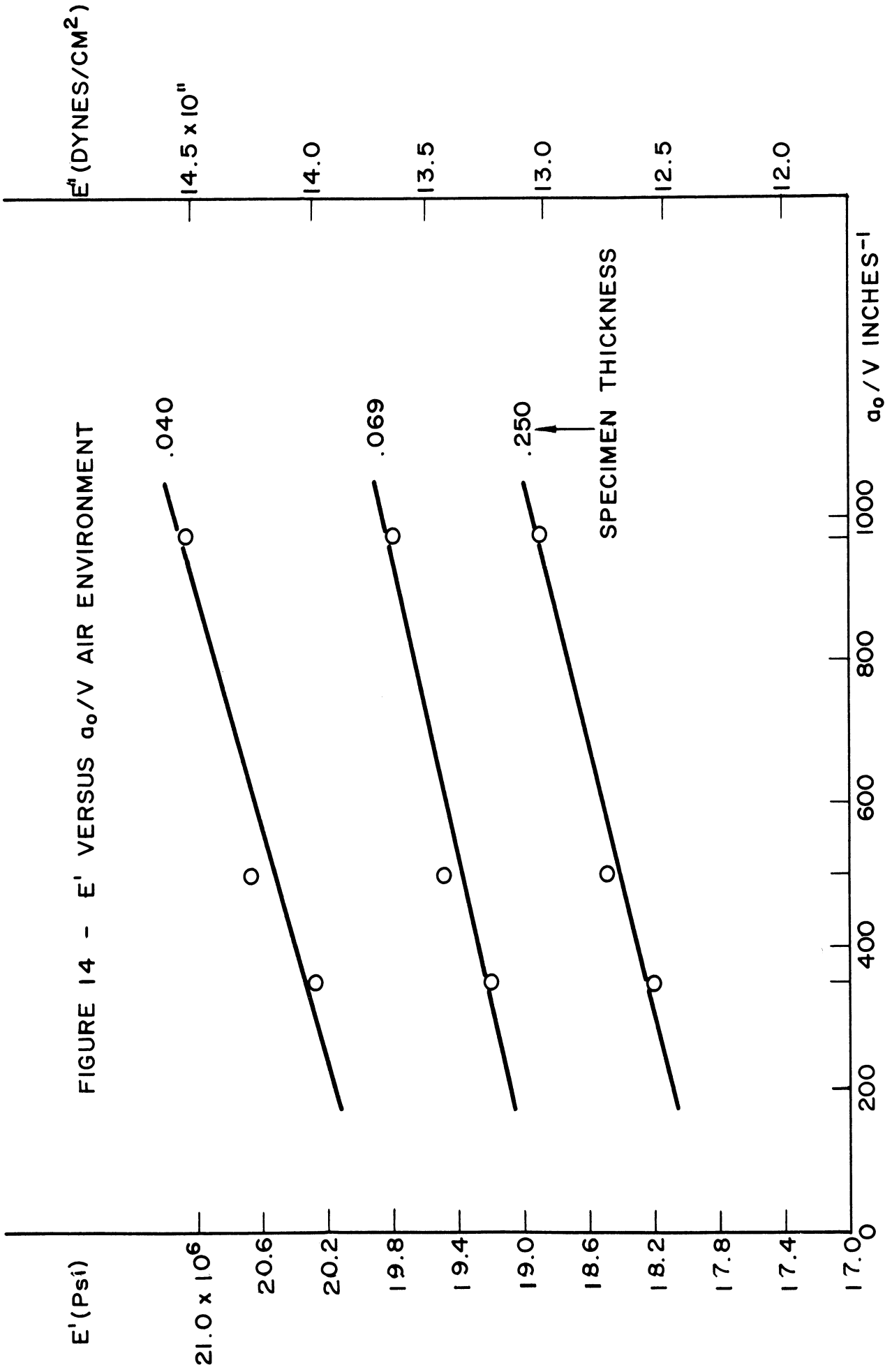


FIGURE 14 - E' VERSUS a_0/V AIR ENVIRONMENT

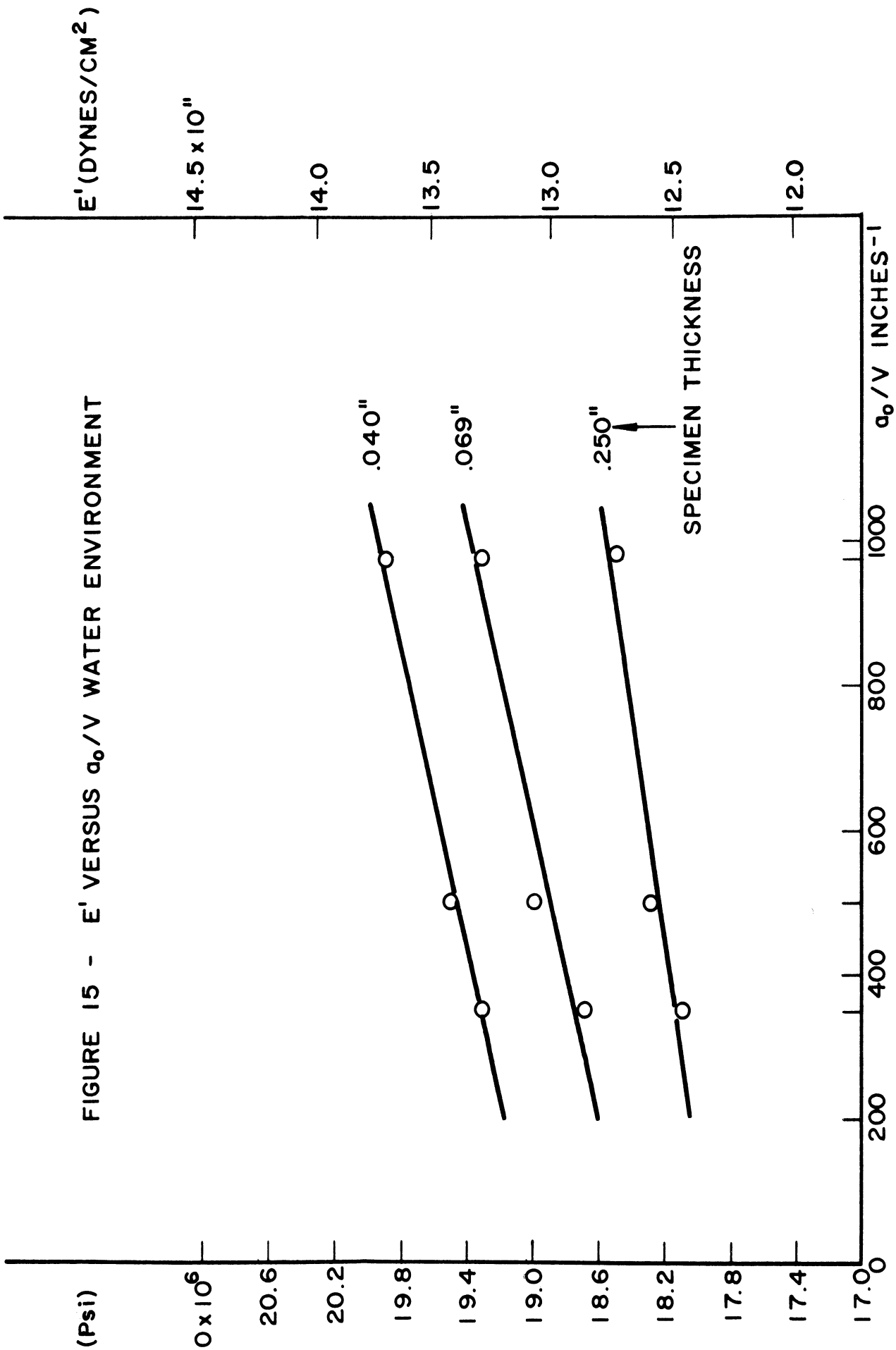


FIGURE 15 - E' VERSUS a_0/V WATER ENVIRONMENT

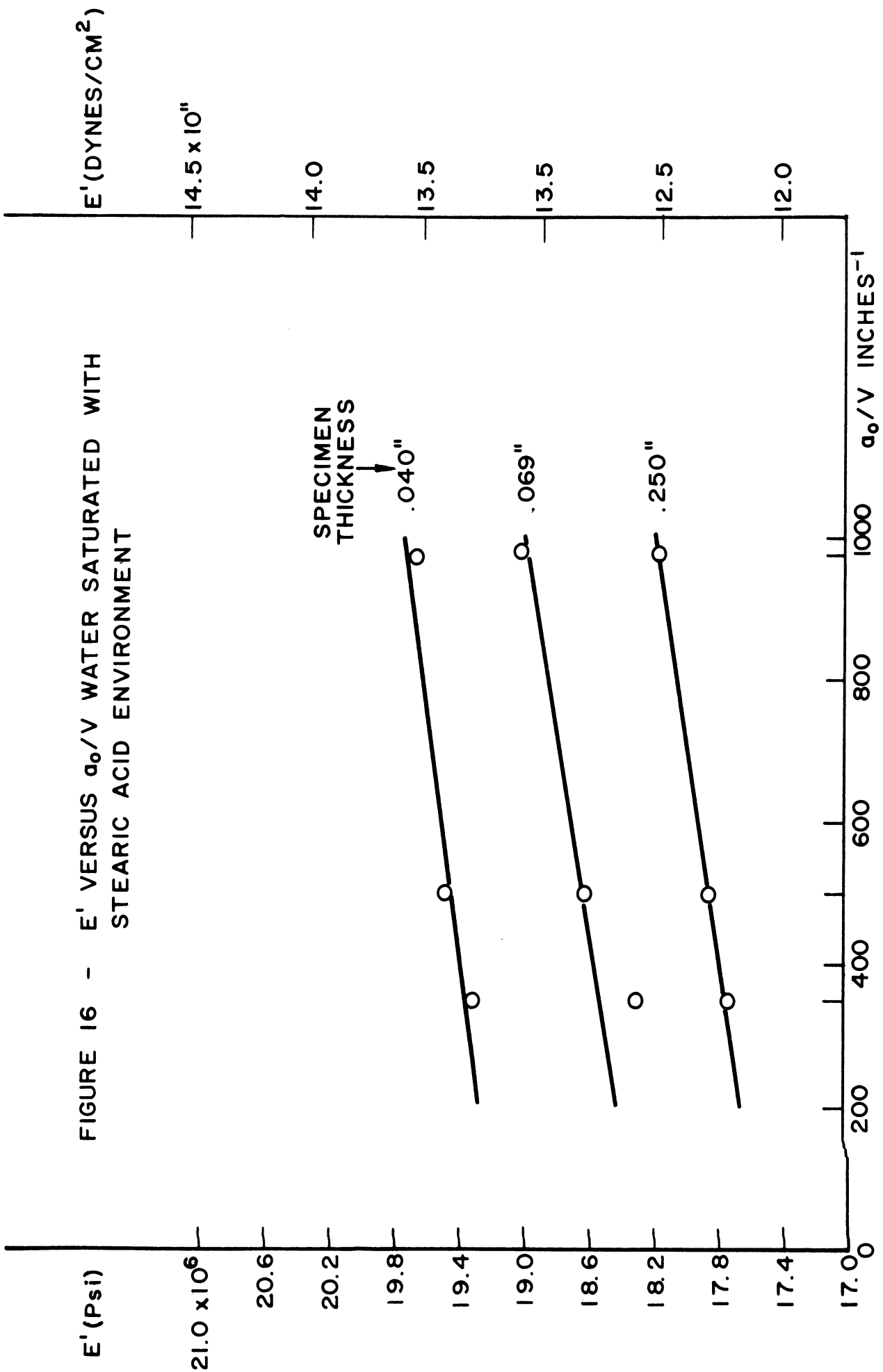


FIGURE 16 - E' VERSUS a_0/V WATER SATURATED WITH STEARIC ACID ENVIRONMENT

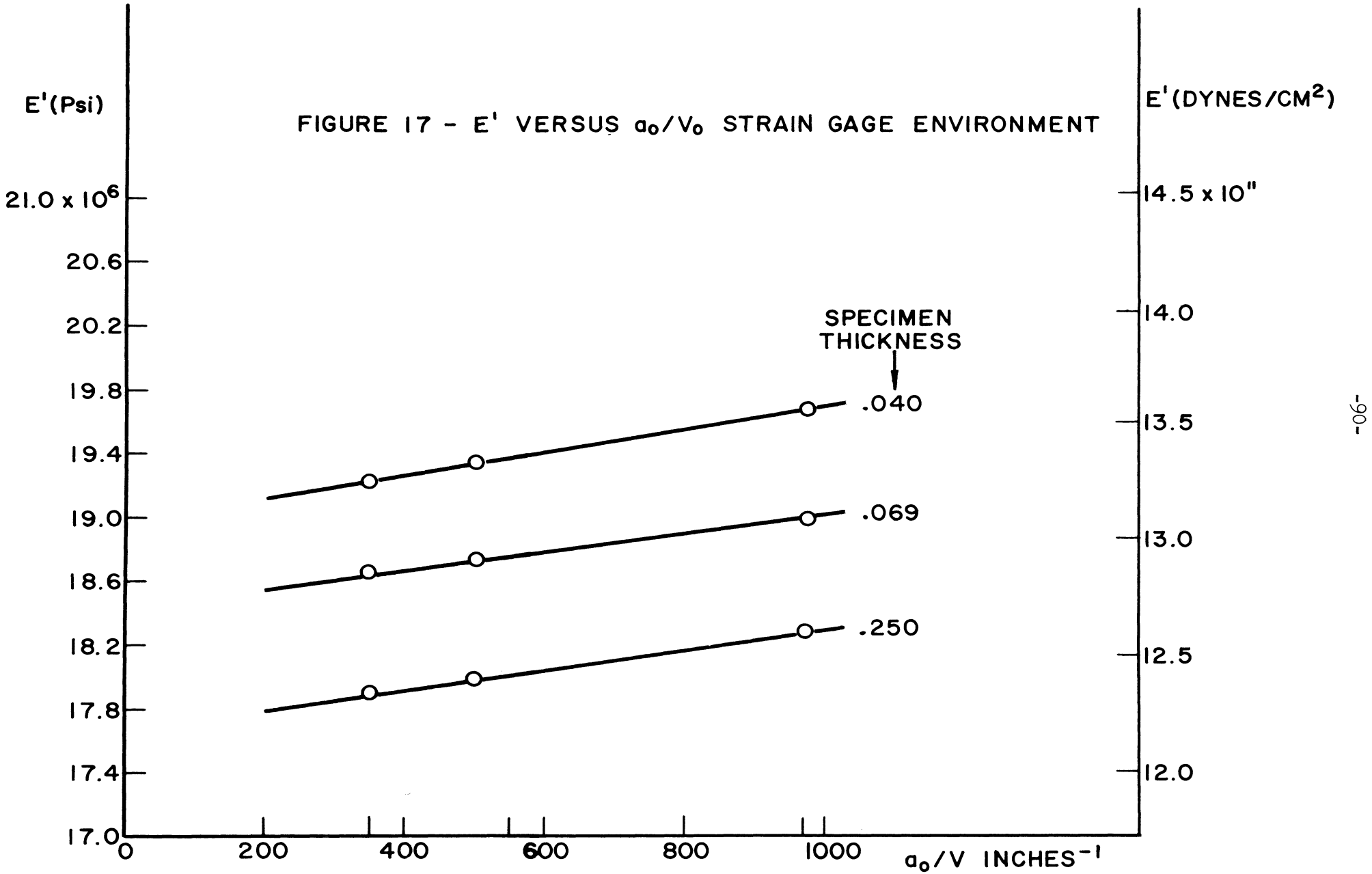


FIGURE 17 - E' VERSUS a_o/V_o STRAIN GAGE ENVIRONMENT

TABLE VI

Values of k and j corresponding to E' values in Table V.

Environment	$k(ergs/cm^2)$	$j(ergs/cm^2)$
air	4.55×10^9	8.20×10^8
dist. H_2O	2.62×10^9	8.80×10^8
dist. H_2O saturated with stearic acid	3.50×10^9	6.02×10^8
strain gage	2.80×10^9	6.13×10^8

The k results are not inconsistent with the tests on wires which indicated the differences between k's to be on the order of 10^8 ergs/cm^2. The results with the copper sheet specimens however, do not agree very closely with those on copper wires as far as differences in k between tests in the same two environments are concerned. This lack of agreement may not be too serious. For one thing the tests were conducted on two essentially different materials, a cold drawn wire of one composition, and an annealed sheet of probably a different composition. Furthermore, as will be brought out, the difference in the cleaning operations that were used can have a marked effect.

In order to check these results the values of E, the elastic modulus, were determined in three bars that had been given the same three annealing heat treatments as the specimens. The values of E were measured by a speed of sound technique. The resultant values of E were 17.62, 17.10, and 17.68×10^6 psi for the bars annealed at 600, 1200, and 1500°F respectively.

On the basis of equation (23) the value $E + 2j\, a_o/V$ should correspond to the intersections of the three E' vs A_o/V curves with the E' axis. Except for the 17.10 value which is somewhat too small, the values of E lie slightly

below the extrapolations of the curves in the various environments. To make a valid comparison the reported values of E should be slightly lower than they are given because the speed of sound technique for measuring E is an adiabatic measurement, while the E' measurements were isothermal ones. In theory, adiabatic values should be somewhat greater than isothermal ones. There is an inherent error of about 2% in the E values, however. In view of this inherent error the values of E cannot be used as a very rigorous check on the E' curves, but within this variation they do support the present results fairly well.

The j results appear somewhat inconsistent because one would expect a constant value of j in all of the environments. This is so because there was no intentional variation of the grain boundary composition between the tests in the various external environments. Yet the values of j range from 6.02 to 8.80×10^8 ergs/cm^2. It may be that there was some changes in the grain boundary compositions near the surface because of diffusion of the external environment into the boundary. With the exception of the strain gage environment however, where the cement was allowed to harden for 24 hours, all of the tests in the various environments were run on the same day and usually within several hours after cleaning and exposure to the environment. Furthermore, except for some slight heating of the specimens during the ion bombardment, the specimens were always at room temperature. Thus the amount of diffusion of the external environment into the grain boundaries should be quite limited. Hence if the variations in j are due to such diffusion then j must be very sensitive to slight changes in composition.

The Russian school of thought, as discussed in the literature survey, attributed the effect of environment on mechanical properties to the penetration of the external environment into the grain boundaries, voids, microcracks and

other regions of discontinuity of the solid. The present changes in j seem in agreement with this idea because they suggest such a penetration took place. There is certainly reason to doubt however, whether this penetration idea is correct as a general explanation of environmental effects. Thus although the present results agree with this idea they are not offered as an endorsement of it.

A more likely explanation for the apparent variations in j in the different external environments is simply that they are due to the local variations in E' values. It may well be that the values of j are the same in all of the environments but that the scatter in the E' results is sufficient to cause slight changes in the observed slopes.

Tests with Changing A_o/V.

In order to furnish an additional check on the linearity of E' with A_o/V the following tests were conducted. The three number six specimens (i.e. those that had been annealed only at 600°F) were re-machined to smaller thicknesses and thereby to new values of A_o/V. The reductions in thickness were as follows: the 250" specimen was reduced to .125", the .069" specimen to .050", and the .040" specimen to .030". These new thicknesses correspond to A_o/V values of 24, 48, and 74 inches^{-1} respectively. The reductions were made only in the center test-sections of the specimens and were made in two equal reductions on each side of the test section

After machining the specimens were given a stress-relief anneal. Strain gages were then applied on the specimens and E' determined with the gages. The Instron recorder was then calibrated in the same manner described before. The values of E' were then determined in the air environment only.

If the present development is correct then E' should be linear with A_o/V. Thus in each environment these new specimens should have E' values that lie on the same line that was drawn through the original E' versus A_o/V results.

The results of these tests are shown in figure 18. The open circles show the values of E' in the two environments, air and strain gage, prior to machining. The crosses show the values after machining to the new thickness. The strain gage environment results show very good linearity of E' with A_o/V, with the three new points lying quite close to the original straight line through the open circles. The air tests show more variation but again the three new points agree reasonably well with the original three points.

These results furnish a good confirmation of the conclusion that E' is linear with A_o/V, for while the validity of assuming linearity with three points may be questionable, it would be difficult to draw anything but a straight line through the six points.

Tests in Other Environments.

In addition to the environments mentioned some tests were performed in other environments. One point that was thought worth investigating was the variation due to adding stearic acid to water. The figures show that adding stearic acid apparently caused some lowering of the individual E' values from those in distilled water. The value of k for the stearic acid solution however, is higher than that of k for water. These results appear inconsistent, and may be due to inaccuracy in the data. In order to check on the effect of stearic acid a new series of tests were conducted using as an environment a 20% saturated solution of stearic acid in water instead of a fully saturated solution. These

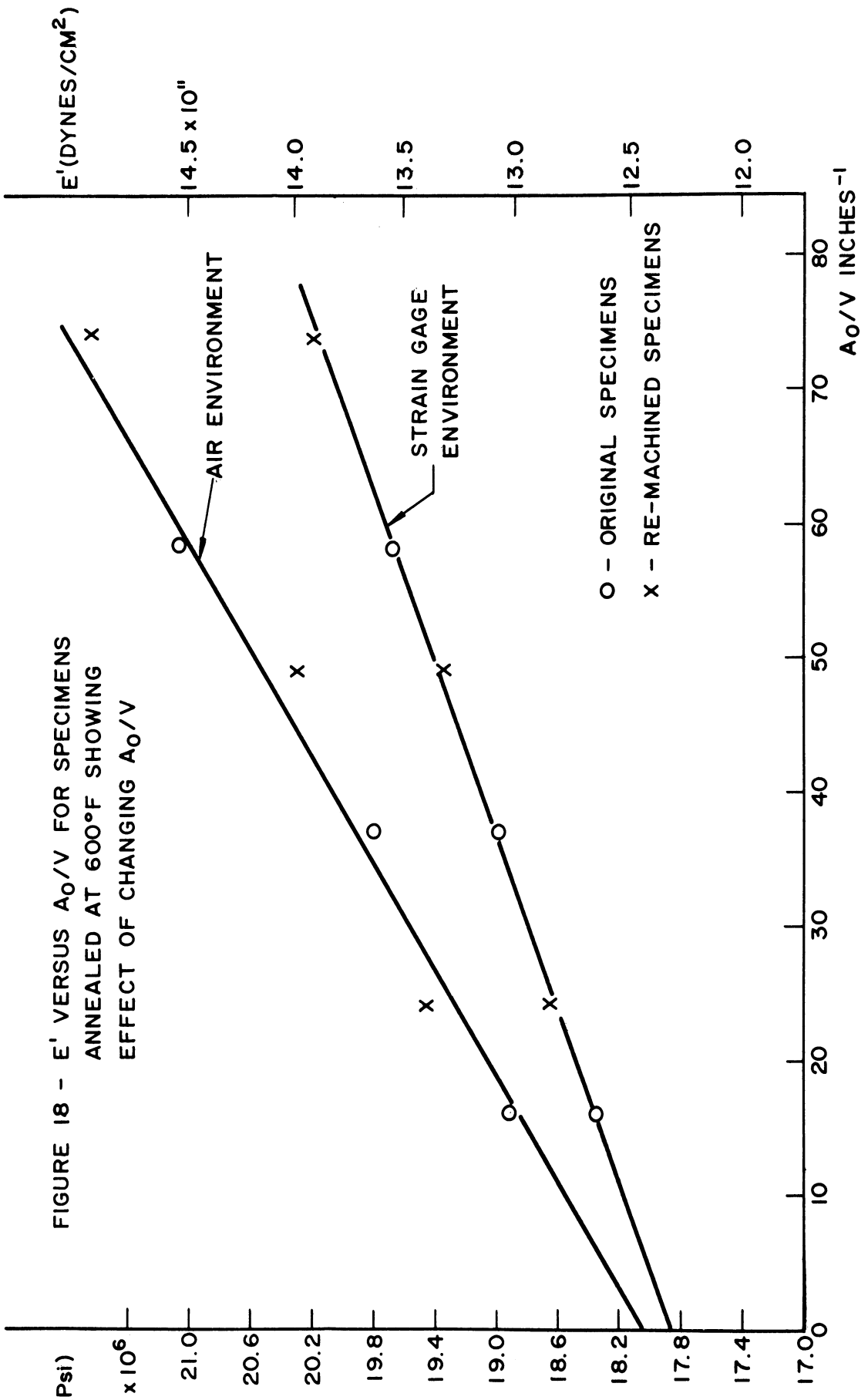


FIGURE 18 - E' VERSUS A_0/V FOR SPECIMENS ANNEALED AT 600°F SHOWING EFFECT OF CHANGING A_0/V

latter tests were conducted only with the number 12 series of specimens, those annealed at 1200°F. The tests were performed in the standard manner described previously.

The results of these tests together with the previous results with the specimens in water and the fully saturated solution are shown in figure 19. As the figure shows, the 20% saturated solution gave results that were almost identical to those found with water. This last result is not too surprising because if the action of the stearic acid is only to enhance wetting it may well be that the copper surfaces were clean enough after ion bombardment so that the wetting effect is no longer significant. This result does not explain however, the fully saturated solution results. It suggests though, that the curve as drawn for the fully saturated solution may be in error, and that these results should also coincide with the water results. Unfortunately the present technique of measuring E' is probably not sufficiently sensitive to determine whether this is so.

Another series of tests was conducted to determine the effect of a mercury environment. A small coil of copper wire was cleaned and dipped in mercury to analgamate the surface. The coil was then inserted in the cleaning chamber in the recessed area in which the specimens rested when being cleaned, and connected through the stopper to an external power supply. The three specimens that had been annealed at 1200°F were then cleaned by ion bombardment in the chamber in the standard manner. After cleaning, and before the chamber was opened, a small current was passed through the amalgamated coil, heating the coil and driving off the mercury which then settled on the specimen surface.

On removal from the chamber the copper surfaces appeared silvery in color indicating that the mercury had covered the surface. This fact is

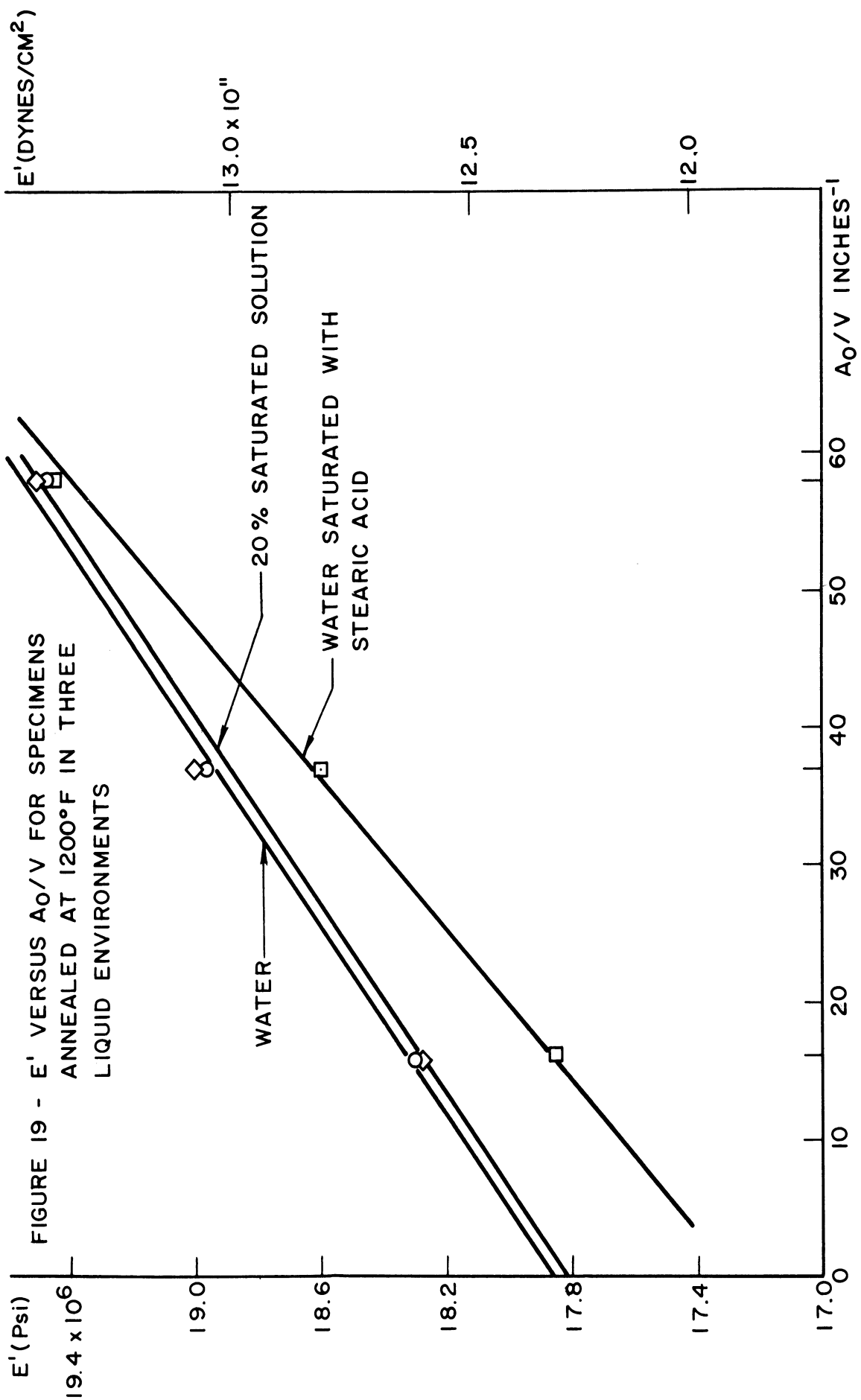


FIGURE 19 - E' VERSUS A_0/V FOR SPECIMENS ANNEALED AT 1200°F IN THREE LIQUID ENVIRONMENTS

additional testimony to the effectiveness of ion bombardment as a cleaning method, because mercury will not wet copper until a fairly high degree of surface cleanliness has been achieved.

The wetted specimens were then tested in the Instron. A container of liquid mercury was not placed around the specimens in this case. The specimens were tested within minutes after cleaning however, to minimize contamination of the surface.

The results of these tests are given in Table VII. Only one test was run on each specimen because of fear of contaminating the vacuum system of the cleaning apparatus on bombarding the amalgamated surfaces. The E' values for these specimens are quite close to those of strain gage and liquid environments.

TABLE VII

Values of E' for specimens coated with mercury. (using specimens annealed $\frac{1}{2}$ hour at 600°F plus $\frac{1}{2}$ hour at 1500°F)

Specimen thickness (in)	E' (psi x 10^6)
.040	19.30
.069	18.45
.250	17.90

Another brief series of tests were made to show the influence of the ion bombardment cleaning. The three specimens annealed at 1200°F were left standing in air for several days after their last cleaning and testing. The surfaces were then cleaned only by removing the excess tarnish with dilute HCl and degreasing with acetone. The specimens were then tested in the standard way in the distilled water saturated with stearic acid environment. This procedure was repeated several times.

The resultant values of E' are listed in Table VIII together with the values of E' for specimens that had been previously tested in air. The results clearly indicate that when the specimens were not ion bombarded the values of E' in the water plus stearic acid environment were very close to those found in air. The previous tests using ion bombardment cleaning though, showed marked differences in the E' values between the two environments. Thus the ion bombardment cleaning appears to play a significant part in showing changes in E' with environment.

TABLE VIII

Values of E' for specimens tested in distilled water saturated with stearic acid without prior ion bombardment cleaning. (using specimens annealed $\frac{1}{2}$ hour at 600°F plus $\frac{1}{2}$ hour at 1200°F)

Specimen thickness (in)	E' ($\times 10^6$ psi) in H_2O + stearic acid	E' ($\times 10^6$ psi) for specimens tested in air (from Table V)
.040	20.41 ± .25	20.68 ± .22
.069	19.50 ± .20	19.54 ± .15
.250	18.55 ± .23	18.50 ± .15

± values are mean deviations

The preliminary tests on the wire specimens however, showed marked changes in E' in different environments without prior ion bombardment cleaning. The reason for this is probably because of the much higher surface to volume ratio of the wires. On the basis of equation 23 the changes in E' should be proportional to A_o/V. For the sheet specimens the largest value of A_o/V was 58 inches^{-1}. For a .010" diameter wire A_o/V is 400 inches^{-1}. It could well be that the negligible changes observed in the sheet specimens would reach the magnitude of the E' changes found in the wires if the results were extrapolated to 400 inches^{-1}.

The tests also indicated that if the wires were cleaned by ion bombardment that the relative changes in E' would be much larger than those that were observed. To check this idea two groups of .010" copper wires from the same stock used in the preliminary work were cleaned by ion bombardment. One series of wires was exposed to air, the other to water saturated with stearic acid. The wires were then tested by the same method used before. With ion bombardment cleaning the difference in E' in the two environments was 2.43×10^6 psi. The original difference in E' was 0.69×10^6 psi. Thus the ion bombardment cleaning increased the environment effect by over 3 fold.

These results clearly show the importance of surface cleanliness in measuring the effect of environment. They also cast some doubt over some of the results reported in the literature in which large changes in E' with environment were observed in bulk specimens without any special surface cleaning. It may be that these tests were done with solid-environment combinations in which surface cleanliness was not as important as with copper.

During the course of the investigation several specimens that had been cleaned and then stored in distilled water were accidently exposed to air for several minutes before testing. These specimens were later tested in the water and the values of E' agreed with the normal tests in water where the specimens had not been exposed to the air. A few additional tests were made to study this effect. It was found, within the limits of accuracy of measuring E', that the specimens could be left in air for several hours without changes in E' when they were subsequently tested in water. Specimens left in air for about 12 hours however, did not have the same E' values. In the latter case the values of E' were higher than those in distilled water.

The most likely explanation for these results is that water and copper form a fairly stable interface after ion bombardment, and that exposure to air does not immediately affect this interface. With standing in air however, it is likely that there is a gradual change in the chemical composition at the surface, either by changes in adsorption or by a chemical reaction such as oxidation. A certain length of time must elapse though, before these changes have progressed enough to be detected by the E' measurement.

Fracture Tests.

As a final test several of the sheet specimens were fractured in order to study the effect of environment on fracture strength. Several investigations have reported that mercury amalgamation of the surface does not significantly alter the mechanical properties of copper (339,356). The cleanliness of the surface might have influenced these results, however since mercury does not wet copper unless the surface is very clean. Therefore the specimens that had

been exposed to mercury after ion bombardment cleaning were fractured to see if the better cleaning would promote embrittlement by the mercury.

Only the two thinner specimens, those .040" and 069" thick, were fractured. The cross-sectional area of the .250" specimen was too large to allow it to be fractured by the D load cell. As a basis for comparison the .040" and .069" specimens of series number 12 (annealed at 1200°F) were fractured in air. The tests were made using the standard gripping arrangement. A strain rate of 0.2" per minute was used.

The fracture strengths and reductions in area of these four specimens are listed in Table IX. It was found that the mercury wetted specimens had slightly lower fracture strengths and reductions in area than the specimens tested in air. These small differences in properties however, may have been due to the differences in grain size between the two sets of specimens. The specimens tested in air had a finer grain size, which might be the cause of the slightly better properties of these specimens. Thus no significant changes in fracture behavior can be attributed to exposure to mercury.

TABLE IX

Fracture strengths and reductions in area for specimens tested in air and after wetting with mercury.

Specimen thickness(in)	Heat treatment	Environment	Fracture stress(psi)	%R.A.
.069	12	air	32,300	23
.069	15	Hg	30,000	17
.040	12	air	31,500	16
.040	15	Hg	28,700	12

heat treatment code
12 = annealed $\frac{1}{2}$ hour at 600°F plus $\frac{1}{2}$ hour at 1200°F.
15 = annealed $\frac{1}{2}$ hour at 600°F plus $\frac{1}{2}$ hour at 1500°F.

DISCUSSION

On the basis of the experimental results it seems fairly well established that E' does change with A_o/V, a_o/V and also with environment. Furthermore the magnitude and direction of these changes agree fairly well with results derived from published information, and also with the relationships developed in the theoretical section. It would seem therefore, that the conclusions in the theoretical section concerning the changes in the various surface energies and surface tensions with strain are well supported, and also that estimates are now possible of the magnitudes of these changes.

Perhaps some remarks should first be made concerning some of the immediate results of this investigation. One point that is worth mentioning is the variations in the E' apart from the consequences concerning surface energy. It is only in extreme cases, as for example, very thin filaments of glass, that large changes in E' have been noted and studied. This fact probably explains why changes in E' in bulk materials have been overlooked. The smaller changes, when they were noticed, were probably attributed to errors in the E' measurements or to variations in structure. From a practical point of view the changes in E' that do occur with varying overall size, grain size, or environment are probably too small to be of concern in general engineering studies.

Although the practical consequences of the changes in E' are not very great there is one point worth mentioning. In a specimen of finite A_o/V the value of E' should be different from that of E by some amount. That is, the stress-strain slope E' should not equal the modulus E. It might not always be possible however to detect noticeable differences between E and E' by normal testing techniques.

Some mention should also be made of the variations or k or j in the changing environment. One point needing clarification is just how changing the external environment should affect the value of k. In the same manner, the possible variations in j with changes in grain boundary composition can also be considered.

One way to visualize the physical meaning of k and j is to consider them as surface modulii. That is, just as E is a measure of the work required to deform the bulk of a solid, k and j may be considered as measures of the amounts of energy necessary to deform thin layers of material at the external surface and grain boundaries respectively. By this analogy then, k and j are measures of the bonding strength of the respective layers.

Using this idea of bond strength it is possible to at least qualitatively understand the variations in k or j with environment. The relative value of k or j will depend on how the environment affects the bonding energy of these thin layers. To a first approximation, adsorption at a solid surface results from the excess bonding energy of the solid that is available at the surface. When a foreign atom is adsorbed on the surface, part of the solid atom-solid atom bonding energy is converted to a solid atom-foreign atom bonding energy. Thus adsorption causes some lowering of j or k because it weakens the bond strength of the surface layer to some extent.

The relative values of j or k therefore, depends upon the quantity and kind of adsorbed atoms on the surface or grain boundary. If the adsorbed atoms are such that they become tightly bonded then k or j will be relatively low because more bonding energy between the surface layer atoms is converted into bonding energy with the adsorbed atoms. Conversely if the adsorbed atoms are

not tightly bonded then k or j should be larger. The highest possible values of k and j would represent completely clean surfaces. In this respect it would be interesting to measure E' of a clean specimen in a vacuum environment, although the experimental problems might prove difficult. In a vacuum and with a clean surface the value of k should be the maximum value for the particular solid tested.

When adsorption takes place on a surface there is some lowering of the interfacial energy. To a first approximation the lowering of the surface energy should be proportional to the amount of bonding between the solid and the adsorbed atoms. Thus one would expect lower values of k with environments that form lower energy interfaces with the solid. The present results seem to support this conclusion. The values of k in the various liquid environments are approximately the same, but all are lower than the k for the air environment. One might expect the liquids to form lower interfacial energy surfaces with the solid. The one surprising result is the strain gage environment, where the value of k is also rather low. It may be that the cement used for bonding the gages also forms a relatively low interfacial energy surface.

The present explanation also shows why the changes in E' with changing environment are sensitive to the cleanliness of the surface. If the surface is contaminated it is likely that a fairly stable environment is already present on the solid surface. Exposure of the solid to various new environments therefore, would generally produce only small changes in composition at the surface. If the surface were clean however, exposure to different environments would produce much greater changes in the chemical composition at the surface and hence much greater changes in k.

Just as it is possible to change k by changing the surface environment it should also be possible to show variations in j by changing the grain boundary composition. As in the case with external surfaces, the greater the lowering of the grain boundary energy the greater the lowering of j should be. It would be interesting to study variations in j with composition by diffusing in foreign atoms along the grain boundary or perhaps by grain boundary segregation from solid solution.

Thus far the only mechanism for changing the bonding energy of the surface layers that has been mentioned is adsorption. Other mechanisms are of course possible. One might also have diffusion of the external environment into the surface of the solid, or conversely diffusion of a component out of the solid. Examples of this type of phenomena are carburization and decarburization. One might further have a chemical reaction between the solid and the environment. In this latter case the problem becomes complicated because the chemical reaction may produce a new surface phase of finite thickness and strength, and thus one would be replacing the original surface layer by a new one having different properties. Furthermore, a new internal boundary would be created between the solid and the new phase at the surface.

With these considerations in mind some attention can now be given to some of the consequences of the changes in surface and grain boundary energy with strain. As mentioned in the introduction, one field that is of particular interest is that of mechanical properties.

The literature review has attempted to describe some of the results and theories concerning the effects of environment on mechanical properties. One of the more prevalent ideas that has been used to attempt to correlate these

results is that surface energy is the significant variable. It would now be interesting to compare the present ideas with the results and theories that have been offered. Instead of dividing the present discussion to cover different classes of solids however, it would seem wiser to treat separately some of the phenomena that have been studied. In this way a more general approach can be made to the problem.

One area that is of considerable interest is that of brittle fracture. To go into this problem in detail would require a lengthy discussion. Most of the current theories of brittle fracture however, are based on dislocation models, while thermodynamic models are macroscopic ones. Thus the present relationships which have been derived thermodynamically are not directly adaptable to dislocation models of fracture. It is possible though, to compare some of the conclusions based on dislocation models to those based on thermodynamic considerations.

The thermodynamics of brittle fracture are quite straight-forward. The major premise is that a solid will fracture when the increase in free energy required to create a new surface is less than the increase in free energy to further elastically deform the solid. Both the volume free energy and the surface free energy increase linearly with the square of the strain. The volume free energy increases proportionately to E, and the surface free energy increases proportionately to k. Since $E > k$ the changes in the two energies become equal at some value of ϵ^2. At this value of ϵ^2 the free energy to further deform the volume of the specimen equals that to create a new surface. Hence the solid favors fracture after this strain.

This principle also illustrates the effect of changing environment on the fracture strength. A second, higher surface free energy environment should have a higher value of k and thus a somewhat greater slope. In this case the

change in surface energy becomes equal to the volume free energy change at a larger value of ϵ^2. Thus one can see how changing the surface environment can affect the brittle fracture strength, or the mode of fracture if the value of k is high enough so that plastic deformation takes place before brittle fracture occurs. This principle of course is nothing more than a representation of the Griffith criteria except that in this case the surface free energy per unit area increases instead of remaining constant. Because of this increase however, the value of the surface energy at fracture may be considerably higher than the value of f_o^s.

In this respect it is interesting to note some of the results of dislocation theory. It has become obvious in recent years that brittle fracture below the transition temperature in polycrystalline metals may not occur by an instantaneous fracture of the entire cross section (445-451). Instead the process seems to be that first there are individual, localized fractures formed across various single grains in the specimen. With increased stress these local cracks propagate into adjoining grains and finally meet and failure of the whole test piece occurs soon afterward.

On the basis of dislocation theory the surface energies to propagate these local cracks are an order of magnitude or two greater than the nominal values of surface energy for the materials (448,449,451-454). Orowan has attempted to reconcile this difference by assuming that localized plastic deformation takes place in the region ahead of the crack (455). The Griffith equation by this modification then becomes

$$\sigma = K\sqrt{\frac{(f_o^s + P)E}{c}} \qquad (39)$$

where P is the amount of plastic work in the region ahead of the advancing crack. Orowan has shown that the value of P may be large enough to reconcile the measured fracture stresses with the Griffith equation.

The point of course, is that this increase in the energy to extend a crack may be due simply to the increase in f^s with elastic strain prior to fracture. For example, the brittle fracture strength of iron is approximately 6×10^9 dynes/cm^2. The calculated effective value of $f_o^s + P$ at fracture is 1.5×10^5 dynes/cm^2 (451). Then taking E for iron as 2×10^{12} dynes/cm^2 the strain at fracture is 3×10^{-3}.

Now assuming that the effective value of f^s is due only to elastic strains, then

$$f_o^s + k\epsilon^2 = 1.5 \times 10^5 \text{ dynes/cm} \qquad (40)$$

Taking approximate values of f_o^s and k

$$2000 + 10^9 \epsilon^2 = 1.5 \times 10^5 \qquad (41)$$

and the corresponding value of ϵ is 12×10^{-3}, which compares well with 3×10^{-3}, especially when one considers that higher strains may have developed in front of the advancing crack. It would seem then, that the calculated values of $f_o^s + P$ are not far greater from what could be achieved by the increase in f^s alone prior to fracture, and that it may not be necessary to introduce plastic work to reconcile the results.

The question might be raised that if fracture begins internally why should the external environment affect the results. It should be pointed out that the internal microcracks appear to form primarily below the transition temperature of the metal. In many cases the reported environmental effects were

observed with normally ductile metals, and microcracks need not have been formed internally in these cases. Thus there is no conflict in many cases. It may still be possible however, to form internal microcracks as the initial step in fracture and still have an environmental effect. One reason for this is that it may be possible for the environment to wet the first microcracks and promote their propagation. A second reason is that although the fracture was initiated at internal sites the environment could still affect the fracture of the external regions of the specimen. In this case the effect of environment on fracture strength would be much smaller but some effect might still be seen.

With respect to internal cracking some results of Wessel are of interest (456). Wessel studied the fracture strength of a tool steel heat-treated to various hardnesses and then fractured in air and distilled water. He found that with lower hardnesses the fracture strengths in the two environments were identical, and that fracture was initiated internally . At higher hardnesses the strength in water was less than that in air, and also fractures were initiated in either the center or on the surfaces of the test pieces. At the highest hardness values the strength in water was again less than that in air, and fractures were initiated at the surface only.

The variations in fracture behavior with hardness are interesting and agree with some other results that show that the effect of environment increases with increasing hardness of the solid. The reason for the hardness effect might be connected with the changes in yield stress of the specimen.

In general the harder the specimen the greater is the extent of the elastic deformation. Therefore the probability becomes greater that the surface free energy curve will intersect the volume free energy curve in the elastic

region. With regards to Wessel's work, the ductility of the low hardness specimens was fairly high. When the ductility was decreased however, at higher hardnesses, the elastic deformation may have become sufficient to allow brittle fracture and an environment effect.

There is another important point with regards to brittle fracture. If brittle fracture begins internally in various grains then local changes in internal composition may become important because of their effects on the surface energy. This question leads to the general problem of embrittlement. It would seem that much of the problem of embrittlement might be explainable in terms of surface energy changes at certain localized regions within the specimen. Several investigators have suggested that segregation of the solute atoms to preferred lattice planes may lead to embrittlement along certain orientations within the grains (457-462). Mention has already been made of the current theory which ascribes hydrogen embrittlement to the formation of low surface energy microcracks.

The grain boundaries however, are usually the chief sites of embrittlement, because a grain boundary can more readily accomodate foreign atoms than the lattice. Thus in any metal the grain boundaries generally contain an excess of foreign atoms, and in some cases these atoms may cause embrittlement.

It would be a lengthy task to catalog all of the solvent-solute combinations which have been found to promote brittleness. In many cases this embrittlement may be associated with the appearance of a precipitate in the grain boundaries. In these cases brittleness cannot be related directly to grain boundary energy changes because the mechanical properties of the precipitate could also be the cause of brittleness. There are a number of well known examples however, where marked embrittlement has been found without the formation of a

visible precipitate. Examples of this type include antimony and bismuth in copper (463-465) and various solutes in iron (466-471). A recent investigation by Crussard and co-workers is also of interest (472). Crussard studied the embrittlement of nickel due to segregation of solute atoms to the grain boundaries. It was found that embrittlement coincided with the adsorption of the foreign atoms on the boundary surfaces. The adsorption itself caused local striations which was attributed to the lowering of the interfacial energy on certain low index planes of the adjacent grains. Embrittlement then, apparently coincided with lowering of the grain boundary energy.

When the grain boundaries become embrittled the resultant fracture is then of course primarilly intergranular. With adsorption in the grain boundary f_o^B and j would be lowered, and thus the energy required to create a new surface becomes much smaller in the grain boundaries. Hence the fracture would proceed across the grain boundary interfaces.

An interesting result that was reported in the environment studies was the formation of small cracks on the surface of ceramics upon exposure to various environments. It is easy to see how the presence of these cracks would lower the strength, but it is not so easy to explain how these cracks form in the first place. One possibility is that adsorption on the fresh surfaces causes the formation of local surface striations. Several investigators have found that metal surfaces develop local irregularities after oxidation (473-477). It has also been suggested that adsorption alone on the surfaces may cause striations to appear (478-480). The explanation for the appearance of these striations is that the surface prefers to adsorb foreign atoms on certain lattice planes because of the consequent decrease in surface energy that is possible. The striations

then result from local adjustments of the surface atoms to allow adsorption on these preferred planes. Whether such a mechanism is possible in the case of ceramic materials, and whether the resultant striations would be of sufficient size to affect the mechanical properties is uncertain.

It has also been suggested that the changes in mechanical properties are due to the formation of a surface film by some chemical reaction between the environment and the solid. Just what reaction takes place, and what is the composition of the resultant film has not yet been discovered. It might be interesting to determine if a surface with microcracks but without a surface film could be prepared, and then measure the strength of such a specimen. In this way one might be able to determine whether cracking alone causes the decrease in strength, or whether a surface film is required to produce the effects. It may also be possible that adsorption alone of impurities on the surface may be sufficient to cause some of the observed effects.

The question of environment penetration before or during testing should also be mentioned. As pointed out in the literature review a certain amount of grain boundary adsorption is thermodynamically favorable because of the lowering of f^B.

It also appeared in the case of liquid metal environments that adsorption was promoted by the application of a tensile stress. An increased adsorption with stress could be due simply to an increased rate of grain boundary diffusion. It could also be due to an increased driving force. If the grain boundary energy increased with strain, then adsorption of foreign atoms into the strained boundary should cause a greater decrease in energy. These two possible causes of adsorption are intrinsically different, for one is based on a kinetic effect while the other

is based on a thermodynamic effect. Thus it should be possible to differentiate between the two possibilities.

An easier approach to the problem however, might be to study variations in surface adsorption with strain. Mention was made in the theory section of the work showing that adsorption caused elastic strains. An interesting experiment would be to test the complementary question, do elastic strains cause adsorption. If an elastic strain causes an increase in surface energy then one should detect changes in adsorption.

With regards to mechanical properties, if penetration to a sufficient extent can take place then one could find environment embrittlement with exposure. That is, exposure of a solid to certain environments and under suitable time, temperature, and stress conditions could lead to embrittlement of the solid. The embrittlement need not be the result of corrosion but merely to adsorption of the environment at preferred sites within the solid. This possibility may be important in various practical problems. One example that has been given is the case of hydrogen embrittlement of steel. In such cases the mechanical properties of the solid could be significantly changed, and yet the solid might appear undamaged.

Conventionally the causes of embrittlement have been broken down into two general types, those due to internal changes in the material, eg. cold work, grain size, alloy content, and those due to testing conditions such as strain rate, triaxial stresses, or temperature. A new variable should be added, that of environment. Its contribution may be due to internal changes in the material, in the case of prolonged exposure prior to testing, or it may be only a testing condition if penetration is restricted. In most cases the environment will not

be a significant variable with regards to embrittlement. In certain cases however, the environment could be the predominant variable.

In order to proceed further with environment effects some attention must be given to the problem of plastic deformation. At this point the present relationships are now longer strictly applicable because all of the developments have been made in terms of elastic deformations. It is possible though, to make a qualitative estimate of the variations in surface energy in the plastic region.

To begin with, in the plastic region there is still an elastic component of the total deformation. To appreciate this one has only to plastically deform a material and then release the load. On release of the load, or on application of a new load, the solid will show an elastic deformation which will be greater than the amount of elastic deformation prior to the plastic deformation.

Now one might assume that the surface free energy change with elastic strain is still governed by the equation: $f^s_\epsilon = f^s_o + k\epsilon^2_{elastic}$ (42).

In this case the subscript "elastic" is added to point out that only the elastic component of the total strain is to be used in calculating f^s_ϵ. The general variation in f^s with strain on this basis is shown in figure 20. As the figure shows, f^s rises sharply in the elastic region, and then gradually in the elastic region. Of course, a number of assumptions are implied in this approximation, and figure 20 should be taken as only an estimate of the variation of f^s in the plastic region.

Figure 20 also includes a second curve representing the variation in f^s in a second environment. What is of interest is the area between the two curves because this area represents the difference in surface work in deforming the solid in the two environments. Many of the investigations of the effects of environment showed that the plastic deformation characteristics of a solid could

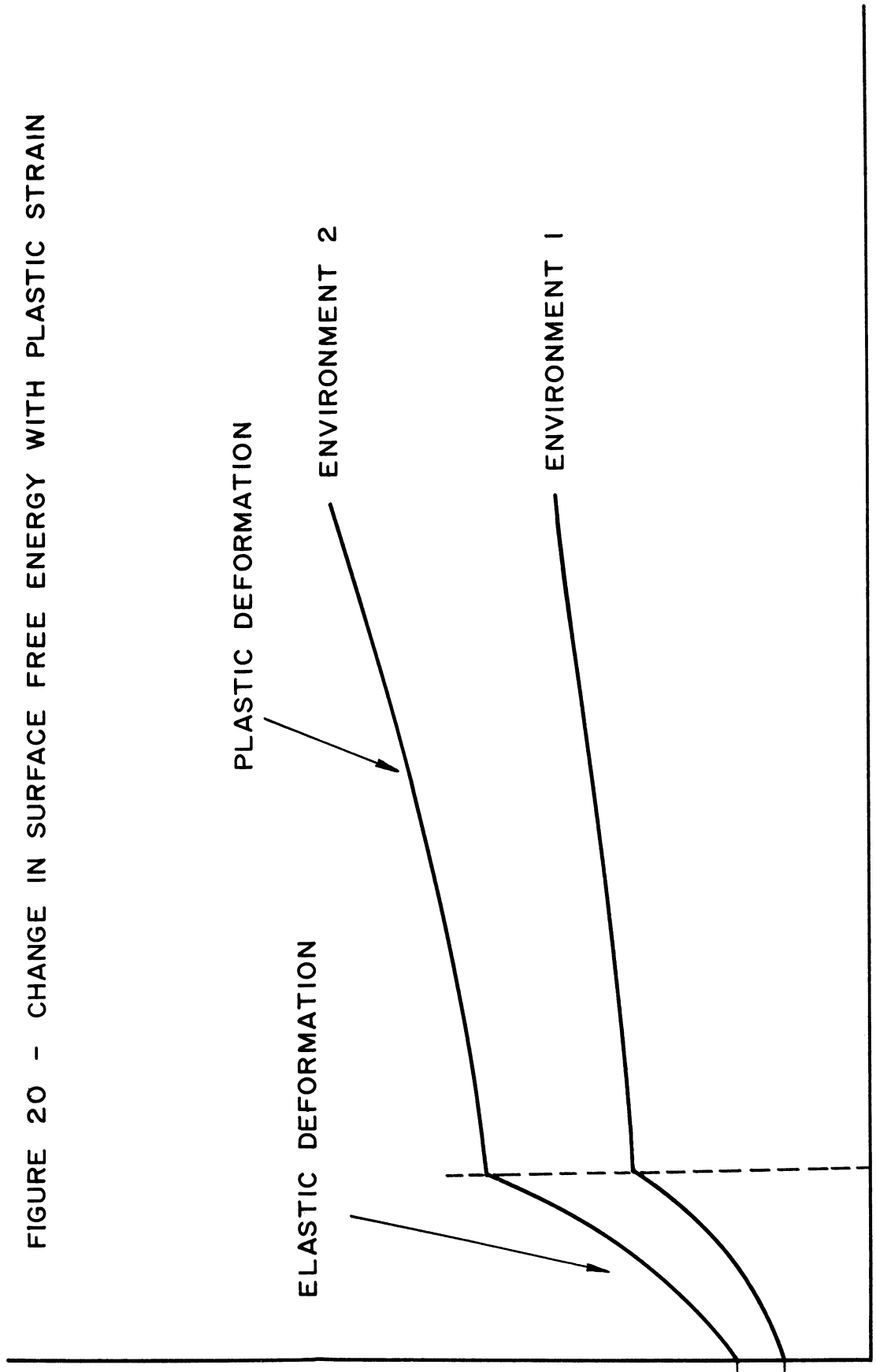


FIGURE 20 - CHANGE IN SURFACE FREE ENERGY WITH PLASTIC STRAIN

be altered by changing the environment. It may be that these differences are due simply to the differences in the amounts of surface work required to deform the solid. The area between the two f^s curves therefore, should be proportional to the differences in total work to deform a solid in two environments.

Unfortunately the uncertaintities involved in extending the f^s curves make it almost impossible to make a quantitative check of this idea. A rough calculation does show that the difference in the amount of surface work because of the possible differences in f^s could be large enough to cause observable changes in the stress-strain curves. In some cases however, the reported changes in the stress-strain curves appear too large to be accounted for by this means.

Rebinder and others of course have already claimed that the surface energy differences were the cause of the differences in plastic behavior. These previous theories however, assumed that f^s was independent of strain and thus the differences in behavior were due only to variations in f^s_o. It is easy to show that the possible difference in values of f^s_o is much too small to allow any visible change in the stress-strain curve. In order to account for the changes in behavior by this means one must assume that the surface area is much larger than the external area of the specimen. Thus one is forced to the conclusions that the environment penetrates into the solid in order to achieve a large enough contact area between the environment and the specimen. The present work shows that the differences in f^s alone may become large enough so that measurable changes in the stress-strain characteristics can become visible.

Another important aspect of the plastic deformation is the possibility of dislocation movement within the specimen to minimize the surface energy. As a solid is deformed the dislocations within it will move so as to lower the energy

of the solid. If there is a large increase in surface energy it is possible that there may be some dislocation motion to relive this energy. Herring (1) and van der Merwe (481) have shown that certain arrangements of dislocations within the solid will tend to lower the surface energy. One such arrangement, shown in figure 21, consists simply in a series of edge dislocations lying parallel to the surface and some finite distance below it.

It may be that during plastic deformation there will be some dislocation movement within the solid to create an arrangement of dislocations such as that in figure 21. This movement will of course lower the value of the surface energy somewhat. Furthermore, an arrangement of dislocations such as that in figure 21 would tend to act as a barrier to subsequent dislocations moving toward the surface from the interior of the solid. Thus previous dislocation movement to lower the surface energy might create a surface barrier to further dislocation flow. This barrier would be similar to that proposed to explain the effects of surface films. In this case however, a barrier can be established without the presence of a film.

This idea suggests that some of the effects that have been attributed to films might be explainable without the requirement that a film itself acts as the dislocation barrier. It does not seem possible, though, to interpret all of the film observations in this manner. For one thing, it does not seem possible to account for the large increases in yield strength or critical shear stress with surface films by this means.

Another interesting aspect of the work on environment are the changes in mechanical properties with size. The general result has been that the strength of a material is greater the smaller the size of the test specimen. One explanation

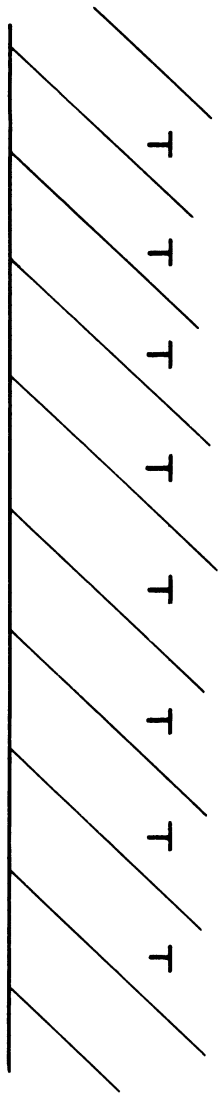


FIGURE 21 - RELIEF OF SURFACE ENERGY BY INTRODUCTION OF AN ARRAY OF EDGE DISLOCATIONS

for this result has been that the strength depends upon surface defects on the specimen. This explanation holds especially well for more brittle materials, and it is easy to see why surface imperfections should have a significant effect. It has never really been shown however, whether surface defects are the only significant variable. For example, several investigations have shown that bulk specimens of glass or various less-ductile metals approach the strength of whisker size specimens with careful surface polishing. What would happen however, if one polished to the same perfection the surface of a whisker size specimen. Would the strength of the small specimen be about the same, or would there be a corresponding increase in strength? To put the question another way, if one could prepare a bulk size specimen and a whisker size specimen of glass having identical volume structures, and so that both specimens had surfaces completely free from microcracks, would there be any difference in strength between the two specimens.

There is one reason to think that there should be a difference in strength. The reason is that there should be a difference in the relative amounts of surface work necessary to deform the two specimens. The total work to deform a specimen may be considered as the work to deform the volume plus the work to deform the surface. If the interior structures of the two specimens were identical then the volume work per cross-sectional area should be the same in both specimens. The surface work per cross-sectional area will not be the same however, because the smaller specimen has a greater amount of surface area. Thus it should take relatively more work to deform the smaller specimen.

This conclusion may be shown another way. If for cylindrical specimens

$$E' = E + \frac{4k}{r} \qquad (31)$$

and

$$E' = \sigma/\epsilon \qquad (43)$$

then the stress required to elastically deform a specimen to a strain ϵ is

$$\sigma = \left(E + \frac{4k}{r}\right)\epsilon \qquad (44)$$

Thus the stresses required to deform the two specimens to the same strain would vary with the radii of the specimens, assuming E and k are constant for the two cases.

It is interesting to note that if one assumes the fracture strain to be constant with varying size then the fracture stress becomes inversely proportional to the radius A number of investigators of glass fibers found such a relationship between the strength and the size. The agreement may be fortuitous however, because the surface microcracks may have been the dominating effect. In this respect these considerations may be of more theoretical than practical consequence. The present results do indicate however, that there should be a size effect in addition to that due to the surface perfection.

The same point is also applicable to the size effects in more ductile materials. In this case several other possible causes for the size effects have been suggested. The proposed reasons are of two types, attributing the observed changes to variations in the internal structure or to the surface effects. The internal variations include changes in dislocation density or the three dimensional dislocation network. The surface effects are those due to surface films or local imperfections.

The suggestion that a surface film controls the mechanical properties of course implies the same type of size effect as just described, for the effect would again be inversely proportional to the diameter of the specimen In the present case however, it may not be necessary to have an actual film on the

sample to produce a size effect. The strengths of whiskers of some metals for example, have been found to be inversely proportional to the diameter. Some of the observed size effects though, such as the variations in yield strength or critical shear strength with size, are difficult to explain by any other means.

In many instances it is difficult to ascribe the results to a size effect either with or without the presence of a film. This is especially true in connection with some of the rather bizarre effects found in whiskers. In cases such as these some major change in the internal structure is probably the predominant cause of the changes in properties. Thus, as in the more brittle materials, a size effect may be masked by more dominating variations. Still, with suitable conditions a size effect should also be observable in ductile materials, and some of the variations that have been observed may be due to this effect.

The idea of an intrinsic strengthening due to size alone represents the other side of the coin with respect to the common idea of why small specimens are stronger than bulk ones. The commonly accepted idea is that small specimens are stronger because they contain certain special deviations from bulk materials. The present idea suggests that small specimens may be inherently stronger than bulk ones, but that special deviations do not allow the specimens to achieve their maximum strength. At the present time the results are not sufficient to allow a conclusion one way or another.

The higher strengths found in very fine fibers of metal or glass have prompted many people to propose that larger sized pieces with high strengths could be made by suitable combinations of smaller pieces. To the author's knowledge the only successful application of this idea has been in the manufacture of glass fishing rods by the bonding together of long glass fibers with a cement.

The reason this particular application is successful is probably due to the fact that a fishing rod has to support essentially only bending stresses. Therefore each glass fiber in the rod can support part of the load, and more important, the cement holding the fibers together does not have to support the load. The only job the cement has is to keep the fibers together. One could also make a good rod by tieing a few pieces of string together around the fibers and ommiting the cement altogether.

This point should be borne in mind in any attempt to incorporate small fibers or films into high strength pieces. As long as the load is supported by the individual high strength components the overall composite should be strong. But if the cement, in whatever form it may be, must support the load then the strength of the overall combination should go down correspondingly. Thus it may take a good deal of ingenuity to successfully make high strength bulk pieces by combining smaller fibers or films.

Summary.

To briefly summarize the foregoing discussion, it would appear that many of the observed effects of environment on mechanical properties are compatible with the idea that the surface and grain boundary energies vary with strain. In addition many of the observed changes in the plastic deformation and fracture behavior with changing environment seem explainable by the present development. In other instances it would appear that the present considerations may be applicable, but that the results to date are not sufficient to allow a conclusion. For example, the effect of environment on the properties of ceramics, or some of the effects of specimen size might be related to surface energy effects, but the information now available is too limited to allow any more than

general speculations on these results. There is clearly a need for future work in fields such as these before the present relationships, or any other general development, can account for the various results.

In other cases it is difficult to relate the observed effects to any surface energy phenomenon. In particular some of the effects of surface micro-cracks and surface films seem independent of surface energy. Thus the present work cannot claim to answer all the problems that have arisen. It would seem though, that the surface energy considerations do furnish a more general mechanism to correlate many of the results that have been observed.

Finally it should be pointed out that the present developments concerning surface energy may be applicable in other fields besides that of the effects of environment on mechanical properties of solids. Various chemical phenomena for example, are influenced by surface energy factors. In some of these cases it might be possible to promote distinct changes in behavior by using an elastic strain to alter the surface energy. Conversely, one should detect elastic strains when a chemical effect takes place which alters the surface energy. One instance that has already been cited of this type of phenomena is the change in dimensions of solids with adsorption and desorption. Considerations such as these indicate that there may be other areas of interest where the present work may be valuable.

CONCLUSIONS

On the basis of the results of this investigation the following conclusions can be made.

1. The surface free energy and grain boundary energy of a solid change with elastic strain in the following manner:

$$f^S = f_o^S + k\epsilon^2$$
$$f^B = f_o^B + j\epsilon^2$$

2. The surface tension changes with elastic strain in the same manner as the surface energy. That is

$$\gamma = \gamma_o + k\epsilon^2$$

3. The values of the constants k and j may be determined by measurements of the slopes of stress-strain curves in the elastic region.

4. Measurements show that there may be distinct changes in the stress-strain slope E' with changing surface environment or with changes in the surface area to volume and grain boundary area to volume ratios of the solid.

5. On the basis of these measurements the value of k is on the order of 10^9 ergs/cm^2 and that of j is on the order of 10^8 ergs/cm^2.

6. The individual values of k and j should vary somewhat with changes in the surface composition at the respective interfaces. In general higher values of the surface and grain boundary energies before straining should give higher values of k and j.

7. The cleanliness of the solid surface prior to exposure to an environment may significantly alter the value of E'.

8. A review of the literature shows that the surface environment may have a pronounced effect on the mechanical properties of solids, but that no general mechanism exists to correlate the various results that have been observed.

9. The present finds suggest that many of these results are explainable in terms of surface energy effects. Other results that have been observed however, do not seem to be easily accounted for by surface energy considerations.

REFERENCES

1. C. Herring, The Physics of Powder Metallurgy, McGraw Hill Co., New York, 1950, p. 168.
2. R. Shuttleworth, Proc. Phys. Soc., 63A, 444, 1950.
3. C. Benedicks, Pittsburgh Int. Conf. on Surface Reactions, 1948, p. 196.
4. G. C. Benson, P. Balk, and P. White, J. Chem. Phys. 31, 109, 1959.
5. A. A. Griffith, Phil. Trans. Roy. Soc. 221A, 163, 1920.
6. A. A. Griffith, First. Int. Conf. on App. Mech. Delft, 55A, 1924.
7. F. O. Anderegg, Ind. Eng. Chem. 31, 290, 1939.
8. A. Joffe and A. Walther, Phys. Zeit.Sowjetunion, 1, 132, 1932.
9. E. Rexer, Z. Tech. Phys. 20, 4, 1939.
10. A. J. Holland and W. E. S. Turner, J. Soc. Glass Tech. 18, 225, 1934.
11. E. J. Gooding, J. Soc. Glass Tech. 16, 145, 1932.
12. K. Wirtz, Zeit. Phys. 93, 292, 1935.
13. O. Reinkober, Phys. Zeit. 32, 243, 1930.
14. O. Reinkober, Phys. Zeit. 38, 112, 1937.
15. O. Reinkober, Phys. Zeit. 33, 32, 1932.
16. S. Jurkov, Tech. Phys. USSR, 1, 386, 1935.
17. S. Schurkow, Phys. Zeit. Sowjetunion, 1, 123, 1932.
18. S. S. Brenner, Science, 128, 569, 1958.
19. E. N. Andrade and L. C. Tsien, Proc. Roy. Soc. 159A, 346, 1937.
20. W. C. Levengood and W. E. Fowler, J. Am. Cer. Soc. 40, 31, 1957.
21. J. E. Gordon, D. M. Marsh,M.E.M. Parratt, Proc. Roy. Soc. 249A, 65, 1959.
22. W. C. Levengood, J. App. Phys. 30, 378, 1959.
23. W. C. Levengood, J. App. Phys. 29, 820, 1958.
24. A. J. Holland and W. E. S. Turner, J. Soc. Glass Tech. 20, T279, 1936.
25. E. Orowan, Zeit. Phys. 82, 235, 1933.

26. A. Blackie, Trans. Faraday Soc. 7, 158, 1911.

27. W. A. Weyl, Research 1, 50, 1947.

28. R. N. Harwood, J. Soc. Glass Tech. 28, T133, 1944.

29. E. U. Condon, Am. J. of Phys. 22, 224, 1954.

30. C. Gurney, Nature 161, 729, 1948.

31. W. H. Otto and F. W. Preston, J. Soc. Glass Tech. 34, 65, 1950.

32. J. J. Bikermann and G. H. Passmore, Glass Ind. 29, 144, 1948.

33. J. B. Murgatroyd, J. Soc. Glass Tech. 32, 291, 1948.

34. R. K. Banerjee, J. Am. Cer. Soc. 36, 294, 1953.

35. R. T. Brannan, J. Am. Cer. Soc. 36, 230, 1953.

36. L. H. C. Tippett, Biometrika, 17, 364, 1925.

37. F. T. Pierce, J. Textile Ind. 17, 355, 1926.

38. W. Weibull, Ingen Vestensk Akad (Stockholm) Proc. No. 151 and 153, 1939.

39. J. Bailey, Glass Ind. 20, 21, 59, 95, 143, 1939.

40. J. Frenkel and T. A. Kontorova, J. Phys. SSSR 7, 108, 1943.

41. C. Gurney, Nature 155, 273, 1945.

42. J. C. Fisher, and J. H. Hollomon, T. AIME, 171, 546, 1947.

43. B. Epstein, J. App. Phys. 19, 140, 1948.

44. P. Gibbs and I. B. Cutler, J. Am. Cer. Soc. 34, 200, 1951.

45. C. H. Greene, J. Am. Cer. Soc. 39, 66, 1956.

46. E. Orowan, Repts. Progress in Physics, 12, 185, 1949.

47. G. M. Bartenev and L. P. Tsepkov, Sov. Phys. Dok. 121, 260, 1958.

48. S. Bateson, J. App. Phys. 29, 13, 1958.

49. G. F. Stockdale, F. V. Tooley, and C. W. Ying, Am. Cer. Soc. Journal, 34, 116, 1951.

50. F. Deeg and A. Dietzel, Glass Tech. Ber. 28, 221, 1955.

51. S. Bateson, J. Soc. Glass Tech. 37, 302T, 1953.

52. F. W. Preston, Bul. Am. Cer. Soc. 33, 355, 1954.

53. H. E. Powell and F. W. Preston, J. Am. Cer. Soc. 28, 145, 1945.

54. G. Apelt, Zeit. Phys. 91, 336, 1934.

55. L. V. Black, Bull Am. Cer. Soc. 15, 274, 1936.

56. A. J. Holland and W. E. S. Turner, J. Soc. Glass Tech. 24, T46, 1940.

57. B. Vonnegut and J. L. Glathart, J. App. Phys. 17, 1082, 1946.

58. F. W. Preston and J. L. Glathart, J. App. Phys. 17, 189, 1946.

59. T. C. Baker and F. W. Preston, J. App. Phys. 17, 170, 1946.

60. C. Gurney and S. Pearson, Proc. Phys. Soc. 62B, 469, 1949.

61. R. H. Kropschot and R. P. Mickesell, J. App. Phys. 28, 610, 1957.

62. R. J. Charles, J. App. Phys. 29, 1549, 1958.

63. C. Gurney, Proc. Phys. Soc. 59, 169, 1947.

64. E. Orowan, Nature, 154, 341, 1944.

65. E. Orowan, Zeit. Phys. 86, 195, 1933.

66. A. Silverman and L. G. Ghering, Glass Ind. 15, 339, 1942.

67. E. B. Shand, Am. Cer. Soc. Jour. 37, 559, 1954.

68. C. Gurney and S. Pearson, Proc. Phys. Soc. 192A, 537, 1948.

69. H. Jebsen-Marwedel and K. von Stoesser, Glass Tech. Ber. 17, 1, 1939.

70. F. W. Preston, J. App. Phys. 13, 623, 1942.

71. T. C. Baker and F. W. Preston, J. App. Phys. 17, 162, 1946.

72. T. C. Baker and F. W. Preston, J. App. Phys. 17, 179, 1946.

73. K. Moorthy and F. V. Tooley, Am. Cer. Soc. Jour. 39, 215, 1956.

74. G. R. Pulliam, J. Am. Cer. Soc. 42, 477, 1959.

75. C. Benedicks, Phys. Zeit. 32, 561, 1931.

76. C. Benedicks and P. Sederholm, Jern. An. 129, 107, 1945.

77. L. H. Milligan, J. Soc. Glass Tech. 13, 351, 1929.

78. Florenski, Vestnik Elektrotekh, No. 2, 1930.

79. J. W. Obriemoff, Proc. Roy. Soc. 127A, 290, 1930.

80. W. C. Levengood and W. H. Johnston, J. Chem. Phys. 26, 1184, 1957.

81. D. G. Holloway, Cambridge Conf. on Strength of Whiskers and Thin Films, 1958.

82. W. P. Berdenikov, Phys. Zeit. Sowjetunion, 4, 397, 1933.

83. C. Gurney, Properties of Metallic Surface, Inst. of Metals Monograph No. 13, London, p. 145, 1953.

84. W. Weibull, Proc. Roy. Swed. Inst. Eng. Res. Stockholm No. 149, 1938.

85. P. Joos, Zeit. F. Angew Phys. 9, 556, 1957.

86. P. Rebinder, Nature 159, 866, 1947.

87. H. Muller, Phys. Zeit. 25, 223, 1924.

88. E. Jenkel, Zeit. Elekt. 38, 569, 1932.

89. C. A. Stearns, A. E. Pack, and R. A. Lad, NASA Technical Note D-75, 1959.

90. A. S. Mekal, Zeit. Phys. 93, 166, 1934.

91. W. W. Webb and W. D. Forgeng, Acta Met. 6, 462, 1958.

92. W. W. Piper and W. L. Roth, Phys. Rev. 92, 503, 1953.

93. G. L. Pearson, W. T. Read and W. L. Feldman, Acta Met. 5, 181, 1957.

94. C. C. Evans, D. M. Marsh and J. E. Gordon, Cambridge Conference on Strength of Whiskers and Thin Films, 1958.

95. J. E. Gordon, Growth and Perfection of Crystals, J. Wiley, New York, p.219, 1958.

96. Z. Gyulai, Zeit. Phys. 138, 317, 1954.

97. W. W. Webb, J. App. Phys. 31, 194, 1960.

98. W. Voight and Sella, Wied. Ann. 8, 636, 1893.

99. K. Kleinhanns, Phys. Zeit. 15, 362, 1914.

100. A. Joffe, 1st Int. Conf. on App. Mech. Delft, 664, 1924.

101. A. Joffe, M. V. Kirpitscheva and M A. Levitsky, Zeit. Phys. 22, 286, 1924.

102. A. F. Joffe, The Physics of Crystals, McGraw Hill, N. Y., 1928.

103. E. Schmid and O. Vaupel, Zeit. Phys. 56, 308, 1929.

104. M. Polanyi and W. Ewald, Zeit. Phys. 28, 29, 1924.

105. M. Polanyi and W. Ewald, Zeit. Phys. 31, 746, 1925.

106. G. Sperling, Zeit. Phys. 74, 467, 1932.

107. K. H. Domerich, Zeit. Phys. 80, 242, 1933.

108. E. Aerts and W. Dekeyser, Acta Met. 4, 557, 1956.

109. A. E. Gorum, E. R. Parker, and J. A. Park, J. Am. Cer. Soc. 41, 161, 1958.

110. E. R. Parker, J. A. Park, J. Washburn, A. E. Gorum and W. Lubman, J. of Met. 10, 351, 1958.

111. R. J. Charles, Fracture, J. Wiley, N. Y., p. 225, 1959.

112. E. S. Machlin and G. T. Murray, J. App. Phys. 30, 1731, 1959.

113. E. S. Machlin, J. App. Phys. 30, 1109, 1959.

114. R. A. Lad, J. App. Phys. 23, 800, 1952.

115. J. B. Wachtman and L. W. Maxwell, J. Am. Cer. Soc. 7, 291, 1954.

116. S. Pearson, Proc. Phys. Soc. 69B, 1293, 1956.

117. F. I. Metz and R. A. Lad, J. Phys. Chem. 60, 277, 1956.

118. H. R. Leider, L. A. Girafalco and R. A. Lad, Acta Met. 5, 216, 1957.

119. R. A. Lad, C. A. Stearns, and M. G. Del Duca, Acta Met. 6, 610, 1958.

120. T. Suzuki, Dislocations and Mechanical Properties of Crystals, J. Wiley, N. Y., p. 215, 1956.

121. J. J. Gilman and W. G. Johnson, Dislocations and Mechanical Properties of Crystals, J. Wiley, N. Y., p. 116, 1956.

122. R. J. Stokes, T. L. Johnston, and C. H. Li, Trans. Met. Soc. AIME 215, 437, 1957.

123. V. P. Bobrikov, Sov. Phys. Tech. Physics 2, 758, 1957.

124. P. L. Pratt, Properties of Metallic Surfaces. Inst. of Metals Monograph No. 13, London, p. 346, 1953.

125. G. A. Bassett, Acta Met. 7, 754, 1959.

126. F. B. Bowden, Properties of Metallic Surfaces. Inst. of Metals Monograph No. 13, London, p. 345, 1953.

127. A.Smekal, Naturwiss., 16, 743, 1045, 1928.

128. A. Smekal, Phys. Zeit. 32, 187, 1931.

129. E. Schmidt and O. Vaupel, Zeit. Phys. 63, 311, 1931.

130. A. Smekal and F. Quittner, Zeit. Phys. Chemie, B3, 162, 1929.

131. R. B. Barnes, Phys. Rev. 44, 898, 1933.

132. R. B. Barnes, Phys. Rev. 43, 82, 1933.

133. F. Erdmann Jesnitzer and F. Gunther, Zeit. Elekt. 56, 446, 1952.

134. F. Gunther and F. Erdmann-Jesnitzer, Zeit. Elekt. 60, 85, 1956.

135. W. Robertson and H. Uhlig, J. App. Phys. 19, 864, 1948.

136. W. Robertson and H. Uhlig, Trans. Electrochem. Soc. 96, 27, 1949.

137. V. D. Kuznetsov, Surface Energy of Solids. Her Majesties Stationary Office, London, 1957.

138. C. Benedicks, Rev. de Met. 45, 9, 1948.

139. C. Herring and J. K. Galt, Phys. Rev. 85, 1060, 1952.

140. S. S. Brenner, Growth and Perfection of Crystals, J. Wiley, N.Y. p.157, 1958.

141. S. S. Brenner, J. App. Phys. 27, 1484, 1956.

142. N. Cabrera, Cambridge Conf. on Strength of Whiskers and Thin Films, 1958.

143. N. F. Mott, Phil. Mag. 43, 1151, 1952.

144. W. C. Dash, Growth and Perfection of Crystals, J. Wiley, N.Y., p.189, 1958.

145. N. Cabrera and P. B. Price, Growth and Perfection of Crystals, J. Wiley, N. Y. p. 204, 1958.

146. J. J. Gilman, Acta Met. 7, 357, 1959.

147. E. N. da C. Andrade, Properties of Metallic Surfaces, Inst. of Metals Monograph No. 13, London, p. 133, 1953.

148. H. Suzuki, S. Ikeda, and S. Takeuchi, J. Phys. Soc. Japan 11, 382, 1956.

149. R. L. Fleisher and B. Chalmers, T. AIME 212, 265, 1958.

150. V. I. Likhtman and V. S. Ostrovski, Dok Akad. Nauk SSSR 93, 105, 1953.

151. V. I. Likhtman and E. K. Venstrom, Dok Akad Nauk SSSR 66, 881, 1949.

152. M. S. Paterson, Acta Met. 3, 491, 1955.

153. J. Garstone, W. K. Honeycombe and G. Greethan, Acta Met. 4, 485, 1956.

154. H. Rebstock, Z. Metallunde 48, 206, 1957.

155. T. L. Wu and R. Smoluchowski, Phys. Rev. 78, 468, 1950.

156. J. E. Gilman, T. AIME 197, 1217, 1953.

157. E. N. da C. Andrade and A. J. Kennedy, Proc. Phys. Soc. 64B, 363, 1951.

158. T. Mukai, J. Sci. Hiroshima Univ. 22A, 99, 1958.

159. T. Evans and D. R. Schwarzenberger, Phil Mag. 4, 889, 1959.

160. K. Karmarsch, Mittheilungen des Gew ver fur Hanover, 138, 1858.

161. G. F. Taylor, Phys. Rev. 23, 655, 1924.

162. P. E. Shlichta, Growth and Perfection of Crystals, J. Wiley N.Y., p.214, 1958.

163. G. L. Pearson, W. T. Read, and W. C. Feldman, Acta Met. 5, 181, 1957.

164. A. Ono, Proc. 3rd Int. Con. on App. Mech. 2, 230, 1930.

165. W. R. Backer, E. R. Marshall, and M. C. Shaw, T. AIME 74, 61, 1952.

166. J. W. Beams, J. B. Breazele, and W. L. Bart, Phys. Rev. 100, 1657, 1955.

167. J. E. Gordon, Growth and Perfection of Crystals, J. Wiley, N.Y. p. 219, 1958.

168. G. A. Bassett and D. W. Pashley, J. Inst. Met. 87, 449, 1959.

169. D. W. Pashley, Phil. Mag. 4, 316, 1959.

170. J. W. Beams, Structure and Properties of Thin Films, J. Wiley, N.Y. p.183, 1959.

171. J. W. Menter and D. W. Pashley, Structure and Properties of Thin Films, J. Wiley, N.Y. p. 111, 1959.

172. M. Charpy, 6th Congress of Testing Mat., N. Y. 4, 5, 1912.

173. R. Stribeck, Stahl u Eisen. 35, 392, 1915.

174. B. Mailander, Stahl u Eisen, 46, 1752, 1926.

175. G. Cook, Trans. Inst. Eng. and Shipbuilders in Scotland, 81, 371, 1938.

176. J. L. M. Morrison, Proc. Inst. of Mech. Engr. 142, 193, 1939.

177. N. Davidenkov, E. Shevandin and F. Wittman, J. App. Mech. 14, 63, 1947.

178. P. E. Shearin, A. E. Ruark, and R. M. Trimble, Fracturing of Metals, ASM, Cleveland, p. 167, 1948.

179. B. B. Chechulin, Zhur. Tekh. Fiz. 24, 1093, 1954.

180. J. G. Docherty, Engineering (London) 133, 645, 1932.

181. J. G. Docherty, Engineering (London) 139, 211, 1935.

182. W. F. Brown, J. D. Lubahn and L. J. Ebert, Weld. Jour. 26, 554S, 1947.

183. E. R. Parker, Fracturing of Metals, ASM Cleveland, p. 82, 1948.

184. Y. Akita, Weld. Jour. 32, 475S, 1953.

185. A. A. Wells, Trans. Northeast Coast Inst. of Eng and Shipbuilders 71, 277, 1955.

186. J. D. Lubahn, Weld Jour. 34, 518S, 1955.

187. E. Dugger and A. Brisbane, Iron Age 177, 82, 1956.

188. E. Me. Shebandin, L. A. Raxov, R. T. Reshetmikova, and V. I. Serpeninov, Dok Ahad Nauk 113, 1057, 1957.

189. J. D. Lubahn and S. Yukawa, ASTM preprint No. 79, 1958.

190. B. M. Wundt, ASME paper No. 59-MET-9, 1959.

191. S. Yukawa, San Francisco meeting of AIME 1958.

192. P. A. Rebinder, 6th Cong. of Rus. Physicists Moscow, 1928.

193. P. A. Rebinder, Z. Physik. 72, 191, 1931.

194. P. A. Rebinder, and N. Kalinovskaya, Zhur. Tek. Fiz. 2, 726, 1932.

195. P. A. Rebinder and N. Kalenowskaya, Phys. Zeit. Sowjetunion 4, 365, 1933.

196. P. A. Rebinder and E. K. Venstrem, Izv. Akad Nank SSSR Otd. Mat. Est. Nauk 4-5, 1937.

197. P. A. Rebinder and V. F. Likhtman, Dok. Akad Nauk 32, 130, 1941.

198. P. Rebinder and G. I. Logginov, Compt. Rend. Acad. Sci. URSS 30, 491, 1941.

199. P. Rebinder, V. I. Likhtman and V. M. Maslennikov, Comtes Rend Acad. Sci. URSS 32, 125, 1941.

200. P. A. Rebinder and E. K. Venstrem, Acta. Physicochimo 19, 36, 1944.

201. V. I. Likhtman and E. P. Zakoshchikova, Dok. Akad Nauk 66, 657, 1949.

202. V. I. Likhtman and B. M. Maslennikov, ibid. 67, 93, 1949.

203. G. V. Karpenko, ibid. 73, 1225, 1950.

204. G. V. Karpenko, ibid. 77, 827, 1951.

205. G. V. Karpenko, ibid. 79, 287, 1951.

206. G. V. Karpenko, ibid. 87, 617, 1952.

207. G. V. Karpenko, ibid. 87, 797, 1952.

208. V. N. Rozhanski and P. A. Rebinder, ibid. 91, 129, 1953.

209. G. V. Karpenko and A. V. Karlashov, ibid. 92, 603, 1953.

210. Y. U. Gorynov, V. N. Rozhanski and P. A. Rebinder, ibid. 105, 448, 1955.

211. S. T. Kishkin and V. V. Nikolenko, ibid. 110, 1018, 1956.

212. P. A. Rebinder, V. F. Likhtman and L. A. Kochanova, ibid. 111, 1278, 1956.

213. V. N. Rozhanski, N. V. Pertsov and E. D. Shchukin and P. A. Rebinder, ibid. 116, 769, 1957.

214. V. I. Likhtman, L. A. Kochanova, and L. S. Briukhanova, ibid. 120, 757, 1958.

215. T. V. Karpenko and R. I. Krpyakevich, ibid. 120, 827, 1958.

216. V. A. Labzin and V. Likhtman, ibid. 121, 442, 1958.

217. M. I. Chaevskii, ibid. 125, 319, 1959.

218. S. T. Kishkin, V. V. Nikolenko and S. T. Ratner, J. Tech. Fiz. 24, 1455, 1954.

219. V. I. Likhtman, Vestnik Akad Nauk SSSR 26, 8, 1956.

220. P. A. Rebinder, ibid. 27, 32, 1957.

221. P. A. Rebinder, Vest Akad Nauk 1, 123, 1947.

222. S. I. Sapiro, Stal 7, 395, 1947.

223. V. I. Likhtman, The Effect of the Medium on the Strength of Metals,(in Russian) Moscow, 1953.

224. A. B. Taubman and E. K. Venstrom, T. 3rd all Union Conf. on Col. Chem. 1953.

225. V. I. Likhtman, P. A. Rebinder and G. V. Karpenko, The Effect of Surface Active Media on the Deformation Processes in Materials (in Russian) Izd. Akad Nauk, 1954.

226. V. I. Likhtman, Uspek Fiz Nauk 54, 587, 1954.

227. V. N. Likhtman, P. A. Rebinder, and G. V. Karpenko, Effect of Active Liquid Agents on the Endurance of Steels (in Russian) 1955.

228. S. I. Gubkin, Zh neorgan khim 1, 1334, 1956.

229. V. N. Rozhunski, Yu. V. Goryunov and V. N. Dekortova, Zh Fiz Khim 31, 888, 1957.

230. P. A. Rebinder, Izv. Akad Nauk OKhN 1264, 1957.

231. G. V. Karpenko, Prikl Mekh 3, 13, 1957.

232. G. V. Kurganov, A. S. Nikishov, L. P. Rink and N. J. Yartenskaya, Takh Trans. Mash. 2, 29, 1957.

233. A. J. Yatsyk and F. B. Yanchisin, Zavods Lab. 24, 229, 1958.

234. N. A. Plateneva and P. A. Rebinder, Dok Akad Nauk 62, 501, 1948.

235. N. A. Plateneva, L. A. Shreiner and P. A. Rebinder, ibid. 62, 653, 1948.

236. T. I. Liubimova and P. A. Rebinder, ibid. 63, 159, 1948.

237. G. I. Epifanov, P. A. Rebinder and L. A. Shreiner, ibid. 66, 879, 1949.

238. G. I. Epifanov, ibid. 75, 415, 1950.

239. G. I. Epifanov, ibid. 75, 555, 1950.

240. S. Ia Veiler and G. I. Epifanov, ibid. 92, 1953.

241. S. Ia Veiler, V. I. Likhtman, and P. A. Rebinder, ibid. 110, 985, 1956.

242. S. Ia Veiler and V. I. Likhtman, ibid. 114, 6, 1957.

243. V. D. Kuznetsov, A. I. Loskutov, and S. N. Pavlova, ibid. 123, 272, 1958.

244. G. I. Epifanov, N. I.Glagolev and P. A. Rebinder, ibid. 123, 663, 1958.

245. P. A. Rebinder, The Effect of Active-Liquid Coating Liquids on Surface Quality in Working Metals by Cutting and by Pressure, Moscow-Leningrad, 1947.

246. V. A. Arshinov and G. A. Alekseev, The Cutting of Metals, 1953.

247. V. D. Kuznetsov and A. I. Loshutov, Fiz. Met i Met 2, 509, 1956.

248. S. Ya Yeiler and V. I. Likhtman, Zhur Tech Fiz 28, 2025, 1958.

249. A. V. Ratner and V. N. Gulyaev, Zavods, Lab. 24, 770, 1958.

250. G. V. Karpenko, Issled. po fiz. tverdogo, Moscow, Akad Nauk SSSR, 1957.

251. G. V. Karpenko, Yatsyuk, and F. P. Yanchisin, Nauch. Zapiski Inst. Michi Aut Akad Nauk Ukr SSR 6, 42, 1957.

252. G. W. Karpenko, Zeit Phys Chemie 208, 309, 1958.

253. V. I. Likhtman and E. D. Shchukin, Sov. Phys. Uspekii 66, 91, 1958.

254. E. D. Shuchukin, Dok Akad Nauk 118, 1105, 1958.

255. D. I. Shilkrut, ibid. 122, 622, 1958.

256. V. N. Rozhanski, ibid. 123, 648, 1958.

257. E. D. Schchukin and V. I. Likhtman, ibid. 124, 111, 1959.

258. A. Pfutzenreuter and G. Masing, Zeit Metallkunde, 42, 361, 1951.

259. G. Masing, La Metallurgia Italiana 43, 467, 1951.

260. W. Klinkenberg,K. Lucke,and G. Masing, Zeit Metalkunde 44, 362, 1953.

261. R. Roscoe, Phil Mag, 21, 399, 1936.

262. D. S. Kemsley, Nature 163, 404, 1949.

263. S. Harper and A. H. Cottrell, Proc. Phys. Soc 63B, 331, 1950.

264. C. L. Smith, Nature 160, 466, 1947.

265. A. H. Cottrell and D. F. Gibbons, Nature 162, 488, 1948.

266. J. Takamura, Mem. Faculty Eng. Kyoto Univ. 18, 255, 1956.

267. E. N. Andrade and R. F. Y. Randall, Nature 164, 1127, 1949.

268. E. N. Andrade and R. F. Y. Randall, Nature 164, 536, 1949.

269. E. N. Andrade and R. F. Y. Randall, Proc. Phys. Soc 63B, 198, 1950.

270. E. N. Andrade, R. F. Y. Randall, M. J. Makin, Proc. Phys. Soc. 63B, 990, 1950.

271. E. N. Andrade and C. Henderson, Phil. Trans. Roy. Soc. 244A, 177, 1951.

272. J. J. Gilman and T. A. Read, J. Met. 4, 875, 1952.

273. J. J. Gilman, Basis Effects of Environments on Strength, Scaling, and Embrittlement of Metals at High Temperatures, ASTM No. 171, 1955.

274. F. R. Lipsett and R. King, Proc. Phys. Soc. 70B, 608, 1957.

275. J. J. Gilman, Nature 169, 149, 1952.

276. R. King, Nature 169, 543, 1952.

277. L. C. Weiner, T AIME 212, 253, 1958.

278. E. N. Andrade, and F. R. Y. Randall, Nature 162, 890, 1948.

279. J. W. Mentor and E. O. Hall, Nature 165, 611, 1950.

280. D. J. Phillips and N. Thompson, Proc. Phys. Soc 63B, 839, 1950.

281. M. R. Pickus and E. R. Parker, J. Met. 3, 792, 1951.

282. E. N. Andrade and R. F. Y. Randall, Proc. Phys. Soc. 65B, 443, 1952.

283. F. D. Coffin and A. L. Weiman, J. App. Phys. 24, 282, 1953.

284. M. Metzger and T.A. Read, Trans. Met. Soc. AIME 212, 236, 1958.

285. S. Shapiro and T. A. Read, Phys. Rev. 82, 341, 1951.

286. C. S. Barrett, Acta Met. 1, 2, 1953.

287. C. S. Barrett, T. AIME 197, 1652, 1953.

288. C. S. Barrett, P. M. Aziz, and I. Markson, T. AIME 197, 1665, 1953.

289. B. I. Edelson and W. D. Robertson, Acta Met. 2, 583, 1954.

290. D. R. Brame and T. Evans, Phil. Mag. 3, 971, 1958.

291. M. Metzger, J. Met. 4, 532, 1952.

292. G. B. Greenough and D. A. Ryder, J. Inst. Met. 84, 467, 1956.

293. L. C. Weiner and M. Gensamer, J. Inst. Met. 85, 441, 1957.

294. L. C. Weiner and M. Gensamer, N. Y. Meeting of the American Chemical Soc. 1959.

295. L. Nanis and J. H. Schulman, New York Meeting of the American Chemical Soc. 1959.

296. S. S. Brenner, J. App. Phys. 30, 266, 1959.

297. W. Weik, J. App. Phys. 30, 791, 1959.

298. L. C. Weiner, Trans. Met. Soc. AIME 212, 342, 1958.

299. C. Benedicks and G. Ruben, Jern. Ann. 129, 37, 1945.

300. M. Sato, Proc. Japan Acad. 31, 620, 1955.

301. M. Sato, Proc. Japan. Acad. 32, 267, 1956.

302. Ove Falck Holm, Draht, 41, 69, 1959.

303. M. Classen-Nekludova, Tech. Phys. USSR, 5, 827, 1938.

304. P. Briedt, J. N. Hobstetter, and W. C. Ellis, J. App. Phys. 29, 226, 1958.

305. T. L. Johnston, R. J. Stokes, and C. H. Li, Acta Met. 6, 713, 1958.

306. R. J. Love, Properties of Metallic Surfaces. Inst. of Metals Monograph No. 13, London, p. 161, 1953.

307. B. P. Haigh, J. Inst. Met. 18, 55, 1917.

308. H. J. Gough and D. G. Sopwith, J. Inst. Met. 56, 55, 1935.

309. H. J. Gough and D. G. Sopwith , J. Inst. Met. 72, 415, 1946.

310. J. W. Martin and G. C. Smith, Metallurgia 54, 227, 1956.

311. K. U. Snowden and J. N. Greenwood, T. Met. Soc. AIME 212, 626, 1958.

312. N. Thompson, N. J. Wadsworth, and N. Louat, Phil. Mag. 1, 113, 1956.

313. M. Hempel, A. Kochendorfer, and A. Tietze, Arch. Eisenhut. 30, 211, 1959.

314. N. J. Wadsworth and E. Hutchings, Phil. Mag. 3, 1154, 1958.

315. R. H. Thielemann and E. R. Parker, Trans. AIME 135, 559, 1939.

316. O. C. Shepard and W. Schalliol, Spec. Tech. Pub. No. 108, ASTM, p. 34, 1951.

317. M. R. Pickus and F.R. Parker, Spec. Tech. Pub. No. 108 ASTM, p. 26, 1951.

318. E. D. Sweetland and E. R. Parker, J. App. Mech. 20, 30, 1953.

319. W. Forestier and A. Clauss, Rev. Met. 52, 961, 1955.

320. P. Shahinain, T. ASM 49, 862, 1957.

321. D. D. Lawthers and M. J. Manjoine, High Temperature Materials, J. Wiley, N. Y., p. 486, 1959.

322. H. T. McHenry and H. B. Probst, ibid. p. 446, 1959.

323. R. Widmer and N. J. Grant, ASME paper 59-A-122, 1959.

324. P. Shahinian and M. R. Achter, NRL Rept. 5037, 1957.

325. P. Shahinian and M. R. Achter, T. AIME 215, 37, 1959.

326. M. R. Achter and H. W. Fox, T. AIME 215, 295, 1959.

327. E. N. Andrade, Nature, 156, 113, 1945.

328. M. Makin, Nature, 174, 752, 1954.

329. E. Schmidt, J. Inst. Met. 82, 604, 1954.

330. L. R. Kelman, W. D. Wilkinson, F. L. Yaggee. Argonne National Lab. Rept. ANL4417, 1950.

331. H. Udin, Metal Interfaces, ASM Cleveland, p. 114, 1952.

332. C. Elbaum, T. Met. Soc. AIME, 215, 476, 1959.

333. J. Huntington, J. Inst. Met. 11, 108, 1914.

334. H. S. Rawdon, Proc. ASTM 18, 159, 1918.

335. J. Rogers, J. Inst. Met. 22, 114, 1919.

336. C. H. Desch, ibid. 22, 247, 1919.

337. J. Rogers, ibid. 23, 244, 1920.

338. J. H. S. Dickenson, ibid. 24, 315, 1920.

339. H. Moore, S. Beckinsale, and C. F. Mallinson, ibid. 25, 35, 1921.

340. L. H. Marshall, U. S. Bur. Stand. Tech. Paper, No. 245, 1923.

341. H. J. Miller, J. Inst. Met. 37, 183, 1927.

342. H. J. Hartley, ibid. 37, 193, 1927.

343. R. Gender, ibid. 37, 215, 1927.

344. D. S. Anderson and G. E. Pool, ibid. 37, 237, 1927.

345. H. Shottky, K. Schichtel, and R. Stolle, Arch Eisenhutt, 4, 541, 1930-31.

346. L. W. Schuster, Proc. Inst. Mech. Eng. 124, 337, 1933.

347. L. J. G. van Ewijk, J. Inst. Met. 56, 241, 1935.

348. O. Patterman, ibid. 56, 254, 1935.

349. G. W. Austin, J. Inst. Met. 58, 173, 1936.

350. W. E. Goodrich, J. Iron and Steel Inst. 132, 43, 1935.

351. P. Ffield ., Trans. Soc. Naval Arch Mar. Eng. 45, 174, 1937.

352. O. H. Henry and R. W. Schroeder, Welding J. Res. Sup. 21, 287, 1942.

353. F. Page, Am. Electroplaters Soc. Proc. of Educational Ser. of 31st Conv. p. 51, 1943.

354. H. A. Campbell, Iron Age, 151, 56, 1943.

355. W. Whitaker, E. Voce, and A. R. Bailey, Metallurgia 39, 21, 66, 1948.

356. W. D. Robertson, T. AIME 191, 1190, 1951.

357. W. H. Brown, W.W. Binger, and R. H. Brown, Corrosion 8, 155, 1952.

358. W. Radeker, Stahl n. Eisen 73, 10, 654, 1953.

359. A. R. Bailey and R. J. King, Bull. Inst. Met. 2, 105, 1954.

360. R. W. Moeller and W. A. Shell, Proc. Am. Electroplaters Soc., p. 189, 1955.

361. H. R. Copson, Stress Corrosion Cracking and Embrittlement, J. Wiley, N. Y. p. 187, 1956.

362. W. A. Wood, J. Inst. Met. 86, 228, 1958.

363. B. Cohen, Plating 45, 1127, 1958.

364. J. C. Spurr, Corrosion Technology 6, 233, 1959.

365. Anon, Metal Progress 76, 123, Dec. 1959.

366. J. B. Wachtman, J. App. Phys. 21, 943, 1950

367. G. Edmonds, Symposium on stress corrosion cracking of metals ASTM and AIME, p. 69, 1944.

368. ASTM Standards pt. 2 Philadelphia, p. 409, 1952.

369. R. Eborall and P. Gregory, J. Inst. Met. 84, 88, 1955.

370. S. L.Archbutt, J. D. Grogan and J. W. Jenkin, J. Inst. Met. 40, 219, 1928.

371. G. Tammann and W. J. Rocha, Zeit. Metal kunde 25, 133, 1933.

372. J. Vero, Metal Ind. Trans. (London) 48, 431, 491, 1936.

373. A. R. E. Singer and S. A. Cottrell, J. Inst. Met. 73, 33, 1947.

374. J. W. Halley, Effect of Residual Elements on the Properties of Metals, ASM Cleveland, p. 71, 1957.

375. F. N. Rhines, Effect of Residual Elements on the Properties of Metals, ASM Cleveland, p. 28, 1957.

376. A. J. Williams, P. J. Rieppel and C. B. Voldrich, Summary Rept. No. AF 33(038)-12619 August 1951.

377. R. P. Sopher, A. J. Jacobs, and P. J. Rieppel, Welding Journ. Res. Supl. 544S, 1955.

378. C. L. Korbin and R. A. Dodd, ASM preprint No. 101, 1958.

379. N. J. Petch, Progress in Metal Physics Vol. V. Pergamon Press, N.Y. 1954.

380. C. S. Smith, T. AIME 175, 15, 1948.

381. W. A. Morgan, Metal Treat and Drop Forging 6, 333, 1959.

382. W. D. Robertson and R. Bakish, Stress Corrosion Cracking and Embrittlement, J. Wiley, N. Y. p. 32, 1956.

383. R. Speiser and J. W. Spretnak, Stress Corrosion Cracking and Embrittlement, J. Wiley, N. Y. p. 92, 1956.

384. J. W. Cahn and J. E. Hilliard, Acta Met. 7, 219, 1959.

385. H. H. Bleakney, Can. Jour. Tech. 30, 340, 1952.

386. D. McLean, Grain Boundaries in Metals, Clarendon Press, Oxford, p.335, 1957.

387. P. W. Davies and J. P. Dennison, J. Inst. Metals 87, 119, 1958.

388. J. Intrater and E. S. Machlin, Acta Met. 7, 140, 1959.

389. P. W. Bridgman, Proc. Am. Acad Arts and Sci. 59, 173, 1924.

390. T. C. Poulter and L. Uffelman, Physics 3, 147, 1932.

391. H. H. Uhlig, Metal Prog. 57, 486, 1950.

392. Anon, Chem. Engr. News 30, 2942, 1952.

393. P. Bastien and P. Amiot, Comp. Rend. 235, 1031, 1952.

394. A. Durkin, Metal Prog. 64, 72, 1953.

395. D. D. Perlmutter and B. F. Dodge, Ind. Eng. Chem. 48, 885, 1956.

396. A. Schuetz and W. Robertson, Corrosion 13, 437, 1957.

397. N. N. Kolgatin, L. A. Glikman, V. P. Trodorovich, Zavod, Lab. 23, 1098, 1957.

398. D. Warren and G. W. Bechman, Corrosion 13, 631, 1957.

399. F. K. Naumann and W. Carius, Arch f. Eisenhut, 30, 283, 1959.

400. F. K. Naumannand W. Carius, Arch f. Eisenhut. 30, 361, 1959.

401. H. H. Uhlig, Physical Metallurgy of Stress-Corrosion Fracture, Interscience Pub. N. Y. p. 1, 1959.

402. P. G. Bastien, Physical Metallurgy of Stress-Corrosion Fracture, Interscience Pub. N. Y. p. 311, 1959.

403. N. J. Petch and P. Stables, Nature 169, 842, 1952.

404. N. J. Petch, Phil. Mag. 1, 331, 1956.

405. H. H. Johnson, J. G. Morlet, and A. R. Troiano, Trans. Met. Soc. AIME 212 528, 1958.

406. M. L. Hill and E. W. Johnson, ibid. 215, 717, 1959.

407. E. A. Steigerwald, F. W. Schuller, and A. R. Troiano, ibid. 215, 1048, 1959.

408. O. Reinkober, Phys. Zeit. 40, 385, 1939.

409. C. V. Boys, Phil. Mag. 23, 489, 1887.

410. R. Threfal, Laboratory Arts, Macmillan and Co, London 1898.

411. C. V. Boys, Dict. Appl. Phys. III, 695, 1923.

412. R. B. Sosman, Properties of Silica, Chemical Catalog Co. N.Y. p. 450, 1927.

413. H. V. Neher and J. Strong, Proc. in Expt. Physics, Prentice Hall, N.Y. Chap.V. 1939.

414. D. J. Tritton, Phil. Mag. 4, 780, 1959.

415. J. B. Murgatroyd, J. Soc. Glass Tech. 38, 368, 1944.

416. M. Sato, Proc. Jap. Acad. 30, 445, 1954.

417. R. Bacon, Cambridge Conference on Strength of Whiskers and Thin Films, 1958.

418. R. V. Coleman, B. Price, and N. Cabrera, J. App. Phys. 28, 1360, 1957.

419. M. Sato, Ark Fysik, 10, 45, 1955.

420. D. W. and R. I. Ruzouk, Proc. Roy. Soc. 166A, 572, 1938.

421. D. H. Bangham and F. A. P. Maggs, Conference on the Ultra Fine Structure of Coals and Coke. Brit. Coal. Utilization Res. Assoc. London, p. 118, 1944.

422. D. J. C. Yates, Proc. Roy. Soc. 224A, 526, 1954.

423. D. J. C. Yates, J. Phys. Chem. 60, 543, 1956.

424. D. J. C. Yates, Advances in Catalysis, 9, 51, 1957.

425. R. S. Haines and R. McIntosh, J. Chem. Phys. 15, 28, 1947.

426. M. L. Lakhanpal and E. A. Flood, Canad. J. Chem. 35, 887, 1957.

427. J. W. McBain and R. F. Sessions, J. Colloid Sci. 3, 213, 1948.

428. T. Kawai, Sci. Repts. Tohoku Univ. 19, 209, 1930.

429. M. Sugihara, Kyoto Imp. Univ. Col. of Sci. Mem. A17, 389, 1934.

430. W. Koster and K. Rosenthal, Zeit. Metallkunde 30, 345, 1938.

431. W. Koster, Zeit. Mettallkunde 32, 282, 1940.

432. D. J. Mack, T. AIME 166, 68, 1946.

433. I. Itaka and T. Morooka, Rept. Castings Res. Lab. Waseda Univ. 9, 55, 1958.

434. R. W. Fenn, Proc. ASTM 58, 826, 1958.

435. L. Holland, Vacuum Deposition of Thin Films, J. Wiley, N. Y. 1956.

436. J. A. Dillon and H. E. Farnsworth, J. App. Phys. 28, 174, 1957.

437. H. E. Farnsworth, R. E. Schlier, T. H. George, and R. M. Burger, J. App. Phys. 29, 1150, 1958.

438. R. Weil, J. Rothman, and L. T. Lloyd, Rev. Sci. Instruments 30, 541, 1959.

439. C. S. Smith, Metal Interfaces, ASM Cleveland, p. 65, 1952.

440. C. S. Smith, and L. Guttman, Trans. AIME 197, 81, 1953.

441. G. Slayter, Am. Cer. Soc. Bul. 31, 276, 1952.

442. W. H. Otto, J. Am. Cer. Soc. 38, 122, 1955.

443. W. F. Thomas, Nature, 181, 1006, 1958.

444. Ia. N. Potak and I. M. Shcheglakov, J. Tech. Fiz. 25, 897, 1955.

445. J. A. Kies, A. M. Sullivan, and G. R. Irwin, J. App Phys. 21, 716, 1950.

446. G. R. Irwin and J.A. Kies, Welding Journal Res. Sup 31, 95, 1952.

447. J. R. Low, Relation of Properties to Microstructure ASM Cleveland, p. 163, 1954.

448. A. N. Stroh, Phil. Mag. 2, 1, 1957.

449. A. H. Cottrell, Trans. Met. Soc. AIME 212, 192, 1958.

450. J. R. Low, Fracture, J. Wiley, N. Y. p. 68, 1959.

451. G. T. Hahn, B. L. Averbach, W. S. Owen and M. Cohen, Fracture, J. Wiley, N. Y. p. 91, 1959.

452. A. A. Wells, Welding Res. 7, 34r, 1953.

453. N. J. Petch, Phil. Mag. 3, 1089, 1958.

454. A. A. Johnson, Phil. Mag. 4, 194, 1959.

455. D. K. Felbeck and E. Orowan, Weld. Jour. Res. Sup. 34, 570s, 1955.

456. E. T. Wessel, Private communication.

457. D. McLean and L. Northcott, J. Iron Steel Inst. 158, 169, 1953.

458. B. C. Woodfine, J. Iron Steel Inst. 173, 229, 240, 1953.

459. E. Perryman, Stress Corrosion Cracking and Embrittlement, J. Wiley, N. Y. p. 61, 1956.

460. C. F. Ransley and D. E. J. Talbot, J. Inst. Met. 88, 150, 1959.

461. N. P. Allen, Fracture, J. Wiley, N.Y. p. 123, 1959.

462. A. R. Troiano, Metal Progress, 77, 112, Feb. 1960.

463. D. McLean and L. Northcott, J. Inst. Met. 72, 583, 1946.

464. E. Voce and A. P. C. Hallowes, J. Inst. Met. 73, 323, 1947.

465. D. McLean, J. Inst. Metals 81, 121, 1952.

466. B. E. Hopkins and H. R. Tipler, J. Iron and Steel Inst. 177, 110, 1954.

467. M. C. Inman, and H. R. Tipler, Acta Met. 6, 73, 1958.

468. B. E. Hopkins and H. R. Tipler, J. Iron and Steel Inst. 188, 218, 1958.

469. W. P. Rees and B. E. Hopkins, J. Iron and Steel Inst. 172, 403, 1952.

470. J. R. Low and R. G. Feustel, Acta Met. 1, 185, 1953.

471. W. P. Rees, B. E. Hopkins, and H. R. Tipler, J. Iron and Steel Inst. 169, 157, 1951.

472. G. Henry, J. Plateau, X. Wache, M. Gerber, J. Bekar, and C. Crussard, Mem. Sci de la Rev de Met. 56, 417, 1959.

473. C. F. Elam, Trans. Faraday Soc. 32, 1604, 1936.

474. A. T. Gwathmey and A. F. Benton, J. Chem. Phys. 8, 431, 569, 1940.

475. A. T. Gwathmey and A. F. Benton, J. Phys. Chem. 46, 969, 1942.

476. B. Chalmers, R. King, and R. Shuttleworth, Proc. Roy. Soc. 193A, 465, 1948.

477. J. Moreau and J. Benard, J. Inst. Met. 83, 87, 1954.

478. J. Moreau and J. Benard, Compt. Rend.Acad. Sci. 241, 1571, 1955.

479. J. Moreau and J. Benard, Compt. Rend.Acad. Sci. 242, 1724, 1956.

480. J. Benard, J. Moreau, and J. Plateau, Z. Elektrochem. 61, 59, 1957.

481. J. H. van der Merwe, Proc. Phys. Soc. 63A, 616, 1950.

Part III - THE EFFECT OF TENSILE STRESS ON DIHEDRAL ANGLES IN LEADED COPPER

Abstract

Experiments were conducted to determine the effect of applied stress on dihedral angles of liquid lead in copper at 900°F. It was found that dihedral angles decrease with increasing stress in the center of test specimens, but that no apparent relation exists between the amount of stress applied and the dihedral angle observed nearer the surface of the specimen. The latter phenomena is attributed to oxygen penetration which changes angles by adsorption on interfaces. It was observed that stress levels resulting in specimen fracture were accompanied by migration of lead to the specimen surface and the fracture surface. A mechanism for this movement is postulated.

Introduction

The purpose of these experiments was to discover what effect applied stress had on interfacial energies in a copper-lead alloy at temperatures where the lead phase was molten. Many phenomena, e.g. "hot shortness" in steels, stress corrosion, etc., can be more readily understood if the possibility is recognized that interfacial energies in metals are changed by stress, affecting in turn the "wettability" of any liquid phase present. Detrimental mechanical properties imparted by a liquid phase are related directly to the extent to which the liquid wets grain boundaries.

The present system was chosen because lead and copper are relatively immisible up the melting point of copper, the temperature needed to maintain a molten lead phase is low, and considerable work has been done by various authors (1, 2, 3, 4, 5) on surface energies in this system.

Theoretical Considerations

The balance of surface tensions at a lead grain in copper is given by the formula $\frac{\gamma \text{ Cu-Cu}}{\gamma \text{ Cu-Pb}} = 2 \cos \frac{\theta}{2}$ where γ Cu-Cu, γ Cu-Pb and θ are as shown in figure (1).

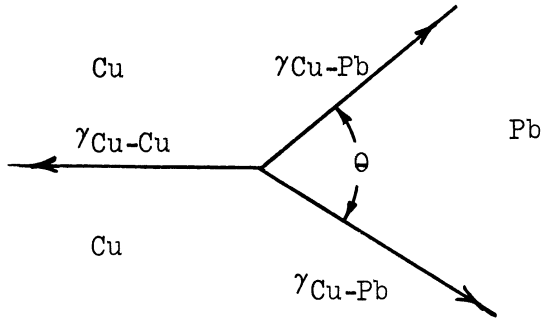


Figure (1)

Any change in the value of γ_{Cu-Cu} and γ_{Cu-Pb} should be revealed as a change in dihedral angle, θ.

The dihedral angle for the lead-copper system is about 65° (from measurements made in this paper). Bailey and Watkins (5) estimated that γ_{Cu-Pb} was 360 dynes/cm, so γ_{Cu-Cu} must be on the order of 609 dynes/cm. The following table gives an appreciation of the size of changes in surface tensions that would be revealed as a 5° change in dihedral angle:

Table (1)

θ	$2 \cos \frac{\theta}{2}$	$\frac{609+x}{360}$	$\frac{609}{360+x}$	$\frac{609+x}{360+x}$
60°	1.732	$x=15 \text{ergs/cm}^2$	$x=-9 \text{ergs/cm}^2$	$x=-20.5 \text{ergs/cm}^2$
65°	1.688	x=0	x=0	x=0
70°	1.640	x=-19	x=+11	x=29.7

Crude as these calculations are they clearly indicate that the dihedral angle, near 65°, is a sensitive measure of changes in surface tensions, although it must still be recognized that fortuitous compensating energy changes could occur which would not change θ.

Floreen, Hucke and Ragone (6) have shown from a thermodynamic analysis that the surface energy and grain boundary energy of a solid changes with elastic strain. Their formula for grain boundary energy is $\gamma = \gamma^{o} + j\epsilon^{2}$ where γ is the grain boundary energy when strained, γ^{o} is the grain boundary energy when unstrained, ϵ is the amount of elastic strain, and j is an unknown constant, probably on the order of 10^{8}.

If the elastic modulus for copper at 900°F is on the order of 10^{6}, a stress of 1000 psi will produce a strain of about 10^{-3}. The product $j\epsilon^{2}$, then, is on the order of 100 ergs/cm^{2}.

From the above discussion it may be seen that it is not unreasonable to expect observable changes in the dihedral angle of lead in copper with applied stress. If changes are observed it is possible to calculate values of j_{Cu-Cu} and j_{Cu-Pb} by assuming $\gamma^{o}_{Cu-Pb} = 360$ ergs/cm^{2}, $\gamma^{o}_{Cu-Cu} = 609$ ergs/cm^{2}, knowing the modulus of elasticity, and assuming the strain is not the same at both interfaces and equal to the bulk strain. These calculations were not made because of the many assumptions that would have had to be made, e.g. no value for the elastic modulus at 900°F is known. Although no calculations were performed, the existance or non-existance of changes in dihedral angle with stress can show whether j is large enough to be important.

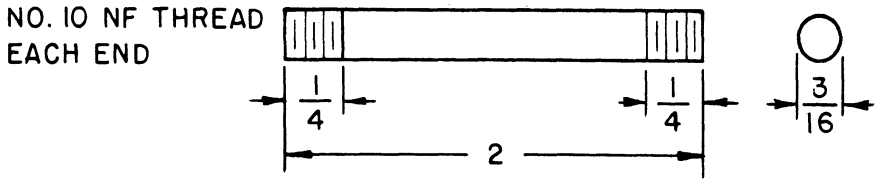
Experimental Procedure

Ingots of 2% lead, 98% copper were prepared by melting about 180 gms of Baker and Adamson Grade 1623 copper and 3.6 gms of Baker and Adamson Grade 1820 lead in a graphite crucible in a Lepel induction furnace under a protective atmosphere of about 50 mm Hg of Helium. The metal charge was kept molten from 5-10 minutes to insure adequate mixing of lead in the copper, then rapidly cooled in the furnace under vacuum. This treatment produced ingots in which the lead was uniformly dispersed through the copper matrix. In only one ingot (No. 1) was there any evidence of porosity, and it was slight in this case.

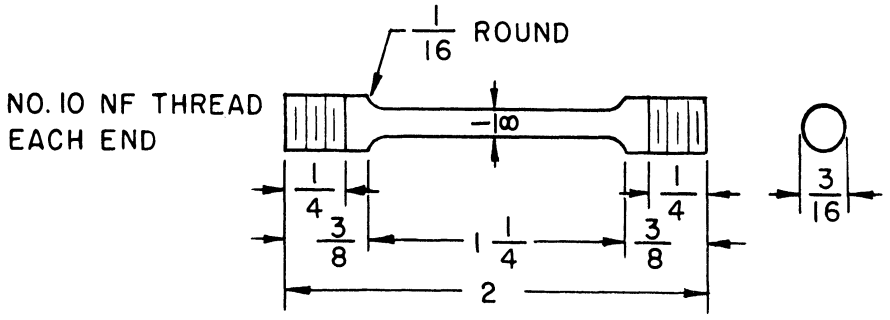
The ingots were cold worked by hand (Ingots Nos. 1 to 3) or by rolling (Ingots 4 to 6) to about 65% of their original crossectional area (except Ingot 4 to about 80% due to cracking of ingot) and annealed for $1\frac{1}{2}$ hours in a salt bath at about 1175°F $\pm$ 75°F.

Tensile specimens were machined from each billet by Knowlson-Gibson Company, Ann Arbor, Michigan to the following dimensions:

Figure (2)



A. SPECIMENS FROM INGOTS NOS. 1, 2, 3



B. SPECIMENS FROM INGOTS NOS. 4, 5, 6

Finished specimens varied up to 1/16" in length; a maximum variation of 0.002" in diameter was noted. (Stresses were calculated on the basis of measured diameters.)

Specimens from ingots (4), (5), and (6) were annealed for 50 hours in evacuated pyrex tubes at 900°F prior to testing; specimens from ingots (1), (2) and (3) did not receive this treatment.

Testing was done in a vertical tube furnace at 900°F. Figures (3,4) show details of the experimental arrangement.

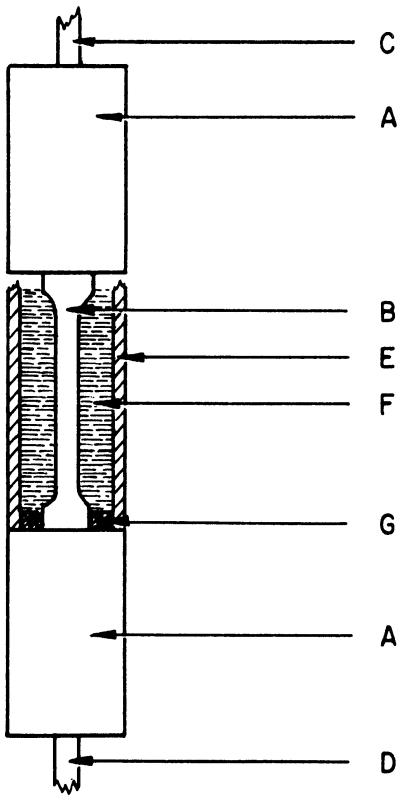


Figure (3). Specimens in Specimen Holders

A. Threaded Fittings holding specimens and steel rods

B. Specimen

C. Steel rod to upper support

D. Steel rod to tray holding weights (Omitted for unloaded specimens).

E. Pyrex glass tube

F. Powdered graphite

G. Sauereisen cement to hold glass tube in place.

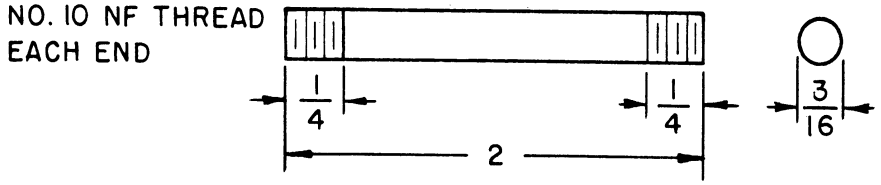
Experimental Procedure

Ingots of 2% lead, 98% copper were prepared by melting about 180 gms of Baker and Adamson Grade 1623 copper and 3.6 gms of Baker and Adamson Grade 1820 lead in a graphite crucible in a Lepel induction furnace under a protective atmosphere of about 50 mm Hg of Helium. The metal charge was kept molten from 5-10 minutes to insure adequate mixing of lead in the copper, then rapidly cooled in the furnace under vacuum. This treatment produced ingots in which the lead was uniformly dispersed through the copper matrix. In only one ingot (No. 1) was there any evidence of porosity, and it was slight in this case.

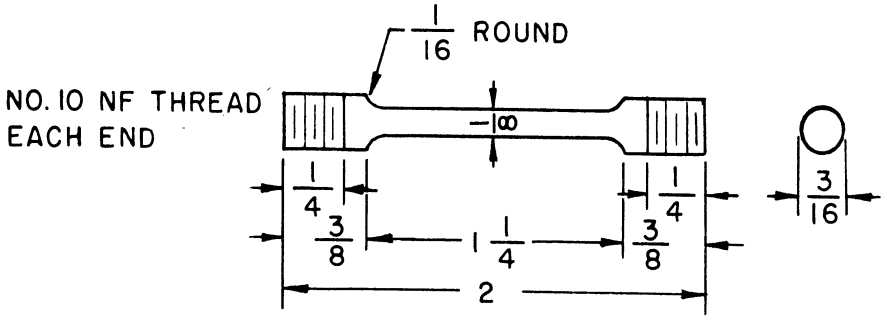
The ingots were cold worked by hand (Ingots Nos. 1 to 3) or by rolling (Ingots 4 to 6) to about 65% of their original crossectional area (except Ingot 4 to about 80% due to cracking of ingot) and annealed for $1\frac{1}{2}$ hours in a salt bath at about 1175°F ± 75°F.

Tensile specimens were machined from each billet by Knowlson-Stevenson Company, Ann Arbor, Michigan to the following dimensions:

Figure (2)



A. SPECIMENS FROM INGOTS NOS. 1, 2, 3



B. SPECIMENS FROM INGOTS NOS. 4, 5, 6

Finished specimens varied up to 1/16" in length; a maximum variation of 0.002" in diameter was noted. (Stresses were calculated on the basis of measured diameters.)

Specimens from ingots (4), (5), and (6) were annealed for 50 hours in evacuated pyrex tubes at 900°F prior to testing; specimens from ingots (1), (2) and (3) did not receive this treatment.

Testing was done in a vertical tube furnace at 900°F. Figures (3,4) show details of the experimental arrangement.

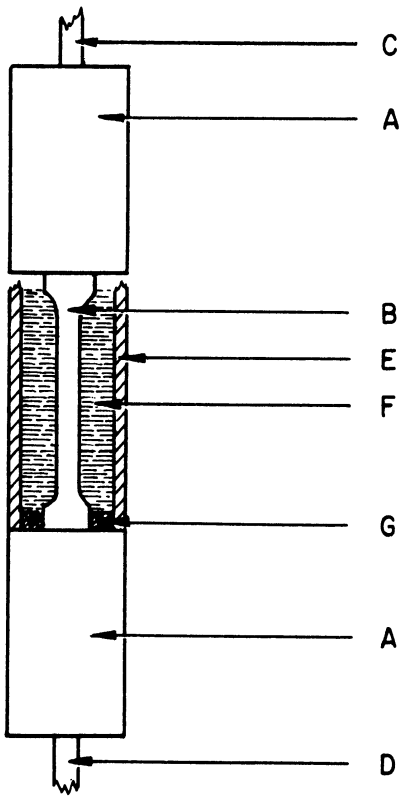


Figure (3). Specimens in Specimen Holders

A. Threaded Fittings holding specimens and steel rods

B. Specimen

C. Steel rod to upper support

D. Steel rod to tray holding weights (Omitted for unloaded specimens).

E. Pyrex glass tube

F. Powdered graphite

G. Sauereisen cement to hold glass tube in place.

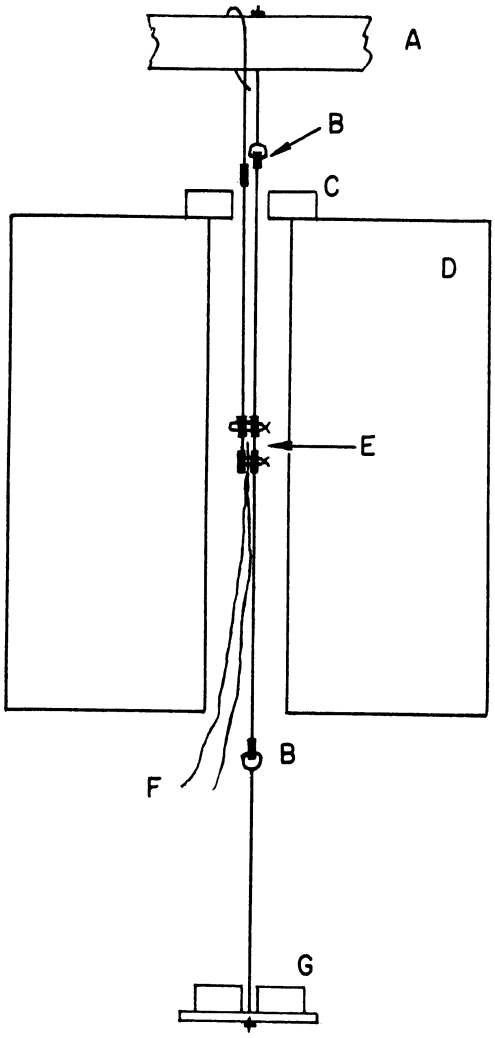


Figure (4). Schematic Arrangement of Testing Apparatus

A. Upper support

B. Universal joints to insure uniaxial loading

C. Insulating brick and loosely packed rock wool insulation

D. Furnace-nichrome wound

E. Specimen arrangement. Thermocouple is located between loaded and unloaded specimens, loosely wired to loaded specimen. Unloaded specimen is loosely wired to top threaded fitting of loaded specimen

F. Thermocouple

G. Weight pan and weights

Specimens were sectioned longitudinally and transversely and mounted in bakelite. Polishing was done on Grade W600A SiC paper, through 1-5 and 0-$\frac{1}{2}$ micron diamond polishing wheels, and finished by polishing for about 12 hours on a Syntron polisher with Linde B aluminum oxide powder.

Dihedral angles of lead in copper were measured on a Baush and Lomb rotating stage metallograph at 2300x. On longitudinal sections traverses were made down the center of the specimen, and all angles of each included lead particle encountered measured. On two specimens (6B and 4D) the angle made by the line bisecting the dihedral angle and the axis of tension was also measured. On transverse sections, traverses were made along a diameter of the specimen, the angles of each lead grain encountered were measured, and the distance of each lead grain from the surface was recorded. Usually, 200 angles were measured on each section of the specimen, although this varied somewhat. (See table 2 for a complete summary of all angles measured).

True dihedral angles were obtained from plots of the distribution of angles measured. The median angle was taken to be a good approximation to the true dihedral angle, following the work of Riegger and Van Vlack (7). In several cases the most frequent angle was also determined and comparisons made on this basis.

Run	Stress in Psi	Time in hrs.	Total No. of Angles measured Longitudinal Section	Median Angle for angles measured on Longitudinal Section	Total No. of Angles measured Transverse Section	Remarks
1A	860	100	100	66	200	
1B	0	100	200	76	200	
2A	860	25	200*	65	200	
2B	0	25	200*	69	200	
3A	2028	$1\frac{1}{2}$				Loaded Specimen broke after $1\frac{1}{2}$ hrs. at exposed thread root
3B	0	$1\frac{1}{2}$				
4A	1940	$2\frac{1}{2}<x<17$				Loaded Specimen broke in center of test section in time x
4B	0	$2\frac{1}{2}<x<17$				
4C	0	25	200	66	200	
4D	1300	25	200**	59.5	200	
5A	428	25	200	66		Specimens 4A through 6B received a 50 hour anneal at 900°F in vacuum prior to testing
5B	0	25	200	65		
5C	837	25	200	66		
6A	0	25				
6B	837	25	100**	66	200	

* Also measured 100 additional angles after chromate etch
** Also measured 200 additional angles noting angle between tension axis and the bisector of the dihedral angle.

Table (2). Summary of Angles Measured.

Discussion of Results

The data obtained from these experiments is at best qualitative, or perhaps, semiquantitative. For this reason, the errors involved in determining true dihedral angles will be discussed first followed by an analysis of the results obtained.

In viewing metallographic samples from the various test specimens it was found that lead particles existed most frequently as lenses and triangles, but grains with four or more corners were not uncommon. The multicornered grains arise from sectioning the lenticular and triangular prisms formed by the lead parallel, or nearly parallel to their prismatic axis. If an unstable structure is present in the copper matrix, e.g. four or more copper grains meeting on an edge instead of the stable three grains, the occurrance of grains on a random section with four or more corners will be much higher.

Harker and Parker's (8) equation for the distribution of angles observed corresponding to a certain true dihedral angle was used by Riegger and Van Vlack (7) to show that the median angle obtained from a cumulative distribution plot of observed angles was within $1\frac{1}{2}^{o}$ of the true angle for any true angle. Accordingly most of the angle measurements made were analyzed on the basis of median angles; the correction for true angles was not applied as the data obtained did not seem sufficiently precise to warrant it.

It was found in all specimens that the median angle for lens-shaped grains alone in a particular specimen was always less than that for triangular grains, which was in turn always less than that for grains with four or more corners. None of the above authors mention this fact, but it appears that in order to obtain a true dihedral angle by these means one must also have a random

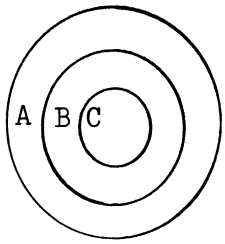
assortment of 2-, 3-, 4-, etc. cornered grains. It is not felt, as Riegger and Van Vlack contend, that a selection of 25 angles is adequate to determine a true dihedral angle, because this probably represents the angles measured from 7-10 grains if all angles on a grain are measured. It is felt that the angles of about 50 grains should give an adequate distribution of grains as well as angles. Unfortunately, due to time limitations not as many angles were measured per sample in these experiments as it is felt is necessary; table (3) gives a summary of the distribution of grain shapes observed on transverse sections in the process of measuring 200 angles per specimen.

In the beginning, dihedral angles were measured on longitudinal sections of all specimens. Table (2) shows the results obtained. The specimens (4C), (5A), (5B), (5C) and (6B) all have about the same dihedral angle; the only departure seems to be (4D), which has the greatest load. These results do not check at all well with (1A), (1B), (2A), and (2B) which indicate a change in dihedral angles should be observed in specimens (5C) and (6B). The reproducibility of median angle in (4C) and (5B) was encouraging, however.

The behavior of (1A), (1B), (2A) and (2B) was difficult to understand, so angle measurements on transverse sections of these specimens were made. The angles measured were arranged into 3 groups on the basis of the depth from the surface of the specimen at which the angle occurred. The results are presented in fig. (5). These results are more erratic than those presented in table (2), but some conclusions may be drawn; a) the distance of the lead grain from the surface of the specimen affects its dihedral angle, b) at the surface, lead grains have about the same dihedral angle regardless of load or time at temperature.

Table 3. Distribution of Grain Shapes Observed on Transverse Sections

A - Outer third of Section
B - Middle third
C - Inner third
Total = A + B + C



Number of Corners

Specimen	2	3	4	5	6	7	8
1A-Total	25	37	7	2			
A	8	18	2	1			
B	11	10	4				
C	6	9	1	1			
1B-Total	36	30	9				
A	4	13	4				
B	11	8	4				
C	21	9	1				
2A-Total	29	39	3	1		1	
A	11	10		1		1	
B	15	10	3				
C	3	19					
2B-Total	29	32	9	2			
A	9	7	3				
B	6	10	3				
C	14	15	3	2			
4C-Total	23	33	10	1		1	
A	9	10	3				
B	6	9	2				
C	8	14	5	1		1	
4D-Total	18	35	12				1
A	4	8	7				1
B	6	17	3				
C	8	10	2				
6B-Total	10	39	12	3			
A	4	9	5	2			
B	3	14	4	1			
C	3	16	3				

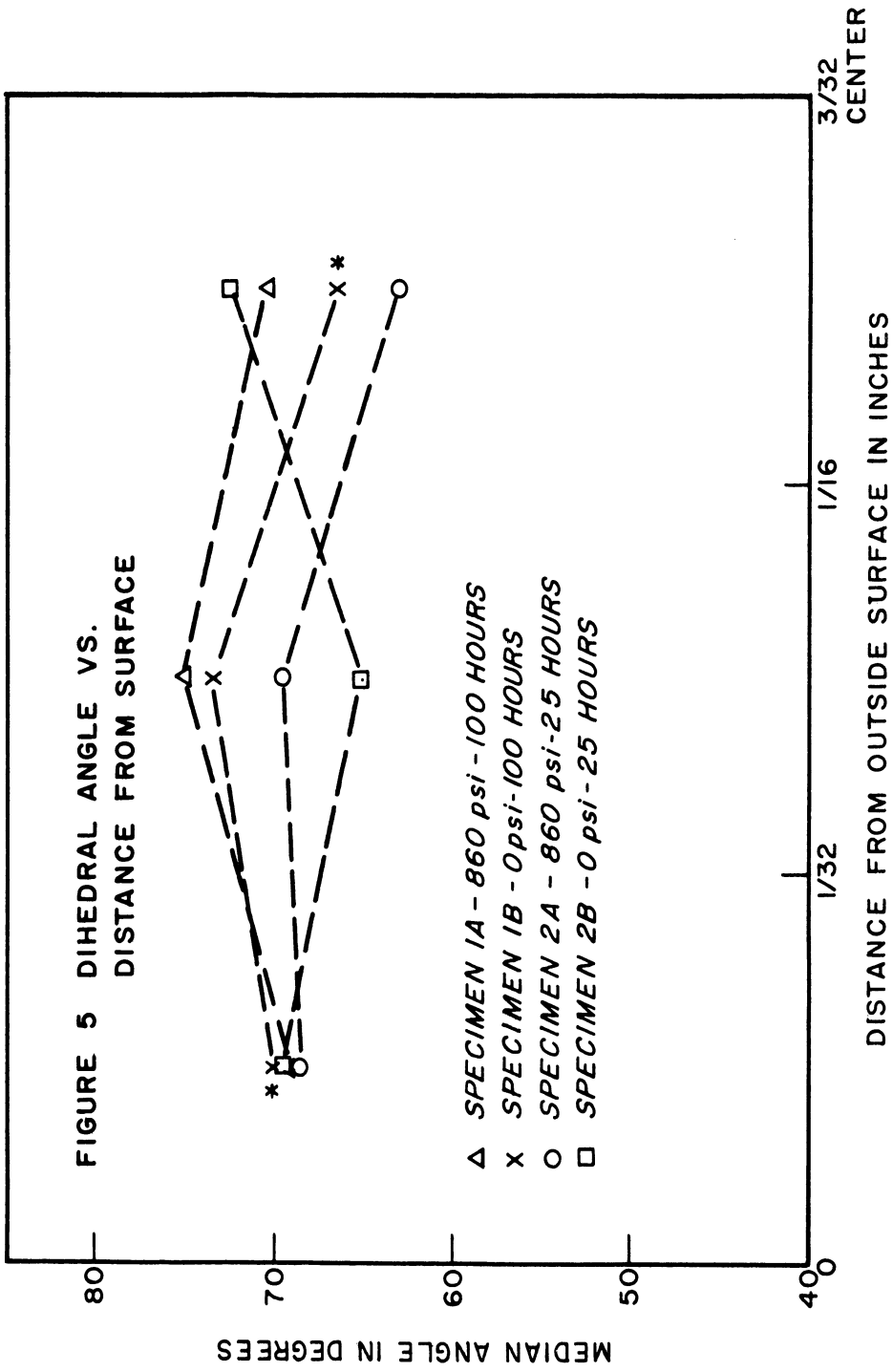


FIGURE 5 DIHEDRAL ANGLE VS.
DISTANCE FROM SURFACE
MEDIAN ANGLE IN DEGREES
80
70
60
50
40
0
1/32
1/16
3/32
CENTER
DISTANCE FROM OUTSIDE SURFACE IN INCHES
△ SPECIMEN 1A - 860 psi - 100 HOURS
X SPECIMEN 1B - 0 psi - 100 HOURS
O SPECIMEN 2A - 860 psi - 25 HOURS
□ SPECIMEN 2B - 0 psi - 25 HOURS

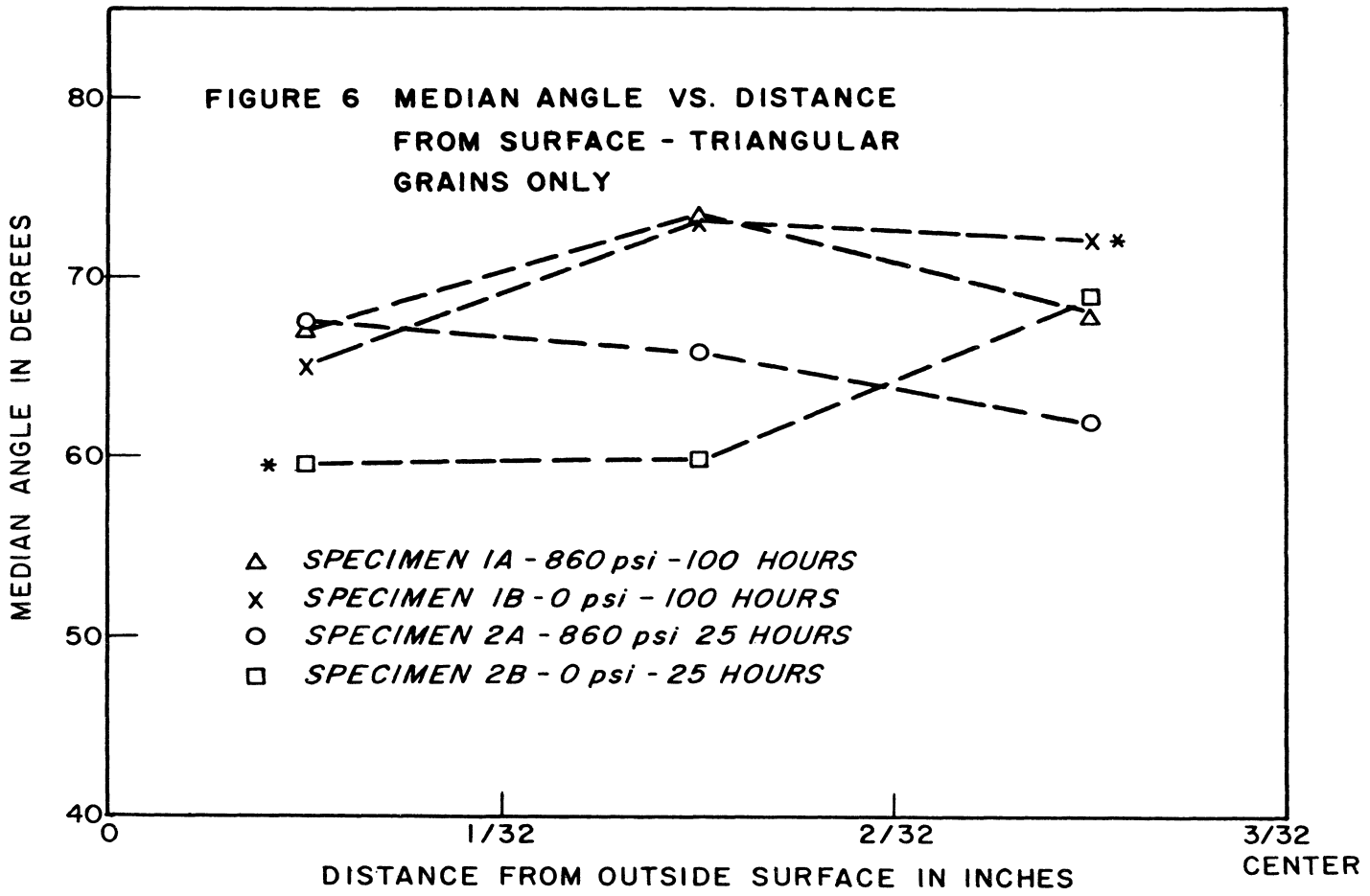


FIGURE 6 MEDIAN ANGLE VS. DISTANCE FROM SURFACE - TRIANGULAR GRAINS ONLY
MEDIAN ANGLE IN DEGREES
80
70
60
50
40
0
1/32
2/32
3/32
CENTER
DISTANCE FROM OUTSIDE SURFACE IN INCHES
SPECIMEN 1A - 860 psi - 100 HOURS
SPECIMEN 1B - 0 psi - 100 HOURS
SPECIMEN 2A - 860 psi 25 HOURS
SPECIMEN 2B - 0 psi - 25 HOURS

The number of angles for each one of these points was relatively small (200 angles total were measured on a transverse section) so another plot was prepared of angles from triangular grains alone (figure 6). (Although each point on this last plot represents still fewer angles, and the median angle of these points should not be a median angle corresponding to the true dihedral angle, comparison of this plot with the previous plot should isolate the effect of a statistically poor selection of 2-,3-,4, etc. cornered grains).

A point for point comparison of the two graphs indicates which points are probably unreliable. The author has starred two points which he feels bear checking. From these last two plots the following generalizations may be made: a) the dihedral angle of a loaded specimen is likely to be smaller than that of an unloaded specimen at the center of the specimen, b) time at temperature and distance from the surface of the specimen affect the dihedral angle. The second observation suggests that penetration of oxygen from the air along the grain boundaries may be changing the surface energies of the Cu-Cu and Cu-Pb interfaces. Loading the specimen undoubtedly accelerates this diffusion to a certain extent; if adsorbed oxygen tends to increase the dihedral angle, and loading tends to decrease it, the net result could easily be as confused as that which is observed. It is possible that interfaces near the surface are saturated with oxygen acting to nullify any effect of stress.

It must be pointed out that specimens (1A), (1B), (2A), and (2B) received no anneal after machining and most certainly did not enter the test run with a dihedral angle characteristic of the temperature (900°F) of the run. The rest of the specimens received a 50 hour anneal in an evacuated pyrex tube prior to the test run, and so began the test in a more uniform condition. No marked improvement in results can be traced to this preliminary anneal, however.

As was noted above, median angles obtained from longitudinal sections of specimens (4C), (4D), (5A), (5B) and (6B) were not consistent with previous results, so angle measurements on transverse sections of (4C), (4D) and (6B) were made. Measurements on the other specimens were not made. Figures (7) and (8) are plots of the median angle as a function of distance from the specimen surface for all grains, and triangular grains only. For purposes of comparison, a plot of most frequent angle versus depth (fig. 9) was also prepared; too much significance should not be attached to this, however, as the total number of angles for each point was not really large enough for this sort of plot, and the grouping of angles (every 10^{o}) was rather coarse.

All of these figures show the same general behavior: a) the dihedral angle at the center of the specimen decreases with increasing stress, b) the dihedral angle at the surface tends to be the same for all specimens. The same explanation as was presented above can account for this behavior.

Miscellaneous Observations.

On longitudinal cross sections of specimens (4D) and (6B), 200 angles were measured along with which were recorded the angle between the tension axis of the specimen and the bisector of the dihedral angle. For each specimen these measurements were arranged in nine groups, each group including all dihedral angles falling within a 10^{o} range of angle off the tension axis, and the median dihedral angle in each range was determined. The results are plotted in figure (10).

The number of dihedral angles making up each group is small and, in the light of factors already discussed, the scatter in data is not surprising.

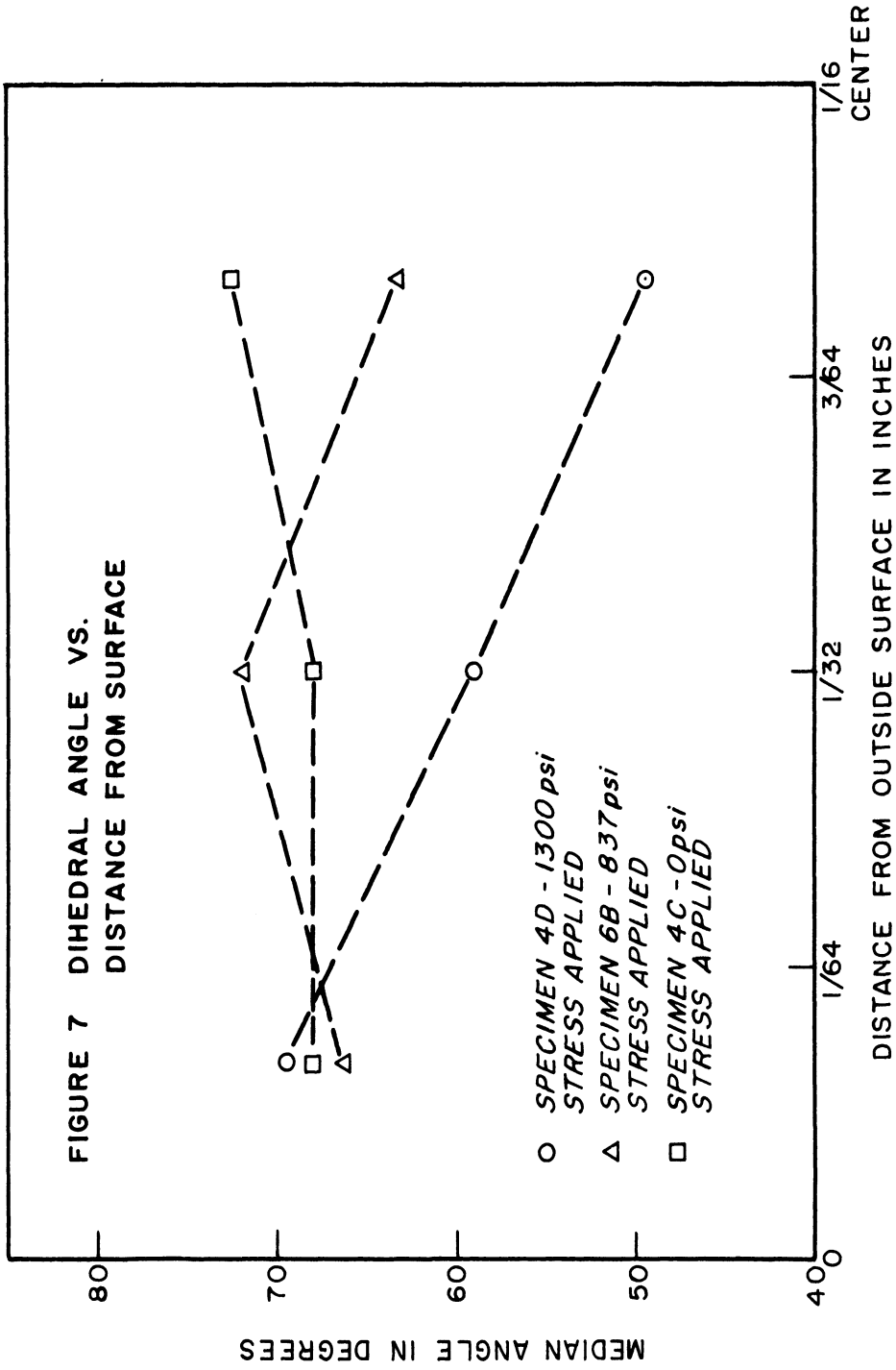


FIGURE 7 DIHEDRAL ANGLE VS. DISTANCE FROM SURFACE
MEDIAN ANGLE IN DEGREES
80
70
60
50
40
0
1/64
1/32
3/64
1/16
CENTER
DISTANCE FROM OUTSIDE SURFACE IN INCHES
SPECIMEN 4D - 1300 psi STRESS APPLIED
SPECIMEN 6B - 837 psi STRESS APPLIED
SPECIMEN 4C - 0 psi STRESS APPLIED

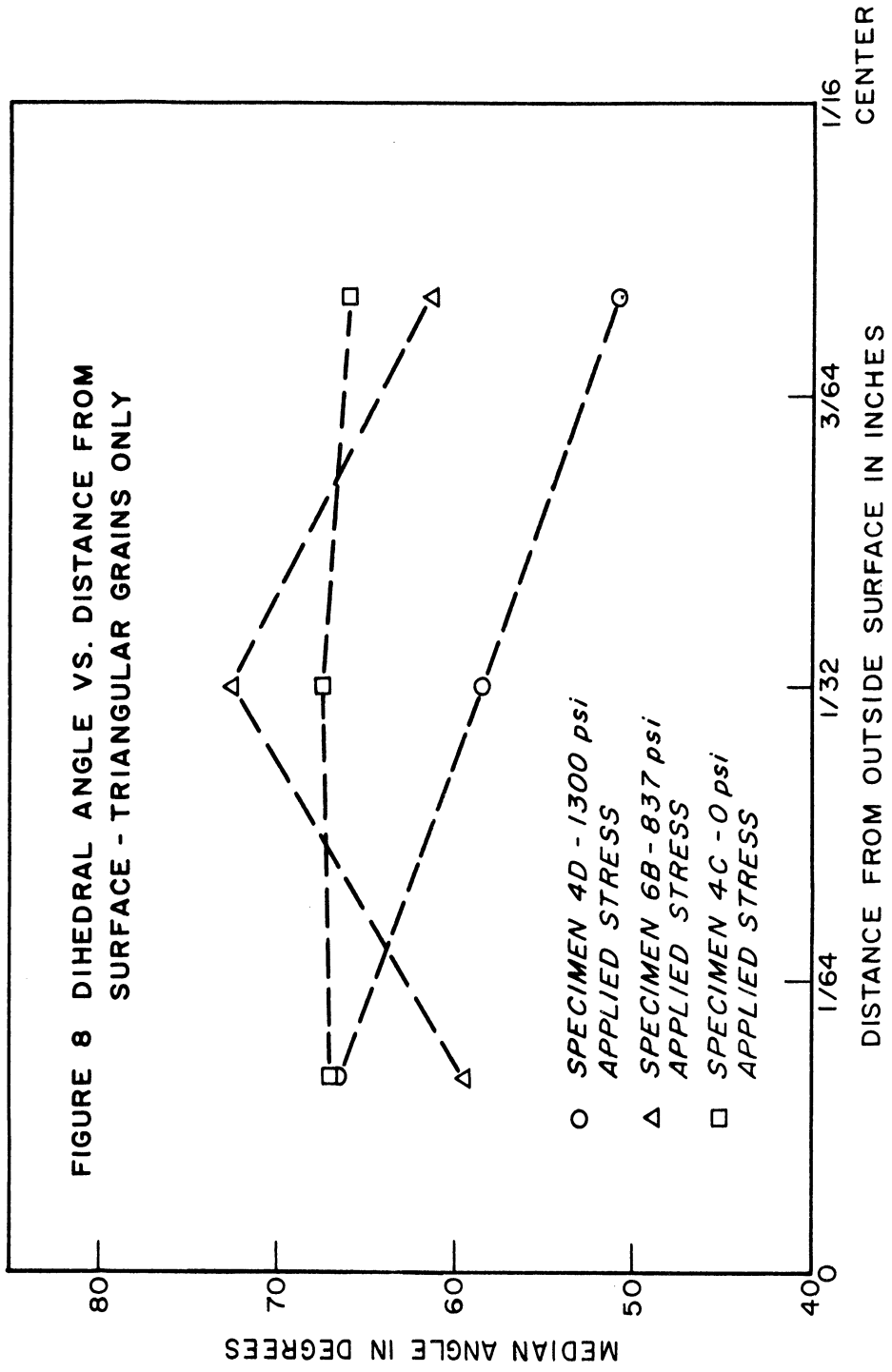


FIGURE 8 DIHEDRAL ANGLE VS. DISTANCE FROM SURFACE - TRIANGULAR GRAINS ONLY
MEDIAN ANGLE IN DEGREES
80
70
60
50
40
0
1/64
1/32
3/64
1/16
CENTER
DISTANCE FROM OUTSIDE SURFACE IN INCHES
O SPECIMEN 4D - 1300 psi APPLIED STRESS
Δ SPECIMEN 6B - 837 psi APPLIED STRESS
□ SPECIMEN 4C - 0 psi APPLIED STRESS

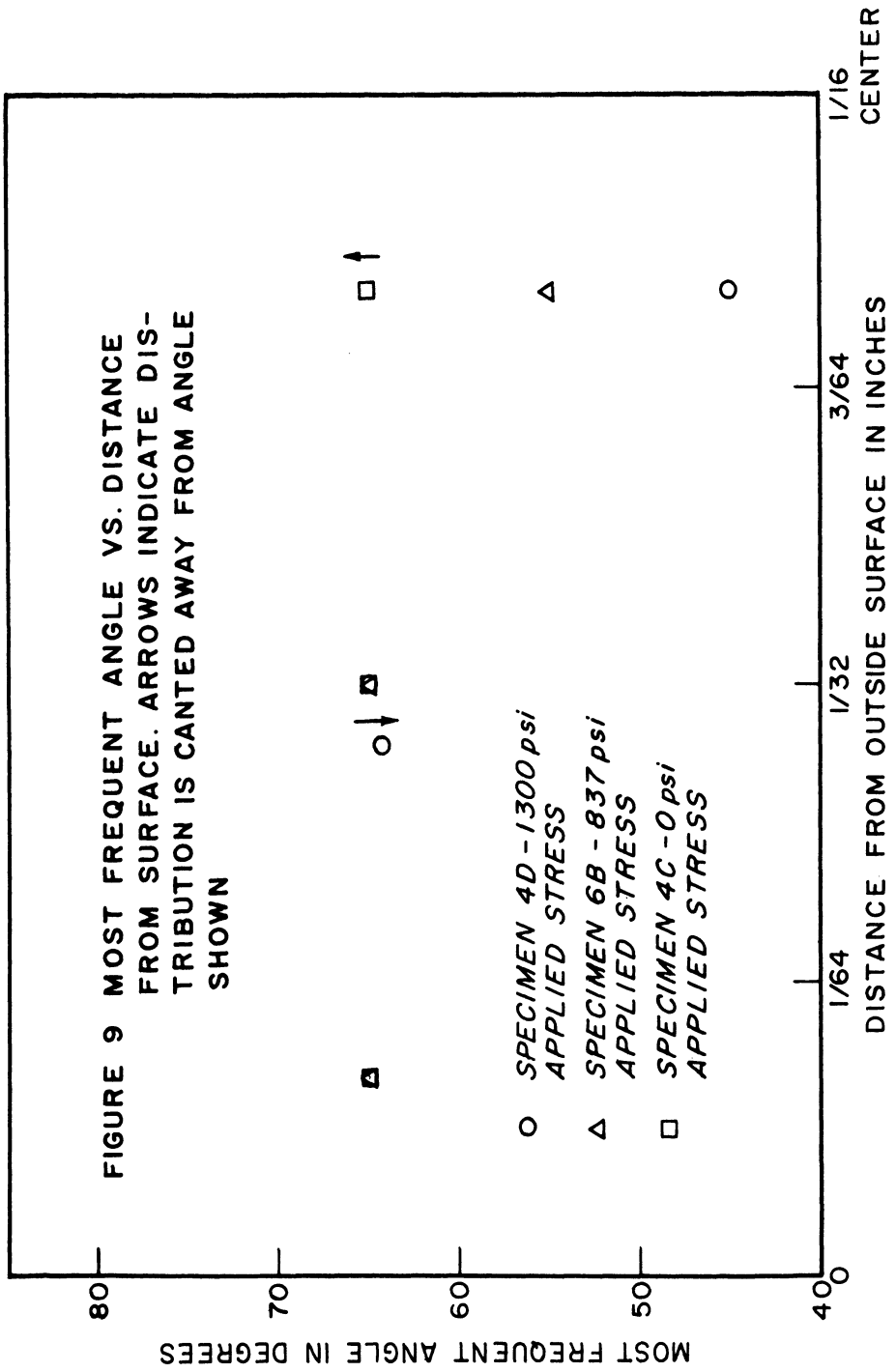


FIGURE 9 MOST FREQUENT ANGLE VS. DISTANCE FROM SURFACE. ARROWS INDICATE DISTRIBUTION IS CANTED AWAY FROM ANGLE SHOWN

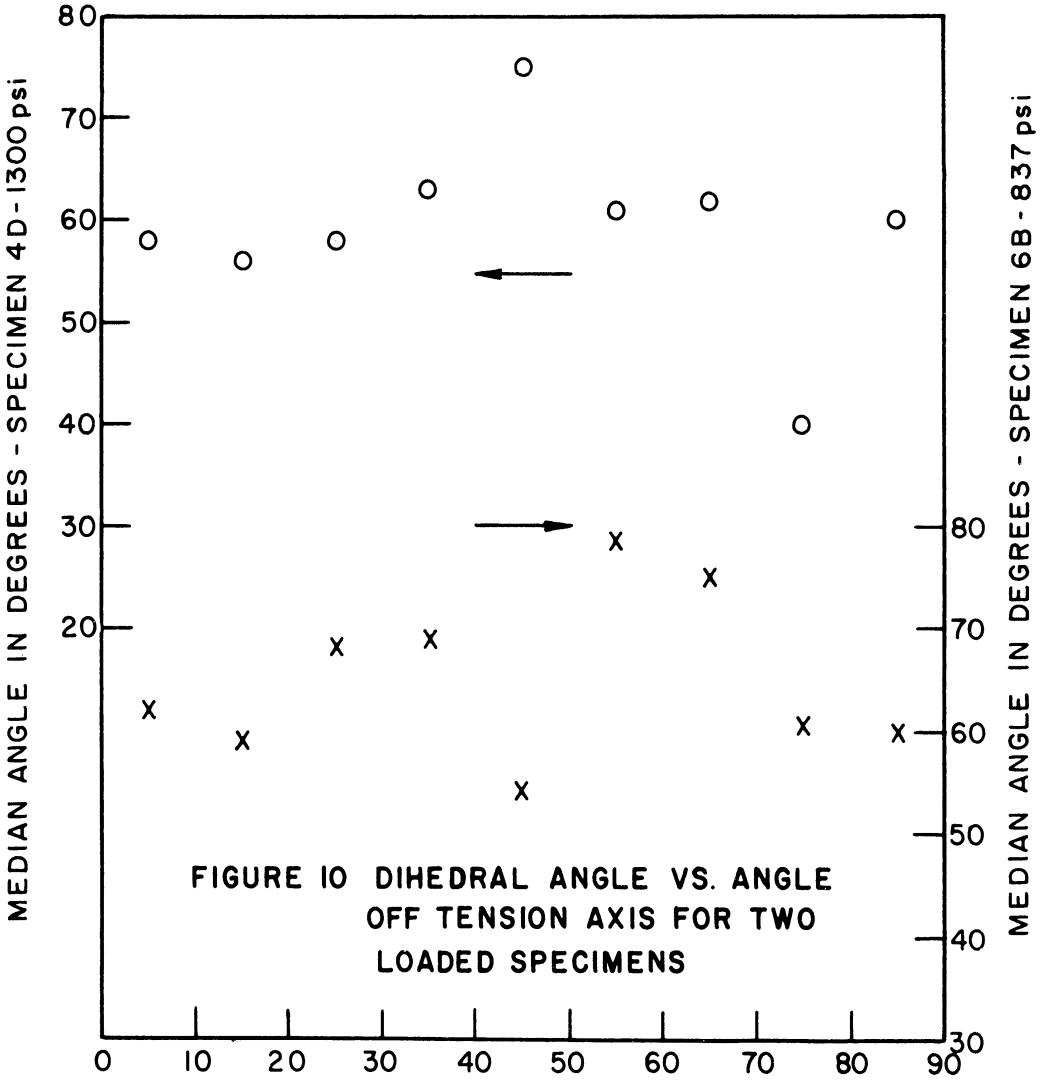


FIGURE 10 DIHEDRAL ANGLE VS. ANGLE OFF TENSION AXIS FOR TWO LOADED SPECIMENS

However, there seems to be a definite trend present; the dihedral angles observed at 45° to the tension axis seem larger than those parallel to or perpendicular to the tension axis. Also, there seems to be no difference in dihedral angles perpendicular to and parallel to the tension axis.

The reason for this behavior is not at all clear. It is probably related to the fact that maximum shear stress occurs on planes making an angle of 45° with the tension axis, and that grain boundary sliding during creep would occur to the greatest extent on planes of maximum shear stress. The liquid lead inclusions distorted by grain boundary sliding would be expected to have an abnormal shape, but it is difficult to imagine how such distortion would result in consistantly larger dihedral angles. Another possibility is that oxygen penetrates preferentially into grain boundaries having maximum shear stress (these measurements were made along the centerline of these specimens; the copper here is not presumed to be saturated with oxygen), causing larger dihedral angles, as was discussed previously.

Before mounting the above specimens in bakelite, they were cleaned in chromic acid to remove any surface oxide that might have formed, then measured to determine whether any necking or elongation had occurred. (No necking was observed; elongation measurements were inadequate to determine the extent, if any, of elongation.)

Specimen (4A) however, was mounted in bakelite without prior cleaning so that fracture surfaces might be examined, and it was found (fig. 11a,b,c,) that all fracture and crack surfaces (including cracks which did not reach the surface) and a considerable portion of the outside surface were covered with lead. (It is reasonably certain this is lead. It is grey in color and under suitable magnification resembles the internal lead particles. None of the oxides of lead or copper are this color).

Eborall and Gregory (4) noted that during hot impact tensile tests of bronzes with varying amounts of lead up to 0.02% that liquid lead films coated incipent cracks behind the fracture surface, and partially coated the fracture surface. They noticed that lead on the fracture surface had time to "de-wet", that is, assume an equilibrium shape during cooling. They confirmed that this spreading would not occur from internal lead particles exposed on the surface by a metallographic polish if the specimen were simply heated at the test temperature in a hydrogen atmosphere.

The alloys used in these tests contained 100 times the amount of lead used by Eborall and Gregory so it is not too surprising that continuous surface films on the fracture surface and on internal cracks were retained down to room temperature. It is somewhat surprising that so much lead was observed to the external surface of the specimen. Assuming the lead was initially uniformly dispersed throughout the specimen and that the film thickness averages 0.01 mm in depth and covers 3/4 of the specimen surface (figures 11a,b,c) calculations show that more than 50% of the lead initially dispersed throughout the specimen is present on the surface. This would mean that internal lead must move up to 0.36mm to reach the surface. If the calculated lead present on the surface is high by a factor of 5 (although observation of microsections indicates this is unlikely) internal lead would have to move up to 0.08 mm to reach the surface.

If these observations are assumed to be accurate, two questions immediately arise: a) what is the mechanism by which the lead reaches the surface?, and b) what is the driving force for this movement? Neither question can be satisfactorily answered on the basis of these experiments, but some guesses can be made.

When specimens are loaded above some critical value it seems likely that liquid lead particles, originally present as discrete grains, spread out

along grain boundaries. Thus, continuous films of lead are present over fairly large distances along grain boundaries. When one of these boundaries intersect the specimen surface, lead flows from the grain boundaries to the surface. Depending on local conditions (depth of crack, stress concentration, etc.), the grain boundary may then either close or open further to form a crack of the sort leading to intercrystalline fracture. Some indication that this might be occuring can be seen in figure (11b). Discrete particles of lead outline grain boundaries adjacent to the large crack. Presumably, boundaries "de-wet" when the tension was released due to fracture of the specimen (lowering of temperature might also cause de-wetting).

It is possible this procedure takes place in intermittant steps; lead at a boundary with a medium level of stress moving to a boundary at a higher stress level (allowing the original boundary to "heal") and through a series of these steps, moving to the surface.

The driving forces for this movement are differences in surface energy. More highly stressed boundaries have a greater surface energy, hence there is a greater tendency for liquid lead to wet these surfaces. On the surface the tendency to wet will be greater yet because the Cu-Cu boundary is replaced by a Cu-atmosphere boundary of much higher energy. (One of the Cu-Pb boundaries will be replaced by a Pb-atmosphere boundary also but the increase in energy should not be as great as in the former case, and even if the increase was as great, better wetting would still be observed on the surface).

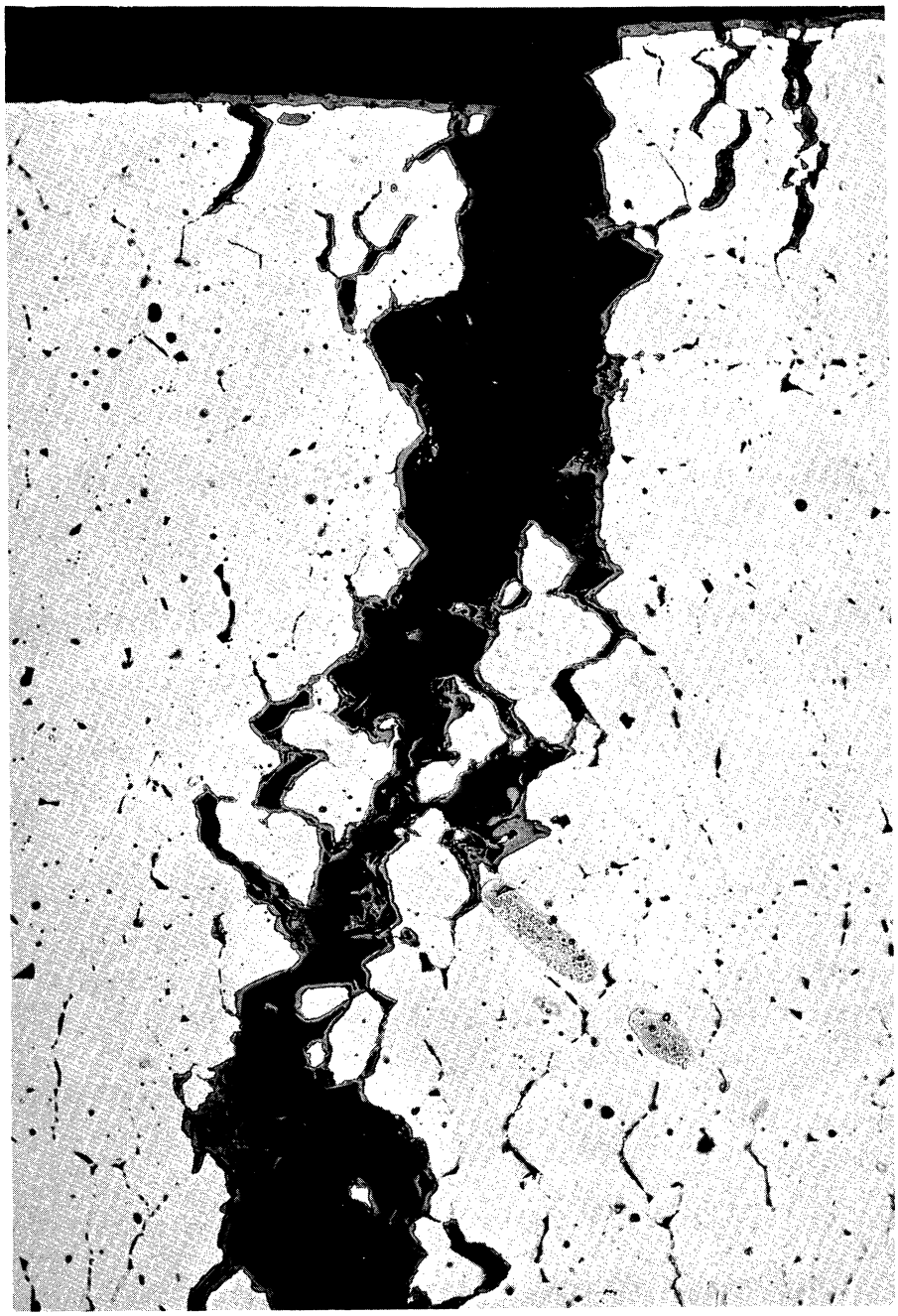


Figure 11a. Fracture Surfaces of Specimen 4A. 100 X. Not etched. Surfaces were fitted together loosely and mounted in bakelite.

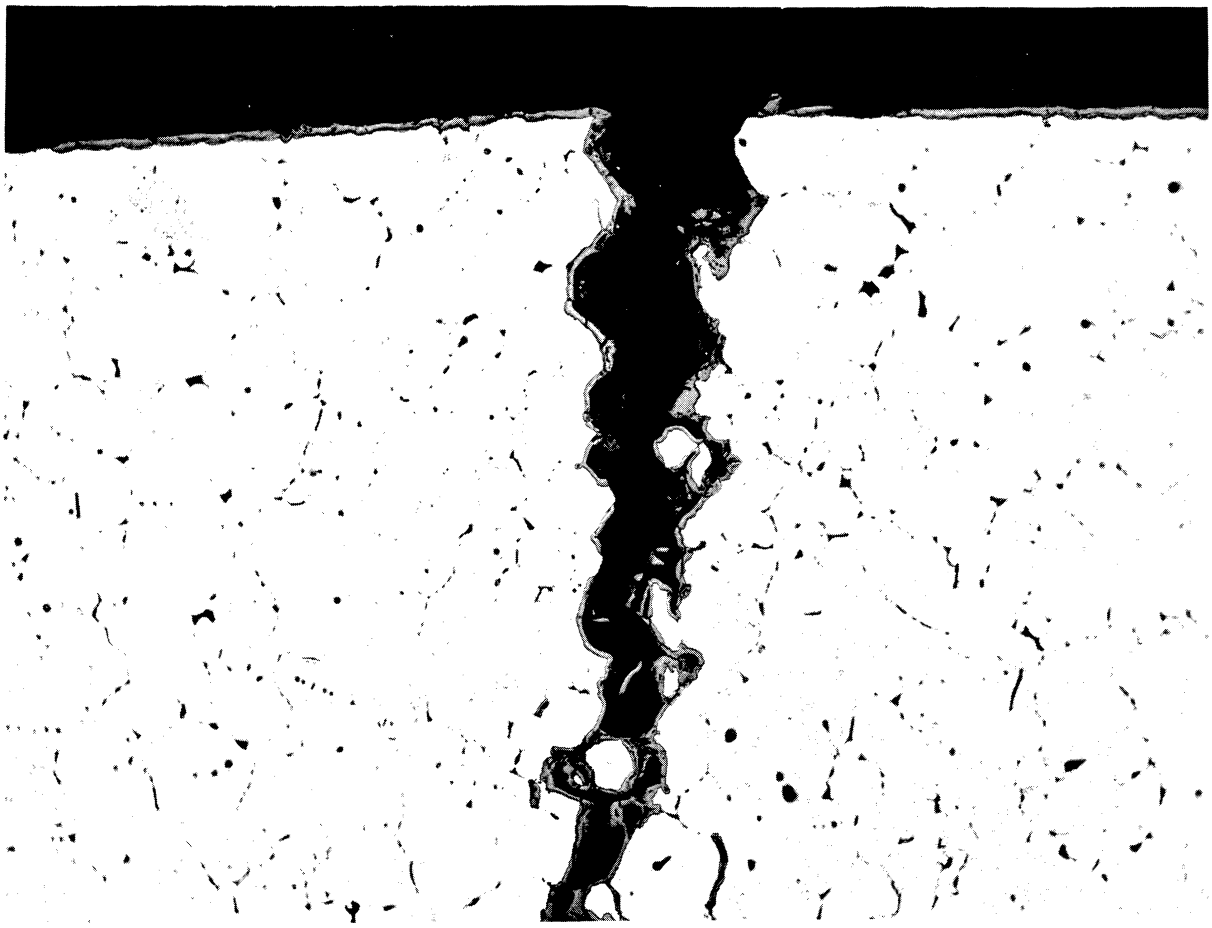


Figure 11b. Large crack on surface of specimen 4A. 100 X. Not etched.

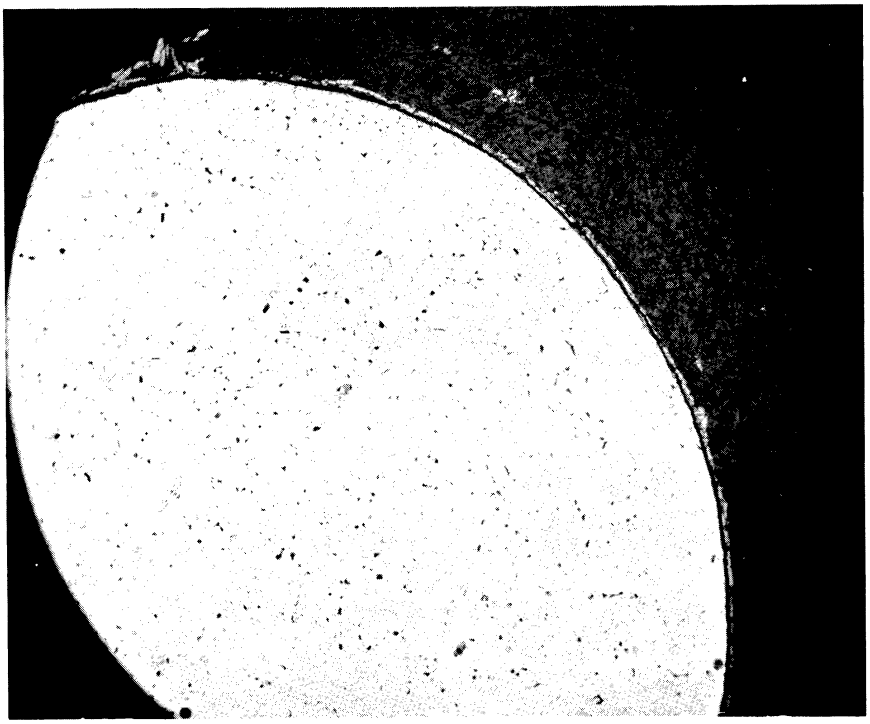


Figure 11c. Transverse section of specimen 4A. 37.5 X. Not etched.

Areas Meriting Further Considerations

Several of the effects observed suggest experiments which would provide more information than has been obtained with more meaning from an engineering and/or theoretical standpoint.

From an engineering point of view, it would be interesting to know what effect an internal liquid phase has on creep properties. A study of this sort would have meaning if results could be obtained which could be applied qualitatively to two phase alloys and cermets operating at very high temperatures under load. Similarly, a study of the short-time high temperature mechanical properties might give some insight into the problem of hot-tearing in castings.

Theoretically, the problem of the combined effect of stress and environment (here an internal environment) is tied in with the general problem of what is usually termed "stress corrosion". Chemically, the phases involved are inert so "corrosion" is a mis-nomer, but the wetting and fracture mechanisms observed in these experiments are almost certainly closely related to those observed in ordinary stress corrosion. Some of the results above suggest that movement of liquid phases occur until the liquid is present on surfaces with maximum surface energy. In particular, it would be interesting to find out whether an internal liquid phase will move out of the boundaries of a loaded specimen when there is a surplus of the same liquid surrounding the specimen, or whether further penetration of boundaries will occur. Further research must be done to determine the influence of gas adsorption on interfacial energies. No control could be exercised over the atmosphere surrounding specimens during loading in these experiments and it is believed that this contributed to some of the anomolies observed.

Summary

The results obtained from these experiments are the sort from which it is difficult to draw any unequivocal conclusions. However, it seems clear that dihedral angles formed by liquid lead in copper in the center of the test specimens are smaller with increasing applied stress.

It is suggested that:

a) Adsorption of oxygen on Cu-Cu and Cu-Pb interfaces changes the dihedral angle of lead in copper, the amount and direction of change varying with the amount of oxygen present.

b) When suitably high stresses are applied liquid lead "wets" copper grain boundaries and external specimen surfaces. Wetting of grain boundaries promotes fracture as discussed by Eborall and Gregory (4).

Bibliography

1. C. S. Smith, Trans. Amer. Inst. Min. Met. Eng., 175: 15 (1948).

2. K. K. Ikeuye and C. S. Smith, Trans. Amer. Inst. Min. Met. Eng. 185: 762 (1949).

3. H. Udin, A. J. Shaler and J. Wulff, Trans. Amer. Inst. Min. Met. Eng. 185: 186 (1949).

4. R. Eborall and P. Gregory, Journ. Inst. of Metals 84: 88 (1955-56).

5. G. L. C. Bailey and H. C. Watkins, Proc. Phys. Soc. (London) 63B: 350 (1950).

6. S. Floreen, E. E. Hucke, and D. V. Ragone, AFOSR TN59 1253, "The Effect of Strain on the Interfacial Energies of Solids" (to be published).

7. O. K. Riegger and L. H. Van Vlack, "Dihedral Angle Measurement" (to be published).

8. D. Harker and E. Parker, Trans. Amer. Soc. for Metals, 34: 156 (1945).