THE UNIVERSITY OF MICHIGAN
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Progress Report

THE EFFECT OF SELECTED MELTING ATMOSPHERES ON THE ELECTRICAL AND TENSILE PROPERTIES OF INGOT COPPER

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SUMMARY

The long range objective of this research is to determine whether wrought copper, equal or superior to OFHC copper, can be produced by control of melting atmospheres or other techniques. The program includes the use of White Pine copper, phosphorus deoxidized copper, and cathode copper as starting materials, but only White Pine copper is considered in this report. The two outstanding characteristics of OFHC copper which are to be duplicated are electrical conductivity and retention of ductility after expposure to reducing atmospheres (bright annealing).

Table I is a summary of electrical conductivity and retention of ductility for eighteen key experimental melts. These were melted and poured under a variety of aphosphorus including H_2, A, N_2, CO, CH_4, Air and with a trial of boron deoxidation.

Electrical conductivity comparable to OFHC (102.6% IACS) was attained by two procedures: (1) melting under hydrogen and pouring under 0.25 mm pressure and (2) melting under argon superheating to 500°F above the liquidus and pouring.

Rentention of ductility after bright anneal (similar to OFHC) was obtained by two procedures: (1) melting and pouring under hydrogen, and (2) deoxidation with boron.

In general, electrical conductivity was probably improved both by distilling off impurity elements and reduction of oxygen level. The retention of ductility after bright annealing required the low oxygen content attained by either hydrogen reduction or deoxidation with boron.

In addition to these positive findings the data provide clear evidence of the deleterious effects of water vapor upon retention of ductility and of impurities upon conductivity.

TABLE I

SUMMARY OF RESULTS

Heat No.	Atmosphere	Pressure Melt	Pressure Pove (mm. Hg)	E. C. c/o IACS	-ΔRA
ln 16	H_2	51	0.25	102.5	1.8
ln 15	H_2	254	254	99.5	4.0
ln 17	H_2	254	254	98.8	2.2
ln 11	A*	534	534	102.1	34
ln 6	A	534	534	98.9	19
ln 12	N_2*	51	51	100.8	32
ln 13	N_2*	381	381	100.8	29
ln 18	CO	254	254	99.2	33
ln 20	CO	254	254	100.6	--
ln 22	CH_4	381	381	100.0	15
ln 21	H_2O	25	25	98.6	45
ln 1	Air	.4	.4	100.9	38
ln 2	Air	.3	.3	100.2	32
ln 4	Air	.3	.3	100.8	37
ln 5	Air	.3	.3	100.9	29
ln 10	Air	.005	.005	99.5	25
8	At Boron	381	381	92.7	2.1
S-1	Air	.25	.25	102.8	14

DEFINITION: Atmosphere: Tank gas used unless an asterisk is shown indicating special purification techniques. Pressure: mm. Hg, 1 mm Hg ≅ 0.04 in Hg. E.C.: Electrical Conductivity. -ΔRA: Reduction in area when annealed in argon minus reduction in area when annealed in hydrogen.

INTRODUCTION, PURPOSE, REVIEW OF THE LITERATURE

OFHC copper is receiving greater acceptance, particularly in the electrical industry. The purpose of this research is to determine whether wrought copper of comparable quality can be produced by a simpler technique than that used for OFHC.

Low impurity ingot copper is readily available; the problem is to attain low levels of oxygen and dioxidants after melting and casting.

A review of the literautre shows that some evaluations have been made of the effects of low pressure of melting atmospheres and of the mechanism of solution of oxygen in copper.

Winkler[4] has discussed vacuum refining of copper. He lists four factors which determine the rate and extent of vacuum purification:

(1) The partial pressure of the impurity
(2) The melt temperature
(3) The area of the melt surface
(4) The length of the diffusion path of the impurities in the melt.

The effectiveness of a vacuum refining treatment is increased by an increase in any of the first three factors or a decrease in the fourth.

Golanka[3] melted several grades of commercially available copper under vacuum in a graphite crucible. He found that with pressures of 10^{-3}atm. he could produce electrolytic copper oxygen free while the other grades were not affected

The solution mechanism of oxygen in copper

$$1/2\ O_2 = \underline{O}^{+1} + 2a\bar{e}$$

has been proposed. This reaction has been experimentally demonstrated in the oxygen-palladium system.

Indirect verification of this solution mechanism in copper has been accomplished by Winkler[5] In vacuum, a D.C. electric field in molten copper caused substantial reduction in oxygen content by attracting the ions to the melt surface where they were drawn off.

Atmospheres that react with copper oxide have been discussed by Girardi and Sieber[2] and Brantley and Schack.[1] The substance of these findings is that the melting atmospheres carbon monoxide, hydrogen, methane, ethane and propane will reduce the oxygen content of a copper melt.

As a result of these investigations it appeared that further work with melt atmospheres and low pressure might lead to a simpler method for producing oxygen-free copper, than the standard OFHC process which involves melting and casting a special grade of copper in controlled atmospheres.

PROCEDURE

The experimental procedures can be discussed conveniently under the following headings: (A) melting and casting, (B) forming, (C) testing, (D) metallographic examination and (E) procedural checks.

A. MELTING AND CASTING

Melting procedures can be outlined under four sections:

(1) atmosphere control
(2) stock control
(3) melt down and atmosphere contact procedure
(4) casting procedure.

(1) Atmosphere Controls.—The gases used for the atmospheres above the melt were obtained and purified as follows:

Tank Nitrogen; O_2 removed by Cu, Ti,Ca at 1300°F; dry with drierite
Tank Argon; O_2 removed by Cu, Ti, Ca at 1300°F; dry with drierite
Tank Hydrogen; dried with drierite
Tank Carbon Monoxide; dried with drierite
Tank Methane; dried with drierite
Generated Water Vapor; produced by low pressure distillation

A needle gauge was used to read furnace pressures above two inches of mercury. Pressures less than two millimeters of mercury were read from a McLeod gauge. The intermediate pressure for the water vapor atmosphere was calculated from the temperature of the liquid water. The vapor pressure of water at 80°F is very close to one inch of mercury. This pressure valve was chosen and the run was made on a day when the ambient temperature was greater than 80°F to avoid condensation in the melting chamber.

(2) Stock Control was necessary to avoid introduction of variation in composition of the melting stock. All the copper was taken from one heat of

White Pine Lake copper. This material was chosen because the Mueller Brass Co. uses it in considerable amounts as a convenient source.

The stock was formed into 1/14 in. x 1 1/4 in. x 3/8 in. pieces for use in the melting furnace. The forming, moving, packaging and shipping should have mixed the stock well enough so that any twenty pounds charge of copper taken for melting should have the same composition as any other twenty pounds.

One exception to the stock control program was the reference sample prepared with OFHC stock. This sample, S-1, will be discussed later in this section.

(3) The Melt Down and Atmosphere Contact Procedures were developed so that they could be used with equal ease with any melt atmosphere.

Each sample was melted and cast in the same furnace (see Fig. 1). Pressures as low as one micron of mercury can be attained or any desired gas can be applied up to .8 atm.

The crucible, F, would not hold the full twenty-pound charge of loose stock, therefore a portion of the stock was held in the charging mechanism, A, and added as melting progressed. The crucible and charging mechanism both were thoroughly cleaned before loading with stock. The tank was given a general cleaning at the same time.

After the stock and the mold were in the tank it was closed and evacuated. When a pressure of 300 microns of Hg was reached the power was turned on and melting proceeded. The vacuum in the tank during melt down was maintained to insure complete out-gassing of the crucible, a process greatly accelerated by increased temperature, and to achieve maximum heating efficiency.

Power was supplied to the system from a 3000 cps, 10 KVA, motor-generator set. The induction coil, G, surrounds the crucible which acts as the susceptor for the field. The coil is copper tubing thus allowing for water cooling. After the sample was completely molten the surface was allowed to freeze to check the difference between the actual and the observed temperature of the bath. The discrepancy was quite large due in part to emmissivity differences and mostly to the shielding by the glass between the bath and the optical pyrometer. The actual temperature was approximated from the equation

$$\frac{1}{T_{actual}} + \frac{1}{C} = \frac{1}{T_{OBS.}}$$

In this case the observed temperature was almost 300°F lower than the actual temperature of the bath.

While the sample surface was freezing the specified atmosphere was being added to reach the proper pressure. After the freeze point was read the sample was heated to the desired temperature. When gas pressure and sample temperature had reached the desired levels the timing of the heat was begun.

(4) Casting Procedure required that the ingot be poured and solidified under the atmospheric conditions prescribed for the run.

The mold is a split graphite block, (Fig. 2) with a silica brick hot-top.

The cast billet was allowed to cool for at least one-half hour before the tank was opened. The hot-top was cut from billet before the latter was sent to the Mueller Brass Co. to be formed into wire.

B. FORMING

The forming procedure was standardized as shown in Table II. The billets were heated in a Hayes air atmosphere furnace, extruded in a Watson-Stillman press, and drawn and scalped on standard draw benches. The size of the drawing and scalping dies is given in in Table II. The rod was annealed in radiant heat air atmosphere furnases. Prior to the final anneal the wire was straightened in a Lesis wire straightener.

After straightening, the wires had to be annealed to a dead soft condition in an atmosphere that would neither oxidize the wire nor introduce a gas soluble in the solid copper. For this reason the section of Table I dealing with argon annealing of the wire merits particular attention. Mr. R. A. Campbell of the Mueller Brass Co. has developed this procedure to insure that the samples were fully annealed in an inert atmosphere. The procedure produced clean, straight wire.

The tensile samples were annealed in a commercial bright annealing atmosphere or in argon in the same manner as the wires as specified.

C. TESTING

Two principal tests conducted were tensil and el ctrical resistivity.

Tensile Testing was carried out on tensile bars with a reduced section diameter of 0.300 in. and 2 in. gauge length. Standard procedures were followed to obtain data for 0.2% offset yield strength, tensil strength percent reduction in area and total elongation at fracture.

The Electrical Resistivity Tests were carried out with a Double Kelvin Bridge according to ASTM specification B193-49. Figure 3 shows the resistivity

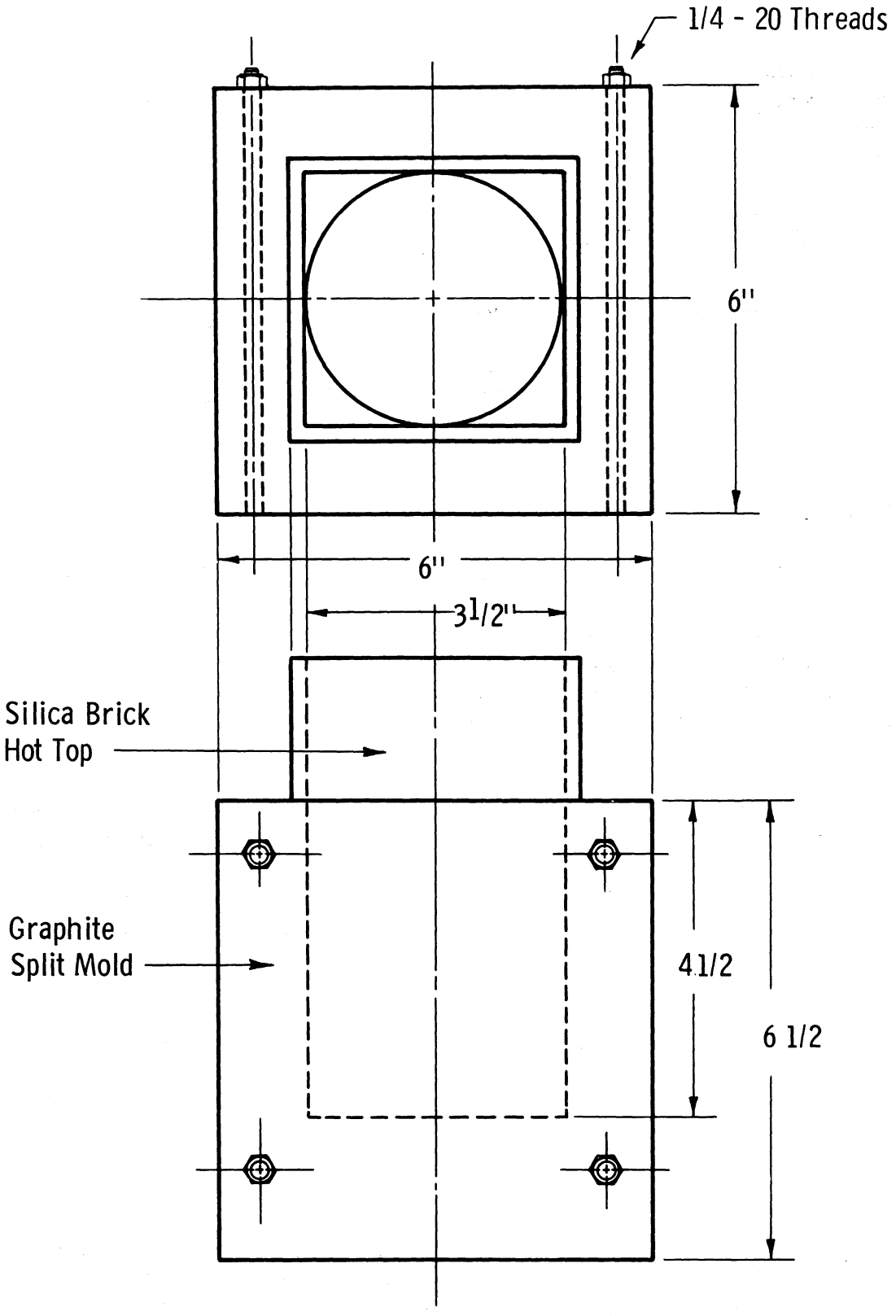


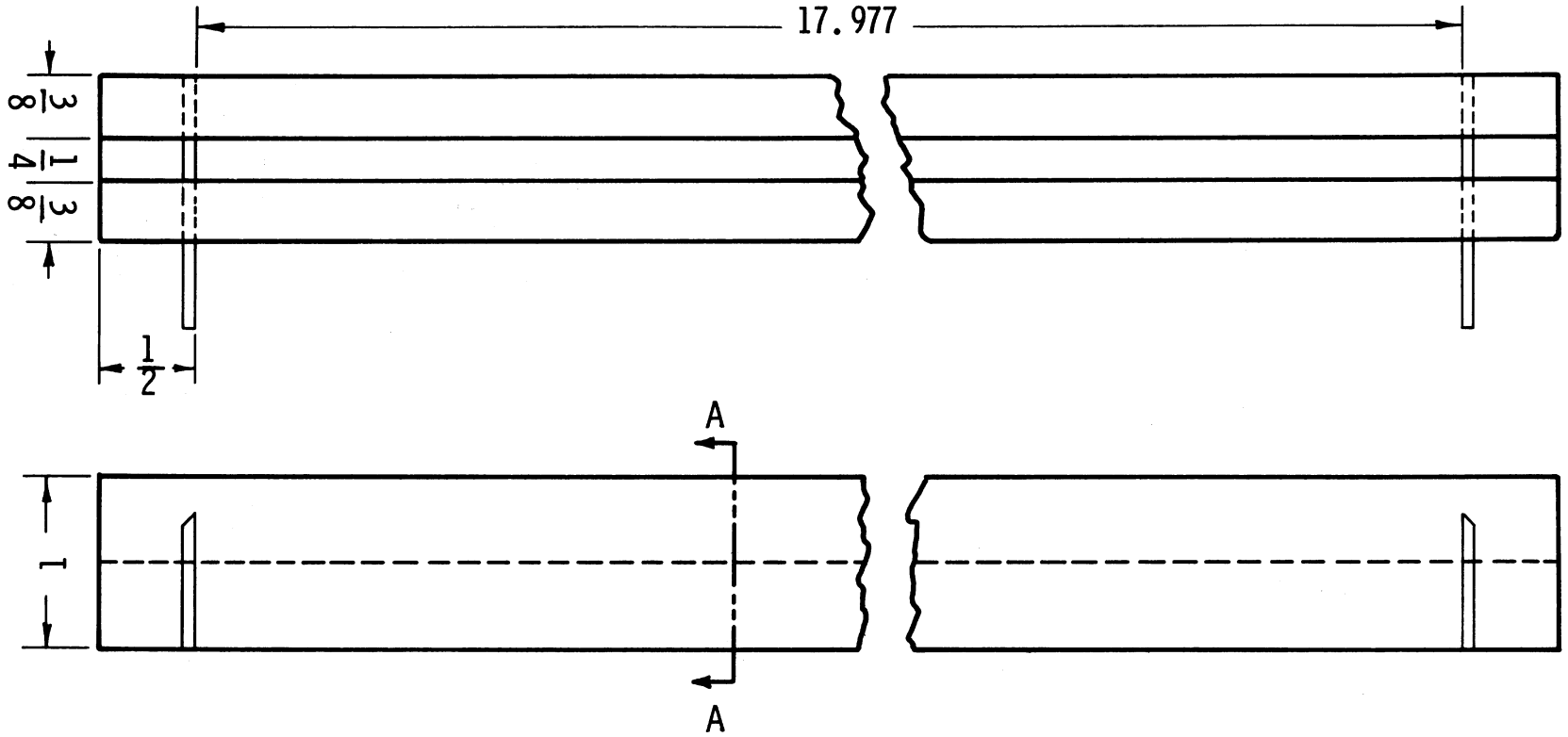
Fig. 2. Graphite mold and silica hot top.

TABLE II

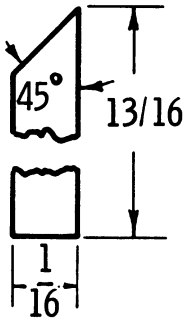
EXTRUSION, DRAWING AND ANNEALING CYCLE

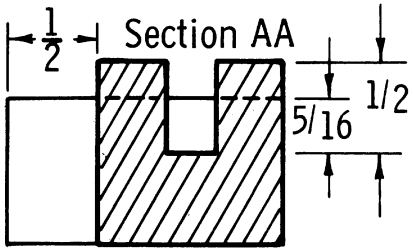
Mueller Brass Co. Extrusion, Drawing and Annealing Cycle

samples:	In 16,17,18,20,21,22,23
billets:	2.93 in. in diameter x 2.75 in. long
billet heating:	temp. 1600°F., 20 min. at temp. Billets stacked on carbon sheets to avoid adhesion. Billets showed extensive surface oxidation.
extrusion:	0.632 in. round die in Watson Stillman press. Central flow pattern developed in butt. Rod was air cooled.
pickle:	12% H_2SO_4, 15 min.
draw:	0.520 in. straight rod
scalp:	0.512 in. rod
anneal:	1200°F 45 min. total furnace time
draw:	0.427 in. straight rod
scalp:	0.415 in. rod
draw:	0.343 straight rod
break:	break out central pipe, cut 20 in. tensile bars
draw:	0.281 in. straight rod
anneal:	1200°F, 45 min. total furnace time
draw:]	0.243 in. coiled rod
draw:	0.187 in. coiled rod
anneal:	1200°F, 45 min. total furnace time
draw:	0.156, then 0.123, then 0.113 in. coiled rod
straighten:	32 in. lengths on Lewis straightener
Note:	Samples in 1,2,4,5,6,7,8,9,10,11,12,13,15, Std. 1, S-A, S-B, S-C, and S-D were given a slightly different and less acceptable drawing schedule. The difference between the two schedules was that in the unlisted schedule the reductions were somewhat greater between anneals.
wire annealing:	hydrogen, annealed at 1200°F, 45 min. total furnace time atmosphere, H_2 .7%, CO .7%, CO_2 11%, N_2 rem. Argon: (1) Cleaned and pickled wires are placed in a 1 in. copper tube that has been pickled and sealed at one end. The tube is completely sealed with a pigtail plug. All plug welding was done while argon flowed into the tube. (2) The tube is drawn down to a pressure not to exceed 150 microns. (3) The tube is charged to a slight positive pressure with argon, and sealed. (4) The assembly is annealed at 1300°F with a total furnace time of 45 min. The tubes were laid at 45° to the belt direction. (5) After annealing and cooling the pigtails were cut. If escaping gas and a clean inner surface on the pigtail were observed the seals were assumed good and the wire sufficiently protected.



Knife Edge





block used in the test. The wire diameter was nominally 0.113; therefore, the length-to-diameter ratio of the specification (at least 10:1) has been easily satisfied as have all other specifications.

Certain ofther checks were made on the wire augmenting the procedure of ASTM B193-49. The wire was cut into 24 in. lengths. E ch length had to pass through a 0.18 in. I.D. tube, thus assuring a departure from straightness of less than 1/16 in. in 24 in. All wires slide easily through the tube.

The diameter of the wire was checked at five locations with two perpendicular measurements with a micrometer that could be read to ±0.00005 in. The average diameter of the ten measurements was used in subsequent calculations.

The wire temperature could not be read directly; therefore, it was necessary to equilibrate the temperature of the wire with a conveniently read temperature room temp. This was done by measuring the resistance of the wire, waiting five minutes, measuring the resistance again. The second measurement could be made quickly; thus, the temperature of the wire was not significantly raised above room temperature by the D.C. current flowing when the m asurements were made. A second five-minute wait revealed no further change in resistence.

The wire was moved as little as possible. When it was put into the resistivity block it was moved directly from its storage tube on to the knife edges, thus reducing to a minimum the cold work in the sample.

An example of the calculation necessary to transform resistance data to conductivity data is given in Appendix B. Conductivity data, complete mechanical testing data and melting conditions are given in Table X, Appendix A.

D. METALLOGRAPHIC PROCEDURE

Samples for metallographic investigation were taken longitudinally from the annealed wires. Each sample was mounted and polished to the condition shown in Fig. 4. The samples were lightly etched with a dichromate etch, 2 gm. $K_2Cr_2O_1$, 1.5 gm. NaCl, 8 ml. conc. H_2SO_4, 100 ml. H_2O, and viewed at 500x.

E. PROCEDURAL CHECKS

To determine whether the tests evaluating controlled atmospheres were producing material comparable to OFHC copper, checks were made using OFHC blanks along with the ingot copper. A change in the properties of the OFHC stock would indicate a change due to the melting or forming operations.

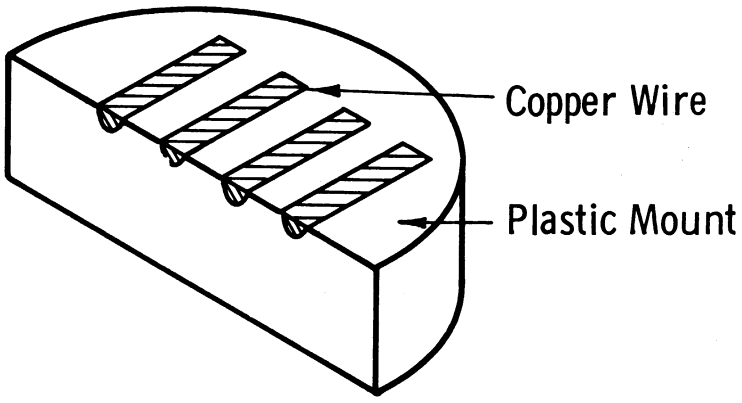


Fig. 4. Section of a metallographic sample showing that half the wire has been ground off to reveal the micro structure near the center.

To distinguish between changes due to melting and changes due to forming two sets of blanks were run with stock taken from one OFHC wire bar. One sample, S-1, was remelted under air at 250 micron pressure, cast, formed and tested with the same procedures as any other sample. Four additional specimens, S-A, S-B, S-C and S-D, were machined directly from the OFHC bar and given the same forming and testing as any other sample.

The procedures outlined have produced samples whose electrical and mechanical properties are reproducible.

RESULTS AND DISCUSSION

The data may be discussed under the divisions, (A) Electrical Conductivity, (B) Mechanical Properties, (C) Micro Examination, and (D) General Discussion.

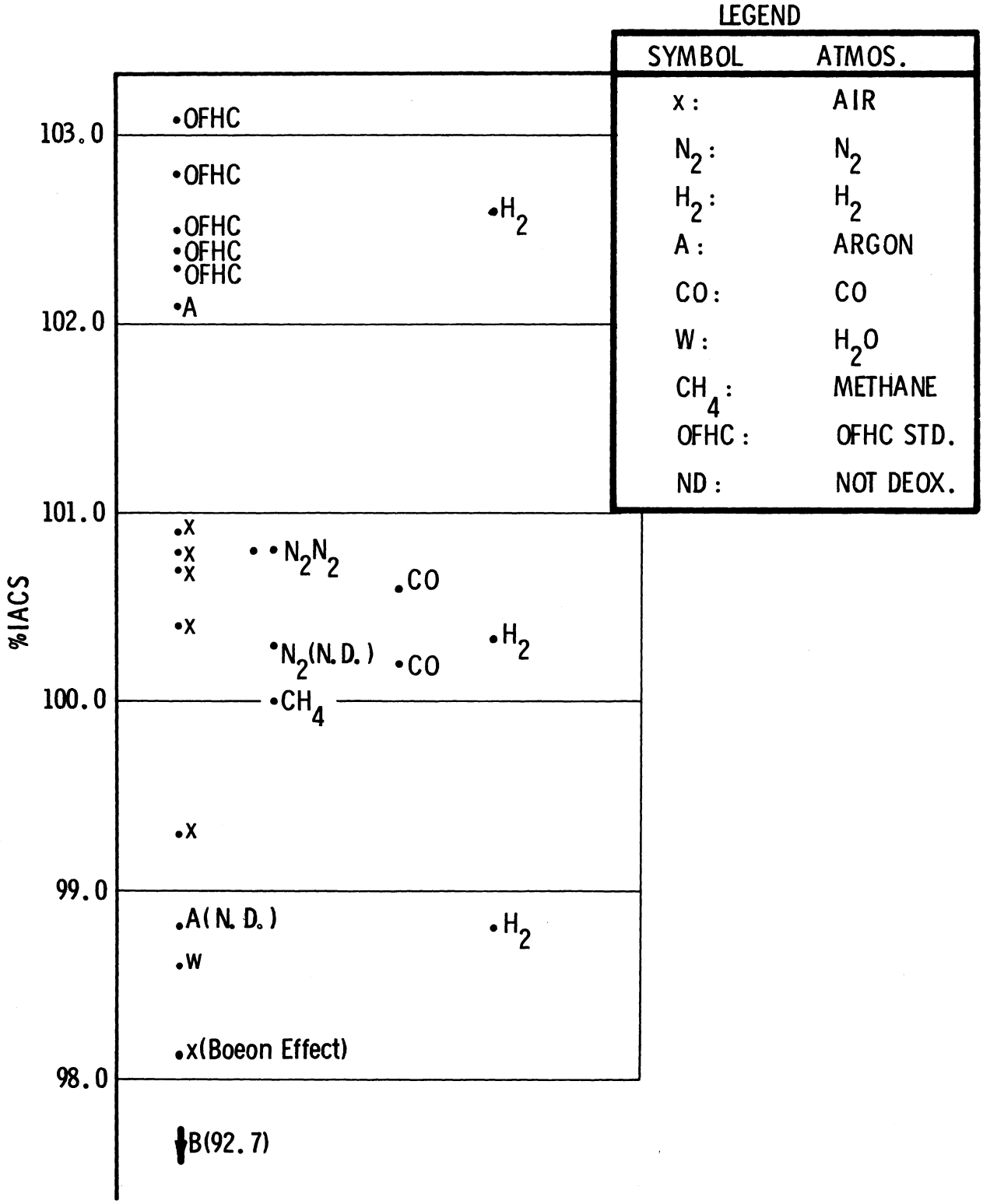
A. Electrical Conductivity

The electrical conductivity of an alloy is a function of composition, temperature, and cold work. Temperature and cold work as variables have been essentially eliminated. The effect of the melting atmosphere on the composition must then be responsible for changes in electrical conductivity. Table III shows the range of conductivities found in the test samples.

The data in three ranges of conductivity, 101.8-103.4%, 99.8-101.0% and below 98.5% IACS.

TABLE III

EFFECT OF MELTING ATMOSPHERES ON ELECTRICAL CONDUCTIVITY



101.8-103.4%

The heats made with OFHC stock fall, as expected, in this range and serve as a procedural check as discussed earlier. In addition, two experimental conditions were successful in attaining this level of conductivity:

(1) Heat In 16: Ingot stock was melted and held at less than 100°F super heat above the liquidus for 1/2 hour under H_2 at a pressure of 51 mm of Hg. The heat was poured under H_2 at a pressure of 0.25 mm of Hg.

(2) Heat In 11: Ingot stock was melted, held at 500°F super heat for 1/2 hour and poured under dried and deoxidized argon at a pressure of 635 mm of Hg.

99.8-101.8%

Heats made under air, nitrogen, carbon monoxide, methane and hydrogen fall in this range. The atmospheres in this group were neither beneficial or deleterious to the conductivity of ingot copper. Melting conditions were as follows:

(1) Air (Heats In 1,2,4,5 and 10): Ingot stock was melted, held at super heat ranging from less than 100°F to 300°F above the liquidus for periods ranging from 15 min. to 2 hours, and cast under air at pressures ranging from 0.005 mm. to 0.4 mm. Hg.

(2) Nitrogen (Heats In 7, 13 and 13): Ingot stock was melted, held at superheats of less than 100 and 300°F for 1/2 hour, and cast under N_2 at pressures ranging from 51 to 380 mm. Hg.

(3) Carbon Monoxide (Heats In 18 and 20): Ingot stock was melted, held at superheats of less than 100 and 300°F for 1/2 hour, and cast under CO at a pressure of 254 mm. Hg.

(4) Methane (In 22): Ingot stock was vacuum melted, held at less than 100°F superheat for 1/2 hour, and cast under CH_4 at 380 mm. Hg pressure.

(5) In 15: Ingot stock was melted, held at less than 100°F super heat for 1/2 hour, and cast under hydrogen at 254 mm. Hg pressure.

98.5% and Below

In this group two treatments were found to have singularly bad effects upon conductivity—a water vapor atmosphere and boron additions. Of course, the effects of water vapor have been known for some time, but a quantitative

evaluation of the effects of water vapor under these experimental conditions was desirable. The boron effect can probably be reduced since an overdose of boron, following the manufacturer's recommendation, was probably used. The details of these data points are:

(1) Water Vapor (In 21): Ingot stock was melted, held at less than 100°F superheat for 1/2 hour, and cast under H_2O vapor at 25 mm. Hg pressure,

(2) Boron Addition (In 8): Ingot stock was melted, held at 300°F superheat for 15 min. while B was added, and cast under A at 381 mm. Hg pressure.

B. MECHANICAL PROPERTIES

Percent reduction in area change in % R.A., yield strength, and tensile strength data for all the melts are given in Tables IV, V, VI, VII. Properties were determined after annealing in an argon atmosphere and in a hydrogen atmosphere. The most significant data are those for the effects of a reducing atmosphere (H_2) upon reduction of area because this has been one of the important engineering advantages of OFAC copper, i.e., no significant change in R.A. with reducing atmosphere.

The data of Table V fall into two groups—specimens showing little or no change in R.A. after annelaing in hydrogen, and specimens showing substantial change.

Specimens with Little or no Change in R.A.

In this group, as expected, are the OFHC specimens. However, the specimens in which the melt was exposed to a hydrogen atmosphere behaved as well as the OFHC group. Also the specimens deoxidized with boron behaved well.

Specimens Showing 10-30% Change in % R.A.

This group combined specimens which probably contain enough residual oxide to result in H_2O vapor formation in the test specimen when annealed in hydrogen, i.e., atmosphere containing air, nitrogen, water vapor and argon. CO and methane (CH_4) also gave poor results, indicating that there was still residual oxide in the melt.

Other mechanical tests are given for completeness but are not particularly significant. All specimens showed a small decrease yield strength, for example, accompanying the hydrogen anneal, the lower yield is probably due to the longer effective annealing time of these specimens relative to those in a closed tube filled with argon.

TABLE IV

EFFECT OF MELTING AND ANNEALING ATMOSPHERES ON
% REDUCTION IN AREA (%R.A.)

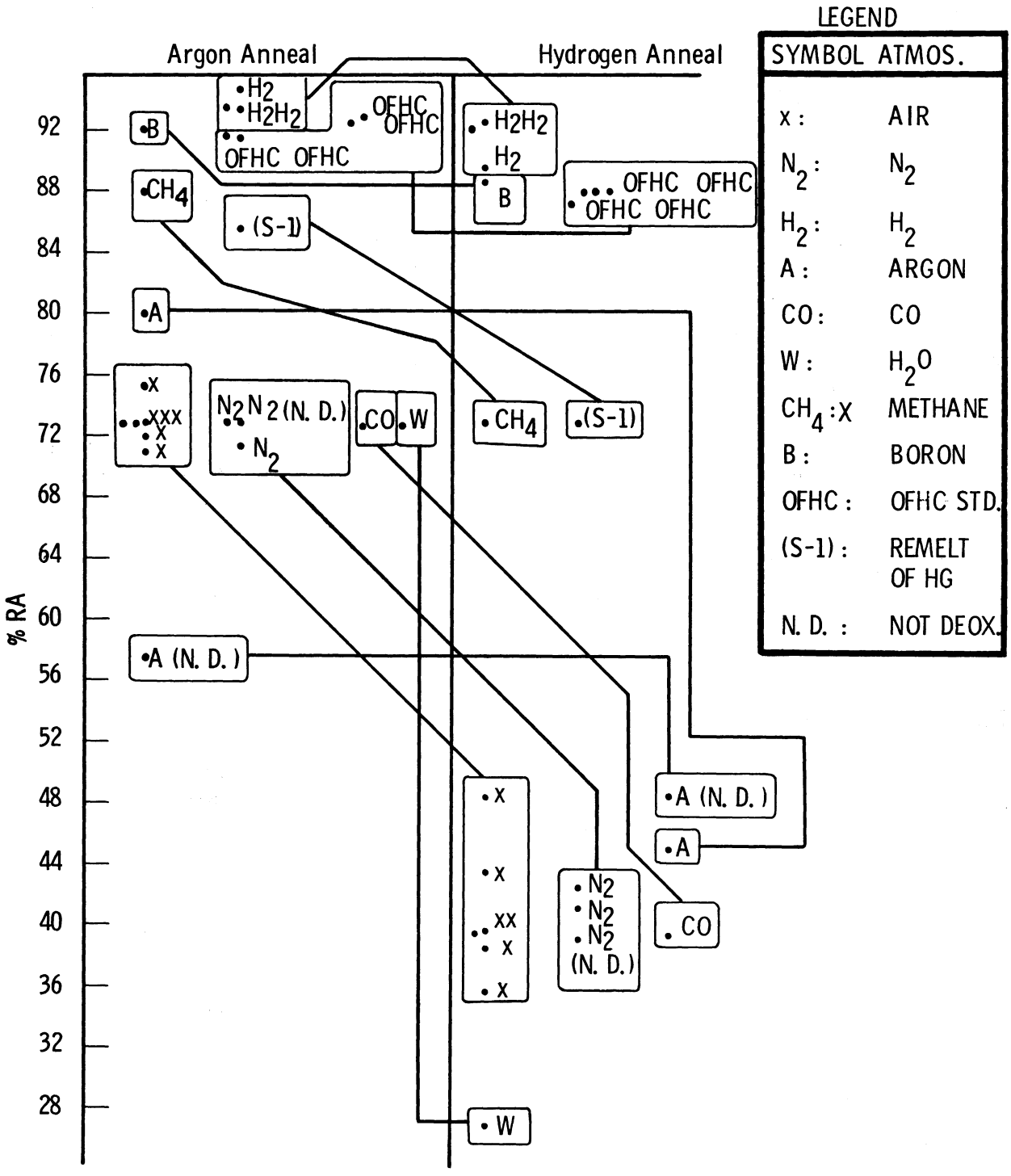


TABLE V

EFFECT OF MELTING ATMOSPHERE ON -ΔR.A.

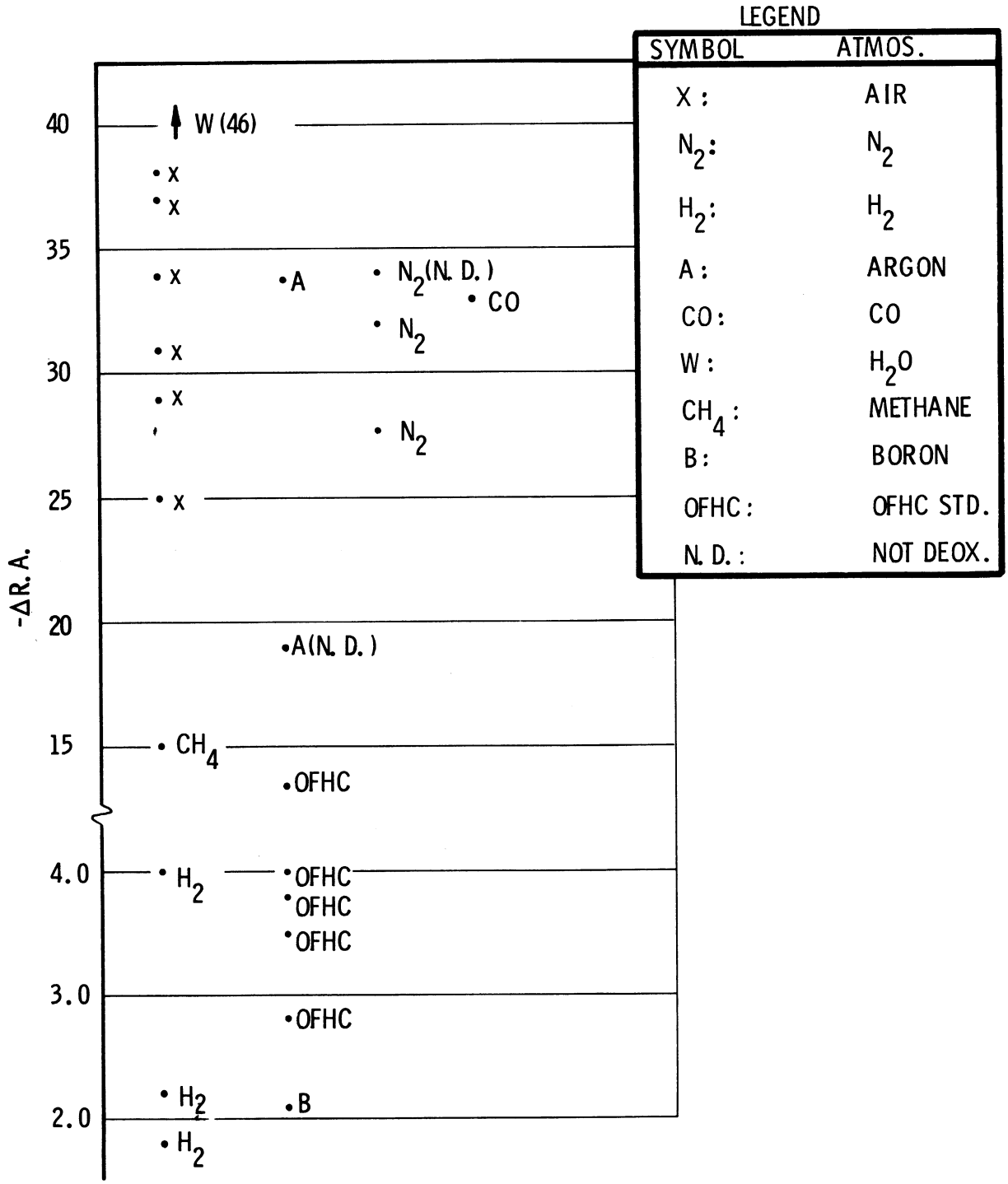


TABLE VI

THE EFFECT OF MELTING AND ANNEALING ATMOSPHERES ON YIELD STRENGTH (0.2% OFFSET)

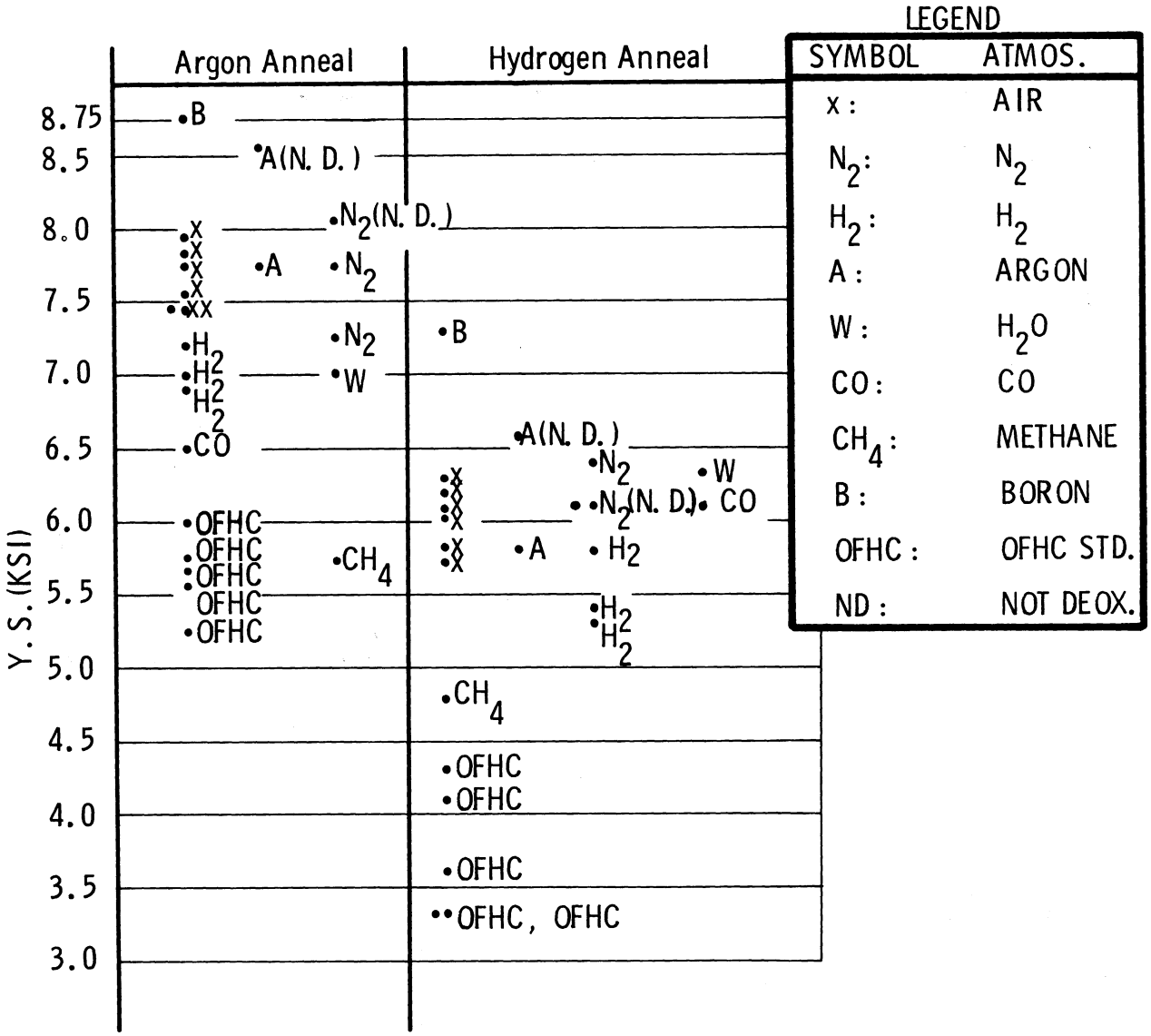
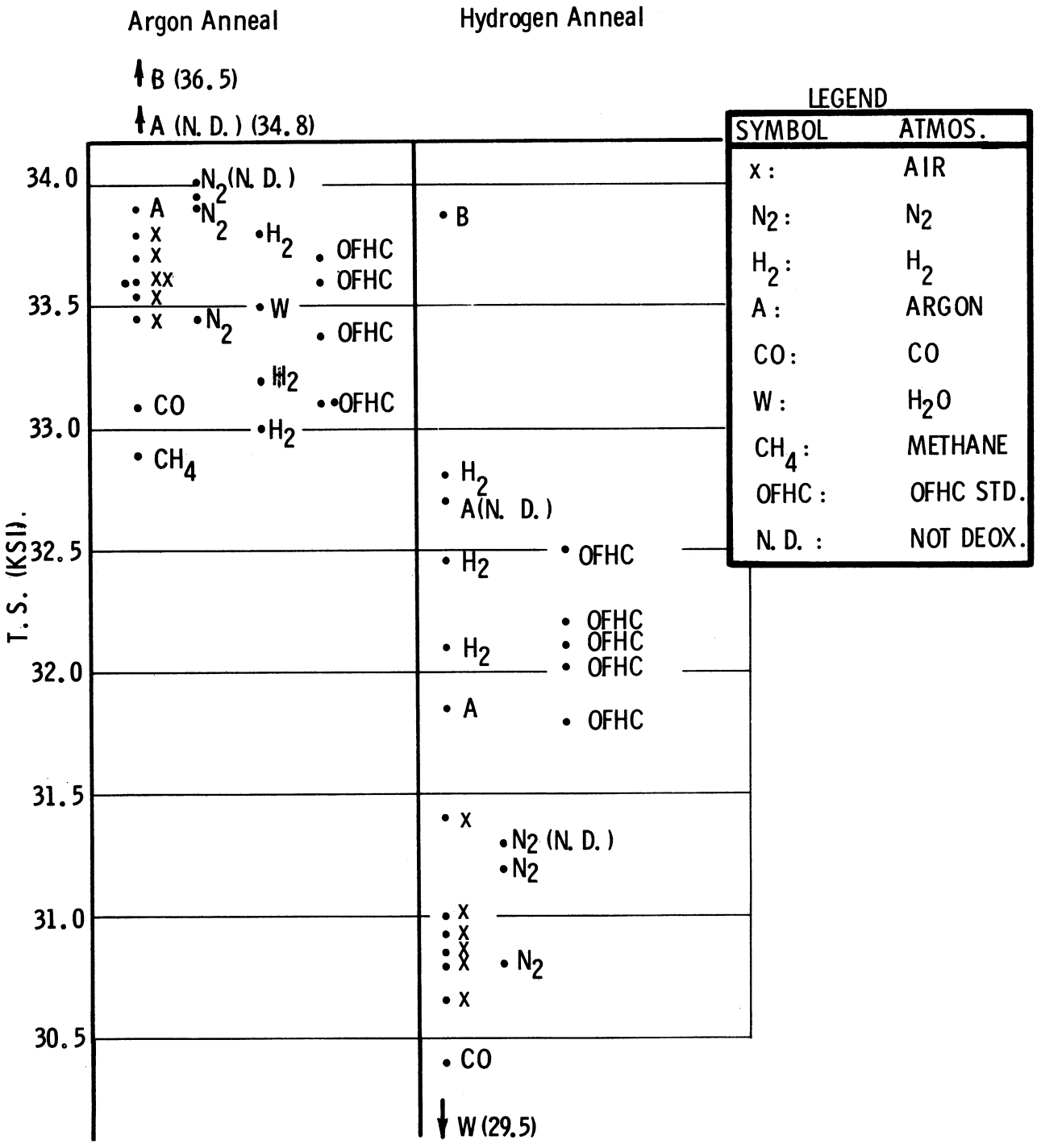


TABLE VII

EFFECT OF MELTING AND ANNEALING ATMOSPHERES ON TENSILE STRENGTH



C. MICRO EXAMINATION

The microstructure of the samples reveals the amount of copper oxide in the sample. After etching, the oxide appears as the black phase in the photomicrographs.

The photomicrographs, Figs. 5-11, were taken to demonstrate the various conditions found in the samples. The data that can be taken from the photomicrographs is conveniently summarized in Table VIII.

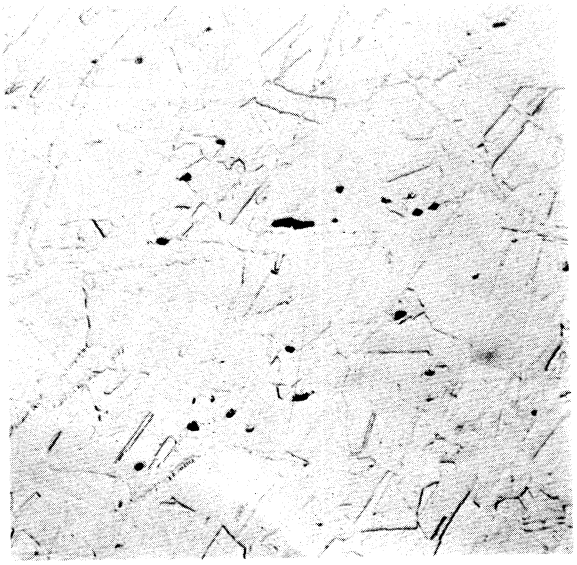
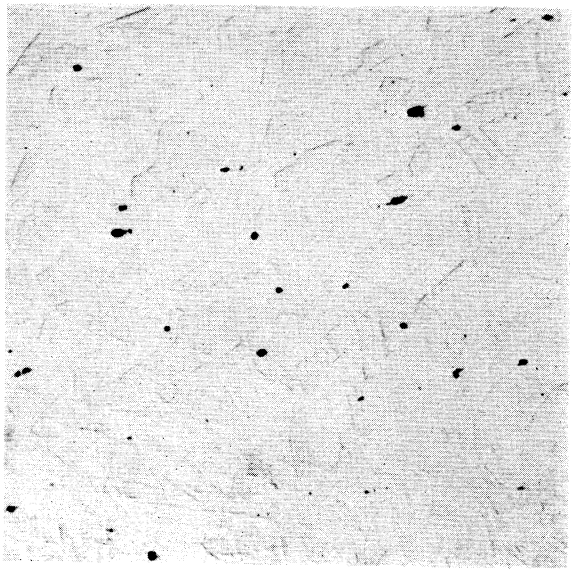


Fig. 5. 500x, dichromate etch. This photomicrograph shows high oxide (black) content and grain boundaries.

Heat: In 1

Melting Conditions: Ingot stock was melted, held 1/2 hour at a 100°F superheat, and poured under air at 0.25 mm. Hg pressure.

Sample Location: Annealed wire

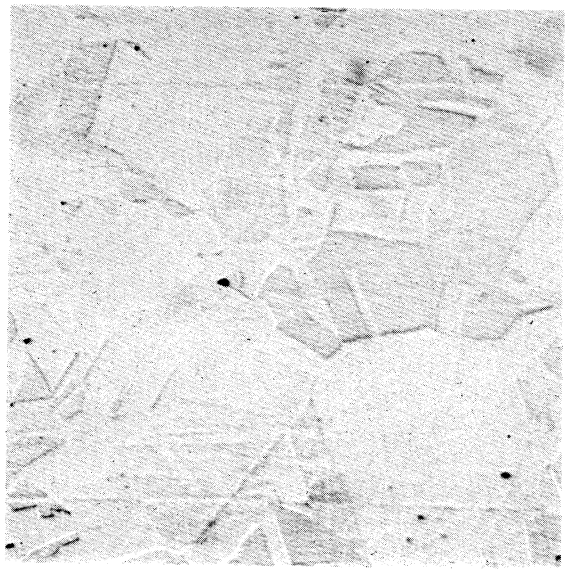


Heat: In 21

Melting Conditions: Ingot copper was melted, held 1/2 hour at a 100°F superheat, and poured under water vapor at 25 mm. Hg pressure.

Sample Location: Annealed wire

Fig. 6. 500x dichromate etch. This photomicrograph shows a large amount of oxide (black) and some grain boundaries.



Heat: In 22

Melting Conditions: Ingot stock was melted, held 1/2 hour at a 100°F superheat, and poured under CH_4 at 381 mm. Hg pressure.

Sample Location: Annealed wire

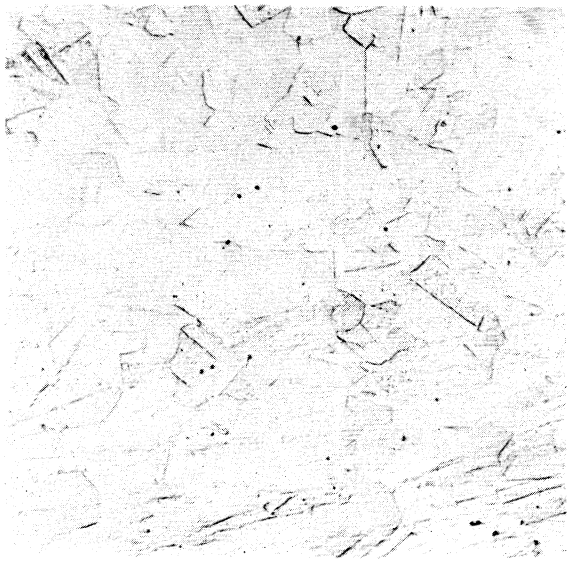
Fig. 7. 500x, dichromate etch. This photomicrograph shows a moderate amount of oxide and grain boundaries.

Heat: In 11

Melting Conditions: Ingot stock was melted, held 1/2 hour at a 500°F superheat, and poured under A at 534 mm. Hg pressure.

Sample Location: Annealed wire

Fig. 8. 500x, dichromate etch. This photomicrograph shows a moderate amount of oxide and grain boundaries.



Heat: In 16

Melting Conditions: Ingot stock was melted, held 1/2 hour at a 100°F superheat under 51 mm. Hg of H_2, and poured under 0.25 mm. Hg of H_2.

Sample Location: Annealed wire

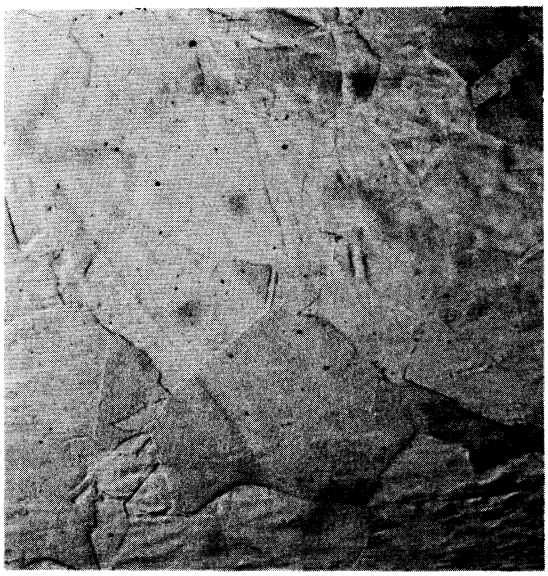
Fig. 9. 500x, dichromate etch. This photomicrograph shows a small amount of oxide and grain boundaries.

Heat: In 8

Melting Condition: Ingot stock was melted, held 1/4 hour at a 300°F superheat with B addition, and poured under A at 534 mm. Hg pressure.

Sample Location: Annealed wire

Fig. 10. 500x, dichromate etch. This photomicrograph shows little oxide and grain boundaries.



Heat: OFHC standard A

Melting Condition: Extrusion built machined from OFHC stock.

Sample Location: Annealed wire

Fig. 11. 500x, dichromate etch. This photomicrograph shows almost no oxide and some grain boundaries.

TABLE VIII

EFFECT OF MELTING ATMOSPHERE ON MICROSTRUCTURE

Fig.	Melt Atm.	Inclusion Size	Amount of Oxide
5	Low Pressure	Large	High
6	Water Vapor	Large	High
7	Methane	Large	Moderate
8	Argon (Bath at 2500°F+)	Small	Moderate
9	Hydrogen	Small	Low
10	Boron Addition	Small	Low practically absent
11	OFHC Std.	Small	Low

The variation in oxide contents of the samples listed in Table VIII is primarily due to different melt-atmosphere interactions. The possible exceptions are the low pressure ingot sample which shows no evidence of changes effected by the atmosphere and the OFHC. Std. which was not remelted.

Water Vapor added oxide to the melts as H_2O dissociates yielding $\underline{H}$ and $\underline{O}$ for the bath. The dissolved oxygen combines with copper at the liquidus temperature of the Cu-O alloy and forms copper oxide.

Methane has been noted for its outstanding deoxidation of copper. Methane has clearly reduced the oxide content of the bath, and the remaining oxide exists as large inclusions. The reaction mechanism (bulk or surface) of the $CH_4+\underline{O}$ is not known, though it is unlikely that a molecule the size of methane could move easily into the copper. Dissociation of the methane is possible.

Argon melting has appreciably reduced oxide content. The lower oxide content is thought to be primarily due to oxide reduction at the crucible surface. The high temperature of the melts and the constant induction stirring both would increase the rate of reduction.

Hydrogen dissolves in copper following Sievert's law. The reaction

$$2\underline{H} + \underline{O} \rightarrow H_2O(g)$$

takes place, removing oxygen from the melt, lowering the oxide content of the sample.

Boron acts in a similar manner. Boron dissolves in the melt and reacts with the dissolved oxygen to form B_2O_3, an oxide stable relative to copper oxide. B_2O_3 rises to the melt surface where it can be skimmed off.

D. GENERAL DISCUSSION

A qualitative evaluation of the properties of the samples is given in Table IX. A high value of electrical conductivity and reduction of area after

TABLE IX

QUALITATIVE EVALUATION OF PROPERTIES OF THE SAMPLES

Sample	Electrical Cond.*	% R.A. After Bright Ann.*	Y.S.*	Oxide Content
Boron Heat	Low	High	High	Low
Water Vapor	Low	Low	Medium	High
Hydrogen (In 17)	Low	High	Low	Medium
Methane	Medium	Medium	Low	Medium
Air (Low Pressure)	Medium	Low	Medium	High
Nitrogen	Medium	Low	Medium	-----
Carbon Monoxide	Medium	Low	Medium	-----
Hydrogen (In 16)	Medium	High	Low	Medium
Argon with 500°F+ SoHo	High	Low	Low-Medium	Medium
Hydrogen (In 16)	High	High	Low-Medium	Medium
OFHC (S-A---S-D)	High	High	Low	Practically None
OFHC (S-1)	High	Medium	Low	Low-Medium

*	High	Medium	Low
Conductivity	$\sigma > 101.8$	$99.8\% < \sigma < 101.01\%$	$\sigma < 98.5\%$ ACS
% R.A.	R.A. > 88%	68 < R.A. < 76%	R.A. < 50%
Y.S.	Y.S. > 7000 psi	5500 psi < Y.S. < 6800 psi	Y.S. < 5500 psi

bright annealing both are desirable. Copper is not usually a structural material, so that yield strength need not be high. The copper oxide content of a sample is not generally a criterion for material selection, but oxide content and yield strength are measures of purity so that low levels of both are desirable.

The evaulations of Table IX contains one set of samples OFHC that has all the desirable characteristics mentioned above. This is what makes OFHC copper particularly desirable to the electronics industry.

Interrelations between the various data is apparent. The oxide content affects both the conductivity and the ductility of the sample. Solid solution impurities lower the conductivity. Alloy impurity content can be qualitatively measured through the yield strength of the sample.

Copper oxide is a brittle ionic compound which would induce the ductility of copper regardless of how it was annealed. The practice of annealing copper in a hydrogen-bearing atmosphere, bright annealing, complicates the situation. Hydrogen embrittlement, reduction of copper oxide leaving voids in the sample, is the main reason that many samples have low ductility after bright annealing.

Copper oxide in a sample is an impurity that will reduce the electrical conductivity of the material. The low ion conductivity of some samples is due to an excess of copper oxide.

Solid solution impurities drastically lower the conductivity of a sample. This effect will override a reduction in copper oxide content. A high yield stress is indicative of solid solution alloying and a high yield stress generally goes along with low conductivity.

The effects of copper oxide and dissolved impurities on copper can be demonstrated through discussion of specific samples. The sample melted under water vapor has an exceptionally high oxide content. This has lowered the electrical conductivity. The percent reduction of area after bright annealing is the lowest found among all the samples. The mechanism of melt oxidation has been discussed previously. The effect of the dissolved hydrogen on the properties of the material would be less than that of hydrogen heat In 15, and can probably be disregarded. The water used was pure so that no other impurity was in the atmosphere; thus, the effect can only be one of increased oxide content. The water vapor pressure employed corresponded to 100% relative humidity at 80°F. This water vapor level in the atmosphere is easily attained on a humid summer day or could be introduced if damp charcoal was used as a melt cover.

The effect of a dissolved impurity is demonstrated by the boron sample. The copper oxide content of the melt is low and the sample is not subject to hydrogen imbrittlement. The yield strength is high and the conductivity is

exceptionally low. The boron addition was made to heat run under low pressure (250 microns) air so no additional impurity is present in the atmosphere. The boron addition was evidently excessive so that a solid solution impurity was added to the sample increasing the strength and lowering the conductivity of the sample.

The argon sample is another example of the effect of alloy impurities on the conductivity of the copper. The copper-oxide content of the sample has been reduced, which should increase electrical conductivity somewhat. The melt was held at 2500°F under deoxidized argon for 30 minutes.

Table X gives the vapor pressure and weight percent of the impurities found in ingot copper.

TABLE X

COMPOSITION OF REPRESENTATIVE SAMPLES OF INGOT AND OFHC AND VAPOR PRESSURE OF CONSTITUENCY

Element	White Pine Ingot	OFHC	Vapor Pressure Near 2500°F
	(wt. %)	(wt. %)	(atm.)
Cu	99.8	99.96(min.)	.0001
Ag	.14	99.96(min.)	.001
O_2	.035	--	--
Fe	.001	--	< .0001
As	.0005	--	1.0
Ni	.008	--	< .0001
Se	.004	--	1.0
Pb	.0008	.0005	0.1
S	.0003	.0013	1.0
Bi	.0001	--	.5
Sb	.001	--	.5
Te	.0002	--	1.0
Zn	.0005	.0003	1.0
Sn	.0006	--	.01
P	--	.0003	1.0
Hg	--	.0005	1.0

Several impurities have substantial vapor pressures at 2500°F and could vaporize. This mechanism is suggested to account for the high electrical con-

ducting of the argon sample.

An example of reduced oxide content leading to high electrical conductivity and high ductility is hydrogen sample In 16. The difference in hydrogen content in the three samples melted under hydrogen has been duscussed and the low hydrogen concentration of In 16 has been established. A moderately low solid solution impurity content and a very low oxide content have coupled to produce a sample with properties approaching those of OFHC copper.

The addition of oxide has lowered the ductility of sample S-1. The other OFHC standards have suffered no loss in ductility or gain in oxide content; therefore, the sample was oxidized by remelting. Apparently air at 250 microns pressure has a sufficient oxygen potential to oxidize copper at 2000°F.

Returning once again to Table IX, it is evident that the samples have been produced with a wide variation of properties. The data from the argon sample and In 16 intimate that a duplex atmosphere heat may yield an exceptionally good sample. The behavior of methane and carbon monoxide leaves much to be desired and some questions unanswered. Further work is needed on both of these atmospheres. Nitrogen as melting atmosphere and low pressure melting are both ineffective and should not require further work with ingot copper.

CONCLUSIONS

While the data give only indications of general effects some particular conclusions can be drawn.

(1) Hydrogen as a melting atmosphere will produce copper which can be bright annealed without fear of hydrogen embrittlement.

(2) Water vapor in the melting atmosphere will lower the electrical and mechanical properties of copper.

(3) Nitrogen in the melting atmosphere does not appreciably effect the properties of copper.

APPENDIX A

Table XI below gives data on the melting conditions and physical properties of each sample. The order of presentation is the chronological order of preparation.

APPENDIX B

Data for electrical conductivity were collected as the resistance of a wire of known geometry at a known temperature. Below is a sample calculation of conductivity from the collected data.

Sample In 4

$R = 1.229 \times 10^{-3}\Omega$, $L = 17.977$ in., $T = 26.5°C$, $A = \pi(\bar{D})^2/4 = 1.012 \times 10^{-2}$ sq. in.

Resistivity at 26.5°C

$$\rho = \frac{R.A.}{L} = 6.919 \times 10^{-7} \text{ ohm in.}$$

Temperature Correction

$$\rho_{20°C} = \frac{\rho T}{1+\alpha(T-20°C)}; \quad \alpha = 3.87 \times 10^{-3}(°C)^{-1}$$

$$\rho_{20°C} = 6.750 \times 10^{-7} \text{ ohm in.} = 1.710 \times 10^{-6} \text{ ohm cm.}$$

Conversion to %IACS

$$\rho = 1.7241 \times 10^{-6} \text{ ohm cm.} \sim 100\% \text{ IACS}$$

$$1/e \; \alpha \; \sigma(\text{conductivity})$$

thus

$$\frac{1.7241 \times 10^{-6}}{1.710 \times 10^{6}} \times 100\% \text{IACS} = \%\text{IACS of In 4} = 100.8\%$$

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