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UNIVERSITY OF MICHIGAN
ANN ARBOR

INTERIM REPORT

HIGH-RESOLUTION AUTORADIOGRAPHY IN METALLURGY

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SUMMARY SHEET

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f. High-Resolution Autoradiography for Study of Grain Boundaries in Metals

g. Object:

The research work under this contract is to be devoted to the development and use of high-resolution autoradiography for the study of grain boundaries of metals. Specifically, the objects are (1) to improve the wet-collodion technique for autoradiography to permit application to the study of metallic systems; (2) to develop protective coatings of optimum thinness to prepare metals for autoradiography; (3) to use various radioisotopes including emitters of both high- and low-energy radiations for autoradiographic purposes and to develop methods for incorporating them into metals; and (4) to apply the techniques developed to the investigation of grain-boundary constituents in alloy systems that contain iron and the other transitional elements, and also to other types of alloys.

h. Summary:

Equipment and techniques used for the autoradiographic study of metallurgical problems are presented in this report. Some results are given showing that high-resolution autoradiographic methods can be a very valuable tool in the study of such problems as the distribution of bismuth in cast and recrystallized copper, grain-boundary diffusion of liquid bismuth in copper, and absorption of hydrogen by copper-base alloys. Sources of artifacts in stripping film autoradiography were also discussed.

i. Conclusions and Recommendations:

High-resolution autoradiography can be used for structural analysis in metallurgy. Technical difficulties which may generate misleading data have been noted. Tests with the copper-bismuth system are not quite completed. The work on copper-hydrogen and iron-nickel systems is still in preliminary stages and should be continued.

It is recommended (1) that the studies of the application of high-resolution autoradiography to metallurgy be continued and (2) that the possibility of resonance electron emission as a method of identifying metallurgical constituents be explored.

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ABSTRACT

Results obtained to date on studies of several metallurgical problems using autoradiographic techniques are presented in this report. These investigations include studies of the distribution of bismuth in copper, the diffusion of bismuth in copper, and the absorption of hydrogen in copper-base alloys. Preliminary studies have also been made of the diffusion of nickel in iron using stable materials.

The changes in the distribution of bismuth in cast copper after cold-rolling and annealing are being studied by contact autoradiography and by stripping film autoradiography. The former is a low-resolution technique, while the latter is one of several available techniques of high-resolution autoradiography. Results indicate that the bismuth initially present in the grain boundaries of cast copper does not preferentially diffuse to new boundaries of the recrystallized grains even after annealing at 1700°F for one-half hour.

Stripping film autoradiographic studies have shown that liquid bismuth diffuses along grain boundaries of copper to a considerable depth. The potentially high resolution of this technique is evidenced by the fact that radioactivity can be detected over grain boundaries where positive identification of the presence of bismuth by microscopic examination alone is difficult.

Equipment has been built for the study of hydrogen absorption in copper-base alloys and a melt of copper-tin alloy has been made under an atomic hydrogen (tritium) atmosphere. Contact autoradiographs of a sectioned surface of this alloy have indicated very low activity in the surface. However, microstructural evidence of hydrogen absorption in the alloy has been found. A tentative conclusion based on these few results is that the absorbed hydrogen is in a very loosely bound state and is lost rapidly from the surface.

Studies of the diffusion of nickel in iron using nonactive nickel have shown that considerable grain-boundary diffusion occurs in this system. Autoradiographic studies using radioactive nickel should yield many data of interest in solid-solid grain-boundary diffusion phenomena.

In the direct evaluation of autoradiographic techniques, sensitivity and possible artifacts were studied. It was found that Kodak stripping film has low sensitivity to bismuth beta radiation, measuring less than that of metallographic plates used for contact autoradiographs. In using Kodak stripping film, it was found that during development, fixing, and washing the emulsion layer can migrate as much as 100 microns, so that the autoradiographic pattern and substrate do not coincide.

INTERIM REPORT

HIGH-RESOLUTION AUTORADIOGRAPHY IN METALLURGY

RADIOACTIVE TRACER TECHNIQUES

At the suggestion of Dr. L. S. Foster, an introductory section on autoradiography has been provided. Metallurgical work is discussed in a later section.

Radioactive tracer elements provide a relatively new and potentially very powerful method of structural analysis in metallurgy. Since radioactive isotopes are practically indistinguishable chemically from stable isotopes, radioactive forms introduced into chemical and physical systems such as metals and alloys will behave, for almost all purposes, exactly like the stable forms of a given element. However, at some time, determined by the structure of the nucleus, the radioactive isotope of a given element will convert itself into an isotope of a neighboring element. Thus, iron-59 changes to cobalt-59, cobalt-60 changes to nickel-60, and nickel-63 changes to copper-63, all by negative beta particle emission, sometimes followed by gamma rays from the excited product nucleus. Copper-61 is converted to nickel-61 by positive beta particle emission, and polonium-210 is converted to lead-206 by alpha particle emission.

It is not the change in chemical element that is of interest, in most cases, as the amount of product is usually too small to be chemically significant. Rather, it is the emitted particle that is significant, since if it can be detected and traced back to its point of origin, the location of the original isotope in the metal structure being studied can be determined.

Thus, by preparing an iron with carbon-14 as part of the carbon content, the location of the carbon on and just below the surface of a metallographic specimen can be determined by detecting the beta radiation from the carbon-14 nuclei as they are converted to nitrogen-14. The effect of

composition, heat treatment, working, and other processing can then be correlated directly with their effect on significant portions of the microstructure.

The value of the tracer technique depends on the sensitivity and spatial resolution of the detectors used to locate the radiation sources. In terms of sensitivity, many methods of detection are available with sensitivities very close to 100 per cent for beta particles. Every beta particle which enters the sensitive volume of a Geiger counter or proportional counter is detected. Scintillation counters also show high sensitivity to beta particles and also to gamma radiation.

However, in spatial resolution there is much to be desired. The atom from which the beta particle came is about 1×10^{-8} centimeter in diameter, and the nucleus of this atom is about 1×10^{-12} centimeter in diameter. Assuming that the nucleus location is not too significant, and taking the atom diameter, 1×10^{-8} centimeter or 1 Ångstrom, as the basic resolvable unit of length, the best present methods of detection will resolve two sources separated by about 100,000 to 10,000 Ångstrom units. One micron, the practical resolution limit of most microscopes, using white light as a viewing medium, is 10,000 Ångstrom units.

This discussion has been introduced so that the techniques and results to be discussed in the following sections may be judged not only on the basis of present results, but also on the results which are theoretically possible using tracer techniques.

AUTORADIOGRAPHY

The radiation detection method with the highest resolution developed to date is autoradiography. In simple autoradiography a radiation-sensitive material, usually photographic film, is placed in contact with the surface to be studied. The radiation from the surface under study produces localized developable areas in the film directly over the radiation source. A great deal has been written on the interaction of ionizing radiation and film,[1] so this subject will not be discussed further here.

After development of the film, the blackened film areas are compared with the surface which produced the blackening in order to locate the radioactive materials.

In the simple contact method, the surface and films must be examined separately and correlation made from recognizable patterns which appear in both surface and film. Figures 2 and 3 and Fig. 4 and 5 are examples of such pairs. It should be noted that the autoradiographs Figs. 3 and 5 are mirror images of the surfaces being autoradiographed. This occurs because the sensitive film layer is in contact with the metal, and image reversal can be achieved only with loss of resolution in the autoradiograph or photomicrograph.

The contact method of autoradiography has severe limitations if high resolution (10-micron resolution or better) is desired. When the specimen and autoradiograph are to be examined under a microscope, the most basic problem is that of register. At 500 diameters, correlation between the specimen and the silver grains in a separate film is virtually impossible.

Other requirements for high resolution and good sensitivity are: very close contact between the surface being studied and the film; high density of sensitive material, such as silver bromide, in the film; and a thin film layer.

Three basic approaches to high-resolution autoradiography have been made. First, there are the commercial stripping films made by Eastman Kodak, British Kodak, and Ilford. Second, there is the emulsion painting technique of Belanger and Leblond. Third, there is the wet process of autoradiography of Gomberg. The three methods differ in certain important aspects, but all attempt to satisfy the requirements listed above.

The modern stripping films consist of a 5-micron layer of silver bromide in gelatin, up to 50 per cent by volume and 85 per cent by weight

of silver bromide grains a fraction of a micron in diameter, supported on a layer of 5 or 10 microns of plain gelatin. The combined gelatin layer is carried on a cellulose acetate or glass base from which it is stripped just before use. The film is commonly applied by floating, with emulsion side down, a piece of the stripped gelatin film on water and then picking it up on the surface to be autoradiographed. The film dries down and forms a thin adherent radiation-sensitive coating on the surface. The film application is done in a dark room. The coated specimen is kept in a cool dark space for the duration of the exposure and then the film is developed. The sensitive layer is in contact with the specimen but the gelatin supporting layer is water-permeable so that developer, wash, and fixer solutions can penetrate through the support layer to the emulsion.

The autoradiograph, in intimate contact with the metal surface, can now be examined under a reflecting microscope. The silver grains can be correlated directly with the metallurgical structure which appears underneath. There are many examples of such autoradiographs in this report, such as Figs. 1, 6, 7, 10, and 11.

There are a number of limitations and difficulties associated with this method, and these will be discussed in detail. Nevertheless, this technique is quite satisfactory and with proper precautions and checks yields very good results.

In the second method, a liquid emulsion consisting of silver bromide grains, gelatin, and water is painted onto the surface to be autoradiographed. When the emulsion has set, the processing becomes identical with that of the stripping film. In the past, the material was not easy to obtain; it had therefore been customary to melt the emulsion from lantern slide plates or Eastman NTB plates. Now, however, Ilford G-5 emulsion can be obtained in the form of dry gelatin "noodles" which are melted over boiling water for use. This painting technique was one of the earliest high-resolution techniques but suffers from technical faults such as high inherent fog due to handling and nonuniform emulsion thickness. The stripping films have largely avoided or overcome these particular difficulties.

The wet autoradiographic process is quite different in approach and execution from the previous two. In the wet process, a sensitive silver bromide layer is formed chemically on the surface to be studied. By controlling formation conditions, the layer produced, containing 80 per cent silver bromide by volume or well over 95 per cent by weight, can be made 1 micron thick, obviously in intimate contact with the surface. The film is developed physically rather than chemically, so that the size of the observed silver grains in the final image can be larger or smaller than the silver bromide grains of the original film. In the wet film,

the silver bromide grains are about 1/2 micron in diameter. When due precautions are taken, excellent high-resolution autoradiographs can be produced. However, this method is more difficult to use than the stripping film method, particularly for personnel who are new to this work. We are therefore using the stripping film routinely and the wet process only when needed.

Having outlined the available high-resolution autoradiographic methods, it is important to re-examine them for difficulties and problems which arise in their use.

First, there is the problem of chemical artifacts. Many metals, iron being an outstanding example, can cause blackening of a film by reacting chemically with the silver bromide. The fact that the film in all the above processes is wet makes the problem more difficult than the case of dry contact autoradiography; it is particularly serious in wet process autoradiography, in which a silver nitrate solution is present. Thin plastic coatings applied by dipping have been developed for use in the wet process and these have been applied to stripping film autoradiography with good results. The plastic film produced is 1-3 microns thick and quite impervious to any of the solutions used. It is essential, however, that the surface be well polished and continuous. The separation of the surface and film leads to some loss of resolution, but no method has as yet been developed to avoid this.

A second problem is dimensional distortion. The stripping films, although 5 microns or less in thickness when dry, swell to 40 microns when wet. In addition, if the directions supplied by the Kodak Company are followed, in which the film is floated on water and then picked up on the specimen, a layer of water is trapped between the film and the specimen surface.

Drying times of several hours have been measured for the stripping film process. Thus if a specimen contains enough radioactivity to produce an image in a few hours, and this is not uncommon in metallurgical work, the exposure time will elapse while the film is separated from the specimen and is swollen. The resulting resolution is naturally poor. This situation has been improved by drawing off excess water with filter paper after the film is in place. Also, rather than float the film on water, a few drops of water are placed on the metal surface and the film simply placed face down on the little droplets. The film absorbs the water, swells, and adheres to the surface. Another method used successfully for rapid removal of excess water is vacuum dessication. However, this accentuates the problem of film peeling, which is discussed in detail later.

The wet process is also subject to distortion of this nature, but it is much less severe. By a change in the amount of collodion used in the first coating solution, the wet film is kept to less than 5 microns when wet and less than 1 micron when dry. The dry dimension is not too important since, in this process, the exposure takes place while the specimen is in a silver nitrate solution and therefore the film is wet. A modification of the process so that the exposure will take place while the film is dry and very thin is under study.

A third problem is film shifting and peeling. It has been found that as the stripping film dries, it often curls and peels off the surface. Extreme care in temperature and humidity control is necessary to prevent this. We have not yet been successful in eliminating it, and recent information from the Kodak Research Laboratories indicates it is a common problem.

Far more serious is the problem of film shifting. In this case the film does not peel off, but during development it loosens slightly, shifts a small distance, and then adheres to the surface again. The resulting autoradiograph looks perfectly good but actually shows radioactivity where it does not exist in the specimen and vice versa. This is particularly striking in Figs. 18 and 19, although it is shown on others as well. In that case the film shifted about 1 millimeter to the right, resulting in complete confusion especially in the high magnification fields. The general pattern and direction of shift are seen most clearly in Fig. 18, where the heavy silver deposits resulting from radiation filtering up through rolling cracks in the specimen can be compared directly with the cracks in the metal.

Subbing solutions to prevent this, as well as peeling, are recommended by British Kodak, but using the chrome alum gelatin solution given in their instructions produced a 40-micron layer between the film and the surface. More work on this is needed but it is obvious that any subbing solution will spoil resolution by increasing the specimen film spacing.

In some new preliminary tests made with the Ilford G-5 emulsion painted on the surface of a Saran-coated microscope slide, the emulsion layer peeled and curled on drying after development and fixing. However, this is the result of only our first attempts to use this material.

By its nature, the wet-collodion process, in which the radiation-sensitive layer of collodion and silver bromide is formed on the surface being studied, is not subject to difficulty with film shift or peeling.

METALLURGY

The fundamental evaluation of autoradiography as a research method in metallurgy can be made only on the basis of studies of specific problems. Four such problems are being studied and are in widely varying stages of progress. The first is a study of bismuth distribution in copper, in cast alloy material, and after diffusion of bismuth from the surface of pure copper. The second is a study of hydrogen (tritium) in copper-base alloys to determine the mechanism of hydrogen embrittlement. The third is a study of nickel diffusion in iron. The fourth is the determination of effect and position of cerium in nodular iron. The first is nearing completion, the second is well started, the third is just begun, and the fourth is still in the discussion and planning stage.

1. Copper-Bismuth Systems (Professor M. J. Sinnott and Mr. S. Yukawa)

a. Diffusion of Bismuth into Copper. Liquid-solid grain-boundary diffusions are known to occur in several metallic systems, including copper-bismuth, iron-copper, and nickel - nickel sulfide. In the past satisfactory data have not been available on these systems, although they are of considerable industrial interest. Because the copper-bismuth system is experimentally the simplest, work has been concentrated on this binary. While these systems are not a common occurrence, their diffusion mechanism is undoubtedly similar to other structure-sensitive diffusion processes of the solid type, and the information would be of interest in this field.

Further, data on the solubility of bismuth and copper are quite controversial due to the difficulty in trying to trace the presence of small amounts of bismuth in copper. The maximum solubility is believed to lie between 0.01 and 0.001 weight per cent. X-ray measurements are not of sufficient accuracy to determine the exact solubility, and the metallographic techniques are of questionable value. Generally, it is believed that the presence of bismuth in copper induces brittleness, due first to the insolubility of the bismuth in copper, and second to its presence as a film at the grain boundaries. Alloying is believed to inhibit the effect of bismuth by changing the surface tension at the grain boundaries and, thereby, the wettability of the boundaries by the bismuth. The difficulty in the past has been that the metallographic techniques are not reliable, some investigators reporting complete boundary encirclement while others claim that the evidence is illusory and the appearance of the grain-boundary phase is merely due to differential etching of the boundaries.

In the work done to date diffusion has been studied by allowing radioactive bismuth to penetrate into more or less columnar-structure copper

produced by a suitable casting technique. The bismuth-210, a beta emitter, is placed in a small cup drilled in one end of a copper block about 1/2 inch square by 1 inch long. The diffusion is allowed to proceed at the desired temperature in an atmosphere of purified hydrogen. Results to date show that the bismuth penetrates through the grain boundaries of copper to a considerable depth below the bismuth-copper interface. Exceptionally good autoradiographs can be made using the alpha radiations of the polonium daughter resulting from the radioactive decay of bismuth. The decay scheme for bismuth-210 is shown below:

$$Bi^{210} \xrightarrow[5\ \text{days}]{} Po^{210} + \text{beta} \xrightarrow[140\ \text{days}]{} Pb^{206} + \text{alpha} + \text{gamma} .$$

Figure 1 is a 500-diameter photomicrograph of a stripping film autoradiograph over a grain boundary showing the presence of alpha activity. The area shown in this figure is at a depth of some 0.15 inch below the copper-bismuth interface, in a specimen held at 1200°F for 60 hours. This same boundary, when examined by regular metallographic techniques, does not show positive evidence for either the presence or absence of bismuth.

The autoradiograph shows definite evidence for the presence of the polonium, the radioactive daughter of bismuth. The short half-life (5 days) of bismuth presents a serious difficulty in evaluating the results of diffusion studies. Since the activity detected by the autoradiograph in Fig. 1 is actually from polonium, the question then arises as to whether the polonium in the grain boundary actually was bismuth that had diffused in and changed to polonium, or whether it diffused in as polonium. A handicap in resolving this question is the low sensitivity of stripping film to the beta radiation which would be associated with the bismuth itself. It is planned to resolve this problem in a number of ways: first, if possible, the bismuth will be purified chemically just before being used in the diffusion study so as to remove all traces of polonium. By making the autoradiograph very promptly after the diffusion run has been completed, the polonium activity will be kept to a minimum, and positive evidence for bismuth should be obtained. Second, other methods will be used to help check results of the autoradiograph. A series of diffusion specimens using nonactive bismuth is being prepared for measurement of the penetration of bismuth that can be detected by the optical and electron microscopes. An identical series will be made using radioactive bismuth, and measurements obtained by autoradiography will be compared to results obtained previously. This will serve as a means of determining the relative sensitivity of each method.

In all this work, wrought or vacuum-cast copper will be used to avoid difficulties experienced previously with porosity in the copper

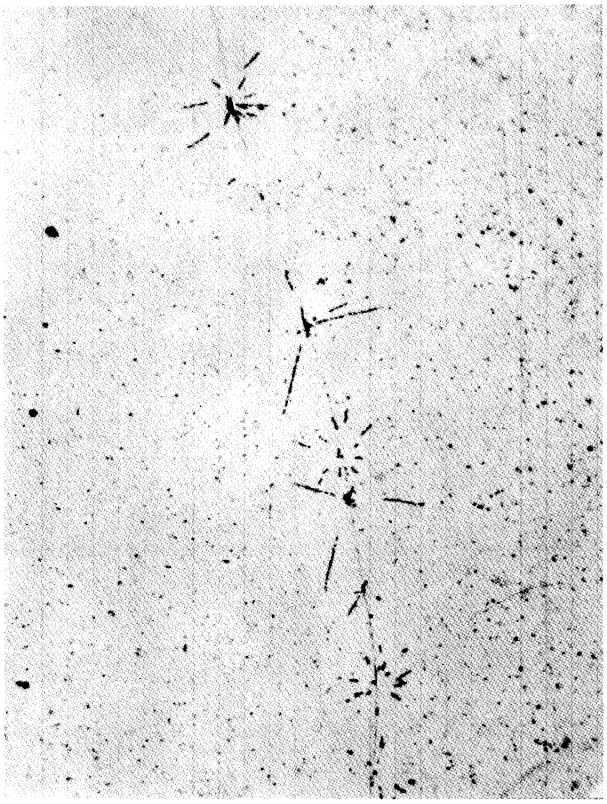


Fig. 1

Grain-Boundary Diffusion of Bismuth in Copper

500x Photomicrograph of Stripping Film Autoradiograph Over Area 0.15 in. from Diffusion Interface.

Diffusion Temperature:	1200°F
Diffusion Time:	60 hrs.
Exposure Time:	114 hrs.

specimens. It is anticipated that further studies will show that diffusion of bismuth along grain boundaries of copper is influenced in some manner by the relative orientation of the adjacent grains that form the boundary. If such a situation is found to exist, studies involving the diffusion of bismuth in copper having grains of known or preferred orientations will be made.

b. Bismuth Distribution in Copper-Bismuth Alloy. A series of studies was made to determine the effect of working and heat treatment on the distribution of bismuth in copper-bismuth alloy. First, a parent melt of copper-bismuth alloy containing 0.02-0.03 per cent of bismuth (Bi^{210}) was made. Geiger counter measurements showed some segregation of the bismuth toward the top of the casting. A sound portion of the casting was cold-rolled to 54 per cent of its original thickness. Specimens from this cold-rolled stock were subjected to annealing treatment of one-half hour at temperatures ranging from 500 to 1700°F. Photomicrographs, contact autoradiographs, and stripping film autoradiographs were made of these specimens so as to follow the changes in structure and bismuth distribution. The structure of the as-cast metal can be seen from the photomacrograph shown in Fig. 2. A 10-diameter enlargement of the contact autoradiograph is shown in Fig. 3.

The autoradiograph shows several distinct features characterizing the bismuth distribution. First, the very dark continuous areas evidently are the grain boundaries; considerable segregation of bismuth is indicated at these boundaries. Since bismuth is practically insoluble in solid copper, this is to be expected. Second, the discrete black spots indicate a conglomeration or concentration of the bismuth within the matrix of the metal. The possibility of a bismuth-polonium separation during solidification has been considered, but it is not believed to be the cause of this observed concentration. Third, the contact autoradiograph shows an overall diffuse but continuous activity pattern, indicating some type of a subgrain or dendritic distribution of the bismuth. Unfortunately, a stripping film autoradiograph of this specimen was not successful. After cold-rolling 54 per cent, a photomacrograph and a contact autoradiograph of a suitable area were made. These are presented as Figs. 4 and 5. To obtain more detailed information, a 75-diameter and a 500-diameter photomicrograph of a stripping film autoradiograph of this specimen were made and are shown in Figs. 6 and 7. The cold-rolling operation has produced fissures and cracks at the grain boundaries of the cast structure. A contact autoradiograph shows intense radioactivity over these cracks due to the tendency of subsurface radiation to escape along low-density paths, and also possibly due to bismuth concentration in the grain boundary which was the original site of the crack.

In Figs. 6 and 7 it can further be observed that the bismuth concentrates along the as-cast grain boundaries and also that some of the

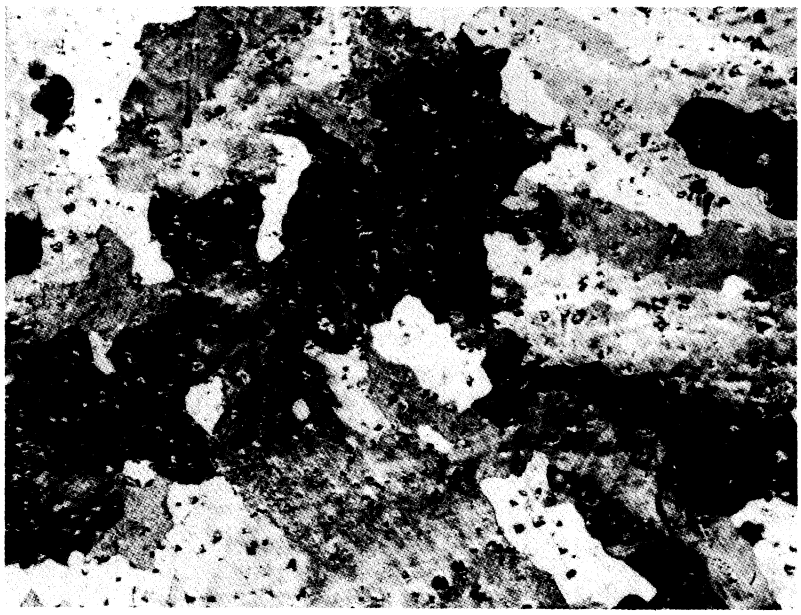


Fig. 2

10x Photomacrograph of Bismuth-bearing Copper, As-Cast

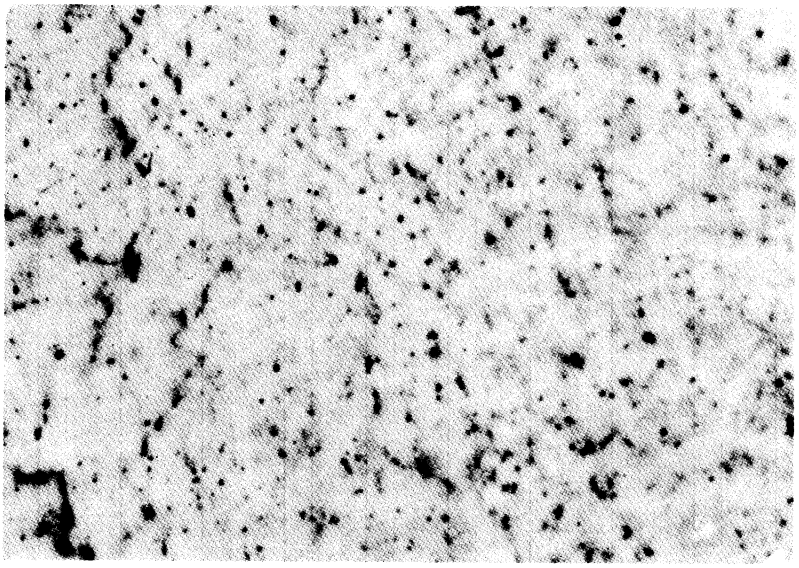


Fig. 3

10x Enlargement of Contact Autoradiograph of Area Similar to Fig. 2

Exposure Time: 72 hrs.

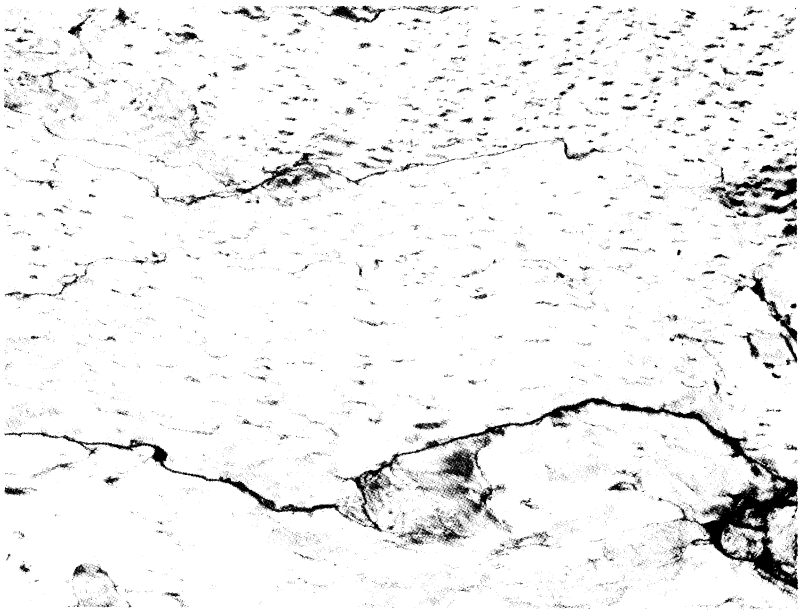


Fig. 4

10x Photomacrograph of Bismuth-bearing Copper Cold-Rolled 54%

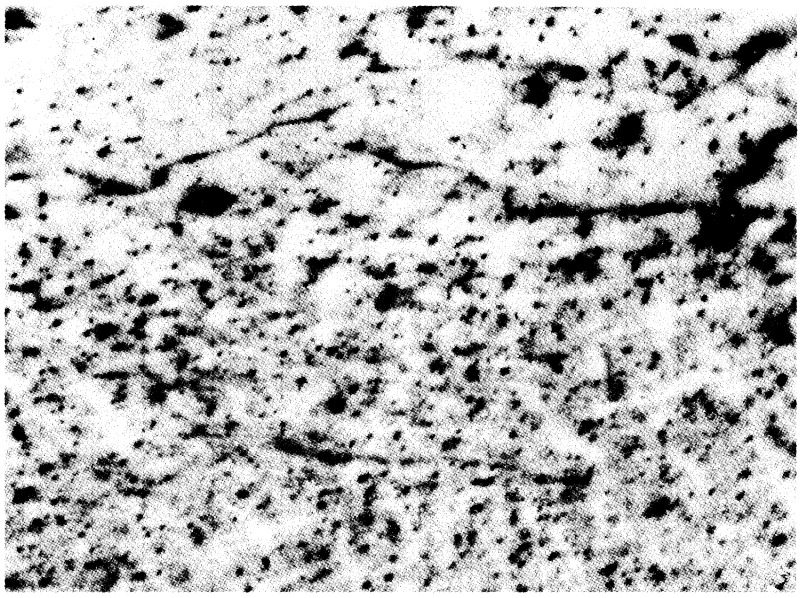


Fig. 5

10x Enlargement of Contact Autoradiograph of Area Identical to Fig. 4 (except Fig. 5 is mirror image of Fig. 4)

Exposure Time: 100 hrs.

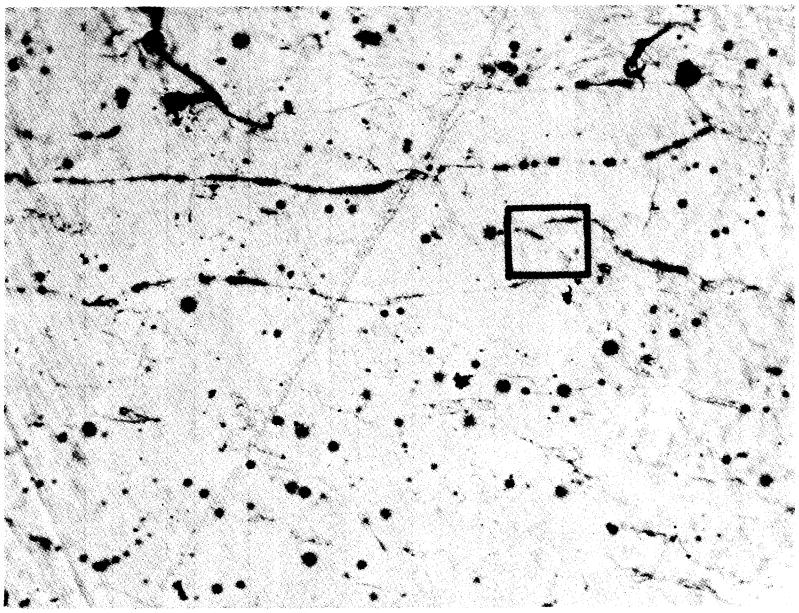


Fig. 6

50x Photomicrograph of Stripping Film Autoradiograph of Bismuth-bearing Copper Cold-Rolled 54%

Exposure Time: 18 days

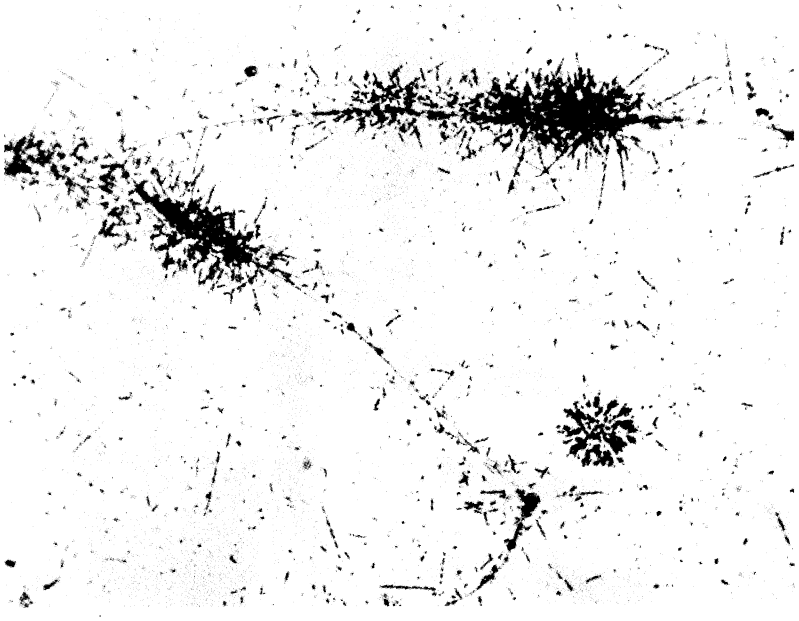


Fig. 7

Area Marked in Fig. 6 at 500x.

bismuth is distributed within the grains. As in the as-cast specimen, the contact autoradiograph of the cold-rolled material shows a subgrain or dendritic distribution of bismuth. However, the stripping film autoradiograph does not show this effect at all. The probable explanation of this anomaly is that the metallographic plate used for the contact autoradiograph is far more sensitive to beta radiation than the stripping film used in the high-resolution studies. As a result, for the time of exposure used (about 72 hours), only the polonium is recorded in the stripping films.

An interesting feature of Fig. 7 is the very compactly shaped alpha star. This star is attributed to a concentration of bismuth (polonium), probably in a subsurface grain boundary. There is no surface structure to correlate with the star and the track angles indicate that the track origin is below the surface plane.

In this autoradiograph there is no evidence of film slippage such as appears in some of the subsequent stripping film autoradiographs.

A similar study of a specimen annealed at 500°F for one-half hour after cold-rolling is shown in Figs. 8, 9, 10, and 11. These figures are respectively a 10-diameter photomacrograph, a 10-diameter contact autoradiograph enlargement, and stripping film autoradiographs at 75 and 500 diameters. At this temperature recrystallization has occurred, creating new grain boundaries, but the bismuth does not appear to have migrated preferentially to these new boundaries. This is shown in Figs. 10 and 11, where the activity is noticeable within the grains as well as at the boundaries. This stripping film autoradiograph again shows activity from subsurface concentrations of bismuth as previously noted. The contact autoradiograph is not very much different from the cold-rolled specimen. Here again it must be noted that the contact autoradiograph and the photomicrograph are mirror images of each other. Any changes in bismuth distribution are not easily discernible from the contact autoradiograph.

A similar series of pictures has been prepared for specimens annealed at 800, 1100, 1400, and 1700°F. These are shown in Figs. 12 through 25; each picture has a title designating its annealing temperature. The stripping film autoradiographs of these specimens show that grain growth and some agglomeration of bismuth (polonium) have taken place with increasing temperature. However, even at 1700°F the preferential migration of the bismuth to the new grain boundaries in the copper is not apparent. The contact autoradiographs show no important changes up to 1700°F. The subgrain or dendritic activity pattern of the cast metals persists despite changes in grain structure and size. At 1700°F the subgrain activity pattern is practically gone. This could mean that the contact autoradiograph is actually more indicative of the true bismuth distribution due to its higher beta radiation sensitivity. However, the low resolution of the contact

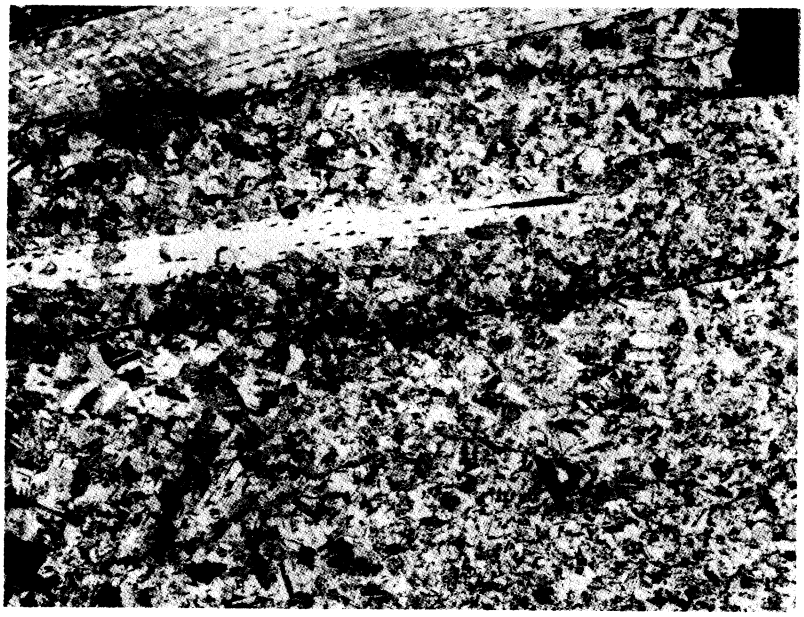


Fig. 8

10x Photomacrograph of Bismuth-bearing Copper Cold-Rolled 54%, Annealed 1/2 hour at 500°F.

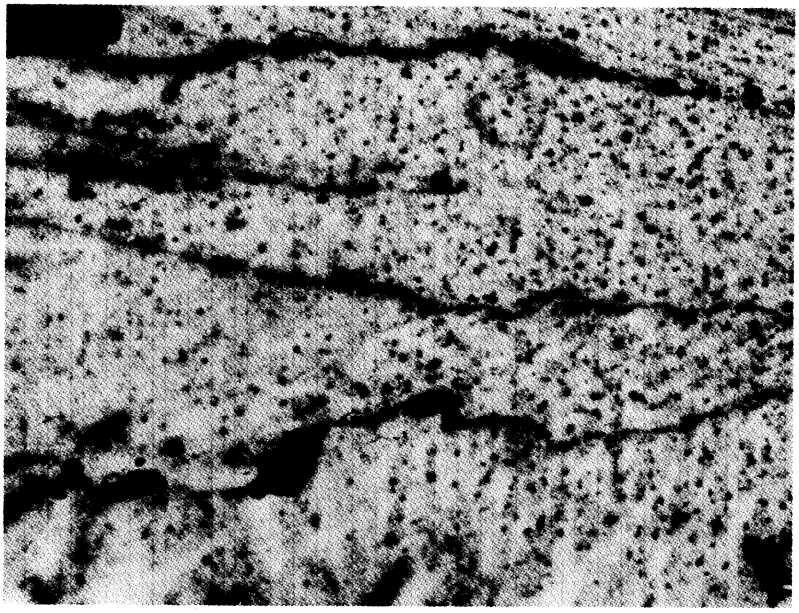


Fig. 9

10x Enlargement of Contact Autoradiograph of Area Identical to Fig. 8 (except for mirror-image relationship)

Exposure Time: 100 hrs.

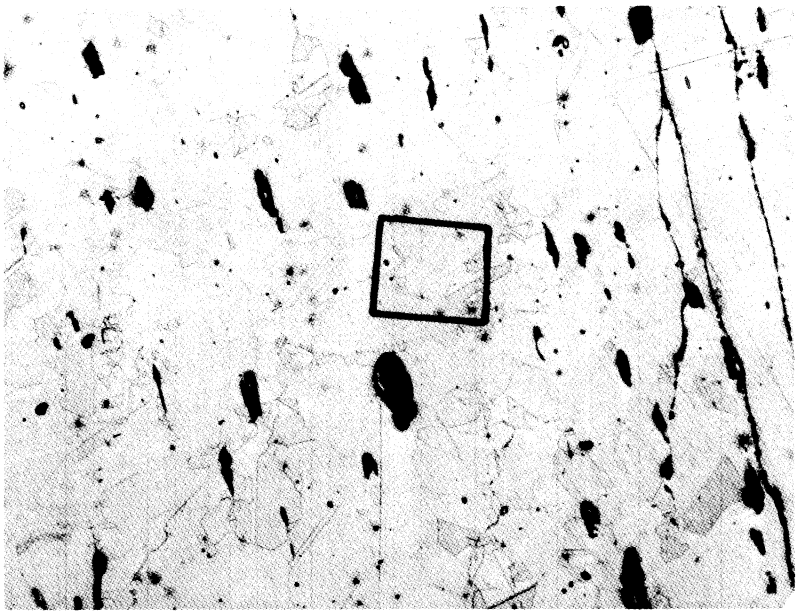


Fig. 10

75x Photomicrograph of Stripping Film Autoradiograph of Bismuth-bearing Copper Cold-Rolled 54%, Annealed 1/2 hour at 500°F

Exposure Time: 4 days

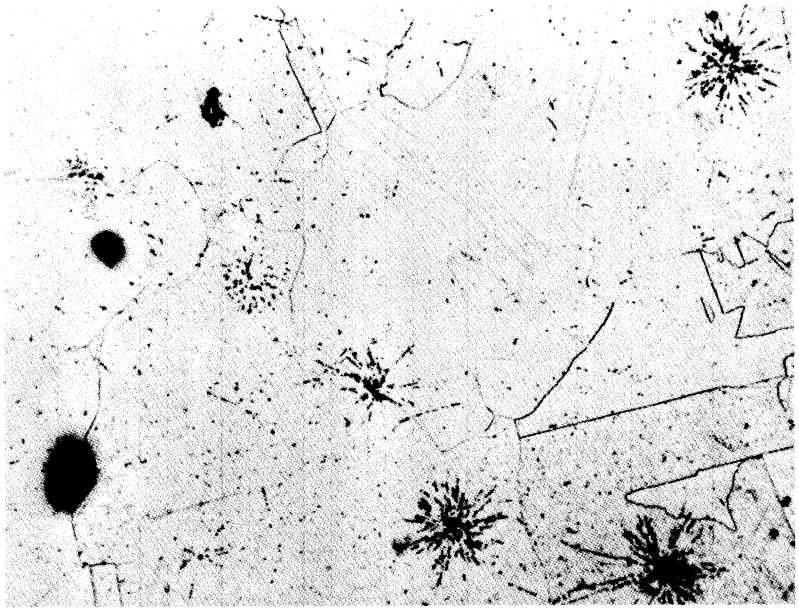


Fig. 11

Area Marked in Fig. 10 at 500x

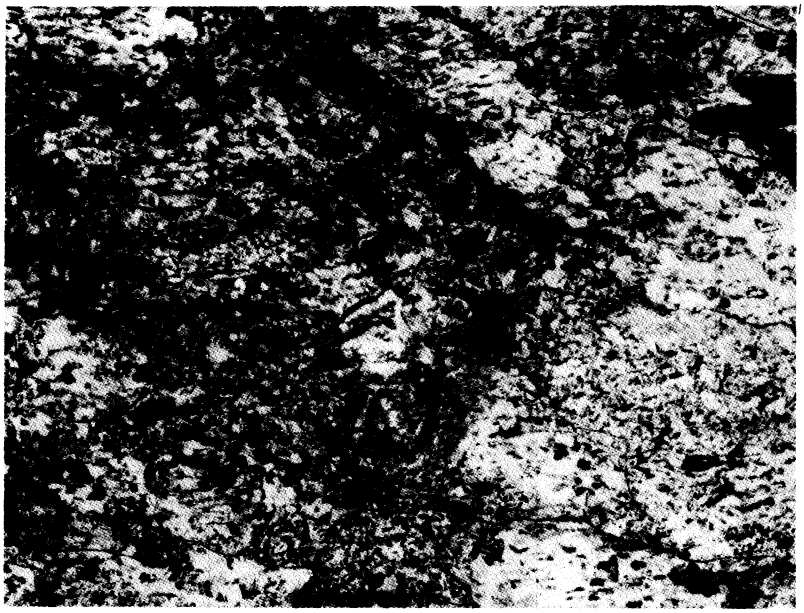


Fig. 12

10x Photomacrograph of Bismuth-bearing Copper Cold-Rolled 54%, Annealed 1/2 hour at 800°F.

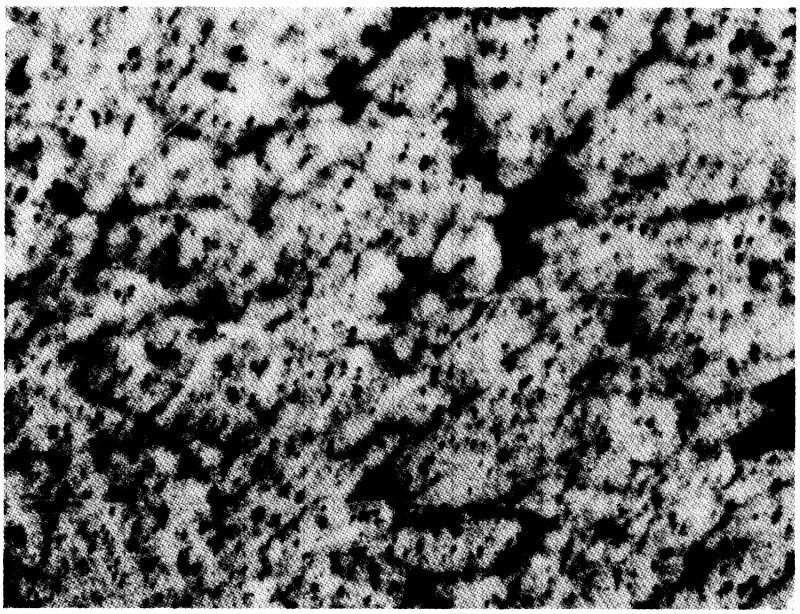


Fig. 13

10x Enlargement of Contact Autoradiograph of Area Identical to Fig. 12 (except for mirror-image relationship).

Exposure Time: 100 hrs.

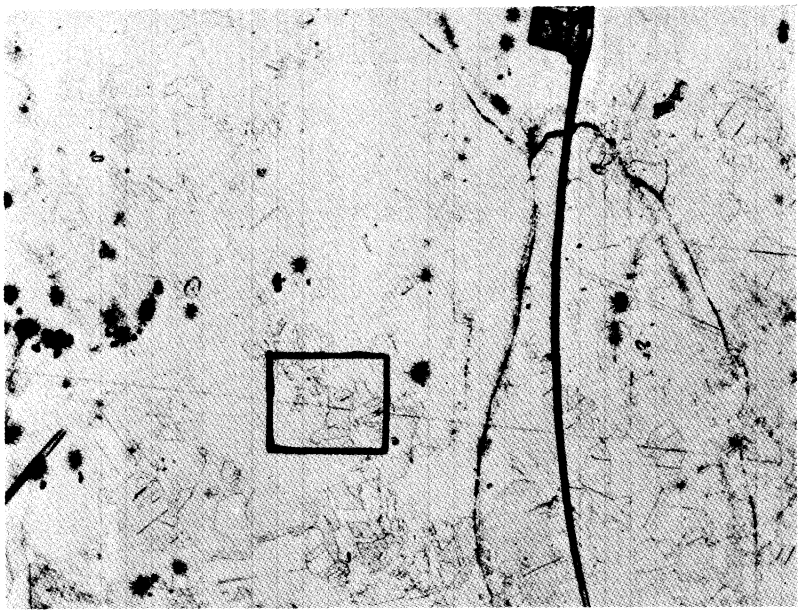


Fig. 14

75x Photomicrograph of Stripping Autoradiograph of Bismuth-bearing Copper Cold-Rolled 54%, Annealed 1/2 hour at 800°F.

Exposure Time: 19 days

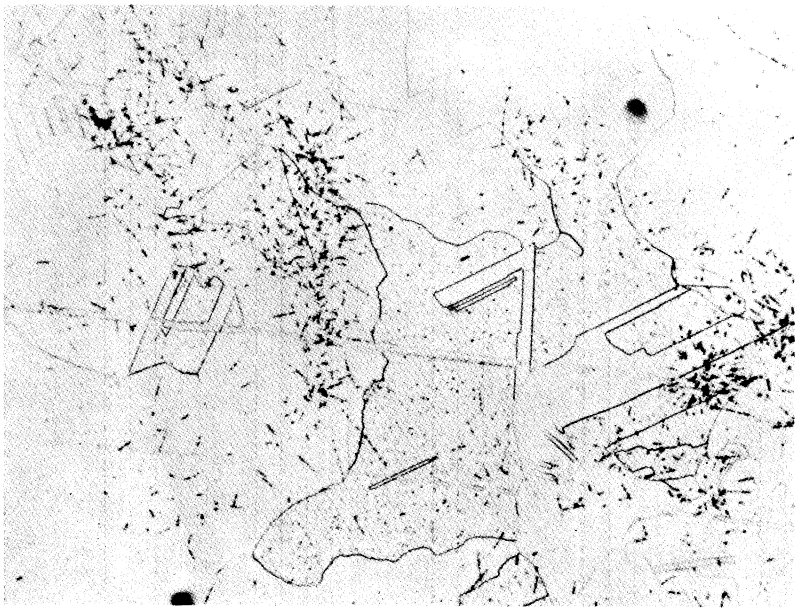


Fig. 15

Area Marked in Fig. 14 at 500x

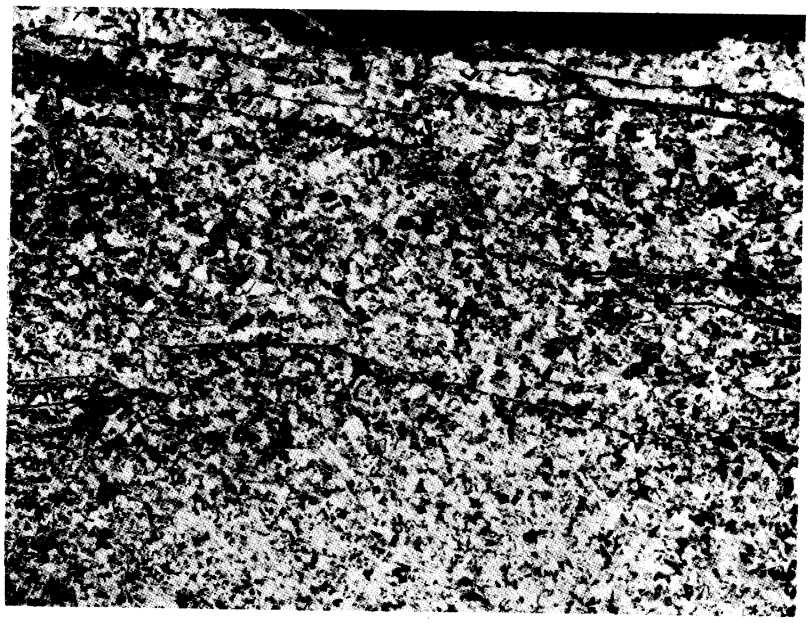


Fig. 16

10x Photomacrograph of Bismuth-bearing Copper Cold-Rolled 54%, Annealed 1/2 hour at 1100°F.

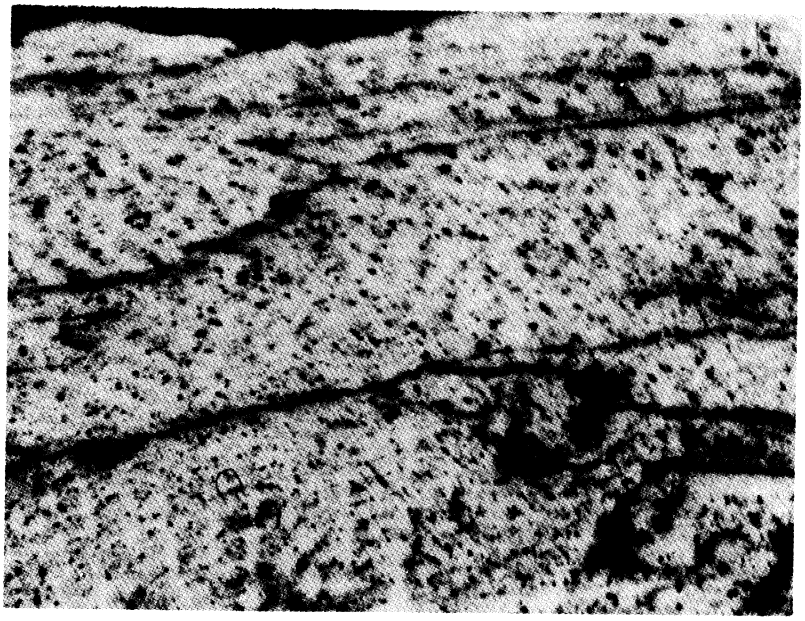


Fig. 17

10x Enlargement of Contact Autoradiograph of Area Identical to Fig. 16 (except for mirror-image relationship).

Exposure Time: 100 hrs.

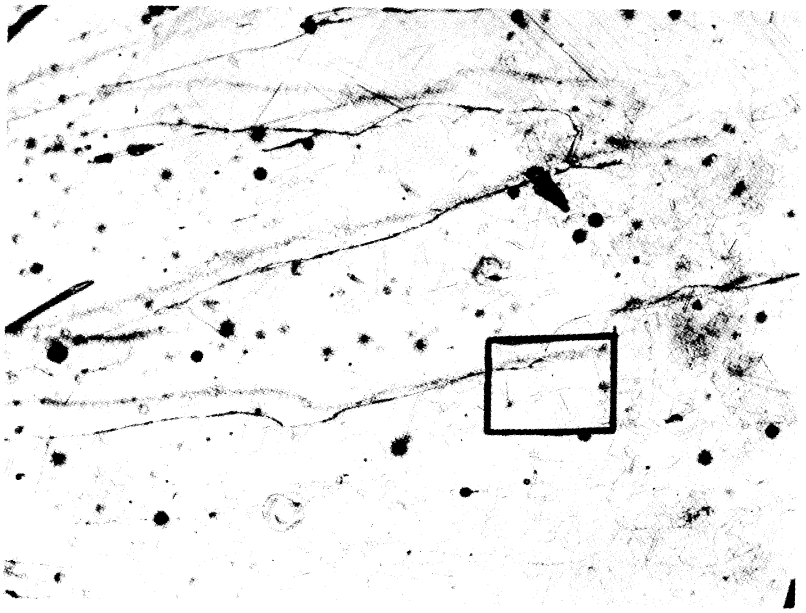


Fig. 18

75x Photomicrograph of Stripping Film Autoradiograph of Bismuth-bearing Copper Cold-Rolled 54%, Annealed 1/2 hour at 1100°F.

Exposure Time: 19 days

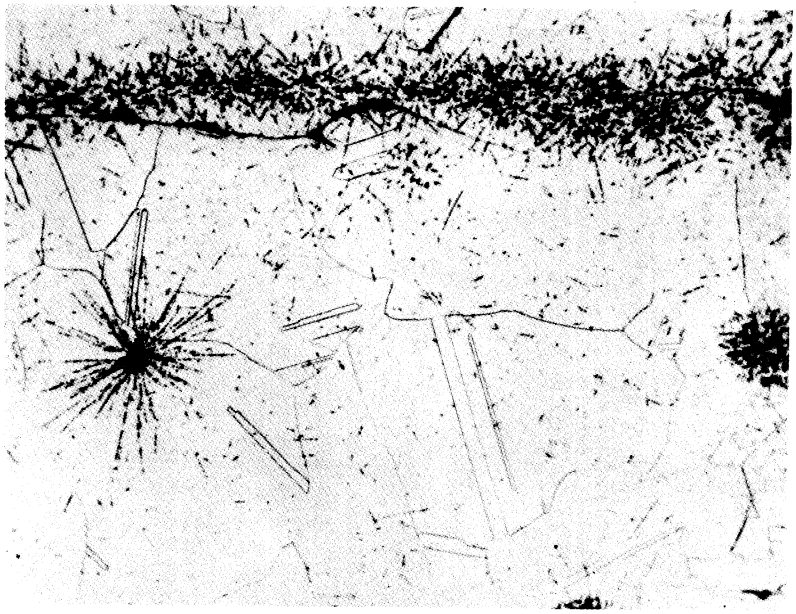


Fig. 19

Area Marked in Fig. 18 at 500x.

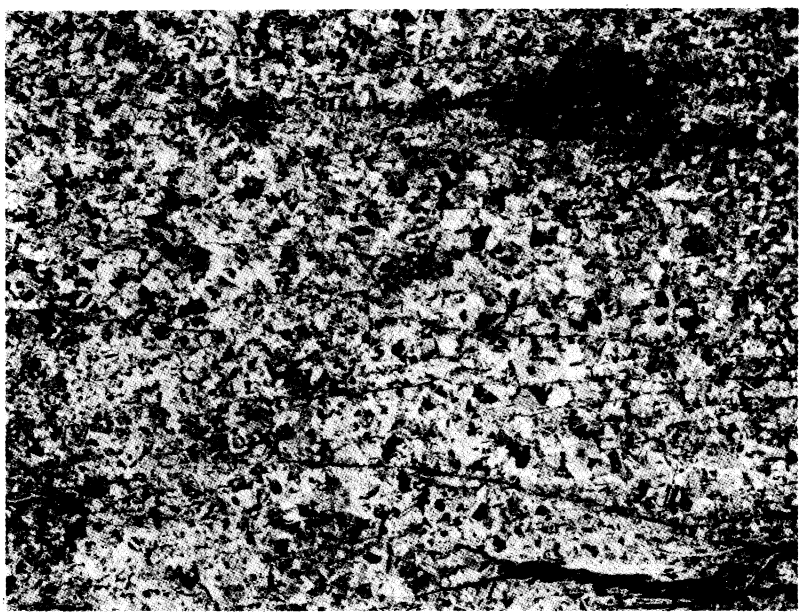


Fig. 20

10x Photomacrograph of Bismuth-bearing Copper Cold-Rolled 54%, Annealed 1/2 hour at 1400°F.

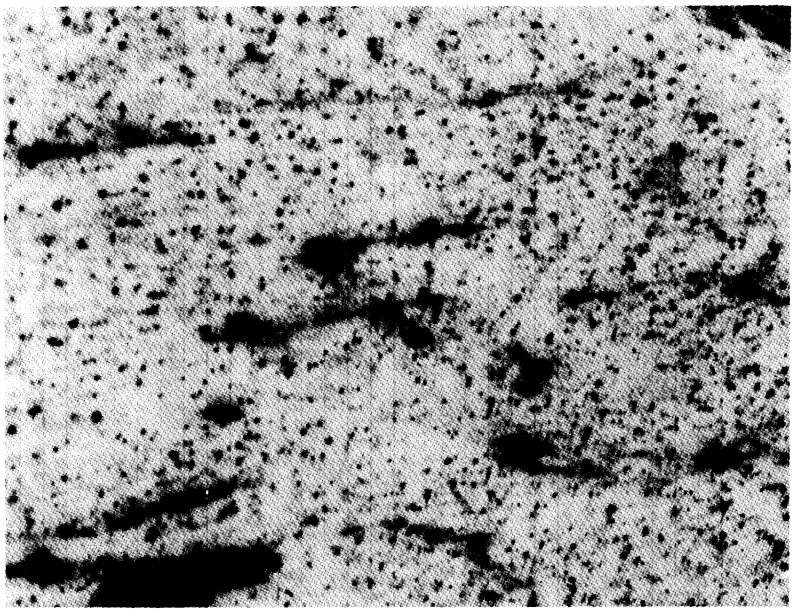


Fig. 21

10x Enlargement of Contact Autoradiograph of Area Identical to Fig. 20 (except for mirror-image relationship).

Exposure Time: 100 hrs.

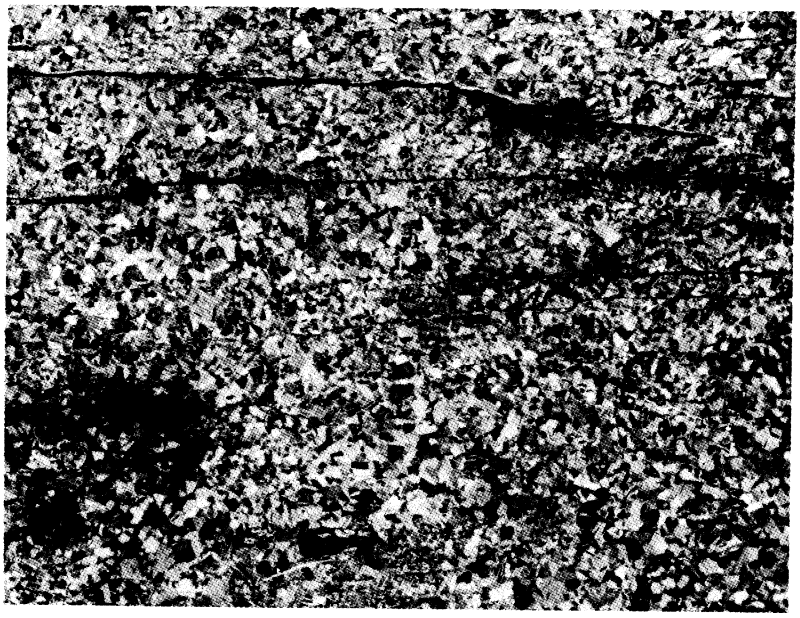


Fig. 22

10x Photomacrograph of Bismuth-bearing Copper Cold-Rolled 54%, Annealed 1/2 hour at 1700°F.

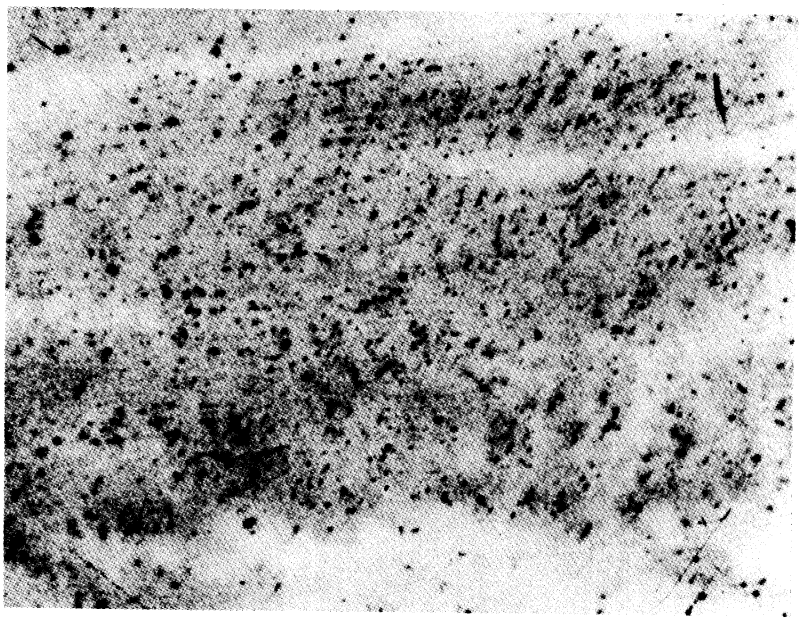


Fig. 23

10x Enlargement of Contact Autoradiograph of Area Identical to Fig. 22 (except for mirror-image relationship).

Exposure Time: 100 hrs.

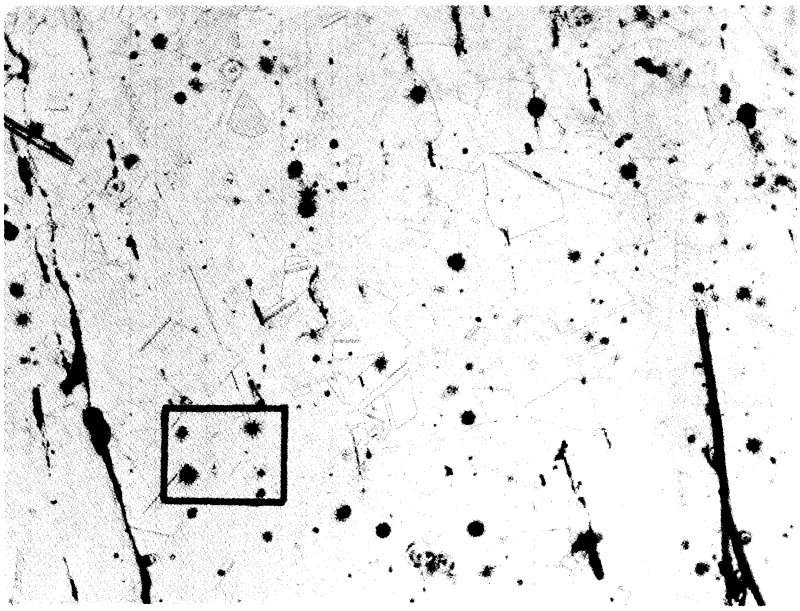


Fig. 24

75x Photomicrograph of Stripping Film Autoradiograph of Bismuth-Bearing Copper Cold-Rolled 54%, Annealed 1/2 hour at 1700°F.

Exposure Time: 18 days

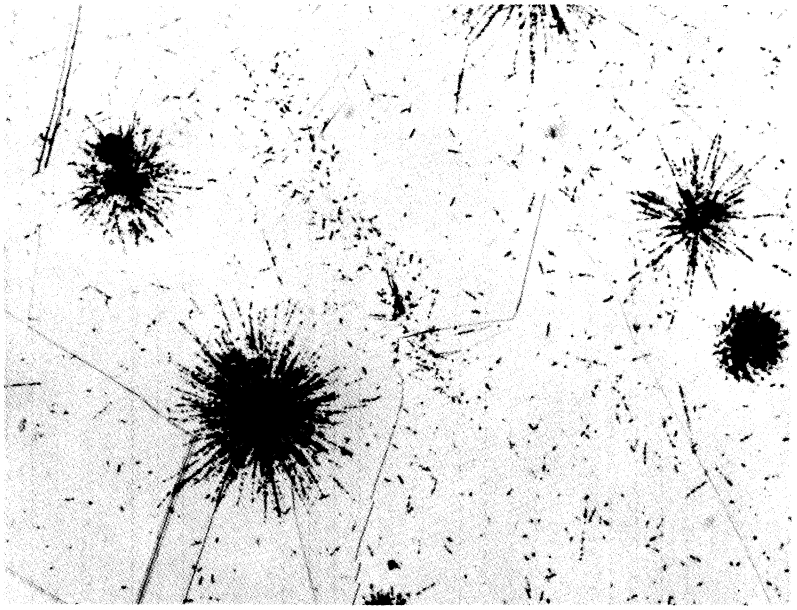


Fig. 25

Area Marked in Fig. 24 at 500x.

autoradiograph does not allow any definite conclusions in this respect. If, as the stripping film autoradiographs show, bismuth does not migrate preferentially to the new grain boundaries during recrystallization, it may be that bismuth-bearing copper is capable of more extensive cold reduction than is usually thought possible. By a light preliminary cold-rolling and recrystallization operation the bismuth will be redistributed away from the boundaries, allowing further cold reduction.

As discussed in the introductory section on autoradiography, serious difficulty has been encountered with slippage, shifting, and buckling of the autoradiographic stripping films during exposure and development. This is particularly noticeable in Figs. 14 and 15 and 18 and 19. These autoradiographs must therefore be interpreted with this factor in mind. From Figs. 14 and 18, the 75-diameter photomicrographs, a sufficient number of landmarks in both the autoradiographic film and the specimen beneath can be established so that fair correlation between the blackening in the film and the structure of the metal can be made.

2. Hydrogen in Copper-Base Alloys (Professor C. Upthegrove)

The major features of this problem were described in our May, 1952, Work Report. For purposes of continuity and convenience, parts of that report are repeated in the introduction below. New experimental work and results follow the introduction.

a. Introduction. The problem of gases in metals has been of interest to the brass and bronze foundrymen for many years. In recent years most foundrymen have come to the conclusion that, in general, better castings with superior mechanical and physical properties are obtained from melts made with oxidizing conditions or atmospheres than those made with reducing atmospheres. Further, the general opinion points to hydrogen as the gas which is largely responsible for defects tracable to variations in melting conditions. The variations in tensile strength and elongation and in density when an 85-copper 5-tin 5-lead 5-zinc alloy is melted under the same conditions, except for the furnace atmosphere, are typical of variations which may be found with other copper-base alloys. Tensile strength may vary from 18,000 to 40,000 psi, elongation from 10 to 35 per cent, and specific gravity from 8.4 to 8.9 as the melting or furnace atmosphere is varied from strongly reducing to strongly oxidizing.

While the furnace atmospheres are designated as reducing and oxidizing, it has been pointed out that hydrogen is considered as the main offender in the reducing atmospheres. It has a measurable solubility in copper in the solid state and is readily soluble in the liquid state. It may be picked up by the melt from the furnace atmosphere and from moisture

in incompletely dried or preheated ladles. Where water vapor is dissociated by contact with molten metal, the atomic hydrogen is readily taken up by the melt.

When the molten metal containing the hydrogen is removed from the melting furnace and poured, some of the gas is liberated previous to and during solidification. Some of the hydrogen remains in the solidified metal, some as trapped bubbles and the remainder in solution. In the case of the oxidizing atmosphere, presumably little or no hydrogen is present in the melt, and consequently little should be retained in the solid state. The "gassed" metal will show shrinkages, sometimes sufficiently large to be recognizable by eye alone, or it may show microporosity in which the voids are so small as to be recognizable only with the aid of the microscope, or the evidence of the gassing may be a more or less fine or lacy type of intergranular shrinkage. Some investigators have reported a difference in the shape of the free lead particles in the leaded alloys depending on whether or not the metal was "gassed". These phenomena appear to be definitely related to the absence or presence of hydrogen in the melt, and in turn to the variations in tensile strength, elongation, and density.

In attempting to provide a rapid and ready means of checking the quality of the melt, as affected by furnace atmosphere, it also has been shown that the fracture characteristic of the cast metal gives a reasonably good indication of the melt quality, as measured by the tensile strength, elongation, and density.

The questions developed by the work on gases in brasses and bronzes are (1) in what way does the hydrogen bring about the variations in tensile strength, elongation, density, and appearance of the fracture characteristic? and (2) is the distribution of the hydrogen remaining in the metal the important factor in determining the final properties?

b. Experimental Work. To obtain maximum control over the environmental conditions, it was decided to make the first test on copper-tin bronze melted in a controlled-atmosphere induction furnace. An 89-copper 11-tin alloy was used rather than a conventional brass in order to avoid vaporization and condensation of zinc and lead from the brass on the furnace wall. The 89-11 bronze is as susceptible to hydrogen absorption and its detrimental effects as is 85-5-5-5 brass. Atmosphere control, in this first test, consisted of evacuating the furnace, sealing it off, and then releasing tritium gas into the evacuated volume. To produce atomic hydrogen for the penetration of the hydrogen into the melt, a pair of electrodes was introduced in the furnace over the melt surface. By setting up a high-frequency discharge in the hydrogen during the melting the amount of atomic hydrogen present and available for diffusion into the melt was increased over that normally present.

A detailed drawing of the controlled-atmosphere furnace used is shown in Fig. 26. A photograph of the completed furnace suspended in the heating coil is shown in Fig. 27 and a special safety hood in which the furnace assembly was enclosed during the melting operation is shown in Fig. 28. The hood was exhausted at the roof of the building in which the work was done. The experimental procedure following in making the melt was:

1) With the furnace partially assembled, 160 grams of bronze (89-Cu 11-Sn) was placed in the graphite crucible (No. 13).

2) The special capsule holder with tritium (No. 3) was hung on a glass hook (No. 1) projecting from the furnace wall.

3) The furnace glass assembly was then completed and the glass envelope sealed.

4) Through the outlet (No. 5), the furnace and gas collection bottle (No. 6) containing palladium foil (No. 7) were pumped down to 5 microns of mercury pressure with a rotary vacuum pump.

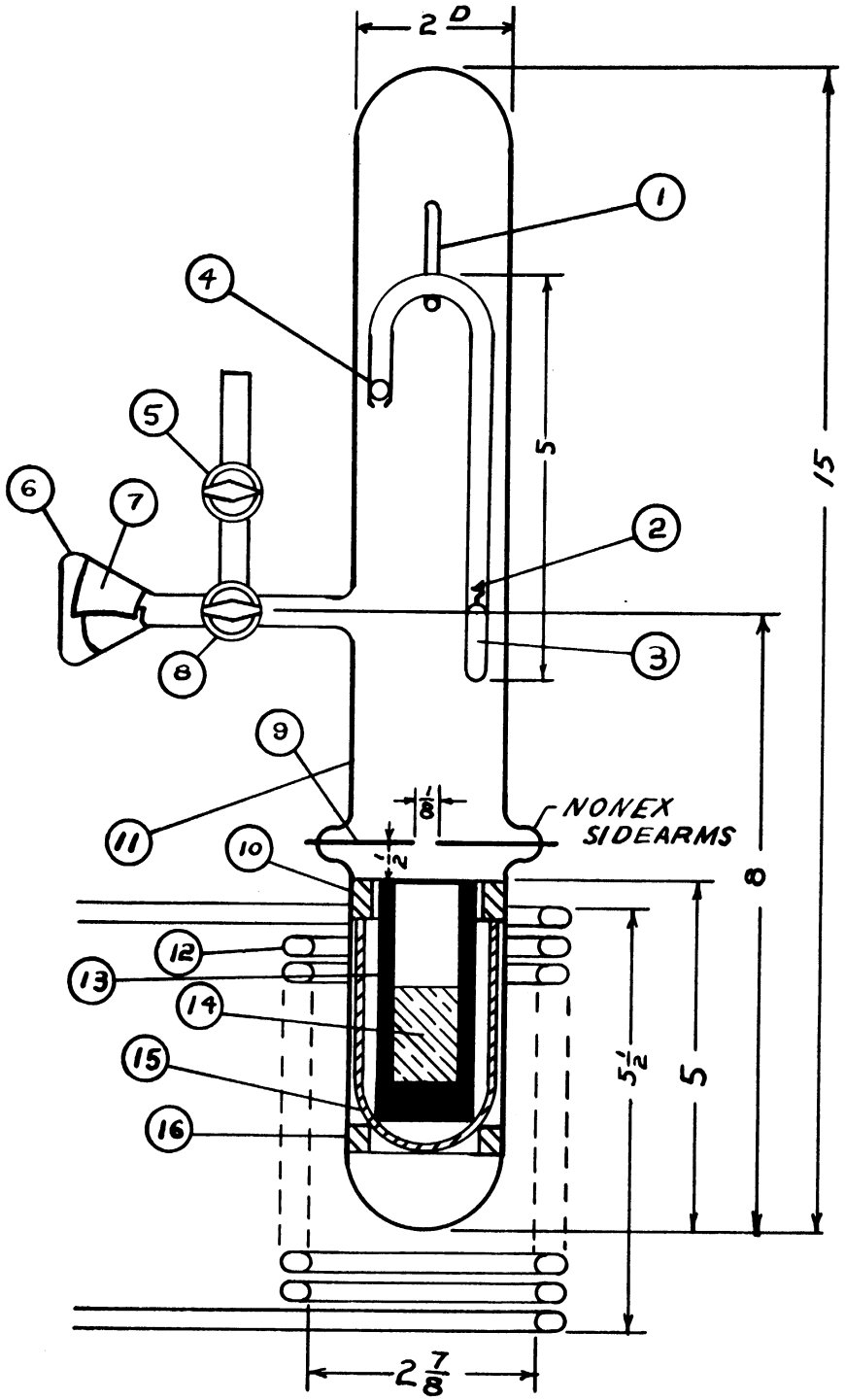
5) Stopcock No. 5 was closed, sealing the system, and three-way cock No. 8 was positioned so that the gas collection bottle No. 6 was isolated from the furnace.

6) The break-off tip (No. 2) of the tritium capsule (No. 3) was broken by dropping the steel ball (No. 4) in the special capsule container on it. The ball was carried from its resting position over the top of the capsule container by a magnet outside the furnace wall. Tritium gas was then released into the whole furnace. For this test, 10 millicuries of tritium gas was used.

7) The water-cooled induction coil (No. 12) was then excited with high-frequency current, with the power input adjusted so as to bring the bronze to the melting point in about 3 minutes.

8) When the bronze was melted, a Tesla coil exciter was applied to the internal arc gap (No. 9) so as to dissociate some of the molecular hydrogen. The discharge was maintained until the melt had cooled.

9) As soon as melting had begun, the power input was increased so as to superheat the melt. In 4 minutes the temperature reached 2250°F, where it was maintained for 7 minutes.



KEY TO FIGURE

1. Glass hook
2. Breakoff tips
3. Tritium capsule in 11-mm tube
4. 1/4-inch diameter steel ball
5. One-way stopcock
6. 25-ml flask
7. Palladium foil, 36 cm^2
8. Three-way perpendicular stopcock
9. 22 gauge tungsten-wire electrodes
10. Alundum ring
11. 2-inch pyrex tube about 1/8 inch thick
12. Induction coil, 20 turns
13. Graphite crucible, 1-3/8 inch O.D. by 1 inch I.D. by 3 inches long by 1/2 inch thick at bottom
14. Bronze charge, 160.5 gm (10% tin)
15. Alundum holder
16. Alundum ring

Note: Mica sheet covers the inside of the 2-inch tube from the bottom to the electrodes.

Scale: 5/12 inch = 1 inch

Fig. 26. Atmosphere Furnace (Pyrex)

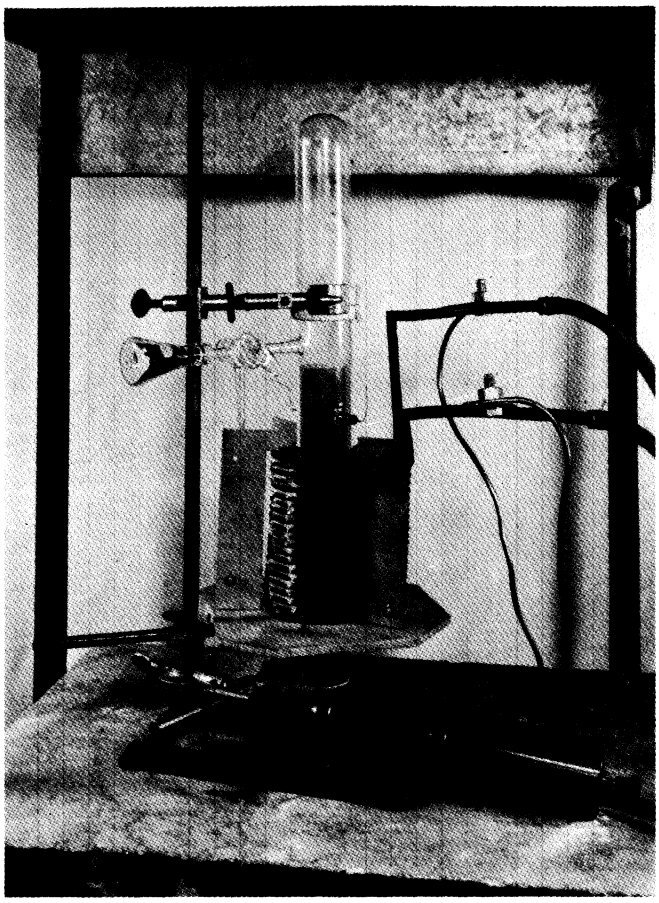


Fig. 27

Controlled-Atmosphere Furnace Assembly. The round dark cylinder with a metal tip, lying on the table, is the high-frequency exciting coil. The crucible enclosed in the Pyrex 2-inch sealed tube extends from about 1 inch from the base to the level of the second copper coil from the top.

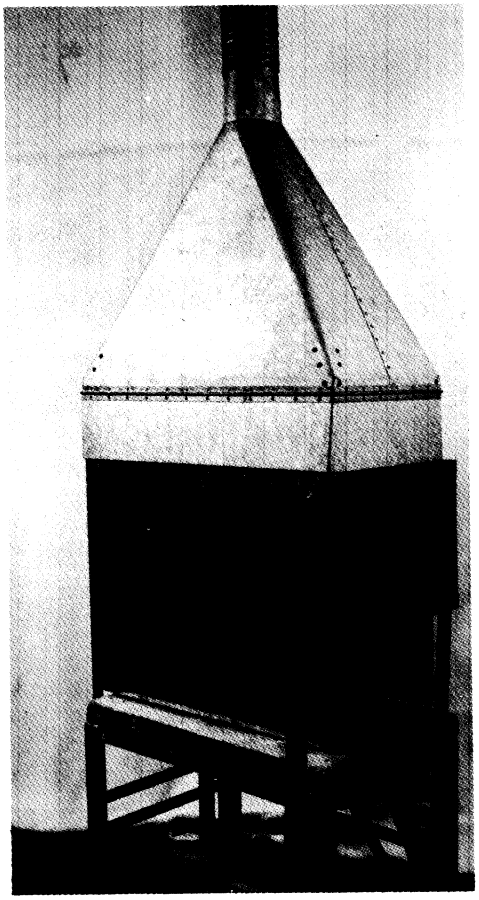


Fig. 28

Exterior View of the Safety Hood Surrounding the Furnace. The exhaust line at the top is attached to the suction end of a blower which discharges outside the building. The dark lines leading in are water lines. Electrical contact is made by mercury cups in the table top. One of the coil wires may be seen sticking into one of the cups.

During this period, a dark "smoke" was observed whirling in the tube, and some of it settled out on the glass wall.

10) The input to the induction coil was cut, but water was kept running in the coil to increase the cooling rate of the melt somewhat. To provide some directional cooling, the furnace tube was raised so that only the bottom half of the crucible extended into the coils used for cooling. This was done to help promote freezing from the bottom up.

11) When the furnace was cool enough to handle, valve No. 8 was rotated so that the gas bottle (No. 6) was connected to the furnace. Using a gas flame, the bottle was heated until the palladium foil reached about 500°C; then it was allowed to cool. A large part of the free tritium was then adsorbed by the palladium foil.

12) The furnace assembly was then transferred to a chemical hood designed for work with radioactive materials. The furnace section was opened to the air and then broken so as to permit removal of the ingot. This operation was carried out in the Phoenix Project Hot Laboratory.

Preliminary runs were made first using the same equipment but with a regular hydrogen atmosphere at 10-20 millimeters of pressure in order to establish melting conditions such as power input and time required to reach and maintain temperature conditions within the melting unit.

c. Results. On breaking the furnace to remove the bronze ingot, smears were made of the inside surface of the glass walls. These were checked in a windowless flow counter and by their high activity certified that the tritium had been released into the furnace.

The bronze ingot, which was about 1 inch in diameter and 2 inches long, was then cut in half longitudinally, using a well cooled cut-off wheel. Some surface chips from this cutting operation were also tested in the flow counter, but these showed activity only slightly above background.

One of the freshly cut sections was polished and etched and then studied metallographically. The surface appearance is shown in Fig. 29. The lacy structure is typical of that attributed to adsorbed intergranular hydrogen. This structure is predominant near the top of the ingot, the last part to freeze.

The two sections were then placed in contact with a Kodak Metallographic Plate in the Phoenix Project Autoradiography Laboratory, and

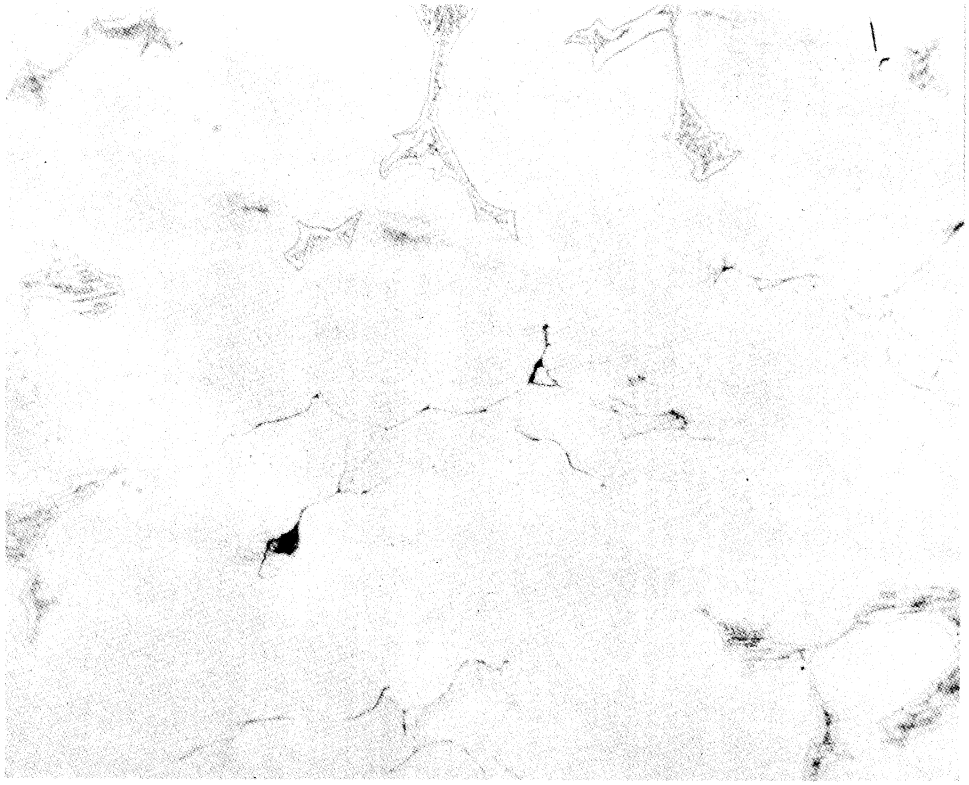


Fig. 29

Typical "Steam" Reaction Microporosity in Copper-Tin Alloy Exposed to Atomic Hydrogen (Tritium) in Controlled-Atmosphere Furnace.

Dichromate etch, 500x

exposed for 64 hours. Both sections produced weak generalized blackening of the plate over their area of contact. There was no concentration of activity associated with the lacy structure at the top of the ingot.

Attempts to repeat this result with 5-hour and 17-hour exposures on No-Screen x-ray film were not successful.

Another very long exposure (73 hours) on metallographic plate also showed a very faint response. The silver grains in the film area under the metal were about twice as dense as the ordinary fog background. This was not detectable with the naked eye, but was revealed only by detailed grain counts of sample film areas under the microscope.

A recheck was made using a freshly polished and etched piece of copper not exposed to tritium atmosphere as a control. After a 73-hour exposure, the treated copper again produced a slight generalized blackening of the film. The control produced a few dark spots, believed to be due to chemical action of the freshly polished surface, but no generalized blackening. The blackening of film by freshly abraded metal surfaces has been known for some time and is discussed in the literature.[2]

At the time of this writing, new longitudinal cuts (parallel to the long axis) of the bronze pieces have been made and polished. These show more porosity and lacy structure, typical of hydrogen absorption, than that observed after the first sectioning. Test autoradiographic exposures are in process and the results will be reported as soon as possible.

d. Conclusions. From metallographic examination of the specimen, it seems definite that tritium (or hydrogen) had entered the bronze during superheating. The microstructure associated with hydrogen absorption is plainly seen in Fig. 29.

However, the level of radioactivity observed at the surface is too low to account for enough hydrogen to produce the effects observed. At the time the autoradiographs were made, the activity was very low. That which could be detected was uniformly distributed and not concentrated at the grain boundaries.

The low activity observed could be due to escape of tritium during the cutting, polishing, and etching operation. The lack of activity at the surface does not necessarily mean that the tritium has been lost from the bulk of the metal.

It would appear that the hydrogen is not chemically bound in any way, but is in a very loosely bound state such that, when a new surface is exposed, the hydrogen near the surface escapes. This is a very tentative

conclusion which will require many experiments to verify. Such experiments are being prepared.

3. Diffusion of Nickel into Iron (Professor M. J. Sinnott)

Nickel and iron are similar in structure and form solid solutions in all proportions. Diffusion of nickel into iron would be expected to take place directly through the iron grains and not show any structural sensitivity or preferred path. However, there is some reason to question this complete structural insensitivity or independence at all diffusion temperatures and for all phases of iron. In preliminary tests, it has been indicated that nickel shows preferential grain-boundary diffusion in the gamma-iron region, using ingot iron as the test base material. No such sensitivity was observed in the alpha-iron region. The observations were based on metallurgical examination by conventional techniques.

However, ingot iron behaves somewhat abnormally in some reactions (e.g., carburization), so a second preliminary test was made using a new base material. Strip steel (0.08% C) was first decarburized in wet hydrogen and then a layer of nickel was plated on the surface. One piece was held at 1400°F (alpha-iron region) for 72 hours. A second sample was held at 1800°F (gamma region) for 48 hours. On metallurgical examination, it was found that no observable diffusion had taken place at 1400°F, but readily observable grain-boundary diffusion had taken place at the higher temperature.

From these preliminary tests, it is felt that new experiments using radioactive nickel should be carried out. By this means, any diffusion in either the alpha or the gamma region will be far easier to detect than is now possible. Thus, direct volumetric diffusion rates can be measured.

In planning the new experiments, some consideration has been given to the preparation of columnar ferrite grains by decarburizing high-carbon steel. Such grain structure and orientation would be very helpful in the diffusion experiments. A similar austenitic structure would also be desirable and can be obtained through grain growth by heating low-carbon steel to 2400-2500°F. The problem of preventing this material's subsequent transformation to ferrite at 1600°F may interfere somewhat with the development of such grains in austenite.

4. Cerium in Nodular Iron (Professor R. A. Flinn)

It has been known for some time that a ductile form of cast iron with mechanical properties approaching those of steel could be prepared by the addition of cerium. The obvious change which occurs is the transformation of the graphite shape from a flake form in the ordinary cast iron to a

spherical form in the cerium-modified iron. However, the exact role of the cerium in bringing about this transformation is not known, nor has the cerium been located within the microstructure of the iron.

By the use of radioactive cerium and autoradiography it is expected that the answers to some important outstanding questions on the role of cerium in cast iron can be found.

NEW RESEARCH: PHOTOELECTRON BACK-SCATTER

In principle, an attractive method for metallurgical analysis would utilize monochromatic x-ray-excited resonance back-scatter of K-shell electrons from the atomic system to be identified. Some successful work has been done using selective absorption of x-rays passing through thin foils, but this technique, with its special requirement of thin sections, is of only minor utility. On the other hand, for all atoms, back-scatter can take place only from a very thin surface layer of a metal specimen, so that the high resolution associated with thin sections can be preserved without the trouble of making such sections. The highly refined techniques of autoradiography such as thin films, sensitive detectors, etc., can be transferred directly to use in this back-scatter detection method.

The obvious objection to the method is the requirement that the exciting x-rays must pass through the detecting layer before reaching the metal surface. The fogging of the film thus produced could obscure the pattern of the back-scattered electrons.

It is at this point that the use of monochromatic x-radiation is important. The photoelectric cross section of atomic systems varies rapidly with the energy of the radiation, jumping from low values at energies just below that to excite K-shell radiation to very high values for energies just at the resonance value. Since these resonance values are unique for every atom, it is possible to excite a particular type of atom very strongly in the presence of other systems less strongly excited.

Preliminary calculations and tests with heterogeneous radiation on materials of different atomic number have been very encouraging. We should like to urge for consideration the extension of the scope of our work to include the evaluation and development of the photoelectron back-scatter technique for metallurgical analysis.

REFERENCES

1. Webb, J. N., Phys. Rev. 74, 1 (1948).

2. Yagoda, H., Radioactive Measurements with Nuclear Emulsions, John Wiley and Sons, New York, 1949.