A study of cast eutectic structures by means of optical and x-ray microscopy

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A STUDY OF CAST EUTECTIC STRUCTURES

BY MEANS OF

OPTICAL AND X-RAY MICROSCOPY

BY

JOHN STANTON WINSTON

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

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Degree of

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Rolla, Missouri

1950

Approved by -

Professor of Metallurgical Engineering
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The author wishes to express his thanks and appreciation to all of the members of the Department and especially to Dr. M. Straumanis, Dr. D. S. Eppelsheimer, his faculty advisor, and Dr. C. S. Barrett of the Institute For the Study of Metals of the University of Chicago for their helpful discussions and encouragement during the progress of this research.
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A Study of Cast Eutectic Structures

By Means of

Optical and X-Ray Microscopy

I

INTRODUCTION

The present research is the result of interest in two rather broad, and at first thought, seemingly entirely separate topics: the structure of eutectics and x-ray microscopy. D. Hanson in 1923 in his correspondence with Albert M. Portevin in regard to his article on the structure of eutectics stated, "A point that always struck him (D. Hanson) in examining eutectics was that one of the constituents always formed a continuous phase round the other one. The orientation of one constituent was either constant or varied in a uniform manner. What, however, was the condition of the 'enveloped' constituent, which formed the small particles which were embodied in the continuous constituent? He had never seen any definite statement on that point, but he believed that, when dealing with the iron-carbon eutectoid, Colonel Belaiew expressed the opinion that the cementite was uniformly oriented throughout what was called a single pearlite grain. Did that apply to eutectics? Was the structure of the discontinuous or enveloped phase uniform throughout the colony or grain of eutectic? He thought that was a somewhat important point, and, if that could be settled, it might help one to understand the method of crystallization of eutectics. The fact that one constituent was continuous and had a uniform orientation was surely important in studying the properties of the whole mass." (1)

To date no completely satisfactory answers have been given to these questions, although the fact that the individual particles in a eutectic are built up into a colony or aggregate, the structure of which is the same as that of any other crystal unit, has been shown in several ways. These will be discussed in a later section.

In working with the application of various x-ray methods to metalurgy a new technique presented by Dr. C. S. Barrett was tried. (2) The results obtained indicated that this method might be useful in determining answers to some of the questions quoted above.

II
REVIEW OF LITERATURE

Early Research. It has been known for a long time that with many pairs of metals it is possible to prepare one alloy which has a freezing point lower than that of any other member of the series. Even better known was the similar behavior shown by mixing a solid salt with ice to produce a liquid in freezing mixtures. Scientific study of this phenomenon dealt mainly with freezing mixtures. Rudorf\(^{(3)}\) in 1864 gave the correct explanation of the production of freezing mixtures when he showed that the point of minimum temperature attained was the intersection of the curve of separation of ice from salt solutions with that of the solubility of salt in water. In 1875 Guthrie\(^{(4)}\) reported the results of his extensive investigations dealing with the freezing points of salt solutions of the above type to which he gave the name cryohydrates. The three observations which led Guthrie to conclude that cryohydrates were chemical compounds are: the constancy of composition and freezing point, and their characteristic appearance. This view was held for some time even though it was disputed as early as 1877.

In his later investigations, reported in 1884-5, Guthrie\(^{(5)}\) was able to show the complete resemblance between the behavior of cooled salt solutions, alloys, and mixtures of fused salts. It was at this time that the term "eutectic" was introduced as a designation for these minimum freezing substances. Although certain of Guthrie's conclusions have had to be discarded, many of his observations and conclusions have been substantiated by later investigators.


\(^{(4)}\) Guthrie, F., Phil. Mag., 49, pp. 206, 266, 1875.

Since the cooling curve of a eutectic has the same form as that of a pure substance and therefore the crystallization of both constituents takes place simultaneously thus producing a very intimate mixture, the mistake of considering it as homogeneous is easily explained. It wasn't until 1895 that Ponsot\(^{(6)}\) proved by microscopic examination that eutectics are heterogeneous, being an intimate mixture of the constituents.

Following these early theoretical considerations the research dealing directly with eutectic structures has not been continual but spasmodic. The topics under investigation may be grouped under the following main headings: the physical appearance of eutectics and the eutectic grain, the mode of growth or factors responsible for the eutectic grain, and classification of eutectics.

**The Physical Appearance of Eutectics and the Eutectic Grain.** The description of eutectic structures are all based upon microscopic examination which is carried out on plane sections. Since eutectic structures are three-dimensional patterns, it is possible then to obtain quite different two-dimensional patterns for similar structures. Lack of appreciation of this fact has led to considerable confusion in the terminology applied to the description of eutectic structures.

The physical appearance of eutectics can be considered in two ways, the gross structure and the fine structure. The individual particles of the phases which make up the eutectic mixture build up the gross structure which has been given several designations, eutectic colony, eutectic grain, or eutectic crystal. The unity of the eutectic grain can be shown in several ways. One method involves etching in such a

way that the individual constituents of the eutectic are not revealed but the eutectic grains are. The fact that this can be done is evidence of the unity of the eutectic grain. Such has been shown by Vogel (7) and Brady (8) for the eutectic of Zn-Cd; Rosenhain and Tucker (9) for the eutectic of Pb-Sn; Eastwood (10) for the eutectic of Cu-S; Straumanis and Braks (11, 12) for the eutectics of Bi-Cd, Sn-Zn, Sn-Cd, Al-Si and Zn-Cd; and Portevin (13) for the eutectics of Pb-Sn and Bi-Cd. See also Figs. 40 and 41 of this paper. With respect to this method Brady says: "This much is quite definitely proved, that the growth of a mass of eutectic material composed of a mixture of two phases is exactly similar to that of a primary crystal. Eutectic grains or crystals are formed, on fairly rapid cooling, which set themselves perpendicular to the cooling surface, and give a structure exactly analogous to that seen in the cross-section of a cast brass bar." (14)

(13) Portevin, A. M., op. cit. Figs. 8, 12 and 34.
(14) Brady, F. L. op. cit., p. 378.
A second method that may enable one to distinguish the eutectic grains is by etching to bring out the constituents and examining at magnifications high enough to bring them out. The variation in the orientation from grain to grain of the constituents making up the eutectic pattern clearly show the eutectic grain boundaries. Illustrations of this method are too numerous to list and additional evidence is presented in Figs. 10, 11, 18, 19, 20 and 21.

A third method depends upon the evidence obtained by straining eutectics. Ewing and Rosenhain (15) observed the behavior of the eutectic alloys of Pb-Sn, Cu-Ag and Pb-Bi under plastic strain. They showed two effects due to such straining. On unetched surfaces the differentiation of the two constituents was brought out by differences of level caused entirely by strain, revealing at low magnifications a surface divided into rather large more or less polygonal areas. This effect on its surface appearance is almost identical with that obtained by etching. This suggests that the eutectic alloy as a whole has a comparatively coarse granular structure. They were also able to show the formation of slip-bands which formed a parallel system over many patches of one of the constituents. This points to the fact that the crystalline elements are similarly oriented throughout considerable areas of at least one of the two constituents of the eutectic alloy.

The fourth method requires etching to reveal the fine structure. In many eutectics the structure so revealed at the outer areas of the grains is much coarser than that in the interior. Thus the demarcation between grains is clearly evidenced. Figs. 16 and 17 of the eutectic

of Cd-Sn is an example of this method.

A fifth method is obtained by the application of x-ray microscopy the details of which are given later.

Mode of Growth of Eutectics. The general consensus of opinion as to the way in which alloys of eutectic composition pass from the liquid to solid state is as follows: Solidification begins at nuclei scattered throughout the melt. From each of these a eutectic grain develops, in a manner similar to that for a primary crystal, and solidification is complete when contact is established between grains growing from different points. Various opinions are expressed as to the order of separation of the two constituents. Portevin (16) suggests three main methods of crystallization: simultaneous, the particles forming together in the liquid and developing at the same or with different velocities; successive, the particles of one constituent forming and developing ahead of the other; and, alternate, crystallization of one followed by crystallization of the other.

He suggests that the determining factors which control the method of crystallization which is to take place are: 1. the spontaneous crystallization velocity as measured by the nuclei number, and 2. the linear crystallization velocity. Tammann (17) has shown these factors to be active during the process of solidification or crystallization.

Vogel (18) in his research dealing with the Zn-Cd eutectic attempted to apply the effect of possible variations in these velocities as an

explanation of what appeared to him as a coarsening of the eutectic structure upon fast cooling. Other investigators, such as Lamplough and Scott (19) and Brady (20) endeavored to repeat his results but without success. It seems probable that Vogel's interpretation of his photomicrographs was faulty. Tammann (21) in his discussion of these photomicrographs drew the same conclusion as did Vogel, that is, apparently a coarser structure is obtained by fast cooling than slow cooling. Close inspection of these photomicrographs and comparison with those obtained by Brady (22) under similar conditions indicates that the interpretation given by Vogel and Tammann was incorrect. Difficulty in the use of these two velocity factors is encountered because of the impossibility of measuring them directly.

Classification of Eutectics. There have been many attempts made to classify eutectics, most of which are based upon micro-appearance. As mentioned previously such plane sections can be misleading; and, therefore, few, if any, of these classifications have been satisfactory. Such classifications generally refer to eutectics as being lamellar, globular, spherulitic, curvilinear, curviplanar, rectilinear, columnar, crystalline, polygonal, etc. As a basis for classification it would be more satisfactory, perhaps, if some less artificial means were used. A few such attempts have been made. For example, Brady (23) sought to correlate structure with surface tension using the values as given by

(20) Brady, F. L., op. cit. pp. 373-76.
(22) Brady, F. L., op. cit., Plate XXIII, p. 384.
Smith\(^{(24)}\) for molten metals. Portevin\(^{(25)}\) attempted to show how the eutectic structure is dependent upon the three interrelated factors of spontaneous crystallization velocity, linear speed of crystallization and the influence of surfusion. Although both of these investigators, Brady and Portevin, recognized the disadvantages of previous proposals for classification, theirs are put in the same category by Desch\(^{(26)}\).

Since more binary eutectics were studied by both Portevin and Brady than by other observers, a brief resume of their methods of classification follow.

\textbf{Brady's Classification.} Class 1. Globular. Eutectic alloys so classified are: Cd-Sn, Cd-Pb, Cu-Ag, Zn-Cd and Zn-Bi. This class includes eutectics between metals both of which are of fairly high surface tension.

Class 2. Lamellar. Eutectic alloy so classified is Pb-Sn. For this class the surface tensions of the component metals much be very nearly equal and they must be present in very nearly equal proportions.

Class 3. Angular. Eutectic alloys so classified are given in two subclasses; A, Sn-Pb, Pb-Bi, Sn-Bi and Cd-Bi; and B, Ag-Pb, Ag-Bi, Al-Sn, Cu-Bi and Cu-Pb. This class occurs in alloys of metals at least one of which has either low surface tension (subclass A) or high cohesion (subclass B). The characteristic appearance of this class is the presence of masses of crystalline contour.

Class 4. Crystalline. One example of a metallic alloy is given,


\(^{(25)}\) Portevin, A. M., op. cit., pp. 239-278.

\(^{(26)}\) Desch, G. H., op. cit., p. 144.
the eutectic between antimony and copper antimoide. This class is made up of eutectics between materials both of low surface tension. This type is much more common amongst the non-metallic eutectics.

Portevin's Classification. Type I. Regular crystals of one of the constituents disseminated in the other constituent which forms the ground mass of the alloy. Examples, the eutectics of Sn-Cu and Sb-Co.

Type II. Dendrites or Skeleton Crystals. The following are given as examples: Ag-Sb, Mg-Cu, Mg-Si and Bi-Pb. The regular compact crystals of Type I are replaced in this type by more or less regularly developed dendrites or skeleton crystals. This type along with Type I may be met with in the same specimen. These two types possess a common characteristic in that one of the constituents of the eutectic retains its own crystalline form. One constituent (the enveloped) seems to exert a directing influence whereas the other (the enveloping) fills in the ground mass. These first two types seem to develop by successive or alternate crystallization of their constituents.

Type III. Arrangement in "eutectic colonies" or as complex grains more or less spherulitic. Examples given of this type are: Al-Zn, Cd-Sn, Cd-Pb, Cd-Zn, Sn-Pb, Sn-Zn and Cu-Cu₂. In this type it is difficult to determine which of the two constituents directs the crystallization, and consequently affects the structural appearance. Evidence as to the mode of growth indicates that simultaneous crystallization of the two constituents takes place. A further subdivision is made on the basis of appearance as spherulitic, fan-like parallel-clustered varieties.

Type IV. Granular. No examples of this type are to be found in the case of metallic eutectics.

Crystalline Orientation of the Constituents. The latest research on eutectic structures deals with the determination of the orientation
relationships existing between the phases. Mehl in a written discussion to the research of Eastwood in 1934 suggested the possibility that a unique relationship in orientation might exist between the lattice of the components in the eutectic and that this relationship might well determine, at least partially, the growth form of the eutectic structure. Evidence for the existence of such a relationship was given by Nix and Schmid who in 1929 examined columnar crystals obtained with various metals and alloys cast in an ingot mold for orientation with respect to the direction of solidification. Included in their investigation were single-phase systems (pure metals and solid solutions) and binary eutectics. The results of their work are given in Table I. F. C. C. metals and one F. C. C. alloy (Al, Cu, Ag, Au, Pb and alpha brass) all gave similar fiber textures with the [100] direction parallel to the length axis of the columnar grain. The tetragonal metal Sn (white) showed the face diagonal of the basal face [100] to be parallel with the length axis. C. P. Hex. metals Ag and Cd gave the hexagonal axis [0001] perpendicular to the length axis. Mg. showed a diagonal axis of the first class [0010] parallel to the direction of the length axis; it differs from Zn and Cd which may have any direction in the basal plane parallel to the length axis of the columnar crystal. Bi, rhombohedral, gave the [111] direction parallel to the length axis. Thus the length axis of the columnar crystals investigated always corresponds to a densely packed crystal direction except with Mn and Cd where the axes on the basal plane are apparently all equivalent. The binary eutectic of Al-Si gave a fiber texture only for the Al which was the


characteristic 100 direction while the Si crystals were random in their distribution. The Zn-Cd eutectic showed the same fiber textures for each phase as they did when alone. Nix and Schmid ascribed the genotypes of the fiber texture of the columnar crystals to an anisotropy in the velocities of growth of the metal crystals.

Straumanis and Braks (29) have investigated the eutectics of Zn-Cd, Bi-Cd, Sn-Zn, Sn-Cd and Al-Si. Ellwood and Bagley (30) observed the relationships existing in eutectics of Ag-Cu, Al-Cu and Al-Ag. In both instances eutectic single crystals were produced by means of regulating the rate of travel of a given alloy through a vertical gradient furnace.

Straumanis and Braks used the rotating crystal method of x-ray analysis to determine the orientation relation between the constituents of the binary eutectic systems indicated above. Ellwood and Bagley used the Laue method of determining the symmetry of single crystals and from this deduced the alignment of the elementary cells one with another. The results of these investigations are given in Table I. The results of Straumanis and Braks are also shown in Figs. 1 through 4.


### TABLE I.

**PHASE RELATIONSHIPS IN EUTECTIC STRUCTURES**

1. **Nix and Schmid**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Metal</th>
<th>Normal to cold surface</th>
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<tbody>
<tr>
<td>B. C. C.</td>
<td>Fe - Si (4.3% Si) θ - Brass</td>
<td>[100] [100]</td>
</tr>
<tr>
<td>F. C. C.</td>
<td>Al, Cu, Ag, Au, Pb</td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td>α - Brass</td>
<td></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>θ - Sn</td>
<td>[110]</td>
</tr>
<tr>
<td>Hex. c. p.</td>
<td>Mg</td>
<td>[1010]</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn, Cd</td>
<td>[0001]</td>
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<tr>
<td>Rhombohedral</td>
<td>Bi</td>
<td>[111]</td>
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2. **Straumanis and Brakh**

<table>
<thead>
<tr>
<th>System</th>
<th>Relationships</th>
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<tbody>
<tr>
<td>Zn-Cd</td>
<td>All planes and directions parallel</td>
</tr>
<tr>
<td>Bi-Cd</td>
<td>(1010)Bi</td>
</tr>
<tr>
<td></td>
<td>[0001]Bi</td>
</tr>
<tr>
<td>Sn-Zn</td>
<td>(100)Sn</td>
</tr>
<tr>
<td></td>
<td>[001]Sn</td>
</tr>
<tr>
<td>Sn-Cd</td>
<td>(100)Sn</td>
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<td>[001]Sn</td>
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3. **Ellwood and Bagley**

<table>
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<th>Phases Formed</th>
<th>System</th>
<th>Relationships</th>
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<td>Two f.c.c. phases</td>
<td>Ag-Cu</td>
<td>All planes and directions parallel</td>
</tr>
<tr>
<td>Al (f.c.c.) θ</td>
<td>Al-Cu</td>
<td>(001)Al</td>
</tr>
<tr>
<td>(b.c. tetragonal)</td>
<td></td>
<td>[100]Al</td>
</tr>
<tr>
<td>Al (f.c.c.) γ</td>
<td>Al-Ag</td>
<td>(111)Al</td>
</tr>
<tr>
<td>(hex. c.p.)</td>
<td></td>
<td>[110]Al</td>
</tr>
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</table>
After Straumanis and Brakas
The present investigation was undertaken in order to ascertain whether the technique of X-ray micrography might not be applied to eutectic structures to give some additional information regarding their genesis beyond that already obtained by the use of the microscope and X-ray diffraction methods. The eutectics used for study were of the binary alloy systems listed in Table II. Pertinent information concerning these alloys is given in Table II. The phase diagram for each system is included in Appendix A.

Preparation of Alloys. All of the alloys, except that of copper and oxygen, were prepared from metals of the highest commercial purity as shown in Table III. Ingots measuring approximately 1 1/8" x 3/4" x 1/2" were cast. In each case the melt was cast into a preheated iron mold and then allowed to cool in air. No further treatment was given, the ingots being used in the as cast condition. The specimen of the copper and oxygen eutectic was cut from a copper pancake, origin unknown although assumed to be a test specimen taken during the fire refining process, which was shown by microscopic examination to be of eutectic composition. No chemical analyses were made as 100 percent eutectic composition was judged by microappearance.

Preparation of Specimens for Photomicrography. Standard A.S.T.M. methods (31) for preparing specimens for microscopic study were used. The usual difficulties were encountered in the preparation of the specimens of the lead, tin and zinc alloys. A complete list of the

<table>
<thead>
<tr>
<th>Alloy System</th>
<th>Eutectic comp.</th>
<th>Eutectic M.P.</th>
<th>Figure Numbers</th>
<th>Source of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Cu</td>
<td>71.9-28.1</td>
<td>779.4°C</td>
<td>5, 6, 7</td>
<td>A.S.M. Hdbk.</td>
</tr>
<tr>
<td>Bi-Cd</td>
<td>60.0-40.0</td>
<td>144.2°C</td>
<td>8, 9</td>
<td>A.S.M. Hdbk.</td>
</tr>
<tr>
<td>Bi-In</td>
<td>33.7-66.3</td>
<td>72.1°C</td>
<td>10, 11</td>
<td>Peretti and Carapella</td>
</tr>
<tr>
<td>Bi-Pb</td>
<td>55.5-44.5</td>
<td>124</td>
<td>12, 13</td>
<td>A.S.M. Hdbk.</td>
</tr>
<tr>
<td>Bi-Sn</td>
<td>57 - 43</td>
<td>139</td>
<td>14, 15</td>
<td>A.S.M. Hdbk.</td>
</tr>
<tr>
<td>Cd-Sn</td>
<td>32.4-67.75</td>
<td>176</td>
<td>16, 17, 39</td>
<td>A.S.M. Hdbk.</td>
</tr>
<tr>
<td>Cd-Zn</td>
<td>82.5-17.5</td>
<td>265</td>
<td>18, 19, 40, 47, 48</td>
<td>A.S.M. Hdbk.</td>
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<tr>
<td>Cu-O</td>
<td>99.61-0.39</td>
<td>1065</td>
<td>20, 21, 44, 45, 46 Hansen, M.</td>
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<tr>
<td>Pb-Sb</td>
<td>88.8-11.2</td>
<td>252</td>
<td>22, 23</td>
<td>A.S.M. Hdbk.</td>
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<tr>
<td>Pb-Sn</td>
<td>38.1-61.9</td>
<td>183</td>
<td>24, 25, 42, 51, 52</td>
<td>A.S.M. Hdbk.</td>
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<tr>
<td>Sn-Zn</td>
<td>91 - 9</td>
<td>199</td>
<td>26, 27, 53, 54, 55, 56</td>
<td>A.S.M. Hdbk.</td>
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</table>
TABLE III
METALS USED FOR ALLOYING

<table>
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<tr>
<th>Metal</th>
<th>Source</th>
<th>Purity</th>
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<tbody>
<tr>
<td>Ag</td>
<td>Handy and Harmon</td>
<td>99.99%</td>
</tr>
<tr>
<td>Bi</td>
<td>Baker and Adamson</td>
<td>99.80%</td>
</tr>
<tr>
<td>Cd</td>
<td>Belmont Smelting and Refining Works</td>
<td>99.90%</td>
</tr>
<tr>
<td>Cu</td>
<td>National Research Corp.</td>
<td>99.99%</td>
</tr>
<tr>
<td>In</td>
<td>Indium Corp. of America</td>
<td>99.97%</td>
</tr>
<tr>
<td>Pb</td>
<td>Eagle-Pitcher</td>
<td>___</td>
</tr>
<tr>
<td>Sb</td>
<td>Belmont Smelting and Refining Works</td>
<td>99.90%</td>
</tr>
<tr>
<td>Sn</td>
<td>Belmont Smelting and Refining Works</td>
<td>99.35%</td>
</tr>
<tr>
<td>Zn</td>
<td>Belmont Smelting and Refining Works</td>
<td>99.99%</td>
</tr>
</tbody>
</table>
etching reagents used and their application is given in Appendix B. Photomicrographs at 100x and 200x were taken of each specimen, see Figures 5 through 27.

**Preparation of Specimens for Macrographs and X-ray Micrographs.** Alloys of Cd-Sn, Cd-Zn, Cu-O, Pb-Sn and Sn-Zn were used for macro examinations and X-ray study. The surfaces prepared for photomicrography were given a deep etch in order to produce extreme contrast between the grains and to make sure that no disturbed metal remained. Macrophotographs of these specimens are shown in Figures 39 through 43. As in the case of etching reagents used for preparation of specimens for photomicrography, those used in the present instance are given in detail in Appendix B.

**Results of Photomicrography.** No attempt was made in the present investigation to compare the eutectic structures observed with the various methods of classification as outlined previously in the review of the literature. The main purpose of the photomicrographs was to use them as a basis for comparison with the X-ray micrographs and to give a basis for comparison between the X-ray micrographs. The eutectic grain or colony is more evident in some of the specimens than in others.

**Theory of the X-ray Method.** The X-ray method used in this investigation was first applied to metal specimens by R. Potvin and C. S. Barrett in 1944 (32). Prior to this a similar technique was used by W. F. Berg (33) in studying the cleavage surface of rock-

---


Fig. 5

Ag-Cu eutectic

50x etchant NH$_4$OH-H$_2$O$_2$
Fig. 6

Ag–Cu eutectic

100x etchant $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2$
Fig. 7

Ag-Cu eutectic

200x etchant NH$_4$OH-H$_2$O$_2$
Fig. 8

Bi-Cd eutectic

100x etchant acid ferric chloride
Fig. 9

Bi-Cd eutectic

200x etchant acid ferric chloride
Fig. 10

Bi-In eutectic

100x etchant 10% nital
Fig. 11

Bi-In eutectic

200x etchant 10% nital
Fig. 12

Bi–Pb eutectic

100x etchant 1% chromic acid
Fig. 13

Bi–Pb eutectic

200x etchant 1% chromic acid
Fig. 14
Bi-Sn eutectic
100x etchant 3% nital
Fig. 15

Bi-Sn eutectic

200x etchant 3% nital
Fig. 16

Cd–Sn eutectic

100x etchant 1% nital
Fig. 17

Cd–Sn eutectic

200x etchant 1% nital
Fig. 18

Cd-Zn eutectic

100x etchant 1% nital
Fig. 19

Cd-Zn eutectic

200x etchant 1% nital
Fig. 20

Cu-O eutectic

100x etchant acid ferric chloride
and NH₄OH-H₂O₂
Fig. 21

Cu-O eutectic

200x etchant acid ferric chloride and NH₄OH–H₂O₂
Fig. 22

Pb-Sb eutectic

100x etchant acetic-nitric
Fig. 23

Pb-Sb eutectic

200x etchant acetic-nitric
Fig. 24

Pb-Sn eutectic

100x etchant 1% nital
Fig. 25

Pb-Sn eutectic

200x etchant 1% nital
Fig. 26

Sn-Zn eutectic

100x etchant 1% nital
Fig. 27

Sn-Zn eutectic

200x etchant 1% nital
salt crystals. His method consisted of illuminating the cleavage surface of a crystal with monochromatic x-rays from a line focus and falling on the crystal surface at the appropriate Bragg angle to give monochromatic reflection. The image formed by these reflected rays were recorded on a photographic film mounted parallel to the crystal surface. Berg was able to show that the striated images thus obtained were the result of deformations caused by the slip of the crystal along slip planes.

The way in which an image is obtained in the present method is best shown by Figure 28 which represents the diffraction of a beam of x-rays of a single wavelength by a small crystal at a point. The incident beam, coming from the left, first passes through a slit $S$ and strikes the crystal at a distance $X$ from the slit. Assuming that the crystal is oriented so that reflection will take place, a ray will be reflected from the crystal along a generator of an imaginary cone diametrically opposite to that of the incident ray. This cone is not that associated with the production of Debye rings in a powder diffraction camera; but, as shown, stands with its axis perpendicular to the reflecting plane of atoms of the crystal.

The image of the point on the crystal from which reflection takes place is shown by the spot width $W$. This width is dependent upon the distance $R$ of the film from the specimen. For greatest detail in the micrograph this spot width $W$ must be made as small as possible. That is to say, the resolving power of this method is limited by the spot width obtainable. By simple geometry it is evident that $W$ is dependent upon $S$, $R$ and $X$ as given by the formula

$$W = \frac{3R}{X}$$

Therefore, in order to make $W$ small $S$ and $R$ must be decreased and $X$ increased. It is not difficult to obtain resolution of lines separated
Fig. 28

Reflecting Conditions for an Atomic Plane
by 2 to 3 microns (0.002 to 0.003 mm.) using, for example, if \( R = 0.1 \text{ mm.} \), \( X = 100 \text{ mm.} \) and \( S = 2 \text{ mm.} \) then \( X = 0.002 \text{ mm.} \).

For study and interpretation the images formed on the film are enlarged. At present useful magnifications of from 100 to 250 diameters can be made. The graininess or resolving power of the film used is the limiting factor in the maximum magnification attainable. For quick preliminary exposures dental film or spectroscopic film has been found useful.

Barrett\(^\text{(34)}\) indicates that the best conditions are obtained by using long wave length, monochromatic radiation from a target having an atomic number equal to or less than that of the elements in the specimen, preferably one of low atomic number such as Cr, Fe or Co; a specimen surface free from scratches and disturbed metal; a fine-grained photographic emulsion placed as close to the specimen surface as possible; and examination or enlargement of the film with a good optical system.

**Apparatus and Procedure.** The camera used is a modification for polycrystalline specimens of the single crystal camera employed by Barrett (Figures 29 and 30). Since polycrystalline specimens will have one or more crystals in position for reflection, no goniometer arrangement was provided. The camera consists of two main parts, a specimen stand and a film support. The specimen stand allows for adjustment in height and surface angle of the specimen with respect to the X-ray beam. The film support is also adjustable for height and is essentially a shelf for supporting the film with emulsion side down in such a way that the incident rays pass beneath and the reflected rays travel upward.

\(^\text{(34)}\) Barrett, C. S., op. cit., pp. 7, 8 and 45.
Fig. 29

X-ray Camera Positioned for Exposure
Fig. 30

Close-up of X-ray Camera
Fig. 31

Alpha Brass 1.75x
Fig. 32

Alpha Brass 100x
from the specimen surface to the film. By trial it was found that by
collimating the beam sharper, more distinct micrographs were obtained.
The collimator used was 48 mm. long and had a pinhole 2 mm. in diameter.

X-rays were supplied by a Baird X-ray diffraction unit equipped
with a demountable gas type tube. Most of the exposures were made with
Co radiation the tube operating at 35 KVP and 8 to 9 ma.

In order to gain proficiency in the method and also to test the
flexibility of the apparatus trial runs were made using a large-grained
annealed specimen of cartridge brass. The specimen used is shown in
Figures 31 and 32. As indicated by the equation for image width,
\[ W = \frac{SR}{X} \]
the resolution is directly proportional to the slit width, 
\( S \), and the distance from specimen surface to film, \( R \); and inversely
proportional to the distance from slit to specimen, \( X \). A series of ex-
posures were made in order to evaluate the effect on the micrograph of
variation in \( R \) and \( X \) by keeping one constant while varying the other.
The results were in accord with those obtained by calculations; namely,
the greater the value of \( X \) the higher the resolution, and the smaller
the value of \( R \) the greater the resolution. Another series of exposures
were made varying only the angle made by the specimen surface with the
incident beam. Again the results were as expected from purely theoreti-
cal considerations showing that the greater the angle the fewer the
images that were formed. Figures 33 through 38 are examples of the
micrographs obtained for the specimen of cartridge brass.

The following measurements were made for each exposure which allowed
approximate duplication of results to be obtained if desired:

1. The height of specimen measured from the surface of the specimen
to the top surface of the specimen holder.

2. The height of the specimen holder measured by the separation
of base and top halves.
3. The total specimen height taken as the sum of 1. and 2.

4. The distance from the back edge of the specimen to the tube.

5. The distance from the back edge of the specimen to the pinhole of the collimator closest to the specimen.

6. The height of the film support measured by the separation of the base and top halves.

7. The distance from the front edge of the film support to the tube.

8. The approximate angle of the specimen surface with the horizontal.

In setting up for an exposure the specimen was mounted in the center of the square plate of the specimen stand in such a way that its prepared surface was parallel with the plate. In order to line up the specimen in the beam of X-rays a fluorescent screen was used by which the beam's path could be followed. The film holder was then placed in such a position that the film made contact with the back edge of the specimen and did not interfere with the incident beam. Exposure time depended upon the type of film used ranging from five to ten minutes for dental film and spectroscopic 35mm. film to 15 to 20 hours for special thin emulsion plates of high resolving power (1000 lines/mm.) donated to the author by Barrett. All micrographs shown are enlargements made from the higher speed films. Three methods were used in making these micrographs. For the first method the X-ray pattern was enlarged by means of a Leitz 35mm. enlarger. Enlargements up to 30x were possible by this method. Figures 33 and 34 were made in this way. The second method, which allowed much higher magnifications to be made, consisted of first taking a photomicrograph and then enlarging further with the 35mm. enlarger. See Figures 36 and 38. In all the micrographs made by this method the initial magnification was approximately 10x, and that obtained by use of the enlarger 5x which gives a total magnifi-
Fig. 33

Alpha Brass

X-ray Micrograph by Method 1, 8.5x
Fig. 34

Alpha Brass

X-ray Micrograph by Method 1, 8.5x
Fig. 35

Alpha Brass

X-ray Micrograph by Method 3, 10x

---

Fig. 36

Alpha Brass

X-ray Micrograph by Method 2, 50x
Fig. 37

Alpha Brass

X-ray Micrograph by Method 3, 10x

Fig. 38

Alpha Brass

X-ray Micrograph by Method 2, 50x
cation of 50X. The third method consisted of making contact prints of
the photomicrographs as shown by Figures 35 and 37.

Interpretation of X-ray Micrographs. X-ray micrographs obtained
by methods one and three above are shown for the eutectic systems of
Cu-O, Cd-Zn, Pb-Sn and Sn-Zn in Figures 44 through 56. All of these are
mounted so that the top edge of the large prints are in contact with the
specimen, the X-ray beam coming from the bottom of the page. The posi­
tion of the sample with respect to the film, the approximate area of
the specimen covered by the X-ray beam, and the direction of the X-ray
beam are indicated in Figures 57 through 62.

Inspection of the X-ray micrographs for Cu-O and comparison of
these with those for the alpha brass shows a close resemblance between
the two. Since in the case of the alpha brass it is obvious that a
grain properly oriented for reflection reflects as a whole, it is pro­
bable that a eutectic grain of Cu-O acts in a similar manner. Compara­
tion measurements of average grain size for the Cu-O specimen and of the
spots on the X-ray micrograph for Cu-O substantiate this conclusion.
The fine spots forming the background in Figures 45 and 46 are due to
the graininess of the film and not to the reflection of X-rays by the
specimen. With the film used the fine structure shown in the photomi­
icrographs (Figures 20 and 21) is not revealed. The possible resolution
of this fine structure by means of finer grained emulsions might offer
more conclusive evidence to support the conclusion stated above.

Similarity of X-ray patterns between alpha brass and the Cd-Zn
eutectic can also be observed. Again measurements of specimen grain
size and X-ray spot size were made, the results showing that the X-ray
spots were of the same order of size as the grains of the specimen.
This led to the conclusion stated above for the Cu-O eutectic, that a
Fig. 39

Cd-Sn eutectic 1.75x
Fig. 40
Cd-Zn eutectic 1.75x
Fig. 41

Cu–O eutectic 1.75x
Fig. 42

Pb–Sn eutectic 1.75x
Fig. 43

Sn-Zn eutectic 1.75x
Fig. 44

Cu–O eutectic - 8.5x

Fig. 45

Cu–O eutectic - 10x

Fig. 46

Cu–O eutectic - 10x
Fig. 47
Cd-Zn eutectic - 10x

Fig. 48
Cd-Zn eutectic - 8.5x
Fig. 49
Cd-Zn eutectic - 10x

Fig. 50
Cd-Zn eutectic - 8.5x
Fig. 51

Pb-Sn eutectic - 10x

Fig. 52

Pb-Sn eutectic - 8.5x
Fig. 53
Sn-Zn eutectic - 10x

Fig. 54
Sn-Zn eutectic - 8.5x
Fig. 55
Sn-Zn eutectic - 10x

Fig. 56
Sn-Zn eutectic - 8.5x
Fig. 57: Cu-O

Fig. 58: Cd-Zn

Fig. 59: Cd-Zn

Fig. 60: Pb-Sn

Area Covered by X-ray Beam
eutectic grain reflects as a whole. Nix and Schmid\textsuperscript{(35)} and Straumanis and Brakss\textsuperscript{(36)} have shown that in the eutectic of Cd-Zn the two phases are oriented with all planes and directions parallel. Therefore both Cd and Zn within a single eutectic grain could be properly oriented for reflection.

A marked difference in the X-ray micrographs of the eutectic of Pb-Sn, Figures 51 and 52, as compared to those of alpha brass, Cu-O and Cd-Zn is quite apparent. The spots on the X-ray micrographs for Pb-Sn (Figures 51 and 52) are much smaller than the apparent grain size as shown by the macrophotograph for Pb-Sn (Figure 42), whereas, in the three cases already discussed (alpha brass, Cu-O and Cd-Zn) there was close correspondence. This dissimilarity of structure between the similar eutectics of Cu-O and Cd-Zn and that of Pb-Sn is also evident by comparison of their photomicrographs. See Figures 18, 19, 20, 21, 24 and 25.

In the case of the Pb-Sn eutectic one phase, dark etching Sn, is quite obviously continuous while the light etching Pb-rich phase is discontinuous. Reflection by the discontinuous phase could account for the pattern of discontinuous spots obtained in the X-ray micrographs. Some grouping of spots into clusters is also evident. This might indicate a similarity of orientation of the discontinuous phase within discreet areas (the eutectic grains).

Similar comparisons can be made in the treatment of the photomicrographs, macrophotographs and X-ray micrographs obtained for the

\textsuperscript{(35)} Nix, F. C., and Schmid, E., op. cit., p. 291

Sn-Zn eutectic as have just been made for the Pb-Sn eutectic. See Figures 26, 27, 43, 53, 54, 55 and 56. The grouping of discontinuous spots into clusters is more prominent and the spots are larger than in the X-ray micrographs of the Pb-Sn eutectic. A study of the photomicrographs of Sn-Zn (Figures 26 and 27) shows the light etching phase (Sn) to be continuous and the dark etching Pb-rich phase to be discontinuous. Again the discontinuity of the spots in the X-ray micrograph might be explained by the reflection of the discontinuous phase.

Summary and Conclusion. The structures shown by the X-ray micrographs indicate groups of similarly oriented crystals. In some cases, particularly those of the eutectics of Cu-O and Cd-Zn, the size of the X-ray spots indicates the eutectic grain as a whole was oriented so as to cause reflection, or that one of the phases was continuous within the grain and properly oriented to give reflection. See Figures 44 through 50. There is a possibility of conclusively proving this point if the phase causing the reflection could be identified. Barrett (37) indicates a possible method for doing this. Since the angle between each reflected ray and the incident beam is characteristic of the crystal structure of the reflecting crystal, a measurement of the direction of the reflected ray would allow the calculation of the Bragg angle \( \theta \); and, therefore, the spacing \( d \) of the reflecting planes.

In other cases clusters of discontinuous spots seem to indicate groups of similarly oriented crystals. This discontinuity might be explained as due to reflection by the discontinuous phase of the eutectic grain. This type of pattern is shown by the X-ray micrographs of Pb-Sn and Sn-Zn, Figures 51 through 56.

(37) Barrett, C. S., op. cit., pp. 34-39
It seems to the author that the present investigation offers additional evidence of the existence of the eutectic grain and the continuity of one phase within this grain.

This present exploratory work indicates that with certain refinements further study of eutectic structures by means of this method could furnish information relative to the crystalline orientation of the two phases existing within a single eutectic grain and the variation in orientation from grain to grain. Particularly, this would require the adaptation of a means of measuring rotation of the specimen in two directions and the obtaining of double films separated by a known distance.
<table>
<thead>
<tr>
<th>Alloy System</th>
<th>Reference*</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver-Copper</td>
<td>A.S.M. Hdbk., 1948</td>
<td>73</td>
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<tr>
<td>Bismuth-Cadmium</td>
<td>A.S.M. Hdbk., 1948</td>
<td>74</td>
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<tr>
<td>Bismuth-Indium</td>
<td>Peretti and Carapella</td>
<td>75</td>
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<tr>
<td>Bismuth-Lead</td>
<td>A.S.M. Hdbk., 1948</td>
<td>76</td>
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<td>Bismuth-Tin</td>
<td>A.S.M. Hdbk., 1948</td>
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<td>Cadmium-Tin</td>
<td>A.S.M. Hdbk., 1948</td>
<td>78</td>
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<tr>
<td>Cadmium-Zinc</td>
<td>A.S.M. Hdbk., 1948</td>
<td>79</td>
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<tr>
<td>Copper-Oxygen (partial)</td>
<td>Hansen</td>
<td>80</td>
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<td>Lead-Antimony</td>
<td>A.S.M. Hdbk., 1948</td>
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<td>Lead-Tin</td>
<td>A.S.M. Hdbk., 1948</td>
<td>82</td>
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<tr>
<td>Tin-Zinc</td>
<td>A.S.M. Hdbk., 1948</td>
<td>83</td>
</tr>
</tbody>
</table>

*References:


Ag-Cu Silver-Copper

By Cyril Stanley Smith

Atomic Percentage Copper

°C  10 20 30 40 50 60 70 80 90 100 2000

Weight Percentage Copper

0 10 20 30 40 50 60 70 80 90 100
Fig. 1  Phase Diagram of the System Indium-Bismuth.
Bi-Pb Bismuth-Lead

By G. O. Hiers

°C
10 20 30 40 50 60 70 80 90
0 Pb 10 20 30 40 50 60 70 80 90 Bi

Atomic Percentage Bismuth

Weight Percentage Bismuth

°F
350 300 250 200 150 100 50

0 10 20 30 40 50 60 70 80 90

α + L
α
α + β
β
β + L
β + γ
γ + L
γ

327°
21.5 322 184°
33 53.5 124°
99.5

271°
Bi-Sn  Bismuth-Tin

BY R. I. JAFFEE* AND BRUCE W. GONSER*

[Diagram of Bi-Sn phase diagram with temperature and composition axes, showing phase boundaries and transition points.]
Cd-Sn  Cadmium-Tin

BY W. T. PELL-WALPOLE

Atomic Percentage Cadmium

Weight Percentage Cadmium

For diagrams on a larger scale, see the next page.
Cd-Zn  Cadmium-Zinc

BY E. A. ANDERSON

Atomic Percentage Zinc

Weight Percentage Zinc

°C  500  400  300  200  100  0  10  20  30  40  50  60  70  80  90
°F

100  200  300  400  500

10  20  30  40  50  60  70  80  90  100

α + L  β + L  β

L

α

α + β

265°  4195°

295°  175°
Pb-Sb  Lead-Antimony

By E. E. Schumacher and G. M. Bouton

Atomic Percentage Antimony

Weight Percentage Antimony

°C

10 20 30 40 50 60 70 80 90

0°F

1200

630°

1000

800

600

400

300

387°

α + L

3.5 11.2

252°

α

L

β + L

β

α + β

100 200 300 400 500 600 700

Pb 10 20 30 40 50 60 70 80 90 Sb
Pb-Sn: Lead-Tin

By G. O. Hiers

Temperature (°C) vs. Atomic Percentage Tin

Weight Percentage Tin

327° C

α + L

α

19.2

183° C

L

61.9

β + L

232° C

400

200

100

0

Pb

Sn

10

20

30

40

50

60

70

80

90

600

500

400

300

200

100

0
Sn-Zn Tin-Zinc

BY E. A. ANDERSON

°C  °F

Atomic Percentage Zinc

Weight Percentage Zinc

20 40 60 80 90

0 200 400 600 800

100 200 300 400 500

419.5°
## ETCHING REAGENTS

Appendix B

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Etchant for Micro-examination</th>
<th>Etchant for Macro-examination</th>
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</thead>
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<tr>
<td>Ag-Cu</td>
<td>5 parts ammonium hydroxide</td>
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</tr>
<tr>
<td></td>
<td>diluted with equal amount</td>
<td></td>
</tr>
<tr>
<td></td>
<td>of water, 1 part 3% hydrogen</td>
<td></td>
</tr>
<tr>
<td></td>
<td>peroxide,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Darkens copper-rich phase.</td>
<td></td>
</tr>
<tr>
<td>Bi-Cd</td>
<td>5 parts ferric chloride</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 parts hydrochloric acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 parts water</td>
<td>Darkens cadmium</td>
</tr>
<tr>
<td>Bi-In</td>
<td>10 cc concentrated nitric acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90 cc ethyl alcohol</td>
<td>Darkens Indium-rich phase.</td>
</tr>
<tr>
<td>Bi-Pb</td>
<td>10 gm. Cr₂O₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90 gm. water</td>
<td>Darkens lead-rich phase.</td>
</tr>
<tr>
<td>Bi-Sn</td>
<td>Immersed in 3% nital</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 parts concentrated nitric</td>
<td></td>
</tr>
<tr>
<td></td>
<td>97 parts ethyl alcohol</td>
<td>Darkens tin-rich phase.</td>
</tr>
<tr>
<td></td>
<td>swabbed with 5 parts ferric</td>
<td></td>
</tr>
<tr>
<td></td>
<td>chloride, 10 parts hydrochloric</td>
<td></td>
</tr>
<tr>
<td></td>
<td>acid, 100 parts water</td>
<td></td>
</tr>
<tr>
<td>Cd-Sn</td>
<td>1 part concentrated nitric</td>
<td>25 gm. ferric chloride</td>
</tr>
<tr>
<td></td>
<td>99 parts ethyl alcohol</td>
<td>25cc conc. hydrochloric</td>
</tr>
<tr>
<td></td>
<td>Darkens cadmium</td>
<td>100cc water</td>
</tr>
<tr>
<td>Cd-Zn</td>
<td>1 part concentrated nitric</td>
<td>1 gm. iodine</td>
</tr>
<tr>
<td></td>
<td>99 parts ethyl alcohol</td>
<td>5 gm. potassium iodide</td>
</tr>
<tr>
<td></td>
<td>Darkens zinc</td>
<td>100 cc water</td>
</tr>
<tr>
<td>Cu-O</td>
<td>Immersed in 5 parts ferric</td>
<td>Same as micro.</td>
</tr>
<tr>
<td></td>
<td>chloride, 10 parts hydrochloric</td>
<td></td>
</tr>
<tr>
<td></td>
<td>acid, 100 parts water, swabbed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>with 10 parts ammonium hydr-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>oxide, 10 parts water, 2 parts</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3% hydrogen peroxide, swabbed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>with acid ferric chloride.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Darkens cuprous oxide.</td>
<td></td>
</tr>
<tr>
<td>Pb-Sb</td>
<td>3 parts glacial acetic</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 parts concentrated nitric</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16 parts water</td>
<td>Darkens lead.</td>
</tr>
</tbody>
</table>
### ETCHING REAGENTS

**Appendix B (contd.)**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Etchant for Micro-examination</th>
<th>Etchant for macro-examination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-Sn</td>
<td>1 part concentrated nitric</td>
<td>25 gm. ferric chloride</td>
</tr>
<tr>
<td></td>
<td>99 parts ethyl alcohol</td>
<td>25 cc hydrochloric acid</td>
</tr>
<tr>
<td></td>
<td>Darkens tin.</td>
<td>100 cc water</td>
</tr>
<tr>
<td>Sn-Zn</td>
<td>1 part concentrated nitric</td>
<td>5 parts ferric chloride</td>
</tr>
<tr>
<td></td>
<td>99 parts ethyl alcohol</td>
<td>10 parts conc. hydrochloric</td>
</tr>
<tr>
<td></td>
<td>Darkens zinc.</td>
<td>100 parts water</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


The author was born February 16, 1916 in Denver, Colorado. Attended the Public Schools of Hinsdale, Illinois graduating from Hinsdale Township High School in 1933. Entered Cornell College in 1933 and graduated with an A.B., majors in mathematics, chemistry and physics, in 1937. Worked in the Industrial Engineering department of Armour and Co., Chicago for one year. Received the degree of M. A. in June, 1939 from the University of Chicago. Held various teaching positions until entrance into the Armed Forces on November 9, 1942. Was discharged January 6, 1946. Resumed teaching and continued to do so until September 1948. Obtained a leave of absence as Assistant Professor of Physics from Morningside College to work on a M.S. at Missouri School of Mines and Metallurgy. Was appointed Instructor in Metallurgical Engineering in June 1949.