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A STUDY OF CAST EUTECTIC STRUCTURES
BY MEANS OF
OPTICAL AND X-RAY MICROSCOPY

BY

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A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

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MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

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1950

Approved by - Daniel S. Eppelsheimer

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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By Means of
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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)

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(1) Portevin, A. M., The Structure of Eutectics, Jour. Inst. Metals, Vol. 29, No. 1, p. 276, 1923.

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 metallurgy 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.

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(2) Barrett, C. S., A New Microscopy and Its Potentialities, Metals Tech., Vol. 12, No. 3, pp. 1-50, 1945.

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.

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(3) Desch, C. H., Metallography, 6th Ed. London, Longmans, Green & Co., 1944, pp. 15-17.

(4) Guthrie, F., Phil. Mag., 49, pp. 206, 266, 1875.

(5) Guthrie, F., Phil. Mag., V, 17, p. 462, 1884; Proc. Phys. Soc., 6, pp. 124, 169, 1884-85.

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

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(6) Ponsot, Bull. Soc. Chim., iii, 13, p. 312, 1895.

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-O; Straumanis and Brakŝs(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)

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(7) Vogel, R., Uber Eutektische Kristallisation, Zeit. Anorg. Chem., Vol. 76, p. 425, 1912.

(8) Brady, F. L., The Structure of Eutectics, Jour. Inst. Metals. Vol. 28, No. 2, Figs. 2 and 4, 1922.

(9) Rosenhain, W., and Tucker, P. A., Eutectic Research: The Alloys of Lead and Tin, Phil. Tran. Roy. Soc., Vol. 209 A, Fig. 39, 1909.

(10) Eastwood, L. W., Structure and Origin of the copper-cuprous oxide Eutectic, Am. Inst. Mining Met. Engrs. Trans. Inst. Metals Div., p. 182, 1934.

(11) Straumanis, M., and Brakŝs, N., Der Aufbau der Bi-Cd, Sn-Zn, Sn-Cd and Al-Si Eutektika, Z.Physikal. Chem. (B) Vol. 38, pp. 140-155, 1937.

(12) Straumanis, M., and Brakŝs, N., Der Aufbau der Zink-Cadmium Eutektikums, Zeit. fur Phy. Chem., (B) Vol. 30, pp. 117-131, 1935.

(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

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(15) Ewing, J. A., and Rosenhain, W., On the Crystalline Structure of Metals, Phil. Tran. Roy. Soc., Vol. 193 A, p. 371-2, plates 27 and 28, 1900.

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 concensus 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

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(16) Portevin, A. M., op. cit., pp. 255-56.

(17) Tammann, G. A., A Textbook of Metallography, N. Y., Reinhold, 1925, pp. 15-30.

(18) Vogel, R., Uber Eutektische Kristallisation, Zeit. fur Anorg. Chem., Vol. 76, pp. 425-36, 1912.

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

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(19) Lamplough, F. E. E., and Scott, J. T., The Growth of Metallic Eutectics, Proc. Roy. Soc., Vol. 90 A, p. 600, 1914.

(20) Brady, F. L., op. cit. pp. 373-76.

(21) Tammann, G. A., op. cit., Figs. 112 and 113, pp. 182-84.

(22) Brady, F. L., op. cit., Plate XXIII, p. 384.

(23) Brady, F. L., op. cit. pp. 369-419.

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 observors, a brief resume of their methods of classification follow.

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, Sb-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,

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(24) Smith, S. W., The Surface Tension of Molten Metals, Jour. Inst. Metals, Vol. 12, No. 2, p. 168, 1914.

(25) Portevin, A. M., op. cit., pp. 239-278.

(26) Desch, C. 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. TypeI. 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 $Cu-Cu_2o$. 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(27) 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(28) who in 1929 examined columnar cyrstals 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 An 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 cyrstals investigated always corresponds to a densely packed crystal direction except with Zn 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

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(27) Eastwood, L. W., Structure and Origin of the Copper-Cuprous Oxide Eutectic., Am. Inst. Mining Met. Engrs. Trans. Inst. Metals Div., 181-195, 1934.

(28) Nix, F. C., and Schmid, E., Uber die Gutztextur von Metallen und Legierungen, Z. Metallkunde, Vol. 21, pp. 286-292, 1929

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 geneses of the fiber texture of the columnar crystals to an anisotropy in the velocities of growth of the metal crystals.

Straumanis and Brakŝs(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 cyrstals were produced by means of regulating the rate of travel of a given alloy through a vertical gradient furnace.

Straumanis and Brakŝs 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 Brakŝs are also shown in Figs. 1 through 4.

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(29) Straumanis, M., and Brakŝs, N., op. cit. pp. 117-131.
Straumanis, M., and Brakŝs, N., op. cit. pp. 140-155.

(30) Ellwood, E. C., and Bagley, K. Q. The Structure of Eutectics, J. Inst. Metals, Vol. 76, pp. 631-42, 1950.

TABLE I.

PHASE RELATIONSHIPS IN EUTECTIC STRUCTURES

1. Nix and Schmid

Structure	Metal	Normal to cold surface
B. C. C.	Fe – Si (4.3% Si) β – Brass	[100] [100]
F. C. C.	Al Cu Ag Au Pb α – Brass	[100]
Tetragonal	β – Sn	[110]
Hex. c. p.	Mg Zn Cd	[10$\bar{1}$0] [0001]
Rhombohedral	Bi	[111]

2. Straumanis and Brakŝs

System	Relationships
Zn–Cd	All planes and directions parallel
Bi–Cd	(10$\bar{1}$0)Bi $\parallel$ (0001)Cd [0001]Bi $\parallel$ [11$\bar{2}$0]Cd
Sn–Zn	(100)Sn $\parallel$ (0001)Zn [001]Sn $\parallel$ [10$\bar{1}$0]Zn
Sn–Cd	(100)Sn $\parallel$ (0001)Cd [001]Sn $\parallel$ [11$\bar{2}$0]Cd

3. Ellwood and Bagley

Phases Formed	System	Relationships
Two f.c.c. phases	Ag–Cu	All planes and directions parallel
Al (f.c.c.) θ (b.c. tetragonal)	Al–Cu	(001)Al $\parallel$ (001)θ [100]Al $\parallel$ [100]θ
Al (f.c.c.), γ (hex. c.p.)	Al–Ag	(111)Al $\parallel$ (0001)γ [110]Al $\parallel$ [11$\bar{2}$0]γ

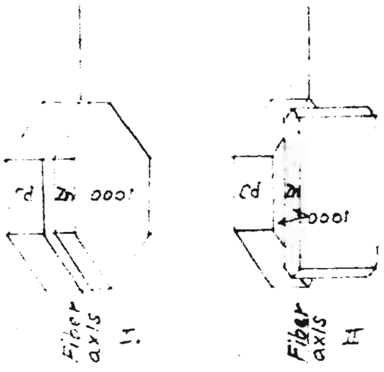

Fig.1

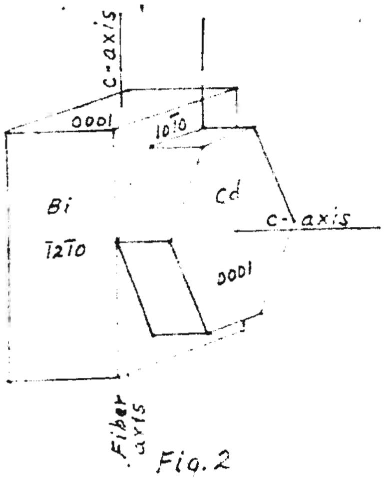

Fig.2

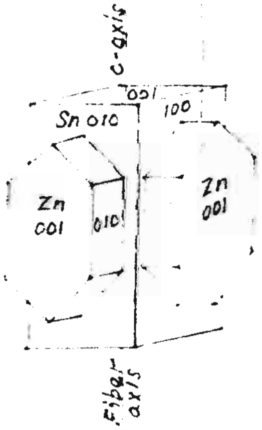

Fig.3

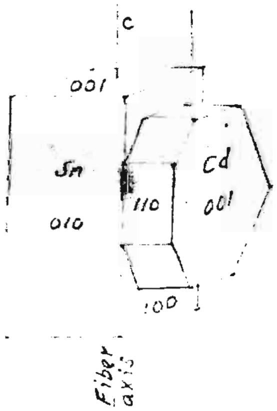

Fig.4

After Straumanis and Brakšs

III

PRESENT INVESTIGATION

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 (30) 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

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(31) A.S.T.M. Standards, Part II, Non-ferrous metals, E 2-49T and E 3-46T, pp 923 and 935, 1949.

TABLE II

EUTECTIC SYSTEMS INVESTIGATED

Alloy System	Eutectic comp.	Eutectic M.P.	Figure Numbers			Source of Data
			Micro.	Macro.	X-ray	
Ag-Cu	71.9-28.1	779.4°C	5,6,7			A.S.M. Hdbk.
Bi-Cd	60.0-40.0	144±2°C	8,9			A.S.M. Hdbk.
Bi-In	33.7-66.3	72.1°C	10,11			Peretti and Carapella
Bi-Pb	55.5-44.5	124	12,13			A.S.M. Hdbk.
Bi-Sn	57 - 43	139	14,15			A.S.M. Hdbk.
Cd-Sn	32¼-67.75	176	16,17	39		A.S.M. Hdbk.
Cd-Zn	82.5-17.5	265	18,19	40	47,48, 49,50	A.S.M. Hdbk.
Cu-O	99.61-0.39	1065	20,21	41	44,45, 46	Hansen, M.
Pb-Sb	88.8-11.2	252	22,23			A.S.M. Hdbk.
Pb-Sn	38.1-61.9	183	24,25	42	51,52	A.S.M. Hdbk.
Sn-Zn	91 - 9	199	26,27	43	53,54, 55,56	A.S.M. Hdbk.

TABLE III

METALS USED FOR ALLOYING

Metal	Source	Purity
Ag	Handy and Harmon	99.99%
Bi	Baker and Adamson	99.80%
Cd	Belmont Smelting and Refining Works	99.90%
Cu	National Research Corp.	99,991%
In	Indium Corp. of America	99.97%
Pb	Eagle-Pitcher	——
Sb	Belmont Smelting and Refining Works	99.90%
Sn	Belmont Smelting and Refining Works	99.85%
Zn	Belmont Smelting and Refining Works	99.99%

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-

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(32) Barrett, C. S., A New Microscopy and Its Potentialities, Metals Tech., Vol. 12, No. 3, pp. 1-50, 1945.

(33) Berg, W. F., About the History of Load of Deformed Crystals, Ztsch. Kristallographie, Vol. 89, pp. 286-294, 1934.

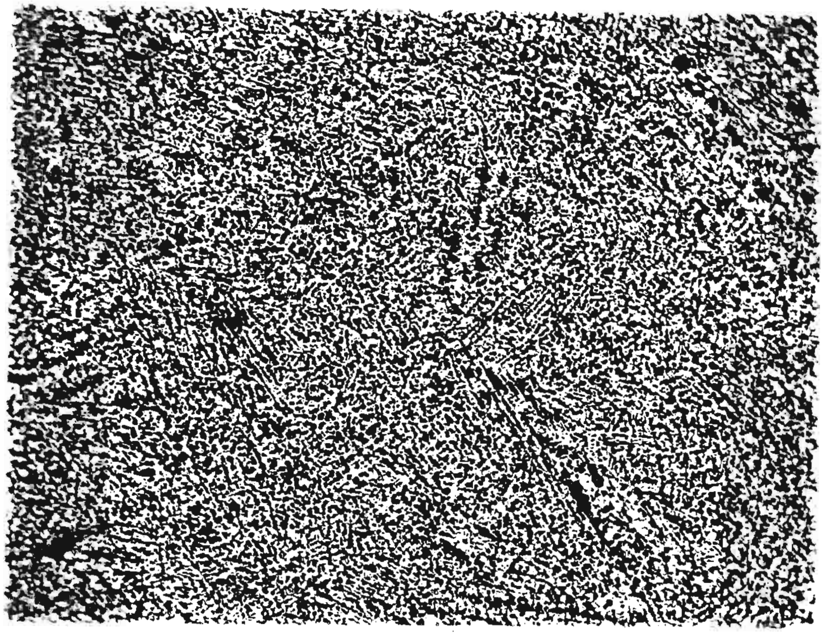

Fig. 5

Ag-Cu eutectic

50x etchant $NH_4OH-H_2O_2$

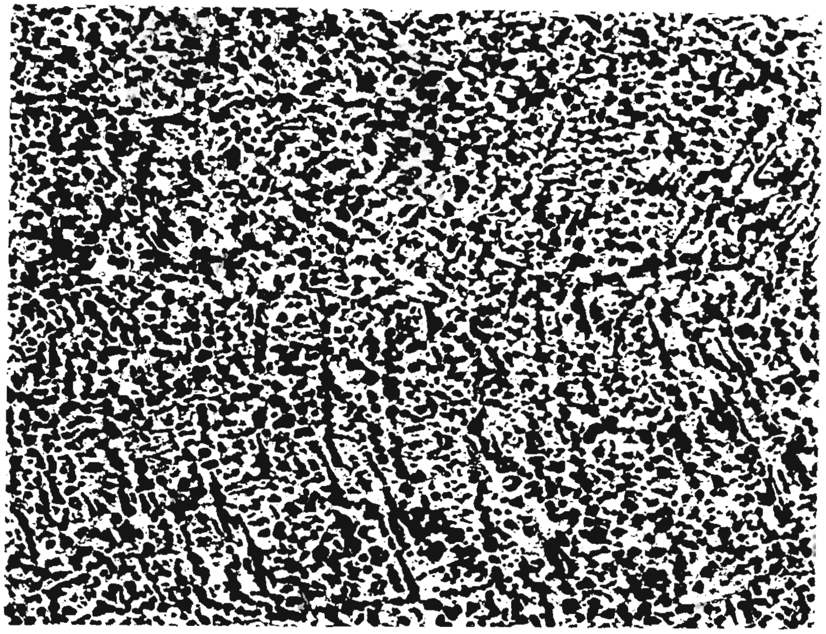

Fig. 6

Ag-Cu eutectic

100x etchant $NH_4OH-H_2O_2$

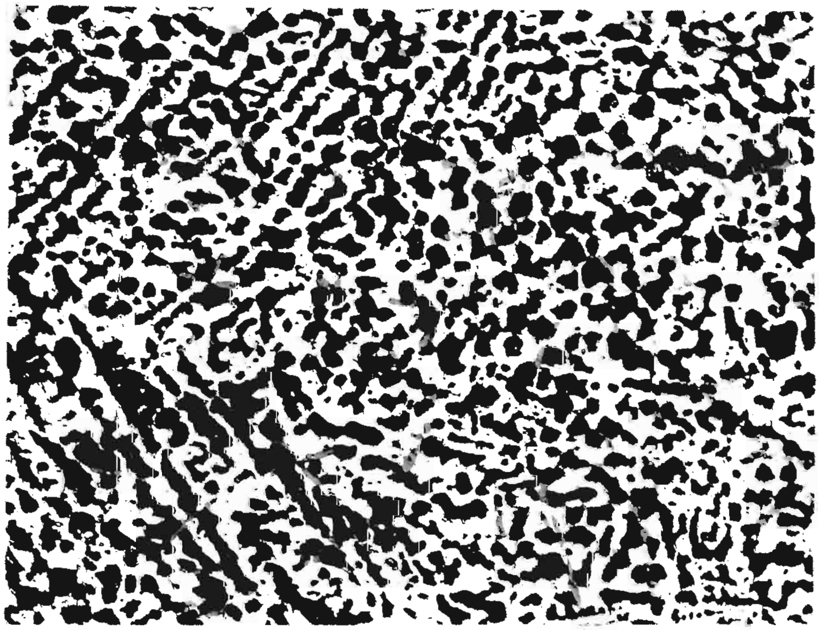

Fig. 7

Ag-Cu eutectic

200x etchant $NH_4OH-H_2O_2$

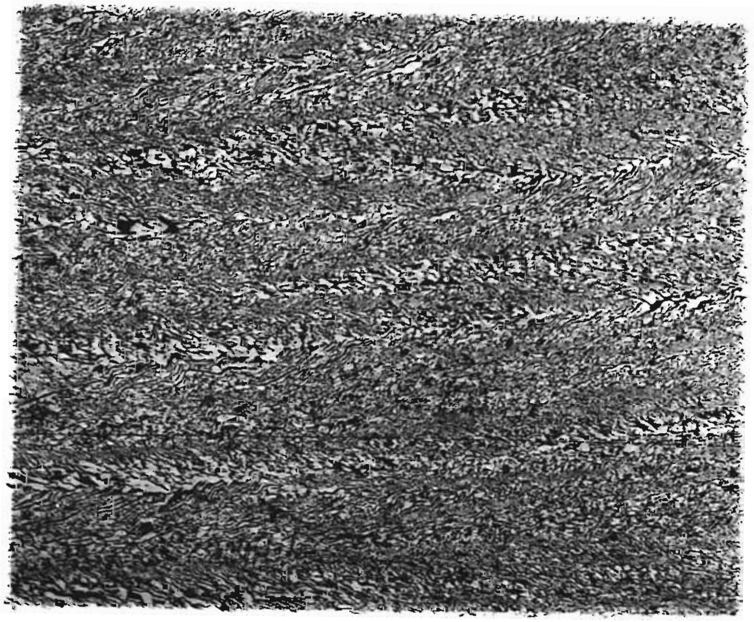

Fig. 8

Bi-Cd eutectic

100x etchant acid ferric chloride

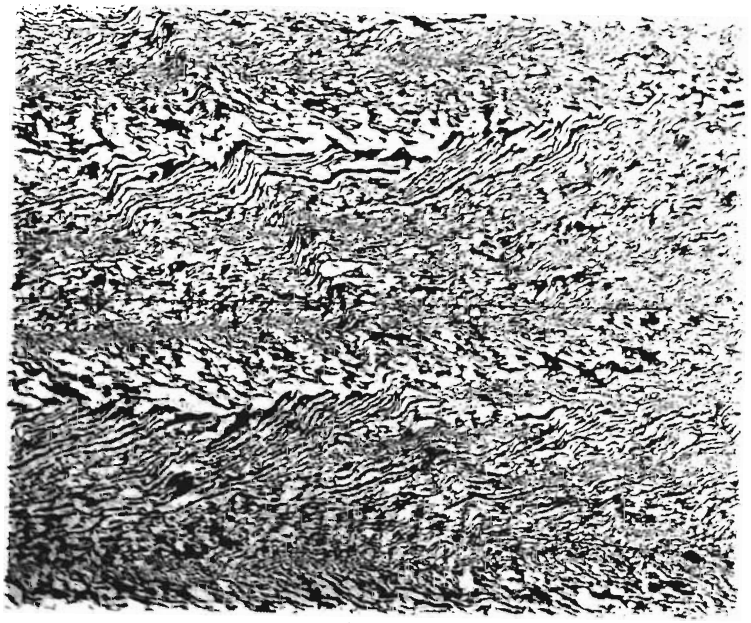

Fig. 9

Bi-Cd eutectic

200x etchant acid ferric chloride

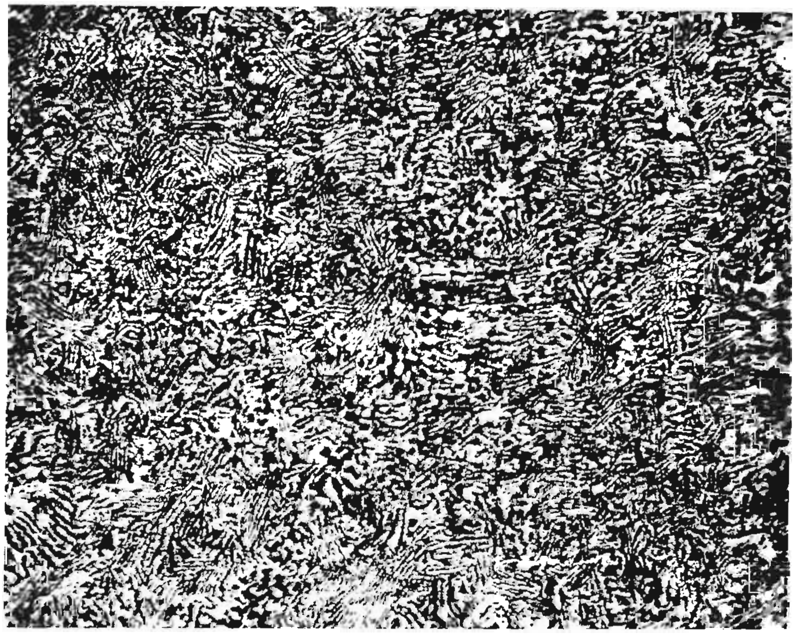

Fig. 10

Bi-In eutectic

100x etchant 10% nital

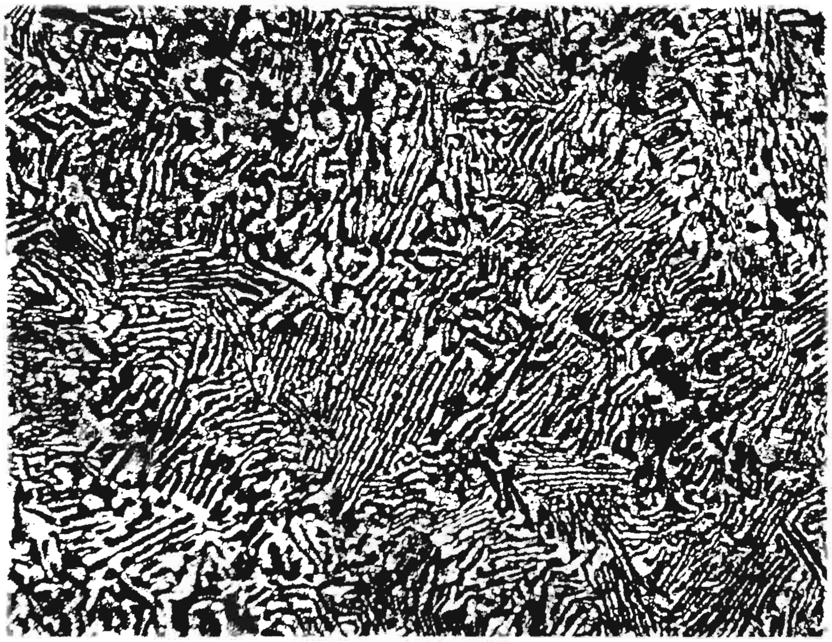

Fig. 11

Bi-In eutectic

200x etchant 10% nital

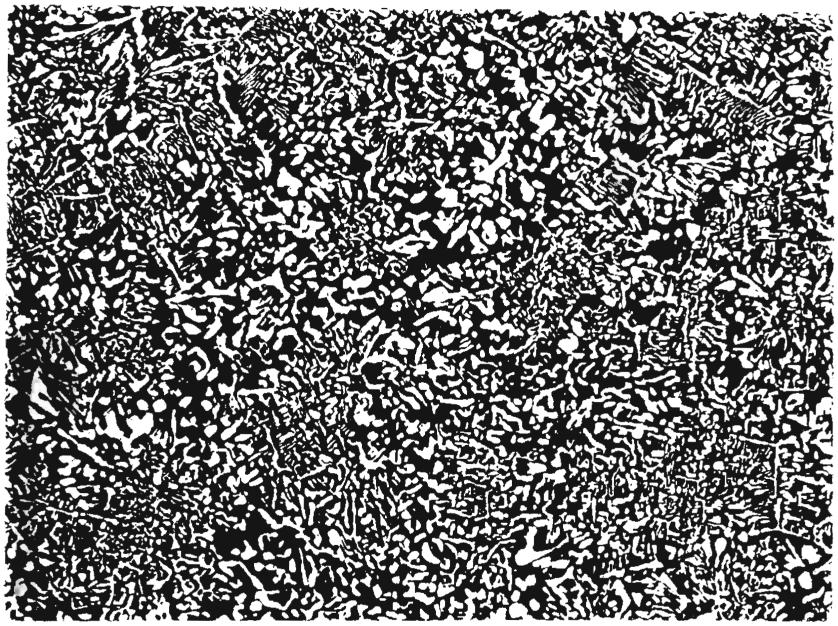

Fig. 12

Bi-Pb eutectic

100x etchant 1% chromic acid

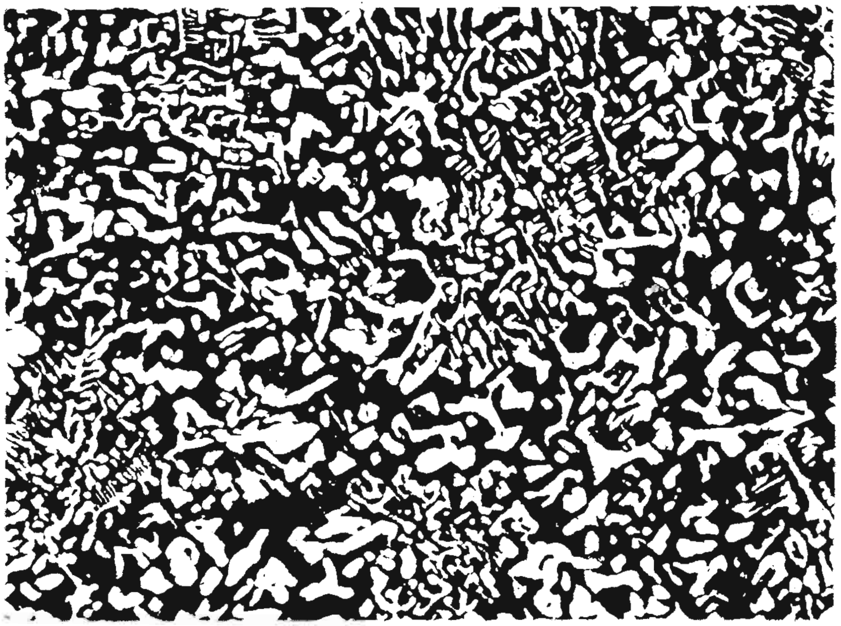

Fig. 13

Bi-Pb eutectic

200x etchant 1% chromic acid

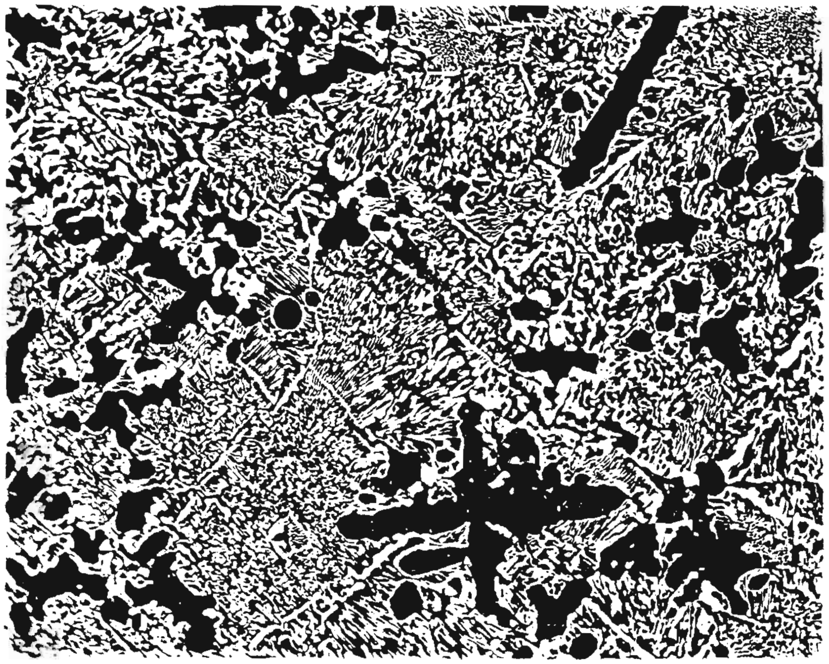

Fig. 14

Bi-Sn eutectic

100x etchant 3% nital

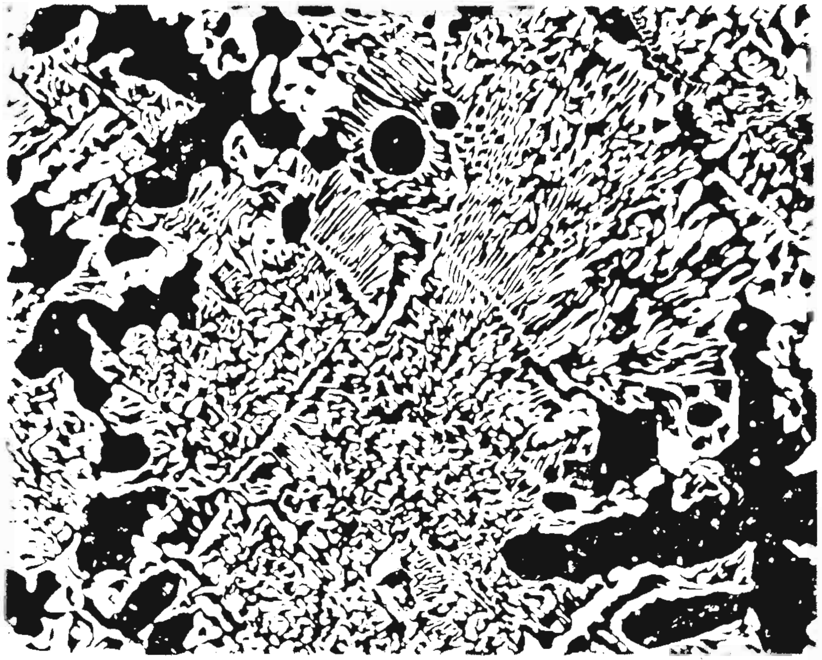

Fig. 15

Bi-Sn eutectic

200x etchant 3% nital

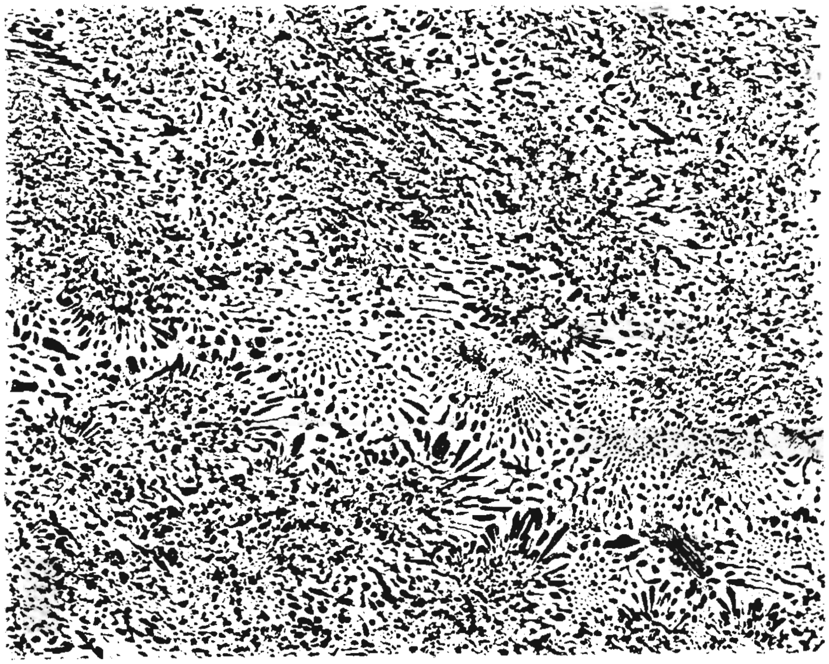

Fig. 16

Cd-Sn eutectic

100x etchant 1% nital

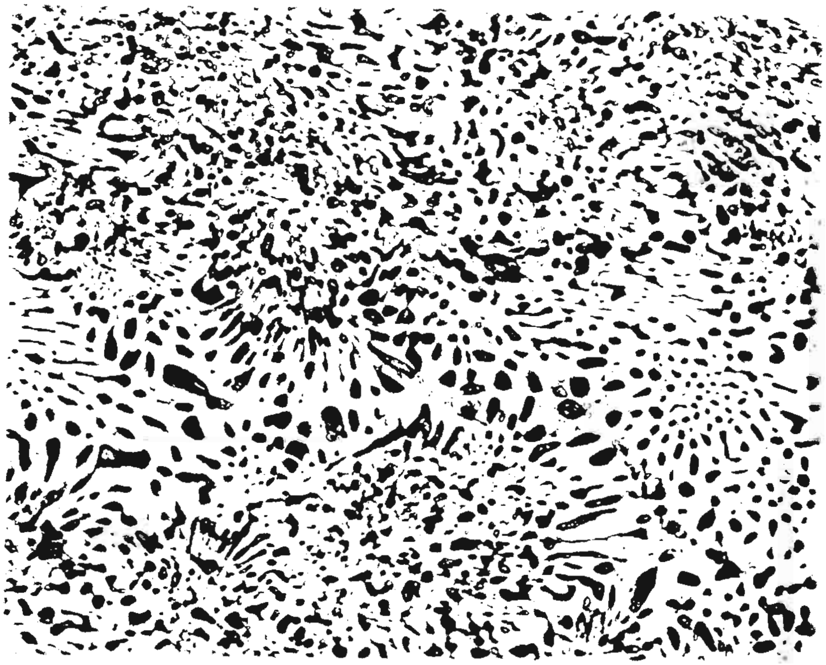

Fig. 17

Cd-Sn eutectic

200x etchant 1% nital

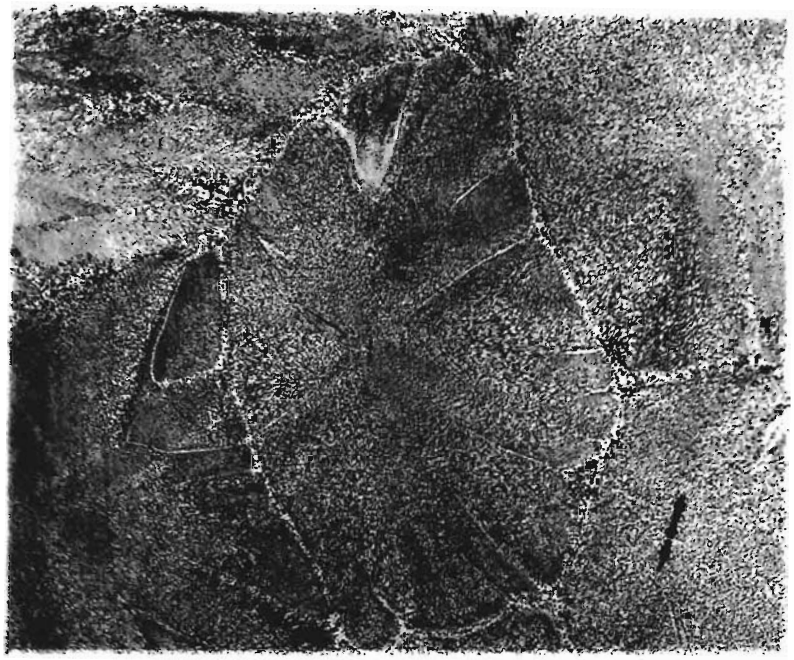

Fig. 18

Cd-Zn eutectic

100x etchant 1% nital

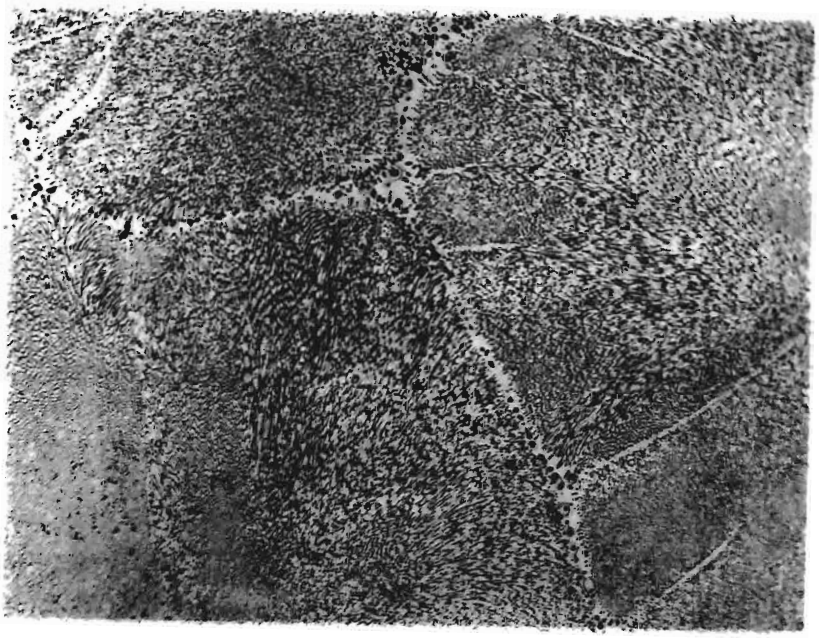

Fig. 19

Cd-Zn eutectic

200x etchant 1% nital

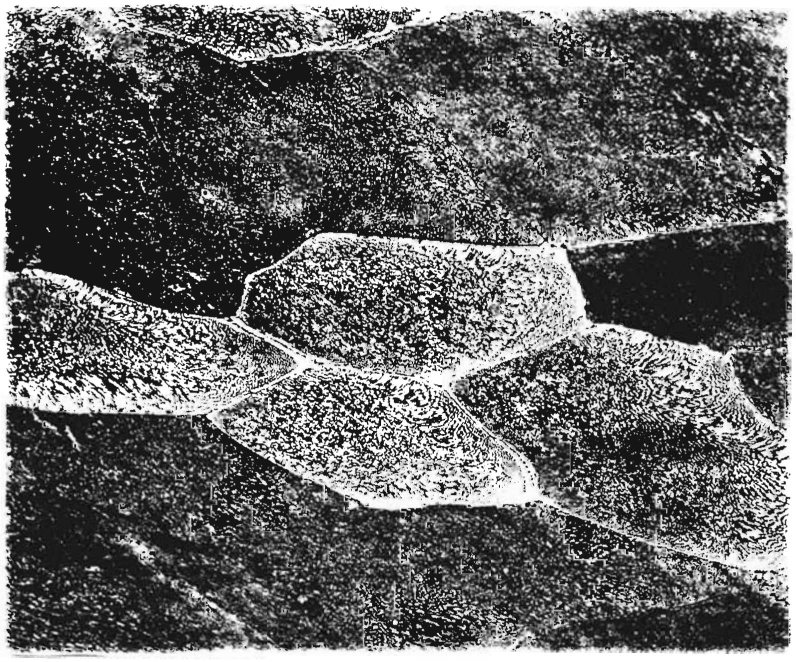

Fig. 20

Cu-O eutectic

100x etchant acid ferric chloride
and $NH_4OH-H_2O_2$

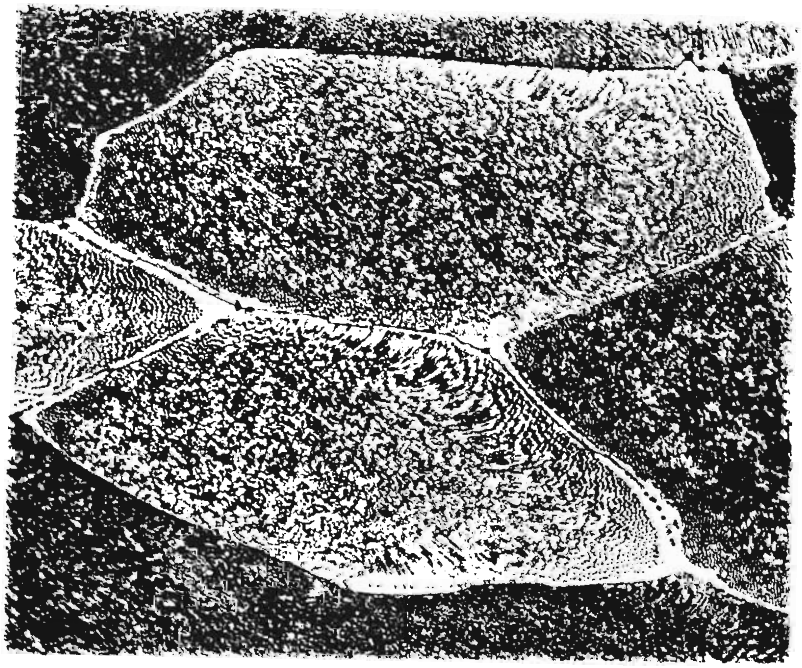

Fig. 21

Cu-O eutectic

200x etchant acid ferric chloride
and $NH_4OH-H_2O_2$

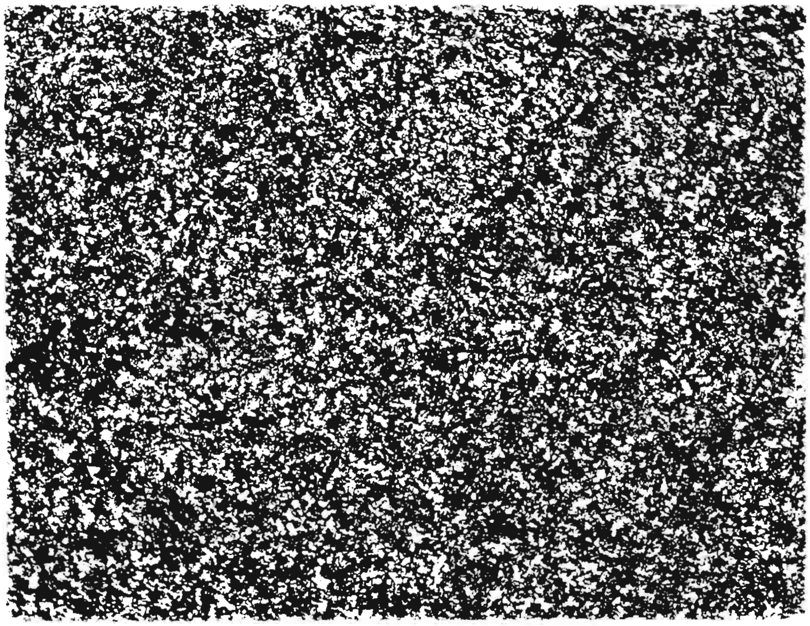

Fig. 22

Pb-Sb eutectic

100x etchant acetic-nitric

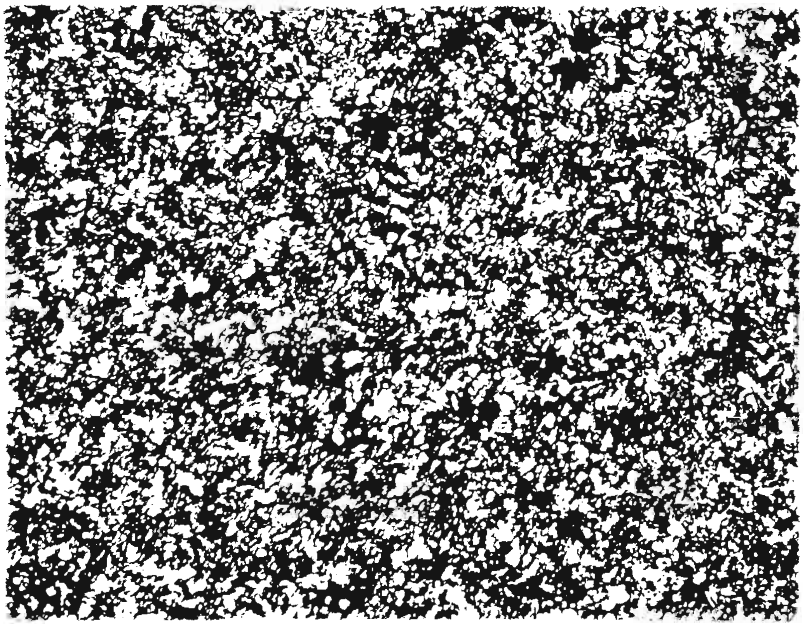

Fig. 23

Pb-Sb eutectic

200x etchant acetic-nitric

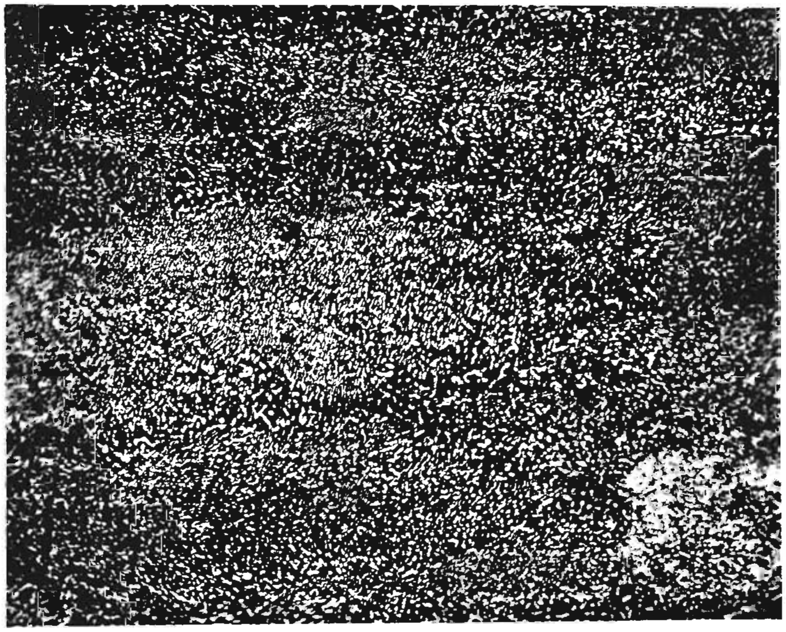

Fig. 24

Pb-Sn eutectic

100x etchant 1% nital

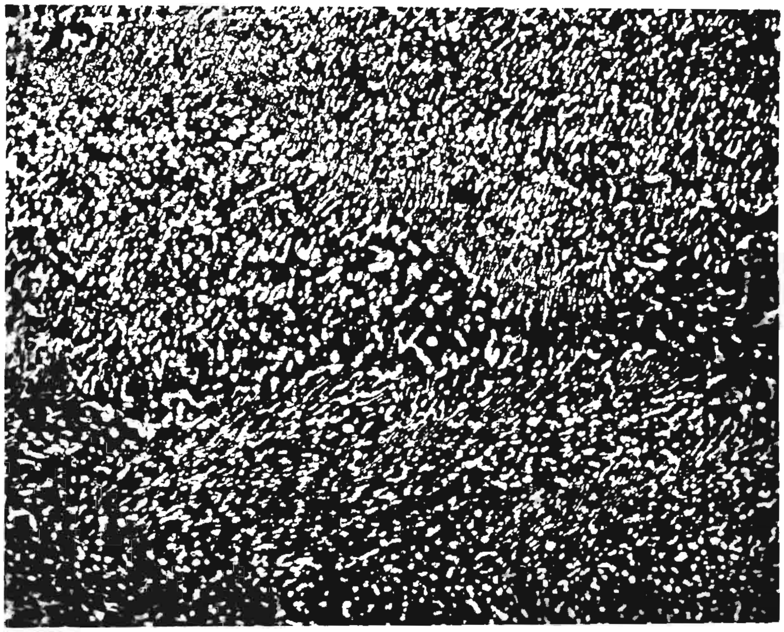

Fig. 25

Pb-Sn eutectic

200x etchant 1% nital

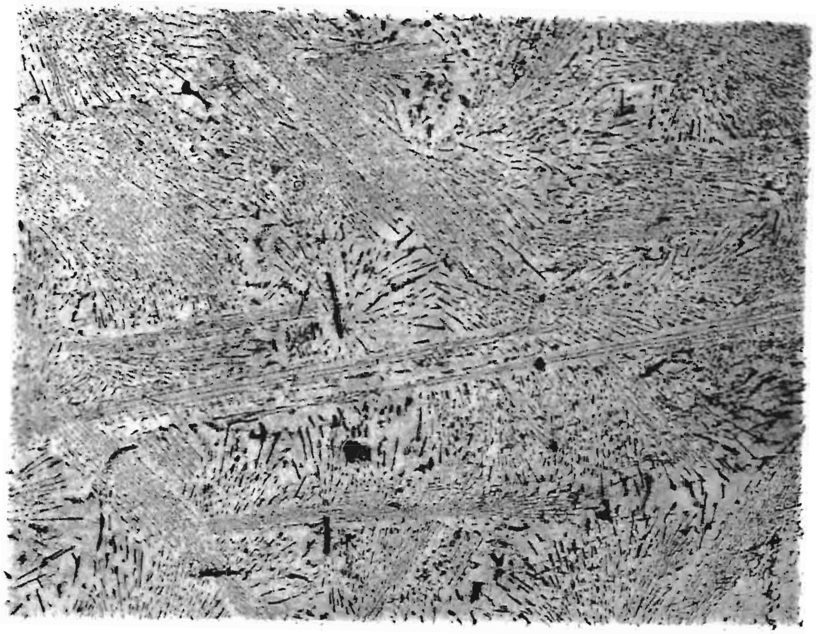

Fig. 26

Sn-Zn eutectic

100x etchant 1% nital

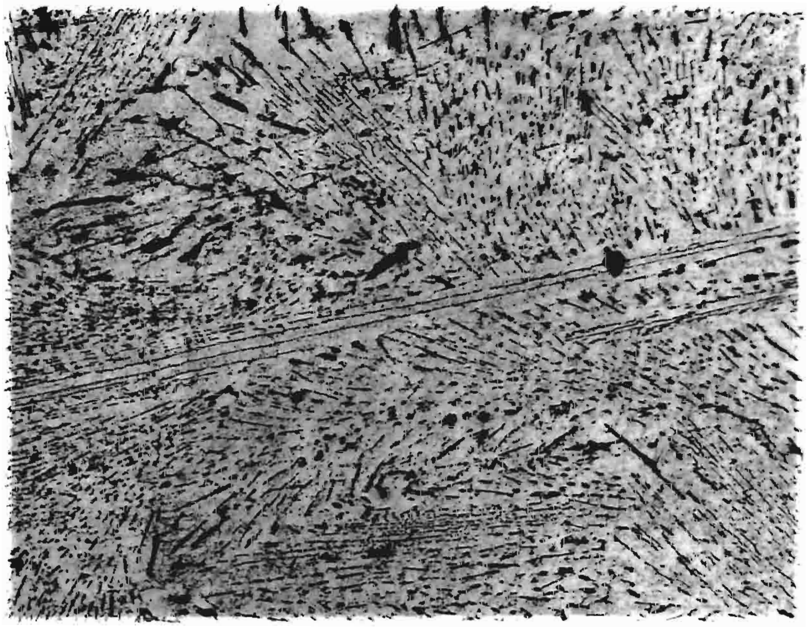

Fig. 27

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

$$W = \frac{SR}{X}$$

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

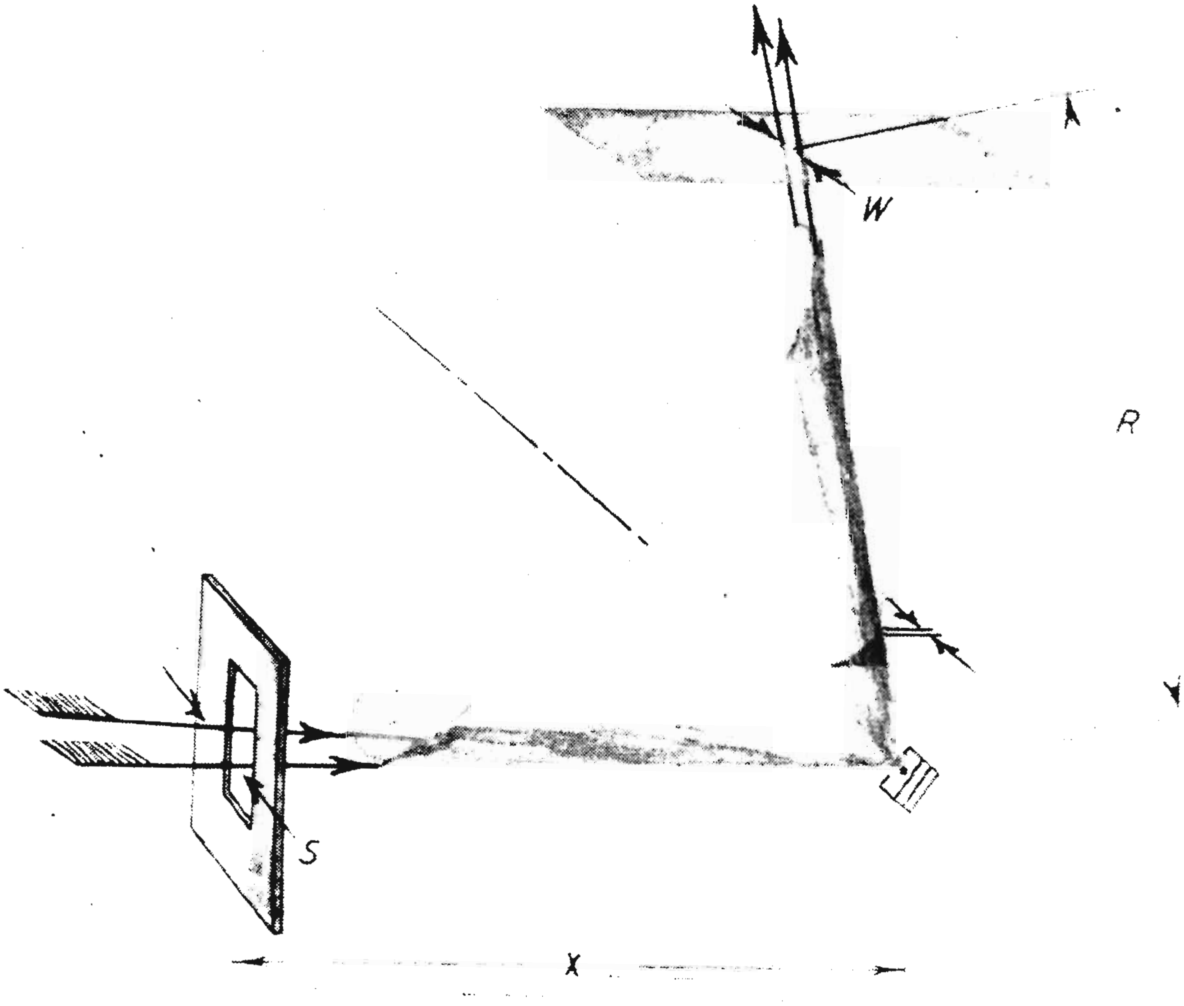

Fig. 28

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

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(34) Barrett, C. S., op. cit., pp. 7, 8 and 45.

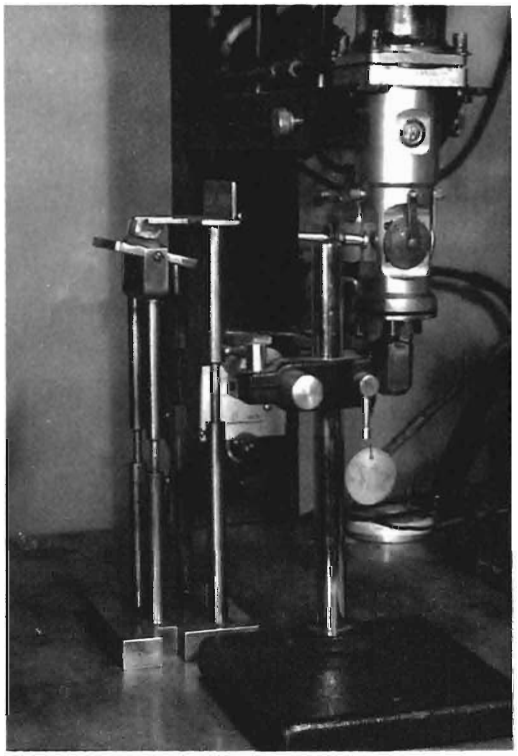


Fig. 29

X-ray Camera Positioned for Exposure

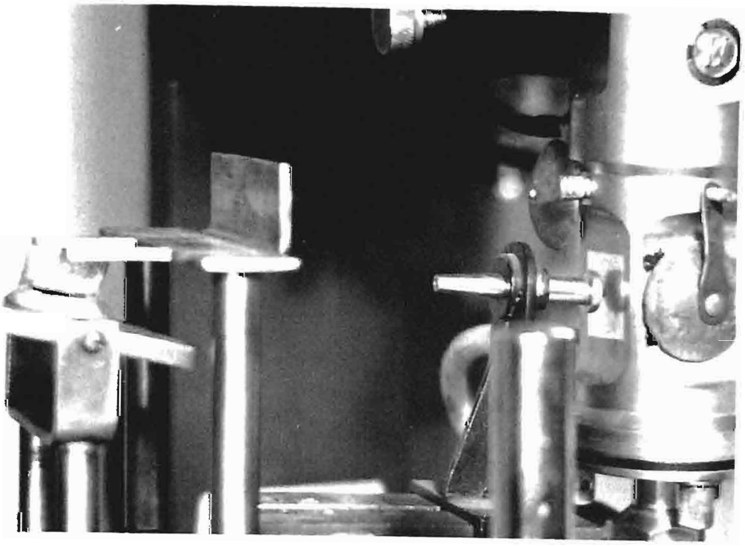


Fig. 30

Close-up of X-ray Camera

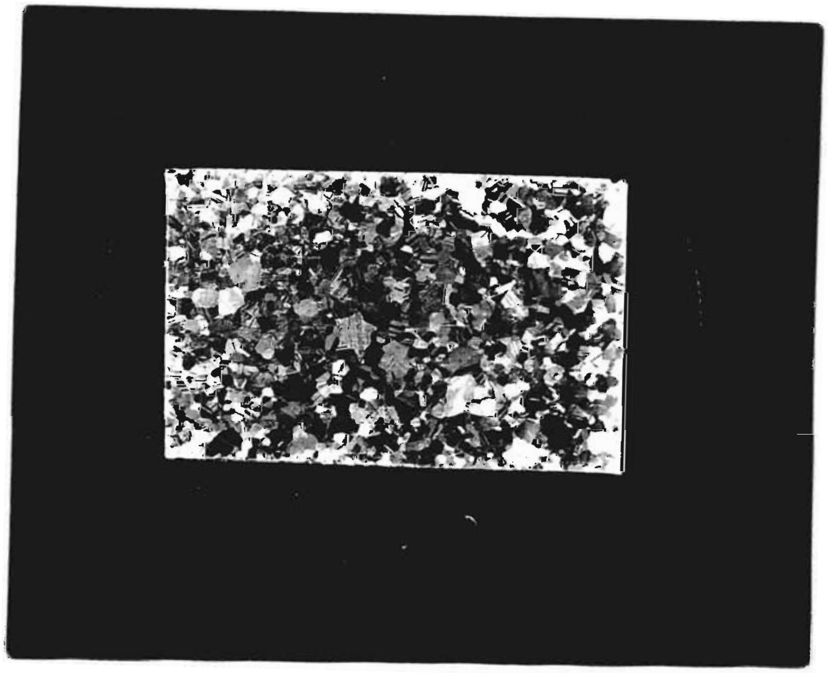


Fig. 31

Alpha Brass 1.75x

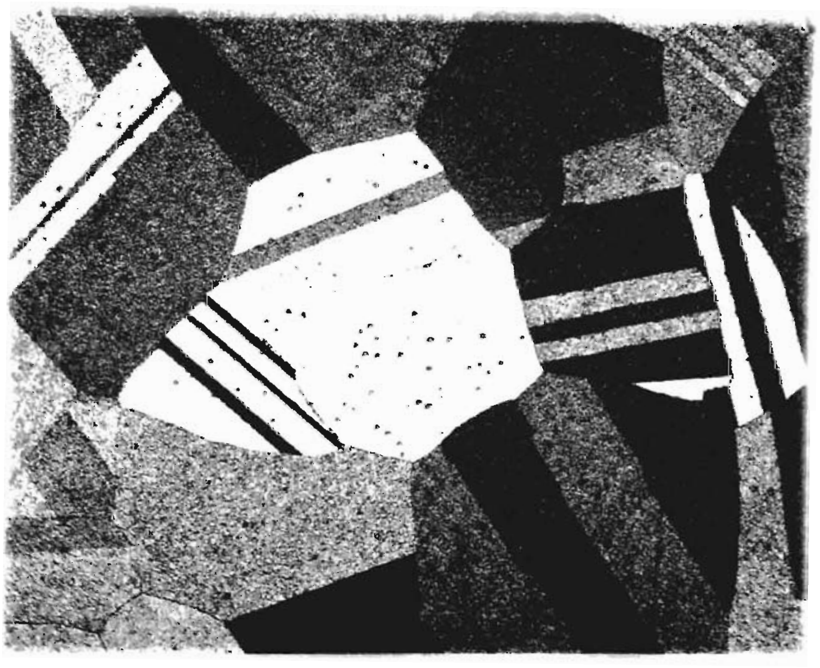


Fig. 32

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 flexability 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 exposures 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 theoretical 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 8½x 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

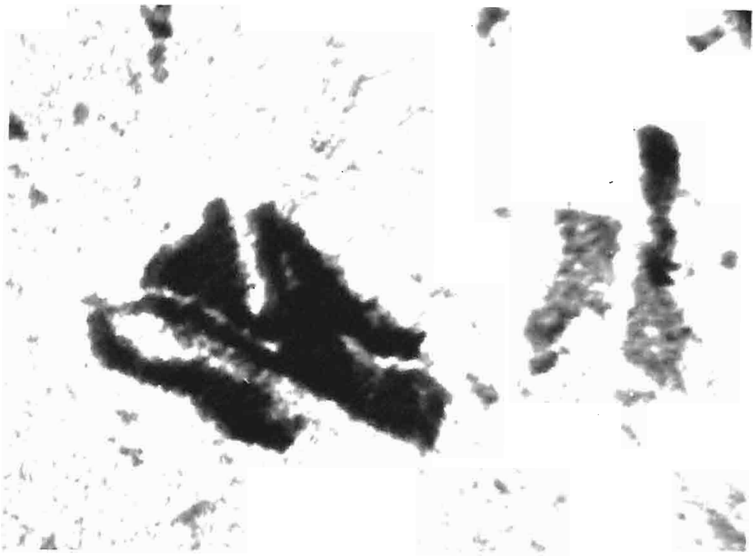


Fig. 36

Alpha Brass

X-ray Micrograph by Method 2, 50x

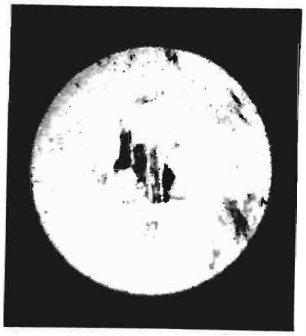


Fig. 37

Alpha Brass

X-ray Micrograph by Method 3, 10x

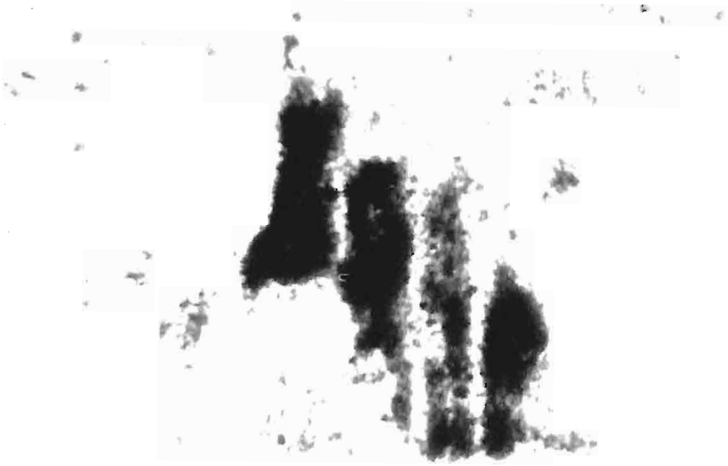


Fig. 38

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 position 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 probable that a eutectic grain of Cu-O acts in a similar manner. Comparison 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 photomicrographs (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

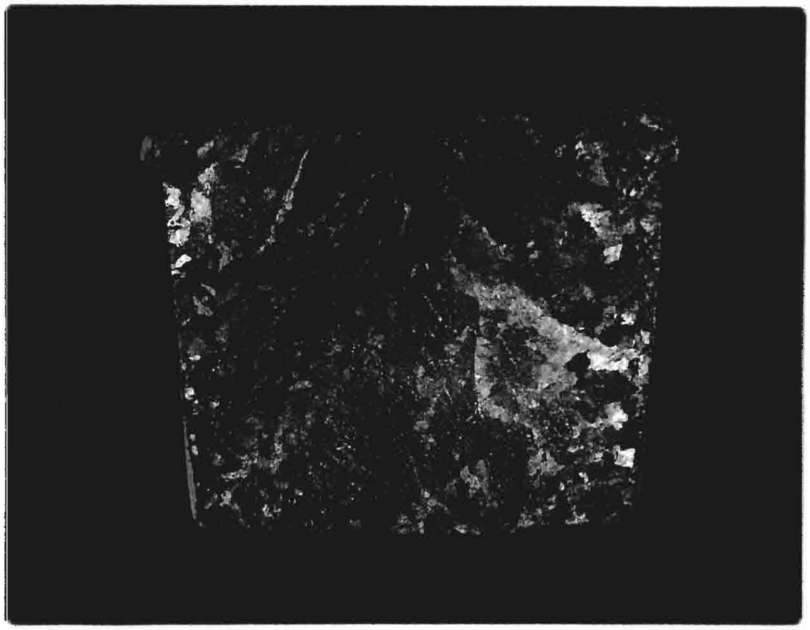


Fig. 39

Cd-Sn eutectic 1.75x

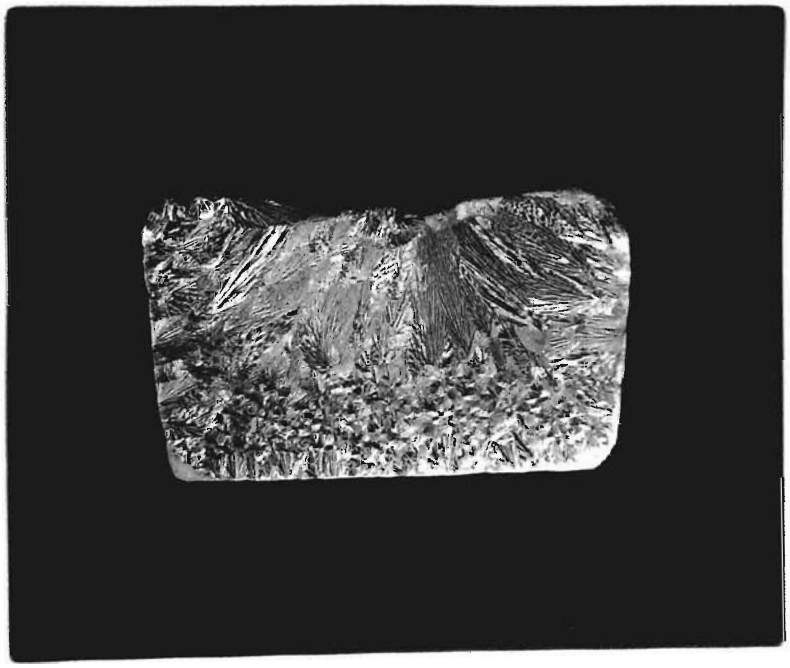


Fig. 40

Cd-Zn eutectic 1.75x

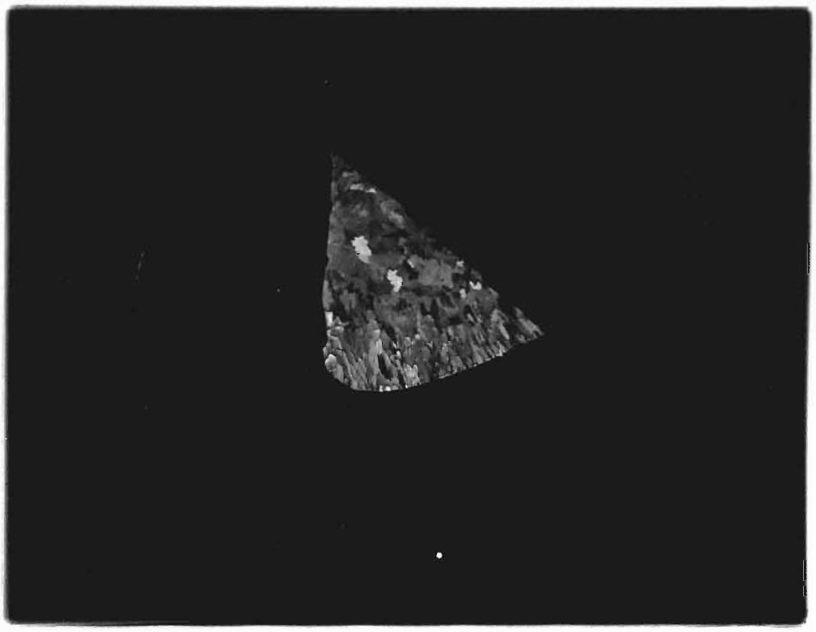


Fig. 41

Cu-O eutectic 1.75x

Fig. 42

Pb–Sn eutectic 1.75x

Fig. 43

Sn-Zn eutectic 1.75x

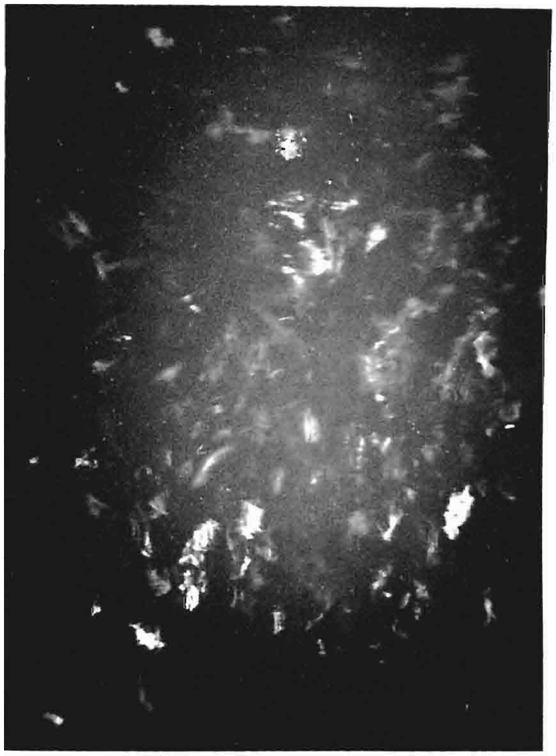


Fig. 44

Cu-O eutectic - 8.5x

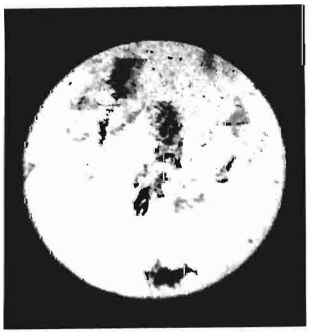


Fig. 45

Cu-O eutectic - 10x

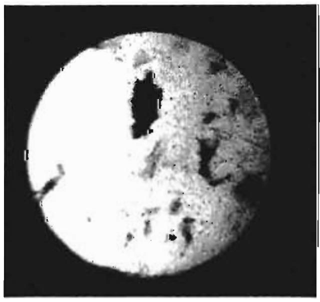


Fig. 46

Cu-O eutectic - 10x

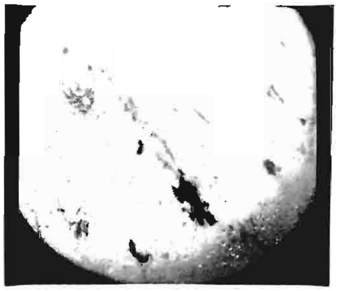


Fig. 47

Cd-Zn eutectic - 10x

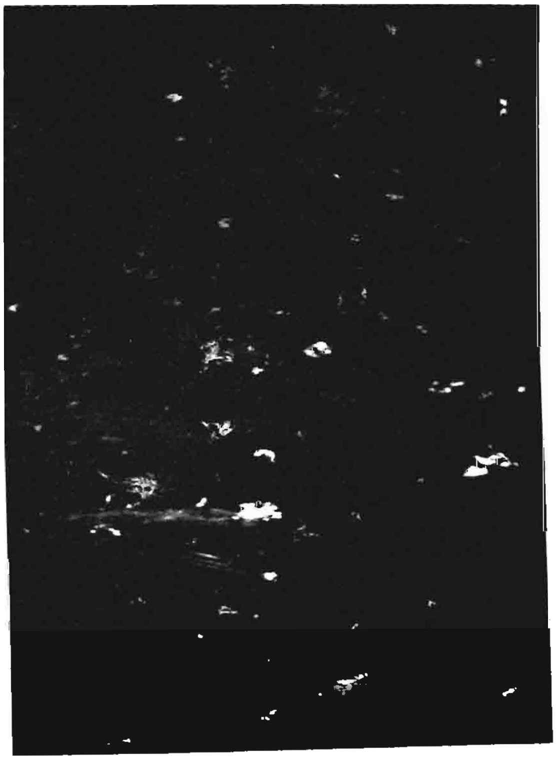


Fig. 48

Cd-Zn eutectic - 8.5x

Fig. 49

Cd-Zn eutectic - 10x

Fig. 50

Cd-Zn eutectic - 8.5x

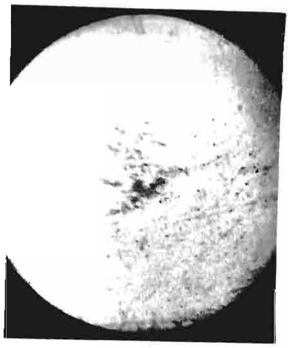


Fig. 51

Pb-Sn eutectic - 10x

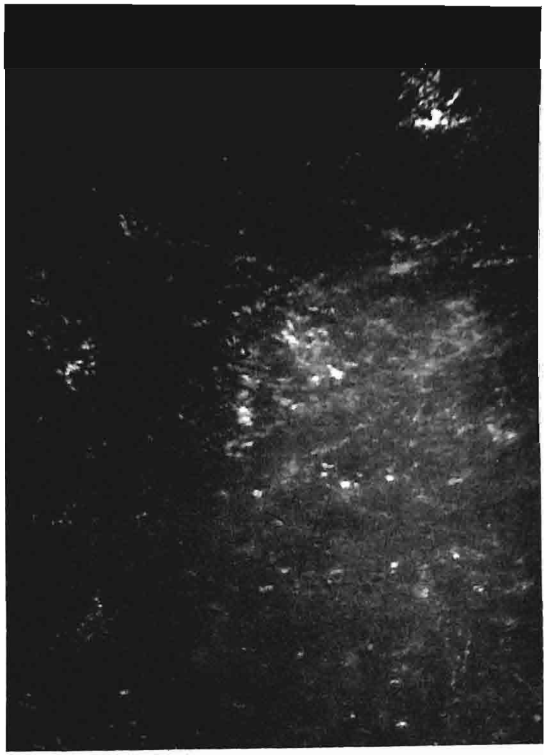


Fig. 52

Pb-Sn eutectic - 8.5x

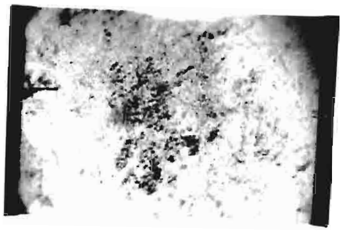


Fig. 53

Sn-Zn eutectic - 10x

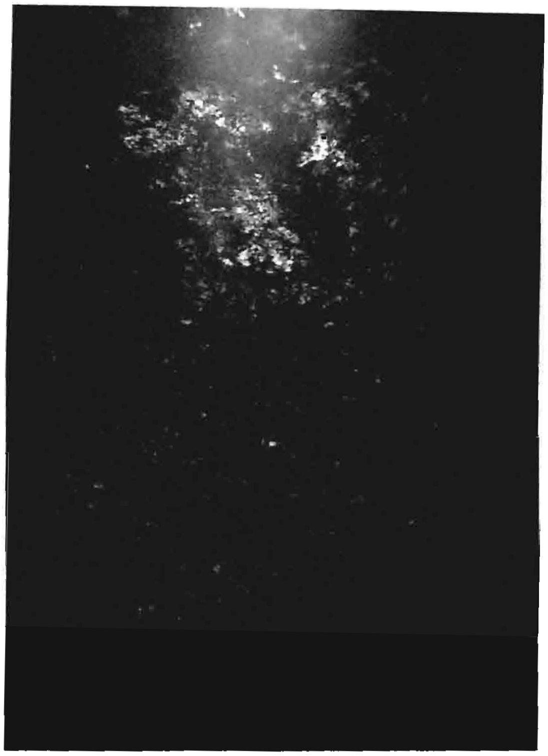


Fig. 54

Sn-Zn eutectic - 8.5x

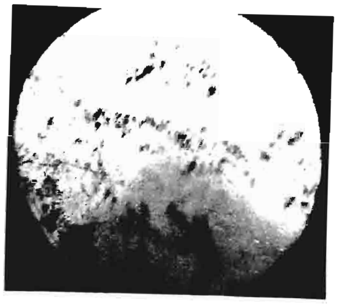


Fig. 55

Sn-Zn eutectic - 10x

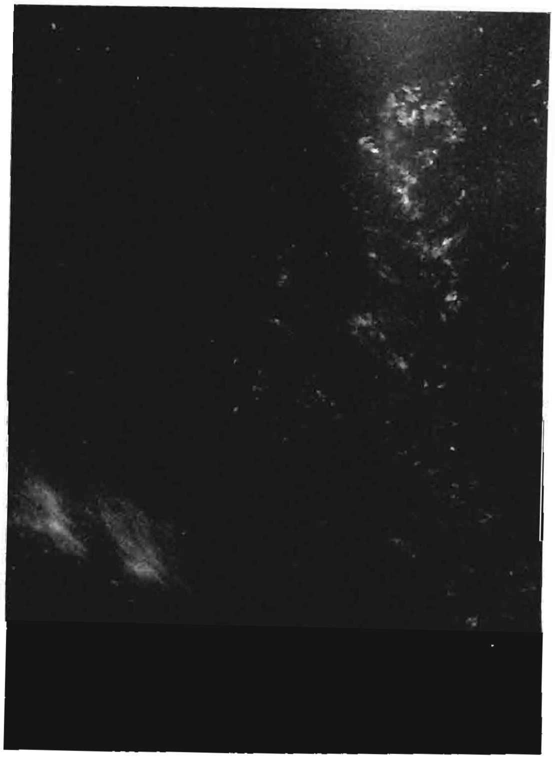
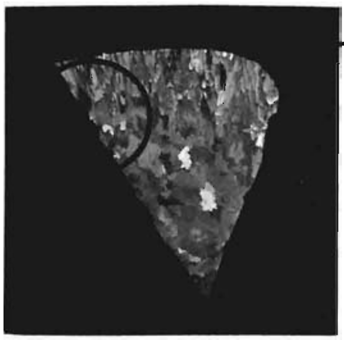


Fig. 56

Sn-Zn eutectic - 8.5x



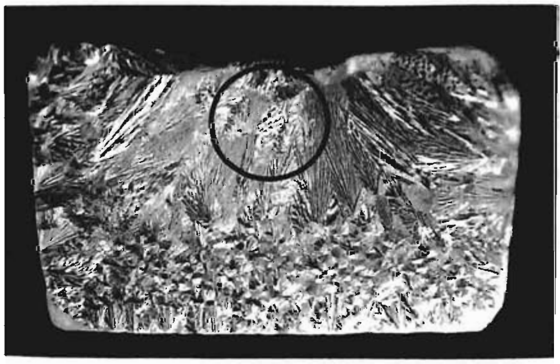
Cu–O

Fig. 57

Cd–Zn

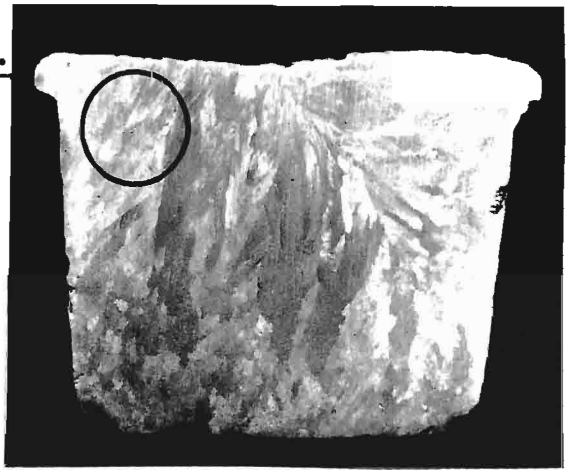
Fig. 58

○ Area Covered by X-ray Beam



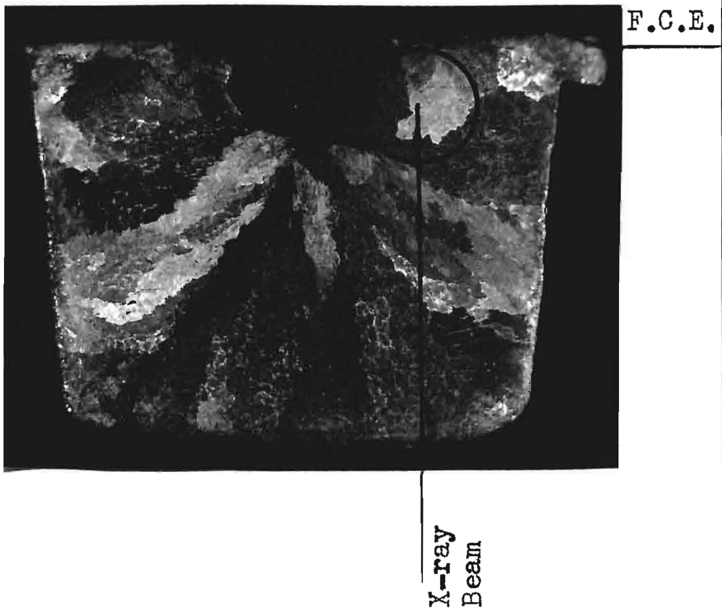
Cd–Zn

Fig. 59



Pb–Sn

Fig. 60



Sn-Zn

Fig. 61

Sn-Zn

Fig. 62

eutectic grain reflects as a whole. Nix and Schmid(35) and Straumanis and Brakss(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

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(35) Nix, F. C., and Schmid, E., op. cit., p. 291

(36) Straumanis, M., and Brakss, N., Der Aufbau der Zink-Cadmium Eutektikums, Z. fur physikal. Chem., (B) Vol. 30, p. 128 1935.

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 θ; 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.

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(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 IV

EQUILIBRIUM DIAGRAMS

Appendix A

Alloy System	Reference*	Page
Silver-Copper	A.S.M. Hdbk., 1948	73
Bismuth-Cadmium	A.S.M. Hdbk., 1948	74
Bismuth-Indium	Peretti and Carapella	75
Bismuth-Lead	A.S.M. Hdbk., 1948	76
Bismuth-Tin	A.S.M. Hdbk., 1948	77
Cadmium-Tin	A.S.M. Hdbk., 1948	78
Cadmium-Zinc	A.S.M. Hdbk., 1948	79
Copper-Oxygen (partial)	Hansen	80
Lead-Antimony	A.S.M. Hdbk., 1948	81
Lead-Tin	A.S.M. Hdbk., 1948	82
Tin-Zinc	A.S.M. Hdbk., 1948	83

*References:

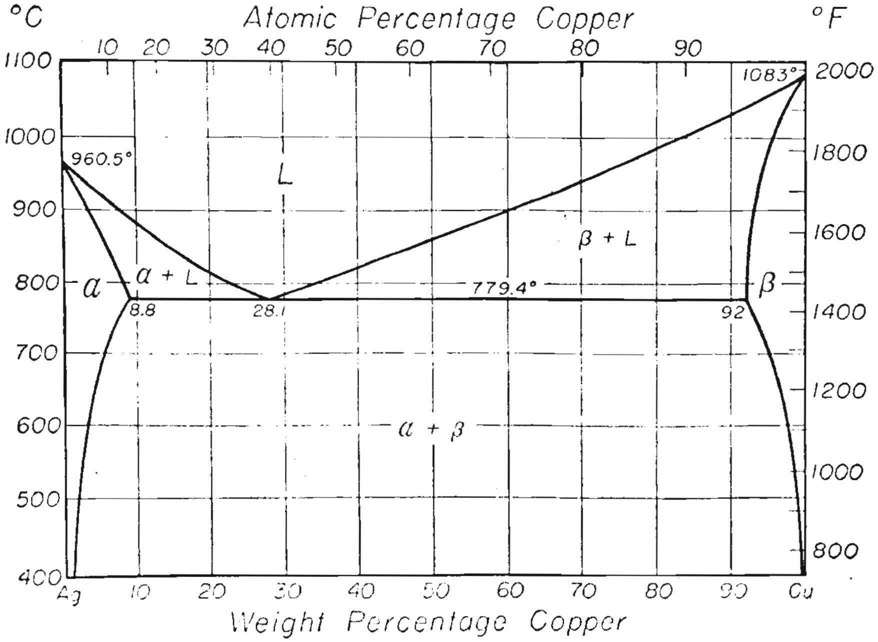
Am. Soc. Metals, Metals Handbook, pp. 1145-1240, 1948.

Hansen, M., Der Aufbau der Zweistofflegierungen, J. Springer, Berlin, p. 590, 1936.

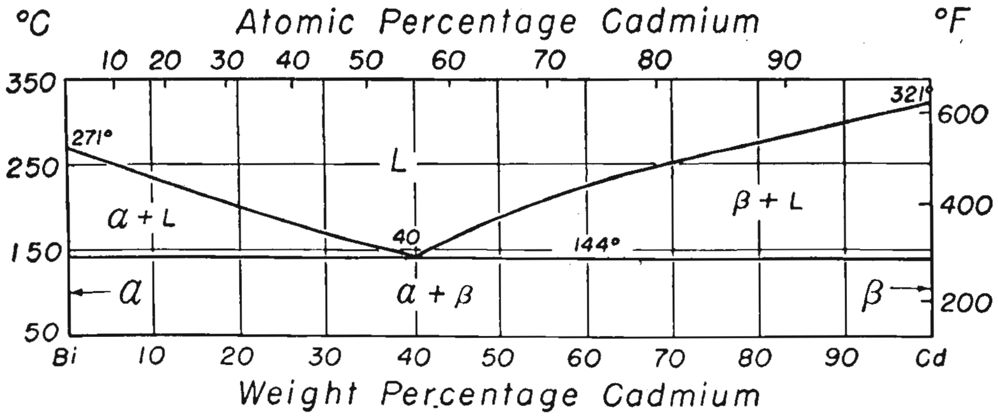
Peretti, E. A. and Carapella, S. C., The Indium-Bismuth Phase Diagram, Trans., A.S.M., Vol. 41, p. 949, 1949.

Ag-Cu Silver-Copper

By Cyril Stanley Smith*



Bi-Cd Bismuth-Cadmium



Bi-Cu Bismuth-Copper

By A. C. Vaughan*

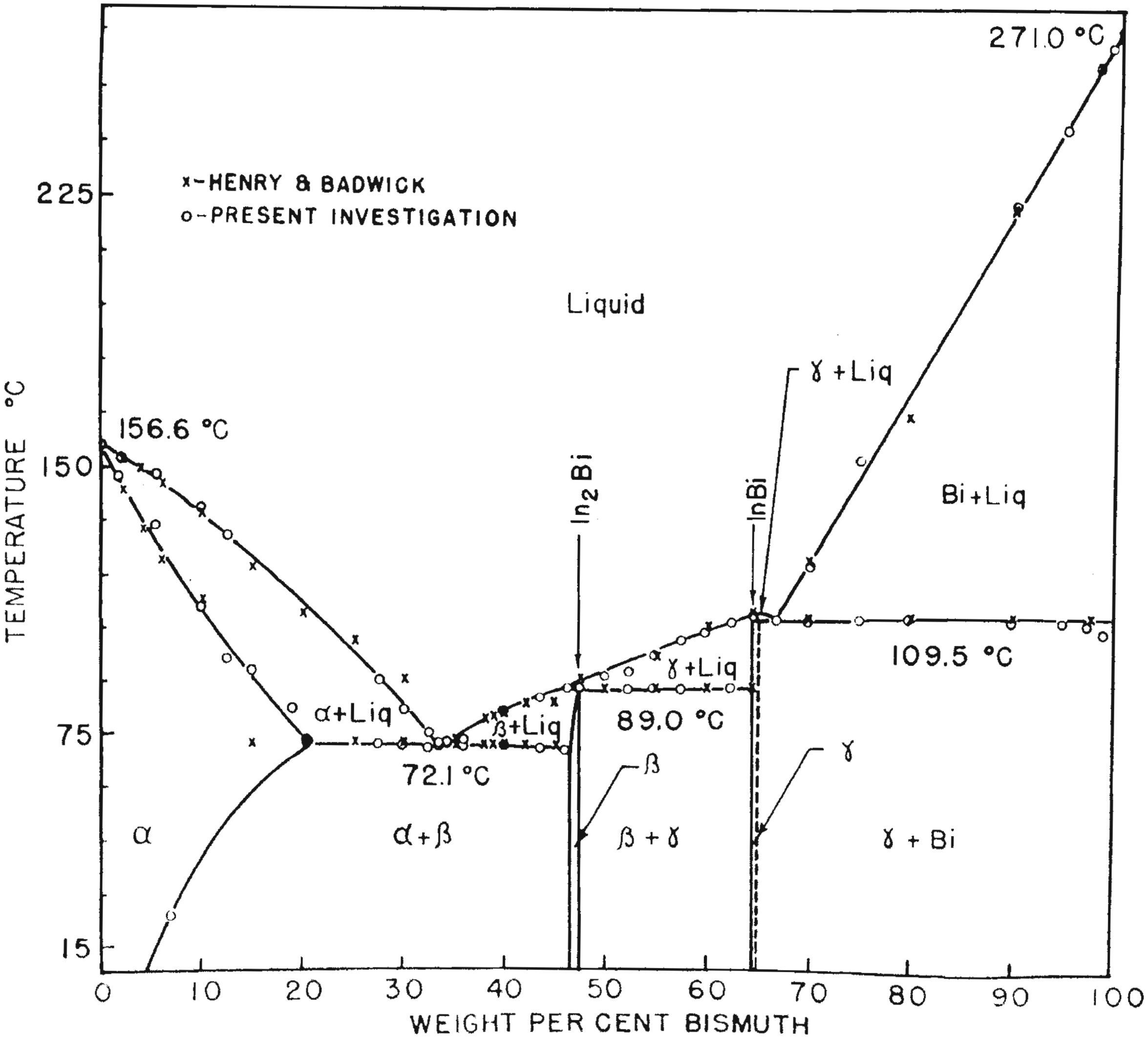
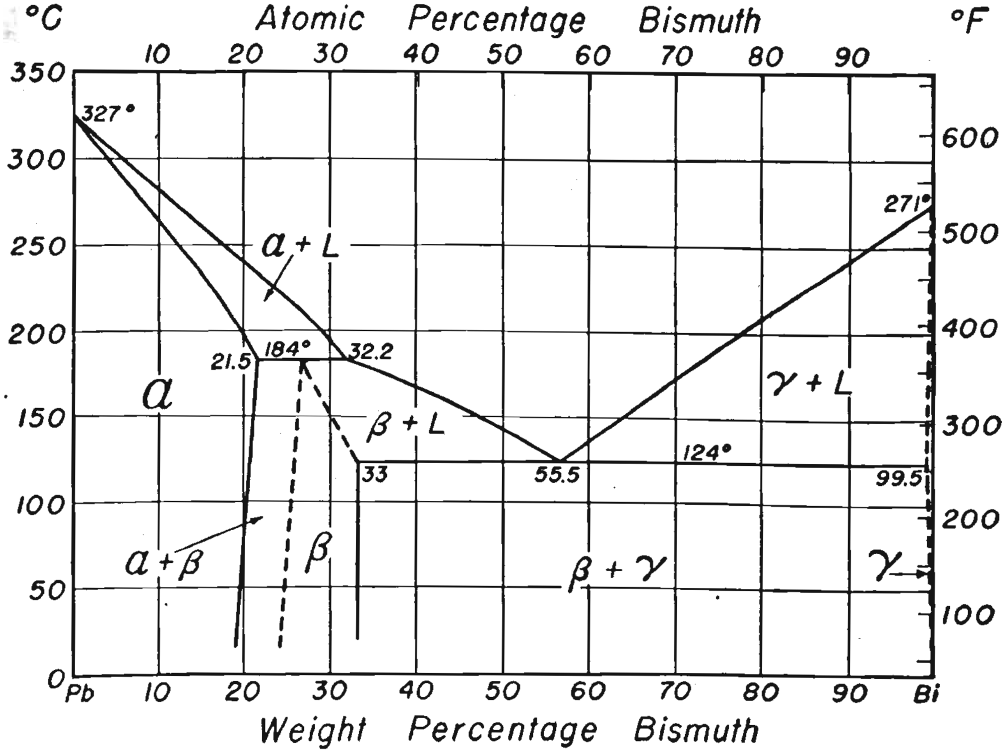


Fig. 1 Phase Diagram of the System Indium-Bismuth.

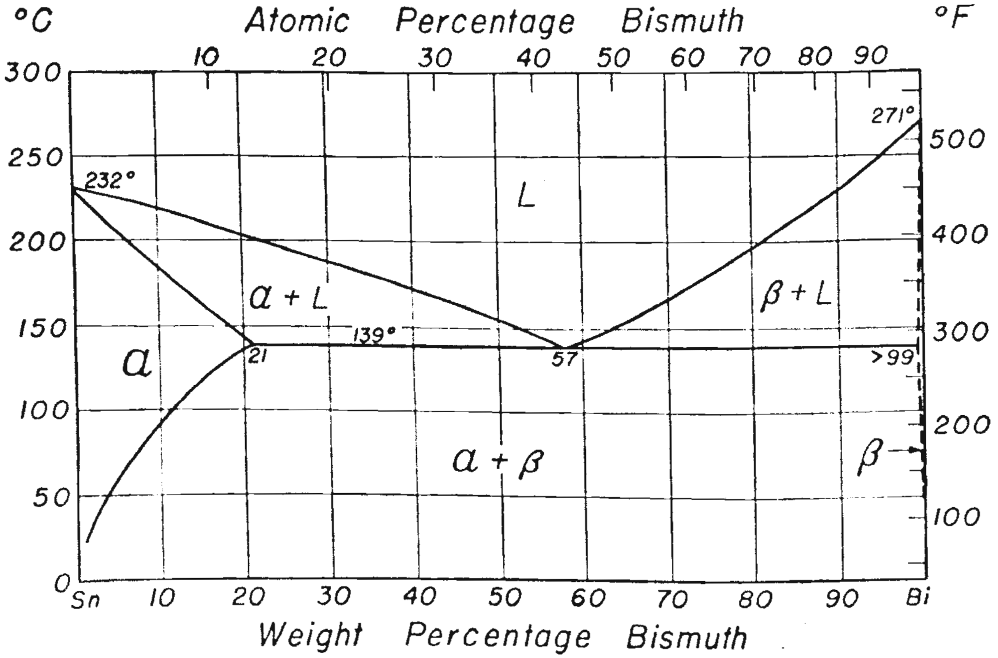
Bi-Pb Bismuth-Lead

By G. O. Hiers*



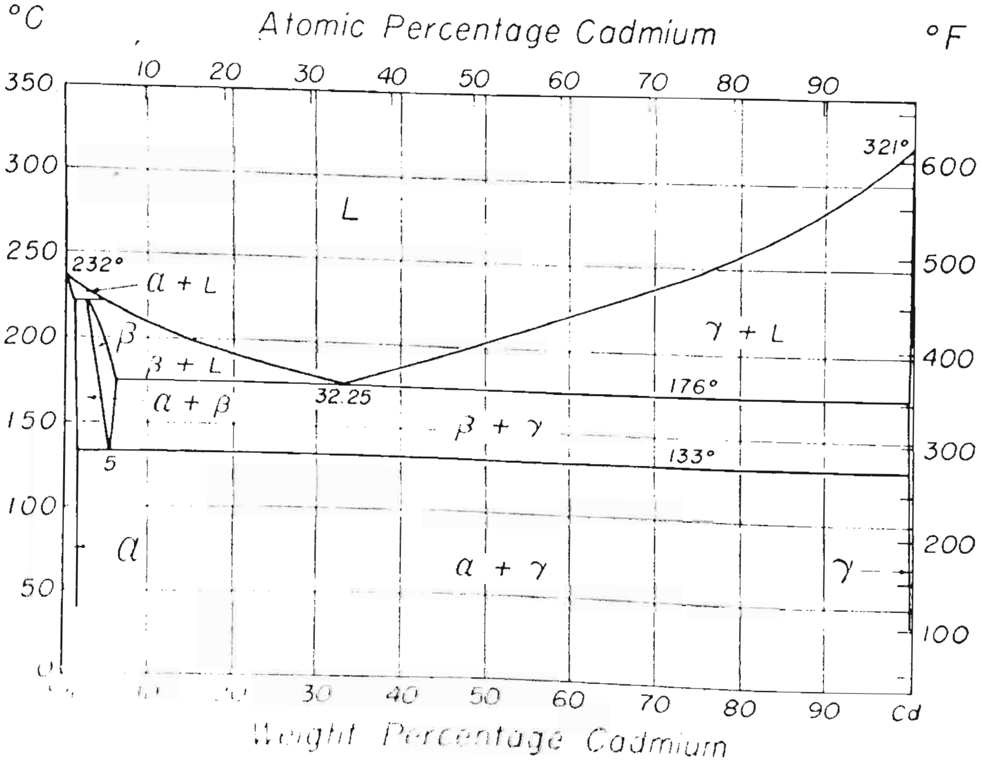
Bi-Sn Bismuth-Tin

By R. I. Jaffee* and Bruce W. Gonser*



Cd-Sn Cadmium-Tin

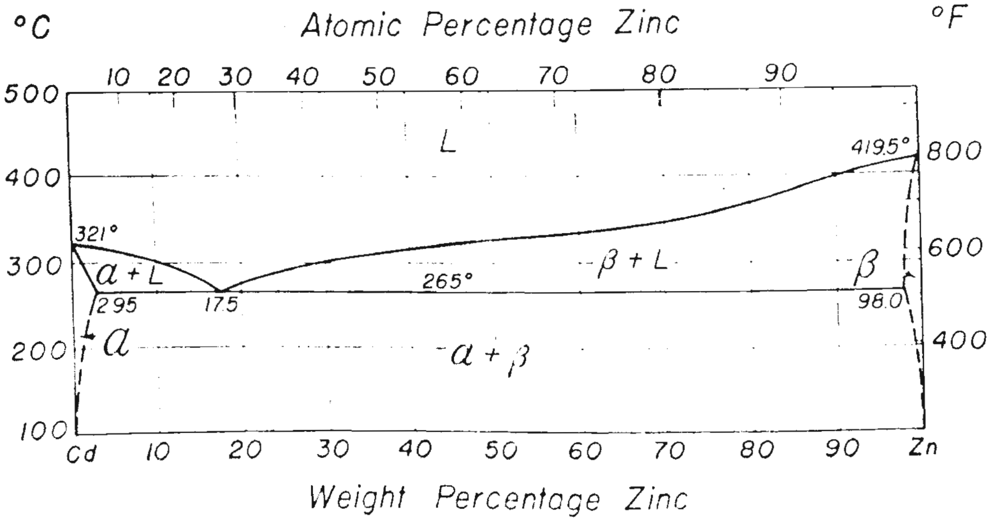
By W. T. Pell-Walpole*



(For diagrams on a larger scale, see the next page.)

Cd-Zn Cadmium-Zinc

By E. A. Anderson*



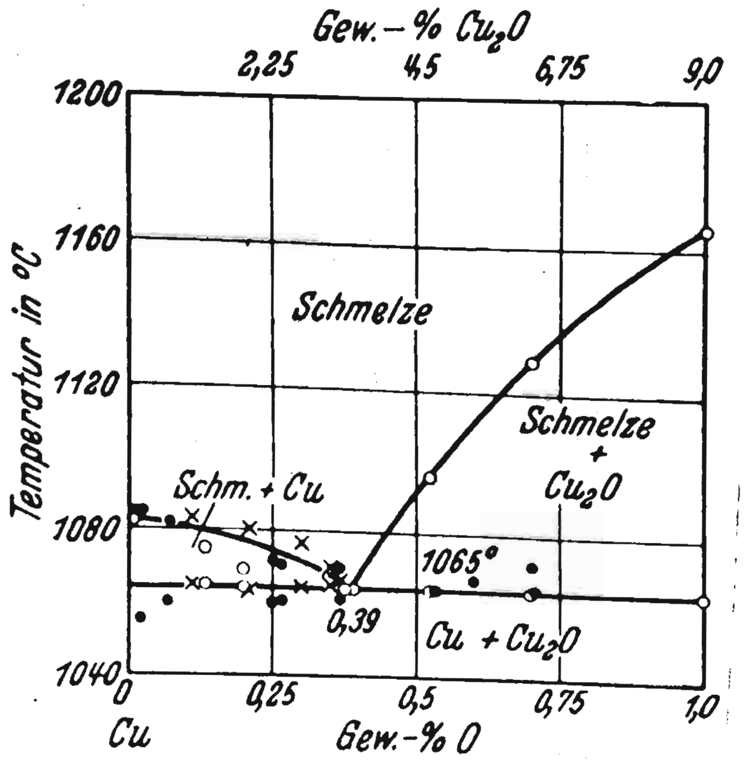
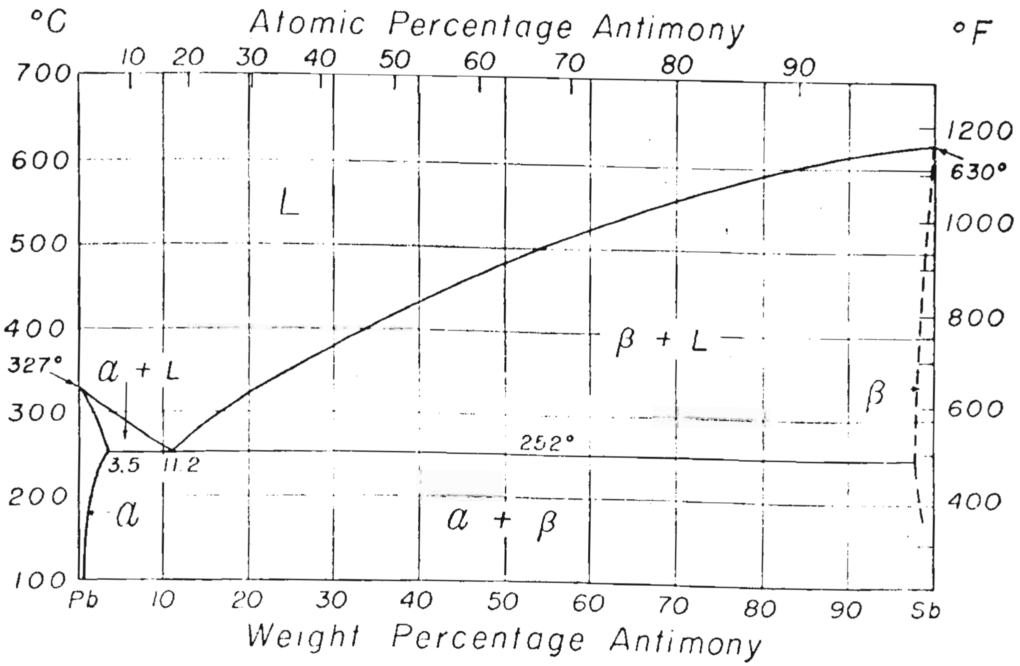


Abb. 251. Cu-O. Kupfer-Sauerstoff (siehe auch Abb. 252).

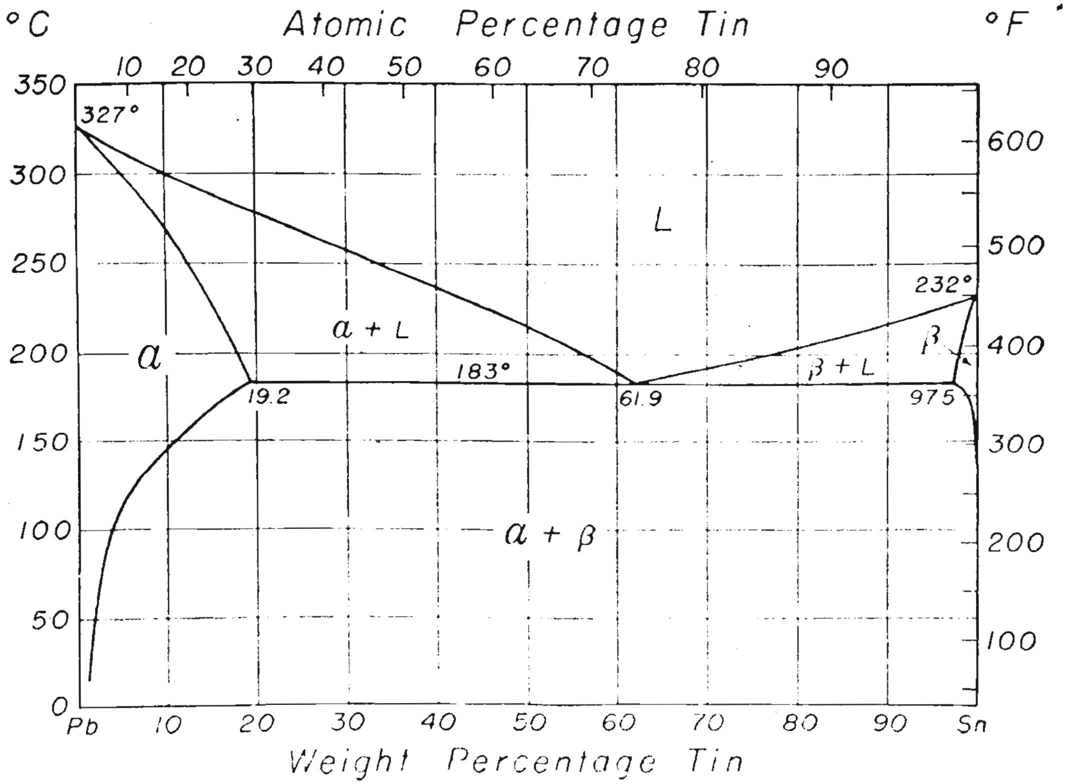
Pb-Sb Lead-Antimony

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



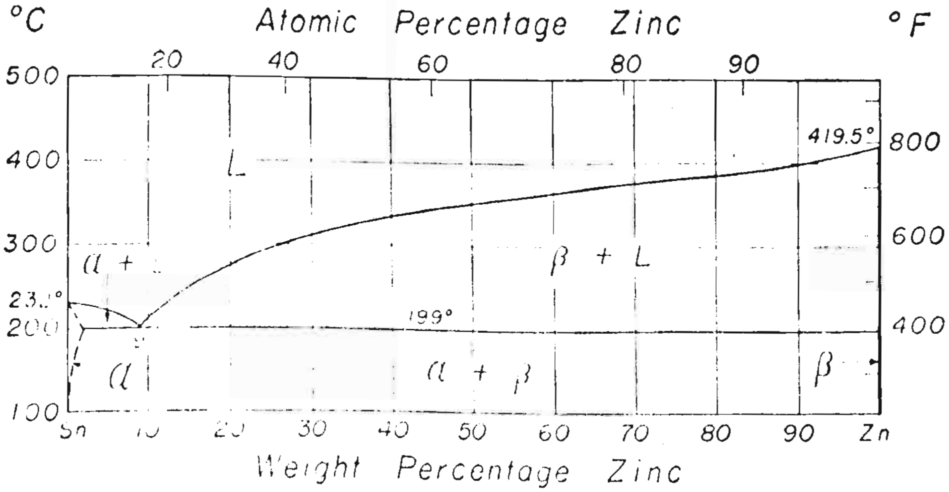
Pb-Sn Lead-Tin

BY G. O. HIERS*



Sn-Zn Tin-Zinc

By E. A. Anderson*



ETCHING REAGENTS

Appendix B

Specimen	Etchant for Micro-examination	Etchant for macro-examination
Ag-Cu	5 parts ammonium hydroxide diluted with equal amount of water. 1 part 3% hydrogen peroxide. Darkens copper-rich phase.	
Bi-Cd	5 parts ferric chloride 10 parts hydrochloric acid 100 parts water Darkens cadmium	
Bi-In	10 cc concentrated nitric acid 90 cc ethyl alcohol Darkens Indium-rich phase.	
Bi-Pb	10 gm. Cr_2O_3 90 gm. water Darkens lead-rich phase.	
Bi-Sn	Immersed in 3% nital 3 parts concentrated nitric 97 parts ethyl alcohol swabbed with 5 parts ferric chloride, 10 parts hydrochloric acid, 100 parts water. Darkens tin-rich phase.	
Cd-Sn	1 part concentrated nitric 99 parts ethyl alcohol Darkens cadmium	25 gm. ferric chloride 25cc conc. hydrochloric 100cc water
Cd-Zn	1 part concentrated nitric 99 parts ethyl alcohol Darkens zinc.	1 gm. iodine 5 gm. potassium iodide 100 cc water.
Cu-O	Immersed in 5 parts ferric chloride, 10 parts hydrochloric acid, 100 parts water, swabbed with 10 parts ammonium hydroxide, 10 parts water, 2 parts 3% hydrogen peroxide, swabbed with acid ferric chloride. Darkens cuprous oxide.	Same as micro.
Pb-Sb	3 parts glacial acetic 4 parts concentrated nitric 16 parts water Darkens lead.	

ETCHING REAGENTS

Appendix B (contd.)

Specimen	Etchant for Micro-examination	Etchant for macro-examination
Pb-Sn	1 part concentrated nitric 99 parts ethyl alcohol Darkens tin.	25 gm. ferric chloride 25 cc hydrochloric acid 100 cc water
Sn-Zn	1 part concentrated nitric 99 parts ethyl alcohol Darkens zinc.	5 parts ferric chloride 10 parts conc. hydrochloric 100 parts water.

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VITA

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