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THE EFFECT OF HEATING CHILL CAST EUTECTICS

BY

ROBERT LEWIS DRESHFIELD

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1959

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THE EFFECT OF HEATING CHILL CAST EUTECTICS

I

INTRODUCTION

This investigation is the result of the author's specific interest in two phase systems. In the past, considerable work has been done investigating the alteration of eutectoid structures; however, eutectic structures have been neglected to a great extent. Tammann did some work on the subject in 1937⁽¹⁾ as did Brown and Guy⁽²⁾ in

-
- (1) Tammann, G. A. and Hartmann, H., Das Gefüge eutektischer Legierungen seine Änderung beim Walzen and Erhitzen, Zeitschrift für Metallkunde, Vol. 29, No. 5, p 141-144, 1937.
- (2) Brown, J. S., and Guy, A. G., The Effect of Working and Heating Eutectic Structure, Trans. AIME, vol 185, p 933, 1949.

more recent times. In both of the above cases the eutectic structure was altered by cold working and subsequent heating of the alloy.

Tammann⁽³⁾ also noted that eutectics chill cast in

-
- (3) Tammann, G. A., op. cit., p 144

liquid air display a vastly different structure than those cast under equilibrium conditions and that there was some shrinkage of the unworked needles after heat treatment.

Eutectic and eutectoid structures show many similarities. Using normal microscopic techniques, one finds it

difficult to note a difference between them except that the eutectoid is usually a finer structure.

In the light of the above, it would seem reasonable that could a fine enough eutectic structure be produced, then it could, perhaps, be expected to respond to spheroidizing heat treatments in a manner similar to eutectoids. This investigation was started in an effort to determine what effect chill casting and subsequent heat treatment has upon eutectic structures.

II

REVIEW OF LITERATURE

Early Research. For many years it has been known that with many pairs of metals and salts it is possible to prepare one alloy or combination which will freeze in the same manner as a pure material at a constant temperature lower than either of the constituents, or any other member of the series. The same effect has been noted in the depression of freezing points of aqueous solutions of various salts. Most of the early research dealt with the latter phenomenon. As early as 1864, Rudorf⁽⁴⁾ noted that

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

the minimum freezing point occurred at the intersections of the curve of separation of ice from salt solutions with that of the solubility of salt in water. Guthrie⁽⁵⁾ in

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

1875 reported the results of his investigations on the above types of solutions which he termed "cryohydrates." He concluded that cryohydrates were chemical compounds because of three things which were similar to known compounds. He noted that these materials had a constant composition, a constant freezing point and a characteristic appearance. Although his view was disputed within two years, it was held for some time.

In 1884-5, Guthrie^(6,7) was able to show the complete

(6) Guthrie, F., Phil. Mag., V. 17, p 462, 1884.

(7) Guthrie, F., Proc. Phys. Soc., 6, pp 124, 169, 1884-84.

resemblance between the behavior of cooled salt solutions, alloys and fused salt mixtures. It was at this time that the term "eutectic" was introduced as a designation for a minimum freezing substance. Although some of Guthrie's conclusions have had to be discarded, many of his findings have been substantiated by later investigators.

Prior to 1895, eutectics were considered to be homogeneous substances. This error appears to be justified as the cooling curve of a eutectic is similar to that of a pure substance and because the phases coprecipitate as a very fine mixture. Ponsot⁽⁸⁾ showed by microscopic exami-

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

nation that eutectics are, in fact, heterogeneous, being an intimate mixture of the constituents.

Since these early investigations, research dealing with eutectics has not been continuous, but rather spasmodic. The investigations generally lie under one of the following topics: the physical appearance of eutectics and the eutectic grain, the mode of growth or factors responsible for the eutectic grain, classification of eutectics, and crystallographic studies of the eutectic grain.

The Physical Appearance of Eutectics and the Eutectic Grain. The nomenclature for the appearance of eutectics has been discussed in detail in many papers. The discussions have been based on microscopic examination of polished sections and at times the terminology appears to have lost appreciation of the fact that the structure is in three dimensions.

The physical structure may be considered in two ways, the gross structure and the fine structure. The particles of the individual phases build up the gross structure which has been termed eutectic colony, eutectic grain, or eutectic crystal. The unity of the eutectic colony can be demonstrated in several ways. Some etchants will attack the colonies, but not the individual constituents of the colonies. The fact that this can be done shows the unity of the colony. This method has been shown by Vogel⁽⁹⁾, Brady⁽¹⁰⁾, Rosenhain and Tucker⁽¹¹⁾, Eastwood⁽¹²⁾,

(9) Vogel, R., *Über Eutektische Kristallisation*, *Zeit. Anorg. Chem.*, Vol. 76, p 425, 1912.

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

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

(12) Eastwood, V. W., *Structure and Origin of the Copper-Cuprous Oxide Eutectic*, *Am. Inst. Mining Met. Engrs. Trans. Inst. Met. Div.*, p. 182, 1934.

Straumanis and Brakss^(13,14), and Portevin⁽¹⁵⁾. As a

-
- (13) Straumanis, M. and Brakss, N., Der Aufbau der Bi-Cd, Sn-Zn, Sn-Cd, und Al-Si Eutektika, Z. Phy. Chem., (B) Vol. 38, pp 140-155, 1937.
- (14) Straumanis, M. and Brakss, N., Der Aufbau der Zink-Cadmium Eutektikum, Z. Phy. Chem., (B) Vol. 30, pp 117-131, 1935.
- (15) Portevin, A. M., The Structure of Eutectics, J. Inst. Met., Vol. 29, figs. 8, 12, and 34, 1923.
-

result of this method Brady⁽¹⁶⁾ states that the solidifica-

-
- (16) Brady, F. L., op. cit., p 378.
-

tion of eutectics is analogous to that of brass in that dendritic growth takes place.

By etching in a manner which develops the individual constituents and examining at the proper magnification, the change in orientation of the phases will give a pattern indicating colony boundaries. This is perhaps the most common technique and its application could be used in most of the photomicrographs in this thesis.

A third method depends on evidence obtained by straining eutectics. Ewing and Rosenhain⁽¹⁷⁾ observed the

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

behavior of eutectic alloys of Pb-Sn, Cu-Ag, and Pb-Bi under plastic strain. They noted that on an unetched specimen, the different phases obtain different levels due

to varying amounts of strain. This effect gives rise to large polygonal areas which are of the same order of size as those obtained by etching. The effect can be seen in the photomicrographs in Appendix I. They also observed that slip bands formed parallel systems over many patches of one phase indicating that the crystals of the phases are similarly oriented over large areas of the eutectic alloy.

A fifth method involves the use of x-ray microscopy. Winston⁽¹⁸⁾ observed that the grain size obtained by x-ray

(18) Winston, J. S., A Study of Cast Eutectic Structures by Means of Optical and X-Ray Microscopy, Thesis, Missouri School of Mines and Metallurgy, Rolla, Mo.

microscopy was essentially the same as that obtained by other methods.

Mode of Growth of Eutectics. The gross mechanism of growth of eutectics is much the same as for single phase alloys. Solidification begins at nuclei scattered throughout the melt. From each of these a eutectic colony results. Solidification of each colony is complete when it comes in contact with another colony. Most investigators concur on the above; but there is considerable difference of opinion on the fine mechanism of the separation of the individual phases.

Portevin⁽¹⁹⁾ suggests three main methods of crystal-

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

lization: simultaneous, the particles forming together in the liquid and developing at the same or different velocities; successive, the particles of one phase forming and developing ahead of the other; and, alternative, crystallization of one phase, then the other. He suggests that the controlling factors are: 1. the spontaneous crystallization velocity as determined by the nuclei number, and 2. the linear crystallization velocity. Tammann⁽²⁰⁾ has

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

indicated that these factors are active during solidification.

Vogel⁽²¹⁾ proposed that the lamellar appearance was

(21) Vogel, R., Uber Eutektische Kristallisation, Z. Anorg. Chem., Vol. 76, pp 425-36, 1912.

caused by polygonal rods of the two phases which grow with their axis perpendicular to the solid-liquid interface. Crystallization of both phases would be simultaneous and the instantaneous condition is shown in figure 1.

In his earlier work, Tammann⁽²²⁾ proposed that crys-

(22) Tammann, G. A., op. cit., p. 182.

tallization starts by nucleation of one phase. This phase crystallizes until the resultant change in the liquid is sufficient to cause the other phase to nucleate. Figure 2 represents the Tammann theory. The lamellae form

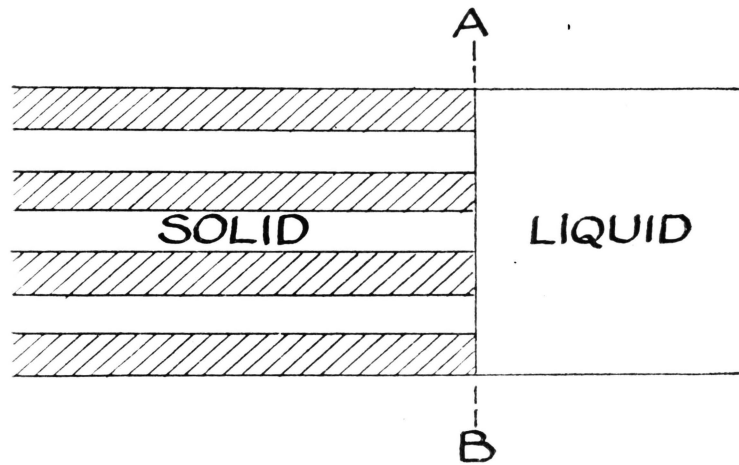


Figure 1. Vogel Theory

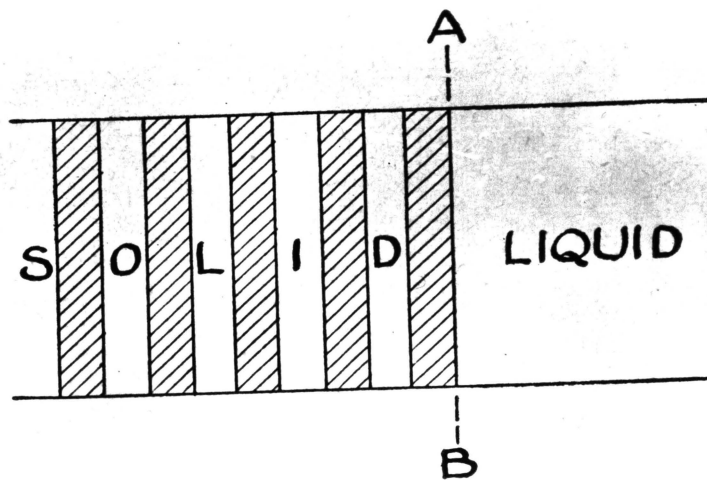


Figure 2. Tammann Theory

perpendicular to the direction of heat flow and crystallization is alternative.

The works of Straumanis and Braaks^(23,24) proved that

(23) Straumanis, M., and Braaks, N., 1937, op. cit., pp 140-155.

(24) Straumanis, M., and Braaks, N., 1935, op. cit., pp 117-131.

in the five alloys studied, the structure was lamellar and the lamellae were perpendicular to the interface.

In explaining the modification of the aluminum-silicon eutectic, Thall and Chalmers⁽²⁵⁾ assumed that the

(25) Thall, B. M. and Chalmers, B., Modification in Aluminum-Silicon Alloys, J. Inst. Metals, Vol. 77, pp 91-96, 1950.

phases crystallize together, but the surface is corrugated as shown in figure 3. The assumption was made on the basis of the fact that the rate of advance of the interface is a function of the latent heat of fusion and the thermal conductivity of the phases.

The above work lead Winegard, Majka, Thall, and Chalmers⁽²⁶⁾ to investigate the mechanism of solidification

(26) Winegard, W. C., Majka, S., Thall, B. M., and Chalmers, B., Eutectic Solidification in Metals, Canad. J. Chem., Vol. 29, pp 320-27, 1951.

of the Pb-Sn eutectic. By using a gradient furnace and decanting the liquid from the solid, they showed conclusively that the lamellae grow parallel to the heat flow.

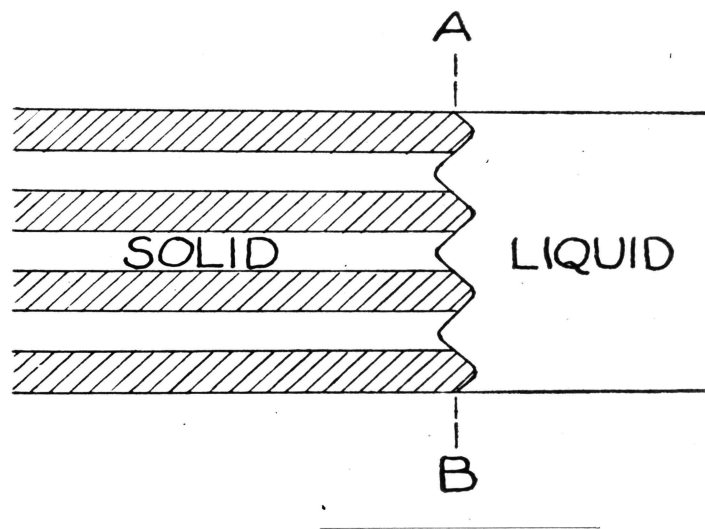


Figure 3. Theory of Thall and Chalmers

They further noted that the leading phase was the tin rich phase. The investigation further showed that the thickness of the lamellae increases with decreasing cooling velocities.

Spiral eutectic structure have been noted in the systems aluminum-thorium and zinc-magnesium. Fullman and Wood⁽²⁷⁾ suggest that this is caused by one phase growing

(27) Fullman, R. L. and Wood, D. L., Origin of Spiral Eutectic Structures, J. Met., Vol. 4, p. 1041, 1952.

faster in all directions in the plane of the spiral and the other phase is growing faster in a direction perpendicular to the plane of the spiral.

More recent works have shown that the solidification of eutectics can further be complicated by the differences in density of the phases. Allen and Isserow⁽²⁸⁾ showed

(28) Allen, B. C. and Isserow, S., Segregation at the Eutectic Temperature, Acta Met., Vol. 5, pp 465-472, 1957.

that a sink and float mechanism can effect the structure and cause segregation in the systems uranium-aluminum, aluminum-silicon, nickel-aluminum, zinc-tin, and lead nitrate-water. They further noted that the segregation is greatly aggravated by cycling through the eutectic temperature.

Classification of Eutectics. Many investigators have attempted to classify eutectics by micro-appearance. The

terms used to classify the eutectics include lamellar, globular, spherulitic, curvilinear, curvilinear, rectilinear, columnar, and many others. As one can see from the terms, all are related to their appearance under the microscope and seemingly neglect the three dimensional appearance of the material.

Brady⁽²⁹⁾ attempted to correlate structure and sur-

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

face tension using the values given by Smith⁽³⁰⁾ for molten

(30) Smith, S. W., The Surface Tension of Molten Metals, J. Inst. Met., Vol. 12, No. 2, p. 162, 1914.

metals. Portevin⁽³¹⁾ tried to show that eutectic structures

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

are dependent upon the three interrelated factors of spontaneous crystallization velocity, linear speed of crystallization and surfusion. Although both investigators recognized the disadvantages of the previous classifications, Desch⁽³²⁾ groups them in the same category.

(32) Desch, C. H., op. cit., p 144.

Crystalline Orientation of the Constituents. Some of the more recent works on eutectics deals with the determination of the orientation relationships between the constituents. In 1934, Mehl in a written discussion on

the work of Eastwood⁽³³⁾ suggested that a unique relation-

-
- (33) Eastwood, L. W., Structure and Origin of the Copper-Cuprous Oxide Eutectic, Trans. AIME, Int. Met. Div., pp 181-195, 1934.
-

ship might exist in the orientation of one component relative to another. Evidence for such relationships were given by Nix and Schmid⁽³⁴⁾ in their study of columnar

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

crystals obtained by casting various metals and alloys in ingot molds. The results of their work is shown in table I.

In more recent work, single colonies have been grown in vertical gradient furnaces. The relationships in these colonies were studied by Straumanis and Brakss^(35,36) and

-
- (35) Straumanis, M. and Brakss, N., 1935, op. cit., pp 171-131.
- (36) Straumanis, M. and Brakss, N., 1937, op. cit., pp 140-155.
-

Ellwood and Bagley⁽³⁷⁾. The results of both investigations

-
- (37) Ellwood, E. C. and Bagley, K. Q., The Structure of Eutectics, J. Inst. Met., Vol. 76, pp 631-642, 1950.
-

are given in table I.

The Alteration of Eutectic Structures. Little work has been done to determine methods of altering eutectic

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	$\frac{\sqrt{100}}{\sqrt{100}}$
F. C. C.	Al Cu Ag Au Pb α Brass	$\frac{\sqrt{100}}{\sqrt{100}}$
Tetragonal	β Sn	$\frac{\sqrt{110}}{\sqrt{110}}$
Hexagonal C.P.	Mg Zn Cd	$\frac{\sqrt{10\bar{1}0}}{\sqrt{0001}}$
Rhombohedral	Bi	$\frac{\sqrt{111}}{\sqrt{111}}$

2. Straumanis and Brakss

System	Relationships
Zn-Cd	All planes and directions parallel
Bi-Cd	$\frac{(10\bar{1}0)}{\sqrt{0001}}$ Bi $\frac{(0001)}{\sqrt{1120}}$ Cd
Sn-Zn	$\frac{(100)}{\sqrt{001}}$ Sn $\frac{(0001)}{\sqrt{10\bar{1}0}}$ Zn
Sn-Cd	$\frac{(100)}{\sqrt{001}}$ Sn $\frac{(0001)}{\sqrt{1120}}$ Cd

3. Ellwood and Bagley

Phases formed	System	Relationships
F.C.C.	Ag-Cu	All planes and directions parallel
F. C. C. and B. C. Tetragonal	Al-Cu	(001) Al $(001)\theta$ $\underline{\underline{100}}$ Al $\underline{\underline{100}}\theta$
F. C. C. and Hexagonal C. P.	Al-Ag	(111) Al $(0001)\zeta$ $\underline{\underline{110}}$ Al $\underline{\underline{1120}}\zeta$

structures. Tammann and Hartmann⁽³⁸⁾ in 1937 studied the

(38) Tammann, G. and Hartmann, H., op. cit., pp 141-144.

effect of cold working and heating eutectic alloys. They noted that one phase is spread in the rolling direction. When the worked material is heated near the melting point the same phase tends to spheroidize. This effect was noted in the following eutectics given the amount of reduction shown: Sn-9 pct. Zn (98 pct.); Cd-82.5 pct. Pb (60 pct.); and Bi-43.5 pct. Pb (90 pct.); but Al-11.7 pct. Si (60 pct.) showed no change after heat treatment. They also noted a distinct shrinkage of the needles in unworked heat treated alloys. As a part of the same investigation, Tammann and Hartmann quenched some ternary eutectic alloys into liquid air. They describe the resulting structure as very fine or microscopically homogeneous. Recently, Brown and Guy⁽³⁹⁾ did similar work on working and heating

(39) Brown, J. S. and Guy, A. G., op. cit., p 933.

eutectic structures. In their investigation the alloys studied were worked in compression about 70 percent. They report results similar to Tammann and Hartmann⁽⁴⁰⁾ in the

(40) Tammann, G. and Hartmann, H., op. cit., pp 141-144.

following alloys: Mg-59.5 pct. Bi, Mg-36.4 pct. Sn, Mg-65.4 pct. Cu, and Bi-40 pct. Cd; but they failed to note any appreciable shrinkage of the needles in unworked heat

treated alloys. Brown and Guy⁽⁴¹⁾ summarized their work

(41) Brown, J. S. and Guy, A. G., op. cit., p 933.

as follows: "In summary, it appears that eutectic structures can be recrystallized into a "spheroidized" condition by heating near the eutectic temperature after severe deformation.....It is reasonable to expect that this tendency towards equiaxed grains from the plate-or needle-like eutectic structure should be general since the energy relations and mode of growth in recrystallization are so different from those that hold for eutectic crystallization."

III

PRESENT INVESTIGATION

This investigation was undertaken to determine whether eutectic alloys could be made to respond to heat treatments in a manner similar to eutectoid alloys. It is a well established fact that when an eutectoid alloy is heated just below the critical temperature for a relatively long time that the structure of the alloy will change to one having spheroids of one phase in a matrix of the other.

EXPERIMENTAL WORK

General: The systems studied are shown in table 2. The materials used are listed in table 3.

The alloys to be studied were prepared by melting the components in a graphite crucible in an electric pot furnace. The alloys were melted and furnace cooled until solid three times to insure homogeneity. The batches were then heated 100° F. above the eutectic and furnace cooled while cooling curve data was obtained. If no liquidous indication was noted the material was assumed to be of eutectic composition. The material to be examined in the furnace cooled condition was then remelted, cast into a No. 3 porcelain crucible, heated 50° F. above the eutectic temperature and furnace cooled to room temperature. All the specimens to be examined in a chill cast condition, except Bi-Cd, were cast into a steel crucible and heated

Table 2.

SYSTEMS STUDIED

SYSTEM	EUTECTIC COMPOSITION (Wt. Percent)	EUTECTIC TEMPERATURE	DIAGRAM ⁴² FIGURE NO.
Bismuth-Cadmium	60 % Bi	144° C.	52
Bismuth-Tin	57 % Sn	139° C.	53
Cadmium-Zinc	17.4% Zn	266° C.	54
Lead-Antimony	11.1% Sb	252° C.	55
Lead-Tin	38.1% Sn	183° C.	56
Tin-Zinc	91 % Sn	198° C.	57

42 Hansen, Max, Constitution of Binary Alloys, 2nd Ed.,
New York, McGraw Hill Book Company, Inc., pp 303,
336, 446, 1100, 1106, 1217, 1958.

Table 3.

MATERIALS

1. Antimony

Source:
Bunker Hill

Analysis:	As	0.00075%
	Pb	0.0003
	Cu	0.0007
	Fe	0.00015
	Sb	Bal (99.998%)

2. Bismuth

Source:
American Smelting and Refining

Analysis:	Cu	0.0003%
	Ag	0.0001
	Bi	Bal (99.999%)

3. Cadmium

Source:
American Zinc Company

Analysis:	Zn	0.016 %
	Pb	0.010
	Cu	0.0014
	Sn	0.0006
	Th	0.001
	In	0.001
	Ni	0.0055
	Au	0.00069
	As	0.00003
	Sb	0.00006
	Cd	Bal (99.963%)

4. Lead

Source:
American Smelting and Refining

Analysis:	Bi	0.0001%
	Cu	0.0001
	Fe	0.0002
	Pb	Bal (99.999%)

Table 3.

MATERIALS (Cont.)

5. Tin Source:
Vulcan Detinning Company

Analysis: Pb 0.0010%
Fe 0.0001
Sn Bal (99.99%)

6. Zinc Source:
American Zinc Company

Analysis: Pb 0.0005%
Cu 0.00025
Cd 0.0004
Au 0.0001
Zn Bal (99.998%)

to 50° F. above the eutectic temperature. The crucible was then plunged into acetone held at -50° C. The procedure for the Bismuth-Cadmium alloy was the same as above except that a brass cup was used to facilitate later handling of the alloy.

Specimens for microscopic examination were prepared by sectioning the cast rod with a hack saw. The specimens were then filed until flat, polished wet on a 240 grit emery paper, a 600 grit emery paper, and a silk cloth with 3-5 micron diamond abrasive. Final polishing was done on a silk velvet cloth using Linde "B" abrasive. The specimens were then etched, examined and the last two polishing steps repeated until the structure remained constant. The etching characteristics of the systems are shown in Table 4.

The specimens which received heat treatment, were held twenty-four hours at the desired temperature either in a furnace or oven depending on the temperature desired. Temperature in the oven was measured by a thermometer; in the furnaces a calibrated chromel-alumel thermocouple was used. All temperatures were controlled to less than $\pm 5^{\circ}$ C.

Bismuth-Cadmium: An alloy containing 60 percent bismuth-40 percent cadmium was prepared by the method previously described. The structure of the furnace cooled alloy is shown in Figures 4 and 5. The microstructure is basically a coarse lamellar structure of bismuth and

Table 4.

THE ETCHING CHARACTERISTICS OF THE SYSTEMS STUDIED

SYSTEM	ETCHANT	REMARKS
Bi-Cd	1I:3KI:10 H ₂ O	Bi - dark Cd - light
Bi-Sn	4% Nital	Bi - dark Sn - light
Cd-Zn	3% Nital	Cd - dark Zn - light
Pb-Sb	4% Nital	Pb - dark Sb - light
Pb-Sn	1HNO ₃ · 1 HC ₂ H ₃ O ₂ = 8 Glycol	Pb - dark Sn - light
Sn-Zn	1HNO ₃ · 1 HC ₂ H ₃ O ₂ = 8 Glycol	Sn - light Zn - dark

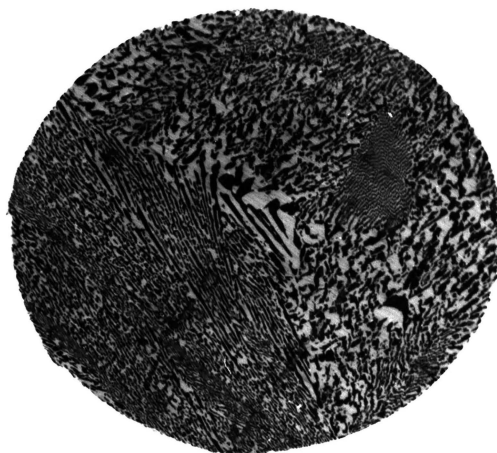


Figure 4. Bi-Cd - Furnace Cooled.

Magnification: 100X
Etchant: 1I:3KI:10 H₂O

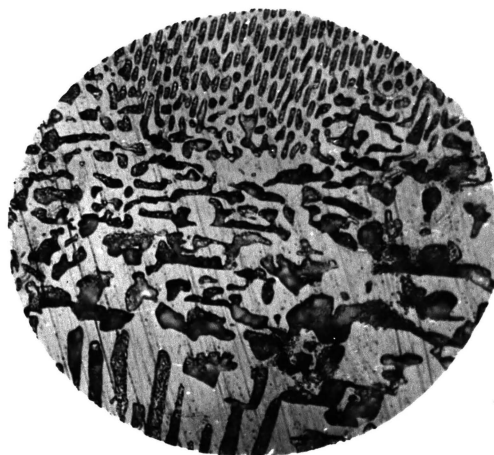


Figure 5. Bi-Cd - Furnace Cooled.

Magnification: 500X
Etchant: 1I:3KI: 10 H₂O

cadmium. The alloy was held at 134° C. for twenty-four hours. The structure after this treatment is shown in Figures 6 and 7. No change in structure resulted from this heat treatment.

The structure of the alloy chill cast at -50° C. is shown in Figures 8 and 9. The alloy contained primarily a fine granular structure of bismuth and cadmium; however, in a few isolated areas a structure resembling the furnace cooled structure was observed probably because the cooling rate was slower in those areas. After heating twenty-four hours at 134° C., the fine granular structure appeared to have coarsened, Figures 10 and 11. The structure appeared similar to the furnace cooled structure, but was somewhat finer and tended to be more granular in appearance. The final structure consisted of rod-like bismuth in a matrix of cadmium.

Bismuth-Tin: An alloy containing 43 percent bismuth-57 percent tin was prepared by the method described earlier. The structure of the furnace cooled alloy is shown in Figures 12 and 13. The structure varied from a lamellar appearance to one containing dendrites of bismuth with the tin solid solution between the dendrite arms. The structure of this alloy after being held at 130° C. for twenty-four hours showed only a slight change, Figures 14 and 15. There appeared to be more tin solid solution in the structure after the heat treatment. This change would be expected because the "as cast" material was

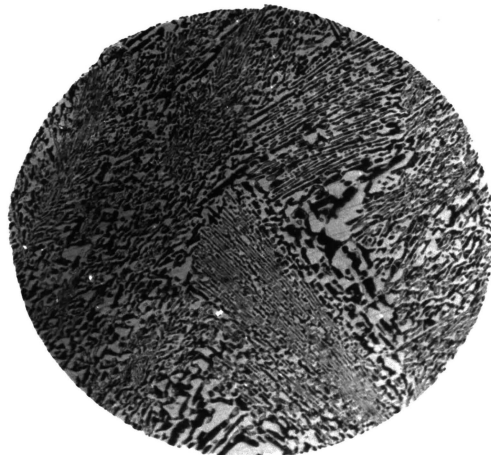


Figure 6. Bi-Cd Furnace Cooled + 24 hours
134° C.

Magnification: 100X
Etchant: 11:3KI:10 H₂O

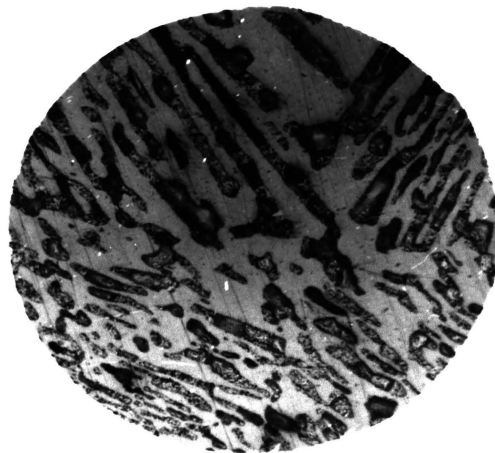


Figure 7. Bi-Cd Furnace Cooled + 24 hours
134° C.

Magnification: 500X
Etchant: 11:3KI:10 H₂O

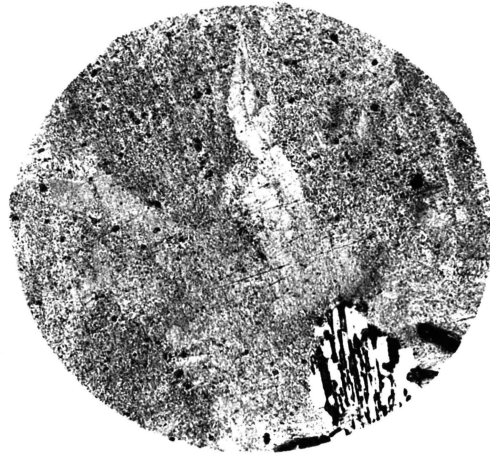


Figure 8. Bi-Cd Chill Cast.

Magnification: 100X
Etchant: 1I:3KI:10 H₂O

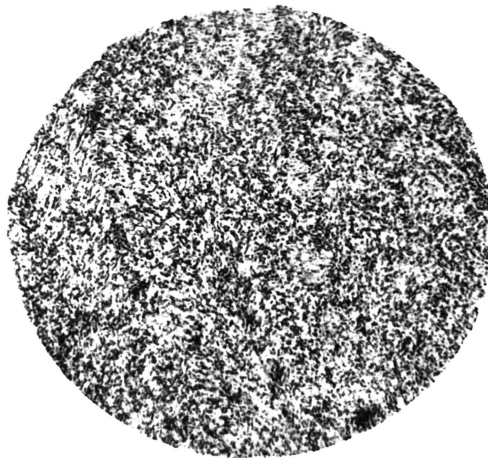


Figure 9. Bi-Cd Chill Cast.

Magnification: 500X
Etchant: 1I:3KI:10 H₂O

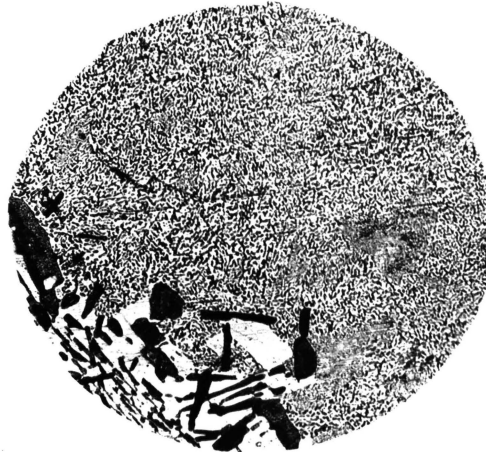


Figure 10. Bi-Cd Chill Cast + 24 hours
134 C.

Magnification: 100X
Etchant: 11:3KI:10 H₂O

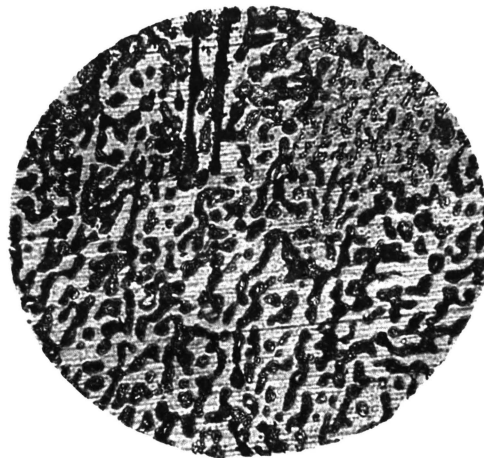


Figure 11. Bi-Cd Chill cast + 24 hours
134 C.

Magnification: 500X
Etchant: 11:3KI:10 H₂O

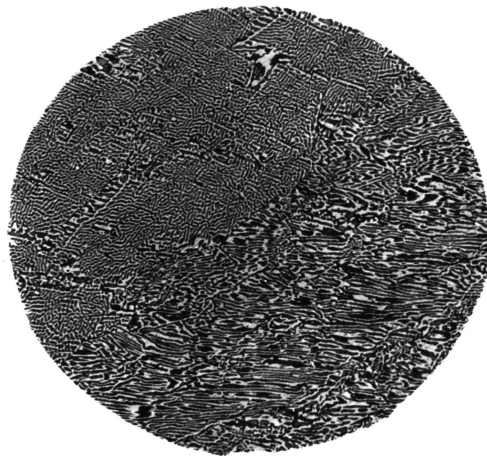


Figure 12. Bi-Sn Furnace Cooled.

Magnification: 100X
Etchant: 4% Nital



Figure 13. Bi-Sn Furnace Cooled.

Magnification: 500X
Etchant: 4% Nital

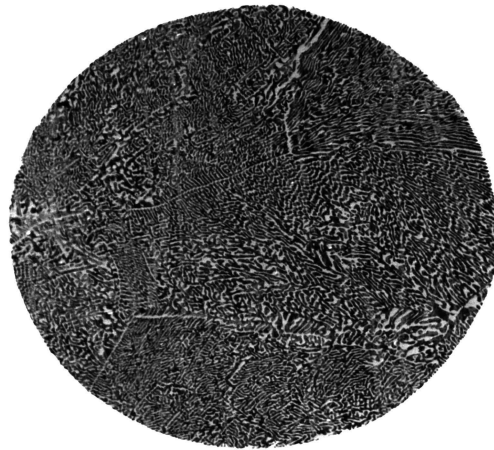


Figure 14. Bi-Sn Furnace Cool + 24 hours
130° C.

Magnification: 100X
Etchant: 4% Nital

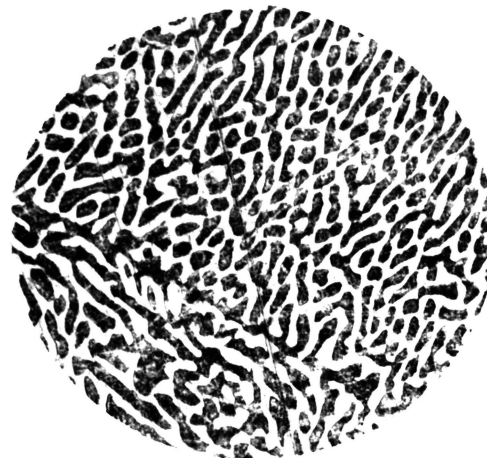


Figure 15. Bi-Sn Furnace Cool + 24 hours
130° C.

Magnification: 500X
Etchant: 4% Nital

furnace cooled to room temperature; but the heat treated material was air cooled from 130° C. where tin has a high solubility for bismuth. The solubility drops sharply at lower temperatures. It is believed that the slight difference in structure was caused by insufficient time for tin diffusion in the heat treated material.

The structure of the chill cast alloy contained dendrites of tin solid solution in a matrix of tin and bismuth solid solutions, Figures 16 and 17. The distribution of the matrix was similar to the furnace cooled alloy, but was considerably finer. The presence of tin solid solution dendrites would indicate that the high cooling rate probably suppressed the crystallization of bismuth solid solution more than the tin solid solution and shifted the eutectic to a higher bismuth concentration. After the chill cast alloy was held at 130° C. for twenty-four hours and air cooled, no change in structure was detected, Figures 18 and 19.

Cadmium-Zinc: An alloy containing 17.4 percent cadmium-82.6 percent zinc was prepared. The structure of the furnace cooled alloy is shown in Figures 20 and 21. The structure of the alloy in this condition consisted of cadmium rods in a matrix of zinc. After the alloy was held twenty-four hours at 240 C., no appreciable change in structure was detected, Figures 22 and 23.

The alloy cast in acetone at -50° C., had primary zinc rich rosettes among needles of finely dispersed zinc

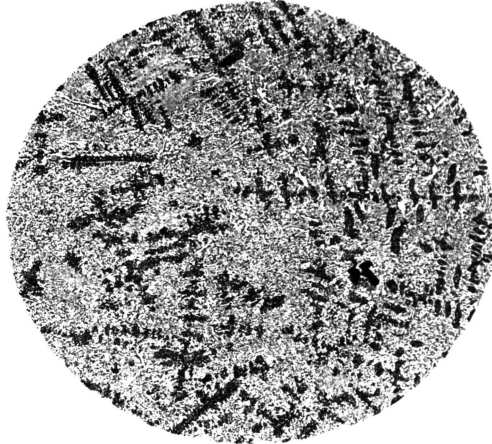


Figure 16. Bi-Sn Chill Cast.

Magnification: 100X
Etchant: 4% Nital

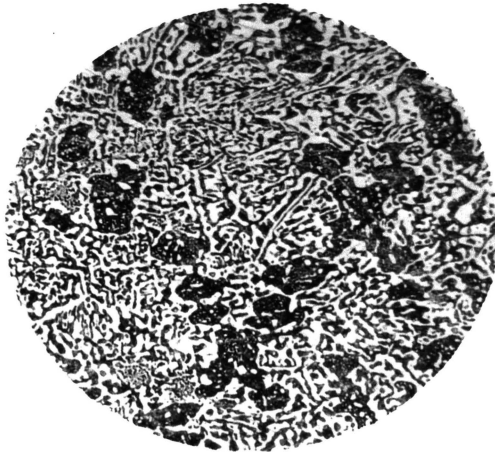


Figure 17. Bi-Sn Chill Cast.

Magnification: 500X
Etchant: 4% Nital

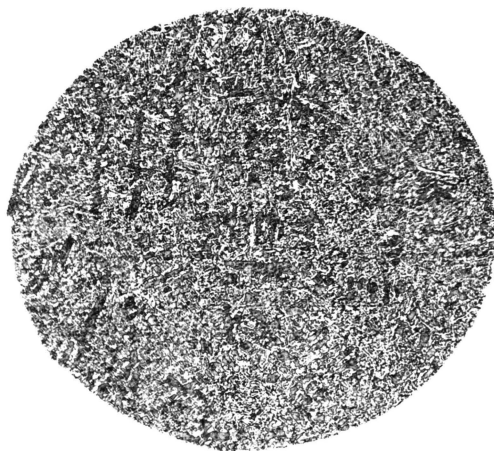


Figure 18. Bi-Sn Chill Cast + 24 hours
130° C.

Magnification: 100X
Etchant: 4% Nital

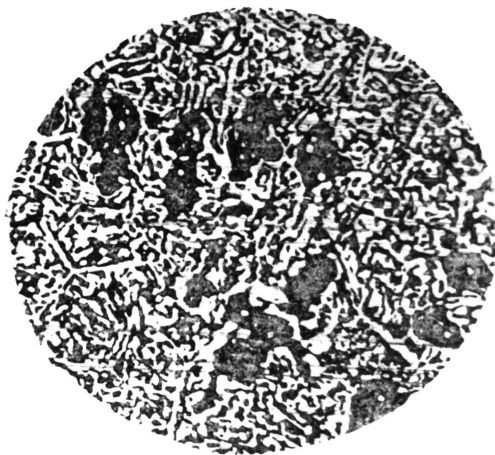


Figure 19. Bi-Sn Chill Cast + 24 hours
130° C.

Magnification: 500X
Etchant: 4% Nital

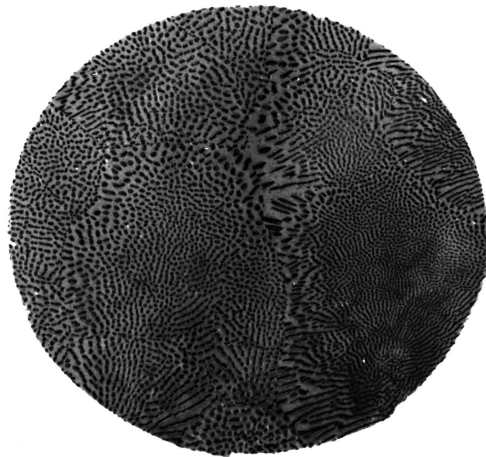


Figure 20. Cd-Zn Furnace Cooled.

Magnification: 100X
Etchant: 3% Nital



Figure 21. Cd-Zn Furnace Cooled.

Magnification: 500X
Etchant: 3% Nital

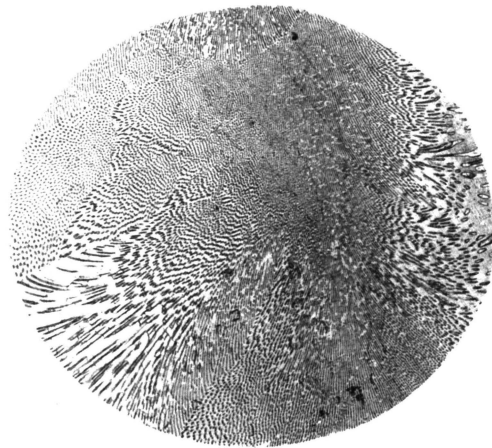


Figure 22. Cd-Zn Furnace Cooled + 24 hours
240° C.

Magnification: 100X
Etchant: 3% Nital



Figure 23. Cd-Zn Furnace Cooled + 24 hours
240° C.

Magnification: 500X
Etchant: 3% Nital

and cadmium, Figures 24 and 25. The zinc rich rosettes probably resulted because the cadmium phase was suppressed more by the high cooling rate than the zinc rich phase. After the alloy was held twenty-four hours at 240° C., the structure consisted of cadmium solid solution spheroids in a zinc solid solution matrix, Figures 26 and 27.

Lead-Antimony: An alloy of 11.1 percent antimony-88.9 percent lead was prepared. The structure of the furnace cooled alloys is shown in Figures 28 and 29. The alloy consisted of script like antimony solid solution in a lead matrix. When the above material was held at 240° C. for twenty-four hours the antimony rich phase tended to agglomerate somewhat, Figures 30 and 31.

The alloy was chill cast in acetone at -50° C. This treatment gave a fine structure of antimony rich rods in a lead rich matrix, Figures 32 and 33. This material was then held twenty-four hours at 240° C. The resulting structure was spheroids of an antimony rich phase in a lead rich matrix, Figures 34 and 35.

Lead-Tin: An alloy of 38.1 percent tin-61.9 percent lead was prepared. The furnace cooled specimen was a lamellar type eutectic containing some primary lead, Figures 36 and 37. When the material was held twenty-four hours at 170° C., no change in structure occurred, Figures 38 and 39.

The specimen which was chill cast in acetone at -50° C. had a very fine structure (not resolvable at 500X),

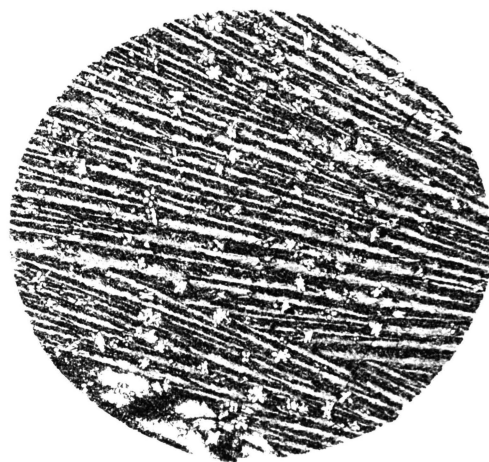


Figure 24. Cd-Zn Chill Cast.

Magnification: 100X
Etchant: 3% Nital

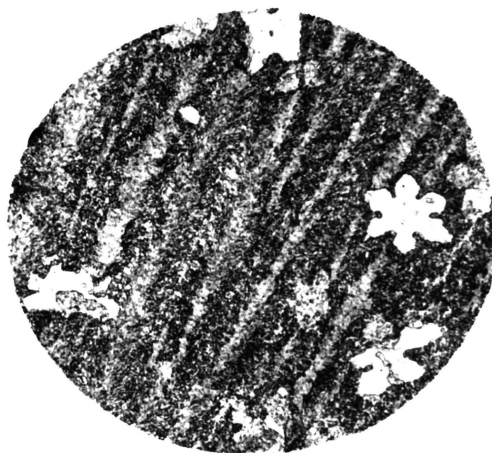


Figure 25. Cd-Zn Chill Cast.

Magnification: 500X
Etchant: 3% Nital

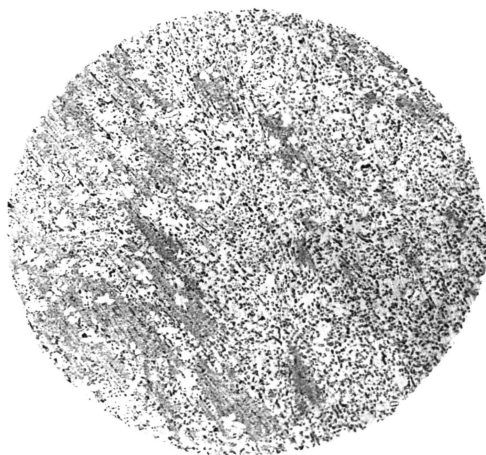


Figure 26. Cd-Zn Chill Cast + 24 hours 240° C.

Magnification: 100X
Etchant: 3% Nital



Figure 27. Cd-Zn Chill Cast + 24 hours 240° C.

Magnification: 500X
Etchant: 3% Nital

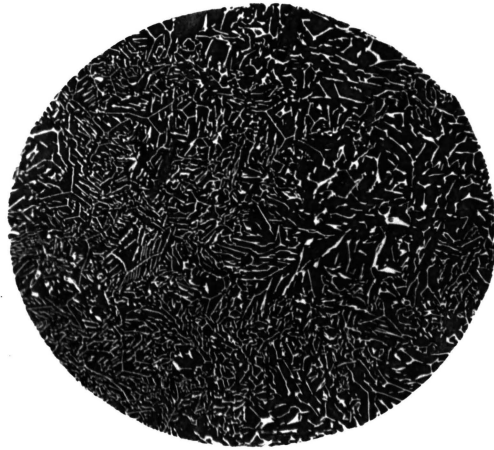


Figure 28. Pb-Sb Furnace Cooled.

Magnification: 100X
Etchant: 4% Nital

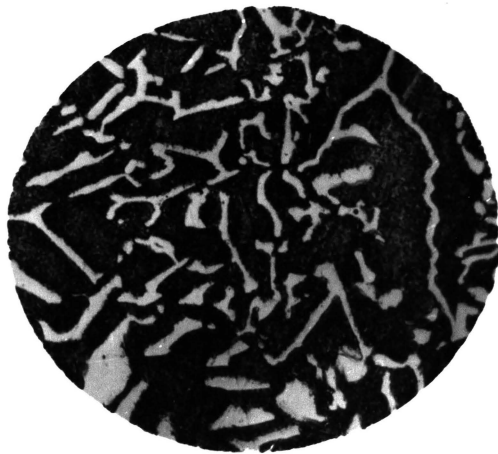


Figure 29. Pb-Sb Furnace Cooled.

Magnification: 500X
Etchant: 4% Nital

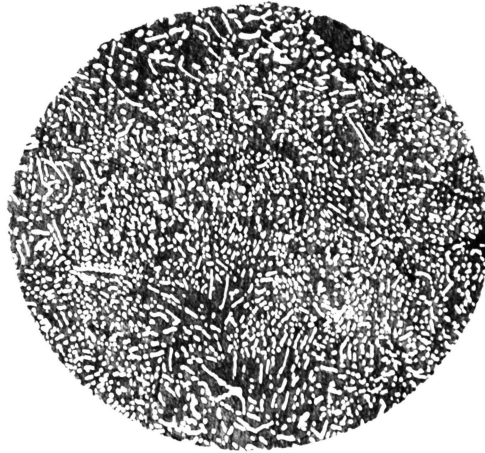


Figure 30. Pb-Sb Furnace Cooled + 24 hours
240° C.

Magnification: 100X
Etchant: 4% Nital



Figure 31. Pb-Sb Furnace Cooled + 24 hours
240° C.

Magnification: 500X
Etchant: 4% Nital

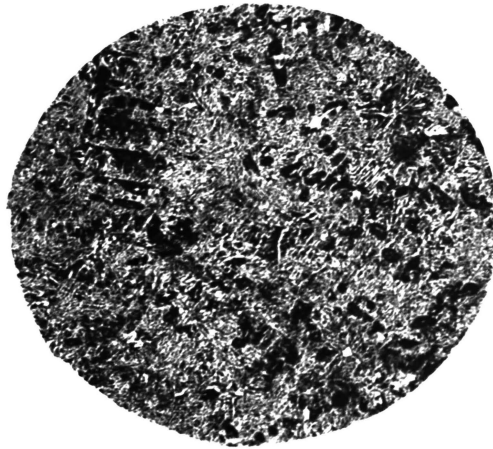


Figure 32. Pb-Sb Chill Cast.

Magnification: 100X
Etchant: 4% Nital

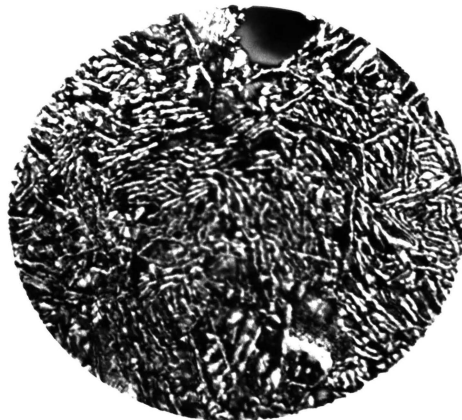


Figure 33. Pb-Sb Chill Cast.

Magnification: 500X
Etchant: 4% Nital

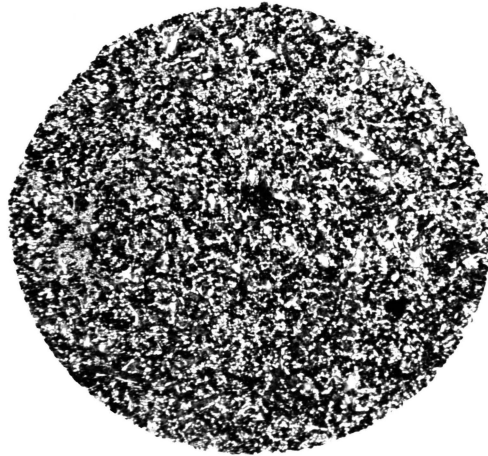


Figure 34. Pb-Sb Chill Cast + 24 hours
240° C.

Magnification: 100X
Etchant: 4% Nital

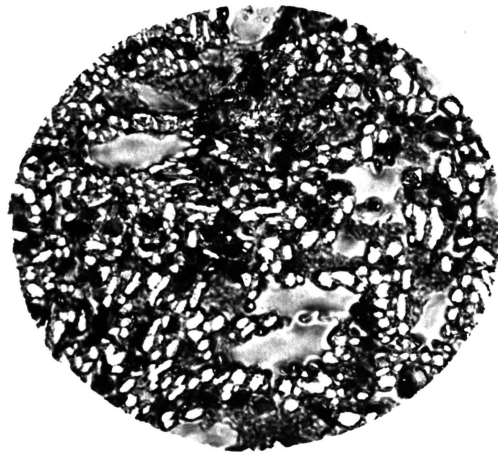


Figure 35. Pb-Sb Chill Cast + 24 hours
240° C.

Magnification: 500X
Etchant: 4% Nital

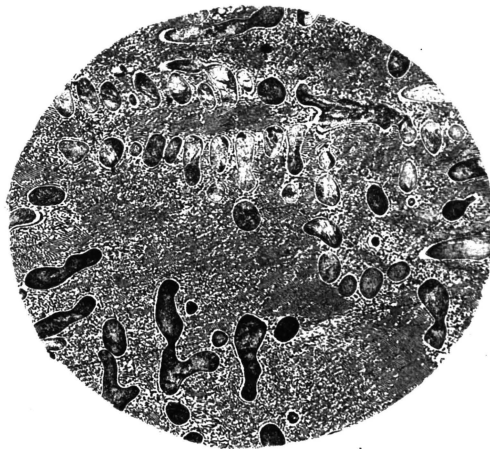


Figure 36. Pb-Sn Furnace Cooled.

Magnification: 100X

Etchant: $1\text{HNO}_3:1\text{HC}_2\text{H}_3\text{O}_2:8\text{Glycol}$

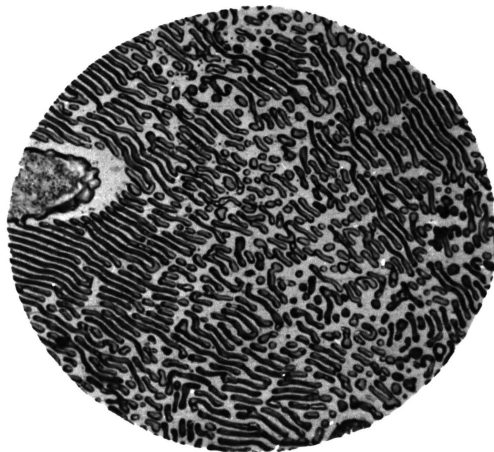


Figure 37. Pb-Sn Furnace Cooled.

Magnification: 500X

Etchant: $1\text{HNO}_3:1\text{HC}_2\text{H}_3\text{O}_2:8\text{Glycol}$

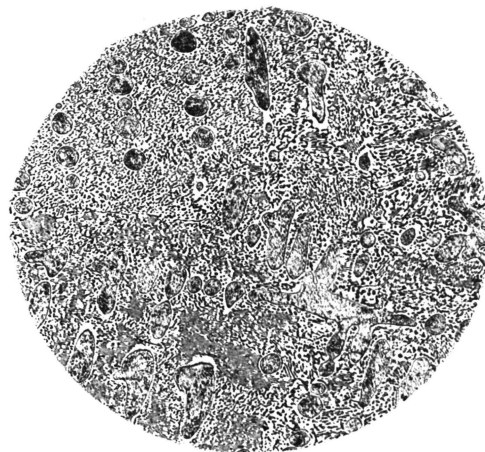


Figure 38. Pb-Sn Furnace Cool + 24 hours
170° C.

Magnification: 100X
Etchant: 1 HNO₃:1 HC₂H₃O₂:8 Glycol

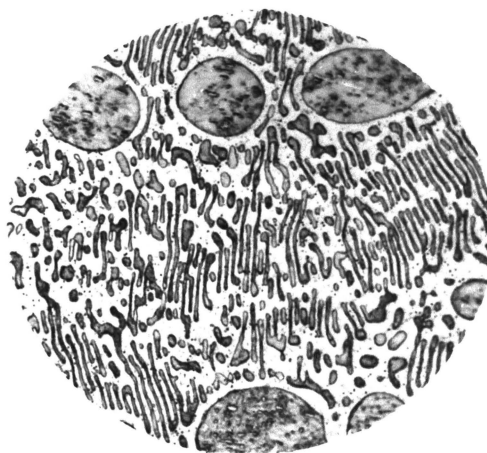


Figure 39. Pb-Sn Furnace Cool + 24 hours
170° C.

Magnification: 500X
Etchant: 1 HNO₃:1 HC₂H₃O₂:8 Glycol

Figures 40 and 41. Holding the material at 170° C. for twenty-four hours caused the lead rich phase to agglomerate into irregularly shaped rods, Figures 42 and 43.

Tin-Zinc: An alloy of 91 percent tin-9 percent zinc was prepared. The furnace cooled specimen had a structure of zinc rods in a tin matrix, Figures 44 and 45. Holding this material at 170° C. for twenty-four hours caused a slight coarsening for the zinc rods, Figures 46 and 47.

The material chill cast into acetone at -50° C. contained columnar grains of a fine dispersion of two phases, Figures 48 and 49. When this material was held at 170° C. for twenty-four hours the zinc rich phase tended to form coarse rods and spheroids, Figures 50 and 51.

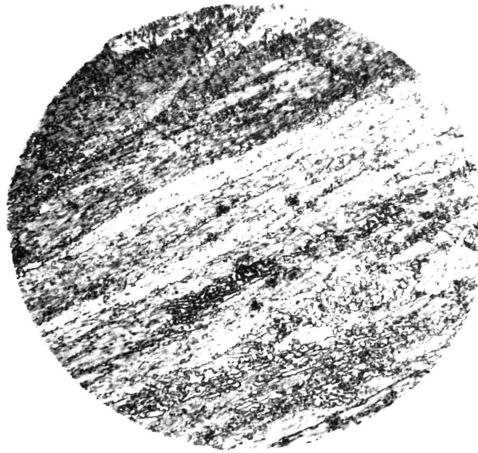


Figure 40. Pb-Sn Chill Cast.

Magnification: 100X
Etchant: 1HNO₃:1 HC₂H₃O₂:8 Glycol

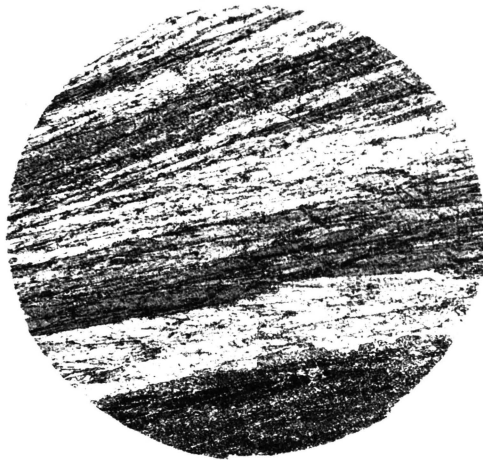


Figure 41. Pb-Sn Chill Cast.

Magnification: 500X
Etchant: 1HNO₃:1 HC₂H₃O₂:8 Glycol

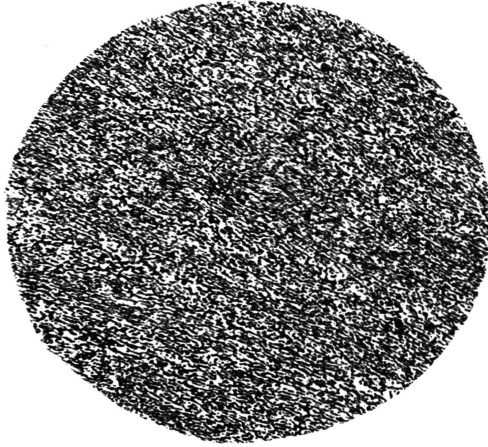


Figure 42. Pb-Sn Chill Cast + 24 hours
170° C.

Magnification: 100X
Etchant: 1HNO₃:1 HC₂H₃O₂:8 Glycol

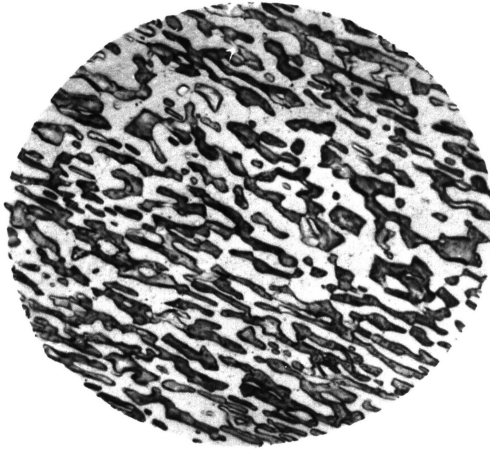


Figure 43. Pb-Sn Chill Cast + 24 hours
170° C.

Magnification: 500X
Etchant: 1HNO₃:1 HC₂H₃O₂:8 Glycol

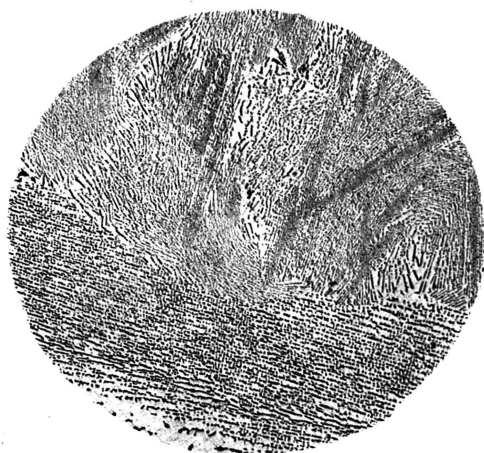


Figure 44. Sn-Zn Furnace Cooled.

Magnification: 100X

Etchant: $1\text{HNO}_3:1\text{HC}_2\text{H}_3\text{O}_2:8\text{Glycol}$



Figure 45. Sn-Zn Furnace Cooled.

Magnification: 500X

Etchant: $1\text{HNO}_3:1\text{HC}_2\text{H}_3\text{O}_2:8\text{Glycol}$



Figure 46. Sn-Zn Furnace Cool + 24 hours
170° C.

Magnification: 100X
Etchant: 1HNO₃:1 HC₂H₃O₂:8 Glycol

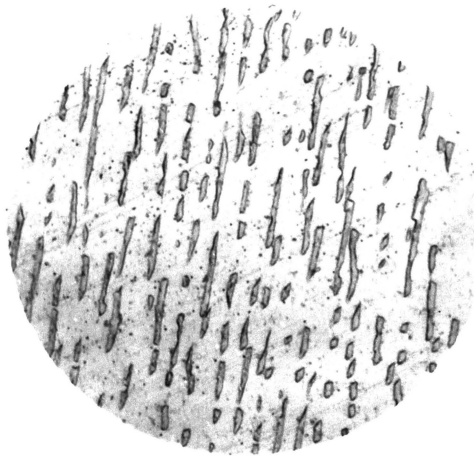


Figure 47. Sn-Zn Furnace Cool + 24 hours
170° C.

Magnification: 500X
Etchant: 1HNO₃:1 HC₂H₃O₂:8 Glycol



Figure 48. SD-Zn Chill Cast.

Magnification: 100X

Etchant: $1\text{HNO}_3:1\text{HC}_2\text{H}_3\text{O}_2:8\text{Glycol}$

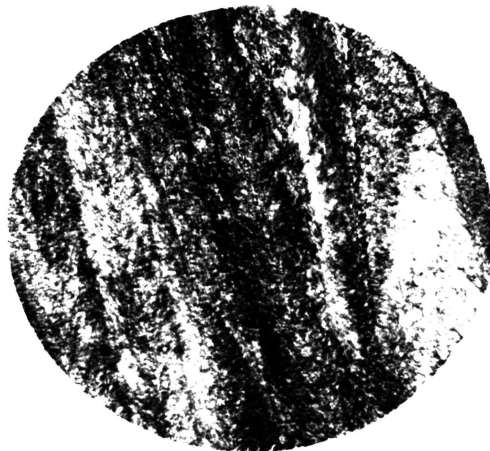


Figure 49. Sn-Zn Chill Cast.

Magnification: 500X

Etchant: $1\text{HNO}_3:1\text{HC}_2\text{H}_3\text{O}_2:8\text{Glycol}$

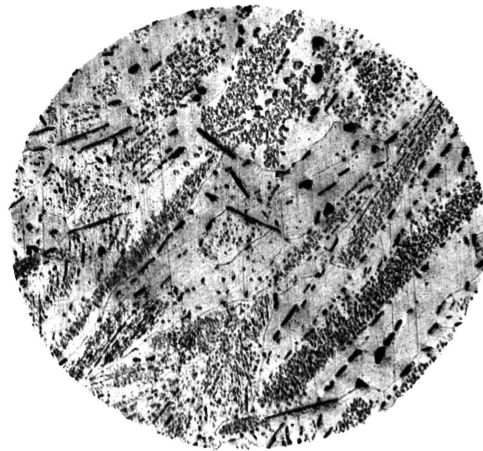


Figure 50. Sn-Zn Chill Cast + 24 Hours 170° C.

Magnification: 100X

Etchant: 1HNO₃:1 HC₂H₃O₂:8 Glycol

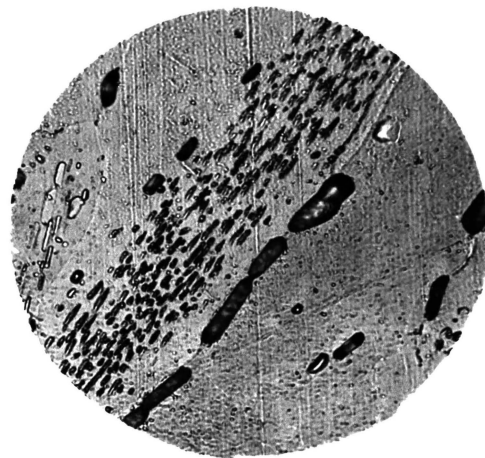


Figure 51. Sn-Zn Chill Cast + 24 hours 170° C.

Magnification: 500X

Etchant: 1HNO₃:1 HC₂H₃O₂:8 Glycol

O. 2694
I. 7306

Bi-Cd Bismuth-Cadmium

The liquidus of Fig. 171 was obtained by graphical interpolation of numerous thermal data [1-9] and has an accuracy of better than $\pm 5^\circ\text{C}$. A slight break at 161°

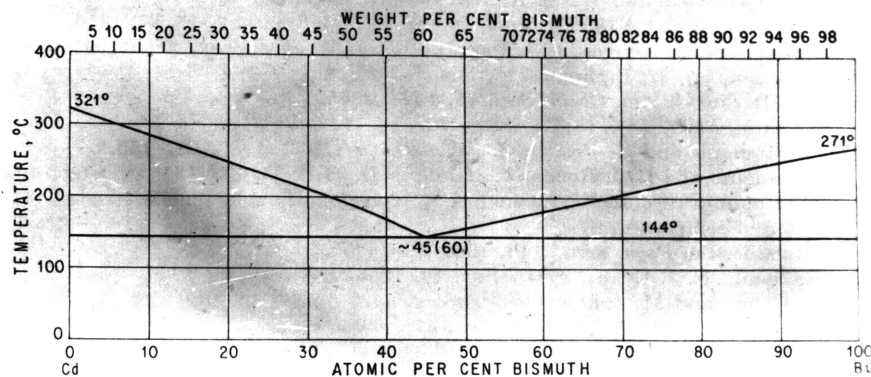


Fig. 171. Bi-Cd. (See also Supplement.)

near the composition Cd_3Bi_2 (due to nonideal activities in the melt; not shown in Fig. 171) was found by [10]. There have been many determinations for the position of

Figure 52. Bismuth-Cadmium

and quenched alloys [7] and 2.4 wt. (4.1 at.) % Sn from emf measurements

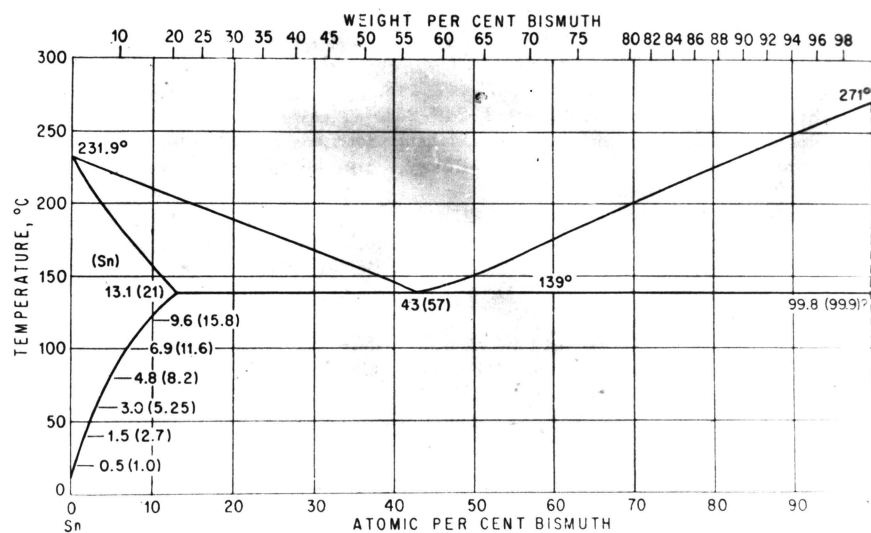


Fig. 195. Bi-Sn

further, [27] could produce single crystals with a Sn content as high as 5 at. [2]

Figure 53. Bismuth-Tin

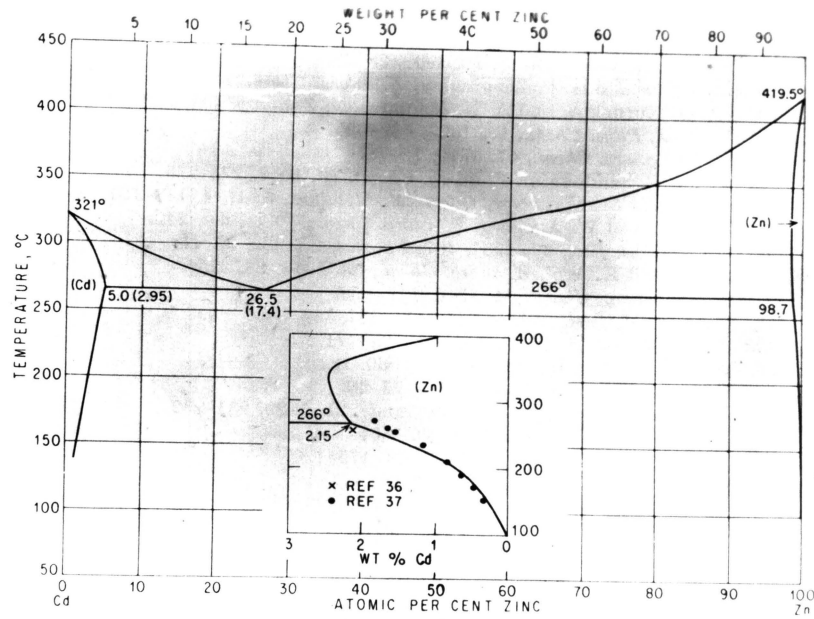


Fig. 256. Cd-Zn

Figure 54. Cadmium-Zinc

[6, 10] were used for Fig. 598. The gap between 16 and 45 wt. % Sb has been bridged over by a smooth line, the fact that it lies up to more than 10°C above the highest

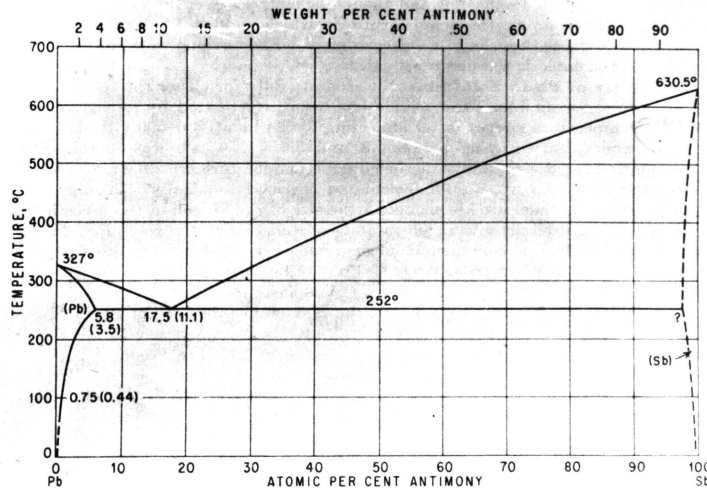


Fig. 598. Pb-Sb. (See also Note Added in Proof.)

experimental data should not be too disturbing in view of the now well-known supercooling effect. In the region 80-100 wt. % Sb, the data by various authors are in good agreement

Figure 55. Lead-Antimony

measurements of resistivity by [33] and has an intermediate position between those found by [16] (resistometric) and [32] (dilatometric, resistometric). For room-temperature solubility, [33] gave the value 0.4 wt. % Pb; however, tensile strength [34] and (qualitative) X-ray diffraction [35] work indicate that the solubility may be even lower (see also [36]), less than 0.3 wt. (0.17 at.) % Pb according to [34].

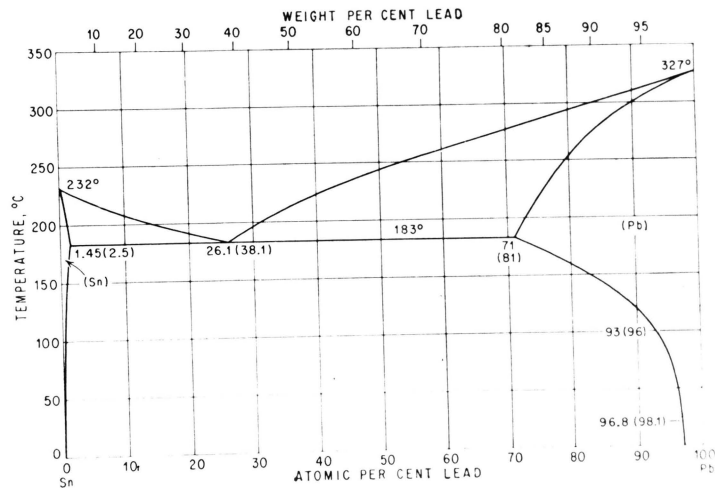


Fig. 601. Pb-Sn

Figure 56. Lead-Tin

ments of tensile strength, [26] concluded the solubility to lie between 0.6 and 0.7 wt. % Sn at the eutectic temperature.

Data reported in the literature for the solubility of Zn in solid Sn at or near the eutectic temperature range from 0 to 7 wt. % Zn. The recent X-ray parametric work by [27] showed clearly that the solubility is at least 0.7 at. (0.4 wt.) %; this eliminates the data 0.2 at. (0.1 wt.) % and 0.325 wt. % reported by [28] (for 180°C) and [29] (for eutectic temperature), respectively. Microscopic work was carried out by [13] and [9]; [13] annealed his alloys for 6 weeks at 185°C and found the solubility to lie between

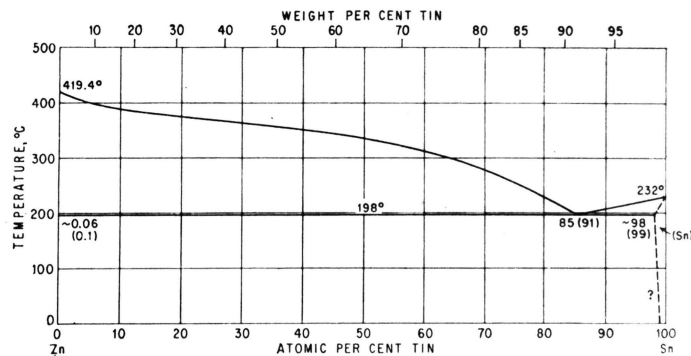


Fig. 659. Sn-Zn

1 and 3 at. (0.5 and 1.7 wt.) % Zn; [9], annealing for 11 days at 150°C, reported the solubility value 2.5 wt. %. Resistometric work by [30] on alloys annealed at 190°C yielded the bracket 1-2 at. (0.5-1.1 wt.) % Zn. For Fig. 659, 2 at. (1 wt.) % Zn has been used as a reasonable estimate.

Figure 57. Tin-Zinc

IV

DISCUSSION

Of the six systems examined, Bismuth-Cadmium, Bismuth-Tin, Cadmium-Zinc, Lead-Antimony, Lead-Tin, and Tin-Zinc, five showed a definite coarsening of their microstructure when a chill cast alloy was heated near the eutectic temperature for twenty-four hours. Only Bismuth-Tin of the systems showed a significant change in the structure of the furnace cooled alloy when it was held near the eutectic temperature.

In an effort to determine some of the factors controlling the phenomenon of eutectic spheroidization, the systems were selected on the basis of certain characteristics in their equilibrium diagrams. The diagrams fall into three distinct eutectic temperature ranges. Bismuth-cadmium and bismuth-tin were treated at 130° C. Lead-tin and tin-zinc were treated at 170° C. and cadmium-zinc and lead-antimony were treated at 240° C. The second consideration in the selection of the systems was the variance in the mutual solubility of the components. The system bismuth-cadmium shows no solubility. In the tin-zinc system, approximately 2 atomic percent zinc is soluble in tin and approximately 0.06 atomic percent tin is soluble in zinc. The remaining systems show larger solubilities at at least one end of the diagram, the greatest being in the lead-tin system in which 19 percent tin is soluble in lead.

The third factor considered to be pertinent in the phenomenon was the original microstructure.

The only system which failed to show a change in the chill cast condition was bismuth-tin. This system was in the lowest temperature group, had low terminal solubilities (0.06 atomic percent and 2 atomic percent) and the chill cast microstructure was the coarsest observed.

Two systems were essentially completely spheroidized by heat treating chill cast alloys. These systems were cadmium-zinc and lead-antimony. Both systems were in the highest temperature group, had intermediate terminal solubilities at both ends of the diagrams, and the chill cast alloys had relatively fine microstructures. The phases of the chill cast cadmium-zinc alloy could not be resolved at 500 X. The phases in the chill cast lead-antimony alloy were not resolvable at 100 X, but were resolved at 500 X.

The systems of bismuth-cadmium, lead-tin, and tin-zinc showed varying amounts of agglomeration of the chill cast material after heat treatment near the eutectic temperature. The lead-tin and tin-zinc systems coarsened from structures not resolvable at 500 X as chill cast to ones easily resolved at 100 X after being heat treated. The coarsened structure of both systems was a rod-like structure. Both systems were in the intermediate temperature range (170° C.). In the lead-tin system, 29 atomic percent tin is soluble in lead and 1.45 atomic percent lead

is soluble in tin. In the tin-zinc system, approximately 2 atomic percent zinc is soluble in tin and less than 0.06 atomic percent tin is soluble in zinc.

The bismuth-cadmium system showed some partial coarsening, but little change in shape of the particles. The chill cast alloy was unique in that it had a fine and coarse structure in it. Only the fine structure showed any appreciable agglomeration. This system was in the lowest temperature group and its equilibrium diagram indicates no terminal solid solubilities.

V

CONCLUSIONS

With the noted exception of the bismuth-tin eutectic, the eutectic systems studied showed agglomeration of one phase when a chill cast alloy was heated near the eutectic temperature. The greatest driving force behind this phenomenon appeared to be the surface energy of the particles. The systems which showed the finest, as chill cast, microstructures had the greatest tendency to spheroidize. The system which showed the coarsest as chill cast microstructure had no tendency to spheroidize. It appears that the mutual solubility of the phases has little or no effect on the process. A system showing no terminal solubilities (Bi-Cd) agglomerated slightly, yet one showing considerable solubility at one end and a slight amount at the other (Bi-Sn) failed to respond to heat treatment.

The systems with higher eutectic temperatures showed the greatest spheroidization, while those with the lowest eutectic temperatures showed the least structural changes. The temperature effect is, however, somewhat masked because those systems which had the highest eutectic temperatures had the finest structures. Because no structural changes were noted at room temperature, it is apparent that some increase in atomic mobility is required to obtain a coarsened structure.

It is suggested that if a eutectic structure can be made sufficiently fine by extreme chill casting that the structure can be coarsened by prolonged heating near the eutectic temperature. As the fineness of the initial structure is increased, the tendency toward complete spheroidization of one phase is increased.

VI

SUMMARY

Six eutectic alloys, Bi-Cd, Bi-Sn, Cd-Zn, Pb-Sb, Pb-Sn and Sn-Zn, were furnace cooled from the melt and chill cast from the melt. The alloys were examined in the "as cast" condition, then held for twenty-four hours near the melting point and examined again.

In all the systems which were examined, the chill cast alloys had finer structures than the furnace cooled alloys. This is in agreement with existing solidification theories because in chill casting diffusion time is greatly reduced. When the furnace cooled material was held near the eutectic temperature for twenty-four hours, only the Bi-Sn alloy showed any significant change in structure, but the structure of this material was considerably finer than the structure obtained by chill casting and heat treating the same material.

All of the chill cast alloys, with the exception of the bismuth-tin eutectic alloy, showed considerable coarsening after being heated near the eutectic temperature for twenty-four hours. It appears that the primary driving force for the phenomenon is the surface energy of the particle. It was noticed that the structure with the finest initial structure exhibited the most spheroidal final structure. The amount of mutual solubility of the components appeared to have little effect on the process

as a system believed to have no terminal solid solubility exhibited coarsening. No correlation could be found between the solubilities in the systems studied and the final structures.

It is suggested that if the structure of an eutectic alloy can be made sufficiently fine, then the structure can be made to respond to heat treatment in the same manner as eutectoid structures. Two techniques for obtaining a sufficiently fine structure are cold working the material and severely chill casting the alloy.

APPENDIX I

In an effort to determine the effect of strain on the spheroidization of an eutectic by cold working a cadmium-zinc eutectic alloy was cast into a preheated graphite tensile specimen mold. The bar was then broken in tension on a universal testing machine. The tensile strength of the specimen was 17,000 psi and it had a 7-1/2 percent reduction in area.

Because of the small strain produced, no spheroidization of the structure could be accomplished.

The specimens did show slip bands in polygonal areas as described by Ewing and Rosenhain⁴³, figures 58, 59, and 60.

(43) Ewing, J. A. and Rosenhain, W., op. cit., p 371-2.



Figure 58. Cadmium-zinc-eutectic-alloy broken in tension.



Figure 59



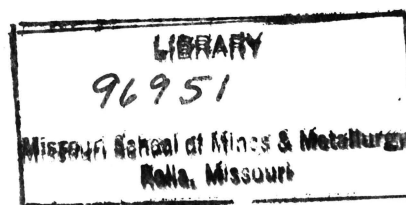
Figure 60

Cadmium-zinc eutectic alloy broken in tension. Note the polygonal area formed by slip bands.

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VITA

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