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Structure of Eutectics

Dilip K. Das

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STRUCTURE OF EUTECTICS

By

Dilip K. Das

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering.

MONTANA SCHOOL OF MINES
BUTTE, MONTANA.
May 4, 1939.
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STRUCTURE OF EUTECTICS.

INTRODUCTION.

The present paper is a result of work done on the study of structures of eutectics of a certain eutectic-forming binary systems. In this research work no systems with intermetallic compounds have been studied. That limited the field, to the study of binaries of the types Va, V and Vc.

Type Va:- In this type of binaries, there is no solubility in the solid state. Liquids are completely miscible. Eutectic is a mechanical mixture of the primary constituents A and B.

Type V :- This type is characterized by partial solubility in the solid state. Liquids are completely miscible. Phase $\alpha$ is a solid solution of primary B in A, and Phase $\beta$ is a solid solution of A in B. Eutectic is a mixture of $\alpha$ and $\beta$.

Type Vc :- This is a modification of the type V. Solid solution $\beta$ is absent. Eutectic is mixture of $\alpha$ and B.
The following binary systems have been selected for the investigation of eutectic structures. Information regarding their equilibrium diagrams, and eutectic compositions and temperatures were obtained from M. Hansen's treatise on Physical Metallurgy.

<table>
<thead>
<tr>
<th>Components</th>
<th>Eutectic Composition</th>
<th>Eutectic Temp.</th>
<th>Type</th>
</tr>
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<tbody>
<tr>
<td>Pb - Sb</td>
<td>13% Sb</td>
<td>247°C</td>
<td>Va</td>
</tr>
<tr>
<td>Pb - Sn</td>
<td>61.9% Sn</td>
<td>183.3°C</td>
<td>Vc</td>
</tr>
<tr>
<td>Sn - Zn</td>
<td>9% Zn</td>
<td>193°C</td>
<td>Va</td>
</tr>
<tr>
<td>Al - Zn</td>
<td>95% Zn</td>
<td>380°C</td>
<td>V</td>
</tr>
<tr>
<td>Bi - Pb</td>
<td>43.5% Pb</td>
<td>125°C</td>
<td>Vc</td>
</tr>
<tr>
<td>Bi - Cd</td>
<td>96% Bi</td>
<td>144°C</td>
<td>Va</td>
</tr>
<tr>
<td>Cd - Sn</td>
<td>67.75% Sn</td>
<td>177°C</td>
<td>V</td>
</tr>
<tr>
<td>Cd - Zn</td>
<td>17.4% Zn</td>
<td>266°C</td>
<td>V</td>
</tr>
<tr>
<td>As - Pb</td>
<td>97% Pb</td>
<td>288°C</td>
<td>Va</td>
</tr>
<tr>
<td>Al - Si</td>
<td>11.7% Si</td>
<td>577°C</td>
<td>Va</td>
</tr>
</tbody>
</table>

As the eutectic alone does not show the structure so well all by itself, it was decided to study the structure as contrasted with the primary crystals. That is why, alloys of compositions A plus Eutectic, B plus Eutectic and Eutectic were separately examined under microscope.
DEFINITION OF EUTECTIC POINT

The following definition is taken from "Physical Metallurgy" by Gilbert E. Doan.

"Usually the two curves (see fig. a), the one dropping from A and the one dropping from B meet and intersect somewhere between A and B as shown at e in the figure. Clearly, the liquid once arrived at this point of intersection e might have approached it either from the A side or from the B side of the diagram; i.e., previous to its arrival at this point, it might have been saturated in either A or B material, depending on what original composition has been chosen. At this point of intersection it is obviously saturated in both kinds of material and must therefore precipitate both kinds of crystals. The result is that it now precipitates alternately a crystal of A and one of B at various points in the remaining liquid, as fast as the heat set free by crystallization can be carried away, until solidification is complete, the temperature and the composition of all three phases (Melt, A crystals and B crystals) remaining constant and unchanged during the process. At any locality in the melt where an A crystal is precipitated the surrounding liquid is left supersaturated in B material and a B crystal precipitates next to the A. Such an intersection of liquidus curves is known as a Eutectic point."
PROCEDURE

For all the alloy specimens were prepared 25 gram samples were chosen as the right weight. In the case of some light metals (metals of low specific gravity), weights had to be reduced to avoid errors that might arise from spilling. For most of the cases, however, 25 gram samples were found to be the most convenient.

From the eutectic composition obtained from Hansen, three samples were chosen to give A plus eutectic, B plus eutectic and eutectic structures. The low melting point metal was first melted in a small porcelain crucible over a Bunsen burner flame and higher melting point metal gradually added and the mass stirred thoroughly with a graphite rod till a homogeneous solution was obtained. In the cases of zinc-aluminum and aluminum-silicon systems a small gas muffle was used. Aluminum was first melted and zinc or silicon slowly added, as the case might have been, and the mass stirred till everything became fluid.

After the fluid alloy was obtained, it was allowed to down slowly to the room temperature. The solid alloy was then weighed and the loss by volatilization estimated.

The specimens as obtained by cooling had the shape of a crucible. A side of the sample was sawed off and was polished in the usual manner.

1. First, a grind was given in the grinding disc to obtain a plane face.

2. The plane face was then polished on four different grades of metallographic paper, 0, 00, 000, 0000, respectively.

3. The face was further polished with alumina emulsion
on a rotating disc and then with water alone.

The polished surface, as obtained was etched for microscopic examination. Different etching agents were tried and the best one is mentioned with the systems. Aluminum alloys were found to be etched best by hydrochloric acid. In some cases, viz. Pb-Bi, Bi-Cd and As-Pb no etching was found necessary, as the polishing alone brought out the micro-structures. Some specimens gave very good results by over-etching them first, and then slightly polishing the surface.

For convenience of showing the structures photomicrographs of the specimens were taken, which accompany each of the systems described.
25 gram specimens were prepared by dissolving antimony in a molten bath of lead. Etching was done by dilute nitric acid.

**Fig. 1.** 45.6% antimony - 54.4% lead. Shows primary antimony crystals (light colored) and dark eutectic filling matter. Magnification 130X.

**Fig. 2a and 2b.** Eutectic composition - 13% antimony. Magnification 130X for fig. 2a and 2b was taken at a magnification 260X. Eutectic has a laminated structure.

**Fig. 3.** 6.4% antimony - 93.6% lead. Dark primary dendritic lead crystals with eutectic filling matter.

Lot of investigation work has been done on the lead-antimony system. Work done before 1890 is considered inaccurate.

Wright and Thomson first showed complete miscibility in the liquid state (1894). Roland and Gosselin were the first to find out the complete course of liquidus (1896) showing an eutectic formation. Later, microscopic investigation by Charpy and Stead and Campbell confirmed Roland and Gosselin's work.
LEAD - TIN

Alloys (25 grams) were prepared by dissolving tin in a molten lead bath. Etching was done by dilute nitric acid.

Fig. 4. 60% lead - 40% tin. Dark crystals of lead in a matrix of eutectic. Magnification 130X.

Fig. 5. Eutectic composition - 61.9% tin. Eutectic shows a pearlitic structure. Magnification 130X.

Fig. 6. 28% lead - 72% tin. Light colored tin crystals with dark fine grained eutectic surrounding the grain boundaries.

Earliest work on this system was done by Kuppfer (1829). Gurtler (1909) showed large solubility of tin in lead at eutectic temperature. He also showed from the results of Mazzotto's work solubility of lead in tin at eutectic temperature.
TIN - ZINC

Zinc was melted over a Bunsen burner flame and tin slowly dissolved in the bath. Etching was done by 10% hydro chloric acid.

Fig. 7. 50% zinc - 50% tin. Dark crystals of primary zinc in a light matrix of light eutectic. Magnification 130X.

Fig. 8. Eutectic composition - 9% zinc. Pearlitic structure. Magnification 130X.

Fig. 9. 6% zinc - 94% tin. Light colored primary tin with fine grained dark eutectic scattered around. Magnification 130X.

Liquidus and solidus of the system was first worked out by Rudberg (1850) Mazzotto (1893) and Gautier (1896) worked on the same subject.

Microscopic examination by Peirce (1923) and El-ectrical conductivity measurements by Tammann and Crone (1930) show that there is no solid solution in the system.
ALUMINUM - ZINC

L2.5 gram specimens were made. Specimens containing 100% eutectic, and zinc plus eutectic were prepared by dissolving aluminum in a molten zinc bath, which was obtained over a Bunsen burner flame. The third was prepared by fusing aluminum in a gas muffle furnace and dissolving zinc in it. All specimens were etched by 10% hydrochloric acid.

Fig. 10. 97% zinc - 3% aluminum. A network of primary zinc (dark) with eutectic filling matter.

Fig. 11. Eutectic composition - 95% zinc. Eutectic has an appearance of finger print. Magnification 130X.

Fig. 12. 60% zinc - 40% aluminum. Rounded primary crystals of aluminum, with eutectic on grain boundaries. Magnification 130X.

Quite a bit of investigation has been done on this system. The accepted equilibrium diagram is due to the work of Rosenhain - Archbutt (1911) and Bouer - Vogel and Hanson - Gayler (1922)
Fig. 10

Fig. 11

Fig. 12
25 gram specimens were prepared by dissolving bismuth in a molten bath of lead. Micro-structure was revealed without etching.

In this system there are two solid solutions on the lead-rich side; one up to 17% bismuth and the other one up to about 33% bismuth. Between 75% lead and 85% lead is a mixture of the two solid solutions. Eutectic is a mixture of the second solid solution and primary bismuth at the composition taken for eutectic plus excess lead.

Fig. 13. 60% lead - 40% bismuth. Dark crystals of solid solution with eutectic along the grain boundaries. Magnification 130X.

Fig. 14. Eutectic composition - 43.5% lead. Eutectic has a laminated structure. Magnification 130X.

Fig. 15. 20% lead - 80% bismuth. In the figure is seen a large grain of eutectic on a bed of primary bismuth. Magnification 130X.

The liquidus curve and the eutectic-horizontal were accurately observed by Wiedemann (1883), Mazzotto (1886) and Heycock-Neville (1892).

The accepted equilibrium diagram is due to the work of Barlow (1910) and Wright (1894) was the first man to recognize the complete miscibility in the liquid state.
BISMUTH - CADMIUM

25 gram specimens were made by melting down a mass of bismuth and slowly adding cadmium to it. In this system there is no solid solution. No etching was necessary.

Fig. 16. 80 % bismuth - 20 % cadmium. Acicular grains of eutectic in a mass of light colored bismuth. Magnification 130X.

Fig. 17. Eutectic composition - 60 % bismuth. Specimen was tried to be prepared at the eutectic composition, but from the figure can be seen a little excess of bismuth. The structure of eutectic is very definitely laminated Magnification 130X.

Fig. 18. 70 % cadmium - 30 % bismuth. Dark dendritic crystals of primary cadmium with eutectic around the grains.

Heycock-Neville (1892) did some work on this system by trying out the effect of small amounts of cadmium and bismuth on the solidification temperature of bismuth and cadmium respectively.

Wright (1894) first observed the complete miscibility of the two liquids.
CADMIUM - TIN

25 gram samples of alloys were prepared by dissolving cadmium in a molten bath of tin. There are two solid solutions in this system on the tin-rich and cadmium-rich sides at high temperatures, but at ordinary temperatures primary metals precipitate out. Specimens were over-etched with conc. nitric acid and then slightly polished to reveal the structure.

Fig. 19. 84% tin - 16% cadmium. White grains of primary tin surrounded by a fine grained eutectic mass. Magnification 130X.

Fig. 20. Eutectic composition - 67.75% tin. Eutectic shows a very fine platy structure. Magnification 130X.

Fig. 21. 40% tin - 60% cadmium. Dark primary cadmium and lighter colored eutectic. Magnification 130X.

Wright first observed the complete miscibility in the liquid state (1894). But before him Heycock-Neville experimented with the influence of small amounts (2.7% at a time) tin and cadmium on the solidification temperature of cadmium and tin respectively (1892).

Kapp was the first to determine the average course of the liquidus (1901), by means of eight alloys. That showed him an eutectic formation.

The accepted equilibrium diagram is a result of Mazzotto's work (1913).
There are two solid solutions in this system on both the sides at higher temperatures, but none at the room temperature.

25 gram samples were prepared by dissolving cadmium in molten zinc. Specimens were etched by conc. nitric acid for a second.

Fig. 22. 10% zinc - 90% cadmium. Light colored cadmium and darker colored, fine grained eutectic. Magnification 150X.

Fig. 23. The specimen for figure 23 was intended to be of eutectic composition (17.4% zinc). But there is too much excess cadmium. However, the structure as seen from the other two specimens has a structure like finger prints. Magnification 150X.

Fig. 24. 28% zinc - 74% cadmium. Dark grains of zinc in perfect dendritic structure with eutectic as the as the intervening matter. Magnification 150 X.

Wright (1894) was again the first one to observe the complete miscibility of the liquids after Heycock-Neville (1892) had done the same experimentation with this system as with the tin-cadmium system.

Roland-Gosselin and Gautier determined the liquidus curve and the eutectic point (1896). Later (1897) Heycock-Neville very accurate work on the equilibrium diagram, and is the accepted one.
There are no solid solutions in this system.

Samples weighing 25 grams were prepared by fusing lead over a Bunsen burner flame and adding arsenic to the molten bath. No etching was necessary.

Fig. 25. 90% lead - 10% arsenic. Shiny, light colored crystals of arsenic with dark colored eutectic. Magnification 130X.

Fig. 26. Lead 97% (eutectic composition) Structure is not very clear, except that it can be seen that it is very fine grained. Magnification 130X.

Fig. 27. 1.2% arsenic - 98.8% lead. Structure is not clear at all. Magnification 130X.

Heycock-Neville (1892) worked on the lowering of melting point of lead by addition of small amounts of arsenic.

Heike's (1914) work is responsible for the accepted equilibrium diagram.
ALUMINUM - SILICON

Solid solution of silicon in aluminum is less than 0.05%.
" " " aluminum in silicon is 4% at eutectic temp.
(577°C) and about 3.5% at 400°C. Equilibrium diagram does not
show solubility at low temperatures.

10 gram samples were prepared by fusing aluminum in a gas
muffle furnace adding silicon to the molten mass. Specimens were
etched with strong hydrochloric acid.

Fig. 28. 80% aluminum - 20% silicon. Cubical, light colored
silicon crystals embedded in a matrix of eutectic of a little darker
shade. Magnification 130 X.

Fig. 29. Eutectic composition - 11.7% silicon. Very fine
grained, platy structure. Magnification 130X.

Fig. 30. 95% aluminum - 5% silicon. Large light colored grains
of primary aluminum, of which the grain boundaries are defined by eutectic
material. Magnification 130X.

Frankel (1908), Roberts (1914), Gwyer-Phillips (1927) and
Broniewski - Smialowski (1932) found aluminum - silicon system to
be a simple eutectic-forming binary.
CONCLUSIONS

In almost all the systems examined the structure of eutectic is very fine grained. In the systems lead-tin and tin-zinc, it is pearlitic.

The idea of examining alloys having excess primary constituents plus eutectic is to study the structure of eutectics by means of a contrast.

For any further work on this subject, it may be suggested that work be done with alloys having fifty percent eutectic and fifty percent primary constituent by volume. This will involve some calculations based on the specific gravities of the component metals and eutectic composition. This procedure, however, might yield better results.
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