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On the Refinement of the Eutectic-structure of Some Alloys by the Addition of a Small Quantity of Foreign Metal¹

By Kaoru Kase and Hajime Kotô

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Abstract

By microscopic and also by X-ray analyses, the normal and modified eutectic structures were examined in connection with various sand-cast and a few chill-cast specimens of lead-bismuth, tin-bismuth and antimony-lead alloys. Moreover, to make clear the mechanism of the modification especially in the case of Sb-Pb alloy, the thermal change, the influence of gas and the amounts of remaining aluminium were determined with regard to the normal and modified alloys.

As the consequence of these examinations, the micro-structures of the alloys of antimony-lead, lead-bismuth and tin-bismuth were found to be considerably refined with the addition of a small quantity of aluminium and calcium respectively.

Introduction

Improvement in the mechanical properties of casting alloys has been made by refining their micro-structure. Especially, it is well known that the eutectic structure of the sand-cast silicon-aluminium alloy becomes strikingly finer by the modifying process of adding a small quantity of sodium, alkali fluorides or the elements analogous to sodium. One of the writers² has previously reported in detail on the modified structure of silicon-aluminium alloy. The writers have undertaken the present investigation, supposing that such phenomena as characterize Si-Al alloys, may also be found in connection with the other eutectic alloys.

Specimens

Under powdered carbon or a mixture of 38%NaCl and 62%CaCl₂, the alloys were prepared in a graphite crucible. In sand moulds (15 mm. in inner diameter, 70 mm. long and about 25 mm. in thickness) castings were carried out at temperatures, respectively, of 450°~500°C in the case of Sb-Pb alloys, and of 300°~400°C in the cases of Sn-Bi

1. This paper was read at the meetings of the Kinki Branch of the Chemical Society of Japan, May, 1937, and of the Institute for Chemical Research, December, 1937.

2. H. Kotô; These Memoirs, A, 18, 17 (1935).

and Pb-Bi alloys. For the microscopical examination, Sb-Pb alloys were cut out longitudinally, but in the cases of Sn-Bi and Pb-Bi alloys transversely at the central part. Each of these specimens was well polished and then etched with a 2~4 per cent. alcoholic solution of nitric acid.

Micro-structures

I. The Sb-Pb System

In the antimony-lead system,¹ the eutectic point lies at 12.5~13% Sb and 247°~250°C, and a slight range of solid solution exists at both ends of the system. Photos 1~7, Plate I, show the micro-photographs of the specimens containing 12.5% Sb, in which the light areas represent the β -constituent (a saturated solid solution at Sb end) and the dark the more readily etched α -constituent (a saturated solid solution at Pb end). It can be seen from Photos 1 and 2 that there is a great difference in grain-size between the micro-structures of the chill- and sand-cast specimens.

(1) *The Effect of Na*

Sodium, as is well-known, is very efficacious for the modification of Si-Al alloy: but contrary to our supposition, this was found not to be effective for the modification of Sb-Pb alloy: e. g., the eutectic is composed of β crystallized in a needle-shape of considerable dimensions. Here, it is noticed that there are various methods of procedure in adding sodium to the melt; among these, the best is to plunge it suddenly into the melt, the sodium being fixed at the end of a carbon rod; and the suitable temperatures, for the melt when it is plunged in, are 600°~700°C.

Sodium gives rise to so slight a modification as to be hardly appreciable with the addition of 0.03% or even 0.1%; but its modifying effect can be detected with the addition of 0.3%: e. g., as shown in Photo 3, the modified alloy is of the coarse micro-structure, in which the β -constituent comes to appear in needle-shaped crystals of considerable dimensions and to be disposed in part in a radiating manner.

(2) *The Effect of Li*

The modifying effect due to the addition of lithium was also microscopically examined. But no sign of the modification could be observed,

1. H. Endô; *Kinzoku no Kenkyu*, 2, 691 (1925).

even when 0.1 or 0.3% of lithium was added at 650°C, except that part of the light cubical crystals of β appear somewhat enlarged.

(3) *The Effect of Ca*

The calcium used is of small scale-like shape, and the part which is ready to undergo a change into CaO is observed. Accordingly, it is very difficult to plunge it thoroughly into the melt; so, under a mixture of 38% NaCl and 62% CaCl₂, calcium enclosed in a thin plate of lead was quickly plunged into the melt at about 850°C. In this way, all exposure to the atmosphere is avoid and the surface of the alloy is perfectly protected from oxidation. Photo 4, Plate I, shows the micro-structure of the specimen, to which 0.5 per cent. of calcium is added, and it is observed to be very fine.

(4) *The Effect of Al*

Aluminium is immiscible to lead even in the melt. Accordingly, when aluminium is to be added, it is reduced to small pieces and thrown into the melt, which is then well stirred, so that it may be uniformly mixed.

Gwyer and Phillips¹ have already found that the aluminium is very effective for the modification of Sb-Pb alloy. The modifying effect due to the addition of aluminium is most efficacious from 0.1 to 0.4%, but almost inappreciable with the addition of more than 0.5%, because the compound between aluminium and antimony is thought to have a tendency to form at the surface of the melt or, if formed below, to float up to the surface, solidifying immediately after forming, so that the aluminium does not remain in the melt. 700°~750°C is the most suitable temperature for adding the aluminium. It is necessary to stir the melt well just before casting. Moreover the casting temperature, efficacious for the modification, is 400°~550°C, but above 550°C or below 400°C, the micro-structure can never be fine. Photo 5 shows the micro-photograph of the specimen with the addition of 0.3% Al.

(5) *The Effect of Mg*

A mixture of 38% NaCl and 62% CaCl₂ was used as a flux. The modifying effect due to the addition of magnesium seems to be almost inappreciable up to 0.4%, but with the addition of a comparatively large amount (0.8%), the micro-structure is seen to become coarse, and the aspects of α and β crystals are somewhat varied, as shown in Photo 6.

(6) *The Effect of Cd*

As can be seen in Photo 7, the micro-structure of the specimen,

1. Gwyer and Phillips; J. Inst. Met., **36**, 283 (1926).

to which 0.3 per cent. of cadmium is added, is certainly finer than that of the normal one.

(7) *The Effect of As*

When arsenic is added at about 600°C, the effect is not only to curve the surface of the melt to a great extent, but to produce a highly fluid alloy. But the effect on the micro-structure is very slight.

(8) *The Effect of Te and Se*

When 0.2% of tellurium is added at about 600°C, its modifying effect was found to be somewhat appreciable, but almost inappreciable with the addition of more than 0.2%. That of selenium seems to be almost inappreciable.

From the results of this experiment it became clear that the metals such as sodium and lithium, which were very efficacious for the modification of Si-Al alloy, are never efficacious for the modification of Sb-Pb alloy: on the contrary, calcium, aluminium and cadmium are most efficacious for the modification. Especially, sodium gives rise to a coarser micro-structure, according to the amount added.

With regard to the modifying effects of some other elements belonging to the same group as Ca in the periodic table, such as Ba and Sr, no examination was made, but we may suppose that modification similar to that caused by calcium might be observed.

II. The Sn-Bi System

In the tin-bismuth system,¹ the eutectic point lies at 42%Sn and 140°C, and a solid solution exists on each side of tin² or bismuth, respectively. As can be seen in Photo 8, Plate I, the micro-structure of the sand-cast specimen is very coarse, in which α -crystal (a saturated solid solution at Sn end) appears in the characteristic large rounded dendritic form and β -crystal in a cubical form. But in an alloy containing 42 per cent. of tin, the β -crystal very seldom appears in such a form, and only the α -crystal is markedly developed. Consequently, this alloy seems to bear the micro-structure of an alloy containing an excess of tin above the eutectic proportion.

(1) *The Effect of Na*

Sodium acts to make coarse the micro-structure of the Sb-Pb alloy, and conversely to make that of the Sn-Bi alloy to some extent fine.

1. H. Endô; *Kinzoku no Kenkyu*, **2**, 682 (1925).

A. C. Davidson; *Techn. Publ. Intern. Tin Res. & Devel. Council, A*, No. 77 (1938).

2. T. Satô, T. Matuhasi; *Japan Institute of Metals*, **2**, 592 (1938).

This fact has already been reported by Felice de Carli.¹ On the whole, such a conspicuous modifying action of sodium seems to be dependent on the formation of the ternary eutectic. As can be seen in Photo 9, Plate I, the micro-structure of the specimen containing 0.3 per cent. of sodium shows that contrary to the case of Sb-Pb alloy, sodium is very efficacious for the modification of Sn-Bi alloy.

(2) *The Effect of Al*

Aluminium is very efficacious for the modification of Sn-Bi alloy, as it is in the case of Sb-Pb alloy. As shown in Photo 10, the amount of added aluminium is sufficient with only 0.3 per cent.

(3) *The Effect of Ca*

As shown in Photo 11, calcium is very efficacious for the modification with the addition of 0.3 per cent. Moreover, if we inspect the micro-photograph more precisely, the α - and β -crystals develop a tendency to arrange themselves generally having a definite orientation towards the centre of the field.

(4) *The Effect of Te*

As is seen in Photos 12 and 13, the micro-structures of Sn-Bi alloys are refined to some extent by the addition of 0.25 per cent. of tellurium; but on the contrary, they are rendered very coarse when the proportion of tellurium is increased to 0.7 per cent. In this case, the light cubical crystals represent the well-developed β -ones.

Study was also made of the modifying effects of the addition of 0.3%Li, of 0.1%Se and of 0.5%Se. But these elements were all found not to be efficacious for modification.

III. The Pb-Bi System

In the lead-bismuth system,² the eutectic point lies at 43.5%Pb and 124°C, and the solid solution extends rather widely on each side of lead or bismuth. As can be seen in Photo 15, Plate II, the micro-

1. Felice de Carli: Atti III Congr. naz. chim. pura appl. Firenze e Toscana, 432 (1929).

2. W. Herold; Z. anorg. Chem., **112**, 131 (1920).

Here, it is noticed that at the 1st great meeting of the Japan Institute of Metals, opened in Tokyo on the 15th of May, 1937, immediately before the present writers read this paper at the regular meeting of the Kinki Branch of the Chemical Society of Japan, opened in Osaka on the 21st of May, 1937, this system was reported by Prof. K. Takahashi and Mr. T. Takase, not to be a simple eutectiferous series as hitherto supposed, but to have a series of solid solution formed by a peritectic reaction.

T. Takase; Japan Institute of Metals, **1**, 143 (1937).

Hans v. Hofe u. H. Hanemann; Zeits. f. Metallk., **32**, 112 (1940).

structure of the sand-cast specimen is considerably coarser, the α - (at Pb end) and β - (at Bi end) crystals appearing in the peculiar angular form. Photo 14, Plate I, shows the micro-structure of the chill-cast specimen; the α - and β -constituents crystallize out only in small dimensions, owing to the rapid cooling.

(1) *The Effect of Li*

As shown in Photo 16, Plate II, the addition of 0.1 per cent. of lithium provides the very fine micro-structure of Pb-Bi alloy.

(2) *The Effect of Na*

Photo 17 shows the micro-structure of the specimen in the case of addition of 0.1% Na, which is refined to some extent. The modifying effect of adding 0.3 per cent. of sodium was also found to be nearly the same as in the previous case. In this case, the α -constituent (the dark) characteristically crystallizes out in a much rounded form.

(3) *The Effect of Mg*

The modifying effect of the addition of 0.3% of magnesium was examined. As is seen from Photo 18, the β -constituent crystallizes in a rather large shape, and consequently the micro-structure came on the whole to be rather coarse.

(4) *The Effect of Ca*

Photo 19 shows the micro-structure of the specimen in the case of addition of only 0.1 per cent. of calcium, and it will be observed to be very fine.

(5) *The Effect of Al*

The micro-structures of the specimens, which were produced by the addition of 0.1~0.3 per cent. of aluminium are all very fine, as was the case with calcium described above.

(6) *The Effect of Se*

Photo 20 represents the micro-structure of the specimen after the addition of about 0.6% of selenium, which is coarser than normal, the β -constituent crystallizing out in a rather large shape.

(7) *The Effect of As*

Photo 21 shows the micro-structure of the specimen produced by adding 0.15 per cent. of arsenic, and it is observed to be very fine. On the contrary, that of the specimen formed by adding 0.45 per cent. of arsenic is very coarse, as is shown in Photo 22.

(8) *The Effect of Te*

The micro-structure of the specimen in the case of adding 0.2% Te is observed to be somewhat fine; while that of the specimen produced by adding 0.5% of Te is coarse, similar to that of the original.

From the results of the experiments above described, both aluminium and calcium were found to be very efficacious for the modification of the alloys of antimony-lead, tin-bismuth and lead-bismuth.

To make clear the mechanism of modification of Sb-Pb alloy, the following experiments were carried out in connection with the normal and modified alloys.

Thermal Analysis

The specimen (12.5% Sb, the remainder Pb) weighing 40~50 grams was first melted in a Tammann tube placed in an electric resistance furnace, and after being transferred into a low temperature furnace previously prepared, it was subjected to thermal analysis under the powdery carbon, being somewhat rapidly cooled. Here it must be remarked that on solidifying pure lead does not show any tendency to undergo undercooling, while antimony generally undergoes very marked undercooling, and even when cooled in furnace, sometimes suffers the undercooling as much as about 60°C lower than its melting point. Consequently slight undercooling is also observed in the normal alloys of antimony and lead.

The curves obtained in the case of the alloys modified with aluminium or sodium indicate greater tendency to undercooling of the specimens at the temperatures of eutectic crystallization, than the curves corresponding to the normal ones do; besides, the eutectic temperature of the former is also somewhat lower than that of the latter. Furthermore, the alloy modified with calcium also has undergone nearly the same undercooling phenomena as was observed with those modified with aluminium or sodium.

Thus the modified structure of Sb-Pb alloys, caused by adding aluminium and calcium respectively can be considered to be due to the undercooling on solidifying. But the alloy modified with sodium, notwithstanding it has undergone the undercooling, is of larger microstructure. Consequently, it may not be confirmed that the undercooling is the only cause of the formation of the refined structure of Sb-Pb alloy.

The Influence of Gases on the Eutectic Structure

All the molten alloys always contain a small quantity of gases. Therefore the following experiments were made in connection with the Sb-Pb alloys, to examine the effect of gases upon their microstructure.

(1) Assuming that the fine structure caused by adding aluminium is due only to the strong deoxidizing action of aluminium, hydrogen was passed into the melt and the oxygen expelled; then the molten alloy was cast into the sand-mould, with the expectation that the fine structure might be obtained. Contrary to our assumption, the larger micro-structure was obtained, as shown in Photo 23, Plate II.

(2) The molten Sb-Pb alloy with the eutectic, first modified with 0.2 per cent. of aluminium and then treated by hydrogen, was cast from 450°C into the sand-mould at the ordinary temperature. As shown in Photo 24, no refinement of the micro-structure was observed, but the β -crystal was observed to segregate at the periphery of the ingot.

(3) In contrast to the former experiment (2), the molten Sb-Pb alloy with the eutectic, first treated by hydrogen and then modified with aluminium, was cast at 450°C. The micro-structure thus obtained is considerably refined, as is seen in Photo 25.

From the results of the experiments above described, it may be concluded that the refined micro-structure of Sb-Pb alloy caused by adding aluminium, is not due only to the deoxidizing action of aluminium, but also to some other effect, such as the change in the surface tension of the melted aluminium on the molten Sb-Pb alloy.

The Amounts of Aluminium Remaining in the Sb-Pb Alloy Modified with It

It is manifestly important to make clear, whether or not the aluminium remains in the alloy modified with it, and if it does, what are both its proportion and state. Therefore, the modified alloy and its slag were both analysed.

It became clear from the results of the chemical analysis that most of the added aluminium was found in the slag, and little or none in the alloy. Consequently, the modified structure in this case seems shown not to be due to the formation of the ternary eutectic of Sb-Pb-Al alloy.

Crystalline Configuration

In this research, the Sb-Pb, Sn-Bi and Pb-Bi alloys of the normal and modified forms with eutectic composition before mentioned were used as the specimens.

The specimens utilized in this examination were prepared as follows: two series of thin plates (about 3 mm. in thickness) were cut out transversely and longitudinally from each ingot, and etched with

conc. nitric acid in the cases of Sn-Bi and Pb-Bi alloys, and with the aqueous solution of 50% HNO_3 and 50% HCl in the case of Sb-Pb alloys, until they were reduced to about 0.15 mm. in thickness to remove the mechanical distortions of the surfaces. When the planed surface of the specimens was set perpendicularly to the incident heterogeneous X-ray beam emitted from the molybdenum anticathode, two series of diffraction patterns were obtained; the one is given rise to by the incidence of X-rays perpendicular to the transverse section of ingot, while the other corresponds to the incidence perpendicular to the longitudinal section.

Some of the diffraction patterns thus obtained are reproduced in Plate III. It is noticed that not only those here reproduced, but all the patterns, produced respectively by the incidence of X-rays perpendicular to the transverse and longitudinal sections of the same specimen, were found not to be essentially different from each other.

Hence only one of the diffraction patterns for the transverse or longitudinal section of a given specimen is here reproduced.

I. The Sb-Pb System

As can be seen in Photo 26, Plate III, the diffraction pattern produced by the normal alloy containing 12.5 per cent. of antimony, consists of a number of radiating bands. We may conclude from the presence of radiating bands, that the larger portion of the specimen is composed of a complex fibrous structure. The micro-structures of the alloys modified respectively with calcium and aluminium are finer than that of the normal one; while that of the alloy modified with sodium is very coarse. All the diffraction patterns taken with these specimens are composed of a number of radiating bands, similar to those of the normal one. This shows us that the larger portion of each of the specimens consists of a complex fibrous structure. Photos 27 and 28 show the diffraction patterns taken with the alloys modified with 0.5%Ca and 0.3%Na, respectively.

II. The Sn-Bi System

Photo 29, Plate III is the diffraction pattern taken with the normal alloy containing 42 per cent. of tin. This pattern consists mainly of a number of radiating bands. It can be concluded from the presence of radiating band, that the larger portion of the specimen is composed of a fibrous structure. The micro-structures of the alloys modified respectively with sodium, aluminium and calcium are smaller than that of the normal one, while that of the alloy modified with

tellurium is coarse or very coarse depending upon the amount of tellurium. As can be seen in Photos 30, 31, 32 and 33, all the diffraction patterns occurring upon these specimens are composed of a number of radiating bands. Thus we may conclude from these patterns that all the specimens are mostly made up of a fibrous structure. Especially, the alloy modified with tellurium has a micro-structure coarser than that modified with calcium, and accordingly may be conceived to consist of crystal-grains of comparatively large size. While, by comparing the radiating bands in their diffraction patterns with each other, it was found that the crystalline configuration with tellurium is not necessarily more regular than with calcium.

III. The Pb-Bi System

As shown in Photo 34, Plate III, the diffraction pattern produced by the normal alloy containing 43.5 per cent. of lead is composed of a number of radiating bands. From this diffraction pattern it can be concluded that the larger portion of the specimen consists of a complex fibrous structure. although all the alloys modified with sodium, calcium or aluminium, are of fine micro-structures, all the diffraction patterns of these specimens have the radiating bands increasing in size and decreasing in number. (See Photos 35, 36 and 37.) Thus we may conclude that the crystalline configuration is somewhat more regular in these specimens than in the normal one.

In consequence of these X-ray analyses in connection with the three eutectiferous specimens of alloys above mentioned, we may conclude that the micro-structure of the specimens concerned does not necessarily give accurate information about the actual size and configuration of the micro-structures: i. e., there are some discrepancies between the actual crystalline configuration in the specimens and their micro-structure.

Conclusion

The experimental results in this research may be summarized as follows:—

(1) The micro-structures of the Pb-Bi, Sn-Bi and Sb-Pb alloys with the eutectic composition, are considerably refined with the addition of a small quantity of aluminium or calcium.

(2) The micro-structure of the Sn-Bi alloy with the eutectic composition is refined by the addition of a small quantity of sodium:

contrary to the above, that of the Sb-Pb alloy with the eutectic composition becomes very coarse.

(3) All the micro-structures of the Sb-Pb, Pb-Bi and Sn-Bi alloys with the eutectic composition become decidedly coarse with the addition of more than 0.5 per cent. of magnesium, selenium or tellurium.

(4) The thermal change, the influence of gas and the amount of remaining aluminium were especially determined in connection with the Sb-Pb alloy with the eutectic composition, and on the basis of the results obtained, the mechanism of modification of Sb-Pb alloy was described.

(5) There are some discrepancies between the actual crystalline configuration in the specimens and their micro-structure.

In conclusion, the writers wish to express their cordial thanks to Prof. D. Uno for his kind guidance, during the present investigations and to Ass. Prof. H. Hirata for his valuable advice in the X-ray analysis.

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Plate I

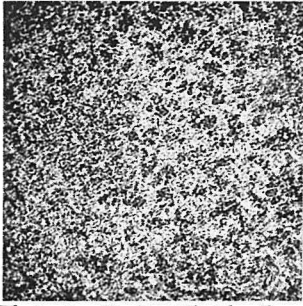


Photo 1. Sb (12.5%)-Pb alloy.
Chill cast $\times 100$

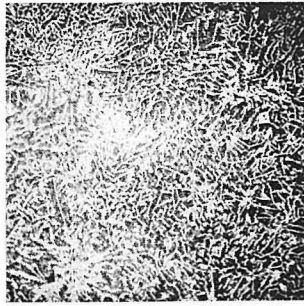


Photo 2. Sb (12.5%)-Pb alloy.
Sand cast $\times 100$



Photo 3. Modified
with 0.3% Na $\times 100$

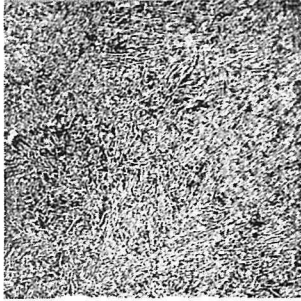


Photo 4. Modified
with 0.5% Ca $\times 100$

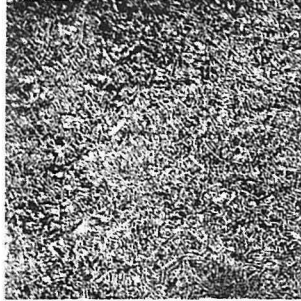


Photo 5. Modified
with 0.3% Al $\times 100$

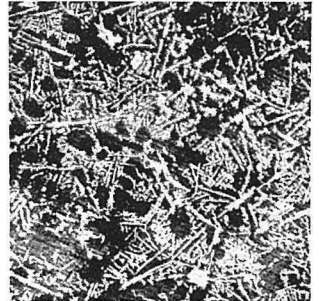


Photo 6. Modified
with 0.8% Mg $\times 100$

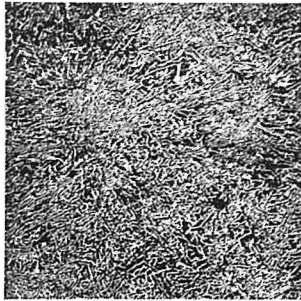


Photo 7. Modified
with 0.3% Cd $\times 100$

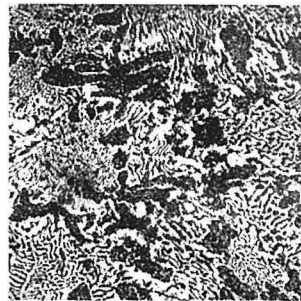


Photo 8. Sn (42%)-Bi alloy.
Sand cast $\times 100$

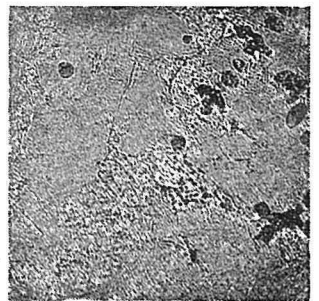


Photo 9. Modified
with 0.3% Na $\times 100$

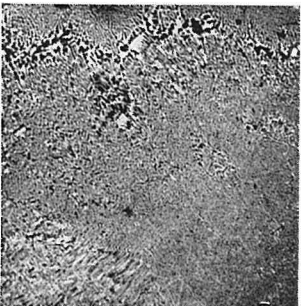


Photo 10. Modified
with 0.3% Al $\times 100$

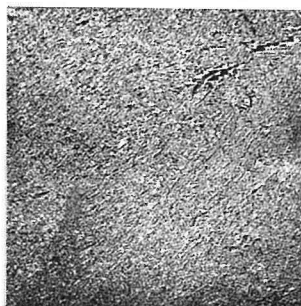


Photo 11. Modified
with 0.3% Ca $\times 100$



Photo 12. Modified
with 0.25% Te $\times 100$

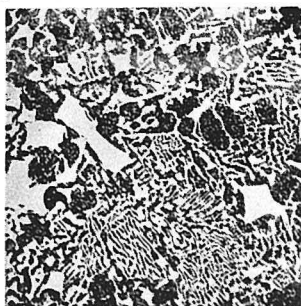


Photo 13. Modified
with 0.7% Te $\times 100$

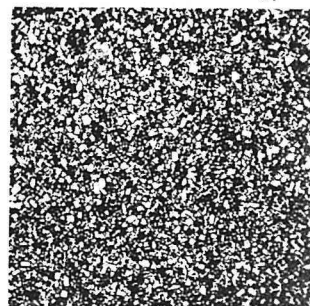


Photo 14. Pb (43.5%)-Bi alloy.
Chill cast $\times 100$

Plate II

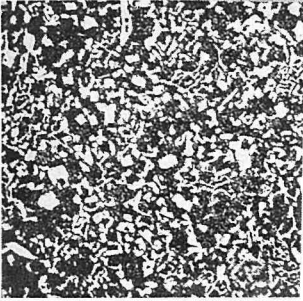


Photo 15. Pb (43.5%)-Bi alloy.
Sand cast $\times 100$

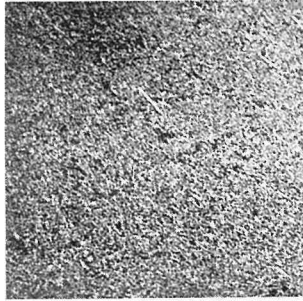


Photo 16. Modified
with 0.1% Li $\times 100$



Photo 17. Modified
with 0.1% Na $\times 100$

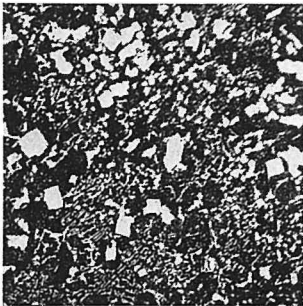


Photo 18. Modified
with 0.3% Mg $\times 100$

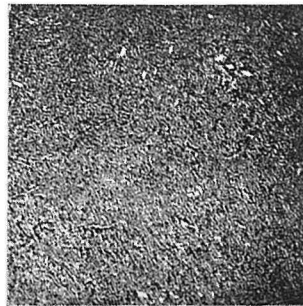


Photo 19. Modified
with 0.1% Ca $\times 100$

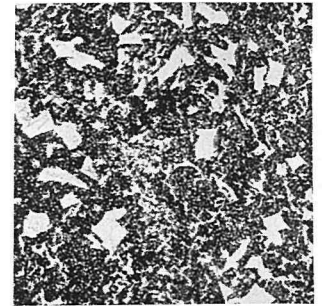


Photo 20. Modified
with 0.6% Se $\times 100$



Photo 21. Modified
with 0.15% As $\times 100$

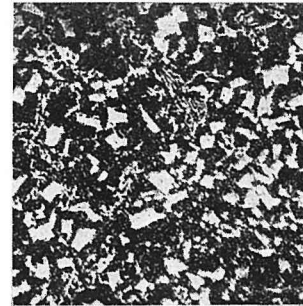


Photo 22. Modified
with 0.45% As $\times 100$



Photo 23. Sb (12.5%)-Pb alloy
(H₂-treated) $\times 100$



Photo 24. Modified with
0.2% Al (H₂-treated) $\times 100$

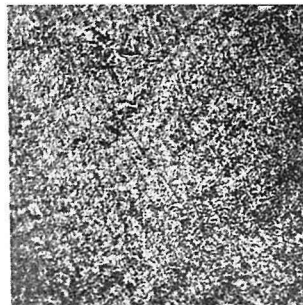


Photo 25. Treated by H₂, then
modified with 0.2% Al. $\times 100$

Plate III



Photo 26. Sb (12.5%)-Pb alloy.
Sand cast.
(Longitudinal section)



Photo 27.
Modified with 0.5% Ca.
(Longitudinal section)



Photo 28.
Modified with 0.3% Na.
(Longitudinal section)

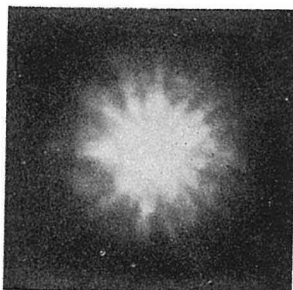


Photo 29. Sn (42%)-Bi alloy.
Sand cast.
(Transversal section)

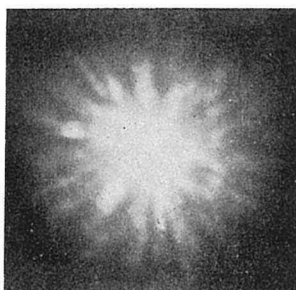


Photo 30.
Modified with 0.3% Na.
(Longitudinal section)

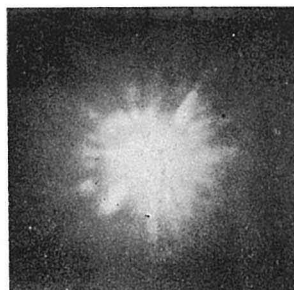


Photo 31.
Modified with 0.3% Al.
(Longitudinal section)

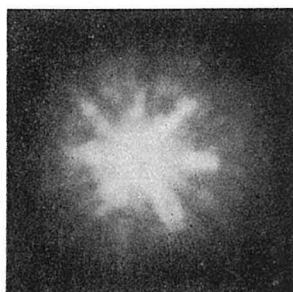


Photo 32.
Modified with 0.3% Ca.
(Longitudinal section)

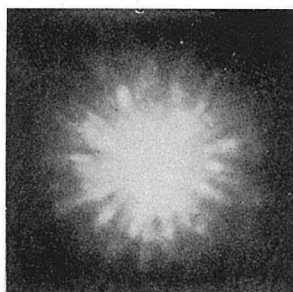


Photo 33.
Modified with 0.7% Te
(Transversal section)

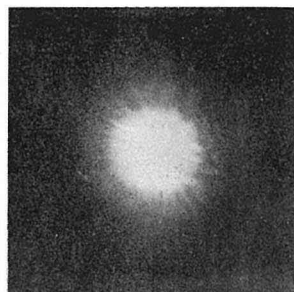


Photo 34. Pb (43.5%)-Bi alloy.
Sand cast.
(Transversal section)



Photo 35.
Modified with 0.3% Na.
(Transversal section)

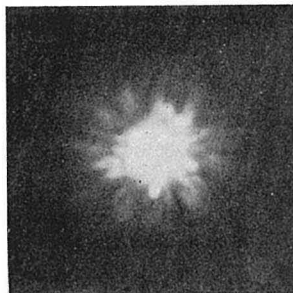


Photo 36.
Modified with 0.3% Ca.
(Transversal section)

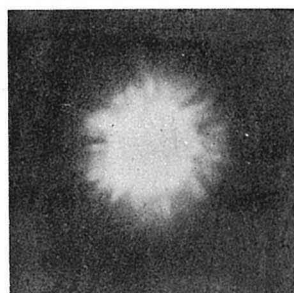


Photo 37.
Modified with 0.1% Al.
(Transversal section)