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On the Refined Structure of the Silver-rich Aluminium-Silver Alloys

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Abstract

Microscopic examination was made in connection with various quenched specimens of the aluminium-silver alloys containing 6.5 per cent. of aluminium and of the same with the addition of a small quantity of Sn and Sb respectively and also of the alloy with 7 per cent. of aluminium. The X-ray investigation was then carried out, to test the crystal structures and the crystalline configurations of the same alloys.

As the consequence of these researches, it was found on the one hand that the micro-structures of those alloys both normal and modified are considerably refined, depending on differences in the quenching temperatures, and the quenching agents and in the concentrations of the added metal; and on the other hand that the micro-structures of these specimens were proved not to be always in agreement with their crystalline configurations.

Introduction

Among the investigations of the refined structures of the alloys, much has been done with those of the Silumin-structure, but up to the present little has been done with those of the other alloys.

Several years ago, in connection with the normal and modified Si-Al alloys the writer² reported that the micro-structures in these specimens were not always in agreement with their inner crystalline configurations. Furthermore, with regard to the eutectic alloys, such as antimony-lead, lead-bismuth and tin-bismuth,³ their refined structures were studied using the method that had been used earlier with Si-Al alloys.

Among the aluminium-silver alloys under consideration, those which bear either $\alpha + \beta$ or β above 600°C, exhibit the refined structure or not, according to the differences in the quenching temperatures and in the quenching media. In the case of the brasses, Bauer and Hansen⁴

^{1.} A part of this paper was read at the 61 st annual meeting of the Chemical Society of Japan, April, 1939.

^{2.} H. Kotô; These Memoirs, A, 18, 17 (1935); The Report of the Institute for Chemical Research, Imperial University, Kyoto, 5, 104 (1935).

^{3.} Presented at the Autumn Meeting of the Institute for Chemical Research, December 11, 1937. These Memoirs, A, 23, 298 (1941).

⁴ Der Aufbau der Kupfer-Zinklegierungen (1927) S. 92.

have previously attempted similar experiments, investigating their micro-structures only.

In the present experiment, the writer made more precise investigation in connection with the aluminium-silver alloys which give rise to such refined structures as described above, and moreover examined their crystalline configurations and crystal structures with X-rays.

Specimens

The silver used was of the highest purity (1000/1000), especially prepared at the Imperial Mint, Osaka; the aluminium was also of the utmost purity (99.996%). Under a layer of sodium chloride the alloys were prepared in a graphite crucible, carefully protected from oxidation and introduction of impurities. After the silver was melted the aluminium was added, then the mixture well stirred, and the alloy cast into an iron mould (6.5 mm. in inner diameter and 60 mm. long). The specimens used were prepared by cutting these ingots to suitable size.

Micro-structures

After several trials, the electrolytic etching process using a 10 per cent. solution of citric acid, was found to give the best results, particularly for the development of the refined structure. A mixture of chromic and nitric acids is suitable for etching the homogeneous alloy. Moreover, for the convenience of comparison all the micro-photographs were taken with a magnification of 160 diameters.

From the constitutional diagram of the system Al-Ag in Fig. 1, it is conceivable that a specimen of the alloy containing 7 per cent. of aluminium gives rise to the transformation of $\beta \not\subset \alpha + \beta$ between 665° and 670°C; i. e., at this temperature of transformation it converts, when quenched into β or $\alpha + \beta$. The numbers in Fig. 1 correspond to those of the annexed micro-photographs and are only appended to represent the positions of the specimens in the constitutional diagram.

To examine the differences of the micro-structures according to the variations in the annealing times, the quenching temperatures and the quenching media, the annealing time was fixed for convenience sake as one hour and the quenching medium as ice-water, while the quenching temperature was varied.

As can be seen in Photo 1, Plate I, the micro-structure of the alloy containing 7 per cent. of aluminium quenched from 750° C in ice-water is composed only of the β -phase. While Photo 2 indicates that the

alloy containing 7 per cent. of aluminium quenched from 600°C in ice-water consists of a small amount of α -crystals finely separated in the ground mass of β -phase. This fact may be explained in the following manner:-When the alloy is plunged into icewater, its temperature suddenly falls to that of the solubility curve as $\alpha + \beta - \beta$, so that the separation represented by $\beta \rightarrow \alpha$ instantly sets in, and the separated *a*-crystals cannot grow and consequently they are fine. Since the quenching temperature in this case is a



little high, the larger portion of the specimen enters into the quenching medium before the temperature falls to that of the solubility curve and consequently the separated α -crystals are very slight. While the specimen quenched from 680°C in ice-water, as can be seen in Photo 3, Plate I, is composed of a large amount of α finely separated throughout the β -grains.

The mechanism of such a refined structure is explainable, and will be described below. When the specimen is immersed in the quenching liquid, the temperature of the larger portion of the specimen arrives at just the transition temperature, because the difference between the quenching-and transition-temperatures is only higher or lower than 10°C, and suddenly the separation as $\beta \rightarrow \alpha$ takes place for a moment throughout the specimen, and consequently such refined structure is given rise to. Photo 4 shows the micro-structure of the

specimen quenched from 670° C in ice-water. When the specimen is plunged into the quenching medium, a large part of it passes through the transformation temperature, since the quenching temperature just corresponds to the transformation temperature. Consequently, the separated crystals are very slight, as shown in Photo 4. While as is seen in Photo 5, when quenched from 660°C in ice-water, the insoluble α -crystals already remain in the β -phase and the α -crystals separated from the β -phase are also very slight, because this temperature of quenching is below the transformation temperature. Moreover, as the quenching temperature is lowered to 650°C and also to 630°C, the amounts of the α -crystals insoluble in β -phase gradually increase, and the α crystals separated in β -phase almost do not appear. The fact above mentioned is observed in Photo 6, which shows the micro-structure of the specimen quenched from 630°C. As the micro-photograph of the specimen quenched from 650°C is similar to that of the specimen quenched from 6_{30} °C, the former is not here reproduced. In the above cases, the annealing time was always fixed at an hour, but even when it was fixed at five hours, the refined structures of the present specimens did not alter. Therefore, for convenience sake the annealing time was fixed at an hour in the following experiments.

Next, for a more gradual quenching castor-oil was used in place of ice-water. In Photo 7, Plate I, the alloy containing 7 per cent. of aluminium quenched from 690°C in castor-oil is observed to consist of the α -crystals finely separated throughout the β -grains, presenting a somewhat different aspect from that quenched from the same temperature in ice-water. Such a refined structure is given rise to by the fact that the greater part of the specimen passes slowly through the transformation temperature in the quenching medium, owing to the heat conductivity of the castor-oil which is smaller than that of icewater and also to other facts. As can be seen in Photo 8, Plate I, the alloy quenched from 680°C in castor-oil bears nearly the same microstructure as that quenched from the same temperature in ice-water. In Photo 9, Plate I, the micro-structure of the alloy containing 7 per cent. of aluminium quenched from 650°C in castor-oil is observed to consist of the insoluble α -crystals and those finely separated throughout the β -grains.

Lastly, for the most gradual quenching, boiling water was used. Photos 10 and 11 show the refined structures of the alloys containing 7 per cent. of aluminium quenched from respectively 690° and 680° C in boiling water; each of them is observed to consist of the *a*-crystals

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finely separated throughout the β -grains, similar to those quenched in castor-oil, while the separated crystals in the former are much larger than in the latter. This may be explainable by the fact that the separated crystals have time to grow, owing to the slow rate of cooling of the specimen after being immersed in the quenching medium. As can be seen in Photo 12, the insoluble *a*-crystals remain in the β -phase in the case of the specimen quenched from 650°C, similarly as in the case of those quenched in the previous quenching media and the state of separated *a*-crystals in the β -phase is also very similar, even though the separated *a*-crystals come to appear very large.

As is seen in Photo 13, the specimen quenched from 680°C in ice-water consists of a considerable amount of the insoluble *a*-crystals and the finely separated ones in the β -phase. Photo 14 shows the micro-photograph of the specimen quenched from 750°C in ice-water; no insoluble *a*-crystals remain, since this temperature is a little higher than that of the solubility curve $a + \beta - \beta$. The reason why the finely separated *a*-crystals in the β -phase should be given rise to, is the fact that as soon as the specimen is immersed in the quenching medium, its temperature falls to that corresponding to the solubility curve above mentioned.

Microscopic examinations have been carried out in our laboratory by T. Ôtsubo,¹ in connection with the specimens of alloys quenched from 680°C in ice-water and containing about 1 per cent. of As, Cd, Cu, Mg, Mn, Sb, Sn and Zn respectively in addition to 6.5 per cent. of aluminium. By these examinations, the micro-structure of the alloys, especially of the specimens containing Sb and Sn, was found to be fine, similar to the Silumin structure. Therefore, further investigation was made by the present writer to see whether their micro-structures are fine or not with regard to the specimens quenched from 680°C and containing $0.1 \sim 2\%$ of Sn and Sb respectively besides 6.5% of aluminium.

The micro-photographs of some of the specimens quenched from 680° C and containing tin in addition to 6.5 per cent. of aluminium, are reproduced in Photos 15, 16 and 18.

The micro-structure of the specimen quenched from 680° C in icewater and containing 0.1 per cent. of tin in addition to 6.5 per cent. of aluminium (not reproduced) scarcely differs from that of the previous

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I. This was read by T. Otsubo at the meeting of the Chemical Society of Japan, April, 1938.

specimen quenched in the same way and containing 6.5 per cent. of aluminium modified with 0.1 per cent. of tin shown in Photo 13. The micro-structure of the specimen quenched from 680° C in ice-water and containing 0.5% Sn besides 6.5 per cent. of aluminium (not reproduced) bears fair resemblance to that of the specimen containing 0.1 per cent. of tin besides 6.5 per cent. of aluminium quenched in the same way, except that the insoluble *a*-crystals increase with the increment of tin-content in the specimen.

While in the specimen quenched from 680°C in ice-water and containing 1% of Sn in addition to 6.5% of aluminium, as shown in Photo 15, no insoluble α -crystals exist, and rather the separation of the fine *a*-crystals takes place throughout the β -phase. The micro-structure of the specimen quenched from 680°C in castor-oil and containing 1% of Sn besides 6.5% of aluminium is almost the same as that of the specimen containing 1% of Sn besides 6.5% of aluminium quenched from 680°C in ice-water. The micro-structure of the two specimens above mentioned bears marked similarity to that of the specimen containing 7% of aluminium quenched from 690°C in boiling water (see Photo 10); the separated α -crystals have a tendency to become somewhat In Photo 16, Plate II, which shows the micro-structure of coarse. the specimen containing 1% of Sn in addition to 6.5% of aluminium quenched from 680°C in boiling water, the separated a-crystals in the β -phase are observed to have become more coarse. Moreover, as is seen in Photo 17, when the alloy containing 0.1% of aluminium and 1% of tin in addition to 6.5% of aluminium was quenched from 680°C in boiling water, the separation of the α -crystals in the β -phase decreased When the same alloy is quenched from 680°C in castormarkedly. oil, its micro-structure bears close resemblance to Photo 17. Consequently, it may be considered that with the increase of only 0.1% Al, the temperature corresponding to the solubility curve falls at least 10°C. Moreover, in connection with the effect of added metal on the refinement of the micro-structure, it may be concluded from the results of these experiments that aluminium was found to be more efficacious than tin. Photo 18 shows the micro-photograph of the specimen containing 2% of tin in addition to 6.5% of aluminium quenched from 680°C in ice-water; no separation of α -crystals in the β -phase takes place.

Photo 19, 20 and 22 show micro-photographs of some of the specimens containing $0.1 \sim 2$ per cent. of antimony in addition to 6.5 per cent. of aluminium quenched from 680° C.

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The micro-structures of the specimens quenched from 680°C in ice-water and containing 0.1 and 0.5 per cent. of antimony in addition to 6.5 per cent. of aluminium (not reproduced), scarcely differ from that of the similarly quenched specimen containing 6.5 per cent. of aluminium shown in Photo 13; i. e., the insoluble α -crystals remain in the β -phase and also the fine α -crystals separate in that phase. The field of the insoluble *a*-crystals increases with the increment of antimony-content, similarly to the case of tin-content. Moreover, as is seen in Photo 19, the micro-structure of the specimen quenched from 680°C in ice-water and containing 1 per cent, of antimony in addition to 6.5 per cent. of aluminium, bears fair resemblance to that of the specimen containing 7 per cent, of aluminium quenched in the same manner (Photo 3). The micro-structure of the specimen quenched from 680°C in castor-oil and containing 1 per cent. of antimony in addition to 6.5 per cent. of aluminium also bears close resemblance to that of the specimen containing 7 per cent. of aluminium quenched in the similar way. Photo 20 shows the micro-photograph of the specimen quenched from 680°C in boiling water; the separated α -crystals in the β -phase seem to become somewhat coarse. As may be seen in Photo 21, when the alloy containing 0.1 per cent. of aluminium besides 6.5 per cent. of aluminium and 1 per cent. of antimony is guenched from 680° C in boiling water, the separated *a*-crystals decrease remarkably. Consequently, in this case, as in the case where tin is added, the aluminium may be easily supposed to be more conspicuous than the antimony, as to the effect on the separation of the α -crystals Furthermore, in Photo 22, which is taken with the in the β -phase. specimen containing 2 per cent. of antimony quenched from the same temperature in ice-water, the separation of the α -crystals from the β phase can scarcely be observed; but if we inspect the micro-photograph in Photo 22 more precisely, its aspect differs somewhat from that caused by tin: i. e., since the amount of antimony in this case is comparatively large (2 per cent.), some separation, which may be supposed to be given rise to by the other phase of the ternary system, seems to take place at the grain boundaries of β . The fact above mentioned, is analogous to the fact that in the case of brasses the separation takes place at the grain boundaries, as was pointed out by Bauer and Hansen.¹ Photos $23 \sim 27$ show the micro-photographs of the specimens containing 6.1 per cent. of aluminium quenched from various tem-

I. Loc. cit.

peratures respectively in ice-water, after annealing at 700°C for 2 hours; each of them consists of $\alpha + \beta$. Photo 23 shows the micro-structure of the specimen quenched from 700°C, after annealing at 700°C for 2 hours; the quantities of α -and β -phases are nearly equal. Photo 24 shows the micro-photograph of the specimen quenched from 760°C in ice-water, raising the temperature up to 760°C in 4 minutes, after annealing at 700°C for 2 hours; it is observed that the insoluble α crystals, though heated for such a short time, considerably decrease, owing to their solubility in the β -phase, and the separation of the a-crystals in the β -phase is more markedly increased than when quenched from 700°C as above described. Photo 25 shows the microphotograph of the specimen quenched from 680°C in ice-water, lowering the temperature to 680°C in 2.5 minutes, after annealing at 700°C for 2 hours; although the quenching temperature differs only 20°C from that in the case of Photo 23, the separation of the α -crystals from the β -phase has already a tendency to decrease, and also the number of insoluble α -crystals in the β -phase seems to increase to some extent. Photo 26 shows the micro-photograph of the specimen quenched from 610°C in ice-water, lowering the tempeature down to 610°C in 1 minute, after annealing at 700°C for 2 hours; the separation of the α -crystals from the β -phase almost does not take place, and notwithstanding the fact that the quenching temperature differs 70°C from that in the case of Photo 25, the quantity of insoluble α -crystals in the β -phase in these specimens does not differ. This is due to the decreasing mobility of atoms in the space lattice with falling temperature. Even in such a case as this, the insoluble α -crystals in the β -phase increase, when the rate of cooling is sufficiently slow. Photo 27 represents the micro-photograph of the specimen quenched from 610°C in ice-water, after being allowed to cool from 700° to 610°C in 8.5 minutes; the α -crystals are observed to be greatly increased.

Crystalline Configuration

X-ray examination was first carried out by means of Laue's method, to see whether the micro-structure of the specimens above mentioned gives any accurate information in connection with the actual size and configuration of the micro-crystals. In this research, the same ingots used for the microscopic examination above described, were used as specimens. To utilize the specimens in this examination, two series of thin plates were cut out transversely and longitudinally from each ingot, respectively and etched by conc. nitric acid until they were reduced to about 0.08 mm. in thickness to remove the mechanical distortions of their surfaces. Then the planed surface of each specimen was set perpendicularly to the incident heterogeneous X-ray beam emitted from the molybdenum anticathode. Now, two series of the diffraction patterns could be 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 due to the incidence of X-rays perpendicular to respectively the transverse and longitudinal sections of the same specimen, were found not to differ essentially from each other.

As can be seen in Photos 28 and 29, Plate III, both diffraction patterns produced by the alloy containing 7 per cent. of aluminium quenched from 680°C in ice-water (see Photo 3), consist of an irregular assemblage of somewhat elongated Laue's spots. We may conclude from this fact that the specimen under examination is composed of crystals of comparatively large size, and bears a fibrous nature of weak degree. The above conclusion does not agree closely with the results of the microscopic examinations; as can be seen in Photo 3, Plate I, the size of crystallites is rather small.

Photos 30 and 31, Plate III, are the diffraction patterns taken with the alloy containing 6.5 per cent. of aluminium and quenched in a similar way to Photos 28 and 29, Plate III. The prominent parts of these patterns consist of a set of the discontinuous Debye-Hull rings and a number of radiating bands. Thus from the presence of Debye-Hull rings in Photos 30 and 31, Plate III, it can be concluded that the specimen under consideration is partly composed of an irregular aggregation of micro-crystals of comparatively small dimension (about 10^{-2} mm. in diameter): but the presence of radiating bands shows us that the larger portion of it has a fibrous structure.

The diffraction patterns occurring upon the specimen containing 0.1 per cent. of tin in addition to 6.5 per cent. of aluminium scarcely differ from those in the former specimen containing only 6.5 per cent. of aluminium. The diffraction patterns in Photos 32 and 33, Plate III, which were produced by the specimen containing 0.5 per cent. of tin besides 6.5 per cent. of aluminium consist mainly of a number of radiating bands. The predominance of such radiating bands in Photos 32 and 33, shows us without doubt that the larger portion of this

specimen has an incomplete fibrous structure. As is seen in Photos 34 and 35, Plate III, both diffraction patterns produced by the alloy containing 1 per cent. of tin in addition to 6.5 per cent. of aluminium, consist mainly of an irregular assemblage of somewhat elongated Laue's spots. Thus, we may conclude from the presence of such Laue's spots that contrary to the results of the microscopic examination (Photo 15), its crystalline structure is comparatively coarse, and has a somewhat fibrous nature. The diffraction patterns in Photos 36 and 37, Plate III, which were taken with the specimen containing 2 per cent. of tin, consist of somewhat regular Laue's spots. Thus it may be said that the crystallites constituting the specimens with 2 per cent. of tin, are of large size, as was concluded from the results of the microscopic examination (Photo 18).

The diffraction patterns occurring upon the specimens containing respectively 0.1 and 0.5 per cent. of antimony in addition to 6.5 per cent. of aluminium, differ almost none from those in the specimen, containing 6.5 per cent. of aluminium, consistent with the results of the microscopic examination.

As can be seen in Photos 38 and 39, Plate III, the diffraction patterns taken with the alloy containing 1 per cent. of aluminium, consist mainly of a number of the discontinuous Debye-Hull rings. From the predominance of such Debye-Hull rings in Photos 38 and 39 it can be conculuded that this specimen is nothing but an aggregation of the finer micro-crystals without any regularity. The above conclusion agrees with the results of the microscopic examinations; as shown in Photo 19, Plate III, the micro-structure is very fine. Photos 40 and 41, Plate III are the diffraction patterns taken with the alloy containing 2 per cent. of antimony besides 6.5 per cent. of aluminium. The prominent parts of these patterns consist of a number of radiating bands. Thus, the predominance of radiating bands in Photos 40 and 41 shows us that this specimen has a fibrous structure.

Crystal Structure

It has been already reported¹ that in the present alloy, when quenched, the β -phase is converted into either $\alpha + \gamma$ or γ according to the composition. To learn whether any change in the β -phase may or may not be observable with the quenched specimens containing $0.1 \sim 2$

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^{1.} H. Kotô and S. Nakamura; Bull. Chem. Soc., Japan, 58, 694 (1937); The Report of the Institute for Chemical Research, Imperial University, Kyoto, 8, 79 (1938).

per cent. of tin or antimony, the writer repeated the X-ray examination. In this examination, adopting the Debye-Scherrer method photographs were taken with the aid of a cylindrical camera of 7.03 cm. in diameter.

Utilizing K_{α} -radiation of copper some of the spectra thus obtained, are reproduced in Photos $42 \sim 50$, Plate IV.

As can be seen in Photo 42, the spectral lines of the specimen containing 6.5 per cent. of aluminium quenched from 680°C in icewater, are composed of lines due to both the α - and γ -phases in diffraction patterns. Photos 43~46 show the powder photographs taken with the alloys containing tin, and Photos 47~50, those taken with the alloys containing antimony. By comparing these figures with Photo 42, it was found that all the spectral lines of these specimens are composed of lines due to both the α - and γ -phases in diffraction patterns. Besides, increasing the amount of tin or antimony contained in the specimens from 0.1 to 2 per cent. gradually intensifies the lines corresponding to the γ -phase.

Thus it was concluded that according to the composition the β phase converts, when quenched, into either $\alpha + \gamma$ or γ , in connection with the specimens containing tin or antimony; i. e., amounts, at least of less than 2 per cent. of tin or antimony, constitute the ternary solid solution with aluminium and silver.

Conclusion

The experimental results which have hitherto been described, in connection with various specimens of the alloys of aluminium-silver and of those containing a small quantity of tin or antimony as the third metal besides aluminium and silver, led us to the following conclusions :—

(1) Contrary to the result of the microscopic examination, the specimen containing 7 per cent. of aluminium quenched from 680°C in ice-water, was found in the X-ray examination to be composed of crystals of comparatively large size.

(2) Such a discrepancy between the crystalline configuration and the micro-structure, could also be observed in the specimen containing 1 per cent. of tin in addition to 6.5 per cent. of aluminium.

(3) Contrary to the above, the crystalline configurations in the specimens containing respectively 1 per cent. of antimony and 2 per cent, of tin, is in good accordance with their micro-structures.

Thus the crystalline configuration in the specimens above men-

tioned, is not always in fair agreement with their micro-structure, as was found to be the case in the Silumin¹ and also in the binary eutectic alloys,² such as antimony-lead, lead-bismuth and tin-bismuth.

(4) It was concluded by the X-ray analysis that according to its composition, the alloy consisting of the β -constituent is converted, when quenched, into either $\alpha + \gamma$ or γ alloy, and also that with respect to the specimens containing tin or antimony, a similar bearing exists.

In conclusion, the writer wishes to express his heartiest thanks to Prof. D. Uno for his kind guidance, during the progress of this investigation and to Ass. Prof. H. Hirata for his valuable advice in the X-ray analysis. The expense for the experiments has been defrayed from a grant made to Prof. D. Uno by the Ministry of Education for the Promotion of Scientific Research, to which the author's thanks are due.

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- I. Loc. cit.
- 2. Loc. cit.

Plate I



Plaet II



Plate III

(Quenched from 680°C in ice-water, after annealing for an hour.)



Plate IV

(Quenched from 680°C in ice-water, after annealing for an hour.)

