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Preferred Precipitations in Some Age-hardened Aluminium Alloys

By

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Introduction

Since A. Wilm, the German engineer, discovered an alloy known at present as duralumin, age-hardening phenomenon has become an important problem in physical metallurgy. In early works, physical and mechanical properties were studied chiefly to explain the cause of hardening during ageing. Other researches were carried out upon the equilibrium diagram of aluminium-copper system, in consequence, the solid solubility of copper in aluminium was found to decrease rapidly with the fall of temperature. On slow cooling the aluminium alloy containing four percent copper, therefore, the precipitation of an intermetallic compound CuAl_2 was confirmed to take place from the uniform solid solution which exists at higher temperatures. By rapid cooling the same alloy as in quenching, however, the precipitation of CuAl_2 will be suppressed and the solid solution supersaturated with copper will be retained at room temperature. The subsequent change in such a supersaturated solid solution is believed to lead to the phenomenon known as age-hardening.

To clarify the phenomenon stated above more definitely, many investigations have been carried out by different means of measurements. From the results of recent researches, it is generally believed that ageing phenomenon in an aluminium-rich alloy containing copper occurs in the following steps¹⁾:

- a. migration of copper atoms in the solid solution,
- b. formation of Guinier-Preston zone,
- c. formation of θ' - CuAl_2 (intermediate phase),
- d. final formation of CuAl_2 (equilibrium phase).

The precipitation phenomenon in other aluminium-rich alloys is also considered to take place through the analogous processes. Many authors have tried to explain this ageing phenomenon from microstructural changes, but the changes could have not been definitely observed under an optical microscope

except some variation in etching characteristics, although the presence of very fine particles may be expected in the alloys according to other informations. Only the results of the observations available are as follows: Fink and Smith²⁾ found a striated structure in aluminium-copper alloy, which is considered to be the result of the formation of Guinier-Preston zones. The revelation of fine precipitates, however, was not evident in a certain region of the crystal grain along which the precipitation was assumed to have occurred. The region appears as faint lines crossing the crystal grains, which seem to be the traces of crystallographic plane {111}. Gayler and Parkhouse³⁾ carried out a detailed microscopic examination of the structure of aluminium-copper alloys being aged and clarified the relation between changes in hardness and in microstructure. Wassermann⁴⁾ observed the striated and the network structures in aged aluminium-magnesium-zinc alloys under an optical microscope.

Thus, the submicroscopic changes in structure that take place during age-hardening cannot exactly be detected by means of an optical microscope. However, the development of an electron microscope in recent years has made it possible to reveal the structures of extremely fine size. For example, A. H. Geisler and F. Keller⁵⁾ examined various light metal alloys by means of oxide film method and discussed the "critical size" of precipitate particles to obtain optimum strength. R. Castaing and A. Guinier⁶⁾ also published the electron micrographs of aged aluminium-copper and aluminium-magnesium-silicon alloys. The present authors⁷⁾ similarly investigated the precipitation behaviors in some age-hardened aluminium alloys by an electron microscope. From these investigations, we conclude that the electron microscope serves to give the direct evidence of the existence of submicroscopic structure, but it is not so suitable as X-ray for identifying exactly what the precipitate is.

The present investigation has been carried out chiefly by an electron microscope to make the localized precipitation evident in some aluminium-rich alloys, and to try to discuss the effect of thermal treatments on ageing.

Experimental Procedure

The alloys were prepared by employing the aluminium of 99.992% purity and the purest alloying elements obtainable. They were treated as described later in this paper. The microstructures were observed under optical and electron microscopes. The method of preparation of the oxide film employed for the study under an electron microscope was similar to that in our previous report.^{5,7)} The specimen was subjected to an anodic oxidation in a saturated solution of ammonium phosphate after it had been polished electrolytically

in a perchloric-acetic acid bath. The oxide film thus obtained on the surface of the specimen was removed in a mercuric chloride solution, then the film was washed with a dilute hydrochloric acid solution and distilled water. Supplementary to these researches, hardness measurement, stress-corrosion test, dilatometric measurement and X-ray analysis were carried out on necessity.

Localized Precipitation Caused by Plastic Deformation*

It is generally accepted that ageing is accelerated by plastic deformation. Some effects of plastic deformation, therefore, were already recognized in specimens in as quenched state. If electrolytically polished specimens are first subjected to the solution treatment and quenched in ice water, and then examined under an optical microscope without repolishing, slip lines are often observed in the grains. This indicates that the specimens are somewhat plastically deformed by quenching. If the same specimens are tempered at comparatively higher temperatures and then etched with a suitable etching reagent, they will show preferential precipitation along the slipping regions produced by quenching. However, if a specimen is quenched not in ice water but in boiling water, or in oil at rather high temperature and subjected to tempering, the precipitation will be observed to occur in localized regions along the network lines, probably due to the lack of slipping. To clarify such preferential precipitation in aluminium alloys, an alloy containing four percent copper was chiefly examined.

The specimens with various grain sizes were prepared by the strain-annealing method. They were quenched in suitable mediums with rapid or slow rate of cooling. Tempering was carried out for 30 hrs. at 200°C., because the sizes of the precipitates under this condition are the most suitable for the electron-microscopic observation.

Photos 1 and 2 represent respectively the optical and the electron micrographs of the aluminium alloy containing 4.02% copper, quenched in ice water from 500°C. and subsequently aged for 30 hrs. at 200°C. Photo 1 shows typical slip lines, but the electron micrograph Photo 2 does not show any distinct preferred precipitation at the slipping regions. It is probably due to the fact that so many slip bands were produced by the plastic deformation resulted from drastic quenching in ice water. Photo 3 is an electron micrograph showing the junction of two different grains in an alloy with the same composition whose grain size was about 3 mm. in diameter. In one grain small plate-like θ' -CuAl₂ particles are seen scattered almost uniformly throughout the grain, but in

* This paragraph in the paper was read on April 1, 1951 at the Spring Meeting of the Japan Institute of Metals.

another grain large precipitate particles are distributed more preferentially than in the former. This fact indicates that the effect of plastic deformation owing to quenching differs according to the orientation of crystal grains and the size of grains. On the other hand, the same specimen, whose micrograph is shown in Photo 1, was quenched from 500°C. in oil bath at about 100°C., then aged and etched similarly. The structure known as "veining" or "sub-boundary"^{4,8,9} was observed instead of slip lines under an optical microscope as shown at upper left corner in Photo 4. This structure is revealed more clearly under an electron microscope as shown also in the same photograph. A few of the plate-like θ' -CuAl₂ particles which are comparatively larger in size, are distributed along rather definite lines, but are not homogeneously in grains. In this case, the rate of quenching was not so great as to produce a plastic deformation accompanied with slipping and, therefore, the preferred precipitation did not take place in the slipping regions. These rather definite lines along which the preferred precipitation has occurred may be considered to be the boundaries of subdivisions in grain, because the orientations of the θ' -CuAl₂ on both sides of the lines are nearly the same.

From the observation of the above electron micrographs, it is evident that, in the case of rapid quenching in ice water, the distribution of the precipitates becomes dense and homogeneous owing to the presence of a large number of slip lines; but in the case of slow cooling, such phenomenon is not observed due to the lack of the occurrence of slipping. It may be concluded that a large number of slip lines produced by quenching play a predominant rôle in the precipitation phenomenon from the supersaturated solution. Even if the alloys are sufficiently homogenized by long annealing at higher temperatures and then quenched mildly, the precipitation will be highly localized at the regions with crystalline defects such as sub-boundaries. The localization of the precipitates is probably due to the fact that the defect of the crystalline structure cannot be eliminated completely.

In order to study further the effect of such imperfections, the specimens whose grain size was about 20 mm. in diameter were prepared by the strain-annealing method. The crystallographic orientations of the specimens were determined by X-ray. They were electrolytically polished and then heated to 500°C. in vacuum glass tubes. From this temperature, they were quenched in oil at 150°C. No slip lines were observed in the specimens on account of their having been slowly cooled. The specimens were then subjected to tension under various rates of loading to produce slipping due to mechanical working. Subsequently, they were tempered similarly as stated above.



Photo 7 Electron micrograph of the same alloy. Solution treated, elongated by 1.8% with a loading rate of 0.75 g. per mm² per second, and aged similarly. Showing preferred precipitation in slipping regions and sub-boundaries. $\times 10,000$

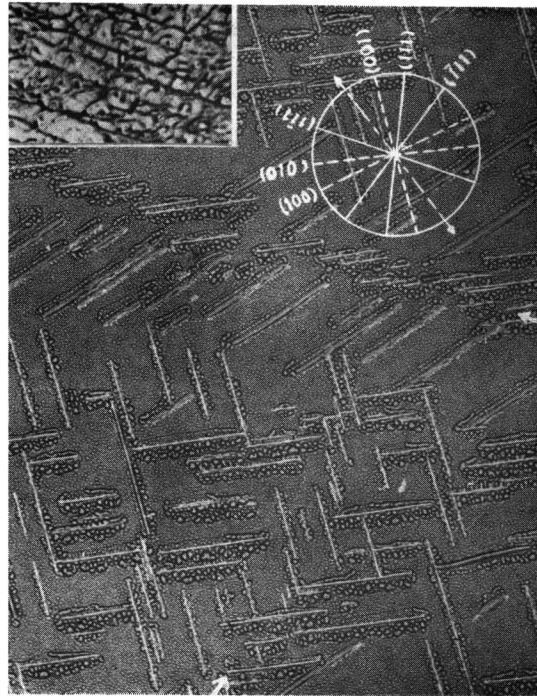


Photo 8 Electron micrograph of the same alloy. Solution treated, stretched by 5%, and annealed at 500°C. for 30 min., and then aged similarly. Showing preferred precipitation in a boundary of polygonization. $\times 10,000$ Its optical micrograph is shown at the upper left corner.



Photo 9 Electron micrograph of the alloy containing 2.85% Cu and 1.09% Mg, quenched from 500°C. and then aged at 250°C. for 5 hrs. Etched slightly in Lacombe's reagent. Showing the formation of plates on two kinds of crystallographic planes of etching pit. $\times 10,000$

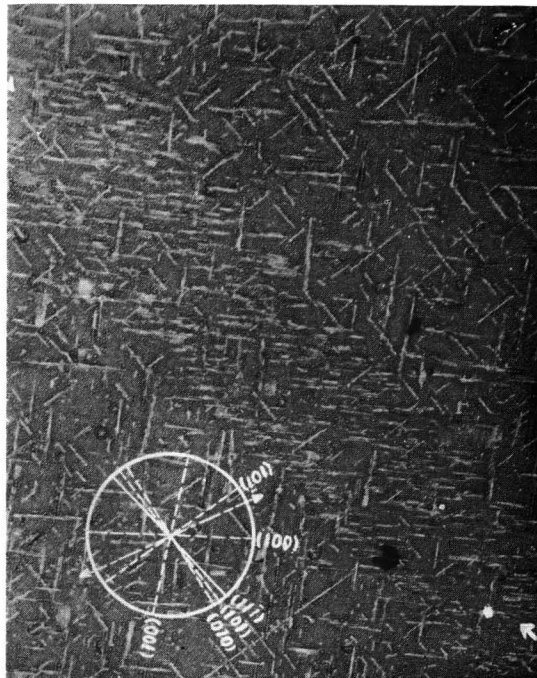


Photo 10 Electron micrograph of the alloy containing 3.12% Cu and 0.97% Mg. Solution treated, elongated by 1% and then aged at 200°C. for 2 days. Showing that the precipitation planes of the alloy are parallel to $\{100\}$ and $\{110\}$ of the matrix crystal, by the aid of the direction of slip band where preferred

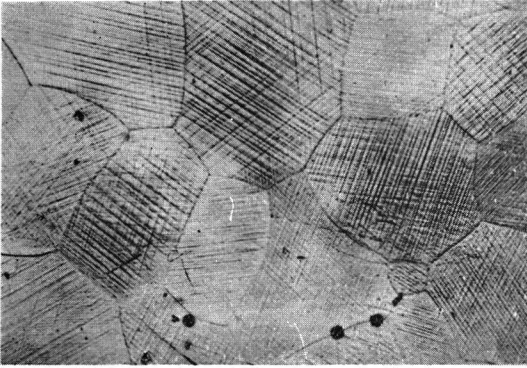


Photo 1 Optical micrograph of the alloy containing 4.02% Cu, aged at 200°C. for 30 hrs. Etched with Keller's reagent. Showing slip lines produced by quenching. $\times 48$

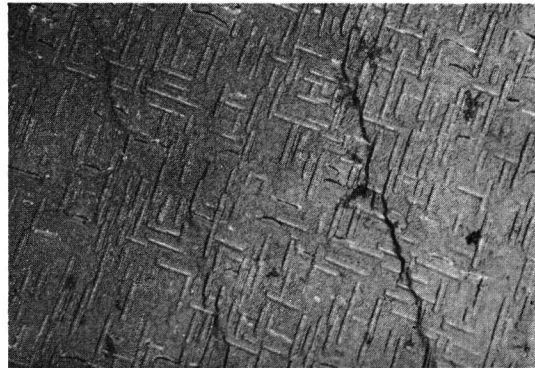


Photo 2 Electron micrograph of the same alloy. The field similar to that of Photo. 1. Showing no distinct preferred precipitation at the slipping regions, probably due to the formation of so many slip bands by rapid quenching. $\times 10,000$

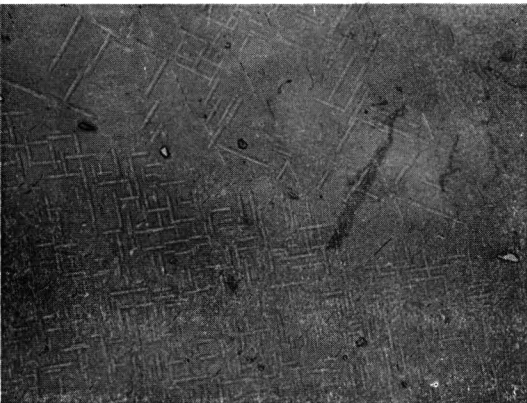


Photo 3 Electron micrograph of the same alloy with larger grain size. Showing the difference of precipitation behavior in grains, depending upon the orientation of crystal and grain size. $\times 10,000$

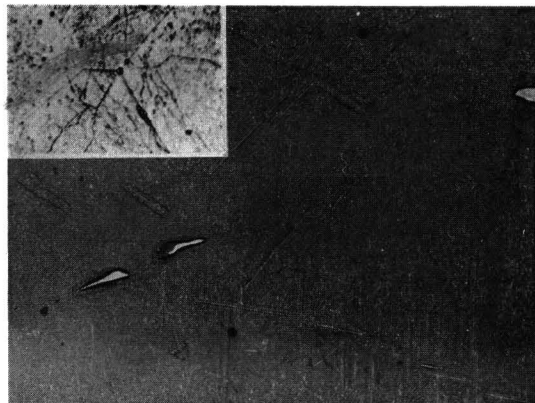


Photo 4 Electron micrograph of the same alloy. Quenched from 500°C in oil bath at 100°C and then tempered similarly. Showing the preferred precipitation in the boundaries of sub-divisions within grains. $\times 10,000$ Its optical micrograph is shown at the upper left corner.

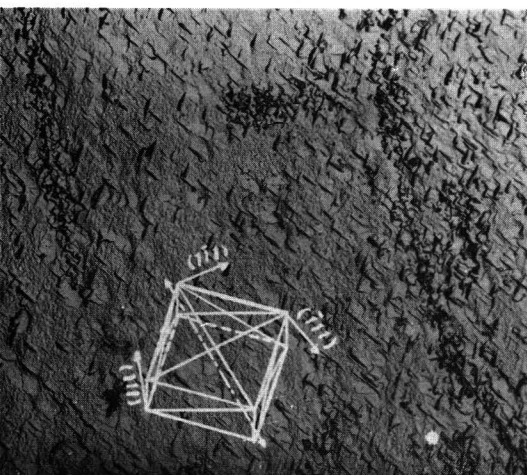


Photo 5 Electron micrograph of the same alloy. Solution treated, elongated by 5.2% with the slow rate of strain, and aged at 200°C for 30 hrs. Etched slightly prior to the preparation of oxide replica. Showing the preferential precipitation of plate-like θ' -CuAl₂ and the fragmentation of mosaic blocks at the regions of slipping. $\times 10,000$

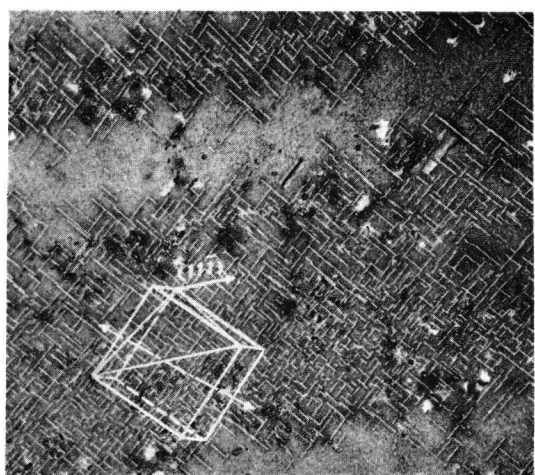


Photo 6 Electron micrograph of the same alloy. Solution treated, elongated 4.7% with the rapid rate of strain and aged similarly. Showing the denuded zones between the regions of slipping where a remarkable preferred precipitation exists. $\times 10,000$

Photo 5 shows an electron micrograph of the aluminium alloy containing 4.02% copper and etched slightly by Keller's reagent. In this photograph, the projection of its crystal lattice obtained from X-ray analysis is so drawn by white lines that the crystallographic directions may coincide with those of the precipitates and slip bands in this photograph. In this specimen, which was subjected to the slow rate of straining and stretched by 5.2% in total length, the occurrence of the preferential precipitation and the fragmentation of mosaic blocks at the regions of slipping are evident. Photo 6 shows an electron micrograph of the alloy with the same composition but with different crystallographic orientation, stretched by 4.7% in total length with a rapid rate of straining. In this photograph, it is apparent that the denuded zone between the regions of slipping, where a remarkable preferred precipitation occurred, exists. Photos 5 and 6 also show a good agreement with the well-known fact observed in pure metal crystals that the breadth of slip bands and their spacing are affected by the straining rate.

The preferred precipitations in slipping regions and sub-boundaries are shown in Photo 7 together with the crystallographic projection of crystal lattice. This electron micrograph was obtained from the specimen of the same composition, quenched in oil at room temperature and then stretched by 1.8% in total length with a loading rate of 0.75g. per mm². per second. The preferred precipitation is observed at the slipping regions of two sets of ($\bar{1}\bar{1}1$) and ($1\bar{1}\bar{1}$) planes, whose crystallographic directions are observed to coincide well with the analytical results by X-ray. Similar precipitates exist at sub-boundaries. These precipitates have almost the same orientation with those on both sides of the boundaries. In comparison with the grain boundaries where only a few coarse precipitates are observed, as shown in Photos 3 and 4, minute, discrete, plate-like θ' -CuAl₂ particles are found to exist along the sub-boundaries. They are an indication that the defects in sub-boundaries are not so marked as in the grain boundaries.

The specimen of the same composition was annealed for 30 minutes at 500°C. after an elongation of about 5 per cent, and then tempered for 2 days at 200°C. As seen in the upper left hand corner of Photo 8, the optical micrograph shows a kind of sub-boundary structure known as "network structure" in Japan.^{8,9)} The electron micrograph is also shown in the same photograph. The preferred precipitation exists in two regions, i. e., one along the slipping regions of ($\bar{1}\bar{1}1$) and the other probably at the boundary formed by polygonization.

The present authors indicated⁷⁾ that the precipitates, in the aluminium alloy containing copper and magnesium and corresponding to the alloy of the

Al-S intermetallic compound quasi-binary system, segregate on the two crystallographic planes $\{100\}$ and probably $\{110\}$. This conclusion was given from the observation of the directions of the precipitates on the etching pits as shown in Photo 9, which is the micrograph of the specimen containing 2.85% copper and 1.09% magnesium and tempered for 5 hrs. at 250°C. From the result of the determination of the directions of slip bands in the present work, it was occasionally found that the conclusion is correct. For example, Photo 10 is an electron micrograph of an alloy containing 3.12% copper and 0.97% magnesium and elongated by about 1 per cent. In this photograph, the crystallographic directions of the matrix crystals determined by X-ray analysis are so described that the predicted results from X-ray analysis may coincide with those observed under an electron microscope with the aid of the direction of slip band at which the preferred precipitation occurs.

On the Preferred Precipitation in Grain Boundary and the Stress-corrosion in Al-Zn-Mg Alloys*

The aspects of grain boundaries affect markedly the properties of polycrystalline materials. Stress-corrosion is such an example. As regards Al-Zn-Mg alloys, P. Brenner and W. Feldmann¹⁰⁾ concluded that the susceptibility to stress-corrosion is diminished by quenching with slow cooling rate, and still more by tempering. According to J. Hérens,¹¹⁾ the stress-corrosion of these alloys is caused by intergranular "décohésion".

As it is evident that stress-corrosion is a phenomenon that occurs along the grains, an electron-microscopic observation is considered to be a suitable means to reveal the phenomenon more distinctly. The present authors, therefore, studied the influence of the preferred precipitation in the grain boundary and also of the addition of copper, manganese and chromium on the stress-corrosion of the aluminium alloys.

For this purpose, an aluminium-rich alloy containing about 10 per cent $MgZn_2$ was prepared by melting aluminium of 99.992 per cent purity, distilled magnesium and electrolytic zinc together, and the alloys containing respectively copper, manganese and chromium in addition were also prepared. After having been homogeneously annealed, they were rolled into sheets. The solution treatment was administered at 450°C. for 10 hrs. and subsequently quenched in ice water from that temperature. They were then tempered at various

* This paragraph in the paper was read on April 1, 1952 at the Spring Meeting of the Japan Institute of Metals.

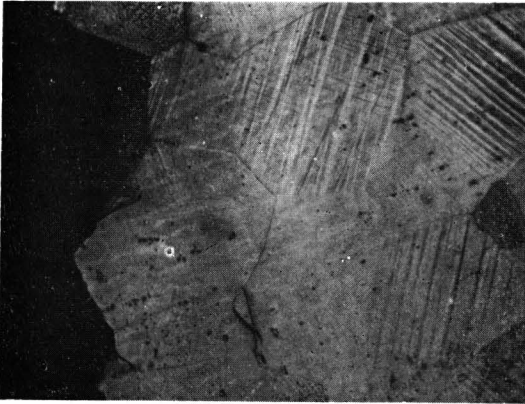


Photo 11 Optical micrograph of the alloy containing 1.54% Mg and 8.51% Zn, quenched from 450°C., aged at 140°C. for 5 hrs., and then subjected to the stress-corrosion test in brine. Showing the intergranular crack in the alloy. $\times 48$

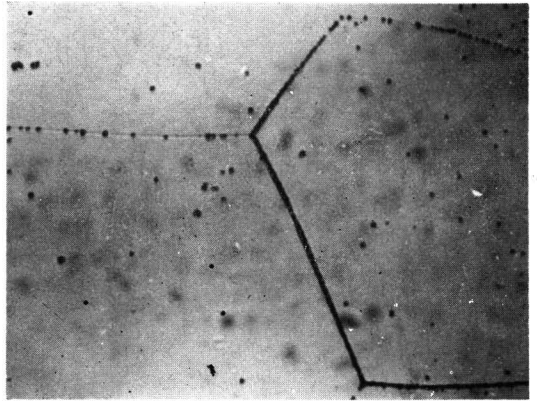


Photo 12 Optical micrograph of the alloy with the same composition as that of Photo 11, aged at 100°C. for 5 hrs. Etched with Wassermann's reagent. Showing the sharply etched grain boundary. $\times 700$

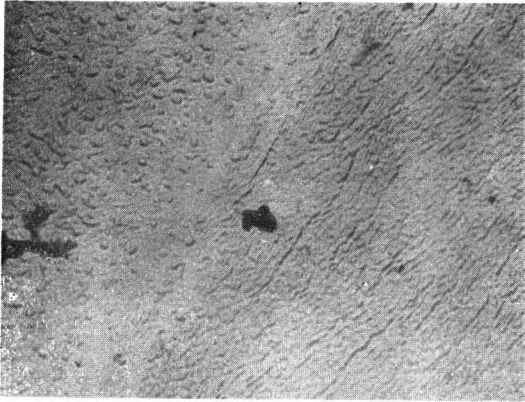


Photo 13 Electron micrograph of the same alloy. The field similar to that of Photo 12. Showing that no sign of any definite precipitates is recognizable in grain boundaries and within grains, though the aspect of the oxide film is not normal. $\times 10,000$

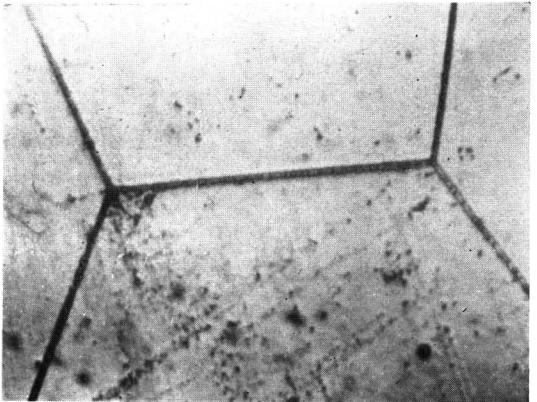


Photo 14 Optical micrograph of the same alloy, aged at 140°C. for 5 hrs., etched with Wassermann's reagent. Showing that the grain boundaries are etched more sharply. $\times 700$



Photo 15 Electron micrograph of the same alloy. The field similar to that of Photo 14. Showing that a greater amount of minute precipitates is present within grains and continuously in grain boundaries. Such aspects of the grain boundaries may probably be related to the susceptibility of stress-corrosion of this alloy. $\times 10,000$

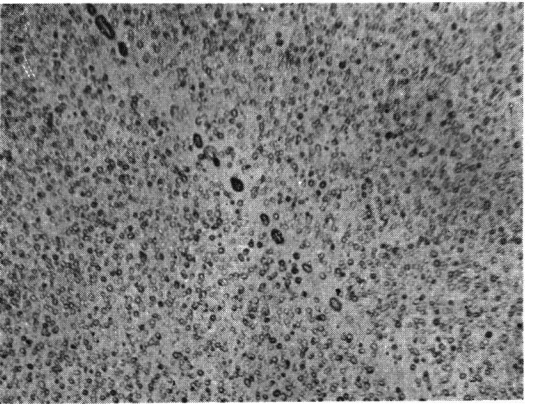


Photo 16 Electron micrograph of the same alloy, aged at 200°C. for 5 hrs. Showing the coagulation of the boundary precipitates and the growth of innercrystalline precipitates. $\times 10,000$

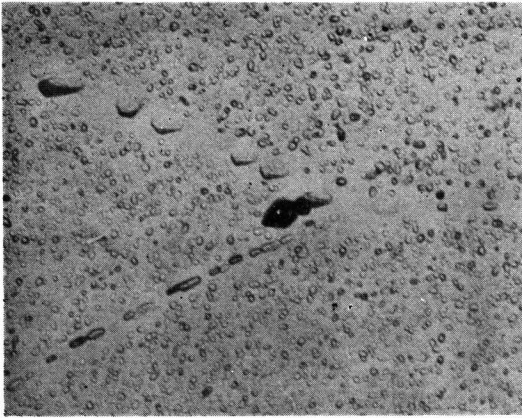


Photo 17 Electron micrograph of the same alloy, aged at 250°C. for 5 hrs. Showing the denuded zones of precipitates in grain boundaries widen and the precipitates within grains grow in size. $\times 10,000$

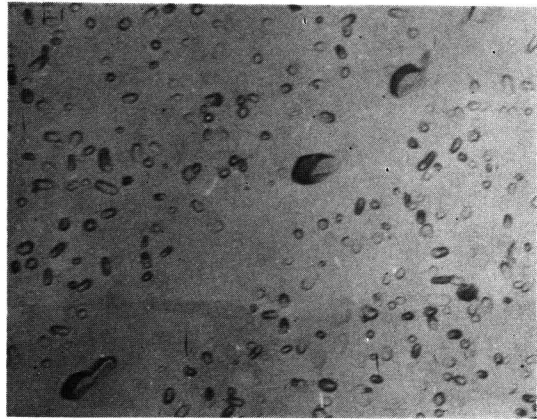


Photo 18 Electron micrograph of the same alloy, aged at 310°C. for 5 hrs. Showing that a part of the precipitates is dissolved again into the matrix. $\times 10,000$

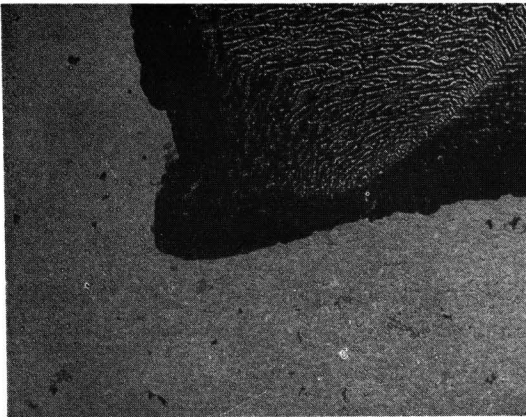


Photo 19 Electron micrograph of the alloy containing 1.52% Mg, 8.47% Zn and 1.57% Cu, aged at 100°C. for 5 hrs. Etched with Lacombe's reagent. Showing the distinct precipitation on the edges of steps in the surface of a large etch pit and the indistinct precipitation at the grain boundary. $\times 10,000$

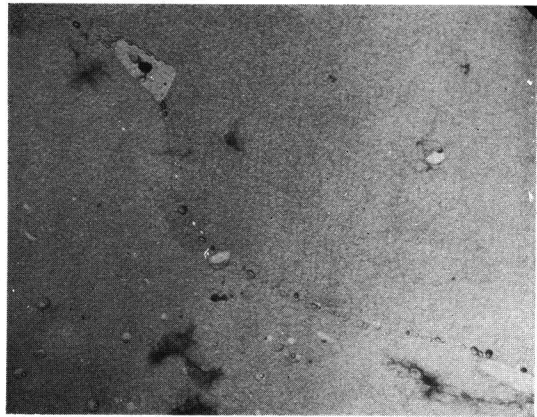


Photo 20 Electron micrograph of the alloy containing 1.63% Mg, 8.75% Zn and 0.47% Mn, aged at 140°C. for 5 hrs., Showing a sinuous grain boundary. This may probably be due to the presence of the intermetallic compound. $\times 10,000$

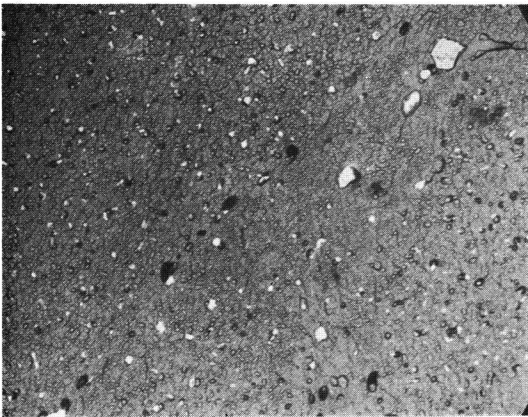


Photo 21 Electron micrograph of the alloy containing 1.57% Mg, 8.57% Zn and 0.39% Cr, aged at 200°C. for 5 hrs. Showing also a sinuous grain boundary and the absence of evident zones denuded of the precipitates. $\times 10,000$

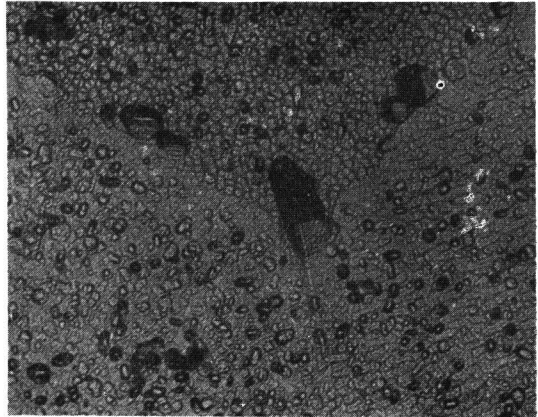


Photo 22 Electron micrograph of the alloy with the same composition as that of Photo 20, aged at 250°C. for 5 hrs. Showing also the absence of denuded zones in grain boundaries. $\times 10,000$

temperatures. The specimens thus treated were examined under an optical and an electron microscope as previously mentioned. The specimens $8 \times 0.5 \times 140$ mm., which were formed in loop shape by gripping the both ends each of which had been bent 20° previously for 20 mm in length, were submerged in brine and the time to produce cracks on them was measured. Thus their susceptibility to stress-corrosion was tested.

Photo 11 shows the intergranular cracks under a magnification of 48 diameters in the alloy containing 1.45% magnesium and 8.51% zinc, tempered for 5 hrs. at 140°C . and then subjected to the stress-corrosion test as described above. In this photograph, it is noted that slip lines exist in each grain.

Photo 12 is a microphotograph of the specimen aged at 100°C ., polished electrolytically and then etched with Wassermann's reagent. It is noticeable that the grain boundaries are etched sharply and that many etching pits exist in the grains and somewhat in the grain boundaries. An electron micrograph of this specimen is shown under a magnification of 10,000 diameters in Photo 13. No sign of any definite precipitate is recognized in the grain boundaries and within the grains, but the aspect of the oxide film is slightly different from that obtained from the quenched specimen. The difference seems to be related to the earlier stage of the precipitation from the saturated solid solution. This conclusion was derived from the change of dilatation of the specimen on heating which was executed separately.^{1,2)}

The microstructure of the specimen aged at 140°C . is shown under a magnification of 700 diameters in Photo 14. It appears that the grain boundaries are more sharply etched and the slip lines are present obviously. Photo 15 is its electron micrograph under a magnification of 10,000 diameters. The aspect of the oxide film is quite different from that of the specimen as shown in Photo 13. A greater amount of minute precipitates is present continuously in the grain boundary on the left of this photograph and within the grains the precipitates may exist also. The continuity of the precipitates in the grain boundaries varies from one grain boundary to another, depending upon the relative orientation of the neighbouring grains. This variation may be due to the fact that the slight difference of orientation between the adjacent grains does not cause the higher rate of precipitation in their boundaries. The relation between hardness or stress-corrosion and tempering temperatures being considered as shown in Fig. 1, the susceptibility to stress-corrosion is evidently related to the aspect of the grain boundaries, although the difference of chemical potential between the precipitates and the matrix may also affect it considerably.

Photo 16 is an electron micrograph of the specimen aged for 5 hrs. at 200°C .

This photograph shows the presence of innercrystalline precipitates which have coagulated as compared with those shown in Photo 15, while at the grain boundaries the precipitates have grown in size, therefore, that there is a zone denuded of the precipitates. The alloy, which shows such a grain boundary, seems to be not very susceptible to stress-corrosion.

The electron-micrographic structure of the specimens tempered at 250°C. and 310°C. are shown in Photos 17 and 18 respectively. They show that the denuded zones become wider and the precipitates grow in size with the rise of tempering temperature. Furthermore, it is to be noticed that in Photo 18 a part of the precipitates has dissolved again. This fact was also proved by the increase in hardness after a lapse of several days. Such a specimen no longer showed the phenomenon of stress-corrosion, even if it had been tested for fairly long time in 3% brine.

The alloy containing 1.52% magnesium, 8.47% zinc and 1.57% copper was examined similarly. No considerable difference was observed in its microstructure. But it was found that the resistance to stress-corrosion had been improved, and compared with the alloy containing no copper, its hardness showed higher value as seen in Fig. 1. Photo 19 is an electron micrograph of the specimen aged for 5 hrs. at 100°C. It is evident that the precipitation at

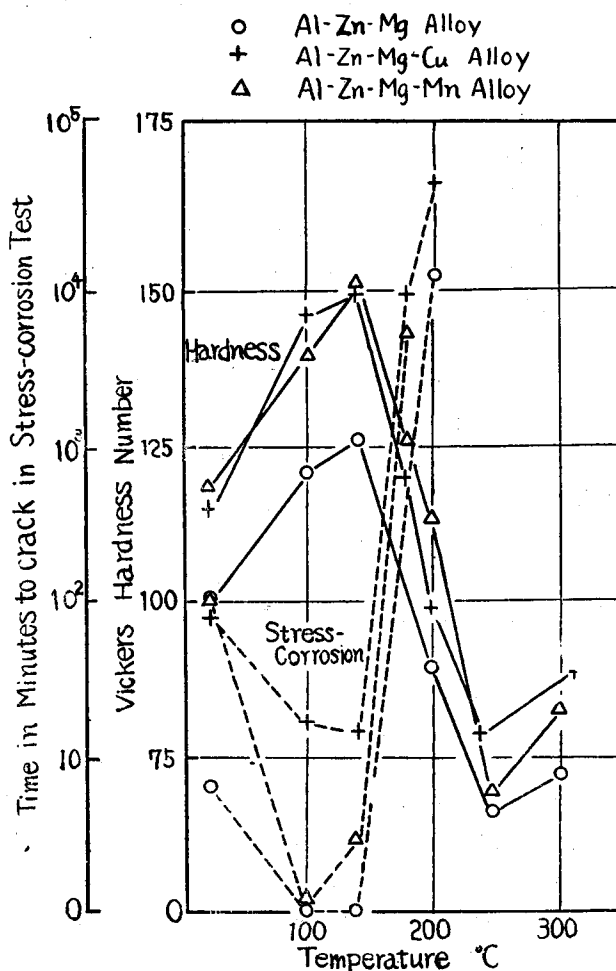


Fig. 1 The relation between hardness and stress-corrosion and tempering temperatures, and the effect of alloying elements.

the grain boundaries becomes indistinct. It may be due to that the precipitation phenomenon differs depending on the content of copper and probably some phase belonging to the Al-Cu-Mg system may be concerned with this phenomenon and also with the susceptibility to stress-corrosion.

The typical electron micrographs of the alloys containing manganese and chromium in addition are shown in Photos 20~22 under a magnification of 10,000 diameters. In the alloy containing 1.63% magnesium, 8.75% zinc and 0.47% manganese aged for 5 hrs. at 140°C., the precipitation has taken place in the grain boundaries, and the boundary becomes sinuous probably by the presence of the intermetallic compound as shown in Photo 20. Photo 21 shows an electron micrograph of the specimen containing 1.57% magnesium, 8.57% zinc and 0.39% chromium. The specimen was tempered for 5 hrs. at 200°C. The shape of grains is also irregular. Intermetallic compounds probably containing chromium are present along the grain boundaries, even if they are not shown in this photograph. It is also noted that at the grain boundaries the zones denuded of the precipitates are not so evident as in the alloy with no addition of the alloying elements. This is probably due to the slow rate of diffusion of these addition elements. Photo 22 shows the microstructure of an alloy containing manganese and aged for 5 hrs. at 250°C. In this photograph, the innercrystalline precipitates have grown in size and the precipitates at the grain boundaries have coagulated, but the denuded zones are not distinct as in Photo 21. By the addition of manganese and chromium, the growth of grains was considerably suppressed and the shape of the grains was very sinuous. The zones denuded of the precipitates at the grain boundaries were not evident. These aspects of the grain boundaries in the alloys containing manganese and chromium may be the reason why these alloys are less susceptible to stress-corrosion.

Micro-segregation in Cast Aluminium Alloys*

Segregation is a phenomenon which takes place during the solidification of alloys, and it has many types called macro- or micro-segregations. Up to the present, little information has been given concerning the micro-segregation known as "cored structure", which is generally observed in cast alloys consisting of a solid solution. P. Brenner and H. Kostron¹³⁾ investigated the macro- and micro-segregation in ingots of two aluminium alloys by measuring their micro-hardness with Zeiss Hanemann micro-hardness tester and obtained some

* This paragraph was read on Oct. 10, 1951 at the Autumn Meeting of the Japan Institute of Metals.

definite idea concerning the variation of the concentration of alloying elements in the crystalline grains of the ingot showing an inverse segregation. The present investigation has been carried out to obtain more definite idea about the cored structure in cast alloys consisting of a solid solution by means of electron-microscopic examination.

For the above purpose, two aluminium alloys containing 4.03% copper, and 8.38% zinc and 1.56% magnesium were cast in cylindrical form, 18 mm. in diameter and 30 mm. in height. They were quenched in ice water immediately after they had solidified to maintain the aspect existing at the moment of solidification. From the middle part of each specimen, a disc 3 mm. thick was sawn off and used for microscopic examination and hardness measurement. The hardness variations within the grains were measured with the load of 50 g. by Akashi micro-hardness tester.

Photo 23 shows the optical micrograph of the alloy containing about 10% $MgZn_2$ (8.38% Zn and 1.56% Mg in chemical composition) in the cast state. In this photograph, the impressions formed on the specimen are shown together with their hardness numbers. The hardness was measured 7 days after casting. The increase in micro-hardness indicates that the concentration of the alloying elements increases from the center towards the boundary of the grains.

Photo 24 is an optical micrograph under a low magnification of the same specimen etched with Wassermann's reagent after tempering it for 16 hrs. at 180°C. The etching characteristic of the cored structure becomes more distinct. This is probably due to the precipitation having occurred in a different way from the boundary region to the cored part. It is also noted that there exist slip lines and sub-boundaries. When this specimen was observed under a higher magnification, the precipitates were more definitely recognized to differ in size and distribution as shown in Photo 25. From these observations, it is evident that the cored structure consists of the following three different parts: an outer unetched white zone adjacent to the grain boundary with a constant breadth; an intermediate zone somewhat more heavily etched; and an inner region slightly etched except in the slipping regions

The electron micrographs of these three parts in the cored structure are shown in Photos 26, 27 and 28 under a magnification of 7,000 diameters. In these micrographs, the conditions of the cored structure may be readily recognized. In the outer unetched white zone, as shown in Photo 26 and on the left hand side of Photo 27, a large number of minute precipitate particles are distributed homogeneously. This may show that the concentration of the

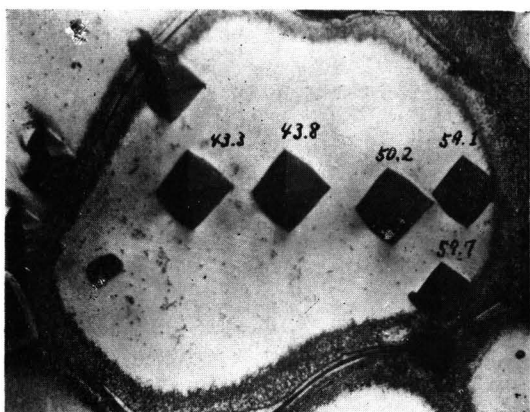


Photo 23 Optical micrograph of the alloy containing 8.38% Zn and 1.56% Mg. Showing the variation of hardness of the cored structure in as cast state measured by Akashi micro-hardness tester. $\times 250$

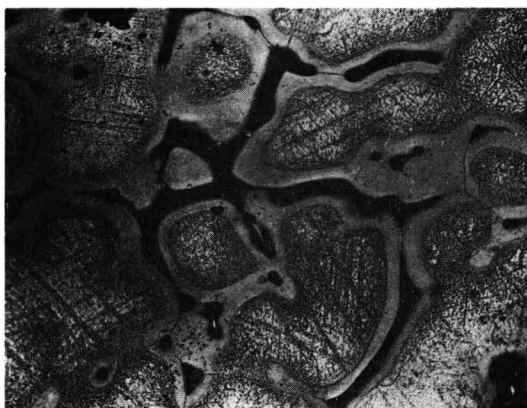


Photo 24 Optical micrograph of the alloy similar as that of Photo 23, aged at 180°C . for 16 hrs. Etched with Wassermann's reagent. Showing the three different parts in the cored structure, i. e. outer white unetched zone, intermediate somewhat more heavily etched zone, and inner region. $\times 96$

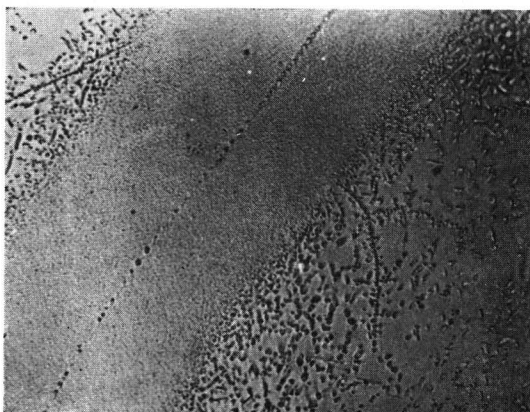


Photo 25 Optical micrograph of the same alloy. The field similar to that of Photo 24 but under a higher magnification. Showing the aspects of the cored structure more distinctly. $\times 1,000$

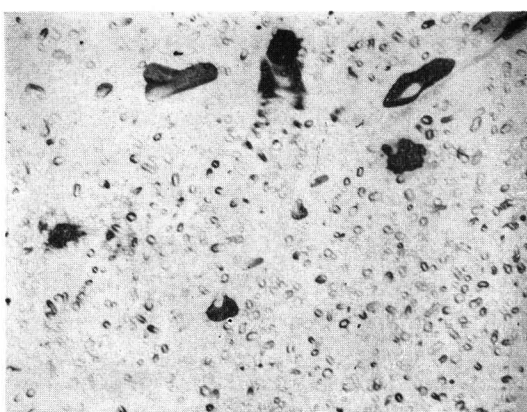


Photo 26 Electron micrograph of the same alloy. The field corresponding to the outer white unetched zone of Photo 24. Showing the homogeneous distribution of minute precipitates. $\times 7,000$

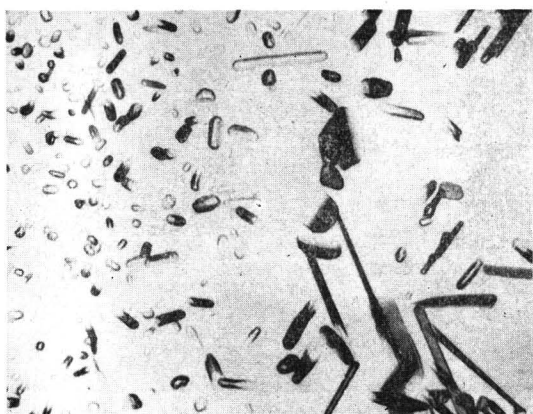


Photo 27 Electron micrograph of the same alloy. The field corresponding to the junction of the outer and the intermediate parts of Photo 24. Showing the distinct differences among the precipitates in size and distribution. $\times 7,000$

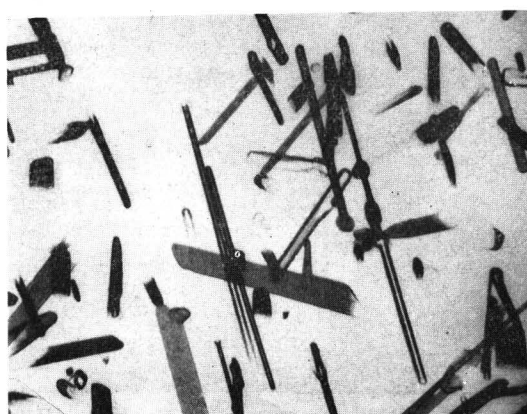


Photo 28 Electron micrograph of the same alloy. The field corresponding to the inner region of Photo 24. Showing that the precipitates in a complete form are distributed in groups at random. $\times 7,000$



Photo 29 Electron micrograph of the same alloy. Showing the subboundary across the junction of the intermediate and inner regions in cored structure. $\times 7,000$

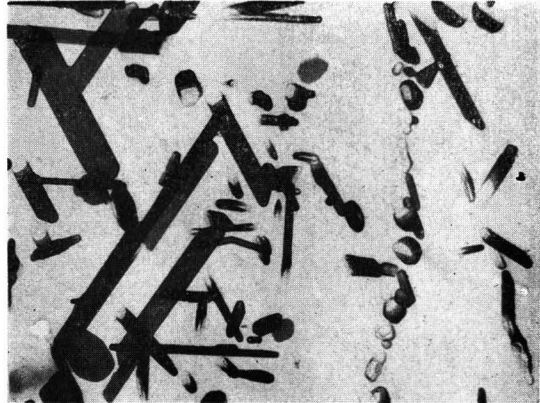


Photo 30 Electron micrograph of the same alloy. Showing the sub-boundary in the inner region. $\times 7,000$

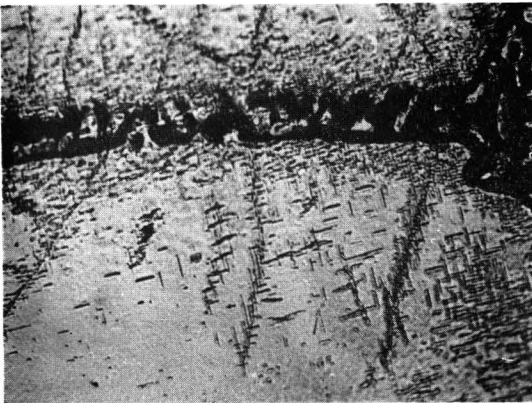


Photo 31 Optical micrograph of the alloy containing 4.03% Cu, aged at 240°C. for 5 hrs. Showing a micro-segregation within grains and a sub-boundary structure. $\times 1,000$



Photo 32 Electron micrograph of the same alloy. The field corresponding to that near the grain boundary of Photo 31. $\times 7,000$

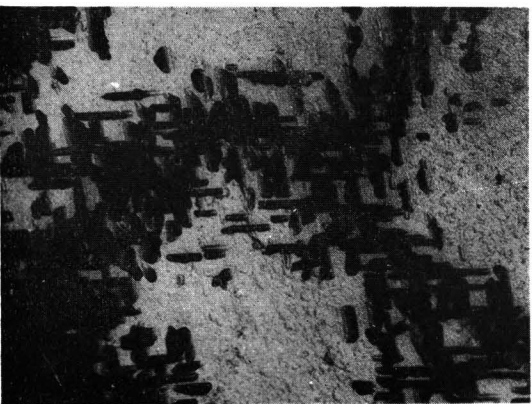


Photo 33 Electron micrograph of the same alloy. The field corresponding to the sub-boundary in the inner region of the core of Photo 31. $\times 7,000$

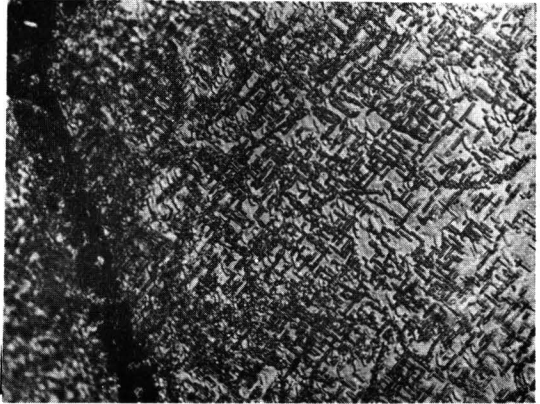


Photo 34 Optical micrograph of the alloy similar to that of Photo 31, annealed at 500°C. for 2 days, and quenched from this temperature, and then tempered similarly. Showing that the subboundaries in the cast structure have a tendency to disappear gradually. $\times 1,000$

alloying elements is almost constant in this zone. Photo 27 shows that at the junction of the outer and the intermediate zones, the precipitate particles distinctly differ in size and distribution. It is also observed that the growth of precipitates occurs probably due to the low concentration of the alloying elements. In the inner region, a few precipitates which have grown up to the complete form are seen to have been distributed in groups at random as shown in Photo 28. These observations indicate that the concentration of the alloying elements in the cored structure is almost homogeneous in the outer zone whose breadth is about 150μ in the present case, then decreases rapidly towards the intermediate zone and again becomes homogeneous in the inner part of the grain. This will give some suggestions to the idea of the solidification of an alloy consisting of a solid solution.

It has already been noted that the preferential precipitation during ageing takes place as a network structure in relation with crystal imperfections along the polygonization boundaries which are produced by annealing. Another kind of sub-division was reported to have been observed in cast alloys.¹⁴⁾ In the present investigation, such a sub-boundary was also observed in the both cast alloys. The electron micrographs of the sub-boundaries in the cast Al-Zn-Mg alloy are shown in Photos 29 and 30. In the sub-boundary through the junction of the outer and the intermediate zone of the cored structure as shown in Photo 29, the aspects of the precipitates are similar to those at the sub-boundaries discussed previously, though the precipitates are different in size according to the variation in concentration. Photo 30 shows the sub-boundary in the inner region of a grain. It is also noted that the precipitates in this region do not show any marked growth.

Photo 31 shows the sub-boundary structure in the core of a cast aluminium alloy containing 4.03% copper, quenched in ice water immediately after the end of solidification, then tempered for 5 hrs. at 240°C . In this optical micrograph, it is evident that the micro-segregation within a grain exists similarly as in the cast aluminium alloy containing 10% MgZn₂. Photo 32 is an electron micrograph showing the grain boundary and the outer zone of the cored structure. The sub-boundaries in the inner region of the core are shown in Photo 33.

These sub-boundary structures in the cast state show a tendency to disappear gradually on annealing. For example, Photo 34 is an optical micrograph obtained from the same specimen after annealing for 2 days at 500°C . and tempered similarly. In comparison with the nature of dynamic movability of the sub-boundaries caused by polygonization, sub-boundaries observed in the cast alloy

do not move so easily. This difference of movability may be interpreted from the presumption that it may have some relation to the segregation of the alloying elements during solidification and the irregular arrangement of atoms or the disorientated region produced during the formation of crystals.

Summary

From the sub-microscopic investigations under an electron microscope, It may be concluded as follows:

The precipitation is accelerated by the irregularity and the defect of crystalline structure which is associated with grain boundary, sub-boundary, slip band and others. The preferred precipitation plays a predominant rôle in the precipitation phenomenon and, in consequence, gives marked effects upon the various properties of the alloys.

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