# On the Electron-Microscopic Study of Age-Hardened Aluminium Alloys

By

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Electron metallography, until recently an unfamiliar and difficult technique, is now becoming accepted as a normal procedure in some metallurgical researches such as precipitation phenomena. In 1947, A. H. Geisler and F. Keller 1) took the electron-micrographs of age-hardened aluminium alloys by the oxide film replicas and discussed the various manners of the precipitate particles. At that time we could not entirely read such a transaction of A. I. M. E. 1) Therefore, in the year of 1948 independently to the above authors, one of us tried to take a micrograph of aged aluminium alloys with an electron microscope which began to be manufactured industrially and to be used generally in Japan. For that purpose an alloy containing 4.2% Cu, which was aged an hour at 250°C, was etched to develope a micro-mosaic structure and then subjected to an anodic oxidation. We obtained a microphotograph in

4.2% Cu alloy aged 1hr. at 250°C

Table 1

| Alloy | Weight Percentage % | | | | | Precipitate phases in equilibrium |
|---|---|---|---|---|---|---|
| | Cu | Mg | Zn | Si | Al | |
| Al-Cu | 4.12 | — | — | — | remainder | $\theta$-$CuAl_2$ |
| Al-Cu-Mg | 3.17 | 1.22 | — | — | 〃 | S ($Al_2MgCu$) |
| Al-Zn-Mg | — | 1.30 | 6.51 | — | 〃 | $MgZn_2$ |
| Al-Zn-Mg-Cu | 2.67 | 2.14 | 5.65 | — | 〃 | $\theta$, S, $MgZn_2$, $Al_2Mg_3Zn_3$ |
| Al-Mg-Si | — | 0.98 | — | 0.51 | 〃 | $Mg_2Si$ |

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which $\theta'$-$CuAl_2$ are observed to precipitate on (100) planes of mosaic blocks, as shown in the figure above Table 1. Recently the investigations on aging of Al-Cu 2) and Al-Mg-Si 3) were reported with some exceedingly remarkable pictures by R. Castaing. These reports encouraged us to continue further on this work to distinguish the precipitation behaviors in various age-hardened aluminium alloys employing Geisler's replica method 1) and others.

*Material and Preparation of Alloy*——For the preparation of the specimens were used 99.992% purity of aluminium and alloying elements as pure as possible to be obtained. The melt was cast in an iron mold (approximately 120 by 20 by 5 mm.). After homogeneity annealing the ingot was rolled to a thickness of 1mm. and the specimens were cut from the sheet. The chemical analyses were made upon each sheets and their results were shown in Table 1. The specimens, prior to quenching and aging in order to insure homogeneity, were heated for 2 days at 490°C for the alloys except Al-Mg-Si alloy which was heated at 550°C, and then were quenched in water at room temperature, and subsequently aged at the desired temperatures between 150°C and 300°C for 0.5 to 48 hours.

*Preparation of Replica and the Interpretation of Electron-Micrograph*——Each aged specimen, after polished electrolytically in a perchloric acetic bath, was subjected to an anodic oxidation in a saturated solution of ammonium phosphate. An oxide film of about 300 Å thick was obtained by employing of the voltage of 18 volts, and it was stripped off by mercury method. Fig. 1 (a) shows diagrammatically the state of the sample with oxide film when the precipitates are very thin. The traces of precipitates remain as vacant space, as shown in Fig. 1 (b), when such an oxide film is stripped and washed. Its density distribution in electron image is shown in Fig. 1 (c). Fig. 2 (a) shows another case for the precipitate of thicker dimension. When such a specimen is polished electrolytically, the trace of precipitate remains already as a vacant hole. In the micro-

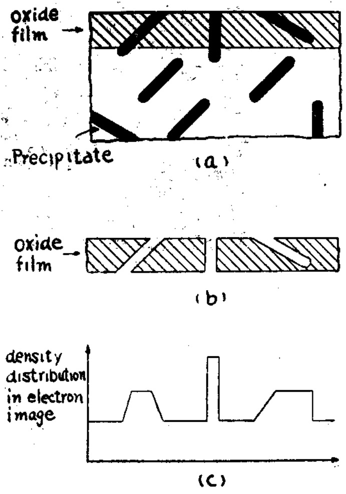


Fig. 1

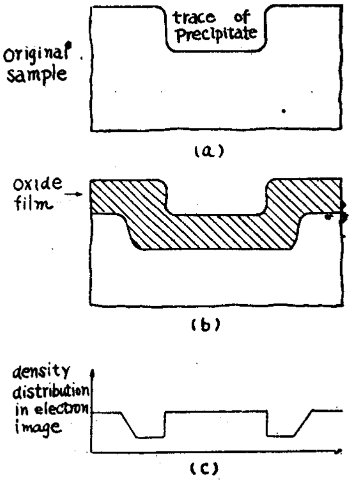


Fig. 2

graph of such a replica, the precipitate would be shown with a dark surrounding band as illustrated in Fig. 2 (b) and (c). The typical case of the former was observed in an intermediate precipitation which the authors want to designate the "coherent" stage of precipitation judging from the micrographic characteristics. These micrographs are shown in Fig. 3, 5, 7 and 10. The latter case is recognized in an alloy, in which precipitates separate out completely from matrix as shown in Fig. 4 and 8. This may be called the second stage of precipitation.

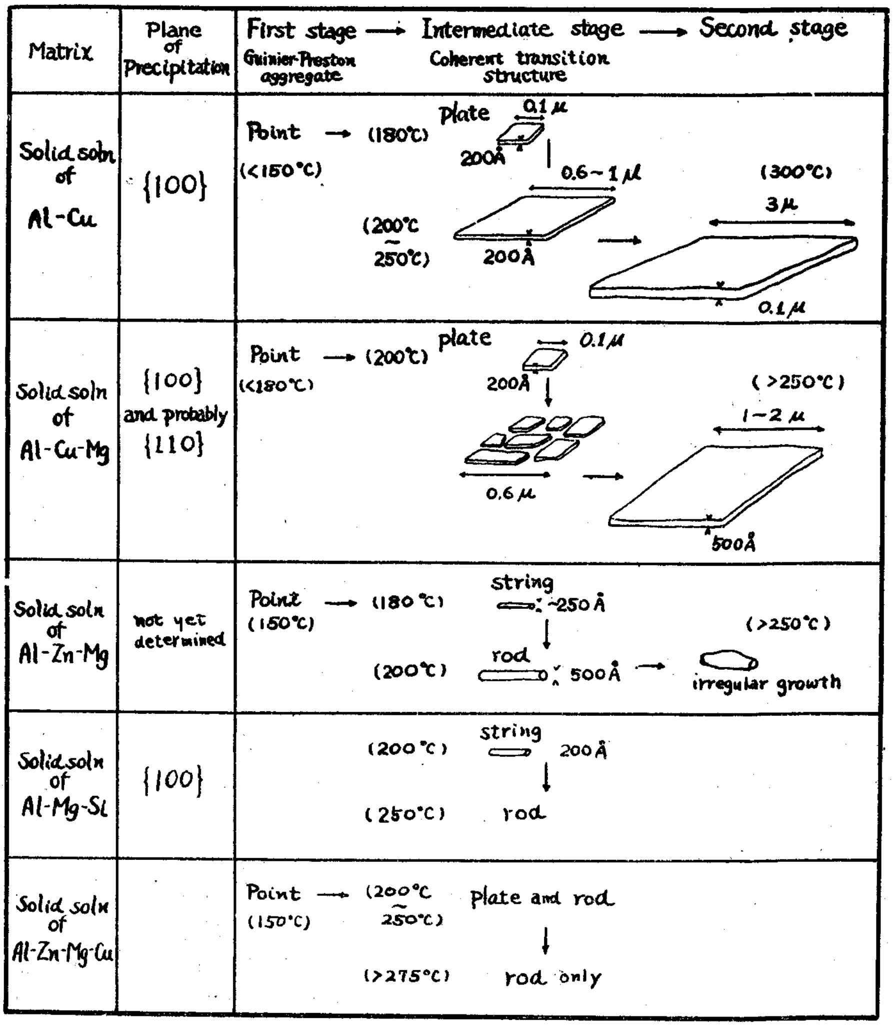
*Results of Experiments*—— In a 4.12% Cu alloy aged 30 hours at 150°C, precipitation was observed to occur in the shape of point of the order 100 Å. Aging at 180°C produced still greater precipitation, in which platelets $\theta'$-$CuAl_2$ are orientated in the two directions parallel to (100) planes of aluminium matrix as already reported by R. Castaing. Fig. 3 shows a precipitation of $\theta'$-$CuAl_2$ platelets in the specimen aged for 30 hours at 200°C. On the left-hand side of this micrograph, precipitation of $\theta'$-$CuAl_2$ platelets is seen to occur parallel to mutually almost perpendicular (100) planes along the slip line which takes place on (111) plane of matrix. At the temperature lower than 250°C, the thickness of the platelet is the order of 200 Å, while its lateral dimension reaches up to 0.6～1 $\mu$. This is the coherent stage of precipitation, and in the second stage, as seen in Fig. 4, $CuAl_2$ will be separated out completely from the aluminium matrix.

In the Al-Mg-Cu system, the alloy corresponding to a composition of Al-"S" quasi-binary system was prepared. The "S" compound whose existence was found by one[4)] of the authors at the first time is recently reported to correspond to a formula $Al_2MgCu$. On the aging lower than 200°C, the earier precipitation is observed to be produced at random in shape of point. The mottling of the micrograph was observed in the specimen aged for 30 minutes at 200°C, which suggests an incipient stage of precipitation at the comparatively higher annealing temperature. In an alloy aged 30 hours at 200°C, precipitates are formed by the congregation of small particles on definite planes, and these planes are parallel to (100) and also probably (110) planes of aluminium matrix judging from the etching pits which are observed in Fig. 5. On aging the above specimen further for 30 hours at 250°C, a marked precipitation is apparently parallel only to (100) plane of aluminium matrix and the congregation of small particles grows into a platelet precipitate as shown in Fig. 6. This micrograph also shows large precipitates at the grain boundary, but no precipitates are seen around them. When aged at higher temperature than 250°C, preferential precipitation takes place on both (100) and (110) plane, which is recognized as the second stage of precipitation.

In Al-Zn-Mg alloy system, the quasi-binary Al-$MgZn_2$ alloy was used. The micrograph of the specimen aged at 180°C shows "coherent" precipitation. Three or four precipitate particles of about 250 Å diameter are situated in a difinite plane which cannot be determined from the photography (Fig. 7). On aging between 200°C and 250°C, this coherent precipitate grows into a rod whose diameter is in the order of 500 Å as shown in Fig. 8. Its orientation seems to have something to do with the slip line which is seen by optical microscope after etching.

In Al–Zn–Mg–Cu alloy system, four phases as shown in Table 1 are to precipitate in consideration of the equilibrium diagram. On aging for 48 hours at 150°C, precipitation is observed to occur densely in the shape of point. When

Table 2 General View of the Process of Precipitation



| Matrix | Plane of Precipitation | First stage → Intermediate stage → Second stage<br>Guinier-Preston aggregate / Coherent transition structure |
|---|---|---|
| Solid soln of Al-Cu | {100} | Point (<150°C) → (180°C) plate 0.1 μ, 200Å<br>(200°C ~ 250°C) 0.6~1 μ, 200Å →<br>(300°C) 3 μ, 0.1 μ |
| Solid soln of Al-Cu-Mg | {100} and probably {110} | Point (<180°C) → (200°C) plate 0.1 μ, 200Å<br>0.6 μ →<br>(>250°C) 1–2 μ, 500Å |
| Solid soln of Al-Zn-Mg | not yet determined | Point (150°C) → (180°C) string ~250 Å<br>(200°C) rod 500 Å →<br>(>250°C) irregular growth |
| Solid soln of Al-Mg-Si | {100} | (200°C) string 200 Å<br>(250°C) rod |
| Solid soln of Al-Zn-Mg-Cu | | Point (150°C) → (200°C ~ 250°C) Plate and rod<br>(>275°C) rod only |

Fig. 3 Al-Cu Alloy aged 30 hr. at 200°C

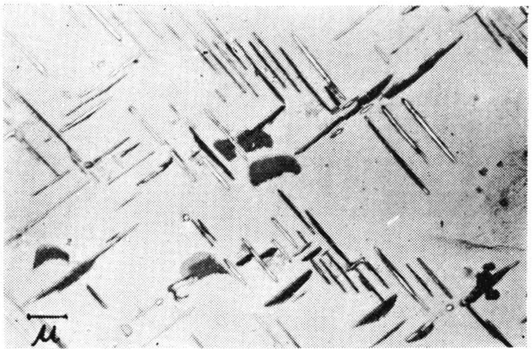


Fig. 4 Al-Cu Alloy aged 2 hr. at 300°C

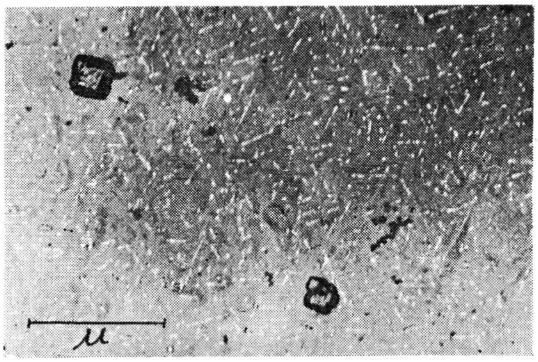


Fig. 5 Al-Cu-Mg Alloy aged 30 hr. at 200°C

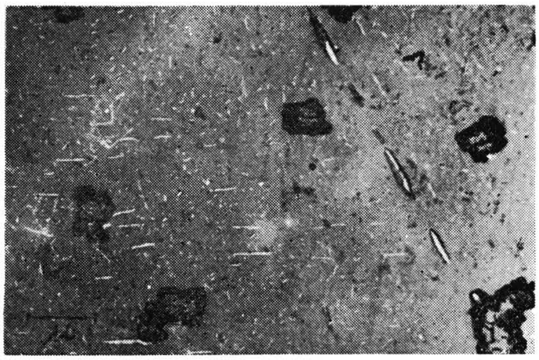


Fig. 6 Al-Cu-Mg Alloy aged 30 hr. at 200°C and furthermore 30 hr. at 250°C

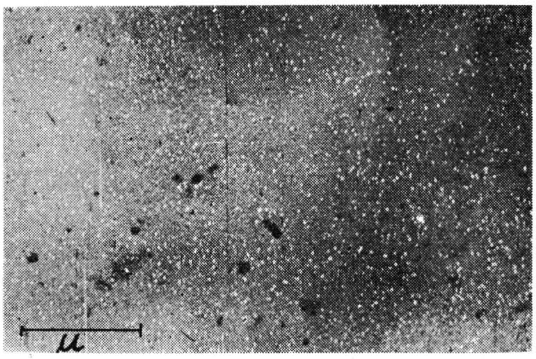


Fig. 7 Al-Zn-Mg Alloy aged 10 hr. at 180°C

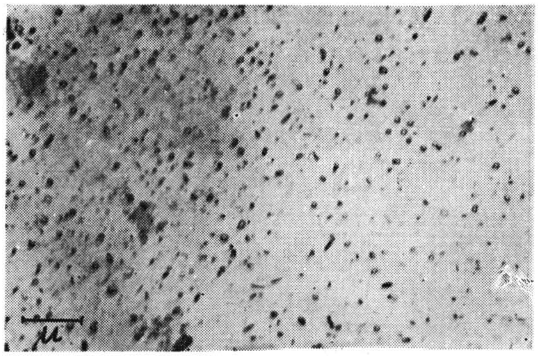


Fig. 8 Al-Zn-Mg Alloy aged 5 hr. at 250°C

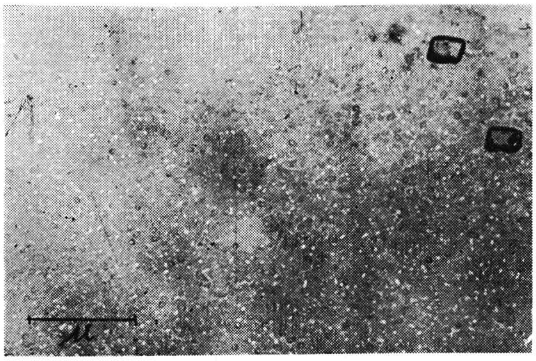


Fig. 9 Al-Zn-Mg-Cu Alloy aged 30 hr. at 200°C

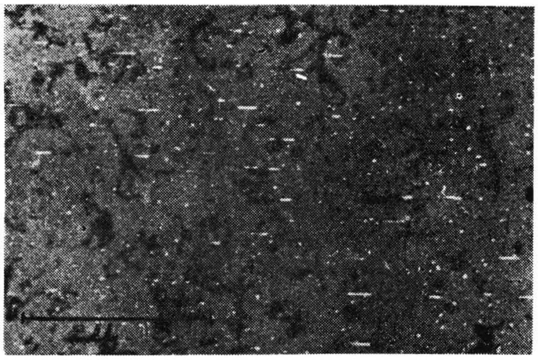


Fig. 10 Al-Mg-Si Alloy aged 30 hr. at 200°C

aged 30 hours at 200°C, two kinds of precipitates are seen to be distinguished clearly for each other as shown in Fig. 9. One of them should be attributed to the "S" compound, for they have the characteristic orientation parallel to (100) and (110) planes of aluminium matrix as above explained. The other one will be the same precipitate as seen in Fig. 8, but it cannot be directly determined to be $MgZn_2$ or $Al_2Mg_3Zn_3$. These manners proceed more intensely at 250°C aging, and when aged at higher than 275°C the latter grows larger while the former almost disappears.

Fig. 10 shows a microstructure of the Al–$Mg_2Si$ alloy aged 30 hours at 200°C, in which the string of $Mg_2Si$ is observed to precipitate perpendicularly with one another.

*Discussion of Results*—— Very early precipitations are naturally too small to be observed under electron microscope. The precipitate is first observable in electron-micrograph when its demension reaches to the order 100 Å. The coherent transition structures are able to be clearly recognized in the course of their growth. They are divided in two kinds of manners, one at which the string structure is well developed and the other at which the plate structure is well developed. The former is observed to occur in Al–Zn–Mg and Al–Mg–Si system, and the latter in Al–Cu and Al–Cu–Mg system. These characteristics in the precipitation behaviors will depend upon the lattice structures of the precipitates. The process of precipitation is summarized in Table 2 from our experimental results.

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## References

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