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Transmission Electron Microscopic Investigation on Recrystallization and Precipitation of Magnesium and Magnesium Alloys

By

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Experiments have been carried out to examine aging characteristics, recrystallization phenomena and effects of plastic deformation after water-quenching on the precipitation of Mg–Th alloys in the composition range from 1.7 to 4.0 wt% thorium as compared with pure magnesium, Mg–Zn and Mg–Al alloys mainly with electron microscopic observations in thin foils.

In Mg–4.0% Th alloys, G. P. zones were confirmed to exist before the appearance of the transition phase Mg_2Th in accordance with the result of measurements of electrical resistance. The presence of thorium in a magnesium alloy greatly retarded such processes as recovery and recrystallization. This slowing up process seems to be reflected in the slow precipitation rate of Mg–Th compounds. The effects of cold working on precipitation in these alloys are not simple but complex.

I. Introduction

This report is a continuation of an earlier one with the title "On Precipitation Phenomena In Magnesium-Zinc Alloys".[1]

Pure magnesium, Mg-Zn, Mg-Al and Mg–Th alloys were investigated mainly by examining thin foils of these alloys with an electron-microscope. These alloys have assumed considerable commercial importance, showing the potent precipitation hardening effects among the magnesium-based binary systems. Especially, magnesium alloys containing thorium are suitable for applications requiring exposures to temperatures greater than 300°C for appreciable length of time.[2] This alloy retains a high level of properties even after exposures of 100 hr at 300°C, although the alloys containing aluminium and zinc are badly overaged by the conditions. Therefore, in order to obtain some insight into mechanism by which thorium produces high temperature stability in Mg–Th alloys, it seems desirable to investigate its aging characteristics at various temperatures after suitable solution-treatment, the effects of plastic deformation on precipitation, and

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recrystallization phenomena in Mg-Th alloys in comparison with pure magnesium, Mg-Zn and Mg-Al alloys.

The studies by L. Sturkey[3] of Mg-Th-Zr alloys in the composition range from 2 to 3% thorium have clarified the structure and orientation of the precipitates in this system. It was confirmed that the age-hardening mechanism in these alloys is probably very complicated, because of the high chemical affinity of thorium for both hydrogen and oxygen and the considerable endothermic solubility of hydrogen in magnesium and that aging in solution-treated Mg-Th alloy precipitated both the equilibrium Mg_4Th and a transition phase Mg_2Th coherent with the magnesium matrix. However, concerning low temperature aging below 300°C no studies were carried out. Therefore, it is one of the purpose of this research to offer experimental evidence to indicate whether the zones occur or not during low temperature ageing in Mg-Th alloys by means of the measurements of the electric resistivity and electron-microscopic observation with thin foils. The actual changes produced by recrystallization in Mg-Th alloys were also investigated by X-ray diffraction methods.

II. Experimental Procedure

The magnesium alloys in these experiments were melted by using 99.99% magnesium in a graphite crucible lined with magnesia under a covering of argon gas in order to prevent oxidation and burning. After the alloying elements were added, they were cast into a chill mould. As for Mg-Th alloys, in due consideration of the pronounced affinity of thorium for both hydrogen and oxygen, an addition of thorium was carried out by using the mother alloy containing about 10% thorium, which was melted from the reactor grade thorium powder with a special dry flux containing $MgCl_2$ 40, KCl 30, MgO 15 and CaF_2 15%.

The composition of the alloys and the solution treatment temperatures are shown in Table I. The gas contents of Mg-Th alloys are given in Table II.

The specimens were cut into 0.7-1.2 mm in thickness for X-ray diffraction technique and electron-micrography, and wire of 0.7 mm diameter for the resistance

Table I. Compositions of the Magnesium Alloys and the Solution Treatment Temperatures.

Alloying Elements wt. pct.	Solution Treatment Temperatures °C
3.2% Zn	330°C
1.7% Th	580°C
4.0% Th	580°C
11.6% Al	430°C

Table II. The Gas Contents of Mg-Th Alloys.

Alloys	N_2 wt. pct.	O_2 wt. pct.	H_2 wt. pct.
1.7% Th	0.00101	0.00718	0.00169
4.0% Th	0.00613	0.01514	0.00283

measurements. The specimens were solution-treated for 24 hr at each temperature as shown in Table I and then water-quenched.

Electron-Micrography

The thin foil specimens were prepared by controlled electro-polishing and chemical polishing at 0°C using a solution containing HNO_3 and ethyl alcohol. Each composition of the solution for the alloys in these experiments is shown in Table III.

Table III. The Compositions of Solution for the Magnesium Alloys.

Alloys	The Compositions of the Solution
Pure Magnesium	33% HNO_3+67% ethyl alcohol
Mg-Zn Alloys	33% HNO_3+67% ethyl alcohol
Mg-Th Alloys	20% HNO_3+80% ethyl alcohol
Mg-Al Alloys	10% HNO_3+90% ethyl alcohol

A small section was cut with scissors from the thinnest parts of the foil and mounted in a microscope specimen holder between two meshes bored at their centers. An Examination was carried out in a Shimazu-SM-D4 type electron microscope operating at 75 KV.

X-Ray Diffraction Method

The polycrystalline Mg-Th alloy specimens 60% rolled after water-quenching were investigated as to recrystallization phenomena by copper radiation with exposures of 1 hr at 60 mA 35 KVP using a collimeter 5.5 cm in length and 0.5 mm bore with a specimen to film distance of 3.5 cm.

Resistance Measurement

The resistance measurements in Mg-Th alloys were carried out immediately after water-quenching, using a potentiometric system. To minimize the contact resistance, the following methods were employed. The wire specimens of 6 cm length and 0.7 mm diameter were spot-welded at two points at each of the two ends with copper lead wire. The voltage and the current were measured precisely with two potentiometers and a standard resistance of 0.01 ohm. The changes in the electrical resistance of the specimen were determined on heating at a constant rate of 2°C per minute.

III. Experimental Results

1) Recrystallization

Photo 1 to 7 show recrystallization processes in the electron micrographs of thin foils of pure magnesium.

Photo 1 shows the deformation structure in the 30% rolled materials after water-quenching. In this photograph, a band of 1μ order and dense networks of dislocations are observed, but new grains are not found. In the 80% rolled specimens after water-quenching, the compression bands[4] by a complex double-twinning mechanism are found clearly and new grains are found locally as shown in Photo 2 (a, b). Photo 3 shows the structure of the specimen 30% rolled and annealed at 70°C for 2 days. There is no remarkable difference between photos 1 and 3. On annealing for 3 hr at 100°C of the 30% rolled specimen a change occurs as shown in photo 4. In the photograph, the matrix is shown to polygonize incompletely. On annealing of the 30% rolled materials, recrystallization proceeds further. The newly recrystallized grains of $0.2–0.5\mu$ diameters appear in the matrix which is still in the stage of polygonization prior to recrystallization. The appearance of a fully recrystallized part of the specimen is shown in photo 5, and of that in the stage of polygonization in photo 6. Photo 7 shows the structure of equiaxed new grains growing up to $3–5\mu$ diameter in the 60% rolled specimens annealed for 10 min at 200°C.

Photo 8 to 11 are electron-micrographs of thin foils of deformed Mg-3.2% Zn alloys. Photo 8 shows a polygonized structure of a 30% deformed specimen after being aged for 5 days at 70°C. In 60% rolled materials aged at 70°C for 5 days as shown in photo 9, the whole area of the specimen is recrystallized and along the sub-boundaries precipitates are observed. Photos 10 and 11 are the electron-micrographs in 40% rolled specimens aged 10 or 30 min at 200°C respectively. Recrystallization being brought to completion, new grains are formed as given in photo 10 and the precipitates exist not only along the grain boundaries but also within the new grains. As aging progresses, the precipitates spread widely as shown in photo 11. In this way, the presence of zinc in a magnesium alloy does not retard such processes as recovery, recrystallization and grain growth.

As for Mg-1.7% Th alloys, even after annealing for 12 hr at 250°C in a 60% rolled specimens, new grains are not observed as shown in photo 12. On the other hand, in the electron micrographs of thin foil of 60% rolled Mg-4.0%Th alloys aged for 6 hr at 250°C, new grains are observed as shown in photo 13. In this photograph, the rolled structure remains at the upper right side but the fully recrystallized grains containing some dislocation lines exist at the bottom side. It seems likely that the tendency of recrystallization in Mg-4.0%Th alloys is larger than that of Mg-1.7%Th alloys. These results of transmission electron microscopic investigations are in accordance with that of X-ray diffraction studies as shown in Photo 14 to 17. These show the X-ray diffraction patterns in the polycrystalline specimens of Mg-1.7%Th and Mg-4.0%Th alloys. At any rate, the presence of thorium in a magnesium alloy greatly retards the rate of the recrystallization as compared with pure magnesium and Mg-Zn alloys.

2) Precipitation

The aging characteristics of Mg-Al alloys were summarized by A. M. Talbot et al.[5] as follows. Mg-Al alloys precipitate the equilibrium $Mg_{17}Al_{12}$. The age-hardening of Mg-Al alloys is due essentially to the precipitation of a second phase from a supersaturated solid solution. And no behavior indicates the presence of any sort of pre-precipitation hardening phenomena.

Photo 18 to 24 indicate the changes of the precipitation process during aging at various temperatures and the effects of plastic deformation on aging in the electron micrographs of thin foils of Mg-11.6%Al alloys. After aging at 70°C for 1 hr, the precipitates are shown along the grain boundaries and within the grains in the electron-micrographs of undeformed Mg-11.6%Al alloys as given in photo 18. And in photo 18 dislocation lines near the grain boundaries are most likely to be observed. The preferred precipitation on the grain boundaries is illustrated in photo 19 on the undeformed specimen aged for 6 hr at 110°C. In this photograph, dislocation lines along the grain boundaries and precipitates within the grain are found.

Photo 20 is an electron-micrograph of undeformed specimens aged for 1 hr at 150°C. In photo 20, the anomalous dislocation array is observed at the center of the photograph and many circular black spots of precipitates are found within the grain. As aging progresses, precipitates grow to large globular shapes and spread extensively in the specimen aged for 3.5 hr at 150°C as in photo 21. Photo 22 shows the 60% rolled structure of Mg-11.6% Al alloys after water-quenching. Photos 23 and 24 show the aged structure of the rolled specimens. No remarkable changes are observed by aging for 3 hr at 70°C in photo 23. But in 60% deformed materials aged for 1 hr at 150°C small amounts of precipitates are found as shown in photo 24. It is probable that the rate of precipitation in Mg-11.6% Al is not accelerated by cold rolling after water-quenching.

As for Mg-Th alloys, L. Sturkey made a detailed study of precipitation mainly by quantitative X-ray diffraction studies and electron diffraction methods[3].

According to this, the precipitation of the equilibrium Mg_4Th compound is preceded by the formation of a transition phase of higher thorium content coherent with the magnesium matrix, having the composition Mg_2Th and a Laves-phase structure. It was confirmed that there is considerable disorder in the transition phase, parallel to one of the {111} planes, indicating that the growth on this {111} plane is parallel to the magnesium basal plane and this disorder is temperature-dependent, and more highly ordered particles may be obtained at higher temperatures. The rate of the precipitation of thorium from solid solution is not remarkable.

On isothermal aging at 250°C in Mg–1.7%Th alloys, the electron micrograph of an undeformed alloy aged for 3 hr shows the preferential precipitation on the grain boundaries as shown in photo 25. Photo 26 shows an electron micrograph of the thin foil of an undeformed Mg–1.7%Th alloy aged for 1 hr at 430°C. Photo 26 shows the preferential precipitation on the dislocation lines. In 60% rolled Mg–1.7%Th alloys, as shown in photos 12 and 27, the precipitation seems to be retarded by plastic deformation after water-quenching. Photo 12 shows the deformed structure in a 60% rolled specimen aged for 12 hr at 250°C. In this photograph, the precipitates cannot be clearly found as compared with photo 25. In photo 27 illustrating newly recrystallized grains, preferential precipitation along the grain boundaries is observed.

On the Mg–4.0%Th alloys, in isothermal aging for 24 hr at 70°C or for 6 hr at 110°C, electron micrographs are shown in photos 28 and 29 respectively. In photo 28, dislocation lines are decorated with solute atoms as shown by an arrow. Photo 29 shows the small circular faint spots which seem to be corresponding to plate-like G. P. zones as in Al–Cu alloys. This result is clearly in accordance with that of the measurements of electrical resistance. Fig. 1 shows the electrical resistance changes of Mg–4.0%Th alloys during heating at a constant rate of 2°C per minute. In Fig. 1, two stage changes were observed: one is the decrease at about 140°C and the other is the increase at about 360°C. It seems that the first stage decrease is due to the growth of G. P. zones and the second stage increase is probably due to the precipitation of transition particles. In the higher aging temperature, for instance, when aged at 150°C for 6 hr, such small circular faint spots perhaps due to G. P. zones are not observed in photo 30, the precipitates are found to be on the dislocation networks. Photo 31 indicates the precipitates on dislocation networks in the electron micrographs of undeformed Mg–4.0% Th alloys aged for 6 hr at 250°C. Photo 13 shows newly recrystallized grains with fine precipitates in 60% rolled materials aged for 6 hr at 250°C. Photos 32 and 33 show a great number of piled up dislocation lines near

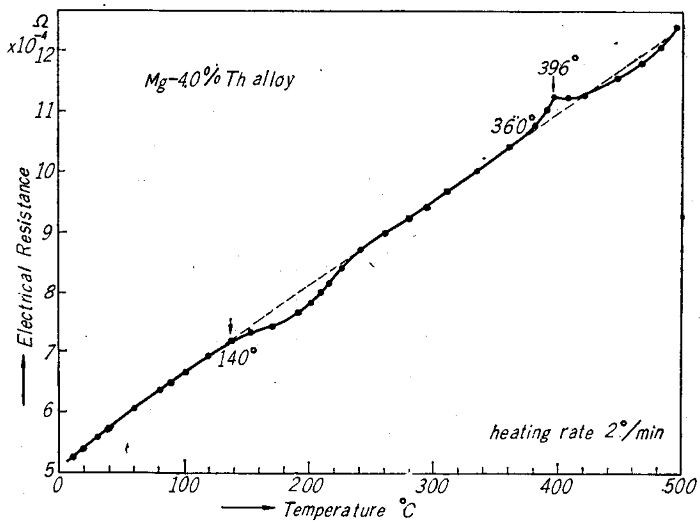

Fig. 1. Electrical resistance change of Mg-4.0%Th alloy in heating at a constant rate. (2°C/min)

the grain boundaries in undeformed Mg-4.0%Th alloys aged for 3 days at 250°C.

The dislocation lines pinned by precipitates and the preferential precipitation on the grain boundary are observed on the electron micrograph of undeformed Mg-4.0% Th alloys aged for 6 hr at 350°C as shown in Photo 34. Photos 35 and 36 emphasize the fact that the rate of precipitation is accelerated by plastic deformation in Mg-4.0% Th alloys. Upon further aging, the anomalous shape of precipitates grow up and spread widely as shown in Photo 37. In general, the precipitation of Mg-Th alloys is not remarkable as compared with Mg-Zn alloys.

IV. Discussion

On the basis of the present studies, the presence of thorium in magnesium alloys greatly retards such softening processes as recovery, recrystallization and grain growth. This slowing-up process is reflected in the slow precipitation rate in the Mg-Th system. L. Sturkey[3)] confirmed that the high chemical affinity of thorium for hydrogen and the relatively high solubility of hydrogen in magnesium provided a basis for an explanation of the low mobility of thorium. According to the present transmission electron microscopic investigation of Mg-4.0%Th alloys aged for 6 hr at 110°C as shown in photo 29, it is clear that G.P. zones occur before the appearance of a transition phase as in Al-Cu alloys. This phenomenon is clearly in accordance with the results of the measurements of electrical resistance.

Guinier[6] studied the shape of G. P. zones in various alloys by the X-ray small angle scattering technique and concluded that in cases where the size difference between solute and solvent atoms is more than 10%, the G. P. zones are plate-like, and where it is less than 10%, the shape is spherical. In Mg-Th alloys, the thorium atom is about 15 to 20% larger in radius than the magnesium atom, so the G. P. zones were assumed to be plate-like. This fact was confirmed as shown in photo 29.

From electron microscopic studies with thin foils in Mg-1.7%Th and Mg-Al alloys, the rate of precipitation seems to be retarded by plastic deformation after water-quenching. On the contrary, in Mg-4.0%Th alloys, the rate of precipitation is accelerated similarly in Al-4%Cu alloys.[7),8)] It is uncertain why the rate of recrystallization in Mg-4.0%Th alloys is larger than that in Mg-1.7% Th alloys, but it is clear that when the matrix is recrystallized the precipitates begin to grow rapidly. It might be supposed that the higher contents of gas in Mg-4.0%Th alloys as shown in Table II have such a particular effect on the recrystallization.

V. Conclusion

Mg-Th alloys were investigated in respect to the precipitation process, the effects of plastic deformation on precipitation and recrystallization phenomena mainly by examining thin foils with an electron-microscope in comparison with pure magnesium, Mg-Zn and Mg-Al alloys. It may be concluded that:

1) The presence of thorium in magnesium alloys greatly retards recrystallization. The tendency of recrystallization seems to be strongly dependent upon the content of thorium and also probably upon gas contents.

2) In Mg-Th alloys, G. P. zones occur before the appearance of the transition phase with the composition Mg_2Th. This is similar to Mg-Zn alloys.[1)]

3) In Mg-Al alloys, the precipitation is found to occur along the grain boundaries and within grains after aging at 70°C for 1 hr. But it is not determined whether the zones occur before the appearance of the more stable precipitates or not.

4) The effects of cold working on precipitation are not simple but complex. The formation of the precipitate is hindered by plastic deformation immediately after water-quanching in Mg-1.7%Th and Mg-Al alloys, though the rate of precipitation is accelerated by plastic deformation in Mg-Zn and Mg-4.0%Th alloys.

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References

1) Yoraro Murakami, Osamu Kawano and Hideaki Tamura : This memoir, 23, 5 (1962).
2) T. E. Leontis : Thorium in Magnesium Technology, Chap. 3 in the Metal Thorium, ASM. pp. 29-53 (1958).
3) L. Sturkey : Trans, AIME 466, Vol. 218, June (1960).
4) C. S. Roberts : Magnesium and Its Alloys, 94.
5) A. M. Talbot and J. T. Morton : "Age-Hardening of Magnesium-Aluminium Alloys". Trans. AIME, **122**, 301 (1936).
6) A. Guinier : Physics, **15**, 148 (1949).
7) Y. Murakami and O. Kawano : This memoir, **21**, 4 (1959).
8) Y. Murakami and O. Kawano : Trans. Japan Inst. Metals, **1**, 27 (1960).

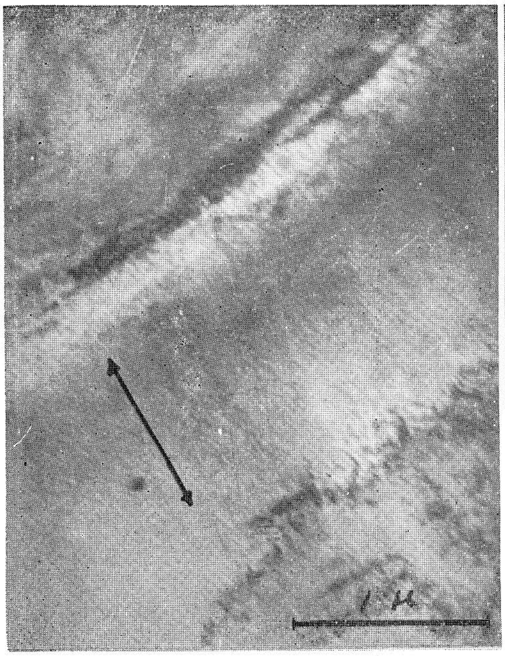

Photo. 1. Pure Mg, W.Q., 30% rolled, showing the band about 1μ wide. (×26,000)

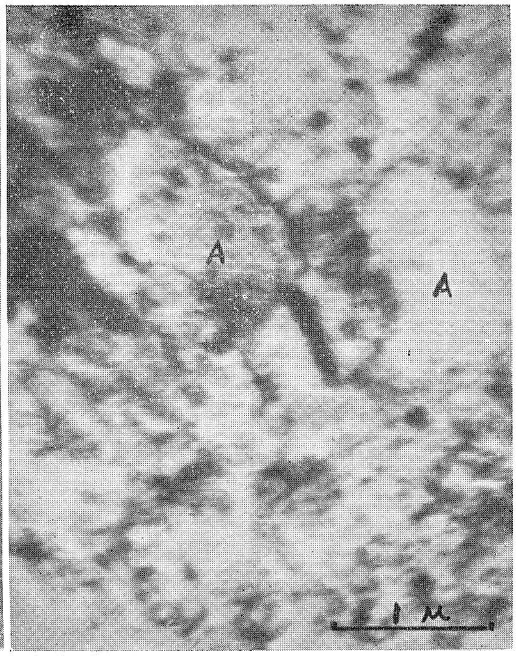

Photo. 2b. Pure Mg, W.Q., 80% rolled. Note new grain A. (×21,000)

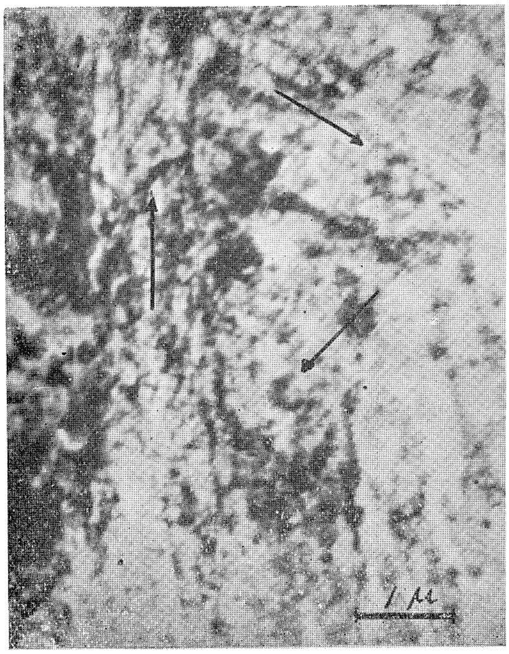

Photo. 2a. Pure Mg, W.Q., 80% rolled, showing the compression bands. (×13,000)

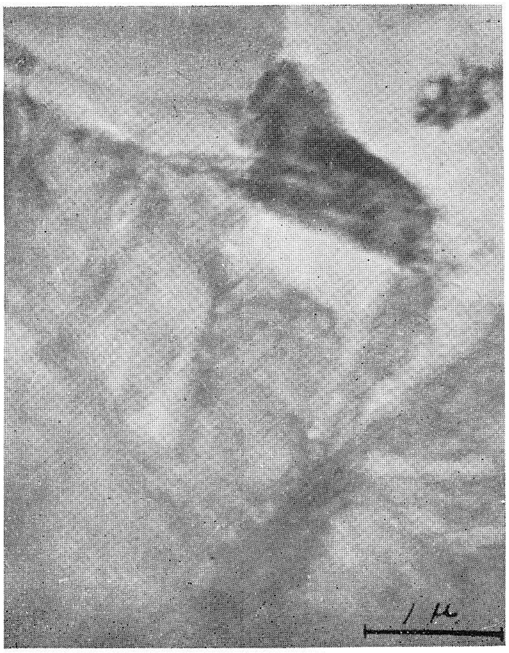

Photo. 3. Pure Mg, W.Q., 30% rolled, aged for 2 days at 70°C (×18,000)

Photo. 4. Pure Mg, W.Q., 30% rolled, aged for 3 hr at 100°C. (×52,000)

Photo. 6. Pure Mg, W.Q., 30% rolled, aged for 30 min at 200°C. (×52,000)

Photo. 5. Pure Mg, W.Q., 30% rolled, aged for 30 min at 200°C. (×52,000)

Photo. 7. Pure Mg, W.Q., 60% rolled, aged for 10 min at 200°C. Fully recrystallized (after grain growth). (×26,000)

Photo 8. Mg-3.2%Zn alloy, W.Q., 30% rolled, aged for 5 days at 70°C. (×27,000)

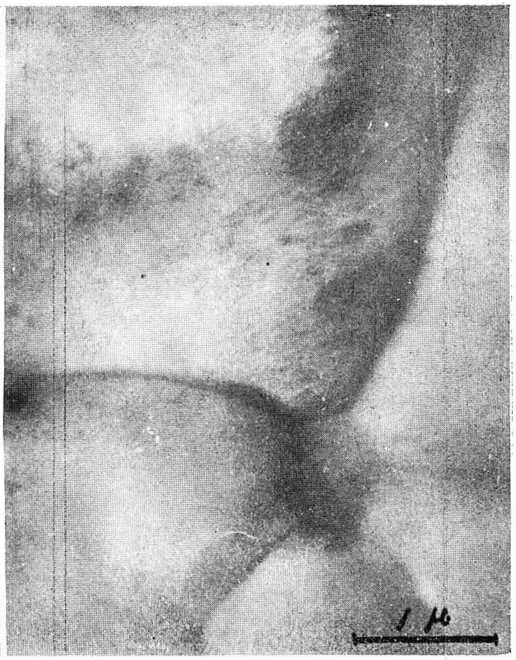

Photo. 10. Mg-3.2%Zn alloy, W.Q., 40% rolled, aged for 10 min at 200°C. (×19,000)

Photo. 9. Mg-3.2%Zn alloy, W.Q., 40% rolled, aged for 5 days at 70°C, showing the precipitates on the sub-boundary. (×19,000)

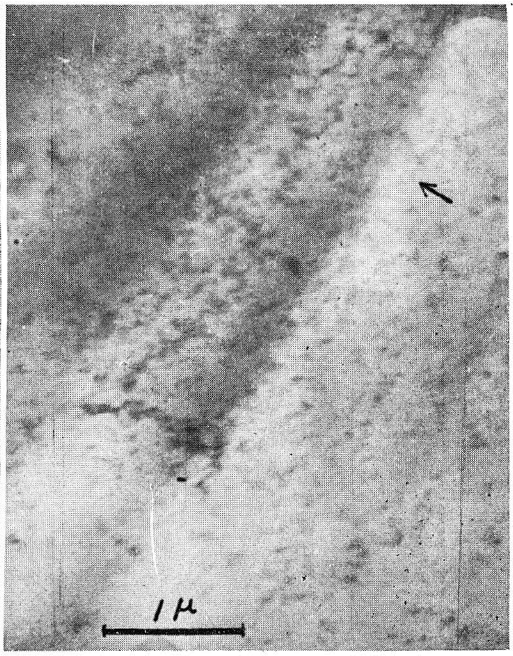

Photo. 11. Mg-3.2%Zn alloy, W.Q., 40% rolled, aged for 30 min at 200°C. (×19,000)

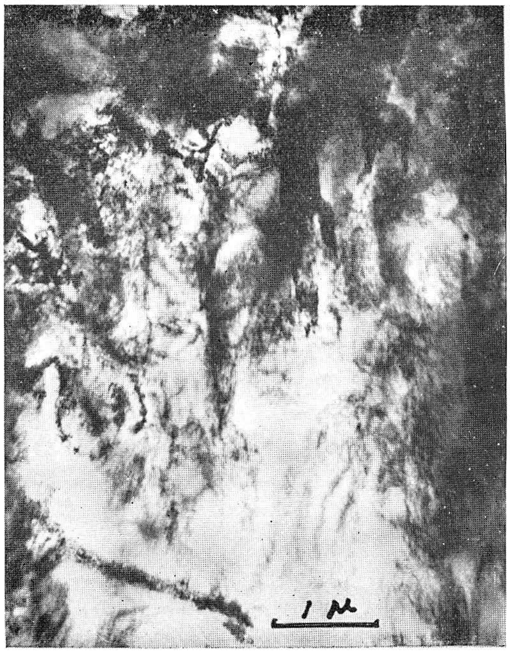

Photo. 12. Mg-1.7%Th alloy, W.Q., 60% rolled, aged for 12 hr at 250°C. (×14,000)

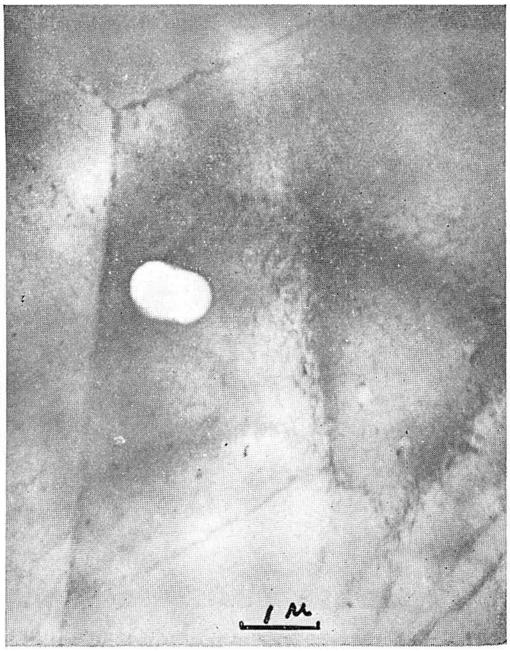

Photo. 18. Mg-11.6%Al alloy, W.Q., aged for 1 hr at 70°C. (×10,000)

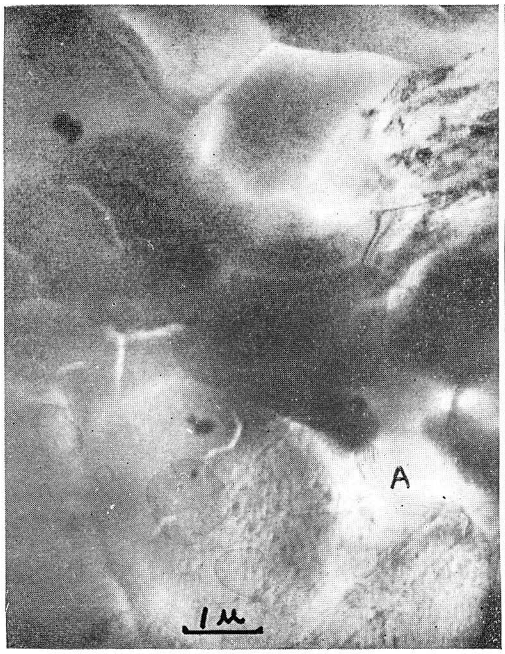

Photo. 13. Mg-4.0%Th alloy, W.Q., 60% rolled, aged for 6 hr at 250°C. Notice fringes along the grain boundary A inclined to the surface of the foil. (×10,000)

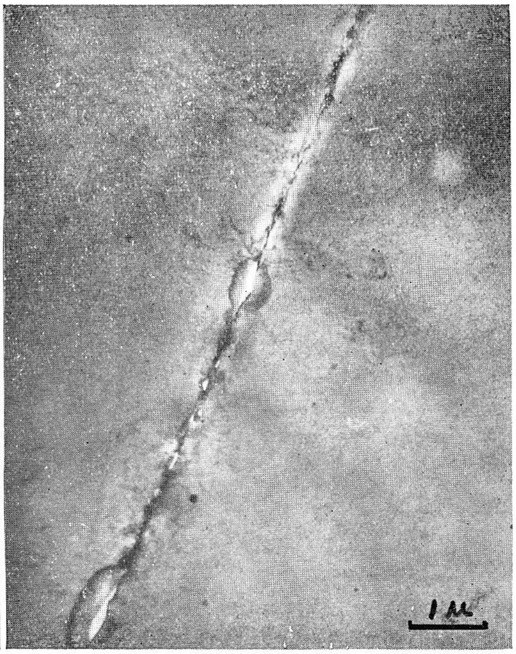

Photo. 19. Mg-11.6%Al alloy, W.Q., aged for 6 hr at 110°C. (×10,000)

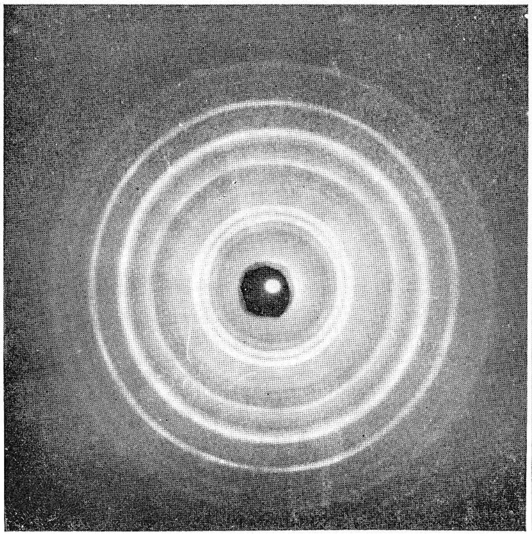

Photo. 14. Mg–1.7%Th alloy, W.Q., 60% rolled, aged for 6 hr at 250°C.

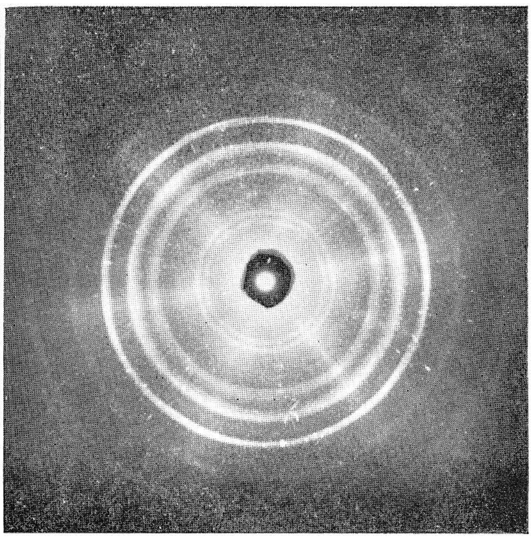

Photo. 16. Mg–1.7%Th alloy, W.Q., 60% rolled, aged for 12 hr at 250°C.

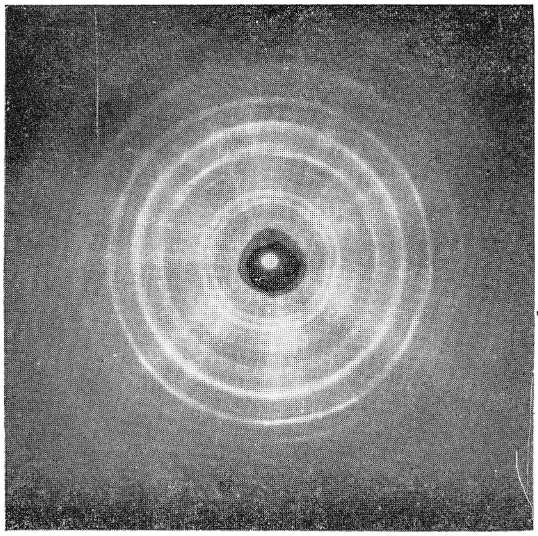

Photo. 15. Mg–4.0%Th alloy, W.Q., 60% rolled, aged for 6 hr at 250°C.

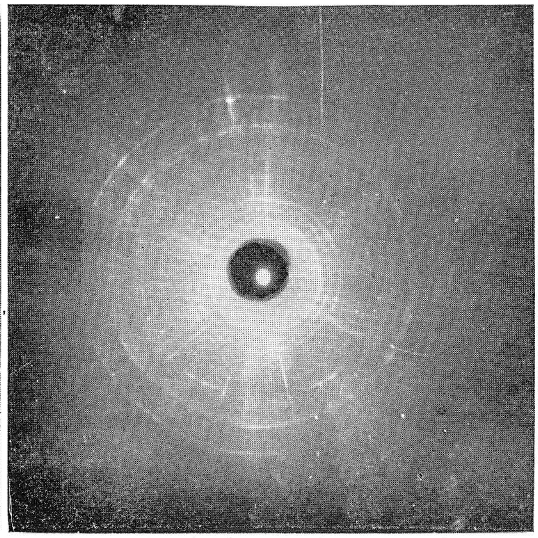

Photo. 17. Mg–4.0%Th alloy, W.Q., 60 % rolled, aged for 12 hr 250°C.

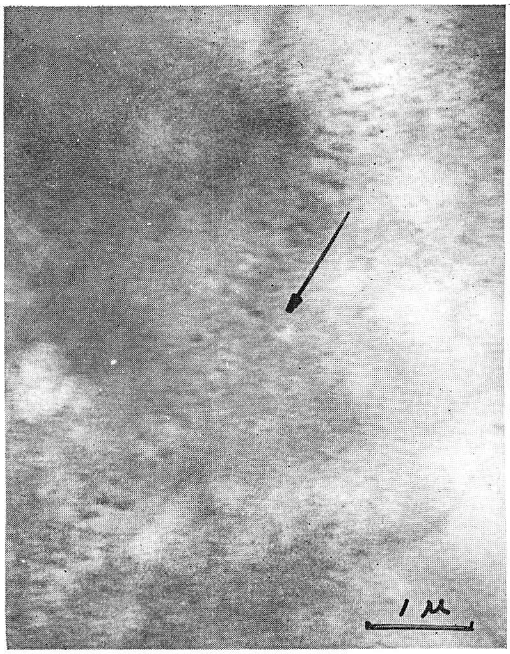

Photo. 20. Mg-11. 6%Al alloy, W.Q., aged for 1 hr at 150°C. The arrow shows the anomalous dislocation array decorated by solute atoms. (×14,000)

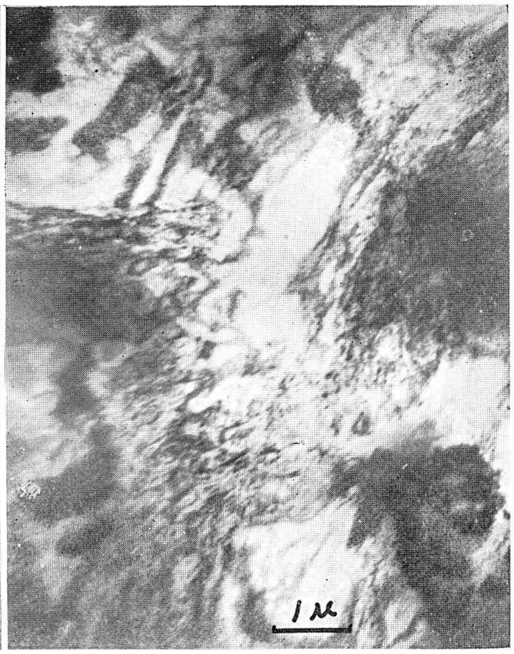

Photo. 22. Mg-11.6%Al alloy, W.Q., 60% rolled. (×10,000)

Photo. 21. Mg-11.6%Al alloy, W.Q., aged for 3.5 hr at 150°C. (×10,000)

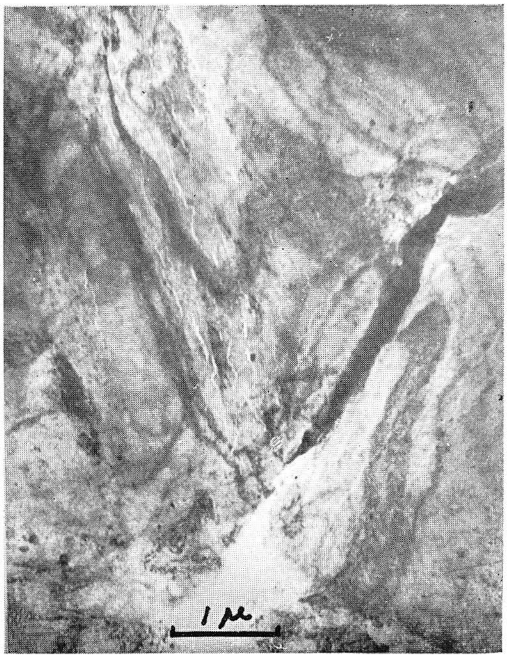

Photo. 23. Mg-11.6%Al alloy, W.Q., 60% rolled, aged for 3 hr at 70°C. (14,000)

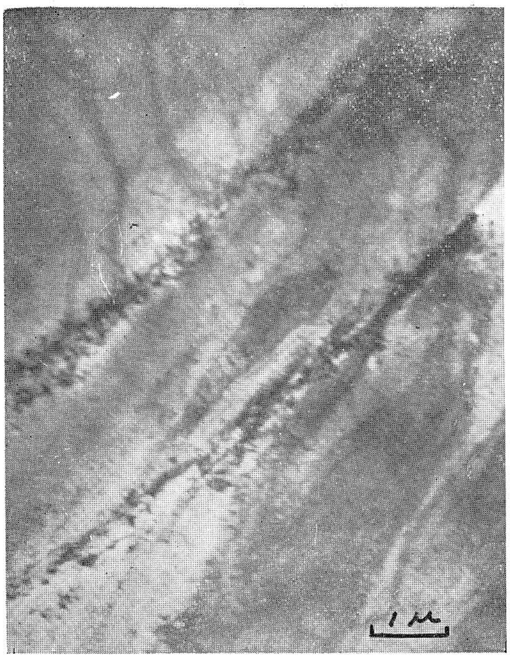

Photo. 24. Mg-11.6%Al alloy, W.Q., 60% rolled, aged for 1 hr at 150°C. (×10,000)

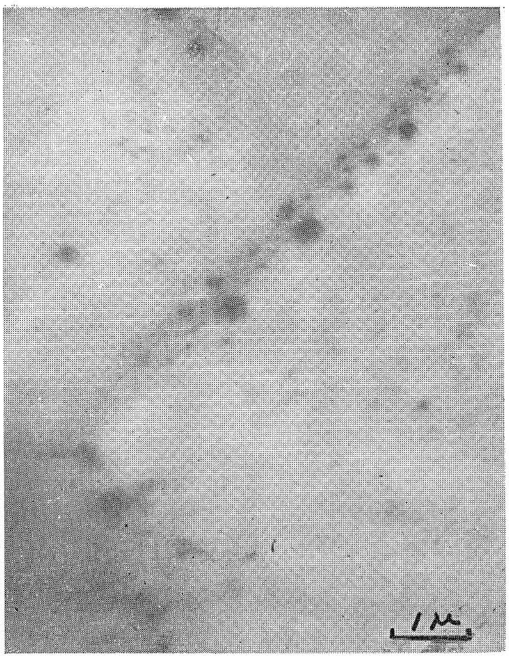

Photo. 25. Mg-1.7%Th alloy, W.Q., aged for 3 hr at 250°C, showing preferential precipitates on the grain boundaries. (×10,000)

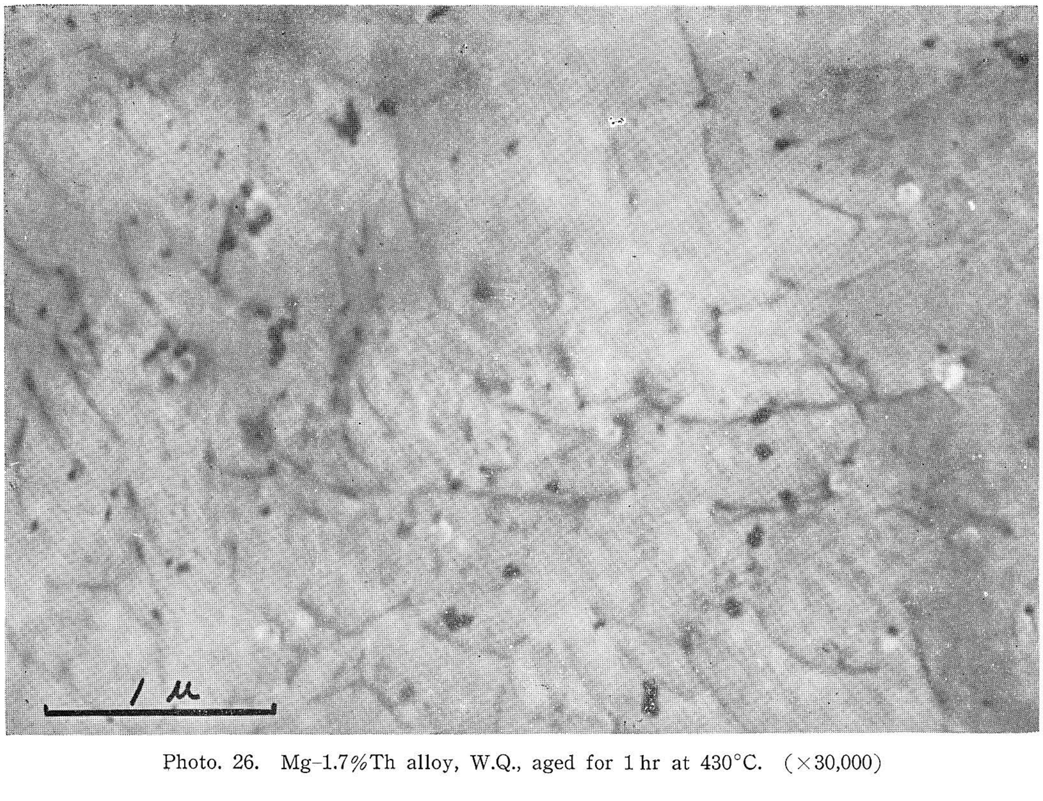

Photo. 26. Mg-1.7%Th alloy, W.Q., aged for 1 hr at 430°C. (×30,000)

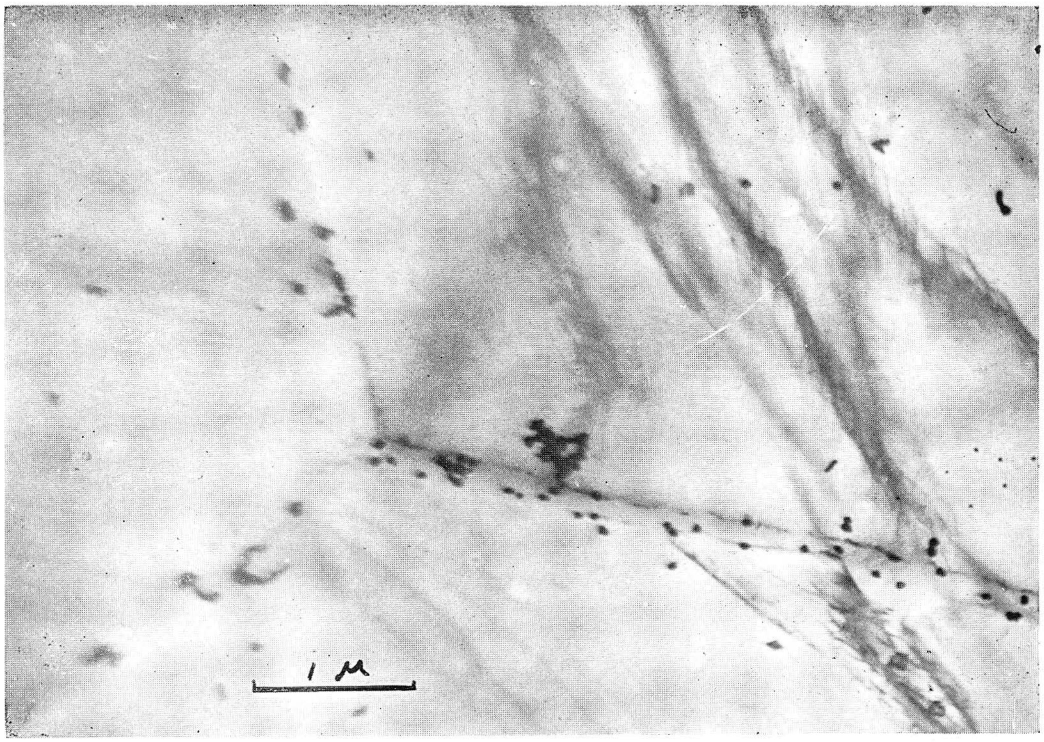

Photo. 27. Mg-1.7%Th alloy, W.Q., 60% rolled, aged for 1 hr at 430°C. (×21,000)

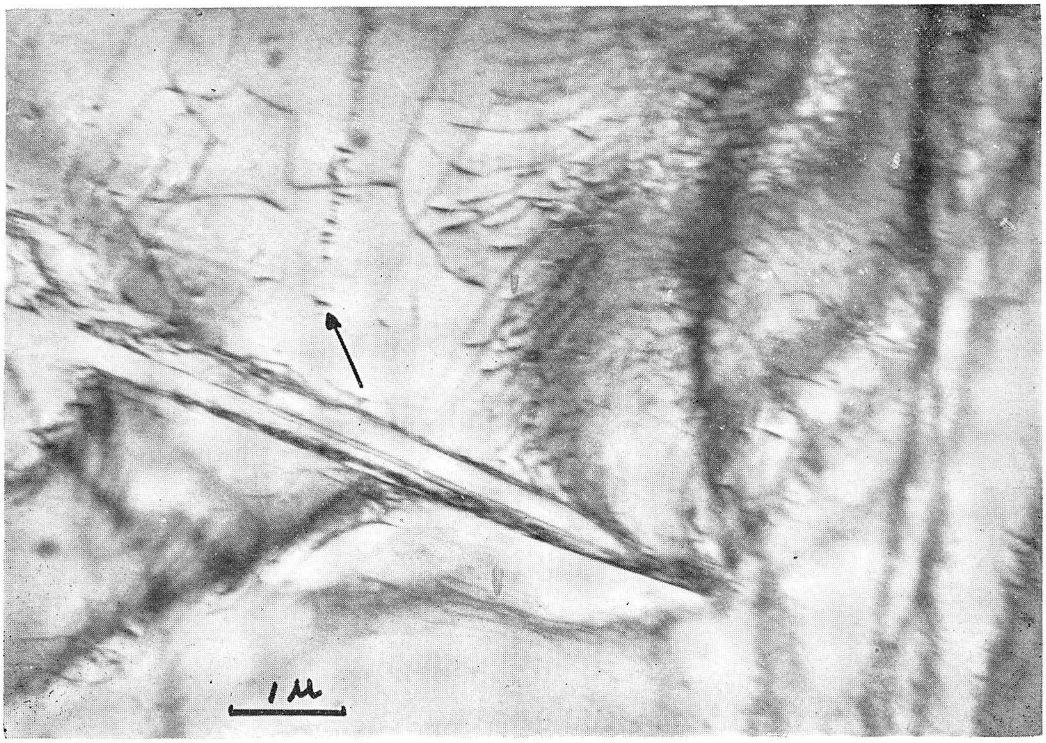

Photo. 28. Mg-4.0%Th alloy, W.Q., aged for 24 hr at 70°C. (×15,000)

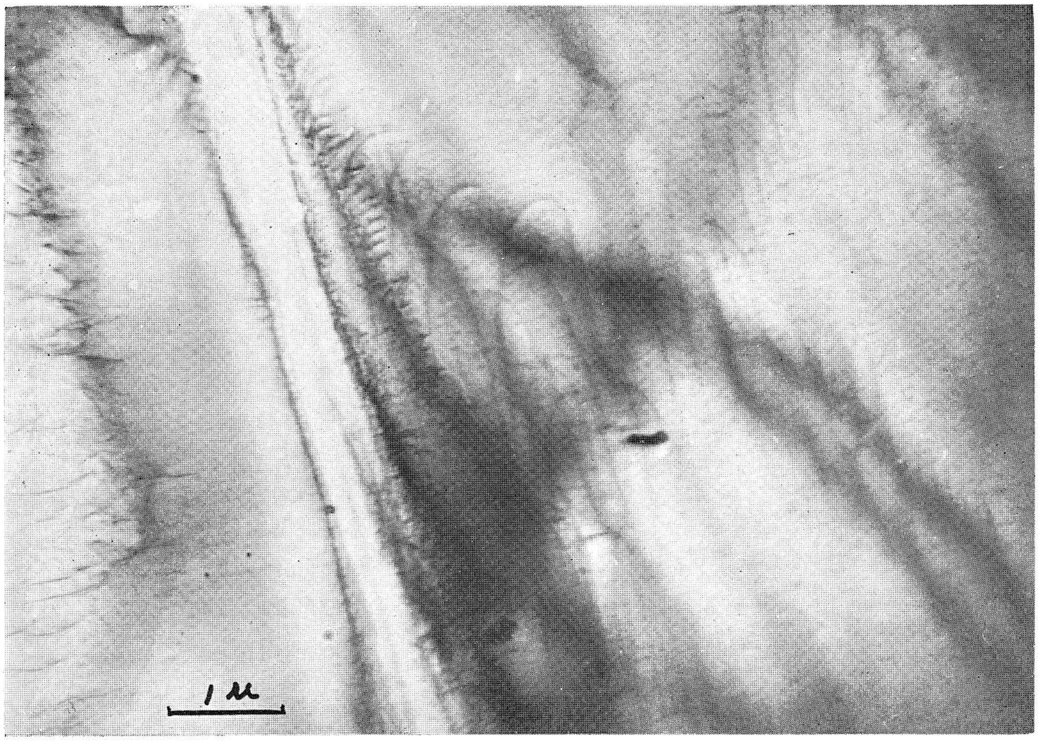

Photo. 29. Mg-4.0%Th alloy, W.Q, aged for 6 hr at 110°C. (×15,000)

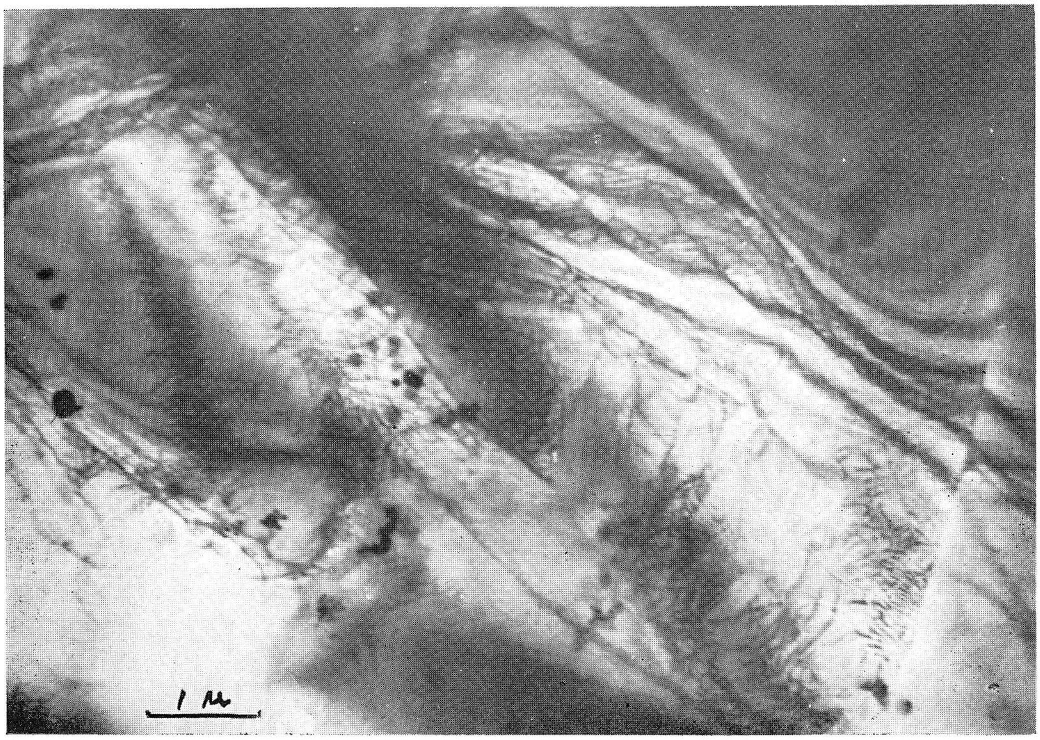

Photo. 31. Mg-4.0%Th alloy, W.Q., aged for 6 hr at 250°C. (×15,000)

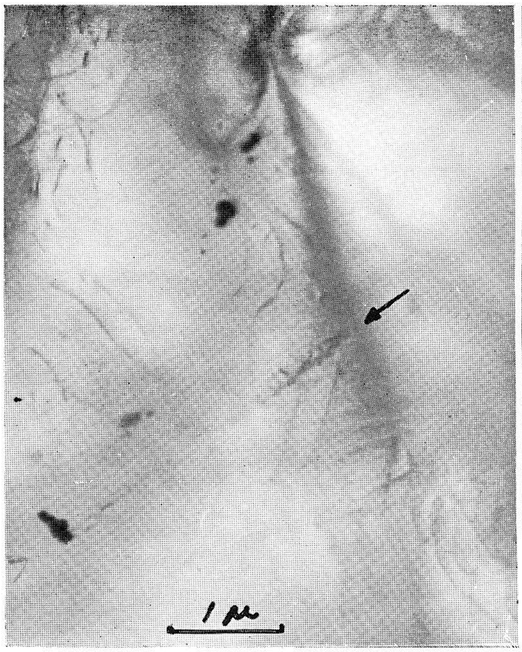

Photo. 30. Mg-4.0%Th alloy, W.Q., aged for 6 hr at 150°C. (×15,000)

Photo. 32. Mg-4.0% Th alloy, W.Q., aged for 3 days at 250°C. (×21,000)

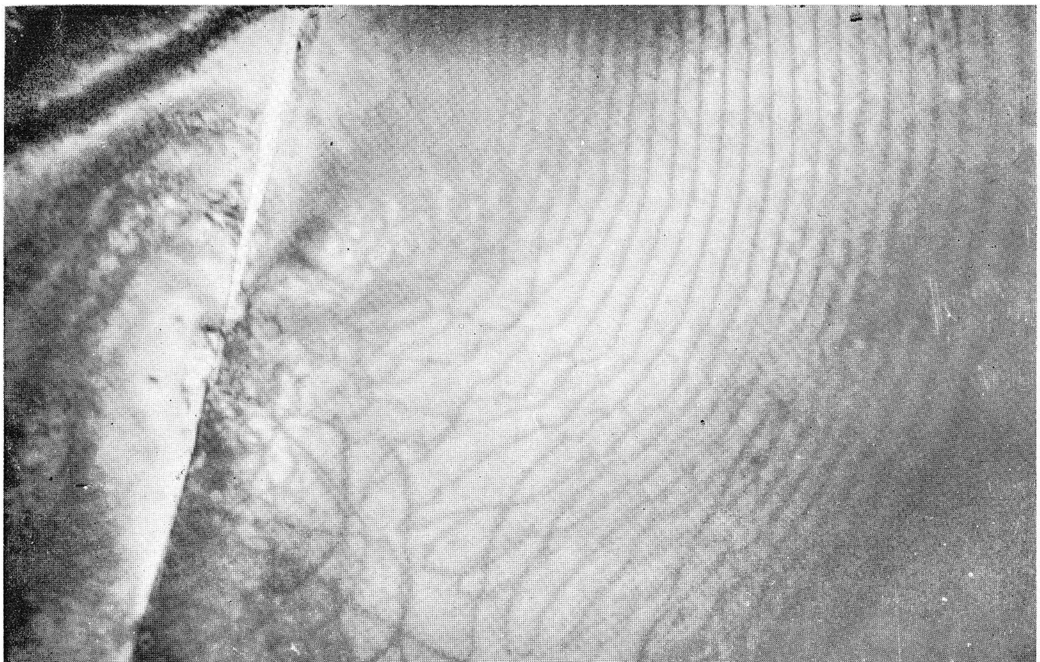

Photo. 33. Mg-4.0%Th alloy, W.Q., aged for 3 days at 250°C. (×21,000)

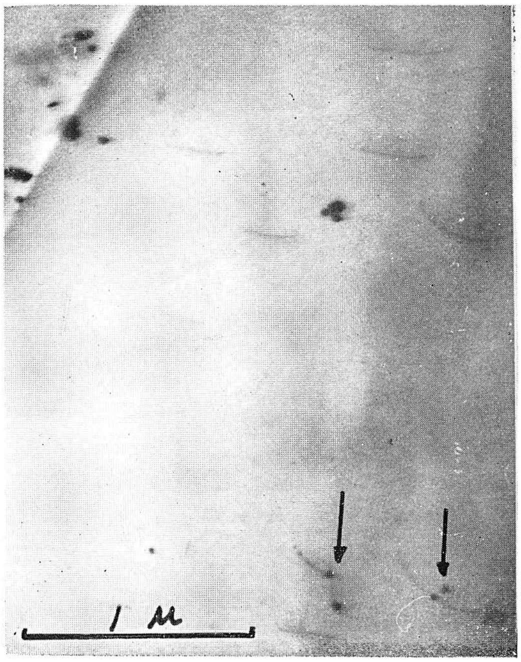

Photo. 34. Mg–4.0%Th alloy, W.Q., aged for 6 hr at 350°C.
Showing dislocations pinned by small precipitates. (×30,000)

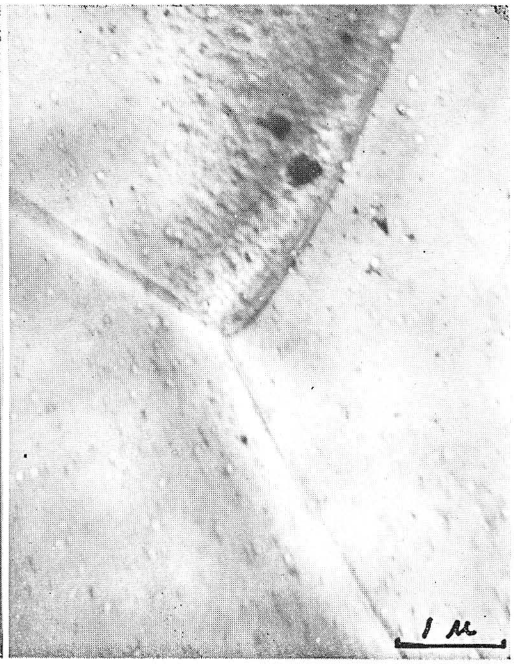

Photo. 36. Mg–4.0%Th alloy, W.Q., 60% rolled, aged for 3 hr at 400°C. (×14,000)

Photo. 35. Mg–4.0%Th alloy, W.Q., 60% rolled, aged for 6 hr at 350°C. (×20,000)

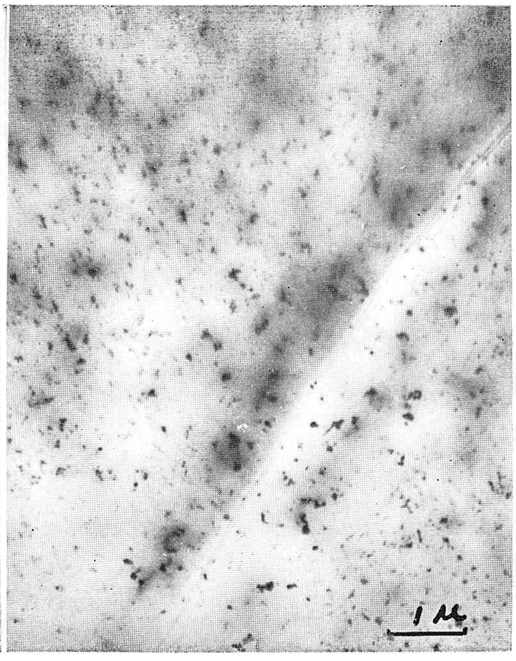

Photo. 37. Mg–4.0%Th alloy, W.Q., aged for 1 day at 400°C. (×10,000)