



Scholars' Mine

Masters Theses

Student Theses and Dissertations

1969

Precipitation hardening of a Mg - 3.5 wt. % Th - 1. wt. % Mn alloy

Adolf Chun-Chiung Huang

Follow this and additional works at: https://scholarsmine.mst.edu/masters_theses

 Part of the [Metallurgy Commons](#)

Department:

Recommended Citation

Huang, Adolf Chun-Chiung, "Precipitation hardening of a Mg - 3.5 wt. % Th - 1. wt. % Mn alloy" (1969). *Masters Theses*. 6848.

https://scholarsmine.mst.edu/masters_theses/6848

This thesis is brought to you by Scholars' Mine, a service of the Missouri S&T Library and Learning Resources. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

PRECIPITATION HARDENING

OF

A Mg - 3.5 wt. % Th - 1. wt. % Mn ALLOY

BY

ADOLF CHUN-CHIUNG HUANG, 1941

541

A

THESIS

submitted to the faculty of the

UNIVERSITY OF MISSOURI-ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1969

171221

T2267
cl
H38

Approved by

(Advisor)

J. B. Clark
P. D. Churney

H. Meant

ABSTRACT

The precipitation process in a Mg - 3.5 wt. % Th - 1. wt. % Mn alloy during aging at 260°, 350° and 400°C was determined principally by transmission electron microscopy. At 350° and 400°C, general precipitation of the equilibrium Mg₄Th phase moderately hardens the alloy. No transition lattice of this phase was seen. The Mg₄Th precipitate forms initially as disc shaped plates parallel either to the prism or basal plane of the matrix, with the following orientation relationship:

$$(110)_{\text{Mg}_4\text{Th}} // (01\bar{1}0)_{\text{Matrix}} \quad (110)_{\text{Mg}_4\text{Th}} // (0001)_{\text{Matrix}}$$

or

$$[\bar{1}10]_{\text{Mg}_4\text{Th}} // [\bar{1}2\bar{1}0]_{\text{Matrix}} \quad [1\bar{1}0]_{\text{Mg}_4\text{Th}} // [1\bar{2}10]_{\text{Matrix}}$$

During prolonged aging at 400°C the plates lengthen into long laths on either of the above planes in the close packed direction $[\bar{1}2\bar{1}0]$. At 260°C an unidentified G. P. zone appearing precipitate forms. Slip dislocations do not shear but bow between the Mg₄Th dispersions, whereas $10\bar{1}2$ twins shear the disc shaped plates of Mg₄Th.

ACKNOWLEDGEMENT

The author is indebted to his thesis advisor Professor J. B. Clark for his guidance and discussion throughout the course of this investigation.

TABLE OF CONTENTS

	page
ABSTRACT.....	ii
ACKNOWLEDGEMENT.....	iii
LIST OF FIGURES.....	v
LIST OF TABLES.....	vii
I. INTRODUCTION & LITERATURE REVIEW.....	1
II. EXPERIMENTAL PROCEDURE.....	4
III. EXPERIMENTAL RESULTS.....	7
A. AGE HARDENING.....	7
B. PRECIPITATION PROCESS.....	7
1. AGING AT 350°C AND 400°C.....	8
2. AGING AT 260°C.....	18
3. EFFECT OF PRIOR COLD WORK ON THE PRECIPITATION PROCESS.....	21
4. PRECIPITATE-FREE REGION AT GRAIN BOUNDARIES.....	24
C. THE HARDENING MECHANISM.....	24
1. TWIN-PRECIPITATE INTERACTION.....	25
2. DISLOCATION-PRECIPITATE INTER- ACTION.....	25
IV. DISCUSSION.....	27
V. CONCLUSION.....	32
REFERENCES.....	33
APPENDIX - PREPARATION OF THIN FOILS OF Mg - 3.5 wt. % Th - 1. wt. % Mn ALLOY BY THE WINDOW METHOD.....	34
VITA.....	36

LIST OF FIGURES

FIGURE	page
1. AGE HARDENING OF A Mg - 3.5 wt. % Th - 1. wt. % Mn ALLOY AS A FUNCTION OF AGING TEMPERATURE....	5
2. DISC SHAPED PLATES (GRAY) OF Mg ₄ Th FORMED DURING A 72 HOURS AGE AT 350°C. BLACK PRECIPITATES ARE UNIDENTIFIED. PLANE OF FOIL CLOSE TO PRISM PLANE. X 23,000.....	9
3a. DISC SHAPED Mg ₄ Th PRECIPITATES ON PRISM PLANE OF MATRIX. SOLUTION TREATMENT 8 HOURS AT 590°C PLUS 15 MINUTES AGE AT 400°C. PLANE OF FOIL-PRISM PLANE OF MATRIX. SMALL DISC SHAPED PLATES OF Mg ₄ Th (GRAY), LYING IN PLANE OF FOIL. BLACK LINES ARE EXTINCTION CONTOURS. X 21,7000..	10
3b. DISC SHAPED Mg ₄ Th PRECIPITATES ON PRISM PLANE OF MATRIX. SOLUTION TREATMENT 8 HOURS AT 590°C PLUS 15 MINUTES AGE AT 400°C. PLANE OF FOIL-PRISM PLANE OF MATRIX. DIFFRACTION PATTERN OF ABOVE FIELD ROTATED TO COINCIDE WITH 3a.....	11
3c. DISC SHAPED Mg ₄ Th PRECIPITATES ON PRISM PLANE OF MATRIX. SOLUTION TREATMENT 8 HOURS AT 590°C PLUS 15 MINUTES AGE AT 400°C. PLANE OF FOIL-PRISM PLANE OF MATRIX. ANALYSIS OF DIFFRACTION PATTERN: ELECTRON BEAM ⊥ TO (01 $\bar{1}$ 0) OF MATRIX AND (110) OF Mg ₄ Th. Mg SPOTS - OPEN CIRCLE; Mg ₄ Th SPOTS - SHADED CIRCLE.....	12
4a. Mg ₄ Th PLATES LYING ON BASAL PLANE OF MATRIX SOLUTION TREATMENT PLUS 24 HOUR AGE AT 350°C. PLANE OF FOIL-PRISM PLANE OF MATRIX. Mg ₄ Th PLATES PARALLEL TO BASAL PLANE ARE SEEN IN CROSS-SECTION. BLACK PRECIPITATE COULD NOT BE IDENTIFIED. X 22,400.....	14
4b. Mg ₄ Th PLATES LYING ON BASAL PLANE OF MATRIX SOLUTION TREATMENT PLUS 24 HOUR AGE AT 350°C. PLANE OF FOIL-PRISM PLANE OF MATRIX. DIFFRACTION PATTERN OF ABOVE FIELD ROTATED TO BRING INTO CONCIDENCE WITH 4a. AS SHOWN BY 4c, FOIL SURFACE IS NEAR PRISM PLANE (01 $\bar{1}$ 0) OF MATRIX. NOTE STREAKS IN [0002] INDICATING PLATES LIE PERPENDICULAR TO BASAL PLANE.....	15

FIGURE	page
4c. Mg ₄ Th PLATES LYING ON BASAL PLANE OF MATRIX SOLUTION TREATMENT PLUS 24 HOUR AGE AT 350°C. PLANE OF FOIL-PRISM PLANE OF MATRIX. ANALYSIS OF DIFFRACTION PATTERN SHOWING MATRIX SPOTS.....	16
5. ELLIPTICALLY SHAPED Mg ₄ Th PRECIPITATES, AGING 8 HOURS AT 400°C. PLANE OF FOIL-NEAR PRISM PLANE OF MATRIX. X 22,600.....	17
6. LONG THIN LATH SHAPED PLATES OF Mg ₄ Th GROWING IN $\langle 1\bar{2}10 \rangle$ CLOSE PACKED DIRECTION. NOTE: (a) DISLOCATION BOWING BETWEEN PLATES (b) DISLOCATION NETWORK IN LOWER LEFT OF PICTURE. SOLUTION TREATMENT PLUS 48 HOURS AGE AT 400°C PLUS HAMMER PEENED. PLANE OF FOIL-NEAR PRISM PLANE. X 22,600.....	19
7. DISPERSION OF PRECIPITATION PRODUCED BY AGING 95 HOURS AT 260°C. BLACK PRECIPITATE IS UNIDENTIFIED, MAY BE α Mn, THORIUM OXIDE, OR Mn-Th COMPOUNDS. NOTE THE VERY FINE TEXTURE ON THE MATRIX INDICATIVE OF A G. P. ZONE TYPE OF PRECIPITATION. X 35,900.....	20
8a. EFFECT OF COLD WORK PRIOR TO AGING. NOTE THE FINER DISPERSION OF Mg ₄ Th PLATES (LIGHT GRAY) IN THE $10\bar{1}2$ TWIN. PART OF THE DISLOCATION NETWORK INSIDE THE TWIN IS SEEN FAINTLY. SOLUTION TREATMENT PLUS HAMMER PEENED, FOLLOWED BY 4 HOUR AGE AT 350°C. X 29,400.....	22
8b. EFFECT OF COLD WORK PRIOR TO AGING. COARSE GLOBULAR DISPERSION OF Mg ₄ Th PRODUCED BY NUCLEATION ON COARSE DISLOCATION NETWORK. NOTE ALSO PRECIPITATE-FREE REGION ADJACENT TO THE GRAIN BOUNDARY PRODUCED BY SOLUTE DEPLETION DUE TO HYDRIDE PRECIPITATION IN THE GRAIN BOUNDARY. SOLUTION TREATMENT PLUS HAMMER PEENED, FOLLOWED BY 24 HOUR AGE AT 350°C. X 22,400.....	23
9. TWIN-PRECIPITATE INTERACTION. DISC-SHAPED PRECIPITATES OF Mg ₄ Th APPARENTLY SHEARED BY $10\bar{1}2$ TWIN. SOLUTION TREATMENT PLUS 48 HOUR AGE AT 350°C, THEN HAMMER PEENED. X 16,700.....	26

LIST OF TABLES

TABLE	page
I. COMPARISON OF PRECIPITATION AND DEFORMATION CHARACTERISTICS OF MAGNESIUM BASE ALLOYS.....	31

I. INTRODUCTION AND LITERATURE REVIEW

In contrast to the extensive knowledge of precipitation process in face centered cubic alloys, comparatively little is known concerning these processes in hexagonal close packed alloys. In an effort to gain more insight into these mechanisms, age hardening studies on a series of magnesium alloys are in progress. In the first investigation on a Mg-5 wt. % Zn alloy⁽¹⁾, which followed earlier work by Sturkey and Clark⁽²⁾, it was shown that the hardening phase was a transition lattice which forms in long thin rods perpendicular to the basal plane. Although these precipitate rods are efficiently orientated to block basal slip, the solubility of zinc in magnesium is too low and the size of the individual precipitate too large to produce a sufficiently small interparticle spacing. Consequently the age hardening response of this alloy is comparatively small. In the second of these investigations, on a Mg-9 wt. % Al alloy⁽³⁾, a modest amount of age hardening is produced by precipitation of the equilibrium phase $Mg_{17}Al_{12}$ parallel to the basal plane. Though this precipitate suppresses $10\bar{1}2$ twin formation unlike the Mg-Zn precipitate, the interparticle spacing is large enough that slip dislocations may bow between and loop around, rather than have to cut the particles. Consequently the age hardening response is small.

The present investigation of Mg-3.5 wt. % Th-1. wt. % Mn is the third in this series of studies. Commercially, the magnesium-thorium-base alloys are modified with ternary

additions of zirconium or manganese, producing the HK and HM series of alloys. These alloys are the high temperature magnesium alloys, maintaining reasonable strength properties up to about 500°F. Thorium appears to block grain growth and the tendency for recrystallization. These effects are not yet completely understood.

In a study of binary Mg-Th alloys, Murakami, et al.⁽⁴⁾ reported formation of both G. P. zones and a transition lattice. Sturkey⁽⁵⁾ established that this transition lattice may be described as a Laves phase Mg_2Th and that the equilibrium precipitate is $Mg_{23}Th_6$ (Mg_4Th), which may be considered as isomorphous with a complex FCC compound Th_6Mn_{23} , analyzed by Florio, et al.⁽⁶⁾. Sturkey reported that Mg_2Th phase forms as plates parallel to the basal plane.

In an investigation of Mg - 3.7 wt. % Th - 0.4 wt. % Zr alloy, Mushovic and Stoloff⁽⁷⁾, also reported the precipitation of plates of the transition phase Mg_2Th , but with the orientation perpendicular to the basal plane rather than parallel as reported by Sturkey.

Mushovic and Stoloff found an additional transition precipitate, a semi-coherent ordered hcp transition lattice of probable composition Mg_3Th ; this precipitate also forms in plates perpendicular to the basal plane. The age hardening is produced by this transition lattice, which must be cut by glide dislocations in order for deformation to proceed. At intermediate stages of aging, long range order disappears and the structure moves toward a Laves phase Mg_2Th . It appears

that additions of zirconium greatly changes the precipitation process seen in binary Mg-Th alloys.

Similarly addition of manganese to Mg-Th alloys, as in the HM series of Magnesium alloys, markedly increases the properties, producing alloys with creep properties far superior to other magnesium alloys. However, although it is known generally that additions of manganese also modify considerably the precipitation process seen in the binary Mg-Th alloys⁽⁸⁾, the details of these modifications are unknown and no systematic study of these alloys has been undertaken. The objective of this thesis is to ascertain the details of the precipitation process and hardening mechanism in an Mg-Th-Mn alloy. A Mg - 3.5 wt. % Th - 1. wt. % Mn alloy was selected for study.

The general kinetics of the precipitation process as a function of aging temperature were determined by hardness testing and the details of the precipitation process by transmission electron microscopy. The identity of the precipitates and their orientation with respect to the matrix were established by x-ray and electron diffraction.

II. EXPERIMENTAL PROCEDURE

The alloy studied in this investigation is commercially designated HM31A, and has the composition Mg - 3.5 wt. % Th - 1. wt. % Mn. Both sheet stock (1-3/4" wide by 0.01" thick) and bar stock (1-3/4" wide by 1/8" thick) were supplied by the Dow Chemical Company.

Thorium in the magnesium alloy tends to combine with hydrogen to form hydrides (ThH_2 and Th_4H_{15}) to the extent that the thorium in the alloy can be completely converted to hydrides and not available for precipitation hardening. Consequently, all heat treatments were carried out in Pyrex vials containing an atmosphere of dry argon.

The solution treatment consisted of an eight hour anneal at 590°C, terminated by a water quench. Aging treatments were carried out at 260°C, 350°C, and 400°C and were terminated by a water quench.

Hardness tests were made at room temperature immediately after quenching from the aging temperature, using the E scale of a Rockwell hardness testing machine. The average of four readings was made for each point on the hardness curve shown in Figure 1. Transmission electron microscopy on an Hitachi HU-11A electron microscope operating at 100 Kv was used to determine the precipitation process. The samples were thinned for the microscopy by the window method. Both electrolytic and chemical thinning procedures were developed

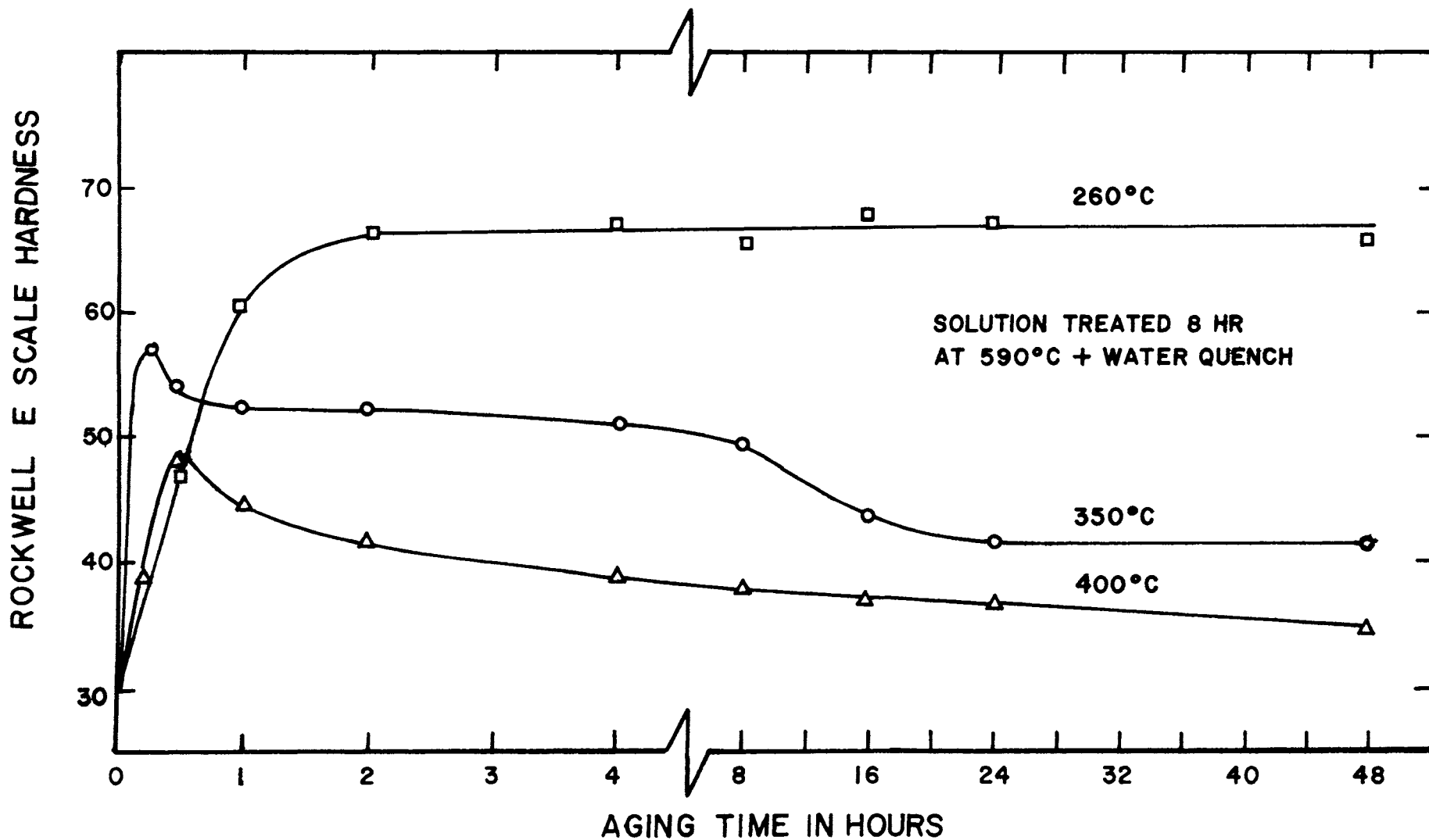


FIGURE 1: AGE HARDENING OF A Mg - 3.5 wt. % Th - 1. wt. % Mn ALLOY AS A FUNCTION OF AGING TEMPERATURE.

as outlined in the appendix. In order to shorten thinning procedure, foil was thinned first by the chemical method down to 0.001", then the electrolytic method was used to complete the thinning.

III. EXPERIMENTAL RESULTS

A. AGE HARDENING

The age hardening curves for the Mg - 3.5 wt. % Th - 1. wt. % Mn alloy are shown in Figure 1. It is seen that at 260°C, the hardness doubles, which is about the maximum hardening seen for magnesium-base alloys. Note the stability of the hardness at this temperature. During aging at 350°C, the alloy rapidly hardens and then over-ages. At 400°C aging, the peak hardness is lower, probably because of less available solute for precipitation. However, classically, the hardness peak at 400°C should lie to the left rather than to the right of the 350°C peak. The reason for this anomaly is not known since, as shown below, the precipitation process at 350°C and 400°C is the same. After 24 hours of aging, the hardness reaches a constant value for the respective aging temperatures.

B. PRECIPITATION PROCESS

First, a few overall observations on the precipitation process in the alloy follow. Only general precipitation occurs during aging between 260° and 400°C. No indication of cellular precipitation was seen. Precipitation occurs preferentially at dislocations and probably on vacancy debris. Precipitation-free regions are seen along the grain boundaries, but many of these appear to be due to local solute depletion of thorium produced by the formation of

thorium hydride in the grain boundary.

The details of the precipitation modes at each aging temperature are discussed below.

1. AGING AT 350° AND 400°C

During aging at both 350° and 400°C, disc shaped plates of Mg_4Th (gray) form first as shown in Figures 2 and 3a. The planes of these foils are near the prism plane and the disc shaped Mg_4Th plates lie parallel to these planes. The identity of generally dispersed black precipitate could not be ascertained. It may be α Mn or possibly thorium oxide. However, the generally random position and variable shape of this precipitate suggests that it is not preferentially oriented and does not play a role in the age hardening of the alloy.

The prism plane habit of the disc shaped Mg_4Th shown in Figure 3a is confirmed in Figure 3b, a diffraction pattern of the same area, showing both precipitate and matrix spots. This diffraction pattern is rotated, using appropriate calibration charts of intermediate lens current verses image rotation, to bring the spots of the diffraction pattern into the same orientation as the bright field image. Analysis (3c) shows that the plane of the foil is the prism plane $(01\bar{1}0)$ and that the (110) plane of the Mg_4Th plates lie parallel to this prism plane. The complete orientation relationship is as follows:

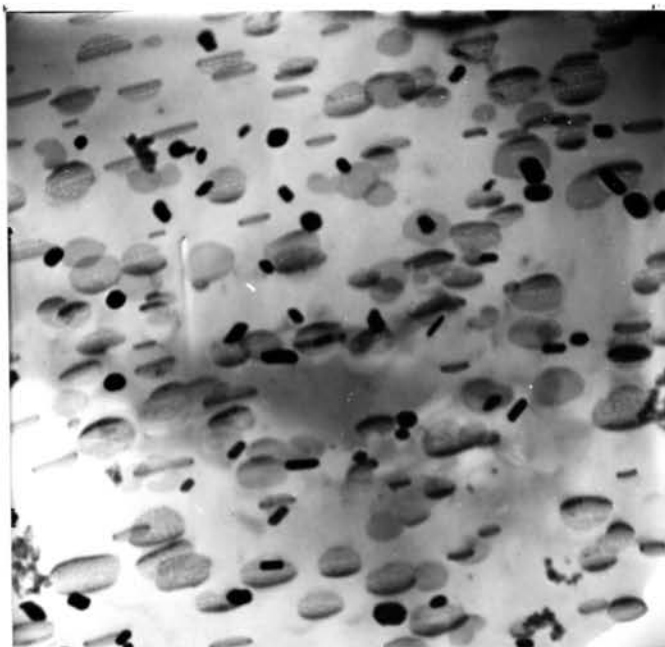


FIGURE 2: DISC SHAPED PLATES (GRAY) OF Mg_4Th FORMED DURING A 72 HOURS AGE AT $350^{\circ}C$. BLACK PRECIPITATES ARE UNIDENTIFIED. PLANE OF FOIL CLOSE TO PRISM PLANE.
X 23,000

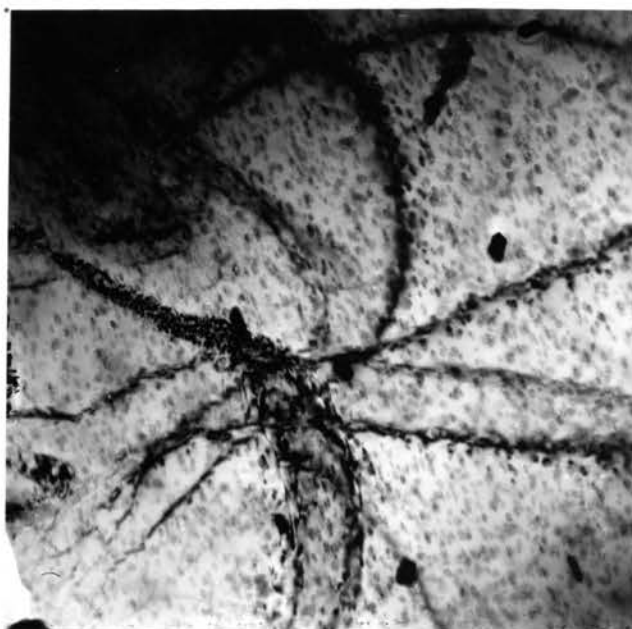


FIGURE 3a: DISC SHAPED Mg_4Th PRECIPITATES ON PRISM PLANE OF MATRIX. SOLUTION TREATMENT 8 HOURS AT $590^{\circ}C$ PLUS 15 MINUTES AGE AT $400^{\circ}C$. PLANE OF FOIL-PRISM PLANE OF MATRIX. SMALL DISC SHAPED PLATES OF Mg_4Th (GRAY), LYING IN PLANE OF FOIL. BLACK LINES ARE EXTINCTION CONTOURS.

X 21,700

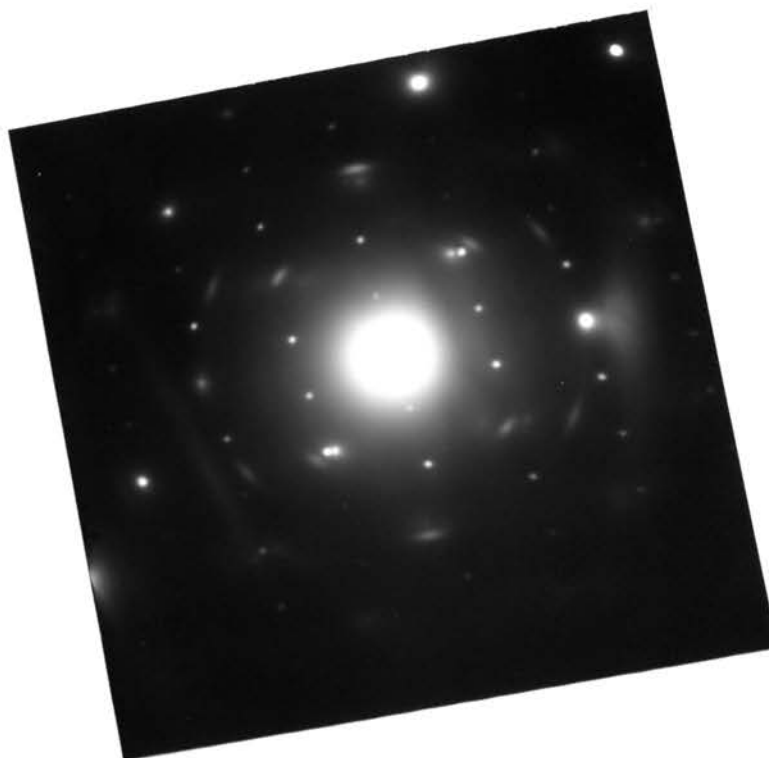


FIGURE 3b: DISC SHAPED Mg_4Th PRECIPITATES ON PRISM PLANE OF MATRIX. SOLUTION TREATMENT 8 HOURS AT $590^{\circ}C$ PLUS 15 MINUTES AGE AT $400^{\circ}C$. PLANE OF FOIL-PRISM PLANE OF MATRIX. DIFFRACTION PATTERN OF ABOVE FIELD ROTATED TO COINCIDE WITH 3a.

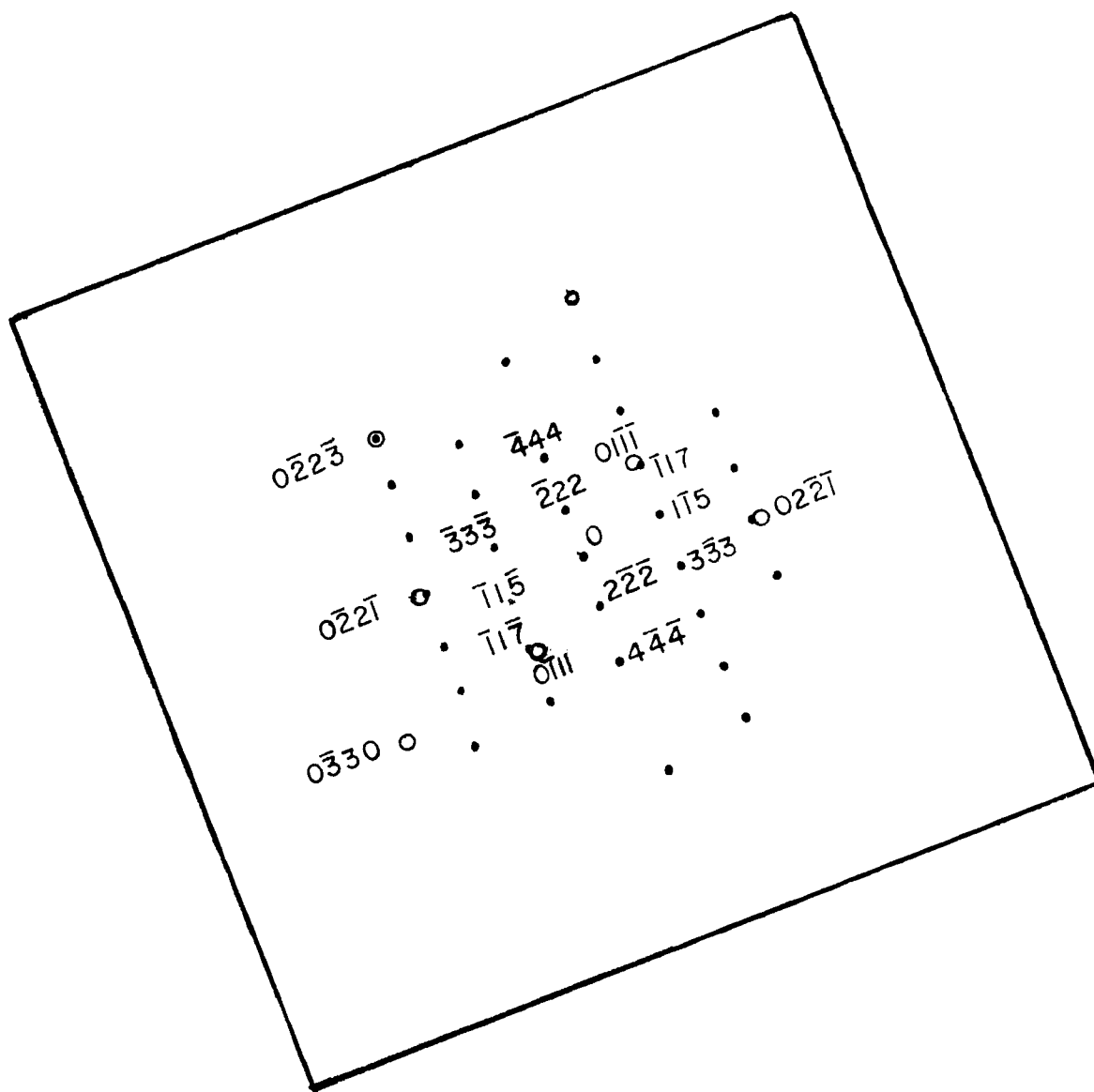


FIGURE 3c: DISC SHAPED Mg_4Th PRECIPITATES ON PRISM PLANE OF MATRIX. SOLUTION TREATMENT 8 HOURS AT $590^\circ C$ PLUS 15 MINUTES AGE AT $400^\circ C$. PLANE OF FOIL-PRISM PLANE OF MATRIX. ANALYSIS OF DIFFRACTION PATTERN: ELECTRON BEAM \perp TO $(01\bar{1}0)$ OF MATRIX AND (110) OF Mg_4Th . Mg SPOTS - OPEN CIRCLE; Mg_4Th SPOTS - SHADED CIRCLE.

$$(110)_{\text{Mg}_4\text{Th}} // (01\bar{1}0)_{\text{Matrix}}$$

$$[\bar{1}10]_{\text{Mg}_4\text{Th}} // [\bar{1}2\bar{1}0]_{\text{Matrix}}$$

The Mg_4Th plates form also parallel to the basal plane. This second orientation is illustrated in Figure 4. In 4a, the plane of the foil is parallel to the prism plane. The Mg_4Th plates are seen edgewise, and as shown by the diffraction pattern (Figure 4b) and its analysis (Figure 4c), these plates lie parallel to the basal plane. In Figure 4b, also note the streaks of the Mg in the $\langle 0002 \rangle$ direction indicative of plates lying parallel to the basal plane. Therefore the complete description of this second orientation is as follows:

$$(110)_{\text{Mg}_4\text{Th}} // (0001)_{\text{Matrix}}$$

$$[\bar{1}10]_{\text{Mg}_4\text{Th}} // [\bar{1}2\bar{1}0]_{\text{Matrix}}$$

For aging at 350° and 400°C, no G. P. zones or transition lattices were detected. Plates of Mg_4Th appear to be the sole hardening precipitate at these aging temperatures.

At 400°C, at early aging times, the Mg_4Th forms in disc shaped plates in either of the two orientations mentioned above. However, after about 8 hours of aging, the disc shaped plates elongate in the plane of the disc and in close packed direction $\langle \bar{1}2\bar{1}0 \rangle$ of the matrix forming elliptically shaped plates (Figure 5). Growth in this direction continues. Until after 48 hours of aging, the

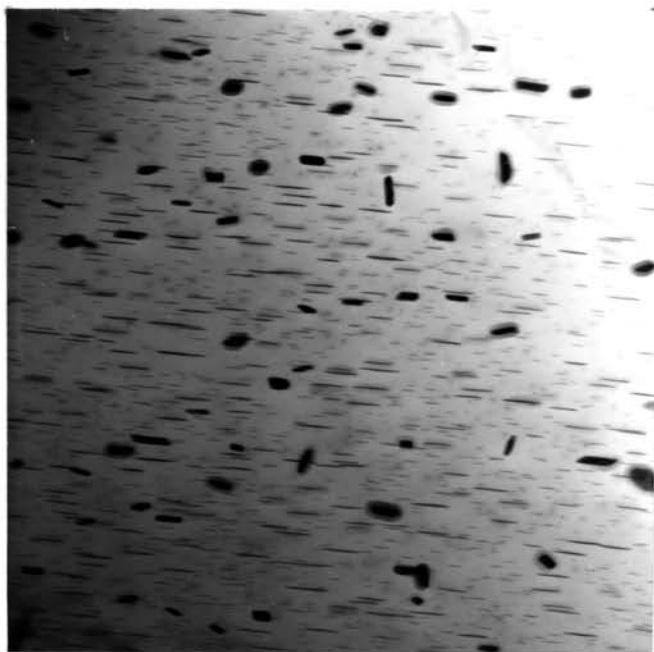


FIGURE 4a: Mg_4Th PLATES LYING ON BASAL PLANE OF MATRIX.
SOLUTION TREATMENT PLUS 24 HOUR AGE AT $350^{\circ}C$.
PLANE OF FOIL-PRISM PLANE OF MATRIX. Mg_4Th
PLATES PARALLEL TO BASAL PLANE ARE SEEN IN
CROSS-SECTION. BLACK PRECIPITATE COULD NOT
BE IDENTIFIED.

X 22,400

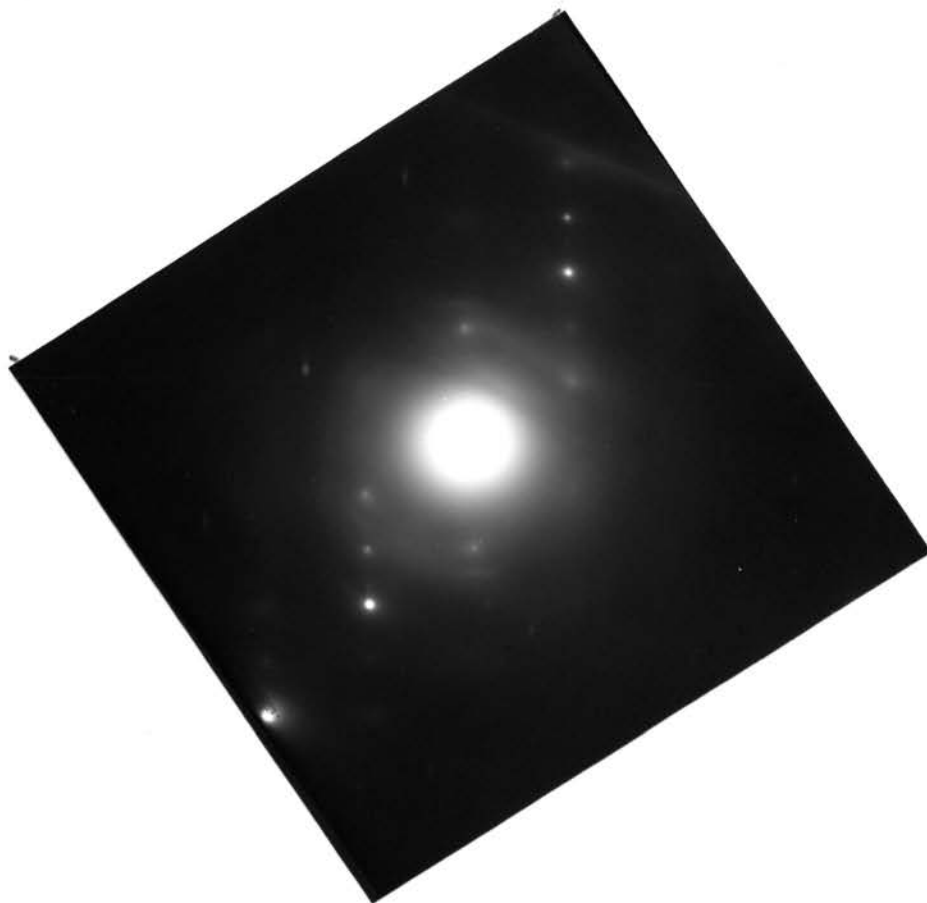


FIGURE 4b: Mg_4Th PLATES LYING ON BASAL PLANE OF MATRIX. SOLUTION TREATMENT PLUS 24 HOUR AGE AT $350^\circ C$. PLANE OF FOIL-PRISM PLANE OF MATRIX. DIFFRACTION PATTERN OF ABOVE FIELD ROTATED TO BRING INTO CONCIDENCE WITH 4a. AS SHOWN BY 4c, FOIL SURFACE IS NEAR PRISM PLANE $(01\bar{1}0)$ OF MATRIX. NOTE STREAKS IN $[0002]$ INDICATING PLATES LIE PERPENDICULAR TO BASAL PLANE.

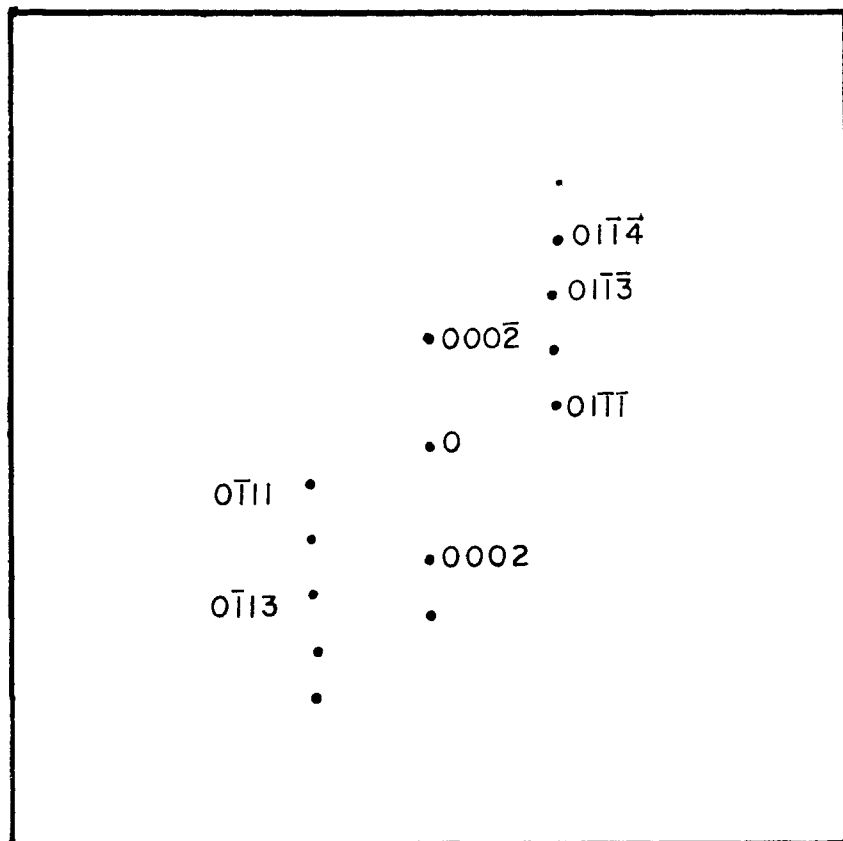


FIGURE 4c: Mg_4Th PLATES LYING ON BASAL PLANE OF MATRIX.
 SOLUTION TREATMENT PLUS 24 HOUR AGE AT $350^\circ C$.
 PLANE OF FOIL-PRISM PLANE OF MATRIX. ANALYSIS
 OF DIFFRACTION PATTERN SHOWING MATRIX SPOTS.

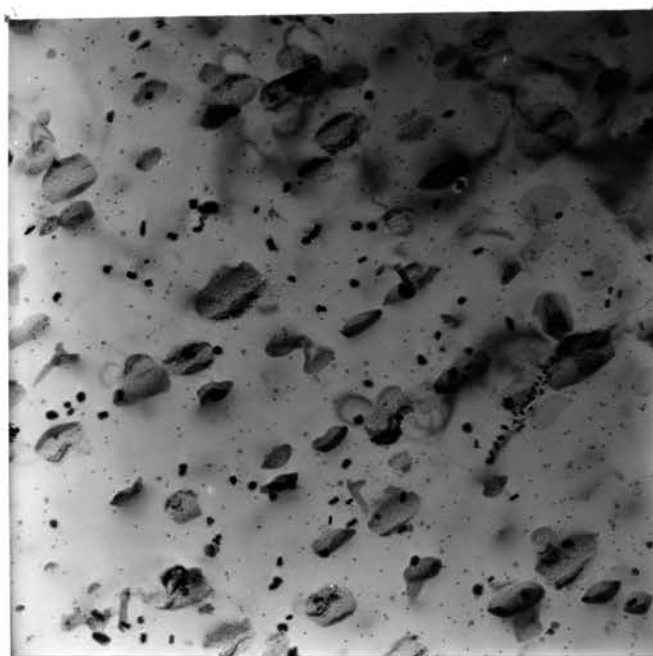


FIGURE 5. ELLIPTICALLY SHAPED Mg_4Th PRECIPITATES, AGING
8 HOURS AT $400^{\circ}C$. PLANE OF FOIL-NEAR PRISM
PLANE OF MATRIX.
X 22,600

elliptical plates are changed into laths parallel to the close packed direction of the matrix as shown in Figure 6. The length to width ratio of these laths can go as high as 40.

2. AGING AT 260°C

Two types of precipitate form during aging at this temperature (Figure 7). A general dispersion of black idiomorphs is seen throughout the grain. Although electron diffraction revealed some weak diffraction spots suggestive of the presence of the FCC transition lattice Mg_2Th reported by Sturkey⁽⁵⁾, conclusive identification was not possible. However, it was established that these precipitates are not thorium hydrides or the equilibrium precipitates Mg_4Th . The second type of precipitate is seen by the fine contrast in the matrix, producing an almost rough texture appearance. This effect, also seen in aluminum alloys with the formation of G. P. zones, suggests that the high hardness produced by the 260°C aging of this alloy, is produced by a fine dispersion of G. P. zones. Note that near the larger black precipitates, the texture appearance disappears similar to the interaction between transition lattice and G. P. zones seen in aluminum alloys. Unfortunately, attempts to identify the nature of the precipitates producing these effects by x-ray and electron diffraction were not successful. Positive identification is left for future study.



FIGURE 6: LONG THIN LATH SHAPED PLATES OF Mg_4Th GROWING IN $\langle 1\bar{2}10 \rangle$ CLOSE PACKED DIRECTION.

NOTE: (a) DISLOCATION BOWING BETWEEN PLATES
(b) DISLOCATION NETWORK IN LOWER LEFT
OF PICTURE. SOLUTION TREATMENT PLUS
48 HOURS AGE AT $400^\circ C$ PLUS HAMMER
PEENED. PLANE OF FOIL-NEAR PRISM
PLANE.

X 22,600

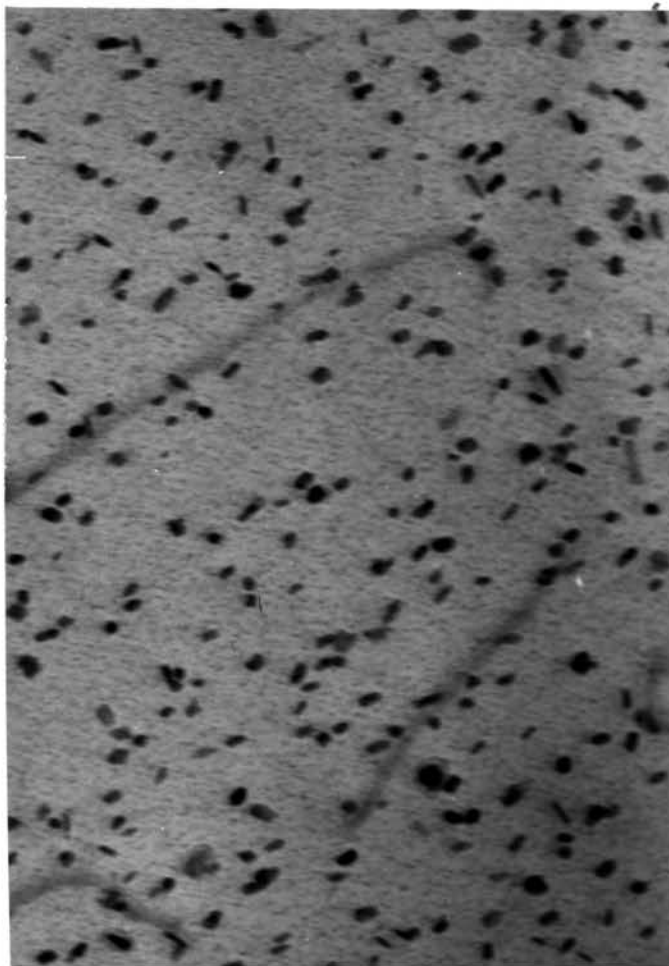


FIGURE 7: DISPERSION OF PRECIPITATION PRODUCED BY AGING
95 HOURS AT 260°C. BLACK PRECIPITATE IS UNIDENTI-
FIED, MAY BE α Mn, THORIUM OXIDE, OR Mn-Th COM-
POUNDS. NOTE THE VERY FINE TEXTURE ON THE MATRIX
INDICATIVE OF A G. P. ZONE TYPE OF PRECIPITATION.
X 35,900

3. EFFECT OF PRIOR COLD WORK ON THE PRECIPITATION PROCESS

Cold work after solution treatment and before aging definitely increases the rate of precipitation. Mg_4Th plates nucleate preferentially on dislocations. Attempts to document the nucleation on dislocation were not successful as the dislocations tended to be out of contrast. However, indirect evidence is available. Figure 8a shows a $10\bar{1}2$ twin in a specimen solution treated, hammer peened, followed by a 25 hour age at $350^\circ C$. Note the heavy dispersion of the fine light gray Mg_4Th plates inside the twin. These twins are filled with dislocations as a result of the shearing action during formation. Toward the right side of the twin, the dislocation network is seen faintly. This fine dislocation network appears to generate the finer dispersion of Mg_4Th plates seen inside the twin.

An area away from a twin in a specimen is seen in Figure 8b. Here the dislocation network is quite coarse. Nucleation occurs on dislocations at early aging times. Growth depletes the surrounding matrix, producing the coarse dispersion of Mg_4Th plates. These heterogeneous nucleation sites evidently tend to destroy the need for epitaxial growth of the precipitate since in most cases, globular rather than plate-like growth of Mg_4Th occurs when dislocations are introduced prior to aging.

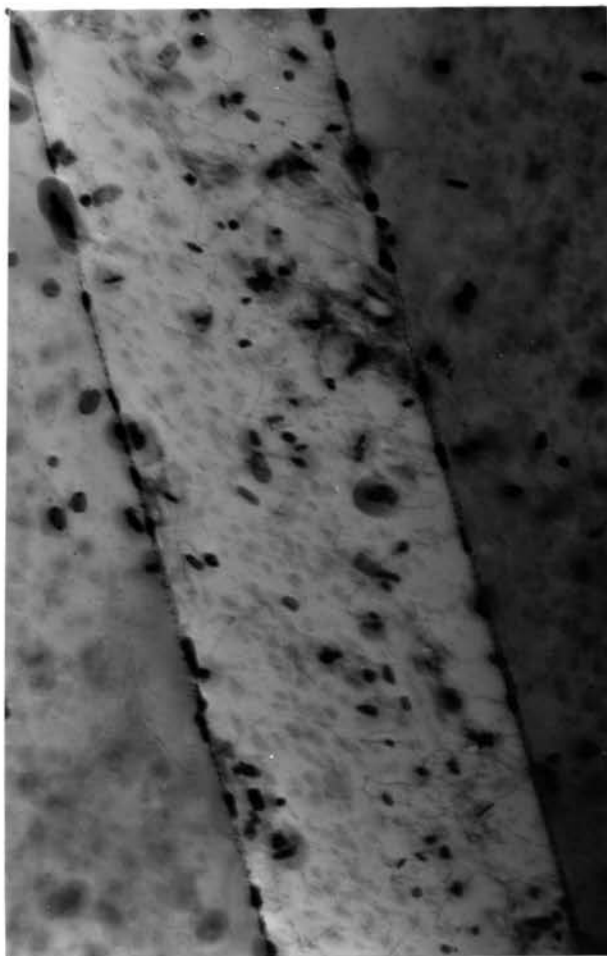


FIGURE 8a: EFFECT OF COLD WORK PRIOR TO AGING. NOTE THE FINER DISPERSION OF Mg_4Th PLATES (LIGHT GRAY) IN THE $10\bar{1}2$ TWIN. PART OF THE DISLOCATION NETWORK INSIDE THE TWIN IS SEEN FAINTLY. SOLUTION TREATMENT PLUS HAMMER PEENED, FOLLOWED BY 4 HOUR AGE AT $350^\circ C$.

X 29,400

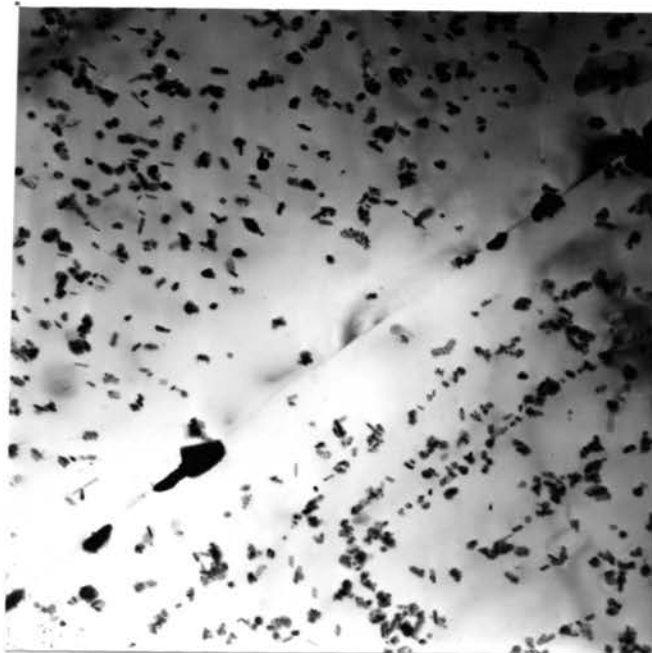


FIGURE 8b: EFFECT OF COLD WORK PRIOR TO AGING. COARSE GLOBULAR DISPERSION OF Mg_4Th PRODUCED BY NUCLEATION ON COARSE DISLOCATION NETWORK. NOTE ALSO PRECIPITATE-FREE REGION ADJACENT TO THE GRAIN BOUNDARY PRODUCED BY SOLUTE DEPLETION DUE TO HYDRIDE PRECIPITATION IN THE GRAIN BOUNDARY. SOLUTION TREATMENT PLUS HAMMER PEENED, FOLLOWED BY 24 HOUR AGE AT $350^{\circ}C$.

X 22,400

4. PRECIPITATE-FREE REGION AT GRAIN BOUNDARIES

In Figure 8b, precipitate-free region is seen. In this case, there is a heavy precipitation of hydride along the boundary, which has depleted the adjacent region of thorium producing the Mg_4Th free regions. However, narrow but definite precipitate-free regions are seen along boundaries containing no hydride precipitate. These regions can be produced by either solute depletion, from heavy grain boundary precipitation or vacancy depletion during the solution treatment quench⁽⁹⁾. In the latter mechanism, the vacancy depletion results in elimination of loops and other vacancy debris necessary for nucleation of the precipitate thereby producing a solute rich, but precipitate-free, region adjacent to the grain boundary. In this study, the vacancy depletion mechanism probably produces the precipitate-free region adjacent to hydride-free boundaries.

C. THE HARDENING MECHANISM

Basal slip and $10\bar{1}2$ twinning are the principal deformation modes in magnesium. Reed-Hill and Robertson⁽¹⁰⁾ also found prismatic slip which might produce a mechanism for cross slip in magnesium. Both prismatic slip and cross slip appear to be relatively rare in magnesium alloys. Of interest in this study is the precipitate interaction with the two main deformation modes.

1. TWIN-PRECIPITATE INTERACTION

In Figure 9, the interaction of disc shaped precipitates of Mg_4Th and a $10\bar{1}2$ twin are seen. Careful examination of plates lying across the twin boundary shows an offset indicative of shearing of the plate as the twin advances. Similar type shearing by $10\bar{1}2$ twin was seen for the transition lattice in Mg-Zn alloys⁽¹⁾. Whether these twins would shear the Mg_4Th when in the form of long rods was not determined but it appears likely. Heavy precipitation of Mg_4Th laths tended to reduce twin formation upon subsequent deformation.

2. DISLOCATION-PRECIPITATE INTERACTION

In all cases, the dislocations bowed between, rather than cut the Mg_4Th precipitate whether in disc shaped or lath-like morphology. Evidently the interparticle spacing is always large enough that the dislocation can by-pass the particles by bowing and are not required to cut the precipitate. In Figure 6, the existence of dislocation networks between the rods can be seen. It appears that bowing of dislocations between the precipitate produces dislocation tangles similar to those seen in Mg-Al alloys⁽³⁾.

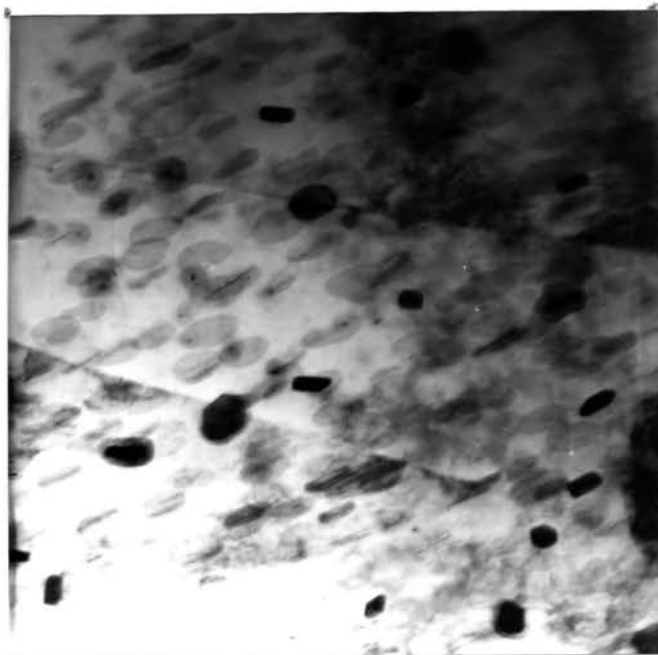


FIGURE 9: TWIN-PRECIPIRATE INTERACTION. DISC-SHAPED PRECIPITATES OF Mg_4Th APPARENTLY SHEARED BY $10\bar{1}2$ TWIN. SOLUTION TREATMENT PLUS 48 HOUR AGE AT $350^\circ C$, THEN HAMMER PEENED.

X 16,700

IV. DISCUSSION

In this investigation, no transition lattice of the Mg_4Th phase was seen, as was reported in Mg-Th-Zr alloys⁽⁵⁾. Roberts⁽¹¹⁾ suggested that the absence of a transition lattice of the Mg_4Th phase in Mg-Th-Mn alloys was due to the prior precipitation of a fine dispersion of α -Mn or Mn-Th intermetallic phases which provide sites for direct nucleation of equilibrium Mg_4Th . This hypothesis seems unlikely for two reasons. First, although in all cases, a dispersion of an unidentified black phase, which could be one of the phases mentioned above was seen; this dispersion was several orders of magnitude coarser than that of Mg_4Th precipitate. Secondly, the Mg_4Th phase was always seen as plates or rods with a definite habit plane and orientation relationship to the matrix, whereas the black precipitate is generally globular with no apparent habit plane. A phase nucleating on this black precipitate would have an equally random habit. Therefore, it appears that the Mg_4Th nucleates on dislocations and other imperfections in the magnesium solid solution matrix rather than on these dispersions.

Although no transition lattice was found, the definite orientation relationship and the rigidly confined growth of the disc shaped plates to produce the long laths indicate a definite lattice matching between planes in the precipitate and those of the matrix and suggests that in the initial stages of nucleation, a transition lattice of Mg_4Th , possibly

the Mg_2Th lattice seen in Mg-Th-Zr alloys⁽⁵⁾, may exist. However, with a small amount of growth, the lattice evidently transforms to the equilibrium Mg_4Th phase. Even though with this transformation the interface boundary between the Mg_4Th precipitate and the matrix may become semi-coherent or even incoherent, some epitaxial relationship must still remain as shown by the generation of long rods only in unique directions, i.e., that of closest packing in matrix. This system is similar to the Mg-Al system in which the equilibrium phase $Mg_{17}Al_{12}$ has a definite orientation relationship without the apparent presence of a transition lattice⁽³⁾.

The existence of two orientations of a precipitate is seen in other magnesium-base alloys. For example in Mg-Zn alloys, Clark⁽¹⁾ found the $MgZn'$, a transition lattice, formed parallel to the prism plane at age hardening temperatures, whereas Gallot⁽¹²⁾ found that $MgZn'$ also formed parallel to the basal plane at higher aging temperatures. In the Mg-Th-Mn alloy, evidently both habits are possible at 350° and 400°C aging temperatures. One can conclude that atom spacing on the (110) plane of the Mg_4Th phase is such that it will match the prism and basal planes of the matrix almost equally well. Even in these planes, however, the fit must not be good as evidenced by the early loss of coherency. Although the Mg_4Th phase may be generally described as an FCC lattice, the structure type is extremely complex, apparently isomorphous with Th_6Mn_{23} as analyzed by Florio, et al.⁽⁶⁾. The unit cell is very large, $a_0 = 14.37 \text{ \AA}$, and

has 116 atoms⁽⁵⁾. Attempts were made to calculate disregistries between Mg_4Th plates and matrix in the two orientations. Matching of unit cell dimensions in the two orientations indicated a disregistry of about 5% which is about right for matching to occur initially with nucleation followed by loss of coherency with slight amount of growth. However, matching the actual planes of atoms in the two structures was not possible because of the complexity of the Mg_4Th structure. Thus attempts to explain the dual orientation relationship on the basis of disregistry arguments were not successful.

As mentioned above, the growth of the Mg_4Th laths with a length to width ratio of 40 or more from initially disc shaped plates is a direct result of atom matching across the habit planes. The interface on the habit plane of disc is a dislocation or ordered interface. Thus this interface can only advance by synchronous climb of the dislocations, whereas the edge interfaces of the discs are disordered and therefore may move easily. Thus with growth, the constraints of the ordered interfaces and ease of movement of the disordered interfaces, first change the initial disc shape to that of an ellipse and then to an elongated plate. Once the plate morphology forms, further lengthening of the plate is aided by the point effect of diffusion. Thus a long lath-shaped precipitate is formed.

Since the Mg_4Th precipitate may lie parallel or perpendicular to the basal plane, the type of precipitate-deformation interaction depends on the precipitate orientation. Precipitates

which lie perpendicular to the basal plane, are oriented efficiently to block basal slip. Those parallel to the basal plane can block twinning. Unfortunately, as in other magnesium alloys, the interparticle spacing is too large to block other forms of deformation efficiently.

However, since Mg_4Th does nucleate on dislocations, possibly cold work prior to aging will produce small interparticle spacing which will require cutting of the precipitate for dislocation motion resulting in higher strength properties. This should be investigated in the future.

The precipitation process and deformation characteristics of several magnesium-base alloys are shown in Table I. The precipitate-dislocation in Mg-Th-Mn alloys is similar to that in Mg-Zn alloys⁽¹⁾. Dislocations bow between widely spaced lath shaped precipitates, though in Mg-Th-Mn alloys, the precipitates are an equilibrium phase and not a transition lattice as in the Mg-Zn alloys. Twin-precipitate interaction in Mg-Th-Mn alloys, however, is similar to that observed in Mg-Al alloys and Mg-Zn alloys. Precipitate is sheared by $10\bar{1}2$ twins as in Mg-Zn alloys; but also the presence of long laths of Mg_4Th precipitate tends to inhibit twin growth as in Mg-Al alloys⁽³⁾.

TABLE I

COMPARISON OF PRECIPITATION AND DEFORMATION
CHARACTERISTICS OF MAGNESIUM BASE ALLOYS

	HARDENING PRECIPITATES	SLIP- PRECIPITATES INTERACTION	TWIN- PRECIPITATES INTERACTION
Mg-Al	Equilibrium Phase $Mg_{17}Al_{12}$	Cross Slip & Tangling of Dislocation	$10\bar{1}2$ Twins Suppressed
Mg-Zn	Transition Lattice $MgZn'$	Bowing	$10\bar{1}2$ Twins Shearing
Mg-Th-Zr	Transition Precipitates Mg_2Th	Shearing	
	Equilibrium Phase Mg_4Th	Bowing	
Mg-Th-Mn	Equilibrium Phase Mg_4Th		
	(Disc shaped)	Bowing	Shearing
	(Long Laths)	Bowing	$10\bar{1}2$ Twins Formation Hindered

V. CONCLUSION

The precipitation process and hardening mechanism involving the precipitation of Mg_4Th phase during aging at 350° and 400°C have been established. Although this phase has interesting precipitation characteristics, the interparticle spacing of this phase is just too large to produce good age hardening properties.

Further studies should be directed at determining the details of the G. P. type precipitate produced at 260°C, especially since the fine spacing of this precipitate produced significantly greater hardness. A knowledge of the precipitation processes and hardening mechanism at lower aging temperature might suggest methods to produce better alloy properties.

REFERENCES

1. J. B. Clark, *Acta Met.* 13, 1281 (1965).
2. L. Sturkey and J. B. Clark, *J. Inst. Metals* 88, 177 (1959-60).
3. J. B. Clark, *Acta Met* 16, 141 (1968).
4. Y. Murakami, O. Kawano and H. Tumara, *Memories Fac. of Engr., Kayoto Univ.* 24, p. 411 (1962).
5. L. Sturkey, *Trans. AIME* 218 p. 466 (1960).
6. J. V. Florio, R. E. Rundle and A. I. Snow, *Acta Cryst.* vol. 5, p. 449 (1952).
7. J. N. Mushovic and N. S. Stoloff, *Proceedings of the International Conference on the Strength of Metals and Alloys, Tokyo*, p. 360 (1967).
8. L. Sturkey, unpublished research, Dow Chemical Co..
9. J. B. Clark, *Acta Met.* 12, p. 1197 (1964).
10. R. E. Reed-Hill and W. D. Robertson, *Trans. Am. Inst. Min. Engrs.*, 209, p. 496 (1957).
11. C. Sheldon Roberts "Magnesium and Its Alloy" John Wiley & Sons, Inc., p. 124 (1958).
12. J. Gallot "Contribution to the Study of Precipitation Phenomena in Magnesium - 6% Zinc Alloy" Thesis, Faculty of Science, University of Rouen, Rouen, France (1966).

APPENDIX

PREPARATION OF THIN FOILS OF Mg - 3.5 wt. % Th -

1. wt. % Mn ALLOY BY THE WINDOW METHOD

A. CHEMICAL THINNING PROCEDURE

Solution: 1/3 by volume HNO₃ (Conc.)

2/3 by volume Methyl Alcohol (abs.)

Rinse Solution: Pure ethyl alcohol

Temperature: Room temperature

Procedure: The thinning solution is maintained in constant agitation by a magnetic stirrer. The specimen is immersed in the swirling thinning solution for about ten minutes until small holes begin to appear in the foil. Then the foil is rinsed in ethyl alcohol and dried. The foil is then masked for electrolytic thinning.

B. ELECTRO-THINNING PROCEDURE

1. Electrolyte: 85% ortho-phosphoric acid H₃PO₄.

Agitated by magnetic stirrer in stainless steel beaker.

2. Dip Solution: 20 g of citric acid (anhydrous) dissolved in 500 ml pure ethyl alcohol.

3. Wash solution (a): Pure ethyl alcohol agitated
by magnetical stirrer.

Wash solution (b): Pure ethyl alcohol.

4. Cathode: Stainless steel beaker
5. Voltage: 15-20 volts at 1-2 amp.
6. Temperature: 20°-30°C
7. Procedure: With the voltage on, the masked foil is immersed into swirling thinning solution (1). When a thin edge has been prepared, the foil is quickly removed and rinsed in wash solution (3a). Until the frothy form of the phosphoric attack has completely subsided. Then the foil is agitated in the dip solution (2) for 3 to 5 seconds and quickly transferred the foil to the wash solution (3b) for a final rinse. Dry the foil between sheets of lintless tissue.

VITA

Adolf Chun-Chiung Huang was born on September 21, 1941, in Taipei, China. He enrolled in Cheng Kung University, Taina, Taiwan, in 1960 and graduated in 1964 with the degree of Bachelor of Science in Metallurgical Engineering.

He has been enrolled in the Graduate School of The University of Missouri-Rolla since September, 1967.

1967