Precipitation Process in a Mg-Ce Alloy*

By Goro Omori**, Shigeru Matsuo** and Hiroshi Asada***

The aging characteristics of quenched Mg-1.3 wt%Ce alloy were studied by electron microscopy and hardness measurements. On isothermal aging at 150°C, precipitates occurred first on the grain boundaries and dislocations, followed by precipitation within grains. At an early stage of aging at temperatures higher than 200°C, precipitation on the grain boundaries and dislocations, and within grains took place simultaneously. The diffraction effect observed in the present experiment suggests that the precipitates formed and dispersed uniformly within the matrix at an early stage of aging were to be of an intermediate phase in which cerium atoms might be enriched on (10 $\bar{1}$ 0) planes of the matrix. In a later stage of aging, the precipitates transformed into the equilibrium hexagonal phase of β , ribbon shaped, with the following orientation relationship with the matrix:

$$(0001)_M \langle 11\bar{2}0 \rangle_M // (0001)_P \langle 10\bar{1}0 \rangle_P, \quad c_M \approx c_P, \quad 3d_{\{11\bar{2}0\}_M} \lesssim d_{\{10\bar{1}0\}_P}.$$

The ribbon shaped precipitates grew predominantly in the direction of $\langle 0001 \rangle$, and, to a much lesser extent, in the direction of $\langle 11\bar{2}0 \rangle$ of the matrix. Significant age hardening observed in the present alloy should be associated with the precipitation of fine particles dispersed uniformly in the matrix. A certain amount of the intermediate precipitates appeared to remain even in a stage where the maximum hardness was attained. An activation energy for the age hardening process was determined to be 30 kcal/mol.

(Received March 11, 1974)

I. Introduction

It has generally been recognized that a magnesium alloy containing about 3% rare earth metals exhibits high strength and creep resistance at elevated temperatures⁽¹⁾⁽²⁾. The partial phase diagram of the Mg-Ce system determined by Haughton and Schofield⁽³⁾ and Weibke and Schmidt⁽⁴⁾ is shown in Fig. 1. According to Haughton and Schofield, the maximum solid solubility of cerium in magnesium is 1.6 wt% at 590°C and it decreases with decrease in temperature. Therefore, the precipitation from super-saturated solid solution is expected to occur. The aging characteristics of Mg-0.2wt%Ce alloy, which exhibited the best workability in this system⁽⁵⁾, were reported previously by the present authors⁽⁶⁾. Some investigations on the precipitation process of this system were also made by Morozumi⁽⁷⁾,

Fig. 1 Magnesium-rich region of the Mg-Ce phase diagram. — by Haughton and ---- by Weibke.

Sturkey⁽⁸⁾ and others. However, the precipitation process in this system has not been well known because of scarcity of electron microscopic observations. In the present investigation, the precipitation phenomena in Mg-Ce alloy, being fundamental of magnesium rare-earth metal alloys, were studied by means of the electron microscopy and hardness measurements.

* This paper was originally published in Japanese in J. Japan Inst. Metals, 36 (1972), 1002.

** National Research Institute for Metals, Meguro-ku, Tokyo 153, Japan.

*** Faculty of Science and Engineering, Nihon University, Chiba, Japan.

II. Experimental

1. Sample preparation

The chemical composition of the alloy used in this work is shown in Table 1. The alloy was prepared by a conventional melting procedure on a laboratory scale. The purity of the starting material was 99.9% or above for magnesium and 99.4% for cerium metals. About 1 kg of magnesium was melted in a mild steel crucible with a flux of Dow No. 311*. The desired amount of cerium was then added to molten magnesium. After being kept at 700°C for 10 min, the melt was cast into a permanent mould and a billet of 75 mm in diameter was obtained. The surface of the billet was scraped for removing defects and the billet was then extruded to 20 mm dia. rod by a 500 ton indirection extrusion press using 75 mm container. Conditions of the extrusion process were; billet pre-heating at 480°C for 20 hr in SO₂ atmosphere, container temperature 400°C, and reduction ratio 14:1. The rod was reduced further by a combination of hot and cold rolling. The ultimate size of specimens was 15 × 15 mm with 0.5 mm thickness for electron microscopy and 10 × 10 ~ 50 mm with 3 mm thickness for the hardness test.

2. Experimental procedure

The solution treatment was made by heating the alloy for 6 hr at 560°C in an argon atmosphere followed by water quenching. As quenched specimens were almost free from precipitation. The specimens were rapidly heated to the aging temperature. Aging at temperatures lower than 200°C was carried out by immersing the alloy into a silicone oil bath

and the aging at higher temperatures was made in a furnace in the argon atmosphere to prevent oxidation. Hardness was measured by a micro-Vickers hardness tester using a 500 g load, each value being the average of at least 5 measurements. Aged specimens were thinned by a modified window method in a solution of 5 parts of ethyl alcohol and 3 parts of phosphoric acid kept at 5°C. A stainless steel cathode was used. The applied voltage was 6 V for the first 30 sec and then lowered to 3 V. The current density was 0.01 A/cm². Thinned specimens were rinsed in pure methanol, dried quickly by filter paper and then observed immediately by an electron microscope.

III. Experimental Results

1. Isochronal aging

A preliminary survey of hardening process in the quenched Mg-1.3wt%Ce alloy was carried out by isochronal aging. Figure 2 shows a hardness-temperature curve obtained from specimens aged for 1 hr at each temperature. The hardening occurred gradually up to about 175°C followed by rapid hardening in a tem-

Fig. 2 Change in hardness on isochronal annealing of quenched Mg-1.3 wt%Ce alloy.

* Dow No. 311 (KCl; 30.5, MgCl₂; 29, BaCl₂; 8.5, CaF₂; 10.5, MgO; 11.5 wt%).

Table 1 Chemical composition of specimen.

Specimen	Nominal composition Ce(wt%)	Result of analysis (wt%)				
		Ce	Al	Fe	Cu	Si
Mg-1.3Ce	1.60	1.30	0.02	0.014	0.006	0.005

Fig. 3 Isothermal aging curves for the alloy after solution treatment.

perature range from about 200 to 250°C, leading to the maximum hardness. Above 250°C, softening took place.

2. Isothermal aging

It has been reported that the age-hardening of magnesium alloys, in general, becomes noticeable only when the alloys are aged at temperatures higher than 150°C. From Fig. 2, it appears that the same is the case for the present alloy. Therefore, the isothermal aging was carried out at temperatures higher than 150°C. Figure 3 shows isothermal age hardening curves at 150, 200 and 250°C. With an increase of aging temperature, the rate of hardening in initial stage increased, but the maximum hardness decreased. The times required to reach the maximum hardness were 3, 20 and 700 hr for aging at 250, 200 and 150°C, respectively.

3. Observation of microstructure

The structural change associated with aging was studied by electron microscopy. A typical microstructure of the alloy aged for 50 min at 150°C after quenching is shown in Photo. 1. The preferential precipitation of the β phase on grain boundaries and dislocations was apparent. Because of the anisotropy in thermal expansion of the hexagonal matrix, there would be a possibility of introducing a number of dislocations during quenching⁽⁹⁾. Although grain boundaries and dislocations were smooth initially but afterwards they became irregular in form due to strains caused by precipitation. As can be seen

Photo. 1 Precipitates on grain boundaries and dislocations observed in Mg-1.3 wt%Ce alloy aged for 50 min at 150°C.

from Fig. 3, the precipitates shown in Photo. 1 do not give any hardening effect on the alloy. The microstructures responsible for hardening are shown in Photos. 2 and 3. Photograph 2 shows the microstructure of the matrix at an initial stage of aging, together with a schematic

Photo. 2 Fine precipitates with diffraction contrast due probably to coherency strain observed in the alloy aged for 5 hr at 200°C. The diffraction pattern was taken from a foil with a matrix zone axis of $\langle 2423 \rangle$. Notice the streaks passing through matrix spots and between them, in the direction of $\langle 1010 \rangle$ of the matrix.

Photo. 3 Precipitates observed in the alloy aged for 16 hr at 200°C. Diffraction pattern was taken from a foil with a matrix zone axis of $\langle 01\bar{1}1 \rangle$. The streaks passing through the matrix spots were observed.

diagram of its electron diffraction pattern. In the pattern, streaks were observed in the direction of $\langle 10\bar{1}0 \rangle$ of the matrix, passing through matrix spots and also midway between them. It was tentatively assumed that a segregation of cerium atoms or precipitation of small dimension of thin platelets occurred on the $(10\bar{1}0)$ plane of the matrix, causing the streaks of the type observed.

The microstructure at maximum hardness is shown in Photo. 3. The fine precipitates were uniformly dispersed in the matrix. In the diffraction pattern taken at this stage, the streaks mentioned above were still observed. Therefore, it was obvious that all the intermediate precipitates did not disappear completely.

Photograph 4 shows a microstructure of the alloy over-aged for 15 hr at 240°C. The precipitates of ribbon shape were apparently arranged along the direction of $\langle 0001 \rangle$ of the matrix (Photo. 4(b)). The growth of precipitates will be discussed later. A precipitate-free region was observed along the grain boundary (Photo. 4(a)), suggesting the participation of vacancies

Photo. 4 Precipitate free region along grain boundary (a), and ribbon shaped precipitates (b), observed in the alloy aged for 15 hr at 240°C. Diffraction pattern was taken from a foil with a matrix zone axis of $\langle 01\bar{1}1 \rangle$.

in the nucleation of precipitates. Photograph 5 shows the electron diffraction patterns and their schematic diagrams for the alloy aged for 15 hr at 250°C.

Photograph 5(a) and (b) were taken from aged specimens with foil planes parallel to the matrix planes of (0001) and $(10\bar{1}0)$, respectively. The indices of diffraction spots are shown in the schematic diagrams in terms of hexagonal structure. The orientation relationship between the matrix and precipitates was found to be $(0001)_M \parallel (11\bar{2}0)_P // (0001)_P \parallel (10\bar{1}0)_P$, $c_M \approx c_P$, $3d_{(11\bar{2}0)_M} \lesssim d_{(10\bar{1}0)_P}$.

Photo. 5 Diffraction patterns taken from specimens aged for 15 hr at 250°C. Matrix zone axes $\langle 0001 \rangle$ for (a) and $\langle 01\bar{1}0 \rangle$ for (b), respectively: $\bullet$: matrix reflections, $\circ$: precipitate reflections.

Photograph 6 shows the microstructure of the alloy aged for 18 hr at 250°C. It was observed from a direction perpendicular to the $(11\bar{2}0)$ plane of the matrix. The precipitates were lengthened in the direction of $\langle 0001 \rangle$ of the matrix, and the diffraction effect due to coherency strain was observed around the planes of ribbon shaped precipitates.

Photograph 7 shows the microstructure of the alloy aged for 18 hr at 250°C. The foil plane was parallel to the (0001) plane of the matrix. Here, the precipitates appeared to be lengthened in the direction of $\langle 11\bar{2}0 \rangle$ of the matrix, though the extent of lengthening was much less than that shown in Photo. 6. In addition, tangled dislocations were observed around some of them.

From Photos. 4, 6 and 7, it was concluded that the precipitates of a ribbon shape, probably of the equilibrium phase, grew predominantly in the direction of $\langle 0001 \rangle$, and to a much lesser extent, in the direction of $\langle 11\bar{2}0 \rangle$ of the matrix.

IV. Discussion

For commercial magnesium alloys containing rare-earth metals such as EK30A* and EK41A**, the solution heat treatment is usually performed for 18 hr at 570°C, at maximum, followed by water quenching, and artificial aging is carried out at 205°C for 16 hr⁽⁸⁾. In the present experiment, the time required to reach the maximum hardness in the case of aging at 200°C was 20 hr as shown in Fig. 3, which was close to that expected from the above specifications.

A semi-logarithmic plot of hardening rates against the reciprocals of absolute temperatures, i.e. $\log 1/t$ vs $1/T^\circ\text{K}^{-1}$ where t is the time to reach the maximum hardness, yields a straight line as shown in Fig. 4. An apparent activation energy for age hardening process obtained

* EK30A Zn 0.3, Zr 0.2, R.E. 2.5~4.4.

** EK41A Zn 0.3, Zr 0.4~1.0, R.E. 3.0~5.0.

Photo. 6 Ribbon shaped precipitates elongated in the direction of $\langle 0001 \rangle$ of the matrix observed in the alloy aged for 18 hr at 250°C . Coherency strain was observed around the precipitates. Foil normal; $\langle 2\bar{1}10 \rangle$.

Photo. 7 Precipitates laid along $\langle 1120 \rangle$ direction of the matrix observed in the alloy aged for 18 hr at 250°C . Tangled dislocations were observed around the precipitates. Foil normal; $\langle 0001 \rangle$. Arrows show the directions of reciprocal lattice.

from the slope of the straight line was about 30 kcal/mol and it was in reasonably good agreement with the activation energy for self diffusion of magnesium⁽⁸⁾.

At lower aging temperatures, e.g. 150°C , the precipitates appeared first along grain boundaries and dislocations, and the precipitation

Fig. 4 Plots of $\log 1/t$ vs $1/T$ derived from the experimental data of Fig. 3; t being the time to reach the maximum hardness and T the aging temperature.

within grains which was found to be responsible for the marked hardening occurred a little later. The results obtained were similar to those reported by Morozumi⁽⁷⁾ on an alloy containing 3wt% cerium.

Based on an investigation of precipitation in Mg-Ce alloy, Sturkey⁽⁸⁾ reported that the cerium-rich phase precipitated coherently, or at least epitaxially with the magnesium matrix. The lattice constants of the coherent precipitates were $a \approx c \approx 10.3\text{\AA}$ and the orientation relationship was; $a_M // a_P$, $c_M // c_P$.

In the present observation by electron microscopy, no direct evidence was obtained for Guinier-Preston zone formation in this alloy.

Figure 5 shows the stereographic projection of the traces of streaks observed in several diffraction patterns obtained at an early stage of aging. From the figure it is obvious that the most of the traces of streaks pass through the matrix spots in the direction of $\langle 10\bar{1}0 \rangle_M$. A close examination of the streaks of diffraction pattern shown in Photo. 2 reveals the intensity maximum along the streaks. Such a phenomenon can be, in general, observed in the diffraction pattern when a diffused periodicity of the solute concentration within the matrix arises. It is reasonable to consider that the

Fig. 5 Stereographic projection of the trace of streaks.

●: foil planes

○: matrix spots through which streaks pass

structure of fine precipitates obtained by the bright field image shown in Photos. 2 and 3 is different from the structure of equilibrium phase as shown in Photos. 4~7 and that intermediate precipitates form at an early stage of aging.

The present results suggests the following sequence of precipitation within grains of Mg-Ce alloy:

Supersaturated solid solution → Intermediate precipitate → Equilibrium precipitate β , (hexagonal).

An attempt to examine the intermediate precipitates more closely has not been successful.

Another diffraction effect caused by coherency strains was also observed in the bright-field image shown in Photo. 2. Since the atomic radius of cerium is larger by 13% than that of magnesium, segregation of cerium atoms on a particular plane of the matrix should exert compressive strains to the surrounding matrix.

In a stage of over ageing, the precipitates were transformed to equilibrium precipitates of a ribbon shape with another hexagonal structure.

The diffraction patterns of such precipitates are shown in Photos. 4~6. Diffuseness or

splitting of the diffraction spots, which suggests presence of some faults in them⁽¹⁰⁾, makes somewhat difficult of precise structural analyses. Nevertheless, the diffraction patterns can be explained fairly well in terms of a hexagonal structure.

According to the phase diagram, the most magnesium-rich intermetallic compound in the Mg-Ce system is the β phase with a complicated structure. The crystal structure of the phase is still not clear, different crystal structures have been proposed for the β phase by several investigators. Vogel and Heumann⁽¹¹⁾ proposed the stoichiometric β phase, Mg_9Ce . Beletskii and Galperin⁽¹²⁾ reported the structure of the β phase being a cubic with $a = 7.302 \text{ \AA}$ or BCC with $a' = 2a$. Evdokimenko and Kripyakevich⁽¹³⁾ also reported the structure of the β phase having a form of $\text{Mg}_{17}\text{Ce}_2$, as hexagonal of $\text{Th}_2\text{Ni}_{17}$ type, with $a = 10.35 \text{ \AA}$, $c = 10.26 \text{ \AA}$. Johnson et al.⁽¹⁴⁾ reported the structure of Mg_{12}Ce as body-centered orthorhombic with $a \approx b \approx 10.33 \text{ \AA}$ and $c \approx 77.5 \text{ \AA}$. According to Lashko and Morozova⁽¹⁵⁾, the structure of the β phase was of hexagonal of ThMn_{12} type with $a = 10.31 \text{ \AA}$, $c = 5.93 \text{ \AA}$. Vogel and Heumann⁽¹¹⁾ and Beletskii and Galperin⁽¹²⁾ suggested that there would be a possibility of the existence of polymorphous structures of Mg_9Ce . Considering the results of thermal analysis by Haughton and Schofield⁽³⁾ and the similarity of the powder patterns of $\text{Mg}_{17}\text{Ce}_2$ and Mg_{12}Ce by Lashko and Morozova⁽¹⁶⁾, Shunk⁽¹⁷⁾ suggested the existence of two closely related structures within the β phase region. Thus, detailed structure of the most magnesium rich intermetallic compound has still not been clear.

It will be adequate that the crystal structure of β phase examined by the electron diffraction method in the present study is of a hexagonal nature as mentioned already. But, the lattice constants are different from the previous results on the hexagonal compound reported by Evdokimenko and Kripyakevich⁽¹³⁾ or Lashko and Morozova⁽¹⁵⁾. Thus, the term, β phase, is used in this paper for the expression of the most magnesium-rich intermetallic compound.

Schematic illustrations of structures for magnesium and the precipitates obtained in

Fig. 6 Schematic illustration of the crystallographic relation between magnesium and precipitate, deduced from the electron diffraction patterns shown in Photo. 5: atomic positions of magnesium; ●: A layer, □: B layer, ----: crystal structure of precipitate.

this work are shown in Fig. 6. It is obvious that the interplanar spacing of the precipitates along the direction of $\langle 10\bar{1}0 \rangle_P$ is a little larger than a value three times that of the spacing along the direction of $\langle 11\bar{2}0 \rangle_M$. The interplanar spacing along the c axis in precipitates agrees well with that in magnesium. Therefore, the precipitates are satisfactorily coherent with the matrix along the common c axis, but not in other directions. It was also apparent from Photos. 6 and 7 that the precipitates grew mainly in the direction of $\langle 0001 \rangle$ and, in much less extent, in the direction of $\langle 11\bar{2}0 \rangle$, but grew little in the direction of $\langle 10\bar{1}0 \rangle$ of the matrix. In addition, a diffraction effect due to coherency strain is observed around the plane of the ribbon shaped precipitates in connection with the spot like or faint streaks extending from the matrix spots to the direction of $\langle 10\bar{1}0 \rangle^{(18)}$, as seen in the diffraction pattern of Photo. 6. Further, tangled dislocations are observed in the vicinity of some precipitates as shown in Photo. 7. These observations, together with the main growth direction mentioned above, can be

consistently explained by the different degrees of coherency strains along different directions.

The mechanism for generation of the tangled dislocations is not well known whether it results merely from the difference in thermal expansion between the precipitates and the matrix, or produced by the misfit exceeding a critical value, say about 5%⁽¹⁹⁾. The misfit, δ , can be expressed by $2\left(\frac{d_1-d_2}{d_1+d_2}\right)$, where d_1 and d_2 are interplanar spacings of the precipitate and matrix, respectively. In the accuracy of the electron diffraction analysis, the interplanar spacing of $\{11\bar{2}0\}_{\text{M}}$, d_2 , is 1.60Å and one-third of $\{10\bar{1}0\}_{\text{p}}$, d_1 , is 1.70Å. As described before, there is no appreciable misfit along the c axis. On the other hand, the misfit, $\delta_{1/3(01\bar{1}0)_{\text{p}}-(11\bar{2}0)_{\text{M}}}$, is estimated to be about 0.06. This is larger than critical value of about 5%⁽¹⁸⁾. Therefore, it seems that the misfit between two lattices of the precipitates and magnesium may possibly be responsible for the generation of tangled dislocations. This is not conclusive since no data on the thermal expansion coefficient of the precipitates is presently available.

The unit cell of equilibrium phase should be of a large scale, because high atom ratio of magnesium to cerium in stoichiometry of the most magnesium-rich phase, β , is included.

V. Summary

The precipitation process of quenched Mg-1.3wt%Ce alloy were studied by hardness measurement and electron microscopy. The results obtained were as follows:

(1) On isothermal aging at 150°C, precipitates appeared first on the grain boundaries and dislocations at an early stage, followed by precipitation within grains. Aging at temperatures higher than 200°C caused precipitation on grain boundaries and dislocations, and within grains simultaneously.

(2) A diffraction effect observed in the present experiment suggests that the precipitates formed and dispersed uniformly within the matrix at an early stage of aging were to be of intermediate phase in which cerium atoms might be enriched on $(10\bar{1}0)$ planes of the matrix.

(3) On a later stage of ageing, the precipitates transformed into the equilibrium hexagonal phase of β , ribbon shaped, with the following orientation relationship with the matrix: $(0001)_M \langle 11\bar{2}0 \rangle_M // (0001)_P \langle 10\bar{1}0 \rangle_P$, $c_M \approx c_P$, $3d_{\{11\bar{2}0\}_M} \lesssim d_{\{10\bar{1}0\}_P}$. The ribbon shaped precipitates grew mainly in the direction of $\langle 0001 \rangle$ and, in much less extent, in the direction of $\langle 11\bar{2}0 \rangle$ of the matrix.

(4) Significant age hardening observed in the present alloy is found to be associated with the precipitation of fine particles dispersed uniformly in the matrix. A certain amount of the intermediate precipitates appeared to remain even in a stage where the maximum hardness was attained.

(5) An apparent activation energy for age hardening process was determined to be 30 kcal/mol.

Acknowledgments

The authors wish to express their cordial thanks to Dr. H. Kimura, Head of Non-Ferrous Metals Division of National Research Institute for Metals, for his encouragement and stimulating discussions. They are also grateful to Professor Dr. R. Horiuchi and Mr. S. Morimoto, Institute of Space and Aeronautical Science, University of Tokyo, for provision of research facilities there.

REFERENCES

- (1) C. S. Robers: Trans. AIME, **200** (1954), 638.
- (2) G. A. Meller and R. W. Ridley: J. Inst. Metals, **75** (1948), 697; **81** (1952-53), 245.
- (3) J. L. Haughton and T. H. Schofield: J. Inst. Metals, **60** (1937), 339.
- (4) F. Weibke and W. Schmidt: Z. Elektrochem., **46** (1940), 357.
- (5) G. Omori, S. Matsuo and H. Asada: J. Japan Inst. Light Metals, **20** (1970), 490.
- (6) G. Omori, S. Matsuo and H. Asada: *ibid.*, **17** (1967), 32.
- (7) S. Morozumi: Reports of Gov. Ind. Res. Inst. Nagoya, **7** (1953), 255.
- (8) L. Sturkey, unpublished results quoted by C. S. Roberts: *Magnesium and Its Alloys*, John Wiley & Sons, Inc., New York, (1960), p. 118.
- (9) J. B. Clark: Acta Met., **13** (1965), 1281.
- (10) Z. Nishiyama, J. Kakinoki and S. Kajiwar: J. Phys. Soc. of Japan, **20** (1965), 1192.
- (11) R. Vogel and T. Heumann: Z. Metallk., **38** (1947), 1.
- (12) M. S. Beletskii and E. L. Galperin: Phys. Met. and Metallog. (USSR), **11** (1961), No. 5, 55.
- (13) V. I. Evdokimenko and P. I. Kripyakevich: Soviet Phys.-Cryst., **8** (1963), 135.
- (14) Q. C. Johnson, G. S. Smith, D. H. Wood and E. M. Cramer: Nature, **201** (1964), 600.
- (15) N. F. Lashko and G. I. Morozova: Ind. Lab. USSR, **30** (1964), 1470.
- (16) N. F. Lashko and G. I. Morozova: Soviet Phys. Cryst., **9** (1964), 209.
- (17) Francis A. Shunk: *Constitution of Binary Alloys*, Second Supplement, McGraw-Hill, Inc., (1969), p. 237.
- (18) P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley and M. J. Whelan: *Electron Microscopy of Thin Crystals*, Butterworths, London, (1965), p. 317.
- (19) G. S. Weathery and R. B. Nicholson: Phil. Mag., **17** (1968), 801.