X-ray Diffraction Study of Ageing Process in Lead-0.4 wt% Magnesium Alloy at Room Temperature*

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The structural ageing process of lead-0.4 wt % magnesium alloy at room temperature has been examined by means of various X-ray diffraction methods. Results obtained are as follows: (1) It has been confirmed from Laue photographs of single-crystalline specimens and small-angle scatter photographs of polycrystalline specimens that G.P. zones are formed in the early stage of ageing at room temperature. Distribution of solute atoms inside G.P. zones seems to be initially disordered and ordered after ageing. (2) The shape of the zones is plate-like, being formed on {100} planes of matrix lead solid solution. (3) From the Debye-Scherrer photograph of the polycrystalline specimens which had been aged for a long time (3500 hr), it has been shown that the stable phase Mg_2Pb is formed in the prolonged stage of ageing at room temperature. The Laue photographs obtained for the single-crystalline specimens in this stage of ageing can be well explained by the following orientation relationships between the matrix Pb lattice and the stable precipitate Mg_2Pb lattice: $(100)_{Pb} // (001)_{Mg_2Pb}$ and $[110]_{Pb} // [010]_{Mg_2Pb}$.

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I. Introduction

A number of investigations of precipitation phenomena have been carried out with various alloys, and several reviews have been published⁽¹⁾⁻⁽⁶⁾. Only few systematic studies, however, have hitherto been made to clarify the ageing process of lead-rich alloys, although Hofmann⁽⁷⁾ has given extensive reviews of

lead and lead alloys. Recently the present author investigated the precipitation process of magnesium from lead solid solution by measuring the mechanical and physical properties, i.e. micro-Vickers hardness, microscopic structure, specific heat, and electrical resistivity of lead-0.4 wt% magnesium alloy. The results obtained have already been reported elsewhere⁽⁸⁾. These results may be summarized as follows: When the ageing temperature is higher than 100°C, the precipitation occurs with the simple nucleation and growth process of stable phase, Mg_2Pb . However, when the ageing temperature is lower than 100°C, the precipitation occurs with a more complicated process in which a decomposition product of lower stability is formed in the early stage of ageing. A reversion phenomenon was detected at about 100°C on the micro-Vickers hardness vs. temperature curves, specific heat vs. temperature curves, and electrical resistivity vs. temperature curves of the alloy which had been aged at low temperature below 100°C. It was considered that the reversion phenom-

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enon observed in this alloy is probably due to the dispersion of G.P. zones into matrix.

In order to investigate the structural change during the low temperature ageing, X-ray diffraction methods were employed for lead-0.4 wt % magnesium alloy aged at room temperature. The equilibrium diagram for the lead-magnesium system is such as shown in Fig. 1, according to Hansen et al.⁽⁹⁾. The solvent metal lead has a *FCC* structure, and the intermetallic compound Mg_2Pb has a cubic structure of the CaF_2 type. The maximum solubility of magnesium in solid lead is 0.73 wt% (5.9 at%) at the eutectic temperature, 253°C. With decreasing temperature, the solubility of magnesium in solid lead decreases to 0.13 wt% (1.0 at%) at 100°C.

Fig. 1 The equilibrium diagram of the lead-magnesium system.

II. Experimental Procedure

1. Specimens and heat treatments

The purities of materials used to prepare specimens were 99.99% lead and 99.95% magnesium. An alloy with a nominal composition of 0.4 wt% Mg was melted in a graphite crucible and cast in an iron mould. The billet of 25×25×70 mm was annealed, 120 hr at 255°C, for homogeneization, and then scalped to a size of 20×20×50 mm. Chemical analysis showed that the actual composition of the billet is 0.36 wt% (3.00 at %) Mg. The alloy specimens of various shapes and sizes suitable for various X-ray works were prepared from this billet. Strips of 3×7×40 mm were cut out from the billet, annealed, strained 5%, slowly heated and held for 6 hr at 260°~280°C in vacuum to produce large-grained specimens. The strips containing crystal grains 3~5 mm in diameter were thinned by electrolytic etching to sheets of 0.1-mm thickness. The large-grained sheet specimens were used for the Laue X-ray work. Polycrystalline specimens in a sheet of 5×10×0.1 mm and in a wire of 20×0.8 mmφ were used for the small angle scattering method and the Debye-Scherrer method, respectively.

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These specimens were solution-heat treated at 255°C for 2 hr in vacuum, quenched in water, and then aged at room temperature for various times.

2. X-ray methods

(1) Laue method

Laue photographs were taken with unfiltered Cu radiation using pin-hole slit of 0.5 mm or 1.0 mmφ, the exposures being 60 mA-hr at 40 kV. The distance from the specimen to the flat-film was 40 mm or 30 mm. The variations in Laue diffraction pattern with ageing time were examined with the $[100]_{Pb}$, $[110]_{Pb}$ and $[111]_{Pb}$ axes parallel to the X-ray beam.

Photo. 1 Laue patterns of Pb-0.4 wt% Mg alloy aged for various times at room temperature, beam along $[111]$, with unfiltered Cu radiation. (a) 20 hr, (b) 1000 hr, (c) 5500 hr.

The arrow $\uparrow$ shows the streak and the intensity maxima in streak, and the arrow $\uparrow$ the new spot observed at a prolonged stage of ageing.

(2) Small-angle scattering method

The photographs were taken with filtered Cu radiation using pin-hole slit of 0.3 mm ϕ , the exposures being 720 mA-hr at 35 kV. The diffraction pattern was recorded on a flat-film 300 mm apart from the specimen.

(3) Debye-Scherrer method

The photographs were taken with filtered Cu radiation using a pin-hole slit of 0.5-mm ϕ and a camera of 80-mm diameter, the exposures being 100 mA-hr at 40 kV.

III. Experimental Results

1. Laue method

Photo. 1 shows the variations in Laue photograph with ageing time, in case the $[111]_{Pb}$ axis is parallel to X-ray beam. The Laue spots in Photo. 1(a) (Specimen aged for 20 hr) are accompanied by one or more streaks running along the zonal ellipses. The streaks develop intensity maxima in Photo. 1(b) (Specimen aged for 1000 hr). The most of the streaks disappear and are replaced by new spots as shown in Photo. 1(c) (Specimen aged 5500 hr). The positions of the new spots are different from the matrix Laue spots. The geometry of these various streaks, the intensity maxima and the new spots are shown in the stereographic projection of Fig. 2. In Fig. 2, the dashed lines show the zone circles, the heavy lines the streaks, the double circles the positions of intensity maxima in the streaks, and triple circles the positions of the new spots, respectively.

Fig. 2 Stereographic projection of one quadrant of Photo. 1. The heavy lines show streaks and the dashed lines zone circles. $\odot$ indicates the position of intensity maxima in streak and $\odot$ the position of the new spot observed at a prolonged stage of ageing.

Photos. 2 and 3 show the variations in Laue photographs with ageing time, in case the $[110]_{Pb}$ and $[100]_{Pb}$ axes are parallel to the X-ray beam respectively. The stereographic projections of these photographs are given in Figs. 3 and 4.

A series of Laue patterns for the specimen at a position which was varied from one exposure to the

Photo. 2 Laue patterns of Pb-0.4 wt% Mg alloy aged for various times at room temperature, beam along $[110]$, with unfiltered Cu radiation. (a) 300 hr, (b) 1000 hr, (c) 5500 hr.

next by 2° or more about the $[110]$ axis were taken. The results obtained for the alloy aged for about 800 hr are reproduced in Photos. 4 and 5. Here, θ_1 and θ_2 are the glancing angle to the Bragg reflexion planes $(\bar{1}\bar{1}1)$ and (002) of matrix, respectively. The Bragg angles θ of $\{111\}$ and $\{002\}$ planes are $15^\circ38'$ and $18^\circ09'$, respectively. Photos. 4 and 5 show that both the shapes and positions of the satellites, incidental to $(\bar{1}\bar{1}1)$ and (002) spots, change with the variations in θ_1 and θ_2 .

2. Small-angle scattering method

Photo. 6 shows a small-angle scattering photograph obtained for the polycrystalline specimen aged for 700 hr. The central streaks are visible.

Photo. 3 Laue patterns of Pb-0.4 wt% Mg alloy aged for various times at room temperature, beam along $[100]$; with unfiltered Cu radiation.
(a) 100 hr, (b) 1000 hr, (c) 5500 hr.

3. Debye-Scherrer method

Except the specimens aged for more than 3000 hr, any additional lines other than the diffraction lines due to the matrix lead solid solution could not be detected in the Debye-Scherrer photograph. Photo. 7 shows the Debye-Scherrer photograph of the polycrystalline specimen aged for 3500 hr. A few additional lines which are considered due to the stable phase Mg_2Pb are observed.

IV. Discussions

1. Precipitation process in the early stage of room temperature ageing

From Figs. 2, 3, and 4 it is predicted that all streaks follow a great circle through the poles of planes of the

Fig. 3 Stereographic projection of one quadrant of Photo. 2.

Fig. 4 Stereographic projection of one quadrant of Photo. 3.

type $\{100\}$. This result suggests that anomalous diffraction effects are correlated with the $\{100\}$ planes of the solid solution. Similar anomalous diffraction effects to these were observed by various workers in aluminium-rich alloys. Two different interpretations have been proposed for these scattering effects; namely (1) these anomalous scattering effects are owing to the G.P. zones where no well-defined new crystalline structure is observed despite the high concentration of solute atom⁽¹⁰⁾⁽¹¹⁾. (2) These effects are owing to the well defined but very fine new crystalline structure⁽¹²⁾⁽¹³⁾. In Photo. 4, when $\theta_1 < \theta (=15^\circ 38')$, the position of the satellite which is incidental to the $(\bar{1}11)$ spot is outside of the $(\bar{1}11)$ spot and the shape of the satellite is a V-shape. When $\theta_1 = 15^\circ 38'$, the satellite coincides with the $(\bar{1}11)$ spot. When $\theta_1 > 15^\circ 38'$,

(10) A. Guinier: Compt. rend., **206** (1938), 1641; Nature, **142** (1938), 569.

(11) G.D. Preston: Proc. Roy. Soc., **A167** (1938), 526; Nature, **142** (1938), 570.

(12) C.S. Barrett and A.H. Geisler: J. Appl. Phys., **11** (1940), 733.

(13) A.H. Geisler and J.K. Hill: Acta Cryst., **1** (1948), 238.

Photo. 4 Series of Laue patterns of Pb-0.4 wt% Mg alloy aged for 800 hr at room temperature. Orientation of crystal given by θ_1 which is angle between direct beam and $[112]$ with $[110]$ vertical. Satellite marked with the arrow.

the position of the satellite is inside of the $(\bar{1}\bar{1}1)$ spot and the shape of the satellite is no longer the V-shape but spotty. If the reciprocal lattice point of matrix lead is elongated along the three principal axes of $\langle 100 \rangle$, the above-described variations in the position and the shape of the satellite with θ_1 can be understood by the way of cutting in which the reflexion sphere cuts the reciprocal lattice rod at various θ_1 values, as proposed by Preston and Guinier⁽¹⁰⁾⁽¹¹⁾. The reciprocal lattice rod in this case is considered due to the relaxation along $\langle 100 \rangle$ of one of the three Laue conditions for matrix lattice. It can be deduced from these results that the solute magnesium atoms segregate on the $\{100\}$ planes of matrix lead solid solution and the plate-like G.P. zones are formed during the room-temperature ageing. This is attributed to the interpretation (1), as observed for the Laue photograph of aluminium-4 wt % copper alloy in the early stage of the low-temperature ageing.

As described on Photo. 1(b), the streaks due to G.P. zones develop intensity maxima in the latter stage of ageing. This would not correspond to the formation of any other new decomposition product of strongly higher stability than G.P. zones. This conclusion can be supported by the measurements of specific heat *vs.* temperature curves which show that the difference in the reversion temperature of each alloy

Photo. 5 Series of Laue patterns of Pb-0.4 wt% Mg alloy aged for 800 hr at room temperature. Orientation of crystal given by θ_2 which is the angle between direct beam and $[110]$ with $[110]$ vertical. Satellite marked with the arrow.

Photo. 6 Small-angle scatter pattern of polycrystalline Pb-0.4 wt% Mg alloy aged 700 hr at room temperature, with filtered Cu radiation.

which reveals the streak and the intensity maxima is less than $20^\circ\text{C}^{(8)}$. The development of intensity maxima in streak has also been observed by the previous workers for aluminium-4wt% copper alloy⁽¹⁴⁾⁻⁽¹⁷⁾. Guinier⁽¹⁴⁾ interpreted the development of intensity maxima as the formation of an ordered structure in G.P. zones, and termed this structure θ'' . Hardy⁽¹⁵⁾ designated this structure G.P.[2], reserving the term G.P.[1] for the first formed G.P. zones. The formation of the ordered G.P. zones was also reported by Nagashima⁽¹⁸⁾ for magnesium-silver alloy. The development of intensity maxima

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- (15) H.K. Hardy: J. Inst. Metals, 75 (1948~49), 707.
- (16) J.M. Silcock, T.J. Heal and H.K. Hardy: J. Inst. Metals, 87 (1953~54), 239.
- (17) V. Gerold : Z. Metallk., 45 (1954), 594; *ibid*, 45 (1954), 599.
- (18) S. Nagashima : J. Japan Inst. Metals, 23 (1959), 381, 460, 465, Trans. JIM, 1(1960), 58.

Photo. 7 Debye-Scherrer photograph of Pb-0.4 wt% Mg alloy aged for 3,500 hr at room temperature, with filtered Cu radiation.

observed in this work is also probably due to the formation of G.P. [2].

From Photo. 6, in which the central streaks are observed, it can be confirmed that the shape of the G.P. zones is plate-like⁽¹⁹⁾.

Guinier⁽²⁰⁾ has classified the G.P. zones into several general types; (1) zones without lattice distortion, (2) zones with strong distortions, and (3) other types of zones. The structural characteristic of the zones with strong distortions (type 2) is that plate-like zones are formed on {100} planes of matrix. Explanations for the plate-like shape of decomposition products with strong distortions were offered by Nabarro⁽²¹⁾ based on strain energy and by Hirano et al.⁽²²⁾ based on the elastic interaction of solute atoms with a cluster of vacancies. Now, in lead-magnesium alloy, the difference in diameters of the solute and solvent atoms is 8.1% of that of the solvent, so that it is expected that the G.P. zones in this alloy belong to the type (2). In fact, the structural characteristic observed in this work represents this type.

2. Precipitation process in the prolonged stage of room temperature ageing

When ageing is continued for about 5000 hr at room temperature, well-defined spots begin to appear at new positions on Laue photographs (Photos. 1(c), 2(c), and 3(c), or Figs. 2~4). Photo. 7, Debye-Scherrer photograph of the alloy at this stage of ageing, shows that the stable precipitate Mg_2Pb has formed. Therefore, the new spots on Laue photographs of the alloy

at this stage may also be due to the stable precipitate Mg_2Pb . The positions of these precipitate spots are regularly distributed in the Laue photographs of Photos. 2(c) and 3(c) or in the stereographic projections of Figs. 3 and 4. This regular array of the precipitate spots suggests that there are definite orientation relationships between precipitate and matrix lattice. In the stereographic projection of Fig. 4, i.e. in the case of the $[100]_{Pb}$ axis of matrix parallel to the X-ray beam, if the positions of the precipitate spots are rotated by 45° about the $[100]_{Pb}$ axis the new positions of the precipitate spots almost agree with poles of some planes of the standard (100) projection for cubic crystals. In the stereographic projection of Fig. 3, i.e. in the case of the $[110]_{Pb}$ axis of matrix parallel to the X-ray beam, the positions of the precipitate spots almost agree with poles of some planes of the standard (100) projection for cubic crystals. The relative positions between the matrix spots and the precipitate spots such as those described above can be understood if the orientation relationships between the matrix Pb lattice and the precipitate Mg_2Pb lattice are such as shown in Fig. 5, namely

$$(100)_{Pb} \parallel (001)_{Mg_2Pb} \text{ and } [110]_{Pb} \parallel [010]_{Mg_2Pb}.$$

The indices of the triple circles which are accompanied by the suffix P in Figs. 3 and 4 were assigned according to these orientation relationships. The lattice constant of matrix lead is $4.94\text{\AA}$, so the length of diagonal of {100} planes of matrix lead lattice is $4.94 \times \sqrt{2} = 6.99\text{\AA}$ ⁽⁷⁾. The lattice constant of the precipitate Mg_2Pb lattice is $6.84\text{\AA}$ ⁽⁸⁾. Thus the difference between the length of diagonal of {100} planes of the matrix lattice and the lattice constant of the precipitate lattice is only 2%. This suggests that the above orientation relationships can occur according to Barrett's criterion⁽²³⁾.

In conclusion, not only the shape and the habit plane of G.P. zones but also the orientation rela-

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Fig. 5 Orientation of Mg_2Pb cell on matrix lead.

tionships between matrix lattice and stable precipitate in lead-0.4 wt % magnesium alloy strongly resemble that in aluminium-copper alloy. The each solvent metal in aluminium-copper alloy and in lead-magnesium alloy has the same *FCC* structure, and the stable precipitate in lead-magnesium alloy is very similar in structure to the intermediate precipitate θ' (distorted CaF_2 type) in aluminium-copper alloy. The size factor in both solid solutions has a very close value, i.e. about 10%. Moreover, the sign of difference of valency between the solute and the solvent atoms in lead-magnesium alloy is negative, being the same as that in aluminium-copper alloy.

Friedel⁽²⁴⁾ has pointed out that the relative valency effect in solid solution is a governing factor in the formation of G.P. zones. The similarity of the structural changes during the precipitation in both alloys appears to originate from the above-described similarity in the natures of both solid solutions.

V. Summary

The results obtained in this work are summarized as follows:

(1) The G.P. zones are formed in the early stage of ageing at room temperature. The distribution of solute atoms inside the G.P. zones seems to be initially disordered and ordered in latter stage of ageing.

(2) The shape of the G.P. zones is plate-like. The zones are formed on $\{100\}$ planes of the matrix.

(3) The stable phase Mg_2Pb is formed in the prolonged stage of ageing at room temperature. The orientation relationships between the matrix Pb lattice and the stable precipitate Mg_2Pb lattice are considered as follows: $(100)_{Pb} // (001)_{Mg_2Pb}$ and $[110]_{Pb} // [010]_{Mg_2Pb}$.

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