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Investigation of Phase Decomposition Process in Mg-Y-Nd Alloys by Small Angle Scattering

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In order to investigate the difference in the age-hardening behavior of Mg-Y alloy and WE54 alloy, SR-SAS measurement was performed. When it is assumed that the shape of β' phase is plate-like, the measured SAS intensities are in good agreement with the calculated intensities and the radius, thickness, interparticle distance and volume fraction can be evaluated. Since in WE54 alloy, β' phase begins to precipitate earlier than in Mg-Y alloy, the hardness of WE54 alloy increases in the early stage of aging. Since the coherency strain between matrix and broad plane of plate-like β' phase became small by Nd addition, the growth rate of thickness of β' phase become large by Nd addition.

Key words: Mg-Y-Nd alloy, Small Angle Scattering, Phase Decomposition Process, β' phase

1. INTRODUCTION

Recently, research of magnesium alloys for application of structural metallic materials is advanced because of their light-weight and high specific strength. Magnesium-rare earth alloy is expected for heat-resistant alloy, since stable metastable phase at high temperature precipitate in the matrix[1]. Since a solubility limit of Y in Mg is 12.5mass% at 839K of eutectic temperature and decrease remarkably with lowering temperature, large precipitation-hardening arises in Mg-Y alloys. Precipitation sequence aged at 473K is reported as follows[2], $Mg_{ssss} \rightarrow \beta'' \rightarrow \beta'$. The hardness of Mg-Y alloy hardly increases in the early stage of aging, but increases rapidly from the middle stage. It is considered that the cause is as follows. In the early stage of aging, β'' phase that has a $D0_{19}$ crystal structure forms in the matrix. From the middle stage, β' metastable phase that has a bco structure precipitates. Since the hardening effect of β'' phase is not so large and that of β' phase is much larger than that of β'' phase, the hardness of Mg-Y alloys suddenly increases from the middle stage of aging[3]. Mg-Y-Nd alloy with which a part of Y of Mg-Y alloy is replaced by Nd is also precipitation-hardening alloy and it is reported that precipitation sequence of Mg-Y-Nd alloy is the same as that of Mg-Y alloy. However, the age-hardening behavior of Mg-Y-Nd alloy differs from that of Mg-Y alloy[3]. That is, the hardness of Mg-Y-Nd alloy gradually increases from the early stage of aging. There is no report detailed about these reason.

In this study, the difference has been investigated the difference in the precipitation and age-hardening behavior between Mg-Y alloy and Mg-Y-Nd alloy by estimating the size, the distribution and the volume fraction of mainly β' phase by synchrotron radiation small-angle scattering (SR-SAS) technique.

2. EXPERIMENTAL

The chemical composition of Mg-Y alloy and Mg-Y-Nd alloy (WE54 alloy) are listed in Table 1. WE54 alloy was a commercial ingot. Mg-Y alloy ingot was prepared from pure Mg, Mg-33mass%Zr alloy and Mg-27mass%Y-0.5mass%Nd alloy in a mixed gas atmosphere of 25% SF_6 and 75% CO_2.

Table 1 Chemical composition of tested alloys.

Alloys	Y	Nd	Zr	Mg
Mg-Y	11.5	0.24	0.68	bal.
WE54	5	4	0.5	bal.

The specimens of Mg-Y alloy and WE54 alloy were solution treated at 823K for 4 hour and at 803K for 2.5 hours, respectively in a flowing Ar atmosphere and quenched into water. Aging treatment was performed at 473K in an oil bath. Mechanical properties were measured by micro Vickers hardness test. SAS intensities were measured by PSPC at beam-line 15A of the Photon factory, Tsukuba Japan. The camera length from the sample position to PSPC is set to 780mm and 1695mm.

3. EXPERIMENTAL RESULTS AND DISCCUSION

The changes in Vickers hardness during aging are shown in Fig.1. The hardness of Mg-Y alloy hardly increases in the early stage till 3 hours of aging and rapidly increases in the middle stage from 6 to 50 hours. The hardness hardly increases from 50hours. On the other hand, the hardness of WE54 alloy increases in the early stages of aging. The hardness increase of WE54 alloy from 0 to 6 hours is 3 times as large as that of Mg-Y alloy. These results are in good agreement with the report that WE54 alloy hardens from the early stages of aging.

The change in SAS intensities during aging is shown in Fig.2(a) and (b). All SAS curves of Mg-Y alloy have a sharp single peak. SAS intensity, $I(k)$, can be described as $F^2(k)$ that is sum of the

SAS intensity from each particle, when inter-particle interference effect can be ignored, that is, the density of dispersed particle is quite low.

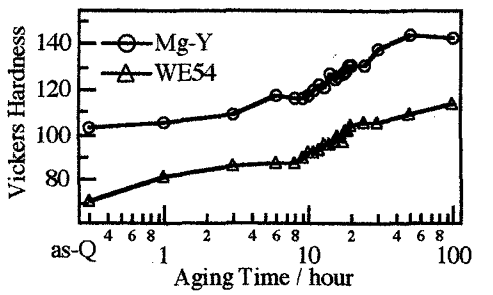

Fig.1 Isothermal aging curves of hardness aged at 473K.

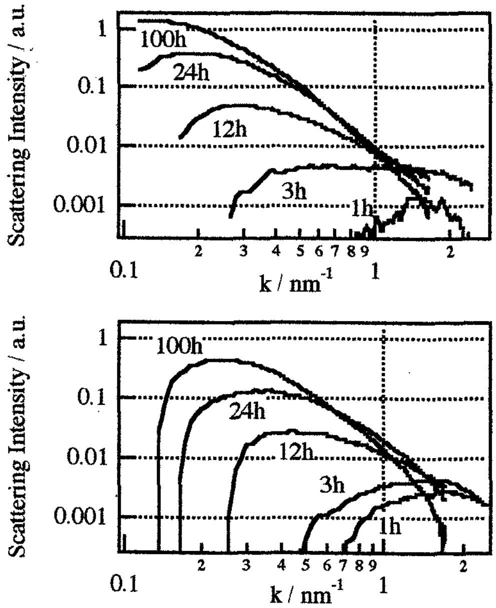

Fig.2 Scattering intensities as a function of scattering vector.
(a) Mg-Y alloy, (b) WE54 alloys

$F^2(k)$ is the function of monotonous reduction to k. However, since the density is high for the precipitation-hardening alloys, the strong inter-particle interference affects the SAS intensity in the small k range and a peak appears in the SAS curve. The scattering vector, k_m, corresponding to the intensity maximum has a following relation to average interparticle distance, l_p.

$$l_p = A/k_m \qquad (1)$$

where A is a constant. It is reported that A is 7.27 in the Al-Zn alloy[5]. Since k_m shifts to the small-angle region with aging time in Mg-Y alloy, average interparticle distance monotonously increase with aging time. On the other hand, SAS curves of WE54 alloy aged for 3 and 6 hours spread horizontally and the peak is not clearly observed. It is considered that the SAS curve of β'' phase has a peak in 1.5nm^{-1} of scattering vector and that of β' phase has a peak in of 0.5nm^{-1}. And these two curves overlapped and became these widely spread curves. That is, it is expected that β' phase is formed from the early stages of aging and β'' and β' phase is in a coexistence state till 6 hours. By the case of Mg-Y alloy, differed from the case of WE54 alloy, broad peaks are not observed. It is expected that only one kind of metastable phase exists in each aging time.

If interparticle interference effect is taken into consideration, when the particle is dispersed at random, scattering intensity, $I(k)$ can be described by the simple multiplication of $F^2(k)$ and $P(k)$.

$$I(k) = F^2(k)P(k) \qquad (2)$$

It is known that radial distribution function, $g(r)$ as a function of radial distance, r, is the Fourier transforms of $P(k)$,

$$g(r) = 1 + \frac{1}{2\pi^2 r(N/V)} \int_0^\infty k[P(k) - 1]\sin(kr)dr \qquad (3)$$

where N/V is the density of precipitate. Therefore, if $F^2(k)$ can be calculated, $g(r)$ can be evaluated and distribution of the particle can be estimated. If particle size and shape are known when it assumes that the particle is distributing at random, $F^2(k)$ can be calculated.

The size of a particle can be evaluated as radius of gyration, R_g. R_g is a moment of inertia of solute and can be defined to a precipitate of any shape. When the scattering vector is nearly zero, $I(k)$ is approximately described as follows,

$$\ln I(k) = \ln I(0) - \frac{1}{3}R_g^2 k^2 \qquad (4)$$

R_g is determined from the inclination in k~0 of $\ln I(k)$ vs k^2 plot. The change in R_g during aging is shown in Fig.3.

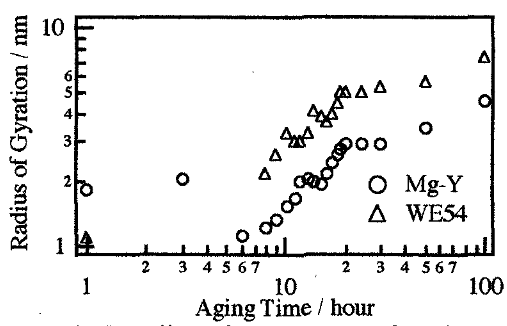

Fig.3 Radius of gyration as a function of aging time.

In Mg-Y alloy, although radius is about 2nm in the early stages of aging, the radius decreases to 1nm in 6 hours. Since it can't be considered that the size of precipitate decreases by isothermal aging when the same kind of phase precipitate throughout the entire period of aging, it is expected that β'' phase precipitate till 3 hours and β' phase precipitate from 6 hours. The radius of β' phase increases exponentially from 6 hour. Compared in same aging time, the size of β' phase precipitated in WE54 alloy is larger than that in Mg-Y alloy. Growth rate of β' phase is almost same as the Mg-Y alloy.

When the shape of a precipitate particles is assumed to be a ellipsoid of revolution of axes $2a$, $2a$ and $2a\omega$, if $\omega >> 1$, the shape of ellipsoid is like needle, if $\omega=1$, the shape is sphere and if $\omega << 1$, the shape is like plate, $F^2(k)$ is described as follows[5],

$$F^2(k)=\int_0^{\pi/2}\Phi^2\left(ka\sqrt{\cos^2\theta+\omega\sin^2\theta}\right)\cos\theta d\theta \quad (5)$$

$$\Phi^2(x)=\left(3\frac{\sin x - x\cos x}{x^3}\right)^2 \quad (6)$$

R_g and a has the following relation in a ellipsoid of revolution.

$$R_g^2=\frac{a^2\left(2+\omega^2\right)}{5} \quad (7)$$

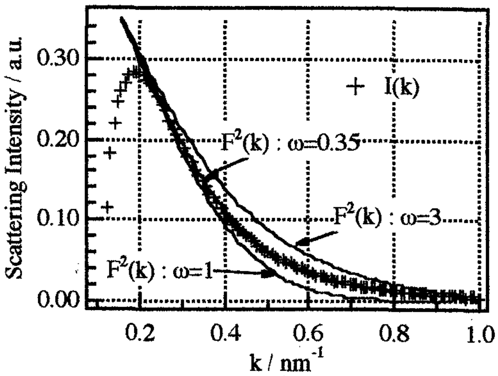

Fig.4 Fitting calculated $F^2(k)$ from ellipsoids of revolution to measured SAS intensity.

As shown in Fig.4, the effect of the shape appears in the degree of decay by the range of large scattering vector. The shape can be evaluated by calculating ω, when $I(k)$ is nearly equal to $F^2(k)$ in the large k range that interparticle interference is small and $P(k)$ is nearly equal to 1. $F^2(k)$ calculated as $\omega=0.35$ is in good agreement with $I(k)$ of WE54 alloy aged for 20hours. Therefore, the shape of β' phase is turn out to be a plate-like and this result is in agreement with the report of Lorimer et.al. [2].

$P(k)$ and radial distribution function, $g(r)$ are calculated by substituting calculated $F^2(k)$ for eq.(2) and (3). The change in $g(r)$ of β' phase in WE54 alloy during aging are shown in Fig.5

As radial distance increases, $g(r)$ gradually increases and shows the maximum. The distance corresponding to the maximum $g(r)$ can be regarded as the average interparticle distance among precipitates, l_p. It is calculable that A=7.86 by substituting this l_p for eq.(1). The changes in the average interparticle distance during aging are shown in Fig.6. l_p exponentially increase till 20 hours and gradually increase after that. Compared to the same aging time, l_p in WE54 alloy is larger than that in Mg-Y alloy.

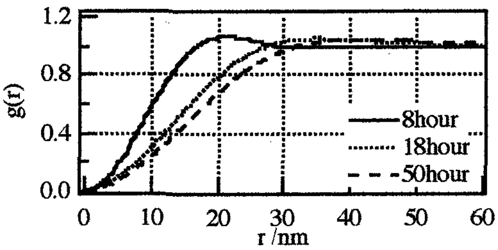

Fig.5 Radial distribution as a function of β' phase as a function of radial distance in WE54 alloy.

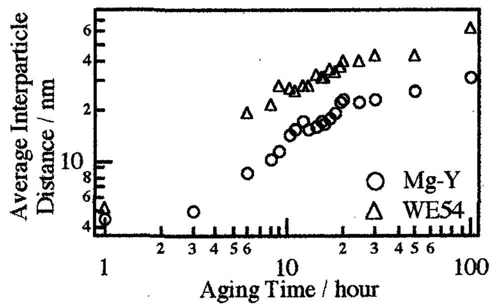

Fig.6 Average interparticle distance as a function as a function of aging time.

Since the shape of a precipitate is turn out to be a plate-like, the radius of the gyration of plate thickness, R_t is determined from the inclination of $\ln I(k)$ vs k^2, so-called Thickness Plot[6],

$$\ln(I(k)\cdot k^2)=\ln(I(0)\cdot k^2)-R_t^2k^2 \quad (7)$$

There are the following relations to R_t and plate thickness, t.

$$t=R_t\sqrt{12},\quad t^2+R^2=R_g^2 \quad (8)$$

Change of radius and thickness of β' phase by aging is shown in Fig.7. The radius and thickness exponentially increase till 20 hours. The growth rate of radius in WE54 alloy is comparable to that in Mg-Y alloy, although the growth rate of thickness in WE54 alloy is much larger than that in Mg-Y alloy. This suggests that the plate-like precipitates grow up more easily to the thickness direction in WE54 alloy than in Mg-Y alloy.

When the plate-like precipitates which radius is R and thickness is t is dispersed at intervals of l_p, the volume fraction of precipitates, V_f is described as follows,

$$V_f=\left(\pi R^2 t\right)\frac{\sqrt{2}}{l_p^3} \quad (9)$$

Change of volume fraction of β' phase by aging is shown in Fig.8. The volume fractions of β' phase in Mg-Y alloy and WE54 alloy monotonously increase till 20 hours and almost remain constant after that. In the period that the volume fraction increases, the growth of β' phase is fast and the increase rate of interparticle distance is also large. And hardness rapidly increases in this period. During the coarsening stage, the growth rate of β' phase become slow and the increase rate of interparticle distance is also small. And hardness almost remains constant in this stage.

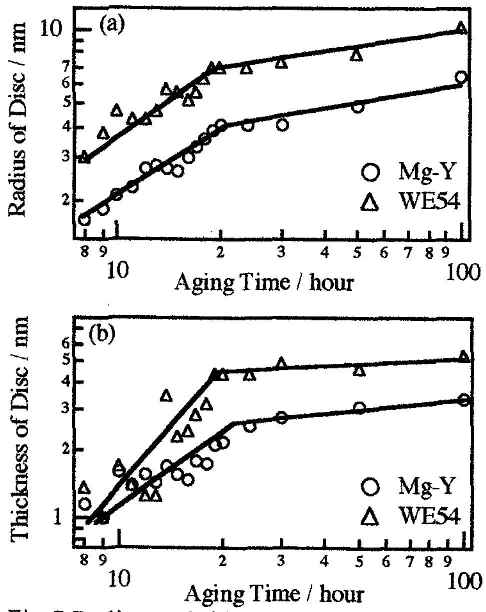

Fig.7 Radius and thickness of plate-like β' phase as a function of aging time.

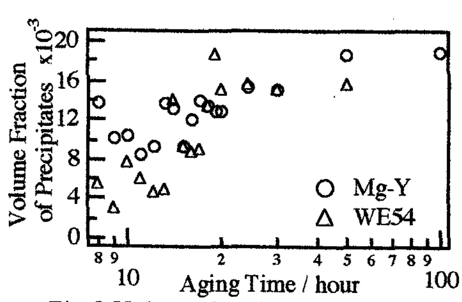

Fig.8 Volume fraction of β' phase as a function of aging time.

It is reported that β' phase is coherent to matrix in the early stage of aging. Coherency strain field is formed by the lattice misfit between matrix and coherency precipitate and it serves as an obstacle of dislocation movement. When the coherency strain is ε, according to Gerold-Harberkorn's coherency strain model, the precipitation hardening effect, $\Delta\sigma$ is described as follows[7],

$$\Delta\sigma = 3MG|\varepsilon|^{3/2}\left(\frac{V_f R}{b}\right)^{1/2} \qquad (10)$$

where G is the shear modulus, M is the Taylor factor and b is Burgers vector. The Vickers hardness is plotted against $(R_g V_f)^{1/2}$ is shown in Fig.9. Change of Vickers hardness is well explained by the coherency strain model. From the gradient of the fitting line, the coherency strain can be estimated. The coherency strain between matrix and β' phase in WE54 alloy is 0.6 times smaller than that of Mg-Y alloy. This result suggest that by the addition of Nd, the coherency strain between matrix and the broad plane of plate-like β' phase became small and the coherency strain between matrix and the side plane hardly change since the growth rate of plate-like β' phase to the thickness direction became large and the growth rate to the radial direction hardly change by the Nd addition. Since Y replaces by Nd in β' phase, it is considered that the lattice constant of phase changed and the coherency strain decreased.

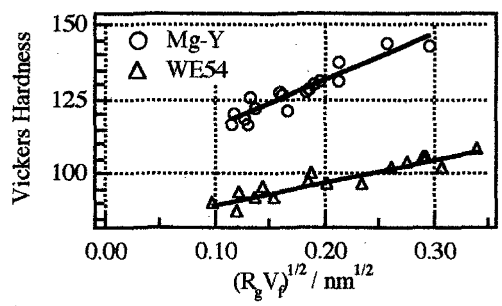

Fig.9 Change of Vickers hardness as a function of radius of gyration and volume fraction.

4. CONCLUSIONS

1, In WE54 alloy, since β' phase begin to precipitate in 3hours of aging, the hardness gradually increase from the early stage of aging.
2, While the volume fraction of β' phase increases in the middle stage of aging, the growth rate of β' phase is very rapid. Growth rate of β' phase decreased in the coarsening stage from which the volume fraction became constant.
3, Since the coherency strain between matrix and broad plane of plate-like β' phase became small by Nd addition, the growth rate of thickness of β' phase become large by Nd addition.

5. References

[1] D. Mizer and B. C. Peters, *Metall. Trans.*, **3**, 3262 (1972).
[2] G. W. Lorimer, Proc. Magnesium Technology, 3-4 Nov., *Inst. metals*, London, 47 (1986).
[3] G. Ohmori, S. Matuo and H. Asada, *J. Japan Inst. Metals*, **36**, 1002 (1972).
[4] K. Osamura, H. Okuda and S. Ochiai, *Scripta METALLURGICA*, 19, 1379 (1985)
[5] A. Guinier and R. Griffoul, *Acta Cryst.*, 1, 188 (1948).
[6] O. Kratly, O. Glatter, ed., *Small-angle X-ray Scattering*, Academic (1982).
[7] V. Gerold and H. Harberkorn, *Phys. Stat. Sol.*, 16, 675 (1966).

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