Proceedings of the 12th International Conference on
Aluminium Alloys, September 5-9, 2010, Yokohama, Japan

pp. 1932-1937

Precipitation Kinetics in an Al-Zn-Mg Alloy by New Rate Equation

Hideo Yoshida[1] and Satoru Yamamoto[2]

[1]R&D Center, Sumitomo Light Metal Industries, Ltd., 3-1-12, Chitose, Minato-ku, Nagoya 455-8670, Japan
[2]Department of Materials Science, Kyoto University, Yoshida-Honmachi, Sakyoku, Kyoto 606-8501, Japan

The precipitation kinetics in aluminum alloys has usually been studied using the Johnson-Mehl (J-M) equation. However, this equation cannot be fitted to experimental data during the early stage or the final one. Furthermore, it is difficult to apply this equation to complicated reactions, in which several reactions simultaneously occur. Yamamoto proposed a new rate equation by improving the J-M equation. Thus this new rate equation was applied to the precipitation kinetics in an Al-6mass%Zn-0.75mass%Mg alloy. It is well known that Al-Zn-Mg alloys have a positive effect on two-step aging, that is, the longer the duration of natural aging, the higher the strength of the artificial aging. The electrical resistivity at 160°C after storage at room temperature for 120min or 10220min was measured. The new rate equation applied to these experimental data showed that two precipitation reactions occur during the artificial aging. The rate equation of these reactions can be written as follows. The parameter, τ, is a time constant related to the evolution of precipitates and n is the exponent related to the morphology of the precipitates. The obtained values of parameters τ and n were consistent with the TEM structures and the change in hardness. ($A + B = 1$)

$$y = y_1 + y_2 = A\left[1-\exp\left\{-\left(\frac{t}{\tau_1}\right)^{n_1}\left[1-\exp\left(-\frac{t}{\tau_2}\right)\right]^{n_2}\right\}\right] + B\left[1-\exp\left\{-\left(\frac{t}{\tau_3}\right)^{n_3}\left[1-\exp\left(-\frac{t}{\tau_4}\right)\right]^{n_4}\right\}\right]$$

Keywords: *precipitation kinetics, rate equation, Al-Zn-Mg alloy, two-step aging, Johnson-Mehl equation*

1. Introduction

Many studies have been done involving the precipitation in Al-Zn-Mg alloys, and the sequences of the precipitation have been investigated and published [1-4]. It is well known that Al-Zn-Mg alloys have a positive effect on the two-step aging (split aging), that is, the longer the natural aging duration, the higher the strength of the artificial aging [5]. However, there are few studies about the precipitation kinetics of these alloys. Precipitation kinetics has been usually studied using the Johnson-Mehl equation or similar ones, and its reaction rate was then analyzed. However, it is difficult to represent the entire reaction process by this equation when multiple reactions simultaneously or sequentially occur. Yamamoto proposed a new kinetics theory and equation [6]. It was proved that this equation can effectively analyze the kinetics reactions by application to the precipitation in Cu-Be alloys [7], the graphitization of cementite [8] and the precipitation from quenched low carbon steel [9]. In this study, the precipitation in Al-Zn-Mg alloys is analyzed using this new equation and the parameters obtained based on this theory are discussed.

2. Experimental

To investigate the precipitation kinetics of Al-Zn-Mg alloys, the changes in the electrical resistivity and hardness were measured. Samples for the electrical resistivity and hardness were prepared from 1mm diameter wire and 1mm thick sheet, which were produced from DC cast slabs on a laboratory scale using a 99.99% aluminum ingot. The content was Al-6%Zn-0.75%Mg (mass %). These samples were solution heat treated in a salt bath for 1 hour at 450°C followed by water quenching. After quenching, they were held for 120min or 10220min at room temperature (20°C) and then aged at 160°C in an oil bath controlled at ±0.1°C. The change in the electrical resistivity was investigated by measuring the difference in the electrical potential at two points. The electric current was 0.5A using a constant power supply. The change in the electrical resistivity was normalized by setting the difference between the final and initial values to unity.

3. Derivation of New Equations

Several rate equations are derived from the model reaction process [6, 10, 11]. In this paper, the rate equation for the precipitation in aluminum alloys is derived as follows. Using the concept of extended volume, V_e, and extended surface area, S_e, according to Johnson-Mehl and Avrami, the ratio of precipitation, y, is given as follows:

$$y = 1 - \exp(-V_e) . \tag{1}$$

V_e was calculated according to the precipitation model. It was assumed that the number of precipitates exponentially decreases with time and each precipitate grows by diffusion based on the TEM structures in this experiment. The number of precipitates, N, is given by the following equation using an exponential function because precipitation is a collective and statistical phenomenon.

$$N = N_0\{1 - \exp(-t/\tau_2)\} . \tag{2}$$

The increasing rate of the number, I, is

$$I = dN/dt = (N_0/\tau_2)\exp(-t/\tau_2) . \tag{3}$$

Parameter N_0 is the number of precipitates at time $t = 0$. Parameter τ_2 is a time constant. According to the diffusion theory, the diffusion distance x is given by the following equation.

$$x \cong \sqrt{Dt} \quad (D\text{: diffusion coefficient}). \tag{4}$$

For a rod-like precipitate with a constant cross-section area, S_0, in which a precipitate grows with the increasing length, the volume of a precipitate at time t is $S_0\sqrt{D(t-t_1)}$ (t_1: the time of precipitate formation) using equation (4). Consequently, the total volume of the precipitates, V_e , and the ratio y of the precipitation at time t are as follows [6, 7]:

$$\begin{aligned} Ve &= \int_0^t S_0\sqrt{D(t-t_1)}\,I dt_1 = S_0\frac{N_0}{\tau_2}\sqrt{D}\int_0^t \sqrt{(t-t_1)}\exp(-\frac{t_1}{\tau_2})dt_1 \\ &\approx \mathrm{S}_0 D^{1/2}N_0 t^{1/2}\left\{1-\exp(-\frac{t}{\tau_2})\right\} = \mathrm{S}_0 D^{1/2}N_0 t^{1/2}N \end{aligned} \tag{5}$$

$$y = 1-\exp(-V_e) = 1-\exp\left(-\mathrm{S}_0 D^{1/2}N_0 t^{1/2}N\right) = 1-\exp\left\{-\left(\frac{t}{\tau_1}\right)^{1/2}\left[1-\exp\left(-\frac{t}{\tau_2}\right)\right]\right\}, \quad \tau_1 = \frac{1}{S_0^2 N_0^2 D} . \tag{6}$$

In a circular disc with a constant thickness, l_0, in which the disc grows in the radial direction by diffusion, the ratio y of precipitation at time t is also derived by the same method.

$$y = 1-\exp(-V_e) = 1-\exp\left(-\frac{\pi l_0 N_0 D}{2}tN\right) = 1-\exp\left\{-\left(\frac{t}{\tau_1}\right)\left[1-\exp\left(-\frac{t}{\tau_2}\right)\right]\right\}, \qquad \tau_1 = \frac{2}{\pi l_0 N_0 D} . \tag{7}$$

In a sphere which grows in the radial direction by diffusion,

$$y = 1-\exp(-V_e) = 1-\exp\left(-\frac{8}{15}\pi D^{3/2}t^{3/2}N\right) = 1-\exp\left\{-\left(\frac{t}{\tau_1}\right)^{3/2}\left[1-\exp\left(-\frac{t}{\tau_2}\right)\right]\right\},$$

$$\tau_1 = \left(\frac{15}{8\pi N_0}\right)^{\frac{2}{3}}\frac{1}{D} . \tag{8}$$

For an arbitrary shape, the next equation is defined.

$$y = 1 - \exp\left\{ -\left(\frac{t}{\tau_1}\right)^{n_1} \left[1 - \exp\left(-\frac{t}{\tau_2} \right) \right] \right\}. \tag{9}$$

Parameter n_1 is related to the morphology of the precipitate which grows by diffusion, n_1 =0.5 for a rod with a constant cross-section area, n_1 =1.0 for a disc or a plate with a constant thickness and n_1 =1.5 for a sphere or a cube. The term $\left[1 - \exp\left(-\frac{t}{\tau_2} \right) \right]$, which does not exist in the Johnson-Mehl equation, is related to the number of precipitates. This term is very important for fitting the experimental data using equation (9). Especially, the change in the early stage is influenced by this term. Yamamoto generalized equation (9) in response to various increasing rates of the precipitates as follows [6][7]:

$$y = 1 - \exp\left\{ -\left(\frac{t}{\tau_1}\right)^{n_1} \left[1 - \exp\left(-\frac{t}{\tau_2} \right) \right]^{n_2} \right\}. \tag{10}$$

Equation (10) is now called Yamamoto's equation. For simultaneous multiple reactions, each reaction rate, y_i is summed to the total rate y as follows:

$$y = \sum_i C_i y_i \qquad (\sum_i C_i = 1). \tag{11}$$

4. Comparison between Experimental Data and the Equations

The experimental data of the normalized change in electrical resistivity aged at 160°C are shown in Fig.1. This figure indicates the occurrence of at least two precipitation reactions. Especially, for the 120min held sample at room temperature, it seemed that the first reaction at 160°C continues to 1000min and the second reaction then occurs. Each reaction was fitted by equation (10) and summed as follows:

$$y = y_1 + y_2 = A\left[1 - \exp\left\{ -\left(\frac{t}{\tau_1}\right)^{n_1} \left[1 - \exp\left(-\frac{t}{\tau_2} \right) \right]^{n_2} \right\} \right] + B\left[1 - \exp\left\{ -\left(\frac{t}{\tau_3}\right)^{n_3} \left[1 - \exp\left(-\frac{t}{\tau_4} \right) \right]^{n_4} \right\} \right] \tag{12}$$

The experimental data in Fig.1 were analyzed by equation (12). Figures 2 and 3 show the calculated curves superimposed on the experimental data for the 120min and 10220min samples, respectively. At 120min, y is given as follows:

$$y = 0.64\left[1 - \exp\left\{ -\left(\frac{t}{490}\right)^{1.2} \left[1 - \exp\left(-\frac{t}{1} \right) \right]^{1} \right\} \right] + 0.36\left[1 - \exp\left\{ -\left(\frac{t}{25000}\right)^{0.5} \left[1 - \exp\left(-\frac{t}{10000} \right) \right]^{1_2} \right\} \right]$$

At 10220min,

$$y = 0.35\left[1 - \exp\left\{ -\left(\frac{t}{290}\right)^{1} \left[1 - \exp\left(-\frac{t}{1} \right) \right]^{1} \right\} \right] + 0.65\left[1 - \exp\left\{ -\left(\frac{t}{4800}\right)^{0.5} \left[1 - \exp\left(-\frac{t}{1500} \right) \right]^{1_2} \right\} \right]$$

The values of the parameters are listed in Table 1.

Table 1 Values of the Parameters in Equation (12) for the 160°C Aging.

Holding time at RT(min)	A	τ_1	n_1	τ_2	n_2	B	τ_3	n_3	τ_4	n_4
120	0.64	490	1.2	1	1	0.36	25000	0.5	10000	1
10220	0.35	290	1	1	1	0.65	4800	0.5	1500	1

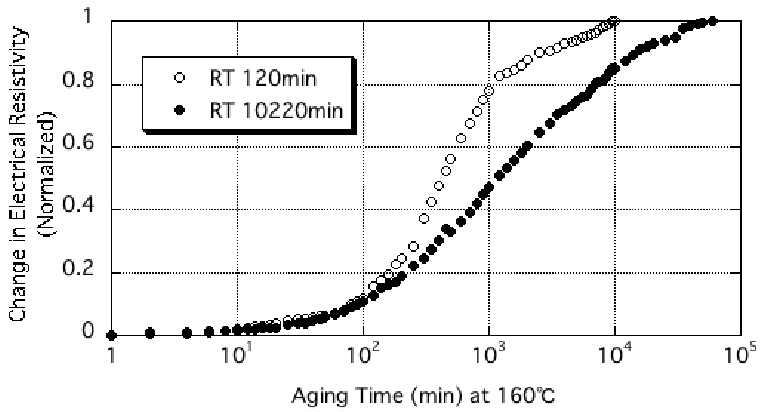


Fig.1 Change in electrical resistivity for holding at 120min and 10220min at room temperature (RT) followed by aging at 160°C.

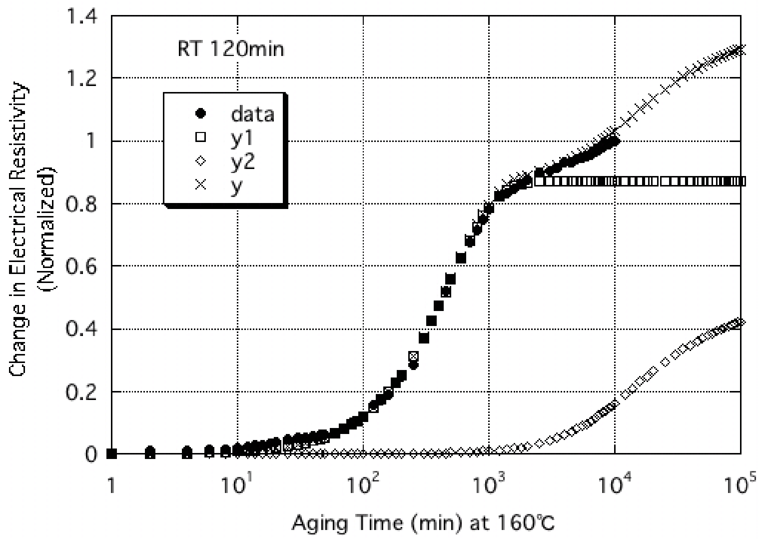


Fig.2 Change in electrical resistivity calculated using Yamamoto's equation for holding at 120min at room temperature (RT) followed by aging at 160°C.

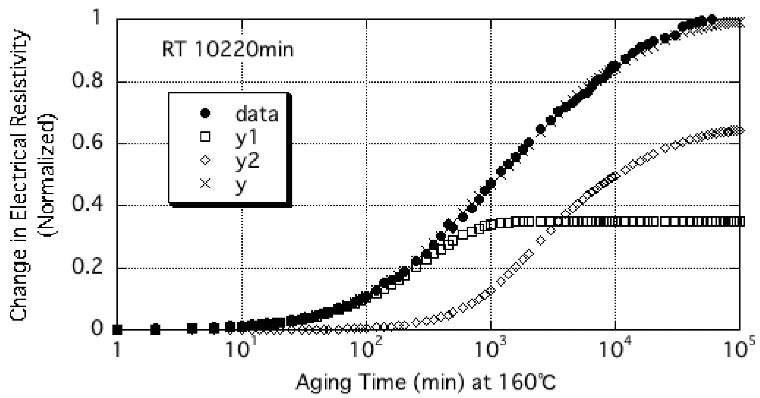
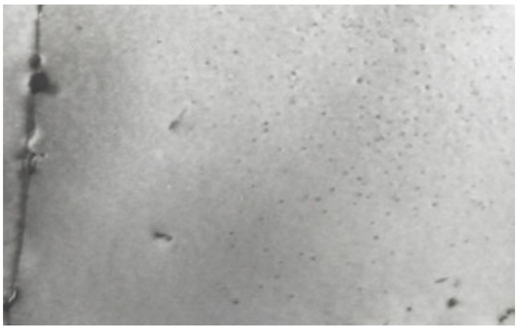


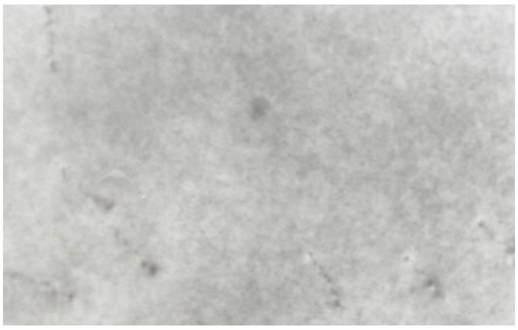
Fig.3 Change in electrical resistivity calculated using Yamamoto's equation for holding at 10220min at room temperature (RT) followed by aging at 160°C.

5. Discussion

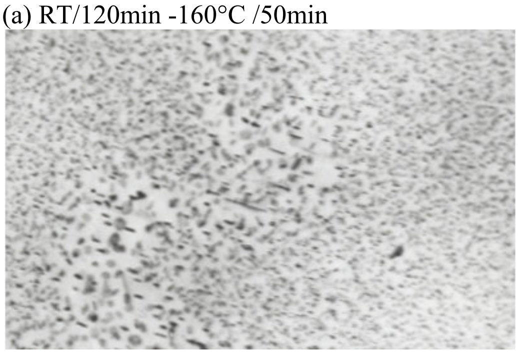
Table 1 indicates that the morphology of the precipitates in the first stage is a plate or a plate-like particle because parameter n_1 is 1.0 to 1.2 and that of the precipitates in the second stage is a rod because n_3 is 0.5. The values of τ_1 and τ_3 for the 120min are higher than that for the 10220min samples. These parameters are in inverse proportion to N_0^m, (m: 2/3 ~ 2) as shown by equations (6), (7) and (8). Therefore, the number of precipitates initiated during the first stage and also during the second one for the 120min is lower than that for the 10220min ones. The values of these parameters are supported by the TEM structures shown in Fig.4. During the early stage (50min) at 160°C, fine precipitates are observed at 120min in Fig.4 (a), but it is difficult to observe the precipitates at 10220min shown in Fig.4 (d) because they are too fine. Figure 5 shows the change in the Vickers hardness during aging at 160°C and the positive effect on the two-step aging. Figure 5 suggests the existence of fine precipitates in Fig.4 (d) because the hardness increases at 10220min compared to 120min. For 1000min at 160°C, the areas containing the plate-like and rod-like precipitates with a 10 to 100nm length surrounded by the one with fine precipitates (probably platelets) are observed at 120min shown in Fig.4 (b), while the distribution and size at 10220min are homogeneous and the length of the plate-like precipitates is 10 to 30nm in Fig.4 (e). For a long duration (~10000min) of aging at 160°C, the distribution of the precipitates at 120min is more inhomogeneous and rod-like precipitates with a 250nm length are observed in Fig.4 (c), while plate-like or rod-like precipitates with a 20 to 50nm length and homogeneous distribution are observed at 10220min in Fig.4 (f).



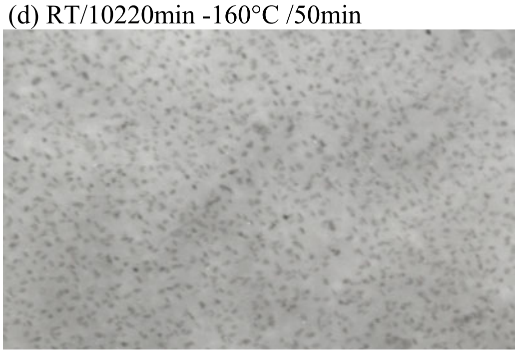
(a) RT/120min -160°C /50min



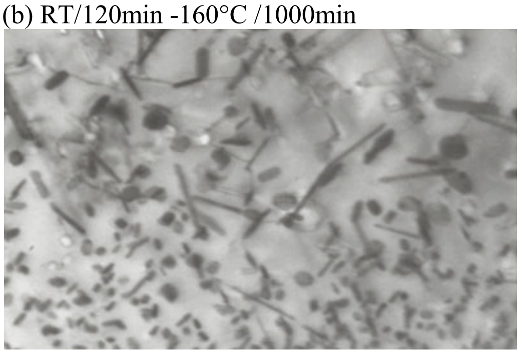
(d) RT/10220min -160°C /50min



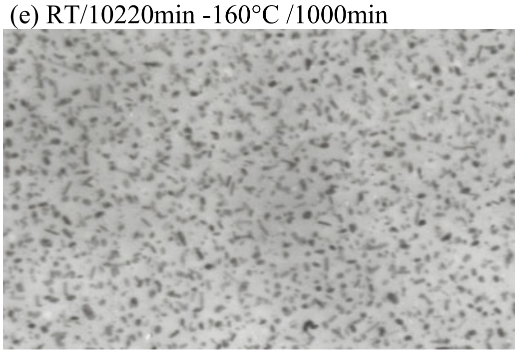
(b) RT/120min -160°C /1000min



(e) RT/10220min -160°C /1000min



(c) RT/120min -160°C /8500min



(f) RT/10220min -160°C /10900min

0.5um

Fig.4 TEM structures after aging at 160°C.

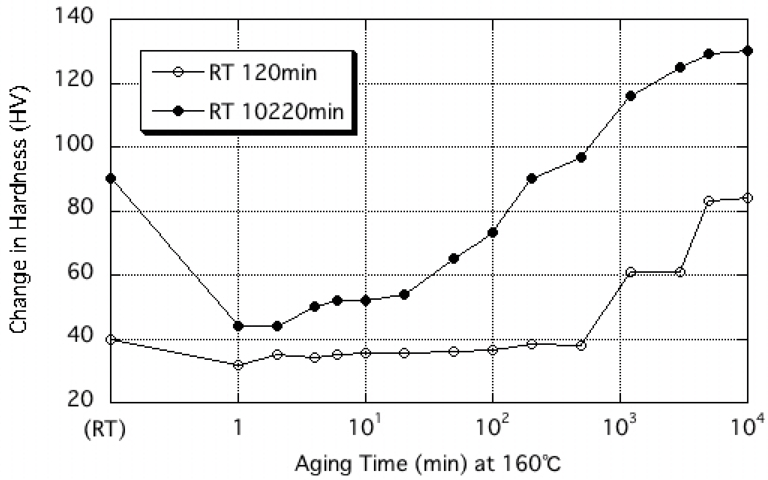


Fig.5 Change in hardness for holding at 120min and 10220min at room temperature (RT) followed by aging at 160°C.

These observed precipitates are estimated as the η' or η phase. The morphology of these precipitates is reported as either plate-like particles or rod-like ones [1-4]. Our result about the morphology of the precipitates is consistent with these previous studies. Figures 2, 3 and 5 indicate that the first stage precipitation contributes to the increase in hardness compared to the second stage one. For the long duration at room temperature, many GP zones formed homogeneously. As a result, the reversion of the GP zones occurred during heating at 160°C shown in Fig.5. It is considered that the reversion of the GP zones accelerates the formation of fine and plate-like precipitates in the first stage. This is the reason why this alloy has a positive effect on the two-step aging.

6. Conclusions

(1) The precipitation kinetics of the Al-6%Zn-0.75%Mg alloy at 160°C contained two precipitation processes. This kinetics was able to be analyzed using a new kinetics equation developed by Yamamoto.

(2) The parameter values in this equation were consistent with the morphology and distribution of the plate-like precipitates in the first stage and rod-like ones in the second stage in the TEM structures.

(3) The reason why this alloy has a positive effect on the two-step aging is that the reversion of the GP zones formed for a long duration at room temperature accelerates the formation of fine and plate-like precipitates in the first stage at 160°C.

References

[1] J.D. Embury and R.B. Nicholson: Acta Met., 13(1965) 403-417.
[2] P.A. Thackery: J. Inst. Metals, 96(1968) 228-235
[3] A.J. De Ardo, Jr. and C.J. Simensen: Met. Trans., 4(1973) 2413-2421.
[4] N. Ryum: Z. Metallkde., 66(1975) 338-343, 344-346.
[5] Y. Murakami, O. Kawano, S. Komatsu, T. Ohnishi and T. Nakazawa: Trans. JIM, 9(1968) 349-354.
[6] S. Yamamoto: *Trial of New Rate Theory* (in Japanese), (Showado, Kyoto, 1979) pp.178-196.
[7] S. Yamamoto and K. Kubota: J. JIM, 46(1982) 917-924.
[8] K. Kubota and S. Yamamoto: J. JIM, 46(1982) 908-916.
[9] K. Hanawa and T. Mimura: Met. Trans. 15A(1984) 1147-1153.
[10] J.W. Christian: *The Theory of Transformations in Metals and Alloys*, Pergamon Press, (1965).
[11] J. Burke: The Kinetics of Phase Transformations in Metals, Pergamon Press, (1965).