KINETICS OF PRECIPITATION IN Al-0.20 MASS% Sc ALLOYS

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ABSTRACT

The precipitation kinetics of equilibrium Al3Sc phases in Al-0.20 mass% Sc alloys was investigated in the aging temperature range from 533 K to 643 K by electrical resistivity and hardness measurements. The average Sc concentration C_{Sc} in the Al-rich matrix was calculated from the resistivity. The results for aging time dependences of C_{Sc} and the degree of precipitation (the fraction transformed) were analyzed form the viewpoint of time scaling and the Johnson-Mehl-Avrami equation. The rapid growth stage of the Al3Sc phsses was successfully scaled and characterized by the model of diffusion-controlled growth.

Keywords: *Al-Sc alloys, precipitation, kinetics, solute in the matrix, resistivity, activation energy and Johnson-Mehl-Avrami equation*

1. INTRODUCTION

Scandium, whose maximum solid solubility in aluminum is 0.21 at.% [1], produces an excellent age-hardening effect in Al-Sc alloys. The use of Sc as an additional element introduces superplastic behavior, a higher tensile strength level with high ductility, a higher heat-resistant property and a higher weldability in other Al alloys. The source of this interesting behavior is the presence of very fine equilibrium Al3Sc precipitates which exists with coherency strain and an ordered Ll2 structure: it is very important to investigate the kinetics of precipitation of the Al3Sc phase in Al-Sc alloys. The resistivity of an aged dilute alloy can be converted into the average concentration of solute in the matrix when the size and volume fraction of precipitates are sufficiently large and low, respectively and the deviation from Mattiessens's rule is negligibly small. It is shown that the conditions are satisfied for Al-Sc alloys [2]. In the present work, the precipitation kinetics in Al-0.2mass% Sc alloys were investigated in detail by converting the value of the resistivity into the average Sc concentration C_{Sc} in the Al-rich matrix.

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

The Al-0.20 mass% Sc alloy was prepared by dilution of the Al-Sc master alloy containing 2.1 mass% with high purity Al. The ingot of 20 mm in diameter was homogenized at 823 K for 0.26 Ms and formed into wire of 0.5 mm in diameter by cold swaging and drawing. According to the result of the chemical analysis, the concentrations of Sc and impurities were as follows: 0.20 mass% (0.12 at.% Sc); 0.006 mass% Mg, 0.004 mass% Fe, 0.001 mass% Cu and 0.001 mass% Si.

2.2 Electrical resistivity measurement and thermal treatment

The specimen for the resistivity measurement was mounted on a quartz specimen holder. The high purity Al wires of 0.5 mm diameter were spot welded to the specimens as potential leads. The resistivity was measured at 77 K by the four-probe method using a precision potentiometer. The measurements were repeated ten times to obtain one data point, reversing the current direction to

eliminate the stray electromotive forces. From the measurement results of the diameter and the distance between potential leads, the specific electrical resistivity was calculated. The specimens were homogenized in air at 913 K for 3.6 ks in a horizontal furnace and quenched into iced water. The quenched alloys were isothermally aged at various temperatures between 513 K and 643 K.

2.3 Hardness measurement

Microhardness tests were carried out using the Vickers method. The measurements were repeated eight times and the mean value was calculated.

3 . RESULTS

3.1 Hardness change

Fig. 1 shows the hardness change plotted as a function of aging time for Al-0.20 mass% Sc alloys. A maximum like a plateau was observed. The maximum hardness and the aging time taken to reach the maximum hardness $H_V{}^{max}$ depended greatly on the aging temperature. The highest $H_V{}^{max}$ was obtained after aging 533 K. This aging temperature is much higher than in usual age-hardenable Al alloys. Another prominent feature of the age-hardening of Al-Sc alloys is the high resistance to overaging. These results suggest that the coherency of the precipitates is fairly stable as would be expected from the fact that they are in their equilibrium state and the diffusion rate of Sc in aluminum is low [3].

3.2 Resistivity change

Fig. 2 shows the resistivity plotted as a function of aging time for Al-0.2 mass%Sc alloys. The resistivity decreases with increase in aging time. The decrease corresponds to the decrease in C_{Sc} in
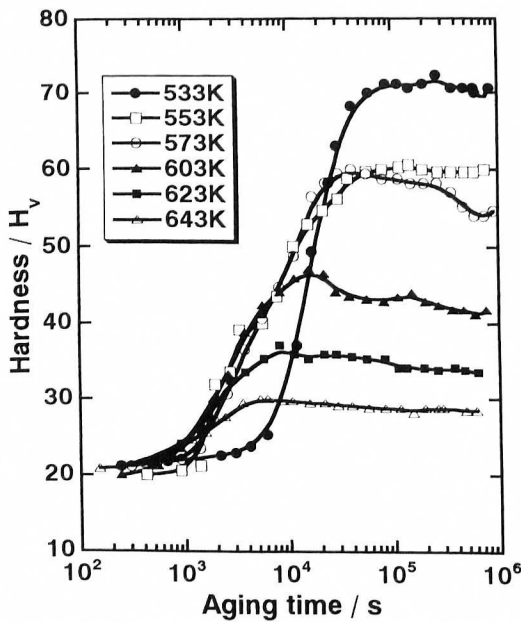

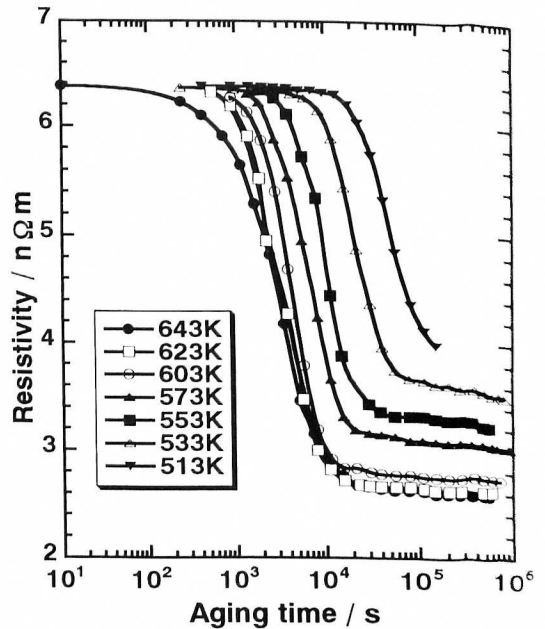Fig. 1 Age-hardening curves for Al-0.20 mass% Sc alloys.

Fig. 2 Resistivity plotted against aging time in Al-0.20 mass% Sc alloys.

the Al-rich matrix owing to the nucleation and growth of Al3Sc precipitates. The change in the resistivity shown in Fig. 2 can be roughly divided into three stages in view of the precipitation process: an early stage with an incubation period, a rapid growth stage and a gradual growth stage with the Ostwald ripening process. The value of 34 nΩ m at.%$^{-1}$ determined by Fujikawa et al. [1] was used in the present work as the resistivity increment $\Delta\rho/\Delta c$ per atomic percent of Sc in the solid solution of the Al-Sc alloys. Fig. 3 shows the time variation in the average Sc concentration of the Al matrix calculated using the results shown in Fig. 2 and the value of $\Delta\rho/\Delta c$.

4. DISCUSSION

4.1 Kinetics and scaling analysis of precipitation process

We have calculated the degree of precipitation (the fraction transformed) using the results shown in Fig. 3 and thereby discussed the kinetics of precipitation process in the Al-0.2 mass% Sc alloys. F can be defined as

$$F = (C_0 - C_t)/(C_0 - C_e) \qquad (1)$$

where C_0 is the concentration of solute in solution at zero aging time, C_t is the concentration at aging time t, and C_e is the equilibrium concentration. The values of C_e are obtained from the results [1,2]. Fig. 4 shows the aging time dependence of F calculated in this way for Al-0.2 mass% Sc alloys. Most of results gave sigmoidal curves for F against aging time, where the value of F increases slowly at first, then much more rapidly and finally slowly again. It is very important to investigate the scaling properties using a normalizing parameter for the kinetics of phase decomposition and to find the universal law of self-similar evolution of the decomposition process. From time scaling analysis,
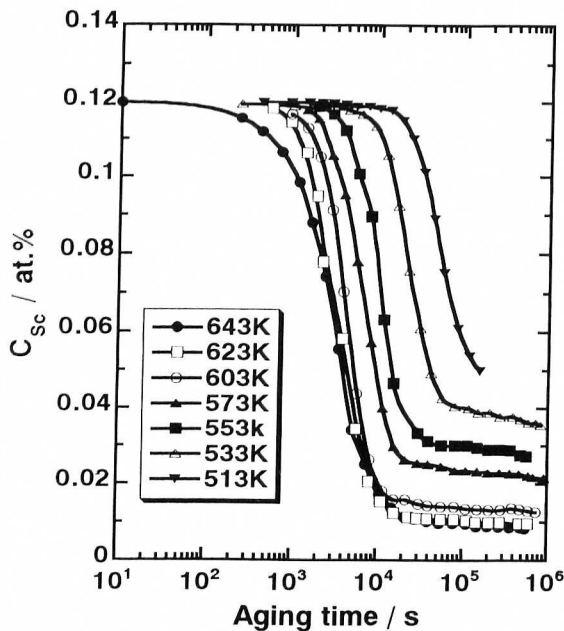
Fig. 3 Average Sc concentration in the matrix
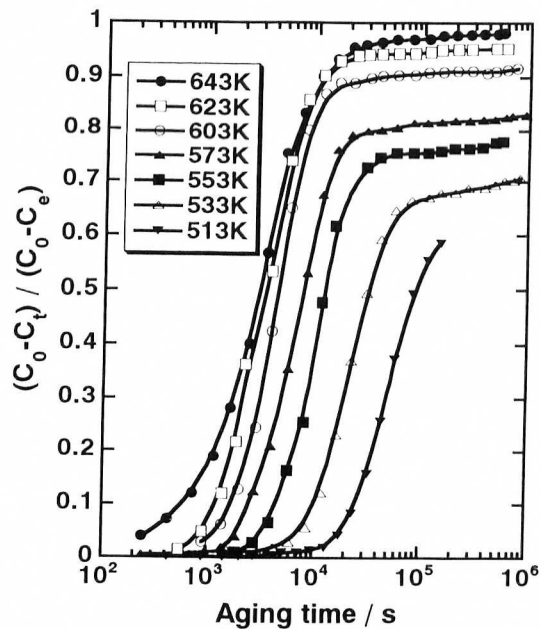   against aging time for Al-0.20 mass% Sc alloys.

Fig. 4 Fraction transformed against aging
        time for Al-0.20 mass% Sc alloys.

a universal time scale may be deduced to evaluate the precipitation kinetics, independently of aging time, aging temperature and composition. In the present work, the aging time was normalized by the time taken to reach $F=0.5$ and time scaling was investigated. Fig. 5 shows the time scaling of the results shown in Fig. 4. It is noted that the values of F in the initial stage and the rapid stage fall on one master curve; hence, the early stage and the rapid growth stage were excellently scaled, independent of aging time and aging temperature. Consequently, the decomposition at the early stage and the rapid growth stage of precipitation in the Al-Sc alloys can be controlled by an universal law, independent of aging temperature and aging time. It is shown that the scaled curves in Fig. 5 is similar to the Johnson-Mehl-Avrami (JMA) equation for three-dimensional nucleation and growth as follows [4,5]:

$$F = 1 - \exp(-kt^n) \qquad\qquad (2)$$

where t is the time, k corresponds to the so-called rate constant, n is the JMA exponent and has the dimensions of $(time)^{-n}$. Avrami pointed out that , if one plots F against $\log t$, all the curves with the same value of n will have the same shape and will differ only in the value of k, which is equivalent to
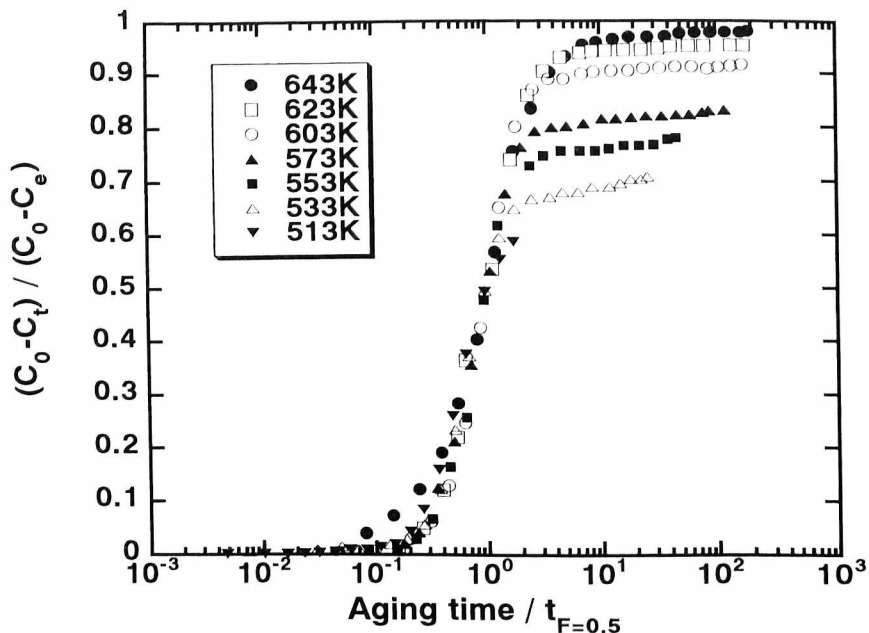

Fig. 5 Time scaling for fraction transformed in Al-0.20 mass% Sc alloys. The aging time is scaled by the time to reach $F=0.5$.

a change in k, corresponding to a change in scale. Here, we analyzed the results shown in Fig. 5 by the JMA equation. When Eq.2 is applied to the result of precipitation, a straight-line relation with the slope n should be found in the maximum observable experimental range of reaction. Therefore, by plotting $\log\{\log[1/(1-F)]\}$ vs. $\log t$ plots, one can obtain the JMA exponentnt n. Fig. 6 shows the $\log\{\log[1/(1-F)]\}$ vs. $\log t$ plots for Al-0.2 mass% Sc alloys. The existence of a straight-line relation was observed in the rapid growth stage. The value of n below 623 K is rather approximately equal to 3/2, which means diffusion controlled growth of a fixed number of crystals irrespective of shape of the crystals [6].

4.2   Time scaling analysis of hardness change

Here, we have calculated the fraction F_H of hardness reached by aging using the results in Fig. 1 and thereby discussed the kinetics of precipitation in Al-0.20 mass% Sc alloys. F_H is can be defined as

$$F_H = (H_t - H_0) / (H_{max} - H_0) \qquad (3)$$

where H_t is the hardness at aging time t, H_0 is the hardness in as-quenched state and H_{max} is the maximum hardness at each aging temperature. Moreover, aging time is normalized by the time taken to reach $F=0.5$. Fig. 7 shows the results of the time scaling analysis and the results are similar to those in Fig. 5. Clearly the hardness changes until the maximum hardness fall on one master curve similar to Eq.2; hence, the early stage and the rapid stage of age-hardening are excellently scaled, independent of aging time and aging temperature and the age-hardening process is controlled by the same process in all aging temperatures.

4.3   Activation energy for precipitation

From the stage where the JMA equation on is valid, the value of activation energy for precipitation Q can be determined from the temperature dependence of the rate constant k:

$$k = k_0 \exp (-Q/RT) \qquad (4)$$

where k_0 is a pre-exponential factor; R and T indicate the gas constant and absolute temperature, respectively. Fig. 8 shows the Arrhenius plots of k in the JMA equation for Al-0.2 mass% Sc alloy. The value of Q obtained using Eq.4 is 200 kJ mol^{-1} and is nearly equal to the activation energy (173 kJ mol^{-1}) of impurity diffusion of Sc in aluminum [3]: hence, it is found that the precipitation process is diffusion-controlled process.
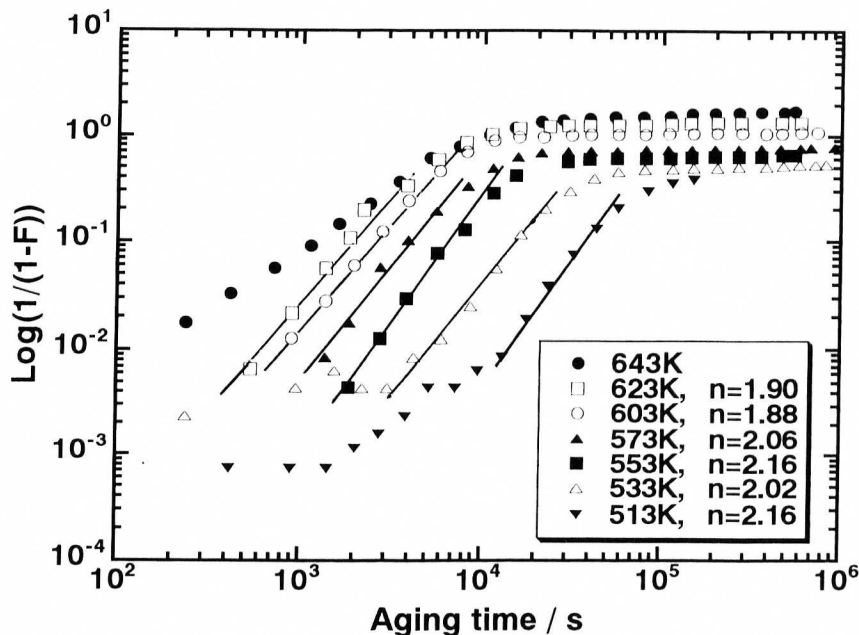

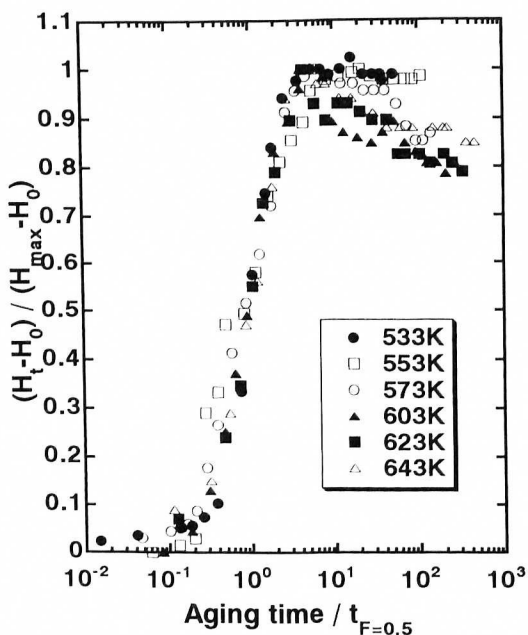Fig. 6   JMA plots for Al-0.20 mass% Sc alloys.

Fig. 7 Time scaling for hardness change in Al-0.20 mass% Sc alloys. The aging time is scaled by the time to reach F=0.5.
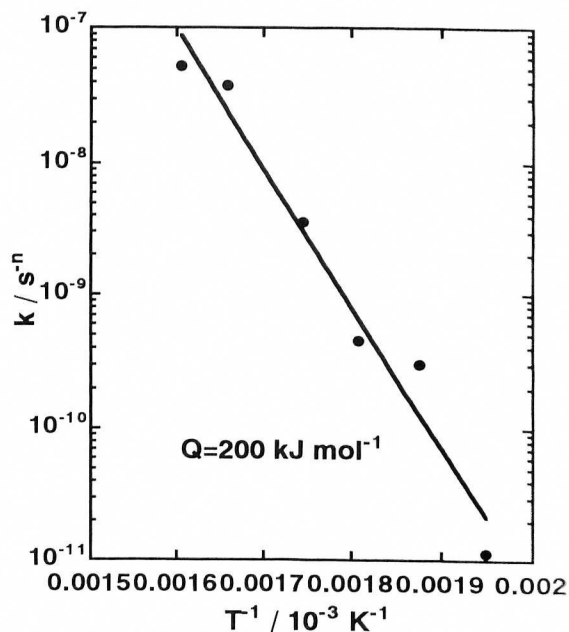

Fig. 8 Relationship between rate constant k in JMA relation and reciprocal aging temperature in Al-0.20 mass% Sc alloys.

5. CONCLUSIONS

(1) The precipitation kinetics in Al-0.20 mass% Sc alloys was investigated by resistivity and hardness measurements.

(2) The average Sc concentration C_{Sc} in the Al-rich matrix at aging time t was calculated from the resistivity results. The curve of C_{Sc} vs. t consists of an early stage with an incubation period, a rapid growth stage and a later stage with the Ostwald ripening process.

(3) The fraction F transformed at different aging times was calculated from the values of C_{Sc}. The curve of F vs. log t was analyzed from the viewpoint of the time scaling and the Johnson-Mehl-Avrami equation.

(4) The time scaling analysis was also carried out for the hardness change.

(5) The activation energy (200 kJ mol^{-1}) for the precipitation of Al$_3$Sc was determined from the temperature dependence of the rate constant k in JMA equation. The value is found to be nearly equal to the activation energy (173 kJ mol^{-1}) for the impurity diffusion of Sc in aluminum.

Acknowledgments

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