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Structure change during heating preaged Al-Li binary alloy samples at a constant rate has been investigated by means of in-situ synchrotron radiation small-angle scattering (SR-SAXS) in order to discuss the differential scanning calorimetry (DSC) results. It was found that the dissolution and the coarsening of δ' precipitates often occurred simultaneously, which affect the shape of the specific heat.

INTRODUCTION

Calorimetric experiments such as differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are useful tools for the quantitative examination of the stability of metastable phase and the kinetics of dissolution. For example, the stability of δ' precipitates and its unidentified precursor is detected by Nozato et al. and Sato et al. using DTA or DSC experiments for Al-Li alloys[1]-[3]. The analysis of the change in the specific heat was also extended by several authors to the determination of the shape or the size distribution of GP zones or precipitates for several Al-based alloy systems[4],[5]. This extension is, however, valid only if the dissolution process consists of one elementary process and the size effect on the dissolution kinetics is negligible. In other words, experimental results on the structure change during DSC measurements are indispensable for the proper interpretation of the calorimetric measurements.

EXPERIMENTAL PROCEDURE

Al-7.9at%Li alloys were used in the present experiment. Samples were solution treated at 823K for 1.2ks in a sealed PYREX tube filled with Ar gas. Then the sample was quenched into iced water and aged in a oil bath at 423K. The DSC measurements were performed in Ar atmosphere at the heating rates of 0.033 - 0.267 K/s. Structure change during heating at the rate of 0.133K/s was examined by in-situ SR-SAXS. The SR-SAXS experiments were performed at BL-15A of Photon Factory, KEK at Tsukuba.

RESULTS AND DISCUSSION

A. DSC RESULTS

Change of the specific heat for Al-7.9at%Li alloy aged at 423K for 86.4ks is shown in Fig. 1 after base line subtraction. As reported by several researchers[1]-[3], the specific heat curve appears to be composed of two peaks and *the higher temperature part is less sensitive to the heating rate.*

Takahashi and Sato[2] made a TEM observation using weak-beam method and found that the strain field around the large precipitates disappeared. They explained the two peaks in the specific heat curve in terms of the coherent and semicoherent δ' precipitates.[2],[3] This explanation seems persuasive, but there still remains several points to clarify. For example, the strain energy is relatively small in this alloy system[6], resulting that the stabilization of the precipitates due to the strain release is small. Considering that the difference in the position of the two peaks (or a peak and a shoulder) in the specific heat is

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about several tens to 100K, stabilization due to the strain release alone is not the enough explanation for the specific heat curve.

In order to inquire into the origin of the two peaks in the specific heat, the structure change during heating was investigated by SR-SAXS.

B. AVERAGE STRUCTURE CHANGE DURING HEATING

Structure change of δ' precipitates during heating at 0.133K/s is shown in Fig.2. The preaging condition for this sample was 423K for 86.4ks. As seen in the figure, spherical precipitates of 6.2nm by Guinier radius were dispersed at the average distance of 21nm at the preaged condition. The integrated intensity remained constant up to about 420K (region I), and then decreased slowly till 450K (region II). The integrated intensity decreased rapidly after 450K (region II'), and then the decrease became slower again at 490K (region III for T>490K). Guinier radius is almost constant till region II, whereas the inter particle distance, L, began to increase in region II. This discrepancy should be mainly due to the fact that the Guinier radius represents the higher moment concerning the size distribution and less sensitive to the small amount of decrease in the average size.[7] Guinier radius decreased and the interparticle distance increased rapidly in region II', corresponding to the rapid dissolution of the precipitates. In region III, Guinier radius began to increase after it remained almost constant of 5.4nm for a while at 485K. The increase in the Guinier radius suggests the simultaneous process of the dissolution and the coarsening. It should be noted that the onset of the increase of Guinier radius almost agreed with the temperature that the slope of the integrated intensity decreased. As discussed above, the structure change of the δ' is divided into three regions using the average structure parameters, Q/Q_0, R_G and L. The first is the region of no change, which is below the aging temperature. The second is the region of dissolution where Q/Q_0, R_G decreased. The third one is the region of decreasing amount of precipitates with coarsening. The onset of region III almost agreed with the position of the shoulder in the DSC results. As seen from the change of the average structure parameters, the shoulder appearing in the DSC curve is closely related to the onset of coarsening. Conventional explanation on this shoulder, i.e., the change in the thermal stability caused by the strain release due to coherent-semicoherent transition of δ' is not sufficient, because the change in the stability caused by the strain energy is small, at most several degrees as measured by the solvus temperature.[8] Another important factor to be considered is that the coarsening in region III suggests that the composition of the matrix is close enough to the position of the miscibility gap, i.e., the specific heat strongly reflect the shape of the solvus itself in this region. Although a simple transition from non-equilibrium to near-equiribrium dissolution can not explain the sharp minimum appearing in several Al-11.8at%Li samples, the specific heat in region III should be mainly explained by the shape of the miscibility gap.

C. INTERPRETATION OF THE AVERAGE STRUCTURE CHANGE

In section B, it was found that the structure change in regions II and II' is a simple dissolution process. In this region, the sequence of dissolution is well understood from the results on the isothermal reversion experiments on the alloy systems.[9]-[11] In order to understand the simultaneous process of the dissolution and the coarsening in region III, understanding both kinetics of isothermal dissolution and coarsening would be helpful.

Figure 3 shows the schematic drawing of the structure change in region III. For simplicity, the heating process is approximated by the sequence of step-heating process as shown in the center of the figure. In each step, shrinkage of the precipitates due to the driving force of dissolution by heating up occurs first, and then the coarsening occurs. The average radius increases if the coarsening rate is larger than the dissolution rate(case (a) in the figure), and decrease if the coarsening rate is less, or coarsening does not occur at all (case (b)). The latter situation of case (b) is realized when the dissolution rate is not fast enough compared with the heating rate, and the driving force for dissolution has been accumulated. For Al-7.9at%Li, we can estimate the dissolution rate, V_d, the coarsening rate, V_c, and the applied dissolution driving force due to heating up(scanning), V_s, using the values in the references.[9]-[16] Dissolution rate constant during isothermal reversion process was used for V_d as defined by[9],[10]

$$dR/dt = V_d. \tag{1}$$

Since the rate constant for the reversion is for the reversion process under large driving force, i.e., the dissolution rate when the sample is heated up directly from the aging temperature, they must be interpreted as the maximum dissolution rate. Assuming that the amount of dissolution is determined by the change in the volume fraction of δ' precipitates at each temperature, T, the change in the radius due to dissolution can be also estimated. Using the definition of the volume fraction in terms of relative change of the average radius, R/R_0, and the phase boundary, the dissolution driving force is defined as

$$V_s = dR/dt = \frac{\alpha \; R_0}{3 \; V_{f0}^{1/3} \; V_f(T)^{2/3}} \; \frac{d}{dT} V_f(T) \tag{2}$$

which is a measure for the additional driving force of dissolution per unit time caused by heating as measured by the dissolution rate of the precipitates of radius R. V_{f0} and $V_f(T)$ are the equilibrium volume fraction at the preaging temperature and at the temperature, T, respectively. The coarsening rate, V_c, was estimated from the experimental data for the coarsening rate constant, K, using

$$V_c = K / 3R^2 . \tag{3}$$

The rate constants of radius for the three process calculated for Al-7.9at%Li are shown in Fig. 4 as a function of temperature. The dissolution rate, V_d, denoted by (a) in the figure, is obtained from equation (2). The dissolution driving force, V_s, denoted by (b) in the figure has two branches. One (denoted by solid line) is the rate calculated for a particle shrinking during heating. The other one (broken line) is for a particle with the same size at each temperature. If the driving force for dissolution is large and all the particles shrink at the same rate, the solid line is the case, and if small particle dissolve selectively due to Gibbs-Thomson effect, then the situation is rather near to the broken line. The solid and the broken lines for the coarsening rate, V_c, derived from (3), also correspond to shrinking R and the constant R, respectively. For Al-8at%Li, it is seen that $V_s > V_d > V_c$ at low temperature region (T<445K), suggesting that the dissolution process cannot catch up the driving force of dissolution and the coarsening never occurs. The dissolution rate, V_d, is the rate-determining one, but the change in the radius is small in this stage because the rate is too small to make an appreciable change in the radius. At higher temperature, dissolution rate catch up the driving force of dissolution, but V_d is still larger than the coarsening rate, V_c, resulting that the average radius continues to decrease. From the constraint that total amount of dissolution is equal to or less than the amount that can dissolve thermodynamically, real dissolution rate should be between V_s and V_d because of the accumulated driving force at lower temperature. In this figure, the coarsening rate exceeds the dissolution driving force at 475K for constant R case, and at 485K for decreasing R case. As seen in Fig. 2, the increase in the Guinier radius was observed experimentally after about 490K, which almost agrees with the present discussion.

If the diagram of Fig. 4 holds, it should be applicable to other aging conditions. The sample with the small initial radius of 1.2nm showed a monotonical increase in the Guinier radius during heating, which agreed well with the suggestion of eqs.(1)-(3). The DSC results by Levendai et al.[17] showed a single dissolution peak for the preaged δ' precipitates although their sample composition and preaging temperature were almost the same as the present experiments. This result can be also explained by Fig.4. Since their heating rate of DSC experiment was ten times faster than the present study, the line (b) increased by ten times according to (2). Then the situation is that the driving force of dissolution is always higher than the dissolution rate, so that the coarsening never occurs.

CONCLUSION

Structure change during heating preaged Al-Li binary alloy is examined by means of in-situ SRSAXS. It was found that

1. Simultaneous process of the dissolution and the coarsening occurred during heating. The onset of coarsening was close to the temperature that the shoulder on DSC curve appeared.
2. The condition for the coarsening with dissolution was qualitatively explained in terms of the isothermal dR/dt for coarsening, dissolution, and the driving force for dissolution.

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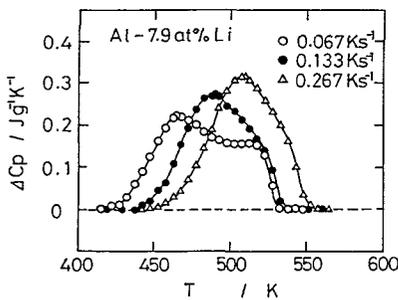[18] Harkness S.P., Gould R. and Hren J.J., Phil. Mag., 19(1969),115.

Fig.1 Change of the specific heat for Al-7.9
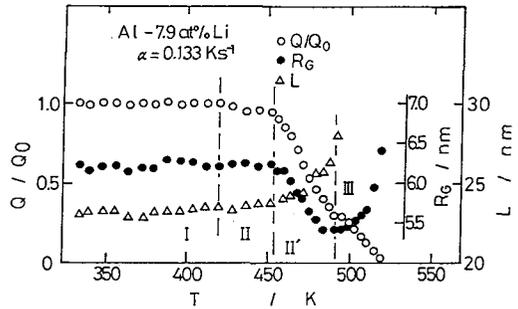   at%Li aged at 423K for 86.4ks.

Fig.2 Change in the Guinier radius, the normalized
      integrated intensity, and the interparticle
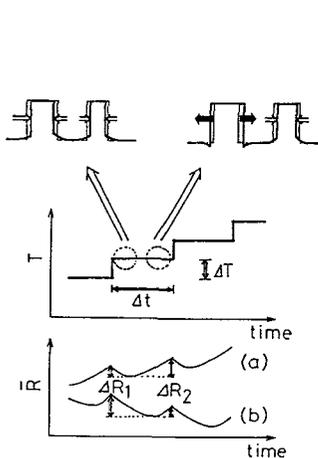   distance. Heat treatment is the same as Fig.1.

Fig.3 Schematic explanation of the simultaneous
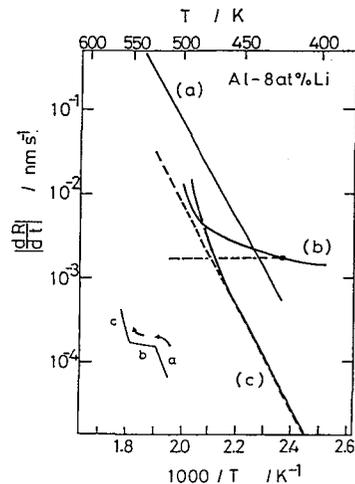   coarsening and dissolution.

Fig.4 Evaluate of the change in the radius due to
      (a)dissolution, (b)dissolution driving force,
      and (c)coarsening