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PRECIPITATION PROCESS OF AI-SC ALLOYS

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Abstract

Precipitation process in an Al-0.25 wt.%Sc alloy aged at 573 K has been investigated by resistivity and hardness measurements, transmission electron microscopy, and atom-probe field ion microscopy. It was found that the equilibrium Al3Sc phase particles precipitate homogeneously from the beginning. The particles coarsen following the Lifschitz-Wagner rule after the completion of the nucleation-and-growth stage. Although the precipitation process seemed to be simple, the composition of the precipitate varied with aging time in an unexpected way. The content of the precipitate was measured to be 27 at.%Sc in the initial stage of aging, and increased to 35 at.%Sc.

1. Introduction

It was recently reported that Al-Sc alloys have excellent age-hardenability. Although the solubility of Sc in Al is very low (1), an age hardening effect is noticeable (2,3). This alloy system is, therefore, a promising candidate for new commercial aluminum alloys. A phase diagram of the Al-Sc system is available now, although it is still regarded as a provisional one (4). A few works have been published on the precipitation process of cast Al-Sc alloys. The precipitation sequence seems to be simple according to the studies by Drits et al. (2) and Blake and Hopkins (3). An equilibrium phase, Al3Sc, with the L12 structure precipitates via a discontinuous precipitation mechanism in chill cast alloy. It was also confirmed that coherent Al3Sc precipitates are formed homogeneously from the solution treated alloy (3).

Discontinuous precipitation is generally not profitable as a means to improve the mechanical properties of alloys. Therefore, it is important to study the precipitation process in the alloy whose concentration of Sc is less than the maximum solubility limit. If such alloys are quenched to a low temperature after the solution treatment, it is expected that small dispersive precipitates of Al3Sc can be formed via homogeneous nucleation as shown by Drits et al (2). The present study is to investigate the precipitation process of a dilute Al-Sc alloy by resistivity and hardness measurements, transmission electron microscopy, field ion microscopy, and atom-probe.
2. Experimental

Al-Sc alloy ingots were prepared by inert-gas induction melting in an alumina crucible. The composition of the alloy ingots were determined to be 0.25 wt.% Sc by chemical analysis. After annealing at 773 K for 7 days for homogenization, the ingots were drawn or rolled to a wire 0.3 mm in diameter for a FIM sample and to a foil 0.1 mm thick for a TEM sample. The samples were solution treated at 910 K for 1 h in Ar atmosphere, and quenched into ice water. They were immediately aged at 573 K for various periods of time in an Ar atmosphere.

The resistivity measurement was carried out in liquid nitrogen using a conventional four terminal method. Hardness was measured using a micro Vickers hardness tester. TEM samples were prepared by twin jet polishing in a solution of $\text{HNO}_3$ 9 part, $\text{H}_2\text{O}$ 1 part. FIM tips were prepared by electropolishing the wire in $\text{HNO}_3$ at 4 V a.c.

An energy compensated time-of-flight atom-probe FIM was used in the present study to determine the composition of the precipitates. The details of the instrument have been described elsewhere (5). Atom-probe analysis was performed under $1\times10^{-10}$ Torr UHV at 40 K with $V_p/V_{dc}=0.2$ to 0.3.

3. Results

3-1. Resistivity measurement

The resistivity of the Al-0.25 wt.% Sc alloy is plotted as a function of aging time, $t_a$, in Fig.1. The resistivity decreases monotonically with aging time. This monotonical decrease of resistivity indicates that the concentration of Sc in the matrix decreased due to the nucleation and growth of the precipitates. At $t_a>10^4$ sec, a plateau region is found during which the resistivity decreases only slightly with longer aging time. Therefore, it can be concluded that the nucleation-and-growth process is completed at $10^4$ sec, and coarsening occurs thereafter.

By measuring the resistivities of as-quenched alloys as a function of the concentration of Sc, it was found that the residual resistivity of Sc in Al was 3.8 $\mu$ $\Omega$ cm/at.% The value of the measured resistivity can be converted to the concentration of Sc in the matrices of the alloys.

According to the Gibbs-Thomson equation and the Lifschitz-Wagner equation, the concentration of the matrix, $c$, can be related to aging time, $t_a$, using the following equation in the coarsening stage

$$c - c_e = (k t_a)^{-1/3}$$

where $c_e$ is equilibrium concentration of Sc in the matrix and $k$ is a constant. The concentration of Sc in the matrix plotted as a function of $t_a^{-1/3}$ is shown in Fig.2. The linear relation can be observed at long aging time, which indicates the coarsening of the precipitates obeys the Lifschitz-Wagner rule. Therefore, it is concluded that the precipitation is in the coarsening stage at $t_a > 3\times10^5$ sec, which is consistent with the result of the resistivity measurement shown in Fig. 1.

3-2. Hardness measurement

Micro Vickers hardness is plotted as a function of aging time in Fig.3. Hardness did not decrease significantly even after it had reached a maximum at $10^4$ sec. This means that it takes a fairly long time for the alloy to reach the over-aged state.
3-3. TEM and FIM observation

Transmission electron micrographs of the sample aged at 573 K for $10^2$ min are shown in Fig. 4. Very fine precipitate particles are homogeneously dispersed in the matrix. The electron diffraction pattern of (110) shows faint superlattice reflections. In Fig. 5, transmission electron micrographs of the sample aged at 573 K for $10^3$ min are shown. The precipitates are observed with coffee-bean-like contrast indicating the existence of coherent strain. Field ion micrographs of the alloy aged under the same condition are shown in Fig. 6. A mixture of Ne and H$_2$ was used as the imaging gas. The precipitates are imaged with bright contrast. The concentric rings are continuous at the interface between the precipitate and the matrix, which indicates that the precipitates are indeed coherent. In the electron diffraction patterns from (001), strong superlattice reflections are observed. Therefore, it is concluded that the precipitates are Al$_3$Sc with the L1$_2$ structure. Transmission electron micrographs of the sample aged for $10^4$ min are shown in Fig. 7. The precipitates have grown in size compared with those formed in the sample aged for $10^3$ min. Coffee-bean-like contrast is still observed. The electron diffraction pattern from (110) shows the superlattice reflections. Field ion micrographs are shown in Fig. 8, which display the precipitates appearing near the (111) and the (200) poles. Since Al$_3$Sc has the L1$_2$ structure, the stacking sequence of the (200) planes should be 0-50-0-50... at% Sc. Since only Sc atoms are brightly imaged in the precipitates, it is expected that brightly and darkly imaged planes should appear in alternate layers of the (200) planes. On the other hand, the concentration of Sc should be constant at 25 at% in the (111) planes if the precipitate has a stoichiometric composition. Therefore, no plane should not be darkly imaged in the precipitates on the (111) plane (Fig. 9). In Fig. 8, the darkly-imaged layers are observed alternatively at the concentric rings in the precipitate appearing on the (200) plane. However, the Sc concentration cannot be determined specifically from this picture. Field ion micrographs of the sample aged at $10^5$ min are shown in Fig. 10. At this long aging time, the precipitates are still coherent with respect to the matrix.

3-4. Atom Probe Analysis

The atom-probe analyses of the precipitates were performed with selected area analysis. The probe hole was located in the center of a precipitate before each analysis. The precipitates were large enough to completely cover the probe hole, so that it was certain that the data were collected only from the precipitate region. Approximately 10 to 30 precipitates were analyzed for each aging condition. The number of Sc atoms collected from each precipitate varied from 50 to 200.

The Sc concentration of the precipitates in various aging conditions is plotted as a function of aging time, as shown in Fig. 11. It is expected from the phase diagram (4) that the equilibrium Al$_3$Sc phase precipitates in this aging condition; however, the atom probe data show the Sc concentration is larger than 25 at.% for all the aging conditions studied. Moreover, the Sc concentration increased with aging time to $10^5$ s, and appeared to reach a maximum value of 35 at.%. 
4. Discussion

The precipitation process of the Al-0.25wt.%Sc alloy is found to be simple. The equilibrium phase, Al$_3$Sc, with the L1$_2$ structure homogeneously precipitates from the beginning. The precipitates are spherical, and have perfect coherency with the matrix. Due to the similarity of the crystal structure of the matrix and the precipitates, the equilibrium phase directly precipitated without the formation of any other metastable phases. Since the L1$_2$ particles remain coherent with the fcc matrix, the nucleation barrier for the precipitation does not seem to be high. Therefore, nucleation could occur homogeneously in the matrix. After the nucleation-and-growth stage, the Al$_3$Sc precipitates coarsened following the Lifschitz-Wagner theory. No transition phases were observed as long as the electron microscopy was concerned.

A question is the composition of the Al$_3$Sc precipitates. As shown in Fig. 11, the atom-probe results indicate that the composition of the precipitates increases from 27 at.% Sc, in the initial stage of precipitation, to 35 at.% Sc in the later stage. According to the phase diagram, the phase region of Al$_3$Sc is extremely narrow, and only the stoichiometric phase can exist. Thus, the present atom-probe results are totally unexpected from the published phase diagram.

Since the evaporation field of Sc would be much higher than that of Al, there is a possibility that some aluminum ions preferentially evaporated without being triggered by the pulse. Therefore, one possibility is that the apparent composition of the precipitates was recorded to be artificially high, and the actual value may be the stoichiometric 25 at.%. However, it should be noted that the composition measured by the atom-probe did not change regardless of the pulse fraction. Another fact is that the atom-probe analysis was performed with essentially the same conditions for the various aging times. Therefore, the apparent composition change of Al$_3$Sc determined by the atom-probe may indeed reflect the concentration of the precipitates as a function of the aging time.

It is possible that the composition of the nuclei is different from the equilibrium value as shown by Goodman et al. (6). Generally, if the interfacial energy is small, nuclei would have a higher composition as shown by Hillert (7). In the case of the present system, however, the thermal equilibrium phase precipitates from the beginning. Furthermore, the equilibrium phase diagram predicts only a stoichiometric value for Al$_3$Sc. Therefore, the free energy curve as a function of Sc concentration would be very sharp. In such a case, it is hard to understand how the composition of the nuclei can be very different from the equilibrium value. Further atom-probe studies are warranted.

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References

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Fig. 1 Electrical resistivity change.

Fig. 2 The Sc concentration of the matrix as a function of $t_a^{-1/3}$.

Fig. 3 Age-hardening curve.

Fig. 4 Transmission electron micrograph and (110) orientation diffraction pattern of the sample aged at 573 K for $10^3$ min.

Fig. 5 Transmission electron micrograph and (002) orientation diffraction pattern of the sample aged at 573 K for $10^3$ min.

Fig. 6 Field ion micrograph of the sample aged at 573 K for $10^3$ min, Ne + a little H$_2$ image.
Fig. 7 Transmission electron micrograph and (110) orientation diffraction pattern of the sample aged at 573 K for $10^4$ min.

Fig. 8 Field ion micrographs of the sample aged at 573 K for $10^4$ min, He image.

Fig. 9 The atomic arrangement in $L_1_2$ structure.

Fig. 10 Field ion micrograph of the sample aged at 573 K for $10^5$ min, Ne image.

Fig. 11 The Sc concentration of the precipitate as a function of the aging time.