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PRECIPITATION HARDENING IN AN AI-2.4Li-0.19Sc ALLOY

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Abstract

Effect of Sc on the precipitation behavior of Al_3Li was studied in an Al-Li-Sc alloy, with particular emphasis on the coprecipitation of Al_3Li and Al_3Sc phases. The main results are ; (1) The present ternary alloy is strengthened by the adoption of the two-step aging, first aging at 573K and second aging at 473K, due to the coprecipitation of Al_3Sc and Al_3Li phases.

(2) when simply aged at 473K, growth rate of Al_3Sc particles is negligibly small and that of Al_3Li is apparently retarded by the presence of Sc. But, (3) when aged at 473K, after preaging at 673K to the overaged state, Al_3Li phase tends to grow around the pre-existing spherical Al_3Sc phase, thus forming composite particles, with Al_3Sc in the core surrounded by Al_3Li . The formation of the composite particles seems to require a critical size for the Al_3Sc core. Mechanism of formation of the composite particles is discussed on the basis of the experimental results.

Introduction

Both lithium(Li) and scandium(Sc) are light elements, and form a L1₂-Al₃X intermetallic compound with aluminum. These intermetallics occur from supersaturated solid solutions and contribute to the hardening of the alloys. The precipitation characteristics in each binary system, Al-Li and Al-Sc, have been considerably studied by the previous authors[1]-[3]. But, the case of ternary Al-Li-Sc alloys has scarcely been studied[4][5]. In the present work, effect of addition of a small amount of Sc on the age hardening and precipitation behaviors in Al-Li alloy is studied. Stress is on the role of coprecipitation of Al₃Li and Al₃Sc phases. Mechanism of the formation of the composite particles is also discussed on the basis of the experimental results.

Experimental procedure

A 3mm thick sheet of a ternary alloy with a composition Al-2.4mass%Li-0.19mass%Sc was prepared from the ingots of each constituent element by melting and casting, followed by hot-rolling and final cold rolling. Cold rolled sheets of binary alloys, Al-0.24mass%Sc and Al-2.6mass%Li, were also prepared by the similar method. The rolled sheets were sectioned into into rectangular pieces for heat treatment. Dimension of the specimen pieces is 3x3x6mm³. The

specimens were solution treated in an argon atmosphere and quenched into cold water. The quenched specimens were aged at 673K or/and 473K for various periods of time. For the ternary alloy, effect of two-step aging (first aging at 673K and second aging at 473K) on the precipitation characteristics was also studied. Hardness tests were carried out using a micro Vickers hardness tester. Foils for transmission electron microscopy were prepared by the electrolytic jet polishing technique using a 20%HClO4/methanol solution. Electron microscopes utilized are JEM-200CX and JEM-2000FX operated at 200kV. Size of the precipitates at each aging condition were measured on dark field electron micrographs.

Results

Age-hardening behavior

Figure 1 and 2 show hardness change during aging at 473K and at 673K, respectively, for the ternary alloy and the binary alloys. At 473K, there are not much difference in age-hardening behavior between the AI-Li-Sc ternary alloy and the AI-Li binary alloy. No substantial hardening is observed in the binary AI-Sc alloy even after a prolonged aging. At 673K, the ternary alloy and the binary AI-Sc alloy show age-hardening curves of similar shape, except that hardness curve of the ternary alloy is shifted upward by a considerable amount. On the other hand, the AI-Li binary alloy shows no appreciable age-hardening. Figure 3 shows the hardness change by the two-step aging for the ternary alloy, together with the curves for 473K and 673K which are included in Fig.1 and Fig.2. In the two-step aging, the specimens were aged at 673K for $3.2x10^3$ s or for 10^6 s at first, and then aged at 473K. Hardness of the ternary alloy is considerably higher in two-step aging than in one-step aging at 473K or at 673K, regardless of aging time. It is also higher than those hardness of the binary alloys aged either at 473K.



Fig. 1 Age-hardening curves for the binary alloys and ternary alloy. (473K)



Fig. 2 Age-hardening curves for the binary alloys and ternary alloy. (673K)

of Al3Li particles

1 shows 110 dark field electron phs showing the precipitates in the Li-Sc ternary alloy and also in the Aly alloy. Specimens were aged at : 10⁵s (peakaged) or 10⁶s(overaged). precipitates seen in the micrographs dered to be Al3Li phase, since Al3Sc not expected to grow large enough to ected by conventional electron opy in this aging condition. It is cognized that Al₃Li particles in the alloy is smaller in size than in the Al-Li alloy for the two aging ns. Growth rate of Al₃Li phase in Li-Sc ternary alloy is apparently by the presence of Sc. In Fig. 5, between mean particle radius (R) and ne(t) is shown.



Fig. 3 Age-hardening curves of the Al-Li-Sc alloy.

oximate linear relation between R3 and

to hold, implying that coarsening of δ' -Al₃Li obeys the Ostwald ripening kinetics[6][7] d by the following equation.

$$R^3 - R_0^3 = Kt$$
 (1)

is the mean particle radius and R_0 is the radius at t=0. K is constant including diffusion ent, interfacial energy and etc.

from Fig.5 that the ratio of the slopes between the Al-Li-Sc ternary alloy and the Al-Li lloy is about 1/30. This rather large difference in the coarsening rate is considered to be nly to the difference in solute diffusivity in the two alloys. By the presence of Sc, n of Li atoms in the Al matrix is largely affected.

tion microstructure

hs of the conventional TEM analysis of the present precipitation microstructure, two Ll_2 ordered compounds are identified, namely Al_3Li and Al_3Sc , besides the fcc α -Al No other compounds were detected. Therefore, it was thought that possibilities of the on of ternary or quaternary compounds are negligible in the present experimental n.

shows the microstruture of the ternary alloy aged at 673K for 10⁶s (overaged). These vere obtained using superlattice reflections. In these dark field micrographs, it is difficult guish images by Al₃Sc phase from those by δ '-Al₃Li phase, because the latter ites finely and rapidly even during quenching and they tend to mask the images of the In a bright field image, they can be better distinguished by taking advantage of the e in coherency strain.

llowing, precipitation microstructure resulted from two-step aging will be shown.



Fig. 4 Electron micrographs showing Al₃Li precipitates for 473K aging..
a:Al-Li alloy, 10⁵s, b:Al-Li alloy, 10⁶s, c:Al-Li-Sc alloy, 10⁵s, d:Al-Li-Sc alloy

Figure 7 shows the microstrutural change for the 473K aging after the first peak aging at 673K for 3.2×10^3 s. Two kinds of precipitates with different size are dispersed in the matrix. They seem to be scattered independently each other. The larger precipitates (20~30nm in radius) are Al₃Li phase, and the smaller (3~5nm in radius) are Al₃Sc phase.

A rather interesting precipitate configuration was observed, when the specimens were overaged in both steps of aging, at 673K and at 473K. The result of such observation is shown in Fig. 8, where spherical composite precipitates with dark cores are seen without any isolated small Al₃Sc precipitates.

The composite precipitates is considered to consist of an inner Al_3Sc core and the outer Al_3Li shell. From the comparison between Fig. 7-c and Fig.8, it can be said that there is some critical size of Al_3Sc core for the formation of the composite structure.



Fig. 5 Mean radius(R) of Al₃Li part in the ternary alloy as a funct of aging time.



Fig. 6 Electron micrographs showing Al₃Sc precipitates in the Al-Li-Sc alloy aged at 673K for 10⁶s. **a**: dark field image **b**: bright field image.

Composite precipitates of this type have been reported to occur in other Al-Li alloys with the addition of a small amount of transition element, such as Zr[8][9][10], Ti[11] and Hf[12]. By an elemental analysis, using an energy dispersive X-ray analyzer attached to TEM, of the composite particles, Sc was detected in the core, supporting the model that the inner core of the composite particles is related to Al_3Sc phase. A close examination of Fig. 8 reveals that some particles appear with core, but some others do not. Tilting the crystal around the <112> axis by a fraction of a degree caused the core contrast to change. Dark core often appears in the precipitates which had no core contrast before.

Discussion

Age-hardening mechanisms

Mechanisms of age-hardening in the present ternary Al-Li-Sc alloys will be discussed on the basis of the observed age-hardening behavior and TEM microstructures of the ternary alloy, as well as of those of the binary Al-Li and Al-Sc alloys.

In aging at 673K, growth rate of Al₃Sc precipitates is high enough and those precipitate particles will make main contribution to the hardness of the ternary alloy. while, Li is supposed to be mostly in solution in this aging condition and contributes to alloy hardness through solution strengthening, because the temperature 673K is well above the solidus temperature.

At 473K, Al₃Sc phase does not grow appreciably within the present aging time, while Al₃Li precipitates grow fast and they make main contribution to the alloy hardness. Possible hardening caused by Li in solution may not be small, but hardening by the small amount of Sc in solution is negligible. This large difference in the growth rates of Al₃Sc and Al₃Li particles can be attributed basically to the large difference in diffusivities of Sc and Li atoms in the matrix. The activation energy for the diffusion of Sc in Al is 286kJmol-1[13], which is much larger than the corresponding value for Li(126kJmol-1)[14].



Fig. 7 Electron micrographs showing Al₃Li and Al₃Sc particles in the two-step aged Al-Li-Sc alloy. The specimens were aged at 673K for 3.2x10³s and at 473K for, a:10⁵s, b: 3.2x10⁵s, c:10⁶s

Growth of Al3Li particles

The experimental results shown in Fig.4 suggest that Sc addition retards the growth rate of Al_3Li , especially when Sc is in solution. This implies that slowly moving Sc atoms trap either vacancies or Li atoms, or both. Further details on the mechanism are not studied in the present investigation. They should be cleared by further investigation.

Formation of the composite particles

The mechanism of the formation of composite particles should be closely related to the nature of coherency of Al₃Sc and Al₃Li phases with the matrix. From the lattice constants of Al, Al₃Sc and Al₃Li,[15]-[17] the misfits at Al₃Sc/Al interface and at Al₃Li/Al interface are estimated to be +1.2% and -0.2%, respectively. Therefore, in the second aging, Al₃Li phase tends to grow preferentially around the preexisting Al₃Sc phase to reduce misfit strain energy and possibly interfacial energy.

From the comparison between Fig. 7 with Fig. 8, it is understood that precipitation of Al_3Li phase occurs only on the Al_3Sc precipitates whose size is larger than the critical. The critical radius falls on somewhere between 5 and 10nm. The growth of Al_3Sc phase to the critical size seems to be necessary for the accomodation of the energy for the heterogeneous nucleation.

Superposition of hardening mechanisms

Factors contributing to the strength of the present ternary alloy are solute atoms (Sc and Li) and precipitates(Al₃Sc and Al₃Li). There is no general rule for the additivity of different hardening



Fig. 8 Electron micrograph showing composite precipitates(Al₃Li/Al₃Sc) in the two-step aged Al-Li- Sc alloy. (at 673K for 10⁶s and at 473K for 10⁶s).

mechanisms. In the followings, yield strength is considered in terms of obstacles for moving dislocations and additivity of contributions from different mechanisms is discussed. It has been understood that frictional obstacles are linearly additive, and also that solution hardening and particle hardening are also linearly additive[16][17]. While, the square additivity will hold for particle hardening, since densities of particles are additive, . Therefore, the strength of the alloy (σ) can be expressed as:

$$\sigma = \sigma_0 + \sigma(Sc) + \sigma(Li) + (\sigma_A^2 + \sigma_B^2)^{1/2}, \qquad (2)$$

Here σ_0 is the strength of pure Al. $\sigma(Sc)$ and $\sigma(Li)$ are the contributions from solution strengthening by Sc and Li, respectively. σ_A and σ_B are the contributions from Al₃Sc and Al₃Li precipitates, respectively.

In the present ternary alloy, after two-step aged, yield strength of the alloy is mainly controlled by the precipitates, and can be approximately expressed as; $\sigma = (\sigma_A^{2+} \sigma_B^{2})^{1/2}$.

Validity of the relation can be examined for the case of the two-step aged condition shown in Fig. 7-c, where the specimen was aged at 473K to the overaged condition after the preaging at 673K to the peakaging condition. Square of the conpressive proof strength measured for this aging condition is in fairly good agreement with the sum of squares of the respective Orowan stresses, which were calculated on the basis of the observed distributions of each particle.

Summary

The results of the present investigation on the effect of Sc on the age-hardening and precipitation behaviors in an Al-Li-Sc alloy are summarized as follows:.

(1) The present ternary alloy is strengthened by the adoption of the two-step aging, prel-aging at 673K and second aging at 473K, due to the co-precipitation of Al_3Sc and Al_3Li phases.

(2) when simply aged at 473K, the growth rate of Al_3Sc particles is negligibly small and that of Al_3Li is apparently retarded by the presence of Sc.

(3) when aged at 473K ,after pre-aging at 673K to the overaged state, Al_3Li phase tends to grow around the pre-existing spherical Al_3Sc phase, thus forming composite particles, with Al_3Sc in the core surrounded by Al_3Li . The formation of the composite particles seems to require a critical size for the Al_3Sc core.

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