Effects of Additional Elements on δ' Phase Stability in Al–Li Alloys

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Abstract

The phase stability of the δ'–Al_3Li phase in Al–Li alloys was investigated in terms of the solvus temperature and coarsening kinetics. The solvus temperatures of the δ' phase for various Li compositions were well evaluated using adiabatic calorimetry(AC) and differential scanning calorimetry (DSC) techniques. The coarsening rate of the δ' phase during aging was determined using an image analysis system on the TEM micrographs. The effects of the additional elements Mg, Ag and Au on the δ' solvus temperatures and coarsening rate were determined. The increments of the solvus temperature are higher for Ag and Au. The coarsening rate of the δ' phase was greatly reduced by the additions of Ag and Au. Mg has a smaller effect. The EDX analysis revealed that the additional elements of Ag and Mg are enriched inside the δ' phase. Thus, the substitutional elements have the effects to increase the phase stability, resulting in the increased mechanical strength even at elevated temperatures.

Introduction

The Al–Li based alloys have been extensively investigated because of the excellent combination of the high specific strength and low density. The high strength of the alloy is achieved by the precipitation of the δ' phase. The δ' phase is a metastable phase coherent with the matrix having the $L1_2$–type ordered structure of Al_3Li composition. To increase strength even at elevated temperatures the thermal stability of the δ' phase as well as the volume fraction should be increased. Deformation behavior of the Al–Li alloys containing the δ' phase has been discussed[1]. In the under–aged condition, the δ' particles are cut by the moving dislocations, while in the over–aged condition dislocations move away by the bypass mechanism leaving Orowan loops at the δ' particles. Therefore, the coherent strain around the

δ' particles and APB(anti-phase boundary) energy are extremely important to improve the mechanical properties. The coarsening behavior of the δ' phase is also important to be taken into account for controlling particle size distributions. The additional elements are known to be effective in changing the properties of the δ' phase[2,3]. In the present work, the effects of the additional ternary elements on the phase stability of the δ' phase were investigated in terms of the solvus temperature and coarsening kinetics. The effects are discussed based on the substitution behavior of the additional elements.

Experimental Procedure

Al-Li and Al-Li-X (X=Ag, Mg, Au) alloys were prepared with high purity materials (99.99%Al, Al-18.5%Li, 99.9%Mg, 99.9%Ag, 99.99%Au) under argon gas atmosphere. The alloy specimens are listed in Table 1 together with their chemical compositions. The ingots were homogenized and solution treated at 773 to 873K in a salt bath, and subsequently quenched into ice water. The adiabatic calorimetry(AC) measurement was carried out at a average heating rate of 0.02K/s with specimens of ~20g in weight. The differential scanning calorimetry(DSC) measurement was also performed at different heating rates ranging from 0.03 to 0.17K/s with specimens of ~80mg in weight. Micro Vickers hardness was measured with an applied load of 500g. The microstructures of the alloys containing the δ' phase were observed by the transmission electron microscope. The δ' particle sizes were determined using an image analysis system on electron micrographs.

Table 1 Chemical compositions of Al-Li and Al-Li-X alloys in mass% (mol%).

	Li	Ag	Mg	Au	Al
Al-2.2Li	2.15(7.87)	-	-	-	bal.
Al-2.7Li	2.70(9.74)	-	-	-	bal.
Al-3.3Li	3.33(11.8)	-	-	-	bal.
Al-Li-1Ag	2.17(8.04)	1.10(0.26)	-	-	bal.
Al-Li-2Ag	2.35(8.68)	1.96(0.48)	-	-	bal.
Al-Li-5Ag	2.37(8.95)	5.14(1.25)	-	-	bal.
Al-Li-1Mg	2.18(7.94)	-	1.13(1.18)	-	bal.
AL-Li-0.2Au	2.31(8.44)	-	-	0.2*(0.026*)	bal.

* nominal composition

Results

1. Effects of additional elements on the δ' solvus temperature

The adiabatic calorimetry (AC) and differential scanning calorimetry (DSC) analyses were

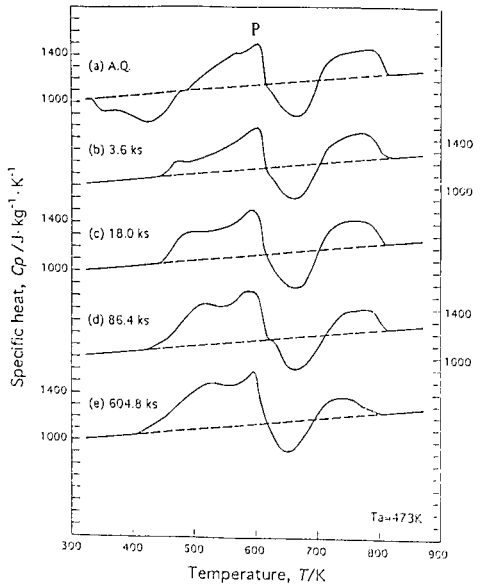

Figure 1 Specific heat curves by adiabatic calorimetry for Al–3.3%Li alloy aged at 473K.

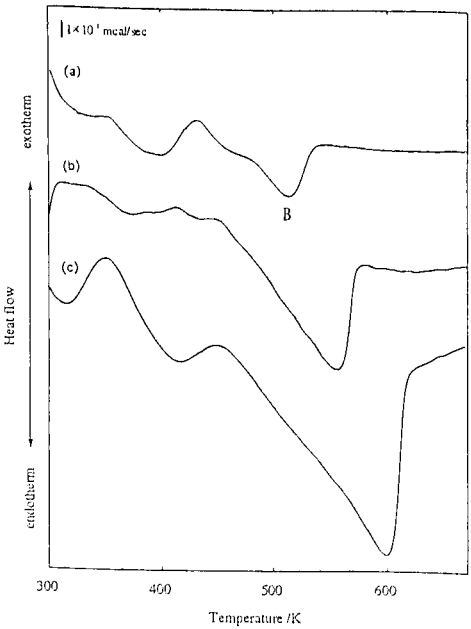

Figure 2 DSC profiles for the as-quenched Al–Li alloys. (a) Al–2.2%Li, (b) Al–2.7%Li, (c) Al–3.3%Li

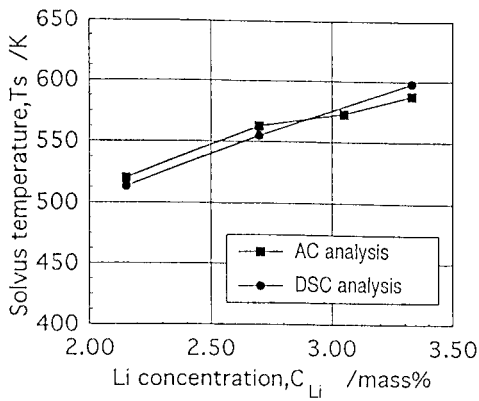

Figure 3 Solvus temperature against Li concentration by AC and DSC analyses.

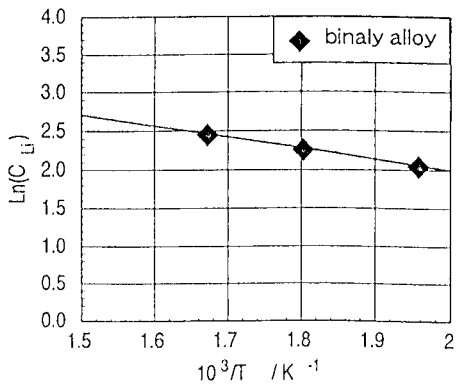

Figure 4 Relationship between $\ln(C_{Li})$ and $1/T$.

performed to determine the solvus temperatures of the δ' phase in Al–Li–X alloys. Figure 1 shows specific heat vs. temperature curves obtained by the AC analysis for an Al–3.3%Li alloy aged at 473K for 0 (A.Q.) to 604.8ks. As discussed previously[4], the heat absorption denoted P is due to the dissolution of the δ' phase. Thus, the temperature at which a peak of heat absorption appears could be referred to the solvus temperature of the δ' phase, Ts. As demonstrated in Figure 1 the solvus temperature is almost unchanged even after aging at 473K for prolonged time. Figure 2 shows DSC profiles for the as–quenched alloys. The endotherm indicated by B is due to the dissolution of the δ' phase, and the temperature of the endotherm–bottom represents the solvus temperature. Thus determined temperatures for Al–2.2%Li, Al–2.7%Li and Al–3.3%Li alloys are almost identical with those determined by the AC analysis as shown in Figure 3, and is well consistent with the reported results[5]. Therefore, the DSC technique is confirmed to be useful to estimate the solvus temperature conventionally. In general, the solubility of a solute atom C is approximately expressed by the following formula,

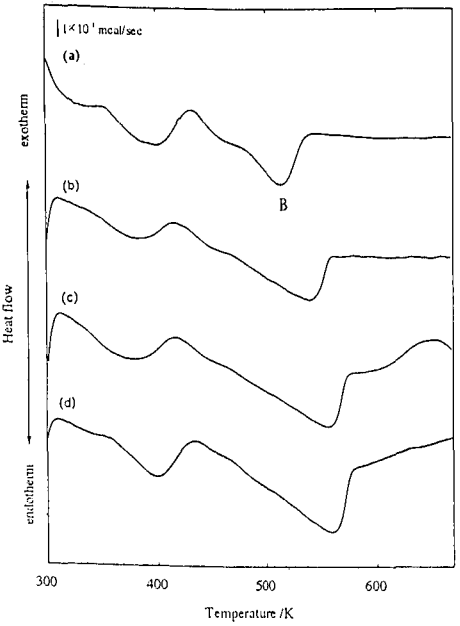

Figure 5 DSC profiles for as quenched Al–Li–Ag alloys.(a) Al–2.2Li,(b)Al–Li–1Ag, (c) Al–Li–2Ag,(d) Al–Li–5Ag

$$C = A\exp(-\frac{Q}{RT}) \quad (1)$$

where, T: temperature, Q: activation energy for solution, R: gas constant and A: constant.
To confirm the above eq.(1) $\ln(C_{Li})$ is plotted against 1/T in Figure 4. The linear relationship is obtained, suggesting that the eq.(1) is applicable to the present case. The obtained Q is ~ 12kJ/mol. According to Figure 4 the solvus temperature for a certain Li concentration can be estimated.

2. Solvus temperatures for Al–Li–X alloys

To determine the effects of the additional elements on the δ' phase solvus temperature DSC analysis technique was applied. Figure 5 shows DSC profiles for Al–Li alloys containing 1 to 5%Ag measured under the same conditions as shown in Figure 2. The endotherm is also clearly detected. The solvus temperature increases with increasing Ag content as shown in Figure 5. Similar analyses were also carried out for Al–Li alloys containing Mg or Au. The increments of the solvus temperatures from those of the original Al–Li binary composition(ΔT) were determined, and are summarized in Figure 6. The specimens containing Ag and Mg were in the as–quenched state, while the specimen containing Au was aged at 473K for 86.4ks before the DSC measurement to obtain a desirable size of the δ' phase. All elements of Ag, Mg and Au contribute to increase the solvus temperature of the δ' phase. The effect of Ag is pronounced, although the effect becomes saturated for higher Ag contents. The element Au also shows marked effect to increase Ts, whereas Mg has a small effect. The effects of Ag and Mg on the solvus temperature are basically identical with the results reported by Baumann and Williams[3].

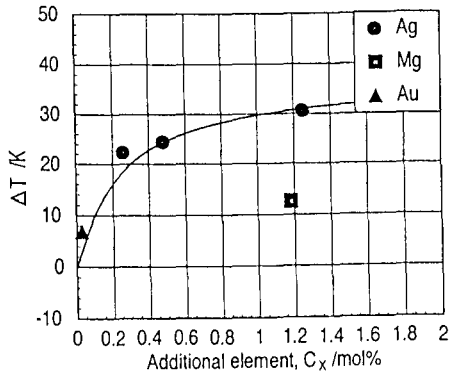

Figure 6 Increments of solvus temperatures, ΔT, against additional elements.

3. Effects of additional elements on coarsening of the δ' phase

The δ' particles were observed with TEM dark field images for Al–Li–X alloys and shown in Figure 7. All specimens were aged at 473K for 604.8ks. The δ' particle sizes were carefully measured and are plotted in Figure 8, the cube of mean particle radius $\bar{r}^3$ against aging time t. All the straight lines intercept the points very close to $\bar{r}^3 = 0$ at $t = 0$, indicating that the coarsening rate is approximately expressed by the simple equation,

$$\bar{r}^3 = Kt \qquad (2)$$

As shown in Figure 8 the slope of a line, i.e. the coarsening rate constant K, is markedly changed with additional elements. The addition of Ag remarkably reduces the K value. The mall addition of Au has also pronounced effect to reduce K, while Mg has a small effect. K

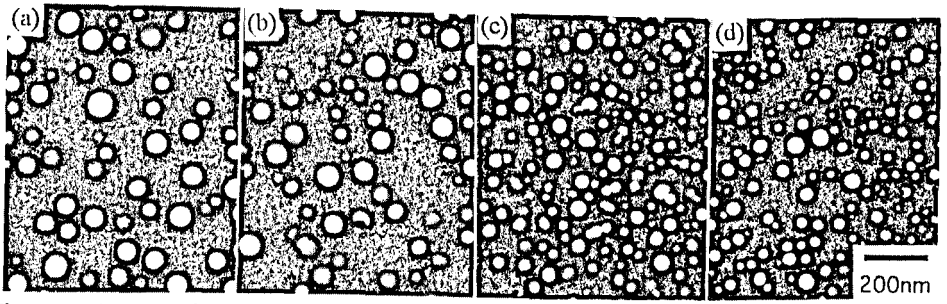

Figure 7 Electron micrographs of the δ' particles in the specimens aged at 473K for 604.8ks. (a) Al–2.2%Li, (b) Al–Li–1Mg, (c) Al–Li–1Ag, (d) Al–Li–0.2Au.

values represented against additional elements change in the manner closely related with the solvus temperature.

Discussion

The solvus temperatures determined using the DSC analysis increase by the addition of Ag, Mg and Au. The crystal structure of the δ' phase in the alloys containing additional elements was confirmed to be unchanged, i.e. $L1_2$–type ordered structure. The increased solvus temperatures indicate that the thermal stability of the δ' phase becomes increased by the additional elements. To make clear partitioning of the additional elements an EDX analysis was performed on both the δ' particles and matrix. An example of the analyses is shown in Figure 9 for an Al–Li alloy containing 1%Ag aged at 473 K for 2592ks. Figure 9 clearly indicates that Ag atoms are enriched inside the δ' particles. Mg atoms are also found to be enriched inside the δ' particles. Hosoda *et al.* [6] suggested that Ag, Au and Mg substitute Al– and Li–sites of the δ' phase respectively based on the calculation for the Pseudo–Ground State of the $L1_2$–type structure. The substituted elements will cause the increased misfit strains as well as the change in enthalpy of the δ' phase predicted by Hosoda *et al.* [6]. Baumann and Williams [3] reported that the change in the solvus temperatures is closely related with the δ'/matrix misfit strains. According to their results Ag has a marked effect to increase the δ' solvus temperature, which is in consistent with

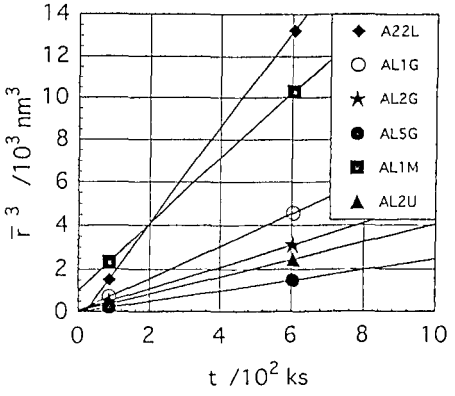

Figure 8 Cube of mean particle size against aging time for specimens aged at 473K.

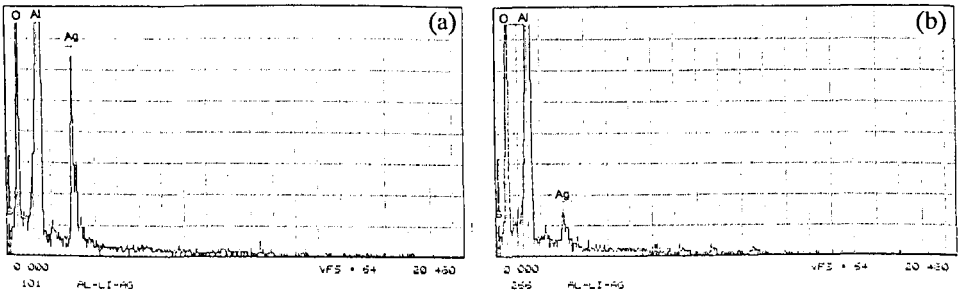

Figure 9 EDX analysis profiles showing enriched Ag for Al–Li–1Ag alloy aged at 473K for 2592ks. (a) a δ' particle, (b) the matrix.

the present result. Mg has also a similar effect on the δ' phase, although the effect is smaller than that of Ag.

Coarsening rate of the δ' phase is reduced by the addition of Ag, Mg and Au. The coarsening rate constant K is expressed as follows for the case of Lifshitz–Slyozov–Wagner(LSW) theory,

$$K = \frac{8\gamma V_m^2 D C_e}{9RT} \tag{3}$$

γ: interfacial energy, V_m: molar volume, D : diffusion constant, C_e: equilibrium concentration of the matrix.

According to eq.(3) the reduced values of γ, V_m , D and C_e result in the decreased value of K. In this work C_e is found to become smaller by the additional elements because of the increased solvus temperature. However, the contribution of the above factors is considered to be not sufficiently large to reduce K values. One of the other possible explanations is to take into account the effect of the δ'/matrix misfit strain. Enomoto and Kawasaki [7] suggested that the attractive elastic field interactions suppress coarsening of particles. Based on their suggestion, the increased δ'/matrix misfit strain will contribute to both the increased solvus temperature and the decreased coarsening rate of the δ' phase. Furthermore, Au was found to have marked effect even with very small amount. At present, our EDX analysis fails to detect any enriched Au atoms inside the δ' phase. The soluble elements to the δ' phase are expected to alter the nature of the δ' phase. According to the calculated results based on the Miedema's semi-empirical formula, the expected highly soluble elements are Ag, Ca, Cu, Ga, Ge, Ir, Mg, Ni, Rh, Si, Sr and Zn [6]. Of these elements Cu, Mg, Si are generally used as the additional elements to Al–Li alloys and markedly contribute to improve properties. In the present work,

Ag and Mg have the effects to alter the nature of the δ' phase. Baumann and williams [3] also pointed out the effect of Zn, which is also soluble to the δ' phase. On the contrary, the solubility of Au in the δ' phase is considered to be limited, thus, the mechanism for Au is not yet clear. The detailed effect of Au addition should be further investigated.

Conclusions

The effects of the additional elements Ag, Au and Mg on the δ' phase stability in Al–Li alloys were investigated in terms of the solvus temperature and particle coarsening kinetics. The obtained results are summarized as follows.

(1) The solvus temperatures of the δ' phase were determined using calorimetric techniques(adiabatic calorimetry and differential scanning calorimetry). Ag and Au have pronounced effects to increase the solvus temperatures, while Mg has smaller effect compared with Ag and Au.

(2) The coarsening rate of the δ' particles are markedly reduced by the addition of Ag and Au. Mg has also a similar but smaller effects than Ag and Au.

(3) EDX analysis reveals that Ag and Mg are enriched inside the δ' phase, suggesting the substitution of elements. The misfit strain between the δ' phase and the matrix is considered to affect markedly the solvus temperature and coarsening rate.

Acknowledgements

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