Precipitation Kinetics in Supersaturated Al-2.0 at% Cu-1.0 at% Mg Alloy

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In Al-2.0 at%Cu-1.0 at%Mg alloy, fine-scale precipitates that occur during aging have been investigated by using differential scanning calorimetry (DSC) to search for the phase transition temperatures (formation and dissolution of precipitates). The microhardness measurements (HV) are used to correlate between the developed reaction peaks in DSC and the observed peaks in the microhardness (HV). The scanning electron microscopy (SEM) is utilized to examine the surface microstructure of the precipitated phases and to confirm the obtained results. During the aging treatment the supersaturation is gradually reduced. The strength increases when fine coherent and/or semi-coherent precipitates nucleate. The precipitation kinetics can be characterized by analyzing the DSC curves. The kinetics of the early stage precipitates were found to be controlled by the migration of Cu and Mg atoms in the matrix. Whereas, the later precipitates as S-phases as the specimens were aged for 240 min at 200 °C.

Keywords: aging, aluminium-copper-magnesium alloy, coherent precipitates, precipitation kinetics

1. Introduction

Abis et al.¹,² had studied the early stage precipitation in Al-4.4 mass%Cu-1.7 mass%Mg; [Cu/Mg ≈ 1 (atomic ratio)] by using DSC, HV and TEM techniques during natural aging at room temperature. They obtained the formation of GPB and GP zones over an extended aging to 500 min. Ringer et al.² had aged specimens of Al-1.1 at%Cu-1.7 at%Mg; (Cu/Mg = 0.65) at temperatures higher than 130 °C and examined by the atom probe field ion microscopy (APFIM), transmission electron microscopy (TEM) and microbeam electron diffraction. They obtained that this alloy exhibits the precipitation of Cu-Mg co-clusters followed by the precipitation of GPB zones + S-phase. The precipitation in Al-0.9 at%Cu-1.4 at%Mg, (Cu/Mg = 0.64), was investigated by Charai et al.³. They found the coexistence of GPB zones, S⁰, S¹ and S-phases as the specimens were aged for 240 min at 200 °C. In this study, we chose an alloy having higher Cu/Mg ratio than those studied in Refs. 1–3. We prepared an alloy of Al-2.0 at%Cu-1.0 at%Mg which has the ratio Cu/Mg ≈ 2. The objective of the present work is to use the nonisothermal DSC analysis of the reaction peaks developed during continuous heating at various heating rates of the quenched Al-2.0 at%Cu-1.0 at%Mg alloys from the solid solution state to determine the activation energies associated with the individual precipitation processes. The obtained activation energies can be successfully used in the characterization of the precipitation kinetics. SEM examinations have been performed after aging at temperatures little lower than the peak hardness temperature.

2. Experimental

An ingot of Al-2.0 at%Cu-1.0 at%Mg was prepared using commercial Al (99.98 purity), Mg (99.99 purity) and Cu (99.99 purity). For DSC measurements, disc specimens of 5 mmφ and 0.5 mm thickness were solution heat treated for 1 h at 803 K and subsequently quenched intiO chilled water at ~273 K. A nonisothermal DSC was carried out for the as-quenched specimens at various heating rates of 2.5, 5, 8, 12, 20, 30 and 45 K min⁻¹.

The microhardness measurements were performed using Vickers method using a diamond square-based pyramid under a load of 0.50 N for a constant duration of 15 s.

For scanning electron microscopy, the quenched specimens were gently polished in order to remove any surface reactions that may occur during heat treatment. The specimens were then etched using the Keller etchant (a solution of 1% HF+2.5% HNO₃, by volume, in H₂O). The SEM examinations were performed after aging for 30 min at temperatures of 450, 555 and 623 K by using JEOL-SEM 5400 LV-Japan scanning electron microscope.

3. Results and Discussion

3.1 DSC

The behaviour of the DSC curves with temperature performed at various heating rates is shown in Fig. 1. The curves exhibit five exothermic reactions referred to as I through V.

The exothermic peak I, could be ascribed to the formation of Guinier-Preston zones (GP zones). Considering the excess vacancies which are quenched in the specimens and the very limited solubility of Cu in Al at room temperature, the Cu-vacancy complexes may form. In addition, the precipitated Cu atoms stimulate the precipitation of solute Mg atoms. Due to the high binding energies between Mg-vacancy and Cu-vacancy,⁴ these complexes may combine forming Mg-Cu-vacancy clusters. Then, the condensed vacancies dissociate with temperature rise and anneal out through the free surface or the grain boundaries in the material leaving Cu-Mg clusters. The Cu-Mg clusters act as preferable sites for nucleation of GP zones. The exothermic peak II; can be characterized by the coexistence of GP zones and $\theta^\prime$-(Al-Cu) phase.
The exothermic process, peak III, could be ascribed to the precipitation of S00 intermediate phase. S00 is a metastable phase (Al2CuMg) which is coherent to the matrix. This process is followed by another process, IV; which could be attributed to the precipitation of S0 (Al2CuMg) intermediate phase which is more stable than S00. The S0-phase (Al2CuMg) has generally been considered as semi-coherent with the matrix.1,3) Both S00 and S0 peaks shift to higher temperatures as the heating rate increases which indicates that these processes are thermally activated, Fig. 1. The exothermic process V; might be ascribed to the growth of S0 and transforms to S-stable phase (Al2CuMg). It is noteworthy to mention that S0 semicoherent phase is slightly distorted version of S-phase,4) so that many authors do not make any distinction between these two orthorhombic phases. Cusait5) had also detected S00 in an Al-1.2 at%Cu-1.6 at%Mg alloy.

In conclusion, from the DSC curves it has been shown that the GP zones and /C1800-(AlCu) phase are formed at temperatures of ~ 392 and 473 K, respectively, and their dissolution takes place at ~ 510 K for Al-2.0 at% Cu-1.0 at% Mg alloy.

3.2 Microhardness measurements
3.2.1 Behaviour of HV during isochronal annealing
The quenched specimens from solid solution state were aged for 1 h at 20 K steps beginning from 333 K up to 773 K and subsequently quenched into chilled water. The HV behaviour with temperature, Fig. 2, shows an approximate similar behaviour as that of DSC, Fig. 1. The first peak hardening appeared at ~388 K is ascribed to GP zones. The next HV peaks developed at ~493 K and ~555 K are attributed to \theta'-Al(Cu) and S'/S''-(Al2CuMg) precipitates, respectively. The small shoulder peak at ~693 K can be attributed to coarsening of S''/S' to form S incohherent precipitates. \theta' and S' are coherent to the matrix, whereas S' is semi-coherent. S'' and S' metastable precipitates can strengthen the alloy by atomic bonding. 5)

3.2.2 Isothermal aging
Age hardening curves obtained during artificial aging of Al-2.0 at% Cu-1.0 at% Mg alloy at 423 K, 448 K and 473 K are shown in Fig. 3. Aging at 423 K produced a lower effect than aging at 448 K and 473 K except in the region from 25 to 75 min (minimum region). Aging up to 1000 min exhibits two main peaks labeled I and II. The first process I could be attributed to GP zones and \theta'' formation, while the second one might be due to the precipitation of S''/S' precipitates. At 448 K and 473 K, the time required for development of S''/S' precipitates and, hence, to the peak hardening is ~ 250 min which is in good agreement with that reported by Silcock for an AlCuMg alloy of Cu/Mg = 2:2 in which the peak hardening was observed at 513 K. 6) Whereas, the time required for formation of S00/S0 peak aged at 523 K is 240 min. in Al-0.9 at%Cu-1.4 at%Mg (Cu/Mg = 0.64) alloy. 7) Comparing our results with those of refs. 3, 4) one can conclude that Cu/Mg ratio has no effect on the aging behaviour on either time or temperature necessary to achieve the peak hardening.

4. Scanning Electron Microscopy
In order to confirm our predictions of the developed processes at the DSC reaction peaks, the SEM specimens...
were aged for 30 min at 450 K, 550 K and 623 K. As the specimen is aged for 30 min at 450 K, fine precipitates characterized as $\theta'$-precipitates are detected by SEM examination, as shown in the micrograph Fig. 4(a). The energy dispersive x-ray spectrometry (EDS) confirms the nucleation of $\theta'$-precipitates, Fig. 4(b). Aging at 550 K for 30 min, the SEM examination exhibits the $S''/S'$-precipitates as shown in the electron micrograph, Fig. 4(c). As the specimen is aged at 623 K for 30 min the SEM revealed the stable S-phase ($\text{Al}_2\text{CuMg}$), Fig. 4(d). The S (or $S'$) is indicated by the XRD, Fig. 5, of the aged specimen at 555 K as $\text{Al}_2\text{CuMg}$.

5. Precipitation Kinetics

To characterize the precipitation kinetics in supersaturated alloys, we used Kissinger method as it is considered as the most accurate one.\(^6\) According to the equation:

\[
(\alpha/T_p^2) = (PRk_0/e) \exp(-E/RT_p)
\]

where $\alpha$ is the heating rate, $p$ is a constant, $k_0$ is the reaction constant, $T_p$ the peak temperature of the given process and $R = 8.314 \text{ (J/mol·K)}$ is the universal gas constant.

Thus the value of the activation energy $E$ for the individual precipitates can be determined from the plot of $\ln(\alpha/T_p^2)$ versus $(1/T_p)$, Fig. 6 shows $\ln(\alpha/T_p^2)$ versus $1/T_p$ relationships. From the slopes of the obtained relationships, we got:

(i) The activation energy associated with formation of GP zones is calculated as $62.8 \pm 0.2 \text{ kJ/mol}$. This energy is in agreement with the values obtained by Ohmori et al. (52.3–63.7 kJ/mol).\(^8\) The determined activation energy is also in agreement with the migration energies of Cu (66.5 kJ/mol) and Mg (62.5 kJ/mol) in Al, respectively.\(^9\) Therefore, the kinetics of this process could be controlled by the migration of Cu and Mg mechanism in the Al-matrix. The calculated activation energy for GP zones precipitation in our alloy
is in fair agreement with the mean value of 67 kJ/mol obtained by Charai et al. for GP zones\(^3\) in Al-0.87 at% Cu-1.44 at% Mg (Cu/Mg = 0.6). In addition, Jena et al. had obtained a slightly lower activation energy of 56 kJ/mol for the same precipitates in Al-0.7 at%Cu-0.9 at%Mg (Cu/Mg = 0.78).\(^{10}\)

(ii) The activation energy of \(\theta''\) for Al-2 at% Cu-1 at% Mg is 112.9 ± 0.2 kJ/mol. This value is moderately lower than the activation energy of diffusion for Cu and Mg in Al (135 kJ/mol) and (131 kJ/mol) respectively.\(^9\) Thus the precipitation mechanism of \(\theta''\) might be controlled by the diffusion of Cu and Mg in Al-matrix. Diffusion is the transport of both Cu and Mg to \(S\) phase.

(iii) The activation energies of \(S''\), \(S\) and \(S\) for Al-2.0 at% Cu-1.0 at% Mg are obtained as 142.1 ± 0.03 kJ/mol, 133.3 ± 0.1 kJ/mol and 146.2 ± 0.1 kJ/mol, respectively. These values are in fair agreement with the activation energies of Cu and Mg diffusion in Al (135 kJ/mol) and (131 kJ/mol) respectively.\(^9\) Therefore, the precipitation kinetics of \(S''\), \(S\) and \(S\) could be controlled by Cu and Mg diffusion in Al. The obtained activation energies for \(S''\), \(S\) and \(S\) are fairly consistent with those obtained for the same precipitates in Al-0.87 at% Cu-1.44 at% Mg (3) and Al-0.7 at%Cu-0.9 at%Mg\(^{10}\) as 134 ± 5 kJ/mol and 130 kJ/mol, respectively. The achieved high hardening of the alloy is attributed to GP zones, \(S''\) and \(S\) phases. The reason of the hardening effect is the interface coherency in Al planes. It can be observed that there is a good matching between the precipitation peaks developed during nonisothermal DSC curves and the hardness peaks appeared in the isochronal annealing of the alloy. The moderate inconsistency of peak temperatures with HV results can be attributed to the lack of equilibrium during the continuous heating in the DSC program.

6. Conclusions

(1) Al-2.0 at% Cu-1.0 at% Mg alloy can be described as having typically fine precipitates structure. The achieved high hardness of it is attributed to GP zones, \(\theta''\), \(S''\), and \(S\) phases.

(2) The SEM examinations have shown that \(\theta''\), \(S''/S\) and \(S\) precipitates are developed as a result of aging at 450, 550 and 623 K, respectively.

(3) The activation energies dictate that the kinetics of the formation of GP zones could be controlled by the migration of Cu and Mg in Al matrix. Whereas \(\theta''\), \(S''\), \(S\) and \(S\) precipitates are controlled by diffusion mechanism of both Cu and Mg in the alloy.

(4) (Cu/Mg) ratio in the alloys has no clear influence on either the time required to achieve peak hardness (at the same temperature) or the kinetics of the precipitates.

REFERENCES