Effect of addition of Ag on the precipitates in Al-Mg-Si alloy by DSC and HRTEM techniques

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The precipitation sequences and kinetics of Al-Mg-Si alloys with the addition of Ag have been investigated by using differential scanning calorimetry (DSC) and high resolution transmission electron microscopy (HRTEM). The activation energies associated with the individual precipitates are determined. Microstructure studies on each peak appearing in DSC curves were carried out on HRTEM to better understand which phases were contained along each peak.

Introduction

Al-alloys are considered an excellent material for automobile and aircraft industries. Al-Mg-Si alloys are important as they can be strengthened by precipitation of several nanoscale metastable precipitates. The understanding and controlling of precipitation during the artificial aging is, therefore, critical for achieving optimum properties. It was reported that Ag had little effect on the aging of Al-Mg-Si alloys, but caused moderate increase in the rates of aging and the amounts of hardening at temperatures close to 200°C. These effects were greater in the case of addition of about 0.5 Ag [1]. Thus, these advantages suggest further investigations of Al-Mg_2Si alloy bearing Ag.

The objective of the present work is to study the influence of the Ag addition on the precipitation sequence and precipitation kinetics in a balanced Al - 1.0wt% Mg_2Si alloy. Both DSC and HRTEM techniques have been used.

Experimental

In order to follow the precipitation processes that take place in a balanced Al - 063% Mg - 0.37% Si (wt%) containing 0.5wt% Ag during continuous heating at constant heating rates, the DSC was used. Disc-shaped DSC samples of 4.5mm diameter and ~ 1.0 mm thick of average weight of ~ 43 mg were machined from the alloy ingot. The specimens were solution heat treated for one hour at 848 K in a standard convection furnace and then quenched into chilled water. An annealed pure aluminum disc of similar shape and weight was used as a reference. Non-isothermal thermograms for the as-quenched specimens (quenching medium temperature ~ 273 K) with a DSC thermal analyzer (DSC 220 - S II, Seiko Instruments, Inc., Japan) at heating rates (α) of 2.5, 5, 10, 20, 30, 60 and 80 K min^{-1} were performed. DSC scans were started at room temperature and completed at 800 K under a purified argon gas atmosphere flowing at a rate of 80ml/min. Specimens for TEM observations were prepared by the conventional twin-jet technique. A solution of 25% nitric acid and 75% methanol cooled to 233 K was used as an electropolisher. The electropolishing technique was performed using a DC current source at ~ 12V. The used TEM was 200 kV - TEM (TOPCON - 002B) operated at 120 kV to avoid damages of electron beam to samples.

Results and concluding remarks

Figure 1 shows selected non-isothermal DSC thermograms of the supersaturated Al – 063 mass% Mg - 0.37 mass% Si - 0.5 mass% Ag performed at constant heating rates of 5, 20 and 30 K/min. Eight main processes can be identified from the DSC thermograms indicated by (I) through (VIII). Six are exothermic and two are endothermic. In the present work, the activation energy associated with the individual reactions is calculated by Kissinger and Starink methods [2,3]. The reaction peaks can be explained as follows: (i) Exothermic reaction I - This reaction can be attributed to the formation of Mg-vacancy, Si-vacancy and Ag-vacancy clusters. Its activation energy has been determined as 60.3 kJ/mol. Figure 2 shows the nucleated fine clusters. (ii) Exothermic reaction II

- This peak is believed to be due the formation of GP-zones [4]. (iii) Endothermic reaction III - The reaction is attributed to the dissolution of the GP zones. (iv) Exothermic reaction IV - This reaction is attributed to the precipitation of β''-phase. These precipitates are coherent to the crystal lattice and, therefore, lead to the strengthening of the material. The determined activation energy for this reaction is 150.8 kJ/mol. This energy is very close to the activation energy of Mg and Si atoms in Al matrix, 131 and 124 kJ/mol, respectively [5,6]. This means that the precipitation kinetics could be controlled by diffusion of both Mg and Si atoms in Al-matrix. (v) Exothermic reaction V - This reaction is attributed to the formation of β'- phase. The activation energy associated with these precipitates is 142.7 kJ/mol. The precipitation process can be controlled by the diffusion of Mg, Si and Ag atoms in Al. (vi) Exothermic reactions VI and VII - These reactions are attributed to nucleation and growth of β- equilibrium (Mg_2Si) plates. (vii) Endothermic reaction VIII - This endothermic reaction can be interpreted by the dissolution of the large β-(Mg_2Si) -phase in the matrix.

Owing to the combined results of DSC and TEM, the following conclusions can be evolved: The precipitation sequence can be concluded as: α_{sss}(supersaturated solid solution) → Mg-Si-Ag-vacancy clusters → GP zones → random precipitates → β''-phase → β'-phase → β-phase.

References

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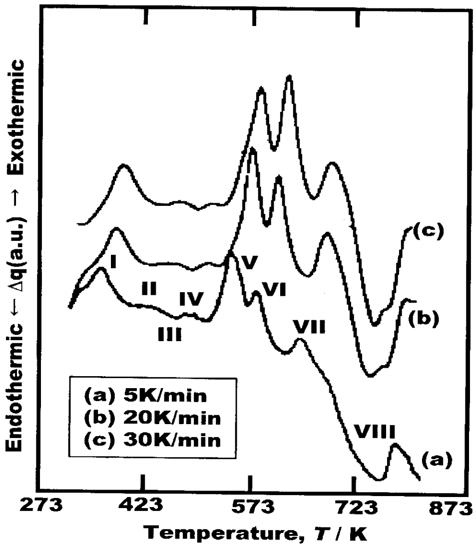

Fig. 1 Typical DSC scans performed at heating rates of 5, 20 and 30 K/min.

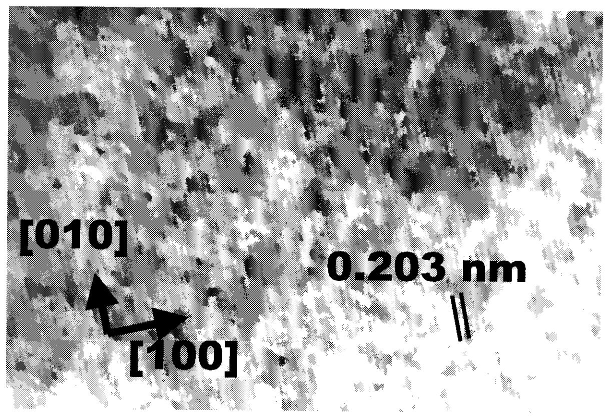

Fig. 2 An enlarged HRTEM micrograph obtained from a specimen heated at 20 K/min up to 383 K and aged at this temperature for 10 min.