STUDY OF PRECIPITATION KINETICS OF AN Al-Mg-Si ALLOY USING DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

This work has been carried out by differential scanning calorimetric (DSC) to study the precipitation kinetics in quenched and natural aging Al-Mg-Si alloy. DSC curves showed exothermic and endothermic peaks corresponding to the precipitation and the dissolution processes. The activation energy of the precipitation process has been calculated using Kissinger model. The results obtained showed a change in the activation energy values, the activation energy for the β″ and β determined for natural aging alloy were higher than that in the quenched alloy.

Keywords: Al-Mg-Si; precipitation; activation energy; natural aging; DSC

1 Introduction

Differential scanning calorimetric is an analysis technique that can be used effectively to study the different solid state and solid-liquid reactions that occur during the main processing steps (solidification, homogenization, precipitation) [1]. The solid-state transformation can be well described by kinetics parameters, namely, the activation energy (E) and the Avrami supporter (n), which reflects the characteristics of nucleation and growth process [2]. The determination of these tow parameters is of great importance to understand the phase transformation mechanism [3].

Al-Mg-Si alloys are widely used in industry due to their excellent plasticity and corrosion resistance, light weight and medium strength after appropriate working processes and heat treatments, quenching and aging treatments. The Al-Mg-Si system is heat treatable class of aluminium alloys that gain their mechanical strength via precipitation hardening. The main hardening phases are precipitated as needle-shaped nano-sized particles from a solid solution of Mg, Si and other added elements. It is known that β″ phase is the main hardening phase in the precipitation sequence [4].

In recent years, many researchers [4, 5] were focused on the kinetics parameters in Al-Mg-Si alloys during the quenching and the aging treatment due to the great importance of understanding the phase transformation mechanisms. Although the precipitation reactions in Al-Mg-Si alloys have been studied extensively, details the precipitation sequence have not been fully understood [6, 7]. Generally, it is believed that the precipitation sequence in quenched Al-Mg-Si alloys occurs the following order:

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Super saturated solid solution (SSSS) → G.P. zones → β″ →β′ → β [7-9]

On the other hand, the precipitation sequence of the Al-Mg-Si alloys stored at room temperature determined by DSC is:

β″ →β′ → β [10]

The aim of this paper is to calculate the activation energy of the precipitation process of the quenched and natural aging Al-Mg-Si alloy; using Kissinger model with the DSC analysis. The results are compared and discussed.

2 Experimental material(s) and methods

The chemical composition of the investigated Al-Mg-Si alloy is shown in **Tab. 1**. DSC tests were carried out using a Q 20 TA analyzer. The samples for the DSC measurements were cut from rods with 3 mm diameter and 2-2.5 mm height. The resulting weight is between 30 and 50 mg. There were two categories of specimens; the first category was homologized 6 h at 550°C and quenched in water before DSC analyses; the second category was natural aging, i. e. it had been stored at room temperature (RT) for 3weeks before DSC testing. Each sample was processed under nitrogen atmosphere, from 20°C to 550°C, with three different heating rates; (20, 30 and 40°C/ min) for the quenched alloy and (10, 20 and 30°C/ min) for the natural aging alloy.

Table 1 Chemical composition of investigated Al-Mg-Si alloy

Elements	Al	Mg	Si	Cu	Fe
at.%	98.45	0.653	0.595	0.014	0.215

3 Results and discussion

Fig. 1 and **2** show the DSC thermo-grams of the quenched and the natural aging Al Mg Si alloy respectively, heated at different heating rate. DSC curves (**Fig. 1**) shows four exothermic peaks which correspond to the formation of GP zones (peak 1), β″ (peak 3), β′ (peak 5) and β (peak 7), and four endothermic peaks (2, 4, 6 and 8) which correspond to the dissolution of GP zones, the metastable phase β″, β′ and the stable phase β respectively. DSC curves (**Fig. 2**) shows three

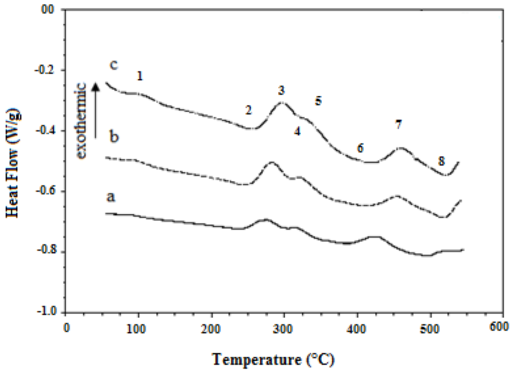

Fig. 1 DSC curves of the quenched Al Mg Si alloy at different heating rates:(a) α = 20 °C/min, (b) α = 30 °C/min and (c) α = 40 °C/min

exothermic peaks which correspond to the formation of β″ (peak 2′), β′ (peak 4′) and β (peak 6′), and four endothermic peaks (1′, 3′, 5′ and 7′) which correspond to the dissolution of GP zones, the metastable phase β″, β′ and the stable phase β respectively. These peaks observed in the Al-Mg-Si alloy (quenched and aged at room temperature for three weeks) are similar to those published in the literature on similar alloys [11, 12]. We can deduce that during the natural aging of Al-Mg-Si alloy, the GP zones form, but during heating in the DSC instrument, the first thing that happens is the dissolution of these particles (peak A) [13, 14].

The main precipitation peaks increase and shift to higher temperatures with the increase of heating rate, which means that this transformation is thermally activated. The maximum peak temperatures of the detected exothermic peaks are indicated in **Tab. 2** (quenched alloy) and **Tab. 3** (natural aging alloy).

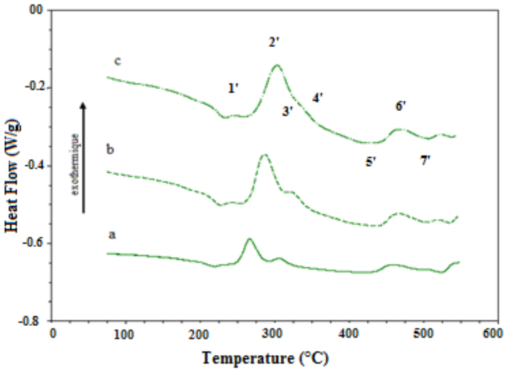

Fig. 2 DSC curves of the Al Mg Si alloy aged at room temperature (RT) for 3 weeks at different heating rates: (a) α = 10 °C/min, (b) α = 20 °C/min and (c) α = 30 °C/min

Table 2 Variation of DSC peak temperature with heating rate α (quenched alloy)

Phase **A**	**GP**	**β″**	**β′**	**β**
20°C/min	90.28°C	261.43°C	315.65°C	424.88°C
30°C/min	95.07°C	281.55°C	323.64°C	454.71°C
40°C/min	100.93°C	295.94°C	328.97°C	460.04°C

Table 3 Variation of DSC peak temperature with heating rate α (natural aging alloy)

Phase **A**	**β″**	**β′**	**β**
10°C/min	267.08°C	307.28°C	455.20°C
20°C/min	287.85°C	323.89°C	463.31°C
30°C/min	302.99°C	334.61°C	464.84°C

The activation energy for precipitation, E, is determined by Kissinger method [14] of the exothermic peaks which have been observed in **Fig. 1** and **2**. This method is basically developed in order to study the variation of the maximum peak temperature with heating rate according to the following expression:

$$ln\left({}^{\alpha}\!/_{Tp^2}\right) = {}^{E}\!/_{RTp} \qquad \text{Kissinger equation} \qquad (1.)$$

where α is the heating rate, Tp is the temperature of the peak maximum, and R is the gas constant (8.314 J mol^{-1} K^{-1}).

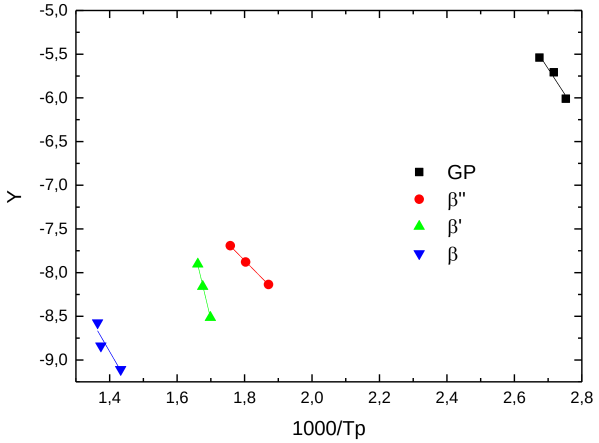

Fig. 3 Plots of Y against 1000/Tp of quenched Al-Mg-Si alloy a) GP, b) β″, c) β′, d) β

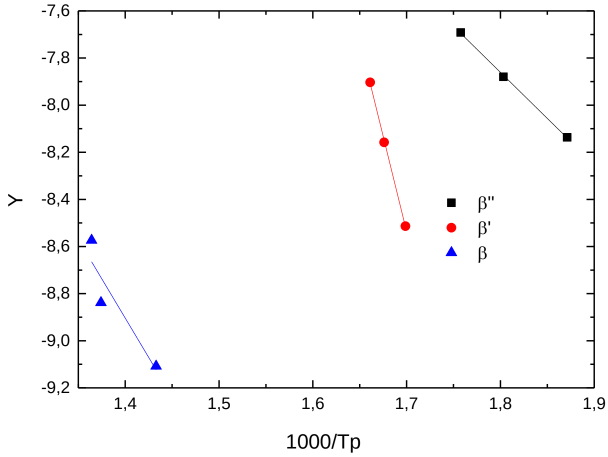

Fig. 4 Plots of Y against 1000/Tp of Al-Mg-Si alloy aged at RT for 3 weeks a) β″, b) β′, c) β

Fig. 3 and **4** illustrate the linear relationships between ln (α/Tp^2) and 1000/Tp for the quenched and the natural aging Al-Mg-Si alloy respectively. The activation energy E is determined from each slope, (**Tab. 4**).

Table 4 Activation energy of precipitates (kJ/mol) calculated from Kissinger method

Phase	**GP**	**β″**	**β′**	**β**
Quenched samples	66.894	41.555	143.059	62.845
Natural aging simples	-	70.263	108.257	454.402

From the quenched alloy results, the activation energy for the first peak (GP zones) is about 66.894 KJ/mol which is much smaller than the ones for diffusion of silicon and magnesium in aluminum and very close to the one for vacancy migration (71.3 KJ/mol) [15]. This reaction can be explained in terms of vacancy cluster formation. A GP zones structure closely related to β″ has been found and is denoted pre-β″ [16, 17]. The activation energy for the second peak, which has been identified as the β″, is determined as 41.555 KJ/mol, is slow than that reported in other literature [18, 19], and it can be explained by the low driving force of β″ precipitate. The activation energy associated with the precipitation of β′ is determined as 143.059 KJ/mol. This value is close to the reported values of diffusion of Mg and Si in aluminum, i.e., 131 to 124 KJ/mol, respectively [20]. The precipitation of β′ particles might be characterised by the diffusion of Mg and Si atoms in Al matrix. This result agrees well with Gaber et al. [18]. The activation energy of β stable is determined as 62.845 KJ/mol, which is significantly smaller than those for the bulk diffusion of Mg and Si in Al.

In the naturally aged specimens, the activation energy associated with the precipitation of the β″ and β′ phase was estimated at 70.263 and 108.257 KJ/mol, respectively. The activation energy associated with the precipitation of the β is determined as 454.402 KJ/mol. In the comparison, the activation energies obtained for the β″ and the β formation in the Al-Mg-Si alloy aged at RT for 3 weeks are higher than that in the quenched alloy 41.555 and 62.845 KJ/mol respectively. It reveals that the formation of these precipitates is really difficult during naturally aged. The increase in the activation energy indicates that the natural aging may have a negative effect on the formation of β″ and β precipitation. When the activation energy obtained for the formation of β′ is smaller than the value in quenched alloy. The decrease in the activation energy indicates that the natural aging may have a positive effect on the formation of β′ phase.

4 Conclusion

In this work the activation energy of all precipitated phases during the precipitation sequence (quenched and natural aging) in Al-Mg-Si alloy has been studied using DSC experiments. The following conclusions can be drawn:

- The activation energy for the formation of GP Zones is very close to that for the migration vacancy.
- The precipitation sequence of the Al Mg Si alloy depends on previous natural aging.
- The activation energy for the GP zones, β″, β′ and the β, in the quenched alloy, are determinate as 66.894, 41.555, 143.059 and 62.845 KJ/mol respectively.
- The activation energy for the β″, β′ and the β, prior natural aged alloy, are determinate as 70.263, 108.257 and 455.02 KJ/mol respectively.
- The activation energy for the β″ and β determined for natural aging alloy were higher than that in the quenched alloy.
- The formation of vacancies during natural aging delays the formation of the β″ and β phase.

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