Effects of TiB$_2$ particles and Ag on the activation energy of Ω phase in Al alloys

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Abstract. This work analyses the effects of TiB$_2$ reinforcement particles and silver additions on the activation energy of the GP zones and the Ω phase in an aluminium matrix composite (AMC). Several additions of TiB$_2$ and Ag were made to a 2xxx series alloy. Differential scanning calorimetry (DSC) was used to identify the temperature peaks and the Kissinger approach used to calculate activation energies. Results showed that the activation energy for the Ω phase was greatly reduced by the addition of both elements; however, the TiB$_2$ particles were more effective. In addition, experimental results show that the lowest value of the activation energy, 68 kJmol$^{-1}$, was not affected by the silver content. This value is lower than any value found in literature and suggests that the formation of the Ω phase is related to the pipe diffusion of Cu in Al.

1. Introduction

Metal matrix composites (MMCs) are used in aerospace industries to satisfy the demand for a lightweight, high performance material. Al-based MMCs play a fundamental role with their great specific strength and improved wear resistance. If a heat treatable aluminium alloy is used as a matrix, the total strength of the aluminium matrix composite (AMC) is the combination of all the strengthening mechanisms, including the ceramic particles and the precipitates.

One of the main effects caused by the addition of ceramic particles is an increase in hardness and a shortening in time to reach the peak-aged condition. However, in a 2xxx series alloy, the addition of silver has shown extremely positive results improving the hardness and reducing the time to peak aging [1, 2]. The reason for this behaviour is the increased number of sites for the heterogeneous nucleation of the Ω phase, which is the main strengthening phase in the alloy [3].

Differential scanning calorimetry (DSC) provides information on a thermally active phase, such as a precipitate, providing a means of analysis of the precipitates present in the alloy, and their nucleation energy and temperature, for a macroscopic sample.

Several reports of the activation energy for the formation of the Ω phase in a non-reinforced Al alloy have been made and most of these experiments found it to be around 150 kJmol$^{-1}$ [4, 5]. This value indicates that the process for the formation of the Ω phase is controlled by the diffusion of Cu in Al ($E_a \sim 140$ kJmol$^{-1}$). However, no studies have been carried out on understanding the effects of ceramic particles (specifically TiB$_2$) on the formation activation energy of the Ω phase.

The major drawback of using DSC is the identification of the precipitates, and in particular being able to link a nucleation or dissolution event to its corresponding phase. For this reason, DSC is used...
in conjunction with microscopy to correctly identify the precipitates. However, for the 2xxx series, an extensive literature exists on the identification and correlation between DSC peaks and precipitates.

The present paper describes the use of DSC to study and understand the effects of TiB₂ particles and Ag content on the activation energy of the GP zones and the Ω phase in an Al-Cu alloy. In particular, the Kissinger-Akahira-Sunose method [6-8], which is known as the generalized Kissinger approach, will be used to study the effects of these two additions on the activation energy.

2. Experimental procedure

Five different alloys were produced by varying the composition of the A205 alloy. This alloy, denoted alloy A, is an Al-Cu-Mg with additions of TiB₂ ceramic particles and silver. Alloys B and C were cast with varying amounts of Ag, resulting in an amount of Ag of 0.5 and 1.5, with respect to that of alloy A. Alloy D was prepared by diluting the amount of TiB₂ in alloy to half that in alloy A. Alloy E was a TiB₂ free alloy with half the amount of Ag of the initial alloy A. The composition variations of the five alloys were analysed by XRF and are summarized in table 1.

The alloys were melted in an induction furnace and poured into sand moulds to obtain test bars of 10 mm diameter and 100 mm length. All alloys used in this work are cast alloys. A solution heat treatment was carried out, and then the alloys were quenched into cold water to achieve a super saturated solid solution. In order to avoid natural aging, samples were stored in a refrigerator until used.

The samples used were machined to 5 mm diameter and 0.5 mm height, with masses of around 28 mg, and then solution heat treated. A Perkin-Elmer DSC 7 was used to measure over a temperature range from 350 K to 650 K, with different scanning rates ranging from 10 Kmin⁻¹, 20 Kmin⁻¹ and 40 Kmin⁻¹.

Table 1. Chemical compositions, given as ratios, of an initial Al-Cu alloy, to which were added varying Ag and TiB₂ additions.

| Alloy | Ag | TiB₂ | Al  |
|------|----|------|-----|
| A    | 1  | 1    | rem |
| B    | 0.5| 1    | rem |
| C    | 1.5| 1    | rem |
| D    | 1  | 0.5  | rem |
| E    | 0.5| 0    | rem |

All DSC samples were run twice; the first run activated the precipitates and the second run was recorded as a baseline. The baseline was then subtracted from the first signal. This experimental procedure was carried out in order to enhance the signal from the DSC and eliminate instrument noise. The Kissinger approach was then used to calculate the activation energy for the formation of the two phases present in the alloy. This approach is based on the theory that the temperature at which the given peak occurs is shifted with increasing scan rate.

3. Results

In a DSC plot of an Al-Cu-Mg alloy, after solution heat treatment, two endothermic and two exothermic peaks were found. These peaks were identified as related to the nucleation and dissolution of the GP zones and the Ω phase, as suggested in the literature [9]. Because each event is connected, the endothermic and exothermic peaks are adjacent to each other, meaning that a phase is first nucleated and then dissolved.
Figure 1 shows DSC curves for alloy D after the solution heat treatment process for three different scanning rates. In an Al-Cu-Mg alloy, the GP zones are the first precipitate to form, at around 370 K. The dissolution of this phase starts at about 430 K reaching a peak at around 470 K. This peak is followed by an exothermic peak at around 540 K, which is correlated to the formation of the Ω phase. The Ω phase is the main strengthening mechanism in 2xxx series alloys, and it nucleates from an Ag-Mg cluster. The Ω phase contributes to the strength of the 2xxx series alloy because it nucleates on the {1,1,1} planes which are the slip plane of the aluminium matrix.

The dissolution of the Ω phase and the nucleation of the θ\textsuperscript{i} phase are not clearly distinguishable in the plot, because they partially overlap [10]. The S phase was not observed in this alloy due to the high Cu:Mg ratio.

Activation energies are derived through the Kissinger methods which correlate the scanning rate (ϕ) to the peak temperature (T\textsubscript{p}) of the process. Equation (1) shows the relationship between these variables. The activation energy (E\textsubscript{a}) for the nucleation of the GP zones and Ω phase, can be derived from an Arrhenius equation by plotting ln(T\textsuperscript{2}\textsubscript{p}/ϕ) vs 1/T\textsubscript{p}, as seen in figure 2. The resulting activation energies are summarized in Table 2. In carrying out the Kissinger analysis, the heating rate (ϕ) must be converted to Ks\textsuperscript{-1}.

In each case, equation (1) fits the data points with an R\textsuperscript{2} value of > 0.98.

\[
\ln \left( \frac{T_p^2}{\phi} \right) = \left( \frac{E_a}{RT_p} \right) + C
\]  

(1)
Figure 2. Comparison of Arrhenius plots for the Kissinger analysis of the exothermic peaks due to the Ω phase nucleation in alloys B, C, D and E. The lines are the fits of Equation (1).

Figure shows that by varying the scanning rate, a peak can be enhanced; in fact, at faster scanning rates (e.g. 40 Kmin^{-1}), the area underneath the peaks is greater. Because of this and because of the partially overlapping peaks, it was not possible to detect an exothermic peak linked to the nucleation of the Ω phase in alloy A.

Table 2. Results for the activation energies of the GP zones and the Ω phase calculated by the Kissinger approach.

| Alloy | GP (kJ mol^{-1}) | Ω (kJ mol^{-1}) |
|-------|------------------|-----------------|
| A     | 63               | ND              |
| B     | 75               | 69              |
| C     | 76               | 68              |
| D     | 87               | 98              |
| E     | 59               | 113             |

ND: not detectable

From the results reported in table 2, it is possible to suggest that the TiB₂ particles are more effective in reducing the activation energy of the Ω phase than the silver. In fact, increasing the TiB₂ content twofold (alloys D and B) lowered the activation energy by almost 30% for the Ω phase, while the addition of Ag, from alloy B to C, did not have any effect on the activation energy for the Ω phase. None of the additions had a significant effect on the activation energy of the GP zones. Alloy E was taken as a reference for the activation energy for non-reinforced alloys.

4. Discussion

The identification of phases by DSC can be difficult, and for this reason most research involves DSC and microscopy to interpret their results. However, in a 2xxx series alloy, with a high Cu/Mg mass ratio, the S phase is suppressed. Therefore, the precipitation sequence in the temperature range studied in this work was: GP zones, Ω phase and θ phase.

Dutta et al. [11] analysed a 2xxx series alloy with addition of Al₂O₃ particles and observed the θ phase nucleating between 550 K and 560 K, at a scanning rate of 20 Kmin^{-1}, which is in the same
range as in this work. In addition, Oguocha et al. [12], studying AA2618 with Al₂O₃ particles, found the nucleation of S and θ phase at around 570 K. As a consequence, it is possible to correlate the exothermic peak found in Figure at around 540-550 K with the nucleation of the θ phase. The exothermic peak found at 500-520 K, must therefore be associated with the nucleation of the Ω phase.

In addition, if a non-reinforced alloy is taken into consideration, the dissolution of GP zones is found at around 470 K [13] and so the nucleation of the Ω phase occurs at 490-500 K [9, 14]. These results are comparable with this work. However, the first endothermic peak at around 370 K was not linked to the dissolution of any phases. In agreement with the literature [12, 15], this work showed that the addition of TiB₂ particles does not affect the nucleation temperature of any phases. In fact, Chang et al. [14] has demonstrated that the shift in the exothermic peak is related to the Cu:Mg ratio.

The value of the activation energy for the Ω phase reported for a non-reinforced alloy is close to that for lattice diffusion of Cu in Al, which is around 140 kJ mol⁻¹ [4, 16]. However, the value reported in this study for a reinforced alloy is well below the lattice diffusion of Cu in Al, suggesting another process occurs, as reported by Dutta et al. [17]. In a reinforced alloy the difference in the coefficients of thermal expansion generates a high density of dislocation lines during quenching. Therefore, the diffusivity of Cu atoms in the alloy is improved because the Cu atoms will migrate through the dislocation lines, in a process called pipe diffusion [18]. The activation energy for pipe diffusion of Cu atoms in Al is 66 kJ mol⁻¹ [15] which, as a consequence, will be the lowest activation energy value possible to nucleate the Ω phase.

The combined effect of both silver and TiB₂ particles in alloy B shows a value for the activation energy lower than any value reported so far for the Ω phase. This reduction due to different alloying additions is also reported in the literature. In fact, Borrego et al. [15] was able to reduce the activation energy of the phases studied by 25% by increasing the volume fraction of the SiC reinforced particles in a 6xxx series alloy. Nieh at al [19] reported decreasing the activation energy by 37% when comparing a reinforced 6xxx series composite with a non-reinforced alloy. The lower activation energy seems therefore to be due to the higher density of dislocations with a higher amount of reinforced particles. This will facilitate the diffusion of Cu atoms and the formation of the Cu bearing precipitates such as Ω and θ phase.

The activation energy for the formation of the GP zones reported in this work was around 68 kJmol⁻¹, and it remained unchanged with alloying additions. The results of this work are comparable to values reported in literature [13, 20].

In summary, this work offers a first examination of the activation energies for the GP zones and the Ω phases in metal matrix composite. In particular, the effects of the reinforcing particles (TiB₂) and the silver content have been analysed with the Kissinger approach. The results suggest that in a reinforced alloy, the activation energy for the Ω phase can be reduced. This value for the activation energy in a reinforced alloy suggests that the formation of the Ω phase is due to pipe diffusion of Cu in Al.

5. Conclusions
1. The activation energy for the formation of the Ω phase is greatly reduced by the addition of TiB₂ particles and silver, while the activation energy for the formation of the GP zones is unchanged.
2. In MMC alloys, the most effective mechanism to reduce the activation energy of the formation of the Ω phase is to increase the volume fraction of the reinforcing particles.
3. The silver additions did not show any effect on the activation energy of the Ω phase.
4. The lowest value for the activation energy was found to be 68 kJmol⁻¹ phase. This value was found when both silver and TiB₂ were added.

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