Precipitation kinetics of GP zones, metastable $\eta'$ phase and equilibrium $\eta$ phase in Al–5.46wt.%Zn–1.67wt.%Mg alloy

A. KHALFALLAH$^{1,2}$, A. A. RAHO$^1$, S. AMZERT$^2$, A. DJEMLI$^3$

1. University of Sciences and Technology Houari Boumediene, Bab ezzouar Algiers 16111, Algeria;
2. Nuclear Research Centre of Birine, BP 180, Ain Oussera, Djelfa, 17200, Algeria;
3. Department of Physics, University of M’sila, M’sila 28000, Algeria

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Abstract: Thermal analysis is one of the most used techniques for analyzing the behavior of aluminum alloys in order to analyze the precipitation of Guinier–Preston (GP) zones and different phases formed. In the present work, the behavior of the Al–5.46wt.%Zn–1.67wt.%Mg alloy was studied. The mechanism and kinetics of precipitation of the GP, the metastable phase $\eta'$ and the equilibrium phase $\eta$ were investigated using DSC carried out between room temperature and 480 °C at heating rates of 5, 10, 15 and 20 °C/min. The apparent activation energies, calculated by DSC from isothermal calculation method using JMAK model, for GP, $\eta'$ and $\eta$ were 56, 79 and 96 kJ/mol, respectively, and those calculated by non-isothermal calculation method using Kissinger methods were 57, 82 and 99 kJ/mol, respectively. The values of Avrami parameter, $n$, from isothermal calculation, during the precipitation of the GP, $\eta'$ and $\eta$ were 1.103, 1.9075 and 1.92, respectively, and those calculated by non-isothermal were 0.86, 2.30 and 2.24, respectively. The results show that GP zones formation is governed by the migration of Zn and Mg atoms while the precipitation of the $\eta'$ metastable phase and the $\eta$ stable phase is governed by both the migration and the diffusion of the solute atoms.

Key words: Al–Zn–Mg alloys; precipitation kinetics; DSC; JMAK model; activation energy; Avrami parameter

1 Introduction

Aluminum alloys of 7xxx series AlZnMg are extensively used in the automotive and aerospace industry because of their low density and high mechanical properties. These age-hardenable alloys provide a high strength in the peak-aged conditions [1–5]. The aging behavior and the precipitation sequence may be studied by different methods such as hardness, resistivity measurement, calorimetry and X-ray diffraction technique.

Physical properties of these alloys are linked with the precipitation of metastable precipitates during aging treatments. The decomposition of supersaturated solid solutions obtained by quenching takes place in several stages. The formation of the metastable precipitates leads to a variation of the alloy microstructure [6–9]. The addition of zinc to the Al–Mg alloy system reduces the solid solubility of aluminum in magnesium, increasing the amount of precipitate phase formed upon aging and thus causing a moderate increase in strength [10]. In such a case, it is interesting to study the microstructural evolution of the alloys to correlate the physical properties with the alloy microstructure. Generally, the kinetics of precipitation and dissolution reactions in aluminum alloys was obtained using resistivity and differential scanning calorimetry (DSC) techniques to study the kinetics under isothermal conditions and under non-isothermal conditions, respectively. The decomposition of the supersaturated solid solution is known to take place via the formation of several phases which may precipitate simultaneously. Depending on thermal treatment, the unmixing processes can be described as follows [11–14]: $\alpha$-supersaturated solid solution ($\alpha$-sss) $\rightarrow$ GP zones (Zn,Mg) $\rightarrow$ metastable $\eta'$ (Hex.) $\rightarrow$ stable $\eta$ (MgZn2) (Hex.).

In the age-hardenable aluminium alloys, the precipitation is the subject of many experimental and theoretical works [11,15–17]. In the AlZnMg alloys, the hardening is attributed to the precipitation of the GP zones and the $\eta'$ metastable phase which, generally but not necessarily, nucleates from the GP zones [18]. The precipitation and the dissolution of all the phases
of the precipitation sequence are accompanied by exothermic and endothermic reactions which may be investigated by the differential scanning calorimetry (DSC) technique [19–21].

In the present work, the transformation kinetics of precipitation of the GP zone and metastable phase \( \eta' \) and equilibrium phase \( \eta \) has been investigated by DSC in order to estimate the activation energies of GP, \( \eta' \) and \( \eta \) formations based on isothermal and non-isothermal methods, the growth morphology parameter \( n \) and the frequency factor for the reaction of GP, \( \eta' \) and \( \eta \) formations.

2 Experimental

2.1 Materials and samples preparation

The Al–5.46wt.%Zn–1.67wt.%Mg alloy studied was prepared from an aluminium powder of 99.98% purity. Its chemical composition is given in Table 1.

| Table 1 Chemical composition of Al–5.46wt.%Zn–1.67wt.%Mg alloy (mass fraction, %) |
|-----------------|---|---|---|---|---|
| Si              | 0.11±0.026 |
| Fe              | 0.107±0.21 |
| Mg              | 1.67±0.4   |
| Zn              | 5.46±0.1   |
| Al              | 92.63±0.4  |

The microstructural structure of Al–Zn–Mg was observed using a metallographic microscope Leica DM2500 M equipped with a photographic camera. X-ray diffraction patterns were registered using a Philips X-Pert PW1500 with a monochromatic Cu K\( \alpha \) radiation of a wavelength of 0.15405 nm. The thermal analysis (DSC) was carried out on a Setaram LABSYS Evo TG–DSC 1600 °C equipment, operated under argon atmosphere.

2.2 Theoretical concept

The determination of the kinetics parameters describing the precipitation kinetics of the GP zones, the \( \eta' \) metastable phase and the \( \eta \) stable phase is based on an isothermal calculation method and on a non-isothermal calculation method.

2.2.1 Isothermal calculation method

The isothermal calculation method is based on the JOHNSON-MEHL-AVRAMI-KOLMOGOROV (JMAK) theory. The evolution of the transformed fraction during a phase precipitation is given by

\[
x(t) = 1 - \exp(-kt^n) = k_0 \exp(-E_a/(RT))
\]

where \( x \) is the transformed fraction at time \( t \), \( k \) is the rate constant which has an Arrhenian temperature dependence:

\[
k = k_0 \exp(-E_a/(RT))
\]

where \( k_0 \) is the frequency factor, \( E_a \) is the activation energy, and \( R \) the gas constant.

The transformed fraction is determined from the DSC thermograms for different heating rates using the relation:

\[
x = A_T/A
\]

where \( A_T \) represents the area under the peak at the temperature \( T \) and \( A \) is the total area of the peak.

The rate of transformation \( dx/dt \) is expressed by

\[
dx/dt = kF(x)
\]

where \( F(x) \) is a function of the transformed fraction [22].

So, Eqs. (5) and (6) exist:

\[
\ln\left(\frac{dx}{dt}\right) = \ln(k_0n) + \frac{n-1}{n}\ln[-\ln(1-x)] + \ln(1-x) - \frac{E_a}{RT}
\]

\[
\ln[k_0F(x)] = \ln(k_0n) + \frac{n-1}{n}\ln[-\ln(1-x)] + \ln(1-x)
\]

From the DSC analysis at different heating rates, the activation energy, the frequency factor and the Avrami parameter can be determined.

For each transformed fraction \( x \) at different heating rates, the apparent activation energy is determined from the slope of the curve \( \ln(dx/dt) \) versus \( 1/T \) and the values of \( \ln[k_0F(x)] \) are given by

\[
\ln[k_0F(x)] = \ln\left(\frac{dx}{dt}\right) + \frac{E_a}{RT}
\]

The Avrami parameter \( n \), is determined by choosing some pairs of \( x_1 \) and \( x_2 \) that satisfy the following condition:

\[
\ln[k_0F(x_1)] = \ln[k_0F(x_2)]
\]

So, \( n \) will be given by

\[
n = \frac{\ln[\ln(1-x_2)/\ln(1-x_1)]}{\ln[(1-x_2)/(1-x_1)\ln(1-x_1)]}
\]

The frequency factor \( k_0 \) could be deduced from Eq. (6) after the determination of \( n \).

2.2.2 Non-isothermal concept

Several methods in the non-isothermal DSC experiment may be used to calculate the apparent activation energy in the non-isothermal DSC experiment. In this work, the single Kissinger [23–26] method was chosen:

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

where \( v \) is the heating rates in the DSC analysis; \( T_p \) is the absolute peak temperature on DSC curves; \( C \) is a constant. The activation energy is deduced from the slope of the curve \( \ln(v/T_p^2) = F(1/T_p) \).

The values of the Avrami parameters are deduced
for each heating rate from the following equation [26–28]:

\[
n = \frac{2.5T_P^2 R}{\Delta T_P E_a}
\]

where \( \Delta T_P \) is the width of the transformation peak at half maximum.

3 Results and discussion

3.1 Optical microscopy

The optical microscopy technique was applied for the analysis of the microstructure of the alloy. The optical micrograph of the homogeneous alloy shows a granular structure including some intermetallic insoluble particles containing Si and Fe (Fig. 1(a)) and that of the homogeneous alloy heated to 290 °C at a rate of 10 °C/min shows stable particles MgZn₂ in the grains and at the grain boundaries (Fig. 1(b)).

3.2 X-ray diffraction characterization

X-ray diffraction patterns show that the diffraction peaks of the as-quenched solid solution are at analogous positions of those of the aluminum and, after a heating from room temperature to 290 °C, the diffraction patterns show the diffraction peaks of the \( \eta \) (MgZn₂) stable precipitate (Fig. 2).

3.3 DSC analysis

During the heating from room temperature to 480 °C, using heating rates of 5, 10, 15 and 20 °C/min, the DSC thermograms (Fig. 3) show exothermic and endothermic peaks corresponding to the precipitation and the dissolution of the GP zones, the \( \eta' \) (MgZn₃) metastable phase and the \( \eta \) (MgZn₂) stable phase in accordance with the precipitation sequence.

The different peaks are noted by \( A \) for the GP zones precipitation, \( B \) for the precipitation of the \( \eta' \) metastable phase and \( C \) for the precipitation of the \( \eta \) stable phase (Table 2).

The shifting of the peak temperatures to the higher temperatures with the increase of the heating rate is due to the fact that the precipitation reaction is thermally activated [29–33].

3.3.1 Isothermal calculation of precipitation kinetics

During the precipitation of a phase, the transformed fraction, \( x \), is determined from the DSC thermograms for different heating rates using Eq. (2). Figure 4 shows the

![Fig. 1 Optical micrographs of as-cast Al–Zn–Mg alloy: (a) Homogenized at 480 °C for 2 h; (b) Homogenized and heated to 290 °C at rate of 10 °C/min](image)

![Fig. 2 XRD patterns of pure aluminum (a), Al–Zn–Mg as-quenched solid solution (b), and Al–Zn–Mg solid solution after heating from room temperature to 290 °C (c)](image)
transformed fraction and rate of transformed fraction during the precipitation of the GP zones, the η' metastable phase and the η stable phase.

The shape of the transformed volume fraction curves suggests that the precipitation kinetics obeys to the JMAK law of the growth controlled by the solute atom diffusion [34−36].

Figure 5 represents the variations of $dx/dt$ versus time during the precipitation of the GP zones, the η' metastable phase and the η stable phase. The rate of transformation increases with the increase in the heating rate.

Figure 6 shows the plots of $\ln(dx/dt)$ and $1/T$ versus transformed fraction $x$ during the precipitation of the GP zones, the η' metastable phase and the η stable phase at different heating rates from DSC experiment.

The values of the apparent activation energy for different transformed fractions, determined from the slopes of the linear curves $\ln(dx/dt)$ versus $1/T$ plotted for different transformed fractions at different heating rates (Fig. 7) are listed in Table 3. The correlation factor, $R^2$, greater than 0.99, indicates that there is a strong linear relationship between $\ln(dx/dt)$ and $1/T$.

Figure 8 shows the plots of $\ln[k_0F(x)]$ versus transformed fraction $x$ during the GP zone precipitation, the metastable phase precipitation and the stable phase precipitation at different heating rates. We could deduce the Avrami parameter by choosing some pairs of $x_1$ and $x_2$ that satisfy the following condition: $\ln[k_0F(x_1)]=\ln[k_0F(x_2)]$. The average values of Avrami parameter $n$, for each heating rate are listed in Table 4 using Eq. (9).

3.3.2 Non-isothermal calculation of precipitation kinetics

In the case of the non-isothermal calculation method, the activation energy is determined by the Kissinger relation. The apparent activation energies, determined by the Kissinger method from the slope of the linear curves $\ln(v/T^2_p)$ versus $1/T_p$ (Fig. 9) are listed in Table 5, which are in the order of 57 kJ/mol during the GP zones precipitation, in the order of 82 kJ/mol during the precipitation of the η' metastable phase and in the order of 99 kJ/mol during the precipitation of the η stable phase. The correlation factor, $R^2$, greater than 0.99, indicates that there is a strong linear relationship between $\ln(v/T^2_p)$ and $1/T_p$.

The obtained results are in accordance with those of OHTA et al and AFIFY et al [37−39].

The Avrami parameter $n$ is determined from Eq. (11) and, the values and average values of $n$ are listed in Table 6. The average values of $n$, during the GP zones formation, are characteristics of a growth of plate after saturation of nucleation, while the average values of $n$, during the precipitation of the η' metastable phase and during the precipitation of the η stable phase are characteristics of a continuous nucleation and diffusion controlled growth [40].

It is well known that the activation energy results from the contribution of the vacancies formation and the
Fig. 4 Transformed fractions and rates of transformed fraction at different heating rates during GP zone precipitation (a), η’ metastable phase precipitation (b) and η stable phase precipitation (c).

Fig. 5 Growth rate \(\frac{dx}{dt}\) of GP zones (a), η’ metastable phase (b) and η stable phase (c) versus time at different heating rates.

Fig. 6 Plot of \(\ln(\frac{dx}{dt})\) and \(1/T\) versus transformed fraction \(x\) during precipitation of GP zones (a), η’ metastable phase (b) and η stable phase (c) at different heating rates.

Fig. 7 Plots of \(\ln(\frac{dx}{dt})\) versus \(1/T\) for each transformed fraction \(x\) during precipitation of GP zones (a), η’ metastable phase (b) and η stable phase (c) at different heating rates.
Table 3 Activation energy ($E_a$) and coefficient of determination ($R^2$) for different transformed fraction $x$

| $x$ | GP zones | | | | | | $\eta'$ metastable phase | | | | | | $\eta$ stable phase | | | |
|-----|----------|-----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|     | $E_a$ (kJ·mol$^{-1}$) | $R^2$ | $E_a$ (kJ·mol$^{-1}$) | $R^2$ | $E_a$ (kJ·mol$^{-1}$) | $R^2$ |
| 0.1 | 59.01 | 0.9999 | 81.10 | 0.99829 | 98.47 | 0.99391 |
| 0.2 | 57.43 | 0.9984 | 80.21 | 0.99839 | 97.49 | 0.99500 |
| 0.3 | 56.41 | 0.9977 | 79.51 | 0.99853 | 96.95 | 0.99527 |
| 0.4 | 55.75 | 0.9958 | 78.99 | 0.99867 | 96.53 | 0.99550 |
| 0.5 | 55.40 | 0.9946 | 78.48 | 0.99868 | 96.24 | 0.99580 |
| 0.6 | 54.77 | 0.9930 | 78.21 | 0.99892 | 95.50 | 0.99550 |
| 0.7 | 54.40 | 0.9921 | 77.74 | 0.99870 | 95.08 | 0.99640 |
| 0.8 | 54.14 | 0.9913 | 77.12 | 0.99863 | 94.18 | 0.99620 |
| 0.9 | 53.44 | 0.9905 | 77.04 | 0.99858 | 93.94 | 0.99600 |
|     | Average | 55.64 | 78.71 | 96.04 |

Table 4 Values of Avrami parameter and frequency factor at different heating rates

<table>
<thead>
<tr>
<th>$v$ (°C·min$^{-1}$)</th>
<th>GP zones</th>
<th>$\eta'$ metastable phase</th>
<th>$\eta$ stable phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$</td>
<td>$k_0/10^5$</td>
<td>$n$</td>
</tr>
<tr>
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</tr>
<tr>
<td>10</td>
<td>1.92</td>
<td>4.86</td>
<td>1.93</td>
</tr>
<tr>
<td>15</td>
<td>1.89</td>
<td>4.94</td>
<td>1.91</td>
</tr>
<tr>
<td>20</td>
<td>1.89</td>
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<td>1.91</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>1.103</td>
<td>5.10</td>
</tr>
</tbody>
</table>

Fig. 8 Plots of ln$k_0F(x)$ versus transformed fraction $x$ during precipitation of GP zones (a), $\eta'$ metastable phase (b) and $\eta$ stable phase (c) at different heating rates

Fig. 9 Plots of $ln(v/T_p^2)$ versus $1/T_p$ at different heating rates during precipitation of GP zones (a), $\eta'$ metastable phase (b) and $\eta$ stable phase (c)
4 Conclusions

(1) The DSC experiments highlight the precipitation sequence in the AlZnMg alloy. The shift of the peak temperature to the higher temperature with the increase of the heating rate confirms that the precipitation and the dissolution reactions are thermally activated.

(2) All JMAK parameters $n$, $k_0$ and the apparent activation energy $E_a$ were determined using both an isothermal calculation and a non-isothermal calculation during the precipitation of the GP zones, the $\eta'$ metastable phase and the $\eta$ stable phase.

(3) The results also show that GP zones formation is governed by the migration of Zn and Mg atoms while the precipitation of the $\eta'$ metastable phase and the $\eta$ stable phase is governed both by the migration and the diffusion of the solute atoms.

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References


[8] STILLER K, WARREN P J, HANSEN V, ANGENETE J, GJONNES J. Investigation of precipitation in an AlZnMg Al alloy after two step aging treatment at 100 and 150 °C [J]. Materials Science and
Al−5.46wt.%Zn−1.67wt.%Mg 合金的 GP 区、亚稳 η′相和平衡 η相的析出动力学

A. KHALFALLAH1,2, A. A. RAHO1, S. AMZERT2, A. DJEMLI3

1. University of Sciences and Technology Houari Boumediene, Bab ezzouar Algiers 16111, Algeria;
2. Nuclear Research Centre of Birine, BP 180, Ain Oussera, Djelfa, 17200, Algeria;
3. Department of Physics, University of M’sila, M’sila 28000, Algeria

摘 要: 热分析是研究铝合金行为最常用的技术之一，用于分析 Guinier−Preston(GP)带的析出及不同相的形成。本文研究 Al−5.46wt.%Zn−1.67wt.%Mg 合金的行为。用 DSC 研究 GP 区、亚稳 η′相和平衡 η相从室温到 480 °C 的析出机制与动力学，升温速率为 5、10、15 和 20 °C/min。根据 DSC 结果，用 JMAK 模型和等温计算法得到 GP、η′和 η 的表面激活能分别为 56、79 和 96 kJ/mol，而用 Kissinger 方法和非等温计算法得到三者的表面激活能分别为 57、82 和 99 kJ/mol。GP、η′和 η 析出过程中，等温计算的 Avrami 参数(n)值分别为 1.103、1.9075 和 1.92，而非等温计算的 n 值分别为 0.86、2.30 和 2.24。结果表明，GP 区的形成由锌和镁原子的迁移控制，而 η′亚稳相和 η 稳定相的析出由溶质原子的迁移和扩散控制。

关键词: Al–Zn–Mg 合金; 析出动力学; DSC; JMAK 模型; 激活能; Avrami 常数

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