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Thermal aging, kinetics and mechanical properties of Al-7 wt% Mg alloy

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ABSTRACT

This work presents the experimental results of the differential scanning calorimetry (DSC), hardness measurements (Hv) and X-ray diffraction (XRD) analysis, investigating the kinetics of precipitation phenomena in Al-7 wt % Mg alloy. In the XRD and DSC curves indicates the formation of the intermediate precipitation of β-(Al_3Mg_2) phase respectively. The activation energies associated with the processes have been determined according to the three models proposed by Kissinger, Ozawa and Boswell. Consequently, the nucleation mechanism of the precipitates can be explained. These phases are confirmed by the XRD analysis.

1. Introduction

Al–Mg alloys are an important group of commercial Al alloys with good combination of strength and formability and therefore they have various applications in transport, packaging and general engineering industries. Strength of Al–Mg alloys strongly increases with addition of Mg. The Mg has a high solubility in solid solutions and therefore it provides the most effective enhancement of strength among all alloying additions in the aluminium solid solution [1–3]. Thermal analysis has been extensively used to study precipitation in metallic materials such as aluminium alloys [4–6] and copper alloys [7]. Addition of Mg to Al is popular in Al industry because Mg is a typical element to introduce significant hardening of Al through a solid solution effect. Although the equilibrium solid solubility of Mg in Al is about 1 wt% at room temperature, an extended solid solubility of Mg in Al can be achieved by rapid solidification as well as by mechanical alloying of elemental powders [8,9].

The kinetics of these transformations was investigated under isothermal and non-isothermal treatments which involve several nucleation and growth mechanisms where the most important kinetic parameters are the activation energy and the growth exponent [10,11]. Studies of the precipitation sequence of this alloy system became important for its further development, and many of these studies have been made by using differential scanning calorimetry (DSC) and microhardness measurement (Hv) [12–14]. Their methods were applied to characterize the precipitation kinetics in Al–Mg alloys. Boumerzoug and Fatmi [15] investigated the effect of heat treatments on discontinuous precipitation kinetics in Al-30 wt% Zn

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alloy through differential dilatometery, DSC, and other techniques. They reported that at all temperatures lower than 180 °C the supersaturated solid solution of the quenched alloy decomposed completely by a cellular precipitation reaction. The activation energy and the Avrami exponent were 58.7 kJ/mol and 1.83, respectively. Two other studies by Sakurai [16] and Moizumi [17] have examined the effect of addition of copper in an Al—Mg—Si. The Θ′ and S′ phases with both active their precursors. The authors of that study note that the addition of 0.5% Mg reveals precipitates β'et S′ and shortens the duration of the heat treatment, while increasing the final hardness of the alloy. The yield stress and strain-hardening properties are studied by Verdier et al. [18] in Al-2.5 wt%Mg alloy as a function of the initial prestrain, temperature and the duration of annealing treatments. The kinetic evolution of the yield stress is related to the variation of the total dislocation density as a single structural parameter.

2. Experimental procedure

The Al-7 wt% Mg alloy used in this investigation was supplied by Cathay Advanced Materials Limited. The chemical compositions of this alloy are presented in Table 1.

The ingot was cold rolled (15% reduction) to introduce deformation to expedite the subsequent homogenization procedure. Once rolled, the ingot was sectioned and encapsulated in Pyrex tubing back-filled with argon. The encapsulated alloy were then placed in a tube furnace at room temperature and heated to 470 °C for one week. After quench in water from the homogenization temperature to obtain a supersaturated solid solution α_0, portions of all samples were sectioned according to the required dimensions of the crucibles for the DSC.

DSC experiments were performed using a NETZSCH 200PC DSC analyzer between room temperature and470 °C,at heating rates of 4, 6 and 8 °C/min. A protective nitrogen atmosphere was used to prevent samples oxidation. X-ray diffraction experiments were carried out using a PAN alytical X'Pert PRO diffractometer. CuKα radiation and a speed of 1°/min were used. The Vickers microhardness was measured byadevice Tukon 2500 type.

3. Results and discussion

a X-ray diffraction study

For studying the heat treatment effect on the discontinuous precipitation in Al-7wt% Mg, the initial samples are homogenized at 470 °C for one week and quenched in water. The X-ray diffraction spectrum of this quenched alloy which corresponds to supersaturated solid solution α_0 is shown in Fig. 1a; the peaks in this figure indicate only a typical structure of Al (CFC). The formation of this new β phase peaks are present in this spectrum after aging 2h and 20 h at 150 °C (Fig. 1). The first deduction is that kinetics of the discontinuous precipitation reaction is fast and the intermetallic phase β(Al_3Mg_2) corresponds to the equilibrium diagram and agrees with the data in the literature [19–21].

At the temperature 200 °C, it was concluded that the kinetics of the precipitation reaction is faster than 150 °C. Note that the peak intensities of β (Al_3Mg_2) phase are more important, which is a significant amount of the precipitated phase (Fig. 2).

The lattice parameter is a useful parameter to know because it can tell us about the stress that would exert any of the samples. The lattice parameter can be derived fromspectra X-ray diffraction. The Table 2 shows the evolution of the lattice parameter of the Al-7wt% Mg alloy en function to temperature and aging time. The analysis of this spectra quenching and aging state at 150 and 200 °C, revealed the existence of two phases ($\alpha + \beta$ (Al_3Mg_2)) and we also confirmed the presence of the β phase decrease the lattice parameter of the supersaturated solid solution which confirms the depletion of the parent phase α_0. From these tables there is a single lattice parameter with a continuous evolution. This assessment was confirmed in Al-12% wt Mg alloy by Ayadi et al. [22].

As would be expected, the time dependence of the transformation rate (which is often termed the kinetics of a transformation) is an important consideration in the heat treatment of materials. With many kinetic investigations, the fraction of reaction that has occurred is measured as a function of time, while the temperature is maintained constant. The kinetics for crystallization in non-isothermal condition a comprehensive study by DSC, curing and reactions has being been a research topic for more than half a century. The theoretical basis for use of the DSC for study of precipitation rates was developed independently by Johnson, Mehl and Avrami. The volume fraction, *y*, of sample crystallized, *y*, as a fuction of time, *t*, is shown in Eq. (1) [23,24],:

$$y = 1 - \exp\left[-(kt)^n\right] \tag{1}$$

where k is the effective overall reaction rate, given by:

Table 1
Chemical composition of Al-7 wt% Mg alloy.

Elements	Al	Mg	Fe	Cu	Si
wt%	92.40	7.00	0.15	0.23	0.22

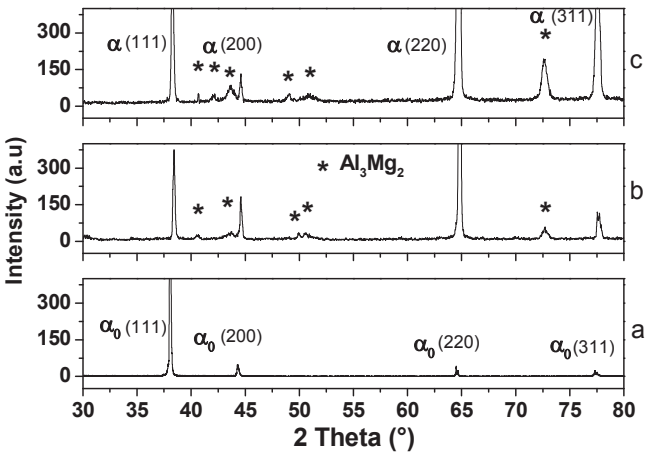

Fig. 1. XRD Spectrum of Al-7 wt% Mg alloy, homogenized at 1 week at 470 °C, quenched (a), aged at 150 °C for 2 h (b) and 20h (c).

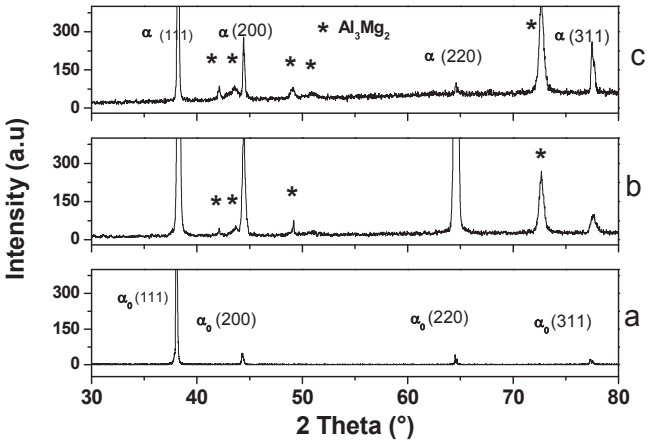

Fig. 2. XRD Spectrum of Al-7 wt% Mg alloy, homogenized at 1 week at 470 °C, quenched (a), aged at 200 °C for 2 h (b) and 4h (c).

$$k = A \cdot \exp\left[\frac{-E_a}{RT}\right] \tag{2}$$

where A is a pre-exponential constant, R is the gas constant, T is the absolute temperature, E_a is the effective activation energy for the overall crystallization process, which combines the nucleation and growth portions of crystallization, and n is the Avrami parameter.

The JMA equation is used to determine the values of k and n at the constant temperature by rapidly heating the sample in a DSC to the desired temperature, and following the evolution of heat during the precipitation process as a function of time. Rearranging the JMA equation yields the expression:

$$\ln(1 - y) = -(kt)^n \tag{3}$$

which is frequently also expressed as:

Table 2
Evolution of the lattice parameter as a function of temperature and aging time.
b The activation energy of precipitation

Aging time (h)	0	2	20	125	175
Lattice parameter a(Å) at 150 °C	4.0766	4.0712	4.0685	4.0672	4.0668
Lattice parameter a(Å) at 200 °C	4.0766	4.0702	4.0684	4.0621	4.0618

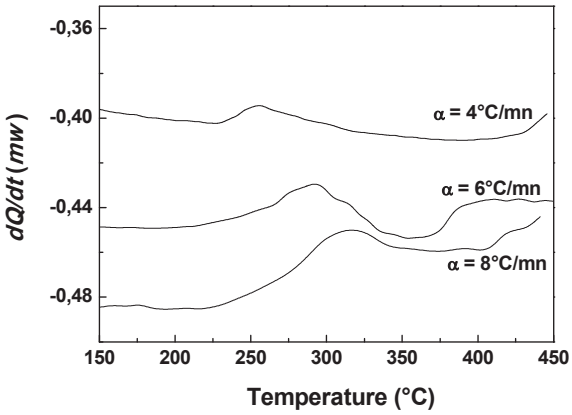

Fig. 3. The DSC curves of the Al-7 wt % Mg alloy quenched and heated 25–450 °C with different heating rates $\alpha = 4$, 6 and 8 °C/min.

$$ln[-\ln(1-y)] = n\ln(k) + n\ln(t) \tag{4}$$

Eq. (2) appears simple but there is no analytical solution that can be devised so far in spite of constant challenging endeavors. However, at a given temperature, the values of n and k are obtained from an isothermal DSC curve using Eq. (4) by least-squares fitting of $\ln[-\ln(1-y)]$ versus $\ln t$. The Avrami exponent is determined traditionally by an isothermal method [25]and its value depends strictly on the incubation time which cannot be given exactly.

In this part of investigation,we present the results of the DSC innon-isothermal conditions of Al-7 wt%Mg previously homogenized and quenched(Fig. 3); at different heating rates ($\alpha = 4$, 6, 8 °C/min. This curve exhibits an exothermic peak in the temperatures range(200–400 °C); corresponding to the dissipation of heat during the discontinuous precipitation [26]. In fact increasing the heating rate leads to an increase in amplitude of the peaks, with a peak top shift to higher temperatures T_m [27].

This suggests that the precipitation process should be considered as a heating rate dependent process, which cannot be characterized by a definite critical temperature independent of the heating rate. These broadened exothermic peaks present asymmetrical profiles; therefore, it was decided to study their crystallization kinetics as a whole, as if it was a single crystallization peak.

The activation energy of crystallization (E_a) for the investigated Al-7 wt%Mg alloy has been estimated using the following methods. The Kissinger model is used generally to determine the kinetic parameters especially for the first order reaction. However, the Kissinger model was modified for the n-order reactions such as Ozawa and Boswell models [28–31]. *Kissinger's* Eq. (5) *Ozawa* et al. Eq. (6) and *Boswell* Eq. (7)which relates the dependence of the crystallization peak temperature T_m on the heating rate (α) by the recent following equations [32–35]:

$$Y = \ln\left(\frac{a}{T_m^2}\right) = C_1 - \frac{E_a}{R\cdot T_m} \tag{5}$$

$$Y = \ln(\alpha) = -1.0518\frac{E_a}{R\cdot T_m} + C_2 \tag{6}$$

$$Y = \ln\left(\frac{a}{T_m}\right) = -\frac{E_a}{R\cdot T_m} + C_2 \tag{7}$$

where C_1,$C_2$and C_3 are constants, T_m is the temperature at DSC-curve maximum, $\alpha = dT/dt$ is the heating rate and E_a is the activity energy.

The value of E_a is obtained from the slope of Y versus $1000/T_{\mathrm{m}}$ plots given in Fig. 4. Activation energies derived from the curves slopes are very close as it is shown in this following Table 3: These values are lesser than those for the bulk diffusion of aluminium, magnesium atoms in aluminium matrix and β (Al_2Mg_3) phase formation are in good agreement with works on Al-12% wt Mg alloy, in which the values lie between 40.70 and 80.86 kJ/mol for temperatures ranging from 200 to 320 °C [22].

The transformed fraction y, which characterizes the running rate of the reaction at a corresponding Tj temperature, is given by the formula$y = \frac{\Delta S_j}{S} = \frac{\Delta H_j}{\Delta H}$, where S is the total surface of the exothermic peak, S_j the partial surface at this temperature, ΔH the total enthalpy of the reaction and ΔH_j the partial enthalpy at this temperature. Fig. 5; shows thefractiontransformed intoa function of temperaturefor differentheating rates. The curves obtained are S-shaped curves or sigmoïdal, showing the

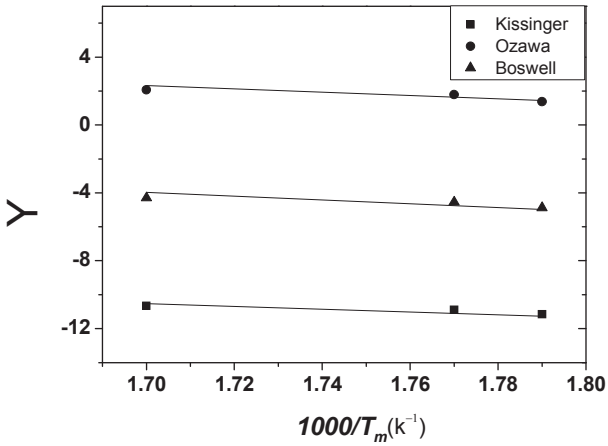

Fig. 4. $Y = f\,(10^3/T_m)$ curves of Al-7wt % Mg alloy using three different methods.

Table 3
Reports the activation energies determined by three different methods of Al-7 wt% Mg alloy, quenched and heated from 25 to 450 °C with different heating rate $\alpha = 4$, 6 and 8 °C/min.
c The Avrami exponent n with Matusita method

Methods	Kissinger	Ozawa	Boswell
Activation Energies (KJoule/mole)	46.18 ± 1.21	67.18 ± 1.02	48.45 ± 2.04

transformed fraction according to the temperature for various heating rates. It is found thatincreasing theheating rateleads toa shift of theexothermic peaksto higher temperatures. The crystallized fraction y at the constant heating rate α is related to the activation energy of crystallization E_a through the Eq. (8) [36].

$$\ln(-\ln(1-y)) = -n\ln\propto - 1.025m\frac{E_a}{RT} + Const \tag{8}$$

Fig. 6 shows the relation between $\ln(-\ln(1-y))$ and $ln\propto$ for four fixed temperatures according to the relation, Eq. (9):

$$\frac{d[\ln(-\ln(1-y))]}{d[\ln(\propto)]} = -n \tag{9}$$

The Avrami exponent, n can be determined using obtained slope of the straight line. The slope values of the four straight lines are quite similar. The slope values, n are 1.87, 1.89, 1.90 and 1.82 are measured for given temperatures of 280, 285, 290 and 295 °C, respectively. The average value of Avrami exponent, n is 1.87. For formation of (β-phase) which may correspond to a phase transformation mechanism driven by diffusion. The value of n is taken to be equal to either (m + 1) or m. The former

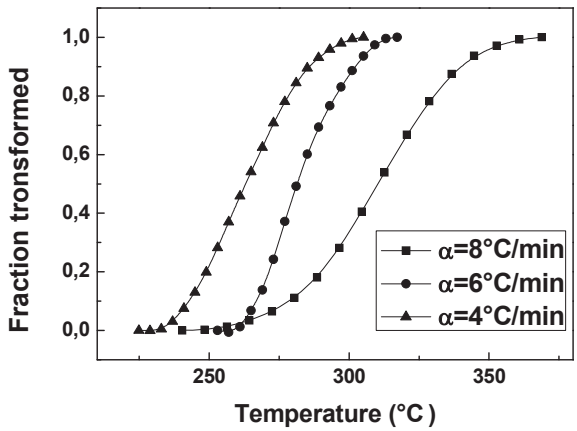

Fig. 5. The transformed fractionof Al-7 wt% Mgalloy at variousheating rates: 4, 6 and 8 °C/min.

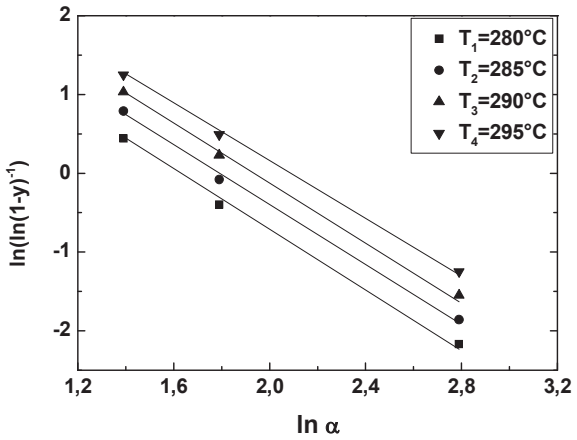

Fig. 6. Plot of the $ln(-ln(1-y))$ versus lnα at four selected temperatures.

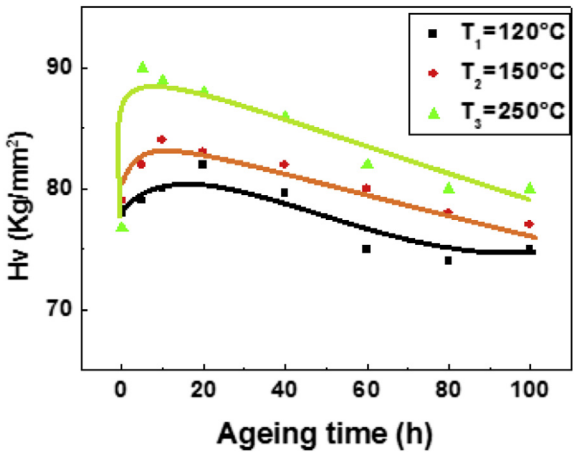

Fig. 7. Vickers microhardness variation Hv of Al-7 wt% Mg alloy, homogenized at 470 °C during one week, water quenchedand aged at 120, 150 and 250 °C.

case is taken when the nuclei formed during the heating run at a constant rate are dominant, while the later case is considered when the nuclei formed during previous heat treatment prior to thermal analysis are dominant.

d The micro hardness measurements

The micro hardness variation curves of Al-7 wt% Mg alloy during aging at 120, 150 and 250 °C is presented in Fig. 7, it was observed that maximum Vickers micro hardness corresponds to the formation of an important quantity of β-phase precipitate particles. Conversely, the hardness peaks are shifted to lower time when the isothermal holding temperature increases, i.e. when the volume fraction of discontinues precipitation was higher. The decline in hardness was thus probably associated with the β′ to β transformation and a progressive coarsening of the structure. The formation of a metastable phase (e.g. the Al(Mg) solid solution) requires that kinetics processes allow the phase to nucleate and grow more rapidly than the stable phase [37]. Considerable long-range diffusion of Al and Mg is needed to nucleate an equilibrium phase with a complex structure and a giant unit cell such as the β-Al_3Mg_2 phase [38]. The alloy becomes soft with prolonging of aging time and its mechanical properties are reduced by the appearance of equilibrium precipitate β. It has been found that a discontinuous precipitation can cause major changes in the microstructure and properties of solid alloys. Among the different discontinuous reactions and discontinuous coarsening are usually deleterious to the mechanical, physical, and chemical properties of a large number of alloys of commercial interest [39].

4. Conclusion

Water quenched and ageing at different heating rates $\alpha = 4$, 6 and 8° C/min. of Al-7% wt Mg alloy has been investigated using DSC, micro hardness measurements (Hv) and X-ray diffraction (XRD) analysis. The results can be summarized as

follows: the spectrums XRD analysis on Al-7wt%Mg samples aged for 2 h at 150 and 200 °C confirmed the presence of β phase precipitate. However, the kinetics of precipitation is very fast in Al–7%Mg alloy. The activation energy of discontinuous precipitation is calculated with three models (E_a = 53.93 kJ/mol), and the n Avrami coefficient that characterizes the transformation mechanism, controlling the discontinuous precipitation in Al-7wt%Mg alloy, is determined (n = 1.87). The maximum hardness corresponds to the formation of an important quantity of β-(Al_3Mg_2) phase.

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