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Research Article

Kinetics and Microstructure of Solid Phase Precipitation in Mg-7 wt. % Al

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Abstract

The kinetics and microstructure of the discontinuous precipitation in Mg-7 wt. % Al has been investigated at different temperatures and time, using the Differential Scanning Calorimetry (DSC), X-ray diffraction, microhardness measurement and optical microscopy. In this paper, we employed methods for calculation of the activation energy, volume fraction and mechanism of precipitation of new phase γ($Mg_{17}Al_{12}$). At 150°C accelerate relatively the diffusion process and the S- mechanism is more dominating in discontinuous precipitation.

Keywords: *Mg-Al alloy, Kinetics, Discontinuous precipitation, DSC*

1. Introduction

The decomposition of a supersaturated solid solution α_0 into a depleted matrix α and new precipitate β (T.T. Song *et al*, 2013; D. Hamana et al, 1998; H.K. Lee *et al*, 1998; H. Olia *et al*, 2012; A.M. Abd El-Khalek, 2008; M.A. Mahmoud, 2001). The earliest occurrence of decomposition was reported in 1930 (N. Ageew, 1930) including Mg-Al in most cases, discontinuous precipitation occurs simultaneously with continuous precipitation.

Most experimental (I. G. Solorzano *et al*, 1984; I. Manna et al, 1991; S. Budurov et al, 1980; W. Gust *et al*, 1979; I. Manna *et al*, 1990; W. Gust *et al*, 1975; W. Gust *et al*, 1978) and theoretical (D. Turnbull,1955; H. I. Aaronson *et al*, 1968; J. Petermann *et al*, 1968; J. W. Cahn, 1959; M. Hillert, 1972; M. Hillert, 1982; B. E. Sundquist, 1973; J. M. Shapiro *et al*, 1968) works on discontinuous precipitation have concentrated on the kinetics of transformation for one nodule, i.e. on the average lamellar spacing in this nodule and on the average velocity v of the reaction front. Duly *et al*, 1992, investigated the macroscopic kinetics of discontinuous precipitation in two Mg-8.5 wt% A1 alloy, with different initial average grain sizes at 220°C by quantitative optical metallography, hardness measurements, X-ray diffraction and other techniques. They reported that the kinetics observed can be described by Johnso~Mehl-Avrami's law, which indicates that a reaction front stops when it meets an immobile grain boundary. Moreover, the precipitation nodule nucleation probably takes place via the mechanism observed and described by Fournelle and Clark, as can be inferred from the grain size dependence of the nucleation rate. In other study in 1994 by Duly *et al*. in Mg-Al alloys, characterized the nucleation rate of discontinuous precipitation as a function of temperature, initial grain size and solute content, at high temperatures (T/> 220°C) all precipitation nodules nucleate via Fournelle and Clark's mechanism, whereas at lower temperatures (T=140°C), the mechanisms identified by Tu and Turnbull or Purdy and Lange is also active (Duly *et al.* 1994).

However, by conventional TEM (morphology) and STEM, the growth of the precipitation nodule is not a steady state process, the mobility of the reaction front would be about 15 times smaller between β and α' than between α and α' (Duly *et al.* 1994). The effect of the temperature on the mechanism of precipitation in Al-8wt. % Mg alloy was investigated by Bensaada *et al.* 2001. In this alloy, the predeformation with aging at 160 °C reveals the structure of Widmannsttaten, with a growth in needles forming and leading to a continuous precipitation. Continuous recipitation is favored at high and low temperatures, while discontinuous precipitation dominates at intermediate temperatures. High temperatures accelerate relatively the diffusion process and the mechanism S is more dominating in discontinuous precipitation. Starink *et al.* 2004, investigate with differential scanning calorimetry (DSC) measurements of the precipitation in an Al–Mg–Mn alloy microalloyed with Cu. The precipitation reactions in an Al–1.3Mg–0.4Mn and an Al–1.3Mg–0.4Mn–0.07Cu alloy in which very small amounts of precipitate, less than 0.3 at.%, are expected to form. The sequence of precipitation processes formed during aging in Al–Mg–Si alloys has been identified by using X-ray diffraction, differential scanning calorimetry and microhardness measurements (N. Afify *et al.* 2008).

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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) (D. Bradai *et al*, 2002; M. Popovi et al, (2008). The precipitation kinetics can be obtained from DSC thermograms. The precipitation kinetics can be investigated for individual reactions (L.C. Doan *et al*, 200). Their methods were applied to characterize the precipitation kinetics in Mg-Al alloys. Bradai *et al.* 200, observed a new mode of dissolution reaction in Mg-10% wt. Al, we have found the reaction starts preferably and occurs faster at the original locations of the grain boundaries. The aim of this study is to determine the kinetics, activation energy and precipitation mode of $Mg_{17}Al_{12}$-phases in binary Mg–7 wt. % Al alloy during no-isothermal annealing, using the optical microscopy (OM), X-ray diffraction (XRD), differential dilatometer, and differential scanning calorimeter (DSC).

2. Materials and Experimental Procedures

The Mg-7 wt. % Al alloy (containing Si, Fe, and Cu at percentages of 0.011, 0.02, and 0.019 respectively) used in this investigation was supplied by Cathay Advanced Materials Limited. The alloy was homogenized in vacuum at 450°C for one week and quenched in water to obtain a supersaturated solid solution α_0. The aging conditions are simultaneously obtained from the literature and from the equilibrium diagram of the alloy Mg-Al system (C. Brubaker *et al*, 2004). Disks (3 mm diameter and 3 mm thickness) were prepared for DSC experiments. DSC experiments were performed using a NETZSCH 200PC DSC analyzer between (25 - 450 °C) at heating rates of 2, 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 metallographic observation was performed using Axiovert 40 MAT Optical Microscopy, after etching in the solution of Keller (07 ml of HF, 09 ml of hydrochloric acid, 20 ml of nitric acid and 85 ml of distilled water). The Vickers microhardness was mmeasured by a device Tukon 2500 type.

3. Results and discussion

3.1 DSC experiments at different heating rates

In this part of study, we present the results of differential scanning calorimetry (DSC) in non-isothermal conditions of Mg-7 wt.% Al previously homogenized and quenched (Fig. 1a); and $\gamma(Mg_{17}Al_{12})$ phase growth rate (Fig. 1b) at different heating rates (α = 2, 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 (Z. Boumerzoug *et al*, 2009; M. Fatmi *et al*, 2011). 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.

On the other hand, the integration of the peak in (Fig. 2) with temperature enables us to plot the evolution of transformed fraction Y with temperature for the different heating rates.

3.2 Determination of activation energies

The activation energy of discontinuous precipitation (E_a) for the investigated of the Mg-7wt.% Al alloy has been estimated using the following methods. Kissinger and Ozawa methods (H.E. Kissinger, 1956; T. Ozawa, 1992). The modified Johnson-Mehl-Avrami equation concerning the kinetics of phase transformation involving nucleation and growth under isothermal conditions is generally used to analyze the crystallization process. For applicability of this equation to non-isothermal crystallization process, several conditions will have to be satisfied (D.W. Handerson, 1979). To check the validity of interpretation of the crystallization data obtained presently in terms of the JMA equation which relates the dependence of the precipitation peak temperature T_m on the heating rate (v) by the following equations:

$$Y = \ln\left(\frac{v}{T_m^2}\right) = -\frac{\boldsymbol{E_a}}{R\boldsymbol{T_m}} + C^{te}$$

Kissinger equation

$$Y = \ln v = -\frac{E_a}{RT_m} + C^{te}$$

JMA equation

$$Y = \ln v = -1.0518\frac{E_a}{RT_m} + C^{te}$$

Ozawa equation

Where, E_a: activation energy ($J.mol^{-1}$), R the universal gas constant (8.314 J/mol K).

Figure 3, represents the evolution of ln(v) versus $1000/T_m$ for JMA method, so simply calculate the slope of these curve to determine the activation energy as it is report on the following table:

Méthode	**(JMA)**	**Kissinger**	**Ozawa**
Energie d'activation ($KJ.mol^{-1}$)	73.76± 0.92	64.57±0.88	70.69±0.79

3.2 XRD study

The X-ray diffraction is the most powerful way to highlight the formation of intermetallic phases and GP zones in various alloys based on aluminum, because they are very sensitive to any disturbance of the periodicity of the crystal lattice. A further study by X-ray diffraction was done on the Mg-7 wt.% Al alloy, previously homogenized one week at 450°C, quenched and aged at 150 °C (Fig. 4) and 200 ° C (Fig. 5), the study of spectra shows the appearance of $\gamma(Mg_{17}Al_{12})$ phase after ageing 20h, 18h at 150°C and 200°C respectively. With extension of the ageing time, the intensity becomes higher with increasing maintain time and this leads to a greater amount of precipitate phase.

The diffraction peaks of the supersaturated solid solution α_0, allowed us to calculate the lattice parameter corresponding to the supersaturated solution of Mg-7wt.%

Al alloy, using the largest diffraction angle 2θ = 99 ° corresponding to the line (114) α_0: a = 3.181 Å and (c = 5.208 Å). This value shows a concordance with Mg-Al alloys. (T.S. Swanson *et al*, 1951; K. Vanna Yang *et al*, 2012; L. Jacques *et al*, 2012).

3.3 Microhardness study

The Vickers microhardness variations versus time of artificial ageing of the Mg-7 wt.% Al alloy, naturally aged for 60 days (after quenched), then artificially aged at 150°C and 200°C, are represents in Fig.6. Initial values of the hardness of the alloy are higher than those of the alloy not was naturally aged (Fig.7). All samples aged at 150°C and 200°C have confirmed our observations by optical microscopy and XRD. The microhardness starts to increase from the value obtained at the quenched condition until a maximum corresponding to duration of 20h then decreases; this corresponds to the formation of the equilibrium γ($Mg_{17}Al_{12}$) phase (J. Hanawalt *et al*, 1938). The increase in temperature accelerates relative to the diffusion process obtained, so better hardening. Beyond a 20h, the hardness tends to stabilize, which means that the formation of the equilibrium $Mg_{17}Al_{12}$ phase is almost complete. This means that precipitation discontinued does not cause hardening of the alloy. This result is in good agreement with the results found by other researchers (W. Gust *et al*, 1979; D. Turnbull, 1955).

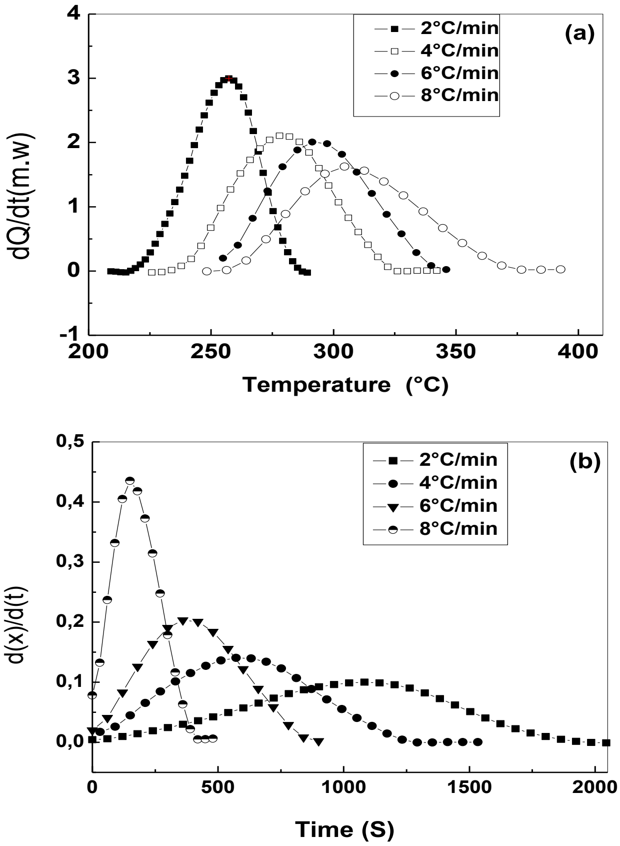

Fig. 1: Typical DSC curves (a) and the growth rate of γ ($Mg_{17}Al_{12}$) phase (b) for the Mg-7 wt. % Al quenched, at different heating rates.

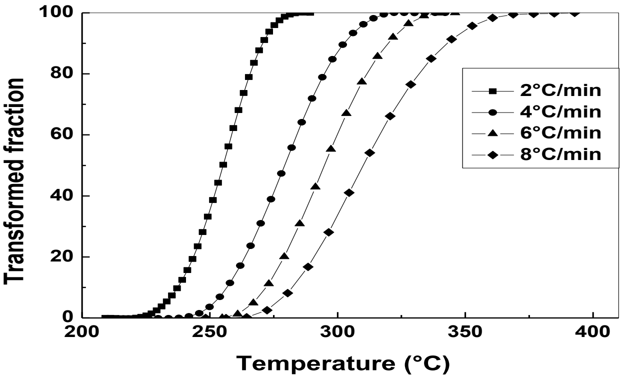

Fig. 2: Transformed fraction Y as a function of the temperature at various heating rate of Mg-7wt.% Al alloy quenched

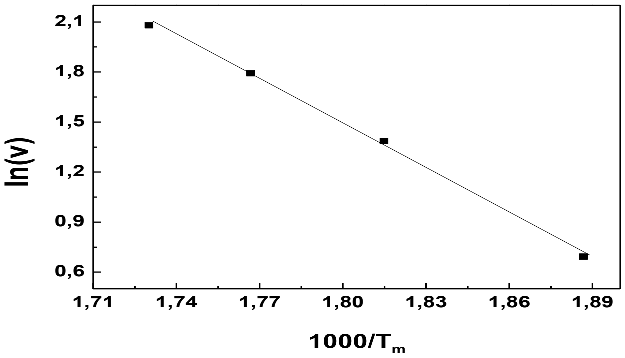

Fig. 3: ln(v) = f (1000/T_m) curve plotted by the JMA method of Mg-7 wt.% Al alloy homogenized at 450 ° C for one week and quenched in water.

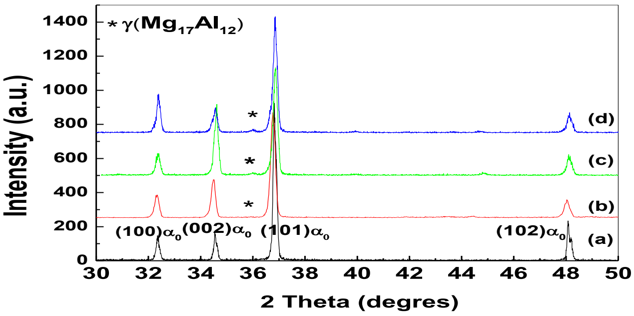

Fig. 4: XRD spectra of the Mg-7 wt.% Al alloy, homogenized at 450 ° C for one week, quenched (a), aged at 150 ° C for 20 h (b), 50h (c) and 100h (d).

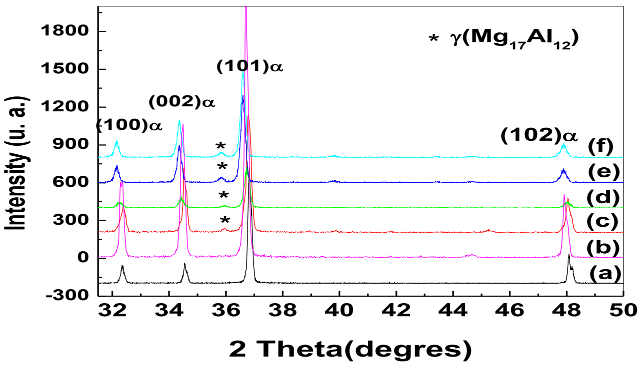

Fig. 5: XRD spectra of the Mg-7 wt.% Al alloy, homogenized at 450 ° C for one week, quenched (a), aged at 200°C for 4h (b), 18h (c), 50h (d), 100h (e) and 150 (f).

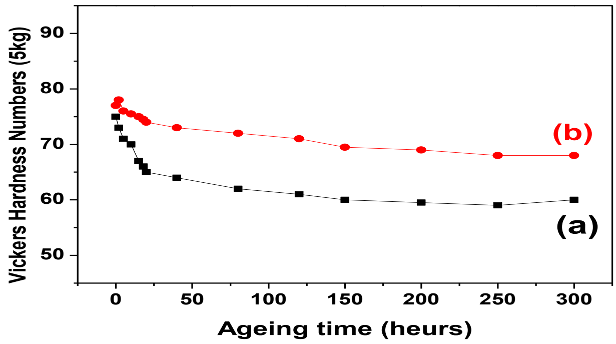

Fig. 6: Microhardness (HV) evolution of Mg-7wt. %Al alloy, homogenized 450°C for 2 week and quenched in water, naturel aged for 60 days and aged at 150 °C (a) and 200 °C (b).

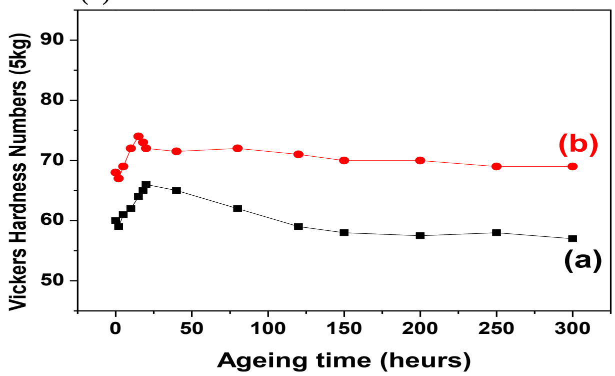

Fig. 7: Microhardness (HV) evolution of Mg-7wt. %Al alloy, homogenized 450°C for 2 week and quenched in water, aged at 150 °C (a) and 200 °C (b).

3.4 Microstructural study

In order to make in evidence the effect of the ageing temperature on the mechanisms of precipitation in Mg-7wt. % Al alloy quenched. We have chosen two temperatures of ageing (150 and 200°C) favorable to this type of transformation. We have confirmed the effect of ageing temperature on kinetic and mode of precipitation on this alloy. Fig. 8 presents an optical micrograph of the Mg-7 wt.% Al alloy after the first ageing at 150°C for 15h. The dark areas represent colonies of the lamellar precipitates growing from the original location of a grain boundary (OGB) (Fig. 8b,c). This growth is accompanied by a lateral expansion, so that the two domains finally come into contact. At 150°C, the same way the S-mechanism morphology is more dominating described by Fournelle and Clark (R.A. Fournelle *et al*, 1972) (Fig. 8b,c).

However, the ageing at the temperature of 200 °C is only favorable to the discontinuous precipitation and with the stable phase $\gamma(Mg_{17}Al_{12})$ which is characterized by an interesting aspect as shown in Fig. 9. The particles of this phase are developed in the form of needles in the grain boundaries and triple points (Fig. 9b). This mechanism mode was found on some alloys as in Al-30 wt.% Zn [34], Al-8 wt.% Mg (S. Bensaada *et al*, 2011) and Mg-10wt.% Al (D. Bradai *et al*, 2002).

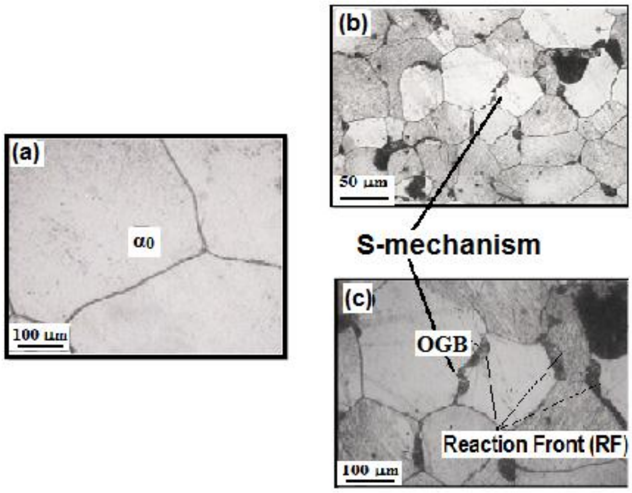

Fig. 8. Optical micrograph of a Mg-7 wt.% Al alloy quenched (a), aged at 150°C for 20h (a,b). *RF is the reaction front of the discontinuous precipitation and OGB is the original location of a grain boundary*.

It is known that the driving force for discontinuous precipitation is an extensive parameter related to several thermodynamic and kinetic functions. Thus, external parameters capable of influencing the driving force (e.g. stress, strain, alloying addition, etc.) may have significant effects on the precipitate nucleation and morphology of discontinuous precipitation (A. Pawlowski *et al*, 1989).

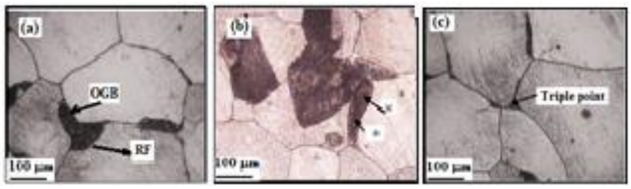

Fig. 9. Optical micrograph of a Mg-7 wt.% Al alloy quenched and aged at 200°C for 18h

4. Summary and Conclusion

The whole results presented in this work reflect in particular the effect of the temperature on the kinetics and mode of precipitation in alloy Mg-7wt.Al. The calculations of the activation energy measured by non-isothermal measurements of precipitation E_c revealed that the results obtained by Kissinger, Ozawa and JMA models, are in good agreement. The spectra of X-ray diffraction clearly show the influence of temperature on the quantity of precipitate γ-$(Mg_{17}Al_{12})$ phase, the latter increases with temperature and aging time. At 150°C, the precipitation of $\gamma(Mg_{17}Al_{12})$ phase most frequently occurring form of lamellar structure. It grows from an original grain boundary by intergranular diffusion according to the S- mechanism. At 200°C, the particles of this phase are developed in the form of needles in the grain boundaries and triple points.

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