

## Analysis Methods for the Determination of Energies Activation and the Study of the Precipitation Reactions in Al-12% Weight Mg Alloys

Hanene Bensouyad and Djamel Hamana

Laboratory of Ceramics, Faculty of Sciences Exacts, University Mentouri, Constantine, Algeria

**Abstract:** The kinetics of transformation (precipitation and dissolution of the precipitates) is always allied to the concepts of energies activation and about the order of reaction. The interest of this study is justified by the existence of a significant number of methods of isoconversionnelle analysis, more or less sophisticated like that of Kissinger-Akahira-Sunose (KAS), Ozawa-Flyn-Wall (OFW) and that of Boswell, which makes difficult the choice of a method particular. The goal of the use of these models of analysis would be to find a description proportioned of the development of the reaction according to time and temperature. In this research, we have interested by the influence of the heating rates on the non isothermal transformations in Al-12% Mg. For this the samples of this alloys have heated with different rates ( $V = 0.5, 1, 2, 3, 4, 5, 6, 7^{\circ}\text{C min}^{-1}$ ) from room temperature until  $530^{\circ}\text{C}$  using the differential scanning calorimetry (DSC) and we will calculate the energy activation of the precipitated phases  $\beta$  and  $\beta'$  by various isoconversionnelles methods.

**Key words:** Precipitation, calorimetry, energy activation, order of reaction n, Al-Mg, isoconversionnelles methods

### INTRODUCTION

Differential scanning calorimetry (DSC) have been applied extensively to the analysis of light metals, especially Al based alloys. Differential scanning calorimetry is used for analysis of solid state reactions, such as precipitation, homogenisation, devitrification and recrystallisation and solid-liquid reactions, such as incipient melting and solidification, are studied by differential scanning calorimetry. In producing repeatable calorimetry data on Al alloys, sample preparation, reproducibility and baseline drift need to be considered in detail. Calorimetry can be used effectively to study the different solid state reactions and solid-liquid reactions that occur during the main processing steps of Al based alloys solidification, homogenisation, precipitation). Quantitative analysis of the kinetics of reactions is assessed through reviewing the interrelation between activation energy analysis methods, equivalent time approaches, impingement parameter approaches, mean field models for precipitation, the Johnson-Mehl-Avrami-Kolmogorov model, as well as novel models which have not yet found application in calorimetry. Differential scanning calorimetry (DSC) represents a rapid qualitative and quantitative means for precipitate characterization in aluminium alloys, this technique can improve understanding of the thermodynamics and kinetics of the precipitation processes. In the present research, a

qualitative as well as quantitative interpretation has been obtained of the precipitates developed in supersaturated Al-Mg solid solutions.

In this research, we were interested to study the kinetics of anisothermal precipitation of the phase's  $\beta$  and  $\beta'$  in alloy Al-12% weight. Mg where each one of these phases can be detected according to the heat treatment applied and selected measurement technique.

### MATERIALS AND METHODS

In this research, we used the analysis calorimetric differential (DSC) (Apparatus Setaram 131), which makes it possible to measure the releases and absorptions of flow of energy of a material during a thermal cycle which consists a heating from  $20^{\circ}\text{C}$  at  $430^{\circ}\text{C}$  with various rates ( $V = 0.5, 1, 2, 3, 4, 5, 6, 7^{\circ}\text{C min}^{-1}$ ) followed by a maintenance of 1 sec at the temperature of homogenisation and a cooling until the ambient one with the same speeds.

The sequence of precipitation in alloys of the system Al-Mg is Kissinger (1957):



where,

- $\alpha \text{ (SSS)}$  = The supersaturated solid solution.
- $\beta'$  and  $\beta''$  = The metastable phases of transition.
- $\beta \text{ (Al}_3\text{Mg}_2)$  = The equilibrium cycle.

**Kinetic theory:** The theory of this research is based on the equation of kinetics:

$$\frac{d\alpha}{dt} = f(\alpha) \times k(T) \quad (1)$$

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where,

$E_a$  : The energy activation of the reaction.

$K_0$  : The exponential pre factor.

$R$  : The gases constant.

To calculate  $E_{a_p}$ , we will use the 3 following isoconversionnelles methods.

**Method of Kissinger-Akahira-Sunose (KAS):** This method rests on the assumption according to which, during the rise in temperature, the reaction passes by a maximum before decreasing (Kissinger, 1957), it based to the following relation:

$$\ln\left(\frac{T_p^2}{V}\right) = \frac{E_a}{RT_p} + c \quad (3)$$

where,

$$c = \ln\left(\frac{E_a}{Rk_0}\right) \quad (4)$$

**Method of Ozawa, Flynn and Wall (OFW):** To calculate the energy activation, we used this isoconversionnelle method of Ozawa (1970) and Flynn *et al.* (1966), which very usual and is based on the change of the temperature  $T_p$  of the exothermic and/or endothermic peak according to the rate heating  $V$  and which is defined by the following relation:

$$\ln V = -1.0516 \frac{E_{act}}{RT_p} + const \quad (5)$$

**Method of Boswell:** This method is defined by the following relation (Boswell, 1980):

$$\ln \frac{V}{T_p} = -\frac{E_{act}}{RT_p} + const \quad (6)$$

**Determination of the order of reaction (N) by the Matusita method's:** Starting from the traditional equation of Johnson-Mell-Avrami-Kolmogorov (JMAK), Matusita and Sakka (1980) found that the equation of kinetics becomes then:

$$\ln\left[\ln(1-a)^{-1}\right] = -n \cdot \ln V + Const \quad (7)$$

where, the transformed fraction  $\alpha$  is given by the relation:

$$\alpha = \frac{S_T}{S} \quad (8)$$

where,

$S$  : The total surface of the peaks.

$S_T$  : The surface partial of the peaks.

## RESULTS AND DISCUSSION

The DSC curves obtained during the heating with various rates of the homogenized and quenched samples (Fig. 1) show two endothermic peaks and an exothermic peak which present 3 effects, respectively related on dissolution of zones G.P. the formation and dissolution of the phases  $\beta'$  and  $\beta$  result already observed by other authors. Because we now during the formation of a phase, the variation of the flux are exothermic, during dissolution the variation is endothermic and the surface of the peak represents an enthalpy of formation (or of dissolution). Each phase has an enthalpy and a temperature of formation which depends on the scanning rate.

The first endothermic peak appears in the interval (40-95°C) and the exothermic peak in the interval (190-350°C) directly followed endothermic peak in the temperature range (350-423°C) the increase of the heating rate leads to the increase in the amplitude of the various peaks, with a shift of the thermo-grams towards the high temperatures.

The curves of DSC obtained for the various heating rates present three effects related to dissolution of zones G.P. the formation and the dissolution of the phases  $\beta'$  and  $\beta$ .

We observe from Fig. 2-4 that the values of the energy activation obtained by the various isoconversionnelles methods are not very different and for the order of reaction  $n$  (Fig. 5), we obtain  $n = 1.33$ , this value close to 1.5 indicates that the mechanism of precipitation occurs everywhere through alloy and that the precipitates grow in all the directions, in more this value of  $n$  suggests that this type of precipitation believes on the existing pre germ So, we can resume all this values of the energy activation in the Table 1.

For the formation of the phases  $\beta'$  and  $\beta$  we have found that the  $E_{act}$  obtained is of (74.60±0.90) KJ mole<sup>-1</sup>, who is close to that of Starink (2004) (78 kJ mol<sup>-1</sup>), Luiggi and Betancourt (2003) (70 kJ mol<sup>-1</sup>), Nozato and Ishihara (1980) (77 kJ mol<sup>-1</sup>); but a little distant from that of van Mourik *et al.* (1989) (90 kJ mol<sup>-1</sup>) and for

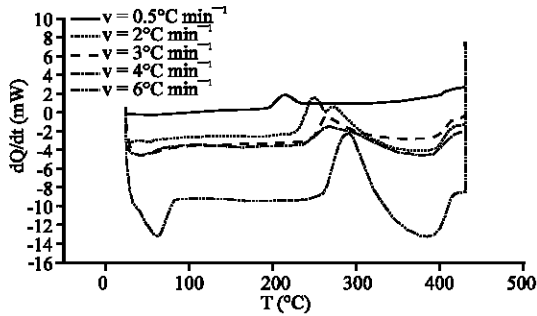


Fig. 1: Curves DSC of alloy Al-12% Mg homogenized, quenched and heated with various speeds

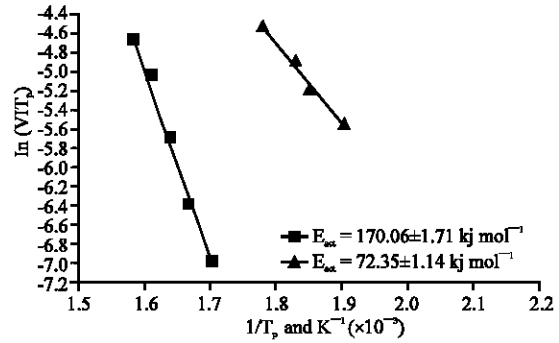


Fig. 4: Curves of Boswell due to: formation of  $\beta'$  and  $\beta$  and dissolution of  $\beta'$

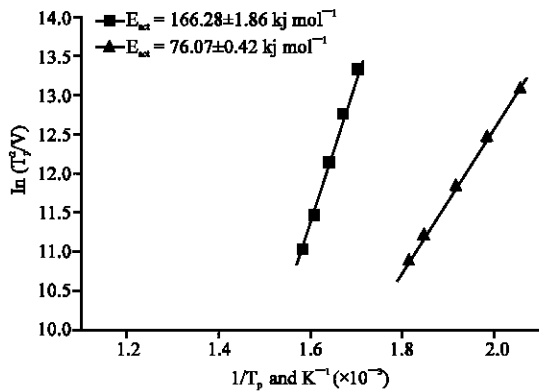


Fig. 2: Curves of Kissinger due to: formation of  $\beta'$  and  $\beta$  and dissolution of  $\beta'$  and  $\beta$

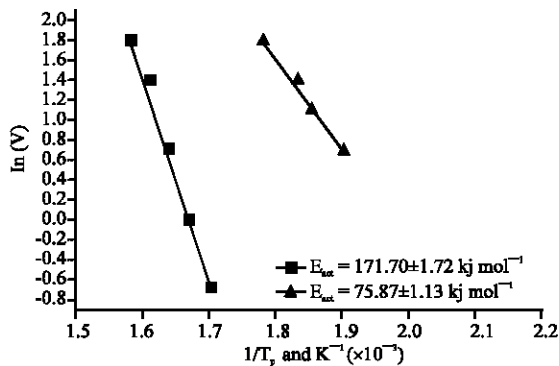


Fig. 3: Curves of Ozawa, Flynn and Wall due to: formation of  $\beta'$  and  $\beta$  and dissolution of  $\beta'$

the order  $n = 1.33$ , this value close to 1.5 indicates that the mechanism of precipitation occurs everywhere, through alloy and that the precipitates grow in all the directions, in more this value of  $n$  suggests that this type of precipitation believes on the existing pre germ.

For the dissolution of the phases  $\beta'$  and  $\beta$  it was found that the  $E_a$  obtained for this process is of

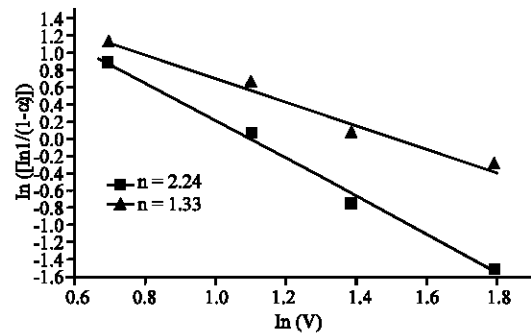


Fig. 5: Order of reaction  $n$  due to: formation of  $\beta'$  and  $\beta$  and dissolution of  $\beta'$

Table 1: Energy activation and the order of reaction  $n$  for different process

Process	Energy activation ( $\text{Kj mol}^{-1}$ )		
	Kissinger	Ozawa, Flynn and Wall (OFW)	Boswell
Formation of $\beta'$ and $\beta$	76.07±0.42	75.87±1.13	72.35±1.14
Dissolution of $\beta'$ and $\beta$	166.28±1.86	171.70±1.72	170.06±1.71
Order of reaction $n$			
Formation of $\beta'$ and $\beta$	1.33		
Dissolution of $\beta'$ and $\beta$	2.24		

169.12±1.76  $\text{Kj mol}^{-1}$ , this energy is consumed for the dissociation of the large precipitates and the migration of the atoms of aqueous solution in the matrix and for the order  $n$  of reaction is equal to 2.27, this value suggests that the speed of dissociation is constant and also affirm that magnesium diffuses and dissolves through all the matrix.

### CONCLUSION

- The study of the kinetics of precipitation made it possible to illustrate the following conclusions.
- Peaks of precipitation and dissolution of the phases ( $\beta'$  and  $\beta$ ) are shifted towards the high temperatures with an increase in their amplitude.

- The increase in the width of the peaks with the increase of the heating rate testifies to the increase of the quantity of precipitates formed during the anisotherme annealing.
- The shift of the peaks is due to the fact that precipitation takes seat with difficulty and this shift can be explained by delays of the formation and dissolution of the phases.
- For the formation of the phases  $\beta'$  and  $\beta$ , we have found that the  $E_{act}$  obtained is of  $74.60 \pm 0.90 \text{ KJ mol}^{-1}$  who is close to that of Starink (2004) ( $78 \text{ kJ mol}^{-1}$ ), Luiggi and Betancourt (2003) ( $70 \text{ kJ mol}^{-1}$ ), Nozato and Ishihara (1980) ( $77 \text{ kJ mol}^{-1}$ ); but a little distant from that of van Mourik *et al.* (1989) ( $90 \text{ kJ mol}^{-1}$ ) and for the order  $n = 1.33$ , this value close to 1.5 indicates that the mechanism of precipitation occurs everywhere, through alloy and that the precipitates grow in all the directions, in more this value of  $n$  suggests that this type of precipitation believes on the existing pre germ.
- For the dissolution of the phases  $\beta'$  and  $\beta$  it was found that the  $E_a$  obtained for this process is of  $169.12 \pm 1.76 \text{ KJ mol}^{-1}$ ; this energy is consumed for the dissociation of the large precipitates and the migration of the atoms of aqueous solution in the matrix and for the order  $n$  of reaction is equal to 2.27; this value suggests that the speed of dissociation is constant and also affirm that magnesium diffuses and dissolves through all the matrix.

In parallel, it seems that the use of the energy activation connects for the estimate of the parameters is indeed very interesting.

## REFERENCES

- Boswell, P.G., 1980. On the calculation of activation energies using a modified Kissinger method. *J. Thermal Anal.*, 18: 353-358.
- Flynn, J., L. Wall and A. Quick, 1966. Direct method for the determination of activation energy from thermogravimetric data. *J. Polym. Sci.*, 4: 323-328.
- Kissinger, H.E., 1957. Reaction Kinetics in Differential Thermal Analysis. *J. Analyt. Chem.*, 29: 1702-1706.
- Luiggi, N. and M. Betancourt, 2003. On the non-isothermal precipitation of the  $\alpha$  and  $\beta$  phases in Al-12.6 mass% Mg alloys using dilatometric techniques *Thermal Anal. Calorimetr.*, 74: 883-894.
- Matusita, K. and S. Sakka, 1980. Kinetic study of crystallization of glass by differential thermal analysis. *J. Non-Crystalline Solids*, 38/39: 741-746.
- Nozato, R. and S. Ishihara, 1980. Calorimetric study of precipitation process in Al-Mg alloys. *J. Trans. Japan Inst. Metals*, 21: 580-588.
- Ozawa, T., 1970. Kinetic analysis of derivative curves in thermal analysis. *J. Therm. Anal.*, 2: 301-324.
- Starink, M.J., 2004. The analysis of Al-based alloys by calorimetry: Quantitative analysis of reactions and reaction kinetics. *Int. Mat. Rev.*, 49: 191-226.
- Van Mourik, P. Maaswinkel, T.H. Keijser and E.J. Mittemeijer, 1989. Precipitation in liquid-quenched Al-Mg alloys: A study using X-ray diffraction line shift and line broadening. *J. Mat. Sci.*, 24: 3779-3786.