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Analysis Methods for the Determination of Energies Activation and the Study of the Precipitation Reactions in Al-4,5% Weight Cu Alloys

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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-4,5% Cu. For this the samples of this alloys have heated with different rates (V = 0.5, 1, 2, 3, 4, 5, 6, 7°C min^{-1}) from room temperature until 520°C using the Differential Scanning Calorimetry (DSC) and we will calculate the energy activation of the precipitated phases θ and θ' by various isoconversionelles methods.

Key words: Precipitation, calorimetry, energy activation, order of reaction n, Al-Cu, isoconversionelles 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, devitrivication 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 (Kissinger, 1957; Ozawa, 1970; Flynn and Wall, 1966; Boswell, 1980), 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 aluminum 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-Cu solid solutions.

In this study, we were interested to study the kinetics of anisothermal precipitation of the phase's θ and θ' in alloy Al-4,5 % weight. Cu where each 1 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 to 520°C with various rates (v = 0.5, 1, 2, 3, 4, 5, 6, 7°C min^{-1}) followed by a holding of 5-10 min at this temperature and a cooling until room temperature, with the same rates.

The sequence of precipitation in alloys of the system Al-Cu is (Starink, 2004):

Supersaturated solid solution (S.S.S)
→ Zones G.P. → Phase θ'' → Phase θ'
→ the equilibrium cycle θ (Al_2Cu)

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Where, θ' and θ'' is the metastable phases of transition.

Kinetic theory: The theory of this research is based on the Eq. of kinetics:

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

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

Where,

E_a : The energy activation of the reaction.

k_0 : The exponential pre factor and r the gases constant.

To calculate E_a, we will use the following isoconversionnelle method:

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:

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

Where,

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

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:

$$\ln\left[\ln(1-\alpha)^{-1}\right] = -n.\ln V + \text{Const} \tag{7}$$

Where, the transformed fraction α is given by the relation:

$$\alpha = {}^{S_T}\!/_{S} \tag{8}$$

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 2 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 θ' and θ 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 (93-241°C) a peak exothermic split appears in the interval (241-378°C) with a maximum located around 349 ° C, which is due to the precipitation of two phases (θ' and θ) this peak followed directly from a peak endothermic split in the interval of temperature (378-514°C) with 2 minimum located around 405 and 483°C, represents the dissolution of these 2 phases θ' and θ. 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 3 effects related to dissolution of zones G.P., the formation and the dissolution of the phases θ' and θ.

Figure 2 and 3 show curves obtained by the kissenger analyzes for the determination of the energy activation of the peaks of the formation and the dissolution of β' and β already shown in Fig. 1 and from that we have found for the formation of the phases θ' and θ we have found that the E_{act} obtained is of

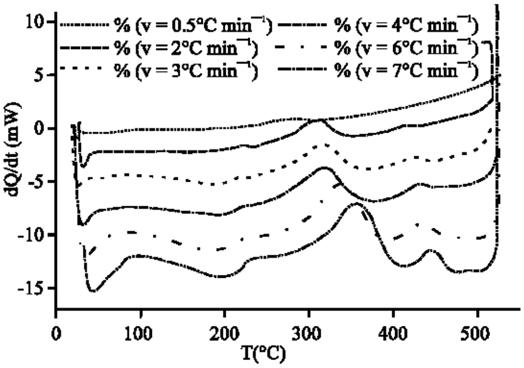

Fig. 1: Curves DSC of alloy Al-4.5% Cu homogenized, quenched and heated with various rates

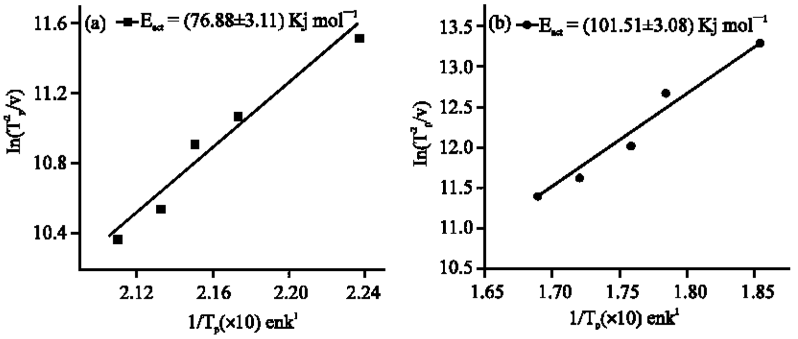

Fig. 2: Curves of Kissinger due to: (a) dissolution of G.P. zones and (b) formation of θ' and θ

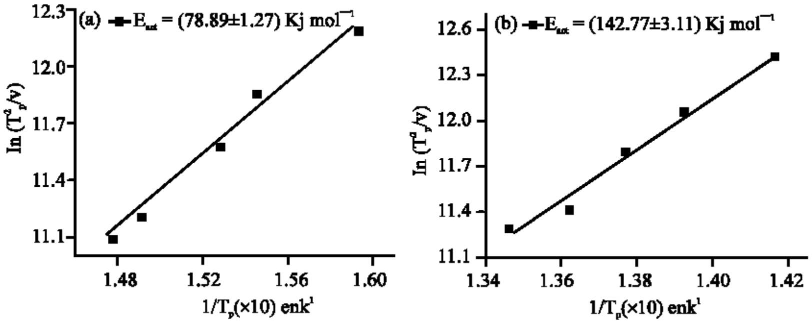

Fig. 3: Curves of Kissinger due to: (a) dissolution of θ' and (b) dissolution of θ

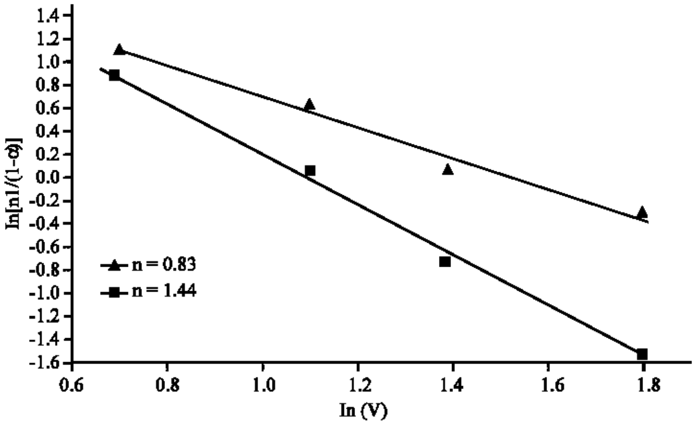

Fig. 4: Order of reaction n due to: dissolution of G.P. zones and formation of θ' and θ

(101.51±3.08) Kj mole^{-1} and for the dissolution of the phases θ' and θ it was found that the E_a obtained for this process is of (78.89±1.27) Kj mole^{-1} for θ' and (142.77±3.11) Kj mol^{-1} for θ ; this energy is consumed for the dissociation of the large precipitates and the migration of the atoms of aqueous solution in the matrix; but for the order of reaction n Fig. 4 and 5 we have for the formation of the phases θ' and θ n = 1.44; 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; and for theirs dissolution the order n of reaction is equal to 1.73 for θ and 0.43 for θ'; this values suggests that the speed of dissociation is constant and also affirm that copper diffuses and dissolves through all the matrix.

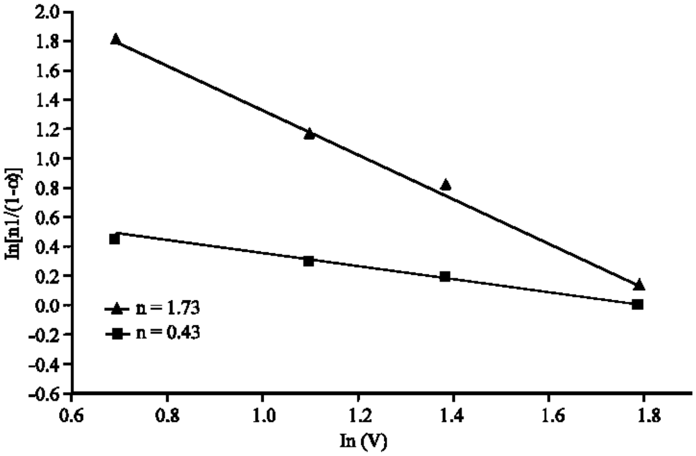

Fig. 5: Order of reaction n due to: dissolution of θ and dissolution of θ'

CONCLUSION

The study of the kinetics of precipitation made it possible to illustrate the following conclusions:

- Peaks of precipitation and dissolution of the phases (θ' and θ) 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 θ' and θ we have found that the E_{act} obtained is of (101.51±3.08) Kj $mole^{-1}$ and for the order n =1.44 ; 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 B' and B it was found that the E_a obtained for this process is of (78.89±1.27) Kj mol^{-1} for θ' and (142.77±3.11) Kj mol^{-1} for θ ; 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 1,73 for θ and 0,43 for θ'; this values suggests that the speed of dissociation is constant and also affirm that copper 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.

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