

ON THE NON-ISOTHERMAL PRECIPITATION OF THE β' AND β PHASES IN Al-12.6 MASS% Mg ALLOYS USING DILATOMETRIC TECHNIQUES

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Abstract

The non-isothermal kinetics of precipitation of an Al-12.6 mass% Mg alloy for different heating rates were studied using thermal expansion techniques. The structural changes associated with the precipitation of the β' and β phases were identified. The conversion degree of each phase was associated with the area under the derivative curve of the thermal expansion with respect to temperature. Using the Kissinger relation and an iso-conversional method we calculated the apparent activation energies associated with formation of the precipitated phases. We report an increasing dependence of the activation energy on the conversion degree, the values obtained being within the range reported in the literature.

Keywords: Al–Mg alloy, iso-conversional method, non-isothermal kinetics, precipitation

Introduction

The study of binary alloys, by assessing the structural changes induced by particular thermal treatments, is a topic of interest because it allows us to determine the particular conditions needed to control and improve the physical and metallurgical properties of the alloys. In the particular case of magnesium in aluminum, recent papers by Boucheur *et al.* [1] and by Starink and Zahra [2, 3], using DSC and optical and transmission electron microscopy, confirm observations by other authors [1–3] and establish the following precipitation sequence:

Solid solution $\alpha \Rightarrow$ GP Zones (δ') \Rightarrow GP Zones (δ'') or $\beta'' \Rightarrow \beta'$ phase $\Rightarrow \beta$ phase

Each one of these phases can be detected according to the thermal treatment used, the aging conditions, and the measuring technique selected. Dilatometry is widely utilized to ascertain critical points of transformation, but its value in identify-

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ing important details of the kinetics and mechanisms of phase transformations is limited [4, 5]. In the present work we use dilatometry to obtain the apparent activation energy of the phase transition of an Al 12.6 mass% Mg alloy using non-isothermal expansion and its derivative with respect to temperature at different heating rates.

Experimental

Standard samples of Al–Mg binary alloys from Aluminium Pechiney, France, containing (12.6 ± 0.4) mass% Mg and impurities of Fe (10 ppm) and Si (40 ppm) were arranged in $26 \times 4 \times 4$ mm³ parallelepipeds and homogenized at $500 \pm 5^\circ\text{C}$ during 15 h in an argon atmosphere. The Al–Mg samples were quenched in water at 0°C and kept at the temperature of liquid nitrogen until ready for dilatometric study. The thermal expansion measurements were performed with a NETZSCH-402E electronic dilatometer with an LVDT-type sensor and automatic data acquisition through an IEEE-488 interface card. The temperature was recorded by means of an S-type thermocouple and the system controlled automatically through a desk computer.

Theoretical aspects

Kinetic theory

The theoretical foundations of the present work are based on the kinetic equation:

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

where ψ is a function dependent on the conversion degree or transformed fraction α of the studied phase, the temperature T , and the elapsed time t at that T . k is known as the rate constant and f is the kinetic or conversion function. While isothermal treatments require the temperature to remain fixed, non-isothermal treatments are carried out varying the temperature, variation which establishes a relation T - t between the temperature and the time of transformation that may define the ψ slope. The experimental kinetic curve contains information of ψ in an integrated form, and there is no basis to separate ψ in K and G functions, as done in the term at right in Eq. (1). However, a frequently accepted approximation considers the reaction constant and the conversion function as independent functions [6], which allows for an easy solution to that equation under isothermal conditions. This generates, obviously, an ambiguity of the kinetic description. However, some physical conditions must be met to guarantee the validity of that approximation. If the temperature varies in linear fashion with the time, a constant heating rate is obtained; and if the transformation process is homogeneous in temperature, mathematical equations applicable to non-isothermal processes can also be deduced from isothermal equations [7]. Any other T - t path renders the tracking of the kinetics difficult. In this case, the separation of the ψ function in Eq. (1) into independent k and f functions is no longer valid. This is evident in the work of Vyazovkin *et al.* [8] who verified that comparing model fitting results for

isothermal and non-isothermal experiments is practically meaningless. More consistent kinetic results seem to be generated by iso-conversional methods [8, 9]; however, any consistency is subject to the strict control of the experimental conditions and to a heating rate sufficiently low to prevent an abrupt change of phases.

Equation (1) in integral form is written:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t k(T, t) dt \quad (2)$$

Exclusive dependence of f on α in the first integral of Eq. (2) produces the different reaction models referenced in the literature [8–10]. The rate constant k , for an activation energy E_a , follows an Arrhenius relation,

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where A and E_a are the Arrhenius parameters characteristic of the reaction to be studied. Obviously different reaction models generate different Arrhenius parameters.

Considering the heating rate β as a constant, we solve the integral (2),

$$I = \int k(T) dt = -\frac{AE_a}{\beta R} \int_{X_0}^X \frac{\exp(-X)}{X^2} \quad (4)$$

where we use the change of variable $X = E_a / RT$, and assuming that for $T = T_0 = 0$ K, $X_0 = \infty$, we write

$$I = \frac{AE_a}{\beta R} \left(\frac{\exp(-X)}{X} - \int_X^\infty \frac{\exp(-X)}{X} dX \right) \quad (5)$$

The remaining integral in Eq. (5), called the exponential or thermal integral, does not have an analytic solution; and numerous studies have been attempted to evaluate it in the most precise fashion [11, 12]. It is common in the literature to use a series expansion to solve Eq. (5),

$$I = \frac{AE_a}{\beta R} \frac{\exp(-X)}{X^2} \sum_{L=0}^{\infty} (-1)^L \frac{(L+1)!}{X^L} \quad (6)$$

Once the solution to the exponential integral is known, either in numeric or approximate form, we still require a reaction model that defines $f(\alpha)$ in Eq. (2) to relate the Arrhenius parameters with the transformed fraction. Again, in that case, we will end up having as many different pairs of Arrhenius parameters as reaction models are used. A criterion often used to select the reaction model is to compare the experimental data with the theoretical fraction α deduced from each model. The best fit will indicate the applicability of the models, but that is not a guarantee for a solid physical support. In this sense Johnson–Mehl–Avrami-type models with free parameters [10, 13] would be the best.

The dilemma that arises once the reaction model is chosen is overcome by resorting to iso-conversional techniques, which, for a fixed α value assume $f(\alpha)$ invariability. Special attention must be paid to multi-value f functions or multi-phase transformations to avoid ambiguity in the interpretation of results.

In a recent work Luiggi [14] includes the consideration of $T=T_0 \neq 0$ K as the upper limit of the integral (5), obtaining results which permit us to propose the following generic, isoconversional equation:

$$\ln\left(\frac{T^N}{\beta}\right) = \frac{E_a}{RT} + C \quad (7)$$

where the exponent N corrects the error in Eq. (6) introduced by the consideration of $T_0=0$. Note that Eq. (7) with $N=0$ and $N=2$ reproduces the iso-conversional equations reported in the literature [14]. The particular case of $N=2$ and $T=T_{\max}$ generates the Kissinger Eq. [15].

Although Eq. (7) permits us to determine how the apparent activation energy of the structural transformation process varies, it is necessary to know the pre-exponential factor A (Eq. (3)) and the kinetic function f so that Eq. (1) can be fully defined. E_a , A and f , also called 'kinetic triplet', have been rigorously studied in the ICTAC Kinetics Project [16–20], where the benefits and deficiencies of the kinetic theory for the analysis of isothermal and non-isothermal data were presented.

Once E_a of Eq. (7) is known, we can deduce the other two parameters of the kinetic triplet using Eqs (1) and (3).

$$A_\alpha f(\alpha) = \beta_i \left(\frac{d\alpha}{dT}\right)_i \exp\left(\frac{E_a}{RT_{\alpha,i}}\right) \quad (8)$$

where the subscript i in β and T is introduced to differentiate the kinetics at different heating rates. All the terms on the right side of Eq. (8) are known. Notice that the effect of N , appearing in Eq. (7), is incorporated to the calculation by means of E_a . The definitive pre-exponential factor A is obtained when we incorporate details of the reaction model; at that moment $f(\alpha)$ is no longer arbitrary.

Characterization by expansion curves

Thermal expansion has been used as a trusted technique to determine critical points of transformation, but it is seldom used as a characterization technique. Luiggi *et al.* [4, 5] propose to analyze the curves of isothermal expansion in binary and commercial alloys by following the conventional approach of associating the structural changes with the changes of isothermal expansion during precipitation.

$$dl(t,T) = \alpha(t,T)dl(\infty,T) + (1-\alpha(t,T))dl(0,T) \quad (9)$$

where $dl(0,T)$ is the dilatation of the material immediately after quenching and $dl(\infty,T)$ the dilatation at the end of the precipitation. Taking into account that the thermal expansion of the lattice, caused by a change in the equilibrium volume as the

temperature is changed, is induced by the anharmonicity of the crystal potential, i.e., higher-order terms in the expansion of the total energy of the system as a function of the positions of all of the atoms, we can separate the volume change of the alloy into two parts: the first, an anharmonic portion corresponding to the volume change due to the expansion of the alloy in the absence of the structural transformation, and the second, associated with the transformation itself [5]. This effect is rendered evident when we apply the derivative with respect to temperature of the thermal expansion, thus generating a constant value when dilatation is attained by a rise in temperature. On the other hand, the temperature derivative of the length change associated with structural changes generates a spectrum with minimum and maximum characteristics of the transformation process. The proportionality between the derivatives with respect to temperature of the length change of the sample and that of the extent of conversion permits us to obtain the $\alpha(T)$ curves by means of the evaluation of the area under the derivative curves.

Results

The homogenized samples were placed inside the thermal chamber of the dilatometer and the temperature was raised at the constant rate of 2, 3, 4, 5, 10, 20 and 25 K min⁻¹ from 25 up to 600°C. Figure 1 shows the relative length change vs. temperature for different heating rates. The expansion, by exclusively thermal effects in each case, increases steadily with the temperature and, depending on the heating rate, a slight departure from the monotonic growth appears in the neighborhood of 100°C. This small separation from the constant growth is properly observed in the derivative curves. Then, between 215 and 420°C, a broad lobe appears. Both anomalous behaviors are associated with structural transformations. The broad lobe appears earlier when the heating rate is lower. This fact can be associated with the diffusive nature of the transformation, which depends on both the temperature and the time that the sample re-

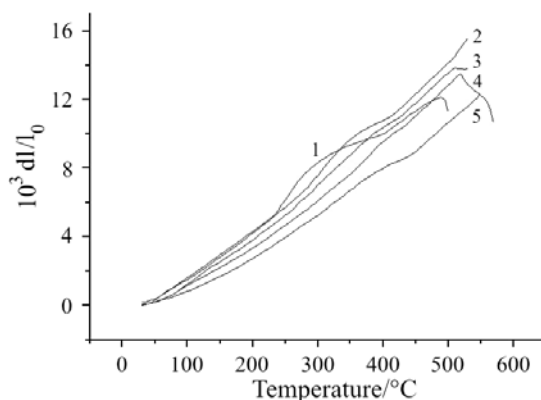


Fig. 1 Relative length change as a function of the temperature for different heating rates. 1 – 2 K min⁻¹, 2 – 5 K min⁻¹, 3 – 10 K min⁻¹, 4 – 20 K min⁻¹ and 5 – 25 K min⁻¹

mains at that temperature. This can be explained as follows: Let the two extreme limits of the heating rate be $\beta=0$ and $\beta=\infty$; when $\beta=0$, T is a constant and the sample remains at the same temperature during the whole time; when $\beta=\infty$, the process occurs very quickly, the structural transformation is very difficult to appreciate, and the sample remains at each temperature for an infinitely short time. A finite β is an intermediate occurrence between those extremes. When the heating rate is raised, the sample remains at a particular temperature for a shorter time than when the heating rate is lower. For that reason, the same structural transformation appears later when β is higher. Some characteristics of these transformations can be deduced directly from Fig. 1; however, better precision on the position of minima and maxima is obtained when we apply the derivative with respect to temperature of the relative length change of the sample.

In Fig. 2 we plot the derivative of the relative expansion vs. temperature for heating rates of 2, 3, 5 and 20 K min⁻¹. These curves confirm a weak transformation in the neighborhood of 100°C, and two maxima associated with the broad lobe. The complete correspondence of these curves with Fig. 2b of the work by Boucheur *et al.* [1], performed under the same experimental conditions but for a different Mg concentration, allows us to associate the first peak with dissolution of the GP zones, the second with the precipitation of the β' phase, and the third with the precipitation of the β phase. This sequence is also reported in the work of Starink and Zhara [2, 3]. Note that the precipitation of the β' phase corresponds to an expansion of the sample and it generates a positive peak in the derivative curves, while the precipitation of the β phase corresponds to a contraction that generates an inverted peak in the derivative.

The similarity of results obtained with DSC and dilatometry allows us to assume that there is a relationship between the area under the derivative with respect to temperature and the transformed fraction. The proportionality between the change of differential expansion during structural transformation and the precipitated fraction associated with that transformation confirms the validity of Eq. (9).

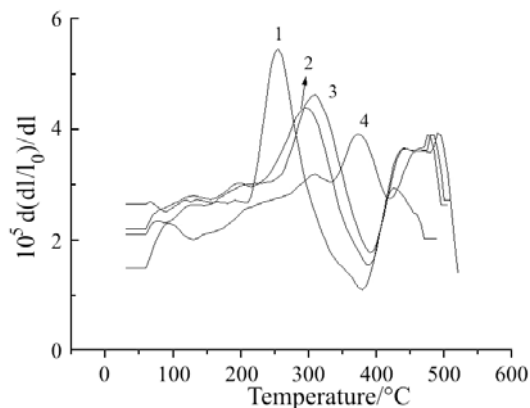


Fig. 2 Derivative of the relative length change with respect to temperature for different heating rates. 1 – 2 K min⁻¹, 2 – 3 K min⁻¹, 3 – 5 K min⁻¹ and 4 – 20 K min⁻¹

Figures 3 and 4 show the conversion degrees (or precipitated fractions) of phases β' and β , respectively, as functions of temperature, obtained from Fig. 2 at different heating rates. These curves indicate that when the heating rate is lower, the structural transformation occurs at lower temperatures. Note that, for the same value of the heating rate the behavior of α is different for the β' and β phases, suggestive perhaps of different precipitation mechanisms.

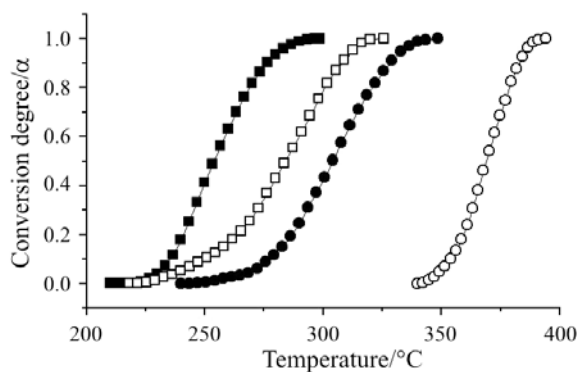


Fig. 3 The conversion degree α as a function of the temperature for the β' phase. $\blacksquare - 2 \text{ K min}^{-1}$, $\square - 3 \text{ K min}^{-1}$, $\bullet - 5 \text{ K min}^{-1}$ and $\circ - 20 \text{ K min}^{-1}$

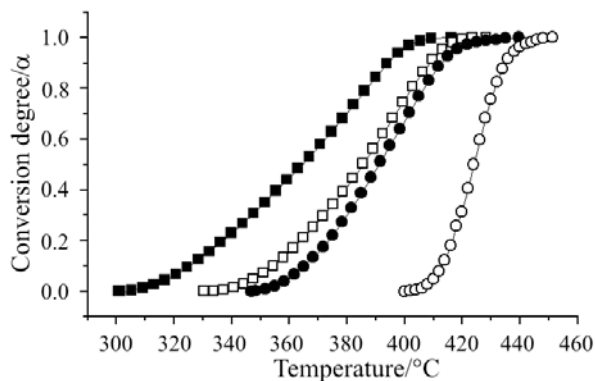


Fig. 4 The conversion degree α as a function of the temperature for the β phase. $\blacksquare - 2 \text{ K min}^{-1}$, $\square - 3 \text{ K min}^{-1}$, $\bullet - 5 \text{ K min}^{-1}$ and $\circ - 20 \text{ K min}^{-1}$

From Figs 3 and 4, by fixing α , we obtain for each different heating rate the temperatures at which the same conversion degree for each phase is reached.

In Fig. 5 we show the variation of the natural logarithm of T^N/β vs. the inverse temperature for the β' phase, for different conversion degrees. The parameter N is fixed at 0 and 2. A linear behavior is shown in both cases and by means of Eq. (7) we can determine the apparent activation energy of the process. A similar behavior, not shown, is obtained for the β phase, but the alignment of points for low heating rates in Eq. (7) is slightly different from that of the high heating rates in the same equation. In Figs 6

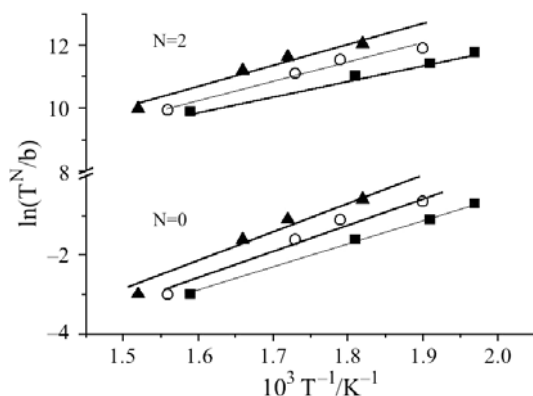


Fig. 5 Natural logarithm of T^N/b vs. the inverse temperature for the β' phase, for $N=0$ and $N=2$. ■ – $\alpha=0.1$, ○ – $\alpha=0.5$ and ▲ – $\alpha=0.9$

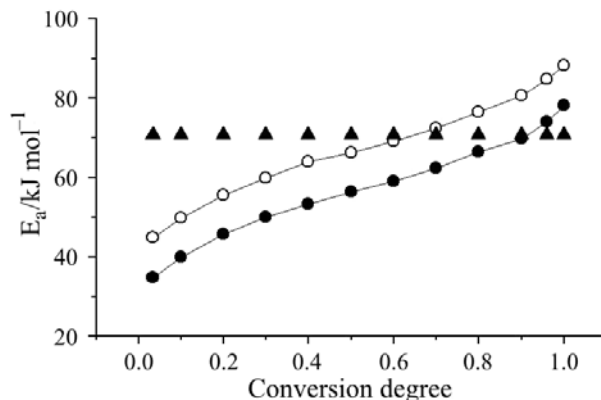


Fig. 6 Apparent activation energy as a function of the extent of conversion for the β' phase, using Eq. (7). ○ – $N=0$, ● – $N=2$ and ▲ – using the Kissinger relation

and 7 we plot the apparent activation energy vs. the conversion degree for phases β' and β , respectively. We also show the activation energy obtained using the Kissinger relation. One observes that the activation energies of both phases increase with the conversion degree, the E_a values obtained with $N=0$ being larger than those obtained with $N=2$. In general form, as shown in [14], N can vary from negative to positive values, its effect on the activation energy being such that when N is lower, the energy increases. The variation of E_a for the β' phase ranges between 30 and 90 kJ mol^{-1} with an uncertainty of 5 kJ mol^{-1} , while the Kissinger relation predicts an E_a value of $(70 \pm 8) \text{ kJ mol}^{-1}$. These values are in agreement with those obtained by the iso-conversional method when $0.4 < \alpha < 0.8$ for $N=0$ and $0.7 < \alpha < 1$ for $N=2$, and with those reported by Starink *et al.* [3], Nozato *et al.* [21], Mourik *et al.* [22] and Luiggi *et al.* [5] using the Johnson–Mehl–Avrami reaction model. With regards to the β phase, we found different variation ranges for E_a for both low and high heating rates,

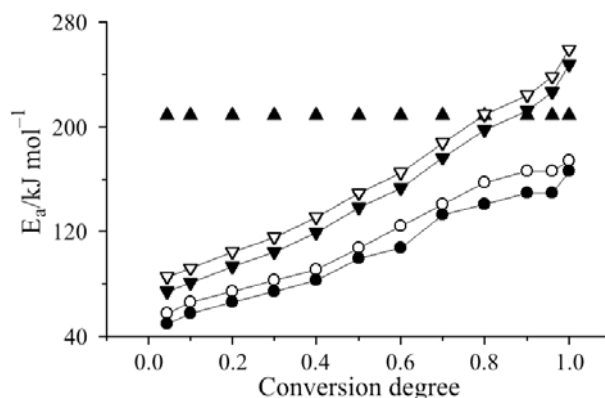


Fig. 7 Apparent activation energy as a function of the extent of conversion for the β phase, using Eq. (7). For low heating rate $\circ - N=0$, $\bullet - N=2$, for high heating rate $\nabla - N=0$, $\blacktriangledown - N=2$ and \blacktriangle – using the Kissinger relation

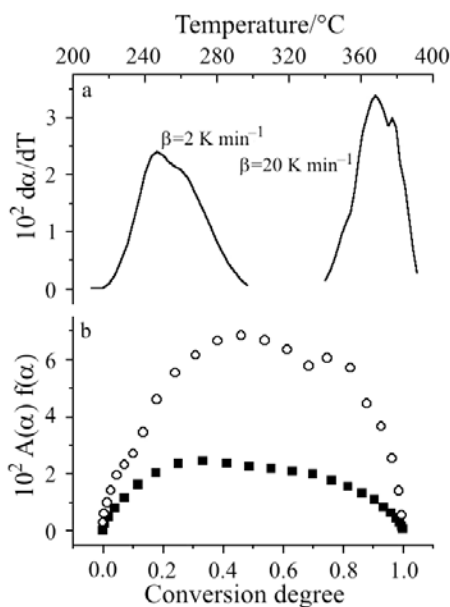


Fig. 8 a – Derivative of the conversion degree of the phase β' respect the temperature for heating rates of 2 and 20 K min^{-1} . b – Product of the pre-factor $A(\alpha)$ by the kinetic function $f(\alpha)$ vs. the conversion degree α , correspondent at the β' phase for $N=2$ and heating rates $\blacksquare - 2$ and $\circ - 20 \text{ K min}^{-1}$

shown in Fig. 7. The effect of the N parameter is similar to that observed for the β' phase, i.e. E_a values for $N=2$ are lower than those obtained for $N=0$. For low heating rates (2, 3, 4 and 5 K min^{-1}) E_a varies between 45 and 150 kJ mol^{-1} . For high heating rates (5, 10, 20 and 25 K min^{-1}) E_a varies between 100 and 320 kJ mol^{-1} . In both cases an uncertainty of up to 10 kJ mol^{-1} is detected. This discrepancy can be explained by

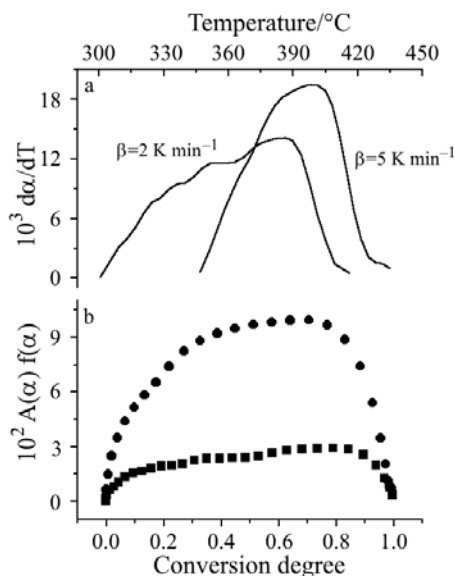


Fig. 9 a – Derivative of the conversion degree of the phase β respect the temperature for heating rates of 2 and 5 K min^{-1} . b – Product of the pre-factor $A(\alpha)$ by the kinetic function $f(\alpha)$ vs. the conversion degree α , correspondent at the β phase for $N=2$. The apparent activation energy used is one shown in the Fig. 7 for low heating rate. ■ – $\beta=2 \text{ K min}^{-1}$ and ○ – $\beta=20 \text{ K min}^{-1}$

the rapidity with which the precipitation at elevated temperatures occurs, as it is very difficult for the dilatometric techniques to discriminate the curves at different heating rates. The E_a value deduced from the Kissinger relation, including each peak, is $(210 \pm 20) \text{ kJ mol}^{-1}$. This value is larger than those obtained for the β' phase and reaffirms the fact reported in [3] that the enthalpies of formation of the β phase are larger than those reported for the β' phase. As for the mechanism of precipitation of the β' and β phases it is difficult to conjecture upon it, since complementary information is necessary, and that is only attainable by use of diverse experimental techniques.

To supplement our results within the demands established by the kinetic theory of reaction, we evaluated Eq. (8) in order to estimate the parameters that complete the kinetic triplet. Part A of Fig. 8 shows the derivative of the conversion degree of phase β' with respect to temperature for heating rates of 2 and 20 K min^{-1} . Although these curves are defined at different ranges of temperature, their extent corresponds to values of α between 0 and 1. Here lies the importance of this derivative to define the functional dependence of the kinetic parameters $A(\alpha)$ and $f(\alpha)$. Part B of the same figure shows the product $A(\alpha)f(\alpha)$ as a function of α for heating rates of 2 and 20 K min^{-1} , respectively, and $N=2$. Because of the presentation, the curve corresponding to $\beta=2 \text{ K min}^{-1}$ is multiplied by 5. In Fig. 9 we repeat this calculation for phase β . In Part A of this figure, derivatives with respect to temperature are carried out for heating rates of 2 and 5 K min^{-1} , while Part B is evaluated for $N=2$, using the apparent activation energy values shown in Fig. 7 for low heating rates. Again, in this

figure, the preponderant character of the derivative on the functional form of the product $A(\alpha)f(\alpha)$ is ratified. Finally, once the apparent activation energy is well known, the consideration of a kinetic model would allow us to know in details the values of the pre-exponential factor A , thus solving the problem of the kinetic triplet.

Conclusions

We have studied the kinetics of precipitation of an Al-12.6 mass% Mg binary alloy by non-isothermal dilatometry and conclude the following:

1) Dilatometry represents a powerful tool to determine kinetic parameters of the precipitation process. The non-isothermal process permits us to determine the temperature range where structural transformations occur. The derivative with respect to temperature pertaining to those changes allows us to define precise minimum and maximum temperatures, the area of the derivative curves being associated with the extent of conversion.

2) The effect of increasing the heating rate is to move the structural transformation towards higher temperatures, indicative that a diffusive process is occurring.

3) The derivative with respect to temperature of the relative length change permits the identification of three different structural transformations: The first, near 100°C, corresponds to the dissolution of GP zones. The second, between 215 and 300°C, corresponds to the precipitation of the β' phase. The third, between 320 and 420°C, corresponds to the precipitation of the β phase. These observations are in concordance with those by Boucheur *et al.* [1].

4) An iso-conversional study makes it possible to evaluate the apparent activation energies of the transformations of the β' and β phases, which increase with the conversion degree α . The energy range obtained for the transformation of the β' phase is between 30 and 90 kJ mol⁻¹, while that obtained for the transformation of the β phase is 100 kJ mol⁻¹ < E_a < 320 kJ mol⁻¹, for high heating rates, and between 45 kJ mol⁻¹ < E_a < 150 kJ mol⁻¹ for low heating rates. The E_a values obtained from the Kissinger relation are 70 and 210 kJ mol⁻¹ for the transformation of β' and β phases, respectively. Our results are in agreement with those reported in the literature.

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