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Comparative study of formation and transformation of transition phases in Al–12 wt.% Mg alloy

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Abstract

The use of various experimental techniques as differential dilatometry, differential scanning calorimetry, optical and transmission electron microscopy, internal friction, electrical resistance and microhardness measurements, shows their importance and their complementarity in the study of the ageing process in Al–12 wt.% Mg alloy. Indeed, their sensitivity to various precipitation stages is different and can give more information to describe the evolution of the structure, the nature and the morphology of the precipitated phases particles and the transition between them, which is not, yet, well established. The obtained dilatometric curves show numerous effects which have been discussed. During ageing of a supersaturated solid solution Al–12 wt.% Mg it seems that β' and β phases do not grow at the expense of GP zones (and/or β'') and β', respectively.

Keywords: Al–Mg alloys; Precipitation; Phase transformation; Internal friction; Hardness

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1. Introduction

The large number of metastable precipitated phases that can occur in age-hardenable commercial aluminium alloys and the wide variety of ageing treatments used can lead to complex microstructural conditions. These complexities allow flexibility in designing microstructures for particular combinations of properties, but they increase the difficulty of totally describing the nature and size distributions of the precipitate present phases. A good description of the microstructure is essential for the understanding of the structure–property relationships.

If a supersaturated solid solution of an Al–12 wt.% Mg alloy is aged at temperatures below 400°C, the precipitation sequence experimentally observed is [1–5]:

$$\text{supersaturated } \alpha \text{ solid solution} \rightarrow \text{GP zones} \rightarrow \beta'' \rightarrow \beta' \rightarrow \beta$$

In the lowest temperature range, the first phase to be formed is β'' just after the appearance of GP zones in the matrix [6]. Then, it is the β' and β particles that would appear in the matrix and on the grain boundaries. Differential scanning calorimetry (DSC), generally, reveals two overlapping endothermic events in the range 50–100°C which are due to the GP zones and β'' phase dissolution [4–6].

As GP zones and β'' phase (Al_3Mg, $L1_2$), (called GP zones 2 or ordered GP zones) [5–7], are coherent and appear at approximately the same temperature interval [1,3–7], it is difficult to separate them. Thus, our attention will be confined, in this work, to the non-coherent stable phase β (Al_3Mg_2, complex fcc), the semicoherent intermediate β' (Al_3Mg_2, hexagonal) and the coherent GP zones.

In a recent work [4], it has been shown that the most important hardening is caused by the formation of the intermediate particles β' which precipitate at temperatures above the reversion temperature of the GP zones. Some authors think that the β' particles nucleation occurs on structural defects as dislocations and vacancy voids/loops [3,4,8]. When the amount of these defects which facilitate the nucleation of β' decreases, a direct formation of β (the equilibrium phase) is observed. However, the mechanism of β' and β particles transformation or dissolution had not

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been, sufficiently, studied. On the other hand, insufficient work has been published about this process [5–11]. However, Starink and Zahra [5] affirm that there is no evidence of nucleation of β′ precipitate on the structure defects. They studied the precipitation of the β′ and β phases in Al–16 at.% Mg by DSC and TEM and showed that there is no direct transformation from β″ to β′, and that β′ precipitates do not form on defects, although, an abundant presence of vacancy type defects (mostly dislocation loops) were observed.

Generally, the β′ phase is formed firstly, the β one appears only in the later stages of ageing when the Mg depletion of the matrix is nearly completed [9–11] and the grain-boundary precipitates can be represented by metastable β′ particles but, more frequently, by the stable β phase [12]. The aim of this work is to study the structural evolution with ageing time and temperature, during the ageing of Al–12 wt.% Mg alloy, using different complementary experimental techniques mainly dilatometric analysis, and try to explain the mechanism of phases transformation.

2. Experimental

An Al–Mg alloy containing 12 wt.% Mg was prepared from 99.99 wt.% pure Al and Mg. Samples were homogenised at 430°C for 17 h and quenched in iced water. X-ray diffraction and metallographic analysis have shown that all magnesium goes into the solid solution and remains there immediately after quenching; no second phase could be detected.

Samples for calorimetric measurements were in a disk shape, 3 mm in diameter and 1.5 mm in thickness. The calorimetric measurements were performed with a Metler TA 4000 DSC controlled by a computer. A protective atmosphere of pure argon was used.

Samples for dilatometry measurements were in a parallelepiped shape of $25\times5\times5$ mm^3. The dilatometry measurements were performed with an Adamel Lhomargy DI 24 differential dilatometer controlled by a computer, under a protective atmosphere of pure argon.

For internal friction measurements (using an automatic inverted torsional pendulum at a frequency of 60 Hz), samples were cylinders of 3.5 mm in diameter and 26 mm in length.

A four-point technique was used for electric resistance measurements. The resistance specimens were in a cylindrical shape of 0.2 mm in diameter and 25 mm in length.

After different heat treatments, samples were prepared for transmission electronic microscopy (TEM) examination. After grinding to a thickness of about 0.10–0.15 mm, 3-mm diameter, disks were cut by sparking and thinned by double-jet electropolishing in a perchloric acid–methanol solution (volume ratio 1:4) at −30°C and a voltage of 12–18 V. The TEM analysis was performed with a Jeol 200CX at 200 kV.

A D8 Advance Brucker Diffractometer has been used to record the X-ray diffraction spectra and to measure the lattice parameters.

3. Results

3.1. Results of the DSC analysis

During DSC scanning, the exothermic peaks are due to the heat evolution associated with precipitate formation, and the endothermic ones are due to enthalpy change associated to the dissolution of precipitates into the matrix.

The starting state of the sample before DSC scanning, has been chosen in such manner that it results from a heat treatment applied to the sample to form a well-determined phase, according to the literature and our experimental data. This starting state can be the appearance of the GP zones during ageing from room temperature until 100°C: the β′ phase from 100 to 200°C; and the β phase from 200°C to higher temperatures [4]. The evolution of each phase (its coarsening, dissolution or transformation into an other phase) is then followed during the continuous heating in the DSC. The quenching state, as starting state of a sample, will serve as reference.

DSC curves obtained during the heating from 20 to 430°C at a rate of 2°C/min for four samples of Al–12 wt.% Mg homogenised 17 h at 430°C, quenched (Fig. 1a) and aged 15 days at 25°C (Fig. 1b), 50 h at 50°C (Fig. 1c)

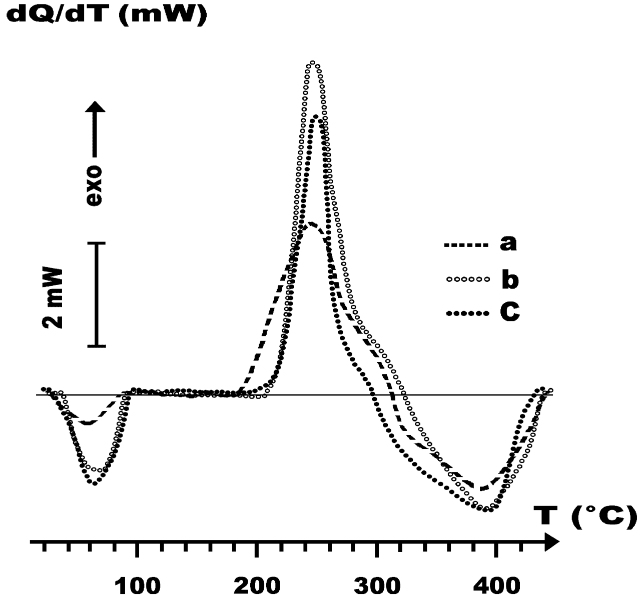

Fig. 1. DSC scanning during heating at a rate of 2°C/min for Al–12 wt.% Mg alloy homogenised 17 h at 430°C: (a) quenched and aged, (b) 15 days at 25°C and (c) 50 h at 50°C.

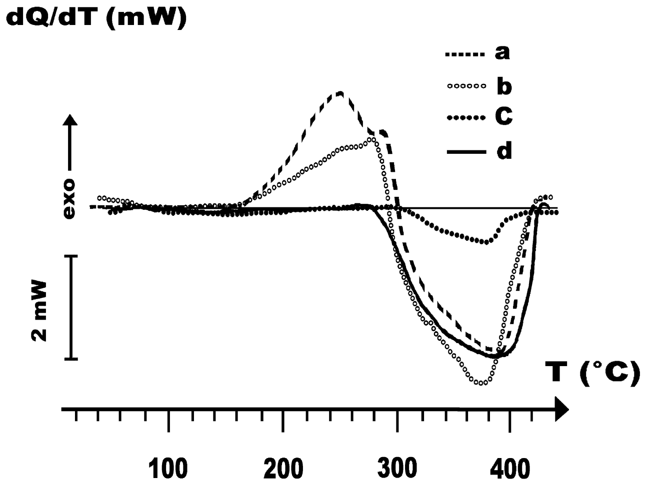

Fig. 2. DSC scanning during heating at a rate of 2°C/min for Al–12 wt.% Mg alloy homogenised 17 h at 430°C, quenched and aged: (a) 30 h at 100°C, (b) 24 h at 150°C, (c) 24 h at 200°C, (d) 7 h at 250°C and (e) 8 h at 300°C.

and 30 h at 100°C (Fig. 2a), present practically the same number and the same shape of peaks: two endothermic peaks in two intervals of temperature, 50–100 and 300–420°C, respectively, and a third exothermic peak in the range 200–300°C.

The first endothermic peak is probably due to the dissolution of GP zones formed just after quenching and during the ageing at 25 and at 50°C. The amplitude of this peak is more important in the case of the ageing at 50°C. It means that the quantity of these zones increases with the temperature and the time of ageing (at least until 50°C). It is very difficult to differentiate the dissolution of GP zones from that of the β″, from these first endothermic peaks. The exothermic peak is complex (one peak overlaps an other), it is certainly due to the precipitation of two phases (in principle β′ and β). Finally, the second endothermic peak (which follows immediately the exothermic peak) represents, usually, the dissolution of the same phases β′ and β. The second endothermic peak (of dissolution) comes just after the exothermic one (of precipitation). It means that precipitated phases (β′ and β) begin to dissolve from 300°C. On the other hand, the first endothermic peak is not followed by any heat effect (it stops at 100°C and the following peak begins at 200°C). It means that GP zones are dissolved before the appearance of β′ and β phases and, therefore, are not transformed into these two phases or do not directly contribute to their formation, as observed by Starink and Zahra [5].

The DSC curves obtained under the same conditions as previously described, for four other samples homogenised 17 h at 430°C, quenched and aged 24 h at 150°C (Fig. 2b), 24 h at 200°C (Fig. 2c), 7 h at 250°C (Fig. 2d) and 8 h at 300°C (Fig. 2e), are different from the ones in Figs. 1a–c and 2a. This difference consists in the absence of the first endothermic peak (due to the dissolution of GP zones) for all samples, and the exothermic peak lack for samples, sufficiently, aged at 250 and 300°C.

During the ageing of 1 day (24 h) at 150°C, one notices the appearance of two peaks, an exothermic and an endothermic one. The exothermic peak, which spreads from 180 to 300°C, is split, indicating the precipitation of the two phases β′ and β (Fig. 2), while the amplitude of the endothermic peak in the temperature interval (300–420°C), which represents the dissolution of precipitated particles, is more important because of the great quantity of the β′ particles, formed during the ageing before the DSC test, in addition to those formed during the heating (i.e. during the exothermic peak). On the other hand, the exothermic peak decreases considerably (Fig. 2b) before disappearing completely (Fig. 2c,d), which suggests that the nucleation and the growth of the β particles is completed during the ageing for 7 h at 250°C and 8 h at 300°C. The consecutive endothermic peak is due to their dissolution (Fig. 2c,d).

It can be deduced from these results that GP zones do not, directly, take part in the precipitation of β′ or β phases because they are dissolved before the appearance of these two phases (no effect is observed between their endothermic peak of dissolution and the first exothermic peak of precipitation). Some results of this study are similar to those observed by Starink and Zahra [5].

For a better understanding of these phenomena, we are going to proceed to dilatometric tests and to compare their results with those of DSC.

3.2. Results of the dilatometric analysis

This method is a way of investigation, which is used to follow changes of the sample length during a heating cycle, as a function of temperature or time. As the dilatation coefficient depends upon the phase composition of the alloy, the dilatometry can give information about the microstructural evolution and the phase transformations of aged alloys.

To compare the structural evolution during dilatometric tests, the same heating and cooling rate, as used in the DSC tests, is performed (2°C/min). The thermic cycle consists of heating up to 430–450°C, followed by an isothermal hold of 5–10 min at this temperature and a cooling to room temperature. Dilatometry curves of the complete cycle and the derivative curve are presented in Figs. 3 and 4. During isothermal ageing at 430°C and cooling from 430 to 20°C, no interesting dilatometric effect has been observed. Therefore, the study will only concern the heating process.

The dilatometric curve of the sample homogenised 17 h at 430°C and quenched (Fig. 3a) presents an important effect during the heating. Nevertheless, it is necessary to notice the absence of any dilatometric effect at the end of the test (when the temperature of the sample reaches the

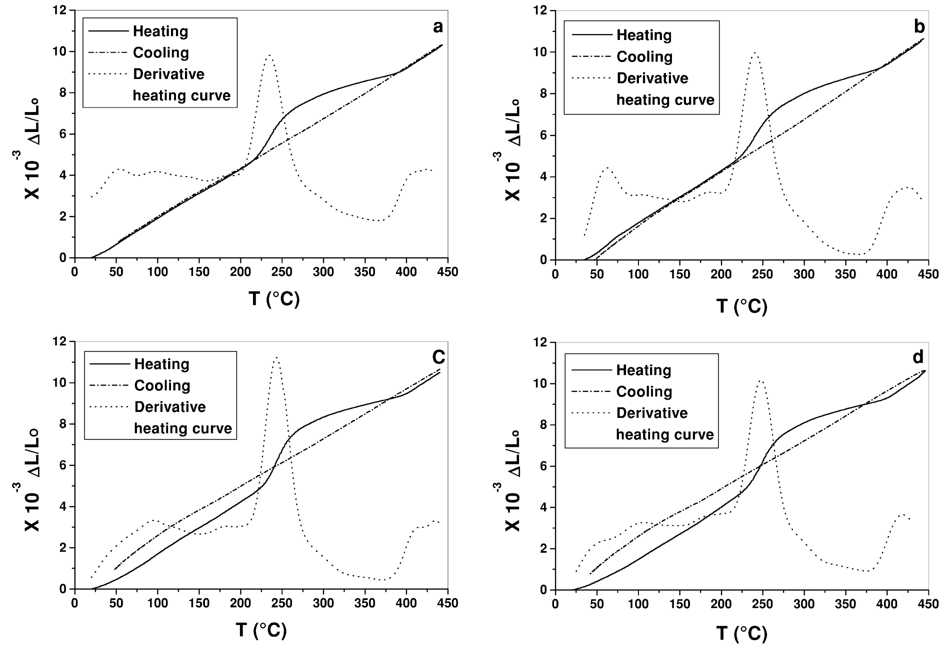

Fig. 3. Dilatometric curves of the complete cycle and the derived curve of the heating one (dotted line) at a heating and cooling rate of 2°C/min of Al–12 wt.% Mg alloy homogenised 17 h at 430°C: (a) quenched, and aged (b) 15 days at 25°C, (c) 50 h at 50°C and (d) 30 h at 100°C.

room temperature after cooling): no 'residual' expansion or contraction is observed. The examination of the derivative curves shows that this effect is composed of an important expansion peak in the temperature range 200–280°C, with a maximum at about 245°C followed by a contraction peak in the temperature range 280–410°C. The observed expansion can be linked to precipitation. It is interesting to make an important remark concerning this expansion which is unexpected, because the precipitation of the second phase (β′ and/or β) is, generally, accompanied by a reduction of the lattice parameter [13]. Thus, during ageing, a contraction and not an expansion of the matrix must be expected. This question will be discussed later when more experimental data will be available.

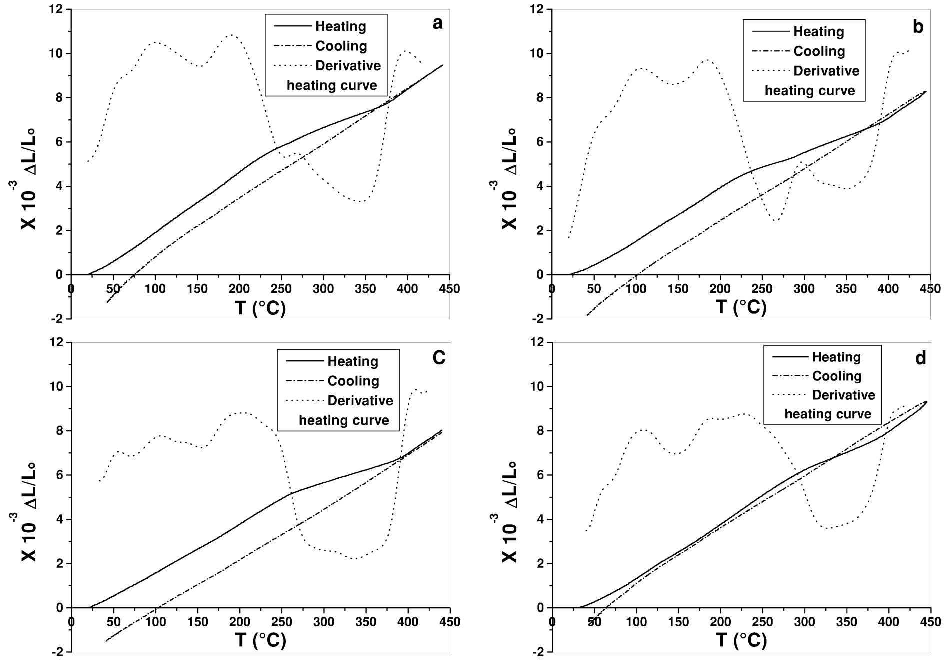

Fig. 4. Dilatometric curves of the complete cycle and the derived curve of the heating one (dotted line) at a heating and cooling rate of 2°C/min of Al–12 wt.% Mg alloy homogenised 17 h at 430°C, quenched and (a) aged 24 h at 150°C, (b) 24 h at 200°C, (c) 7 h at 250°C and (d) 8 h at 300°C.

3.2.1. Temperature interval 25–100°C (formation of GP zones and β″ phase)

Three samples of the Al–12 wt.% Mg alloy, homogenised 17 h at 430°C, quenched and aged at 25, 50 and 100°C, have been heated in the differential dilatometer. The obtained dilatometric curves of the complete cycles, with the derivative heating curves, are presented in Fig. 3b–d. The comparison of these curves leads to the following remarks.

- The general shape for the sample aged at room temperature (Fig. 3b) is identical to that of the quenched sample (Fig. 3a).
- The general shape for quenched and aged samples (at 50 and 100°C) are, practically, identical. A 'residual' expansion persists during cooling between 220 and 50°C (Fig. 3c,d).
- This 'residual' expansion does not exist in the sample aged at room temperature (Fig. 3b).

The derivative heating curves are also interesting. Indeed, more accurate examination leads to the following observations.

- An important effect appears between 220 and 400°C. It is composed of an expansion peak in the temperature interval 220–280°C, with a maximum situated at 240°C and a contraction peak between 280 and 420°C (Fig. 3b,c,d).
- A complementary effect is present in the interval 40–80°C with a peak situated at 60°C for the sample aged at room temperature (Fig. 3b).

The comparison of these results with those of the DSC analysis (Figs. 1 and 2) allows to conclude that this last effect in the interval 40–80°C is, certainly, due to the dissolution of GP zones formed in the course of the natural ageing at room temperature.

According to these results for the three samples, the important dilatometric effect is, undoubtedly, of the same type and of the similar nature than the one observed in the quenched sample: this is due to the precipitation (giving an expansion) followed by the dissolution (giving a contraction) of the β′ and β phases.

3.2.2. Temperature interval 150–300°C (formation of β′ and β phases)

Dilatometric curve of the homogenised sample, quenched and aged 24 h at 150°C (Fig. 4a), presents different effects from those observed for the samples aged below 100°C. Indeed, one can observe:

- two expansions with two maxima situated at 100 and 190°C,
- a contraction with two minima situated at 250 and 350°C,
- a 'residual' contraction at the end of cooling (at room temperature).

In the course of heating of a sample aged 24 h at 200°C (Fig. 4b), similar effects to the preceding case are observed:

- two expansions with two maxima situated at 110 and 145°C,
- two contractions with two minima situated at 180 and 270°C, the amplitude of the first minimum being more important.

However, the heating of a sample aged 7 h at 250°C gives a single contraction with a minimum at 330°C (Fig. 4c).

The first two expansion peaks, more dispersed, and also a single contraction peak with a minimum at 340°C, are present during the heating of the sample aged 8 h at 300°C (Fig. 4d).

These last two curves (Fig. 4c,d) show that the contraction is, certainly, due to the dissolution of all the β phase, entirely, formed during the sufficient ageing at 250 and 300°C.

It is necessary to note the presence of the important expansion (corresponding to higher dilatometric coefficients) between 30 and 240°C (with generally two maxima) for all the samples aged at 150, 200, 250 and 300°C, undergoing the precipitation of the β′ and/or β phases and its absence in the samples aged at 25, 50 and 100°C without any precipitation of these phases.

It seems important to compare all previous results with those obtained by optical and electron microscopy, and microhardness, electrical resistance and internal friction measurements, to identify the phase transformation mechanisms.

3.3. Results of the metallographic observations

3.3.1. Structural state before the dilatometric tests

In the Al–12 wt.% Mg alloy, β-phase nucleation is heterogeneous [13–15]. The structural state observed for each sample, after thermal processing and just before the dilatometric tests, is as follows.

- No evidence of precipitated particles after ageing at 25, 50 and 100°C; this confirms the dilatometric analysis results (Fig. 3b–d), which have shown the absence of important effects (corresponding to higher dilatometric coefficients) in the temperature interval 30–240°C. Therefore, it seems that the dilatation coefficient increase is due to the presence of (β′ and/or β) phases, formed during the preliminary thermal processing.
- At 150 and 200°C, as mentioned in the literature [1,4,8,9], only the formation of the β′ phase occurs. The later which is generally stretched [15], precipitates

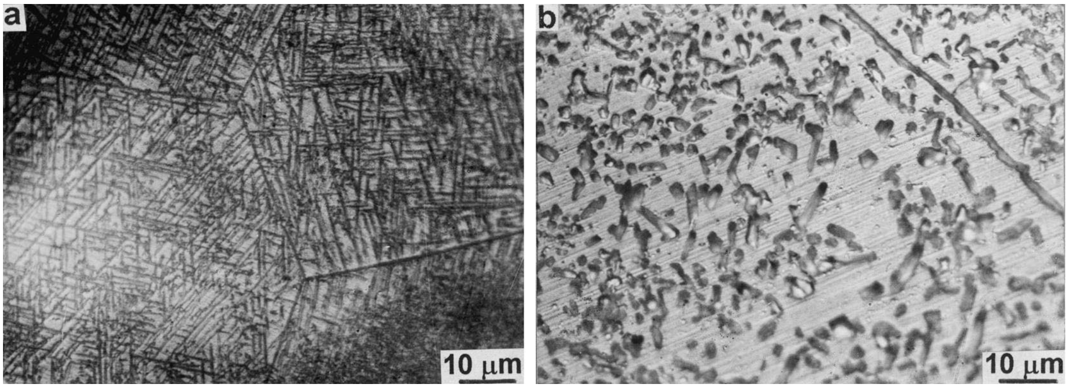

Fig. 5. Microstructure of Al–12 wt.% Mg alloy homogenised 17 h at 430°C, quenched then aged (a) 24 h at 200°C and (b) 8 h at 300°C.

as needles with a structure similar to the Widmanstâtten one (Fig. 5a). These observations are in contradiction to some of the literature [8–10]. Kurtasova and Polyanskiy [16] have already observed particles in the shape of plates up to 80 nm in size, corresponding to precipitates of β′ phase in an Al–9 wt.% Mg alloy aged 50 h at 100°C. Itoh et al. [8] have remarked that β′-precipitate can be distributed more uniformly and densely, frequently showing a rod-shaped morphology in an Al–8 wt.% Mg alloy aged 2.5 h at 200°C. Starink and Zahra [9] have remarked that the characteristic microstructure of the Al–15Mg samples aged at 130 and 190°C consists of lath-like β′ precipitates with slightly irregular shapes.

- At 250 and 300°C, a direct formation of the equilibrium β phase, whose large particles are randomly distributed in the matrix (Fig. 5b), occurred [1,13,15]. The recording of the X-ray diffraction (420) peak, leads to the lattice parameter value $a = 4.067$ Å, which corresponds to the equilibrium state value for this alloy at 250°C [17,18].

3.3.2. Observation of the microstructure corresponding to the exothermic and endothermic DSC peaks

To confirm the origin and the nature of the exothermic and endothermic peaks observed on the DSC curves (Figs. 1 and 2), the same thermal process (identical continuous heating rate of 2°C/min from 25 to 430°C), is applied to homogenised and quenched samples, which are rapidly cooled in water, as soon as they reach the temperatures corresponding to the observed heat effects: 240, 280, 320, 380 and 430°C.

After a continuous heating from 25 to 240°C and to 280°C (Fig. 6a), precipitated particles identical to those of the equilibrium β phase, are noticed. After continuous heating to 320 and 380°C (Fig. 6b), a little larger particles of β phase are observed, without any assertion about their possible dissolution degree. But continuous heating to 430°C gives a microstructure similar to that of homogenised and quenched sample (Fig. 6c), which confirm the dissolution of the precipitated particles formed earlier.

TEM micrographs of a sample homogenised 17 h at 430°C, quenched and aged 5 h at 200°C (to form β′ phase) then 1 h at 250°C (to form β phase) (Fig. 7) confirm the presence of the β′ and β phases particles with different shapes, as observed earlier [5,13,15].

The metallographic study has shown that the precipitate morphology is affected by the ageing temperature. Compared to β phase, which appears as rods at 250 and 300°C [15], the β′ particles formed at 150 and 200°C, are more stretched (as needles) and mainly oriented towards two directions, as in the case of a Widmanstâtten structure.

3.4. Results of the microhardness measurements

Table 1 gives an idea about the variation of the microhardness for different temperatures. The maximum of hardness is observed after 24 h of ageing at 150°C (formation of the semicoherent β′ phase particles (Fig. 5a)). The coarsening of these particles is confirmed by the decrease of the microhardness H_v from 176.8 kg/mm^2 after 24 h at 150°C, to 167.5 kg/mm^2 after 95 h at 150°C. However, this last value is higher than that measured in the presence of the β phase particles: 128.9 kg/mm^2 after 7 h at 250°C and 126.5 kg/mm^2 after 8 h at 300°C.

3.5. Results of the electrical resistivity measurements

Fig. 8 presents the electric resistance variations, as a function of the temperature $R = f(T)$ of a quenched sample, and quenched then aged 5 h at 150°C specimen, during a heating to 350°C at a rate of 2°C/min. In the same figure, the curve α shows the thermal coefficient of linear expansion, which indicates the anomalies of curve $R = f(T)$; it is given by the following formula:

$$\alpha = \Delta R / R\, \Delta T \ (\mathrm{K}^{-1})$$

α presents a peak with a maximum at ~50°C (i.e. an

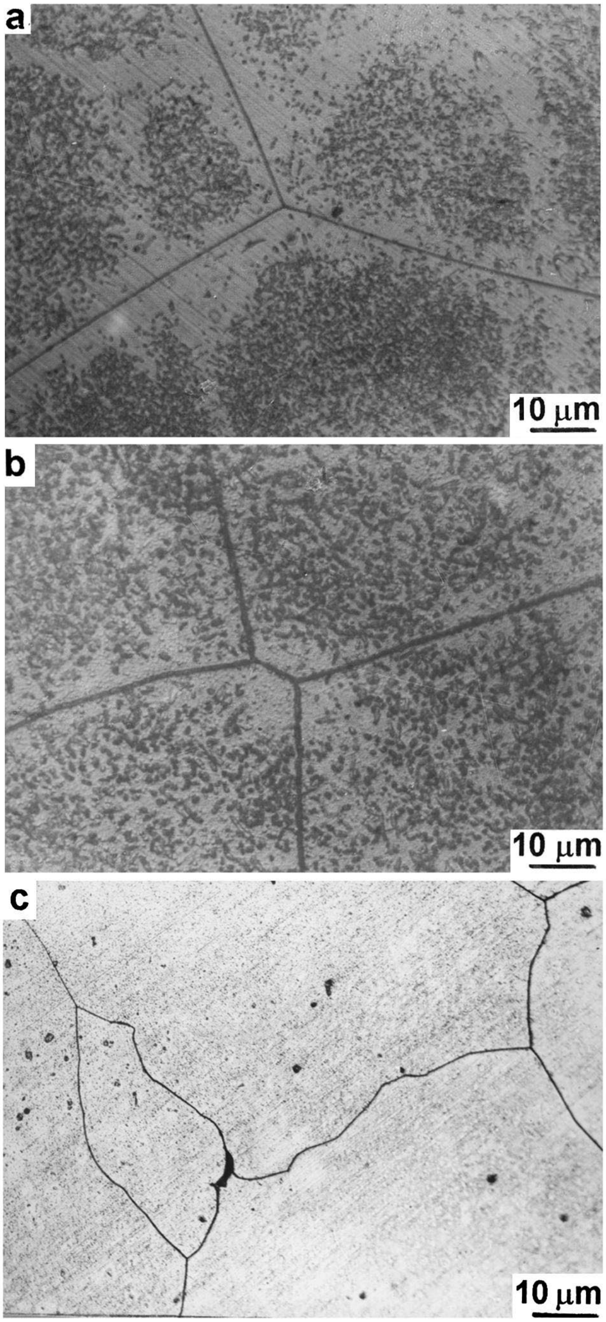

Fig. 6. Microstructure of Al–12 wt.% Mg alloy homogenised 17 h at 430°C, quenched then aged during continuous heating at a rate of 2°C/min to (a) 280°C, (b) 320°C and (c) 430°C.

increase of the electrical resistance) for quenched sample. This maximum corresponds to the endothermic peak observed in the DSC curves in the temperature range 40–80°C (Figs. 1a–c and 2a). Thus, this result confirms the existence of GP zones, whose presence increases the electrical resistance. The two effects giving minima of α observed in the temperature range 200–330°C (i.e. a decrease of the electrical resistance) are due to the formation of coarser phases particles as β' and β.

However, the curve of the electrical resistance variation $R(T)$ of quenched then aged 5 h at 150°C specimen, presents an important effect corresponding to a large peak of α with a minimum at ~300°C (i.e. a decrease of the electrical resistance). The comparison of this result with that obtained with the DSC and the dilatometry methods, confirms that the α minimum can be due to the β phase precipitation. During the ageing at 150°C for 5 h, GP zones are already dissolved and the first peak disappeared.

3.6. Results of the internal friction measurements

The influence of the precipitation on the internal friction (IF) evolution is also interesting, because the IF is particularly sensitive to the evolution of materials microstructure.

Two samples of the Al–12 wt.% Mg alloy homogenised 17 h at 430°C and quenched, are aged during continuous heating at a rate of 2°C/min, with two different deformation amplitudes $\gamma_1 = 3.3 \times 10^{-5}$ and $\gamma_2 = 1 \times 10^{-4}$ (Fig. 9). On the last curves, a peak of the I.F. is observed in the temperature range 180–260°C, where effects have already been noticed on DSC and dilatometric curves, and linked to the precipitation of β' and β phases.

To confirm the effect of the precipitation process on the internal friction, two successive cycles are performed to a sample homogenised 17 h at 430°C and quenched (Fig. 10): a heating from the room temperature until 300°C at a rate of 2°C/min, followed by a cooling and a second heating at the same rate.

The peak observed during the first heating in the same temperature interval 180–260°C, due to the precipitation, decreases during the second heating, which bring proof of the driving force reduction of the precipitation reaction (Fig. 10). The latter is explained by the supersaturation decrease because of the precipitation occurring during the first cycle.

All previous results can explain the IF ones and confirm the optical microscopy observations. The increase of IF, starting at ~190°C, is certainly due to the formation of β' then β phases; its decrease at ~240°C, when a big quantity of β phase is already precipitated, is only due to the presence of β particles. The new IF increase at ~270°C can be due to the beginning of β phase dissolution (Fig. 10). However, the important IF increase at lower temperature (~100°C) (Fig. 10), in the temperature range 180–220°C, when β' phase must be formed, is certainly due to this semicoherent phase.

After the first heating and cooling, a big part of precipitated phases is formed and dislocations can easily oscillate. This leads to an earlier background increase.

The background can, also, be considered as the low temperature part of a high temperature peak, due to dislocations [19]. These results which are in a close correlation with the precedent experimental observations,

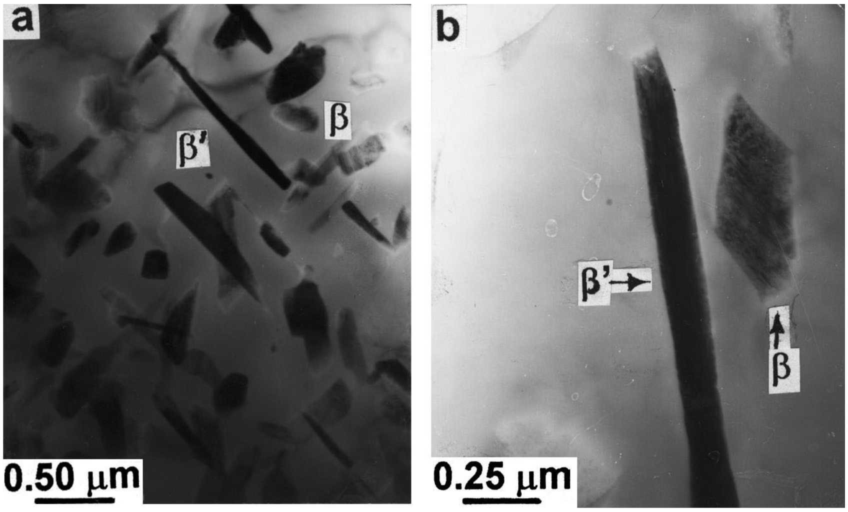

Fig. 7. TEM micrographs of Al–12 wt.% Mg alloy homogenised 17 h at 430°C, quenched and aged 5 h at 200°C and 1 h at 250°C illustrating different particles of (a) β′ and (b) β phases.

Table 1

Sample state	Microhardness H_v (kg/mm^2)
As-quenched	139.5
Aged 30 h at 100°C	110.6
Aged 24 h at 150°C	176.8
Aged 95 h at 150°C	167.5
Aged 100 h at 200°C	153.5
Aged 7 h at 250°C	128.9
Aged 8 h at 300°C	126.5

show that the IF is not very sensitive to GP zone formation or dissolution.

4. Synthesis and interpretation of obtained results

The comparison of the results of the DSC with the metallographic ones leads to confirm that exothermic peaks reflect well the precipitation of the equilibrium β phase (Al_3Mg_2) at 240 and 280°C, as observed in earlier works

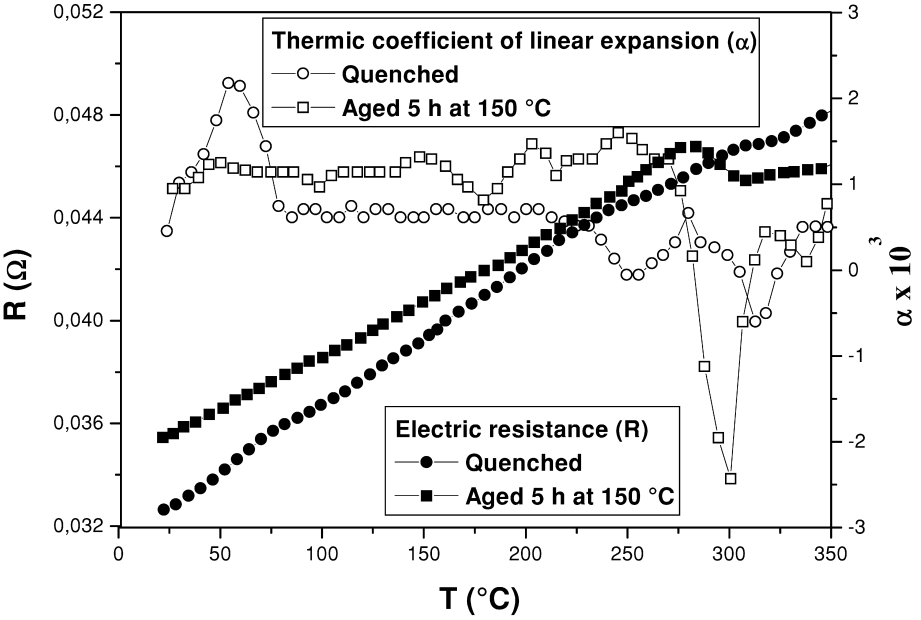

Fig. 8. Temperature dependence of the electric resistance (R) and the thermic coefficient of linear expansion (α) for two samples of Al–12 wt.% Mg alloy treated differently.

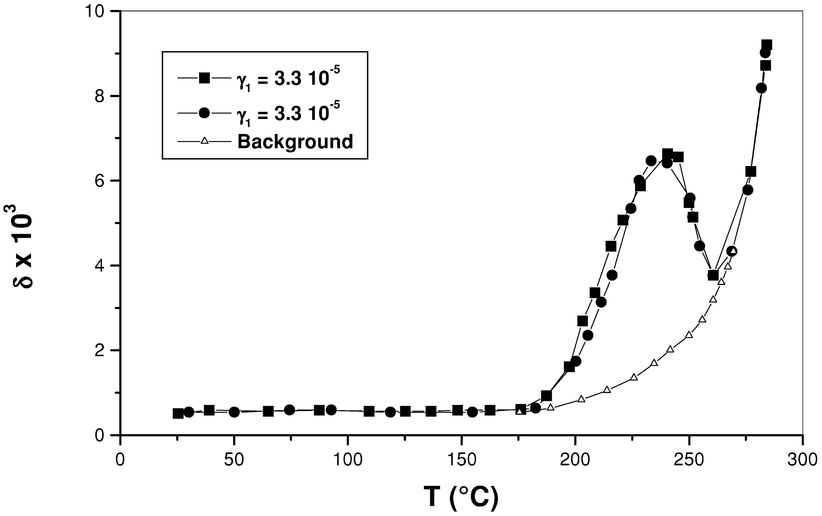

Fig. 9. Temperature dependence of the logarithmic decrement of internal friction for homogenised 17 h at 430°C and quenched Al–12 wt.% Mg alloy, during a heating to 300°C at rate of 2°C/min with two deformation amplitudes.

[1,3,4]. Although Starink and Zahra [6] think that these peaks are due to the formation of β′ phase and the transformation β′→ β.

The dilatometric data are more interesting and lead to the following remarks.

- The precipitation of a phase (exit of Mg atoms from the supersaturated solid solution to form the new phases) leads to an expansion and its dissolution (entrance of Mg atoms in the solid solution) leads to a contraction.
- A first shape of dilatometric curves, without 'residual' expansion or contraction, is given by just quenched and quenched then aged samples at 25°C, a second shape with a 'residual' expansion in the course of cooling is given by aged samples at low temperatures (50 and 100°C), and a third shape with a 'residual' contraction in the course of cooling is given by samples aged at higher temperatures (150, 200, 250 and 300°C).

The results of the metallographic study of the structural state of samples, just before the dilatometric tests starting, confirm that no precipitated particles are observed after ageing at 25, 50 and 100°C, the semicoherent β′ phase is formed at 150 and 200°C and gives the maximum of hardness (after 24 h of ageing at 150°C) and the equilibrium β phase appears at 250 and 300°C. These results are in agreement with the literature ones [1,4,8,9,13,15].

Concerning the electrical resistivity and the internal friction measurements, they confirm the development of the precipitation reaction in the temperature intervals where effects have been observed on the calorimetric and dilatometric curves.

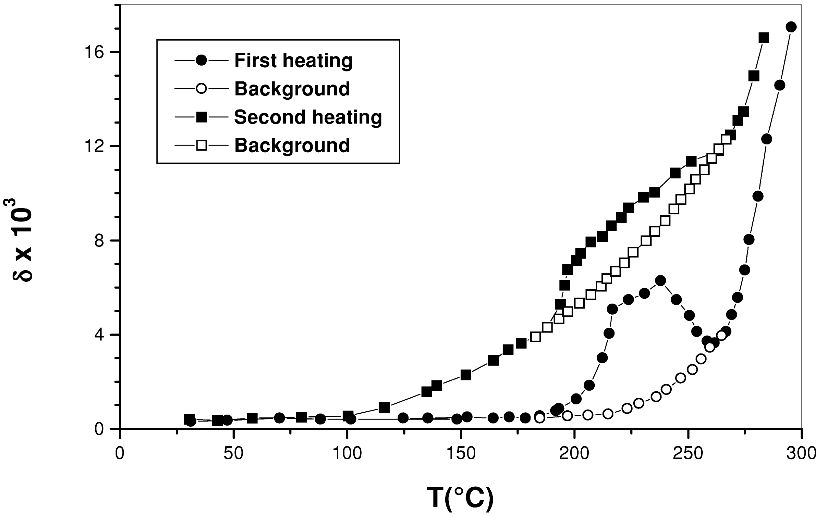

Fig. 10. Temperature dependence of the logarithmic decrement of internal friction for homogenised 17 h at 430°C and quenched Al–12 wt.% Mg alloy, during a first and a second heating to 300°C at rate of 2°C/min.

Thus one can conclude that the expansion during the precipitation is, certainly, due to the presence of β′ and/or β phases. Their contribution to the expansion effect is more important than the one due to the matrix contraction (supported by the diminution of the lattice parameter). In fact, their presence before the dilatometric tests starting, causes important supplementary expansions between 30 and 240°C. This anomaly can be explained by the structure and the values of the lattice parameters of these two phases, which give a specific volume greater than the matrix one: β′ is hexagonal (approximate composition Al_3Mg_2) with $a = 10.02$ Å and $c = 16.36$ Å and β (similar composition Al_3Mg_2) is fcc with $a = 28.24$ Å [10,20].

The supplementary expansions obtained after ageing at 150 and 200°C (giving β′ particles) are composed, in general, of two peaks and are followed by two contractions with two other peaks. This means that there are two different expansions and contractions. Since the expansion is linked to the precipitation and the contraction to the dissolution, one can think that they are due to the appearance and to the disappearance of β′ and β phases, respectively. After ageing at 250 and 300°C (giving β phase particles) two maximum are yet present but only one minimum due to the β-phase dissolution, is observed. Hence, from the preceding observations, the contraction with two minimum is certainly due to the successive dissolution of β′ and β phases and, consequently β′ does not contribute to the formation of β.

- The appearance of an endothermic peak on DSC curves and an expansion on some dilatometric curves, at the first stages of ageing of samples quenched and aged at room temperature and at 50°C, are obviously due to GP zones. As the latter are not immediately followed by an other effect in the DSC and in the dilatometric curves, we can assert that they cannot contribute directly to the formation of the metastable intermediate β′ phase, as observed by Starink and Zahra [5].
- The 'residual' expansion subsisting after cooling in the dilatometric curves of samples quenched and aged at 25 and at 50°C, can be due to the presence of β′ and β phases, formed in the course of heating and not entirely dissolved during the maintain of 5 min at 430°C.
- The 'residual' contraction subsisting after cooling of samples aged at 150, 200, 250 and 300°C, is due to a partial dissolution of precipitated phases during the maintain at 430°C: from the beginning to the end of the dilatometric test, the quantity of phases existing in the matrix must necessarily decrease (reducing the expansion effect). Consequently, the Mg atoms leave these phases and return into the solid solution, increasing its expansion. However, this expansion do not compensate the first effect of expansion due to the presence of the phases initially precipitated (before the dilatometric tests started).

These experimental observations show that the effect of the precipitated phases on the dilatation curves of a binary Al–12 wt.% Mg alloy, is more important than that of the variation of the solid solution concentration. If the specific volume of the precipitate phase is larger than that of the solid solution (matrix), an expansion is expected during the precipitation process, even if an increase of the lattice parameter occurs. Hence we deduce that the dilatometric analysis is more sensitive to the precipitation phenomena than the DSC one.

Conclusion

The interesting experimental results obtained by very complementary, various and rigorous methods, leads to explain the expansion observed during the precipitation on dilatometric curves by the appearance of β′ and/or β phases, because their contribution to the expansion of the matrix is more important than the contraction due to the diminution of the lattice parameter.

On the other hand, it is established that in the Al–12 wt.% Mg alloy, each phase appearing during the decomposition of the supersaturated solid solution, does not, directly, contribute to the formation of the following phase of the precipitation sequence.

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