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Precipitation phenomena in the Mg-31 at% Li-1 at% Al alloy

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Precipitation phenomena produced in the β-phase (b c c) of the Mg–31 at % Li–1 at % Al alloy subjected to different heat treatments have been studied by sensitive single-crystal X-ray diffraction techniques. The variation of the hardness values of specimens quenched and then aged was also examined. It was confirmed that AlLi is a stable phase at room temperature for the examined Al content; AlLi precipitation is only produced for very slow cooling rates from the β-field. Phase reactions for specimens quenched and then aged can be summarized as follows: $\beta \rightarrow \beta + \theta + \alpha$ after ageing at room temperature; $\beta \rightarrow \beta + \theta + \alpha +$ AlLi after ageing at 473 K. A considerable increase of the hardness, which attains its maximum value after about 30 h ageing at room temperature, was observed. Neither the α-phase nor the AlLi-phase precipitation can account for the observed hardening process. The presence of the θ-metastable phase when the hardness reaches its maximum value is verified.

1. Introduction

Systematic research of materials has led to the development of good strength-to-weight ratio alloys, such as the MgLiX alloys, where the third component X is added to the b c c-phase of the MgLi (30 to 100 % Li[†]) binary system. Aluminium, cadmium, zinc and silver are the most effective additions. Several comprehensive studies concerning melting techniques, mechanical properties and the working of heat-treated alloys have been performed [1–5].

The most recent results of McDonald [6–8] obtained from commercial and high-purity alloys with variable concentrations of Li and Al, show that the best mechanical strength–ductility combinations occurs for Al compositions higher than 0.5% and Li compositions lower than 36%. He has interpreted the improvement of mechanical properties in terms of an age-hardening phenomenon connected with a metastable θ-phase precipitation. He proposes that a precipitation-hardening process, similar to that observed in the Al–Cu alloys, is responsible for the detected variations in the mechanical properties. However, he has not confirmed the presence of the θ-phase nor of any other structural transformation that may occur during the changes in the mechanical properties.

Metastable θ-phase precipitation has only been detected for MgLiAl ternary alloys with Al concentrations higher than 4%, by ordinary X-ray diffraction techniques [4, 9].

A better understanding of the nature and conditions of occurrence of structural changes as a function of the heat treatment, is desirable. The present work reports an investigation of the precipitation sequence produced in the Mg–31% Li–1% Al alloy.

The evolution of the heat-treated samples was followed by hardness measurements and by sensitive single-crystal X-ray diffraction techniques capable of detecting very weak diffraction effects, i.e. pre-precipitation phenomena or a small fraction of precipitated phases.

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[†] All compositions given in this paper are in atomic percentages unless otherwise stated.

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2. The MgLiAl ternary system

This section summarizes the relevant phase properties of the composition considered (Mg–31% Li–1% Al). The ternary equilibrium diagram [9, 11] shows a single-phase field (b c c β-phase) above 555 K. Lattice-spacing measurements of this β phase give a value of $a_\beta = (3.5185 \pm 0.0004)$ Å [12] as obtained from samples slowly cooled from β-field to room temperature.

At 475 K, the composition considered is in the $(\beta + \alpha)$-field. α is a hexagonal close-packed solid solution of lithium and aluminium in magnesium. Its lattice parameters are: $a = (3.1908 \pm 0.0004)$ Å, $c = (5.1284 \pm 0.0004)$ Å with $c/a = (1.607 \pm 0.002)$ [12] as determined for quenched samples subsequently aged at 525 K. The α-phase precipitates into the β-matrix with the following orientation relationships [13]:

$$(1\,1\,0)_\beta \parallel (0\,0\,0\,1)_\alpha,$$

$$\langle 1\,1\,1 \rangle_\beta \; 0^\circ \text{ to } 10^\circ \text{ from } \langle 2\,\bar{1}\,\bar{1}\,0 \rangle_\alpha.$$

The $(\beta + \alpha)$-field extends up to an Al concentration of 1.5%. For higher concentrations, the $(\beta + \alpha + \text{AlLi})$-field is formed. The AlLi phase is an ordered stoichiometric phase of the NaTl type (B32), with a lattice spacing of 6.36 Å [14], which grows in the β-matrix with the relationship [10]:

$$(1\,0\,0)_\beta \parallel (1\,0\,0)_{\text{AlLi}}, \langle 1\,0\,0 \rangle_\beta \parallel \langle 1\,0\,0 \rangle_{\text{AlLi}}.$$

There have been no published determinations of the room-temperature isotherm. Nevertheless, the $(\beta + \alpha)/(\beta + \alpha + \text{AlLi})$ boundary behaviour indicates that AlLi precipitation should be possible at room temperature.

The θ metastable phase has been detected [1, 2, 9, 10] for Al concentrations higher than 4%. It has a complex cubic structure, with a lattice spacing of 6.72 Å [9] and it grows in the β-matrix with the same orientation relationship as the AlLi phase.

3. Experimental procedures

3.1. Sample preparation and heat-treatment

Sheet specimens of Mg–31% Li–1% Al* (Mg–11.2 wt % Li–0.9 wt % Al) of 2 mm thickness were supplied by Dr J. McDonald. The melting method and chemical analysis are reported in [7]. (The alloy examined here corresponds to McDonald's designation (B)-11.) The composition of the alloy was confirmed by chemical analysis carried out in our laboratory.

Polycrystalline samples for X-ray diffraction of size 10 mm x 15 mm x 0.5 mm were obtained from the sheet specimens by cold rolling and then solution treated at 660 K for 2 days. Single crystals were prepared from large-grained sheet specimens of β-phase obtained by cold rolling and then annealing for 10 days at 700 K. Crystals of suitable orientation were removed from the sheet by dissolving the surrounding region with a dilute nitric acid solution. They had an average size of 2 mm x 1 mm x 0.5 mm. The selected crystals were again solution treated at 660 K; some of them were slowly cooled; others were quenched and then aged at room temperature and 473 K.

In order to reduce contamination and evaporation of the samples, all the heat treatments were carried out in sealed Pyrex capsules evacuated to 10^{-7} mm Hg and then filled with an excess pressure of high-purity argon. The quenches were performed by breaking these capsules into a water and sodium chloride mixture at 251 K. The isothermal anneals under 525 K were carried out in silicone oil baths.

3.2. Hardness measurements

A Brinell hardness tester was used to study the heat-treated samples of 2 mm thickness. The load applied was 10 kg. All the tests were made at room-temperature. The values reported in Figs. 1 and 2 are each the average of six measurements.

3.3. X-ray examination

A preliminary study of polycrystalline sheets was made in a focusing camera (Guinier's camera) with a transmission mounting, using crystal-monochromatized Cu$K\alpha$ radiation. These polycrystalline techniques did not detect any structural change in the period of time during which an increase in hardness was observed. It was therefore necessary to use more sensitive single-crystal techniques. Single-crystal specimens were held in a two-circle goniometer and oriented on a Läue camera. A single-crystal camera of high sensitivity and intensity designed in our laboratory [15] was used. It works under vacuum and a very fine monochromatic Cu beam is obtained from a focusing LiF crystal monochromator. Diffraction effects are recorded on a semicylindrical film.

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* The exact atomic concentration of Al is 0.70%. For convenience we are considering it as 1%.

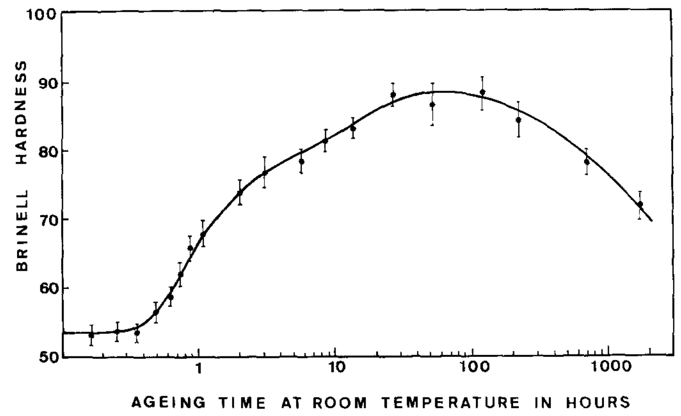

Figure 1 The variation in hardness with ageing time for a specimen quenched from 660 K and then aged at room temperature.

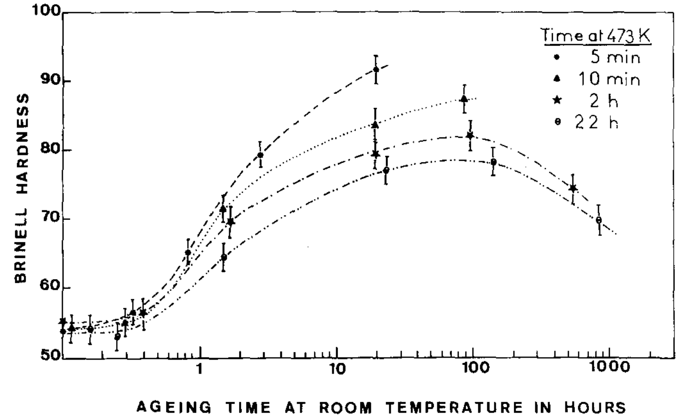

Figure 2 The variations in hardness during room-temperature ageing after various times of ageing at 473 K.

Oscillation patterns were obtained from single-crystals oriented to oscillate about $[1\,1\,0]_\beta$ (vertical), and 35° to each side of the X-ray beam which was initially parallel to the $[0\,0\,1]_\beta$ direction.

4. Results

4.1. Hardness curves

Figs. 1 and 2 show typical hardness variations for the examined alloy. Fig. 1 shows the change in hardness at room temperature of a sample quenched from 660 K. As shown, there is an incubation period of approximately 0.5 h followed by a rapid age-quenching which attains its maximum value within 30 h. After 100 h a slight overageing is observed.

Several specimens were quenched from 660 K and then aged at room temperature for 8 h, producing the same hardness variations as shown in Fig. 1. These specimens were then aged at 473 K for 5 min and this produced a decrease in the hardness to the values obtained immediately after the initial quench. Subsequent ageing at room temperature produced changes in the hardness similar to that shown by Fig. 1. This behaviour was reproduced for longer ageing times (up to 22 h) at 473 K as shown by Fig. 2. The hardness maximums in the subsequent ageings at room temperature were smaller the longer the ageing times at 473 K.

It is worthwhile noting that the hardness values for the samples very slowly cooled from the β-field are equal to the as-quenched value obtained during the initial stages of ageing.

4.2. Precipitation phenomena in β-solid solution

4.2.1. Polycrystalline samples

Polycrystalline samples of 0.5 mm thickness were slowly cooled (2° C h^{-1}) from 660 K. Diffraction patterns showed the presence of three equilibrium phases: β, α and AlLi.

Another group of samples were quenched and then aged at different temperatures ranging from 293 to 423 K. The diffraction patterns for all these samples showed characteristic β-lines immediately after quench; the θ and α lines became visible only after ageing. The ageing times that were

TABLE I

Ageing temperature (K)	Time for appearance of θ-trace	Time for maximum development		Maximum ageing time
		θ	α	
293	15 days	30 days	20–30 days	1 year
328	18 h	40 h	60 h	12 days
373	100 min	N.A.	N.A.	46 days
423	5 min	N.A.	N.A.	2 h

required are summarized in Table I. The AlLi phase was not observed even after the given maximum ageing times.

For the ageing carried out at 373 and 423 K, an inhomogeneous distribution of the grain sizes of the samples prevented an unambiguous determination of the magnitude of the θ and α intensity peaks, that is their actual precipitated fraction.

No variation was observed in the θ-lattice spacing for the different ageing times and temperatures. A rough estimation deduced from $(3\,1\,1)_\theta$ and $(4\,2\,2)_\theta$ (the greatest diffraction angles recorded) gives a value of $a_\theta = (6.77 \pm 0.03)$ Å for all the cases considered.

The variation of the β-lattice parameter for samples quenched and aged at room temperature is shown in Fig. 3. The a_β values have been obtained from Debye–Scherrer X-ray patterns of polycrystalline wires of the examined alloy.

4.2.2. *Single-crystal specimens*

Diffraction patterns obtained from single crystals subjected to different heat-treatments revealed the following facts.

(a) Specimens slowly-cooled ($1^\circ\,\mathrm{C\,h^{-1}}$) from the β-field show three precipitated phases – α, θ and AlLi – in the β-matrix as seen in Fig. 4. The orientation relationships given in Section 2 were confirmed in all cases. The θ-lattice parameter was found to have a value of $a_\theta = (6.74 \pm 0.02)$ Å.

(b) Several specimens were quenched from 660 K and then aged at room temperature for periods of up to 1 year. The patterns corresponding to the as-quenched state show the β-phase spots, broad θ-phase reflections and traces of two α-phase reflections, as shown in Fig. 5a. As the ageing time increased, the θ-phase spots became slightly more intense and also sharper.

Lattice parameter estimations indicate that a_θ decreases continuously from the as-quenched value $a_\theta = (6.87 \pm 0.02)$ Å (corresponding to 20 h at room temperature) to $a_\theta = (6.77 \pm 0.02)$ Å after 265 days at room temperature, as shown in Fig. 6.

The α-phase precipitation, oriented according to the relationship given in Section 2, was produced during ageing. Its maximum precipitated fraction was attained after 50 days. No further modifications were observed for longer ageing times.

The diffraction pattern shown in Fig. 5b, obtained after 1 year ageing, corresponds to the longest ageing time employed.

(c) Single-crystal specimens annealed and quenched from 660 K were aged at 473 K for various periods of up to 170 h. After 2 min at 473 K the α-precipitation was totally developed.

During the first stage of ageing, very broad and diffuse reflections belonging to the θ-phase were detected. After 100 min $(1\,1\,1)_{\mathrm{AlLi}}$ reflections appeared as a consequence of the $(1\,1\,1)$ θ-spots

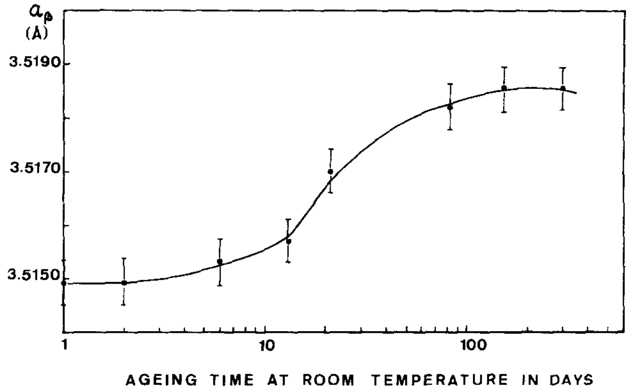

Figure 3 The variation of the β-lattice parameter with room-temperature ageing time.

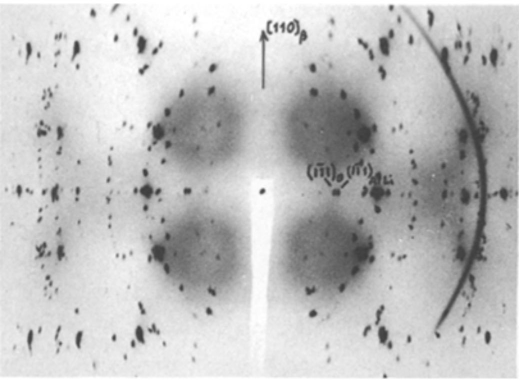

Figure 4 Oscillation X-ray pattern of a Mg–31% Li–1% Al single-crystal specimen slowly cooled from 660 K. (The crystal was orientated to oscillate vertically about $[1\,1\,0]_\beta$, and horizontally through 35° from the position where $[0\,0\,1]_\beta$ was parallel to the X-ray beam.)

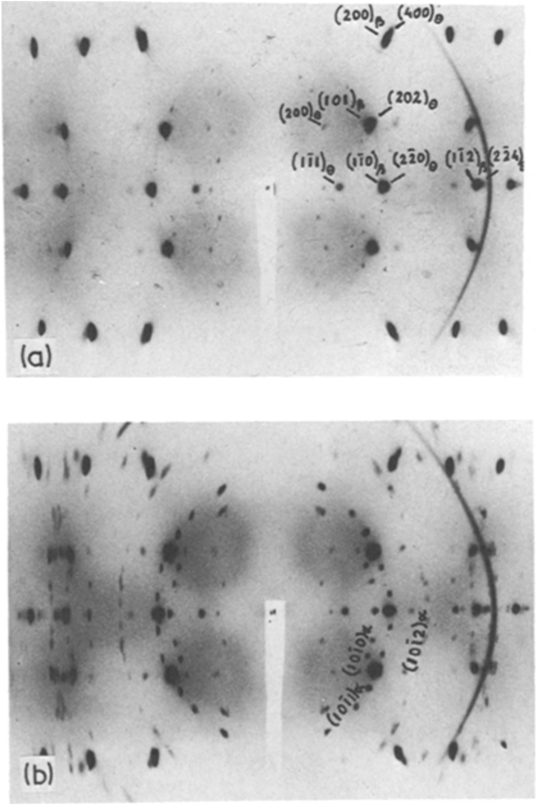

Figure 5 Oscillation X-ray pattern of a single-crystal specimen quenched from 660 K and then aged at room temperature. (The crystal orientation is the same as for Fig. 4.) (a) Aged for 1 day at room temperature. The orientation relationship between the β-matrix and the transition structure θ is shown. (b) Aged for 1 year at room temperature. The α-phase reflections are distributed as spots on discontinuous circles.

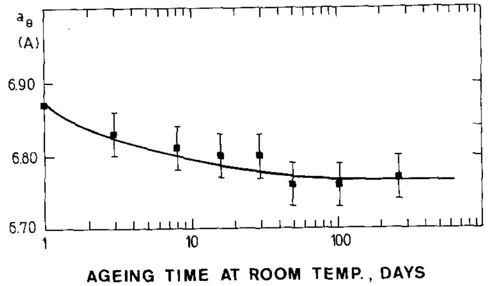

Figure 6 The variation of the θ-lattice parameter with room-temperature ageing time.

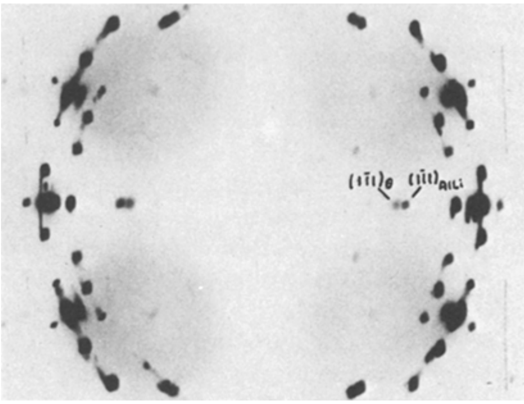

Figure 7 Oscillation X-ray pattern of a single-crystal specimen quenched from 660 K and then aged for 100 min at 473 K. Note the intensity ratio of the $(1\,1\,1)_\theta$-spot and $(1\,1\,1)_{AlLi}$-spot. (The crystal orientation is the same as for Fig. 4.)

splitting, i.e. $(1\,1\,1)_\theta \rightarrow (1\,1\,1)_\theta + (1\,1\,1)_{AlLi}$, as observed in Fig. 7. A decrease in the intensity of the θ-reflections was observed simultaneously to the AlLi-spot reinforcements.

The θ-lattice parameter was not modified during this ageing; the measured value $a_\theta = (6.77 \pm 0.02)$ Å was the same as for the later stages of the room-temperature ageing. The AlLi precipitates exhibited the same lattice spacing and orientation relationship as for the slowly cooled specimens. After 170 h ageing, all four phases (β, α, θ and AlLi) were still detected.

An additional ageing at 525 K for 20 h was performed for these specimens. The AlLi-phase totally dissolved at the same time as the θ-precipitated fraction increased, but there was no detectable changes in its crystallographic characteristics.

(d) The effects of quenching temperature on the different precipitated phases were examined. Quenching from 700 and 760 K did not modify the above-mentioned behaviour of the θ and AlLi phases, during ageings at room temperature, 473 and 525 K.

The α-precipitation rate was accelerated for room-temperature ageing, attaining its maximum precipitated fraction after 1 day. During ageing at 473 K, the α-phase totally lost its orientation relationship with the β-matrix as observed on the X-ray patterns by the almost continuous rings that were formed by reflections from the randomly orientated α-phase precipitates.

It is worthwhile pointing out that circular diffuse scattering domains were present on every diffraction pattern. Apparently, no close dependence on heat treatments exists, since no changes in their size, shape and location in the reciprocal space were observed. Thus they do not appear to be connected with the changes in the hardness values. An interpretation of them as a short-range-ordering into the β-matrix is given in [16].

5. Discussion

5.1. Phase reactions

The phase reactions observed in the preliminary studies of the polycrystalline specimens were slightly different from those in the single-crystal specimens. Any direct comparison between them is not possible because of the difference between the sensitivities of the X-ray techniques. Also, heterogeneous precipitation at grain boundaries may have changed the kinetics and the precipitated fraction of the detected phases in the polycrystalline specimens. Even though some aspects of the results were found to be the same using both techniques, the following discussion essentially concerns the results obtained from the single-crystal specimens.

The patterns obtained from slowly cooled polycrystalline and single-crystal specimens confirm that AlLi is a stable phase at room temperature, for the examined alloy composition.

For single-crystal specimens, the θ-phase is a constituent of remarkable persistency; even cooling at low speeds could not prevent its precipitation. This can be seen from Fig. 4. The fact that the θ-phase was not observed on the patterns of slowly cooled polycrystalline specimens indicates that only a very small precipitated fraction was present, which could not be detected by the technique employed. The patterns of single-crystal specimens, subjected to the same heat-treatment, showed the presence of approximately similar amounts of both the θ- and AlLi-phases, as deduced from the similar intensity of their diffraction spots (see Fig. 4). Only the AlLi line was observed on the polycrystalline patterns; this is thought to be the result of the AlLi precipitated fraction being greater than in the single-crystal specimens. This could be caused by an additional heterogeneous precipitation of the AlLi phase at grain boundaries. Such an effect would be negligible for the single-crystal specimens.

The isothermal precipitation reactions for quenched single-crystal specimens can be summarized as follows. For room-temperature ageing:

$$\beta_q \rightarrow \beta + \theta_q \rightarrow \beta + \theta + \alpha,$$

where q refers to the stage immediately after quenching. The second member corresponds to the first period of ageing and the third member to periods greater than 50 days. θ_q and θ only differ in their lattice parameters: $a_{\theta_q} = 6.87$ Å, $a_\theta = 6.77$ Å. This considerable variation can only be accounted for by a change in the composition of the θ-phase. The Al and Li atomic radii are smaller than the Mg atomic radius ($r_{Li} = 1.520$ Å, $r_{Al} = 1.387$ Å, $r_{Mg} = 1.563$ Å; the values of r_{Mg} and r_{Al} were calculated for a hypothetical b c c state, correcting Goldschmidt radii values for eight-fold co-ordination [17, 18]). Thus, a progressive replacement of the Mg atoms by either or both the Al or Li atoms could explain the observed decrease in the value of a_θ.

The phase reactions produced by ageing at 473 K for 100 min may be written as follows:

$$\beta_q \rightarrow \beta + \theta + \alpha + \text{AlLi}.$$

The θ-phase lattice parameter does not change during this ageing and its value ($a_\theta = 6.77$ Å) is the same as that obtained for the later stages of the room-temperature ageing.

During ageing at 473 K, the AlLi-precipitates grow to the detriment of the θ precipitated fraction, as deduced from a decrease in the intensity of the θ-spots. The opposite process is observed at 525 K; the AlLi is dissolved with a progressive increase in the θ-fraction. These facts and the splitting of the $(1\,1\,1)_\theta$ spots, indicate that the formation of the AlLi phase is closely related to the presence of the θ-phase, which may be partially transformed into the equilibrium AlLi phase.

In quenched and aged polycrystalline specimens, the partial transformation of the θ-phase was not observed. Only the total transformation $\theta \rightarrow$ AlLi was detected, and this for a commercial alloy of higher Li content (36%) after ageing for 46 days at 373 K.

As noted above, the formation of the AlLi phase only occurs during ageing at the higher ($\geqslant 373$ K) temperatures. This may be related to the high Al concentration (50%) necessary to produce the AlLi phase, which must be attained locally from the much lower average Al content (1%) in the alloy as a whole.

The AlLi precipitation times depend on the ageing temperature, which indicates that the nucleation and growth are thermally activated processes. However, atomic diffusion coefficients are not available for this alloy and so it is not possible to compare the observed incubation times with those calculated from a mechanism of growth by atomic diffusion.

The phase reactions described above were not altered by the changes in the quenching temperature. Only the rate of precipitation of the α-phase during room-temperature ageing was altered, the rate increasing with increasing quenching temperature.

5.2. Hardness curves

During ageing at room temperature, the alloy remains at the as-quenched hardness values for a period of 0.5 h, and then age-hardens rapidly, attaining its maximum hardness value within 30 h. A slight overaging is observed after 150 h at this temperature. The form of the present hardness versus ageing-time curve is typical of a precipitation hardening process [19]. In the present case, the phase responsible for the hardening should attain its maximum development after about 30 h ageing at room temperature.

The single-crystal X-ray diffraction technique used in this work required exposure times of 20 h. Thus the so-called as-quenched X-ray patterns obtained immediately after quenching, involved that the single-crystal specimens had remained at room temperature for 20 h, a period in which the hardness had increased to almost its maximum value. In spite of this experimental limitation, it is possible to eliminate the α-phase as being responsible for the observed hardening. Even though it precipitates during ageing at room temperature, the time required to obtain its maximum precipitated fraction is twenty times longer than that required to produce the hardness maximum. Moreover, the α-phase is a typical phase of the Mg–Li binary alloy, where no hardening was observed [2].

The AlLi-phase was not detected after ageing at room temperature. Thus it is not possible for it to account for the described hardening phenomena either.

The X-ray patterns corresponding to 20 h ageing at room temperature showed the homogeneous precipitation of the θ-phase in the β-matrix, with the orientation relationship noted in Section 2.

The θ-spots became slightly sharper and more intense after ageing for 3 to 5 days, but no further variation was detected for longer ageing periods at room temperature. Considering the precipitation characteristics of this phase, which is present at the same time as the hardness reaches its maximum value, it is reasonable to propose that the metastable θ-phase is responsible for the observed hardening produced in the Mg–31% Li–1% Al alloy. The hardening process will be related to the distribution, size, shape and degree of coherency of the θ-precipitates, obtained by quenching and ageing at room temperature.

This proposition is supported by observations in a MgLiZn alloy, where similar behaviour has been found [10]. The transition structure of this alloy has the same characteristics as the θ-phase of the MgLiAl alloy, and the increase in hardness, after an incubation time of 10 h, has been confirmed as occurring simultaneously with the precipitation of that metastable phase.

The overageing observed in the present experiments cannot be accounted for by the transformation of the θ-phase into the equilibrium AlLi phase, as has been proposed elsewhere [4, 10]. The simultaneous decrease in the θ-lattice parameter with the increase in the β-parameter could indicate a modification in the atomic misfit between both structures. If we assume that two unit cells of β-solid solution were coherent across the cube face with one unit cell of θ-phase, the calculated atomic mismatch increase from 2% to 4%, from the as-quenched state to the longest time of ageing at room temperature.

6. Conclusions

The AlLi-structure is a stable phase at room temperature for Al-concentrations as low as 0.70 at %.

The so-called θ-metastable phase is a very persistent constituent for single-crystal specimens; the variation in the θ-lattice parameter indicates that important compositional changes occur during heat treatment.

The phase reactions for specimens quenched and then aged may be summarized as follows:

$\beta \rightarrow \beta + \theta + \alpha$ at room temperature,

$\beta \rightarrow \beta + \theta + \mathrm{AlLi} + \alpha$ at 473 K.

Hardness increases during ageing at room temperature and reaches its maximum value after about 30 h ageing.

Neither the α-phase nor the AlLi-phase precipitation can account for the observed hardening process.

The presence of the θ-phase when the hardness reaches its maximum value is verified.

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