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Elastic Moduli Variations during the Decomposition of Aluminium–Magnesium Solid Solutions

Application to the Study of Guinier-Preston Zones

By

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Elastic moduli E and G have been measured during the decomposition of supersaturated solid solutions of aluminium based alloys with 11, 12.5, and 15 weight % magnesium. Ultrasonic (2 and 10 MHz) and resonant rod (70 kHz) measurements for isothermal ageings at various temperatures show an increase of the moduli during the formation of Guinier-Preston zones, and a decrease during the precipitation of β′ and β phases. In the particular case of GP zones, the ageing kinetics clearly show two different decomposition modes. Finally the reversion of the GP zones and their instability with increasing temperature is followed in situ.

Les modules d'élasticité E et G ont été suivis au cours de la décomposition de solution solides sursaturées d'alliages aluminium–magnésium de teneurs 11%, 12,5%, 15% en poids. Les mesures effectuées en ultrasons (2 et 10 MHz) et en barreaux résonnants (70 kHz) au cours de vieillissements isothermes à différentes températures ont montré que les zones de Guinier-Preston font augmenter les modules, alors que les phases β′ et β entrainent une diminution. Dans le cas particulier des zones GP, les cinétiques de vieillissement montrent clairement l'existence de deux modes de formation distincts. Enfin la réversion des zones GP a pu être suivie in situ et a montré l'instabilité des zones au cours d'une élévation de la température.

1. Introduction

Guinier-Preston zones with ordered internal structure have been previously observed by X-ray diffraction [1], neutron scattering [2], and by electron microscopy [3, 4] in aluminium–10 to 15 wt% magnesium alloys. However little is known of their characteristics such as shape, internal order, coherence error, and volume concentration. In complement to these crystallographic studies, we are interested in the kinetics of ageing and the decomposition stages of the solid solutions, and in the conditions of the existence of Guinier-Preston zones.

Of the many experimental methods available, low angle X-ray scattering is not appropriate for studies of Al–Mg alloys, though low angle neutron scattering can be usefully carried out. However, massive specimens are required which are less readily compared with the thin specimens used in the other experimental methods such as resistivity. This type of precipitation with a high residual concentration in the matrix and a low internal concentration in the zones, is difficult to examine by experimental methods such as yield point, Portevin-Le Chatelier effect variations or magnetic susceptibility changes.

Here, we try to show that dynamical elastic moduli measurements are well suited to the study of precipitation kinetics. In the particular case of Guinier-Preston zones, our results are compared with those obtained by hardness, resistivity and electron microscopy studies.

2. Experimental

Measurements have been carried out on two experimental units. The principle of the first [5, 6] concerns the propagation of a pulsed ultrasonic longitudinal or transversal wave emitted and received by a piezoelectric transducer in a specimen having two parallel faces. Frequencies from 2 to 20 MHz are used. The round-trip time τ of the pulse in the specimen is measured by a pulse echo overlap method. The velocity of ultrasound in the material is

$$V = \frac{2l}{\tau},$$

where l is the specimen length.
If V_L and V_S are longitudinal and shear ultrasonic wave velocities, Young's modulus E and shear modulus G are

$$E = \varrho \frac{3V_L^2 - 4V_S^2}{\frac{V_L^2}{V_S^2} - 1} \quad \text{and} \quad G = \varrho V_S^2 ,$$

where ϱ is the density of the material.

The second apparatus [7] (resonant rod) uses the longitudinal resonance of a bar (the length of which is large compared to its diameter) attached at its centre. Both emission and reception systems are electrostatic transducers.

If N is the fundamental mode frequency and l the specimen length:

$$E = 4\varrho l^2 N^2 .$$

The sensitivity for the two experimental sets may attain 10^{-5}. Measurements may be performed from -196 °C to 300 °C.

It must be noticed, in the case of measurements in polycrystalline specimens, that the moduli strongly depend upon the texture of the material. Consequently results are generally presented as relative variations of moduli or ultrasonic velocities.

Specimens were prepared of three aluminium–magnesium alloys containing 11, 12.5, 15 wt% Mg, and were homogenized for 15 h at 445 °C, cooled in the furnace, and annealed for 2 h at 445 °C, then quenched in air. Water quenching of the higher concentration alloys of the massive specimens caused fracturing.

3. Changes of Elastic Moduli in Connection with Precipitation Phenomena

An aluminium–magnesium supersaturated solid solution can decompose in three stages with ageing temperature. Fig. 1 for Al–12.5 wt% Mg shows that Young's and shear moduli vary during the three stages. The specimen was a $20 \times 20 \times 20$ mm³, and ultrasonic measurements with longitudinal (10 MHz) and shear waves (2 MHz) in three perpendicular directions revealed no texture. Density is 2550 kg/m³ ($\pm 0.2\%$) and as-quenched values for E and G are:

$$E = 7.5 \times 10^{10}\ Pa , \qquad G = 2.86 \times 10^{10}\ Pa .$$

Relative variations for E and G are presented here only for the three more characteristic ageing temperatures: 20 °C for Guinier-Preston zones growth, 150 °C

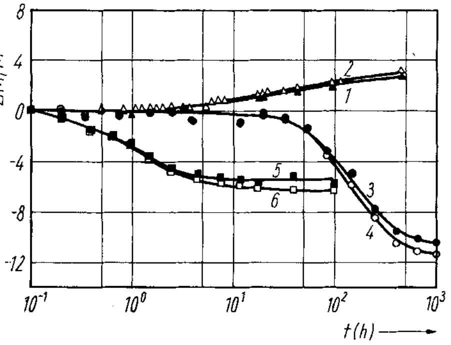

Fig. 1. Relative changes of Young's and shear moduli with ageing time at three ageing temperatures for Al–Mg 12.5 wt%. $\Delta E/E$ (curve 1) and $\Delta G/G$ (curve 2) at 20 °C, $\Delta E/E$ (curve 3) and $\Delta G/G$ (curve 4) at 150 °C, $\Delta E/E$ (curve 5) and $\Delta G/G$ (curve 6) at 300 °C

for metastable β′-phase precipitation, and 300 °C for equilibrium β-phase formation. The type of precipitation according to ageing temperature in good agreement with Bernole's results [9], has been determined by electron microscopy [8] of thin strips cut from the massive sample used for the ultrasonic measurements.

Further, the hardness of the sample increases with ageing time for each ageing temperature [8]: the relative increase at 20 °C is not achieved and reaches 20% after 1000 h. At 150 and 300 °C ageing temperatures the relative increases reach maximum values of 30 % at 600 h and 10% at 10 h.

Previous results have shown that the greatest value for hardness is reached when the β′-phase is developed and this agrees well with the present interpretation. Furthermore the hardness reaches a maximum value and the moduli their minima at the same time. However the moduli do not subsequently vary and so appear to be insensitive to precipitate rearrangement and coalescence.

In the next part, the reversion experiments and resistivity measurements confirm that the moduli variations observed during ageing at 20 °C are caused by Guinier-Preston zones growth. Thus the ultrasonic velocities measurements in specimens aged after quenching is a method of following the formation of Guinier-Preston zones, which causes an increase in the moduli, and also of following β′ or β precipitation which causes a decrease in value of the moduli.

4. Investigation of the Guinier-Preston Zones

The formation and growth of the Guinier-Preston zones will now be followed in detail with concentration of the alloys, quenching rate and ageing temperature.

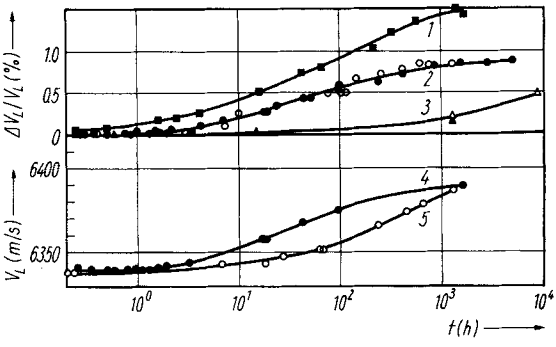

Fig. 2. Relative change of ultrasonic longitudinal wave velocities with ageing time at 20 °C: Curve 1 for Al–Mg 15 wt %, curve 2 for Al–Mg, 12.5 wt %, curve 3 for Al–Mg 11 wt %. Light points in curves 2 and 3 are for the water quenched specimens. Ultrasonic longitudinal wave velocities with ageing time at 20 °C in Al–Mg 12.5 wt % for the as-quenched specimen (curve 4) and for the reverted specimen (10 mm at 100 °C) (curve 5)

4.1 Ageing at 20 °C, quenching rate and measurement frequency dependencies

Curves 1, 2, and 3 in Fig. 2 show the relative changes of the ultrasonic longitudinal 10 MHz wave velocity with ageing time for the three air quenched alloys aged at 20 °C. The relative increase $\Delta V_L/V_L$ is very small in Al–11% Mg, about 0.2% after 1000 h, whilst reaching 1.45% for the same length of time in Al–15% Mg.

Points obtained after water-quenching in 11 and 12.5% alloys have been plotted on the same figure: it has not been possible to observe any differences between the kinetics in air or water quenched alloys. Thus, the dependence on quenching rate may be ignored and massive air-quenched specimens may be used. However this peculiarity of Al–Mg alloys will be investigated with greater precision using resistivity measurements which are more sensitive to the initial decomposition stages.

Curves 4 and 5 for 12.5% Mg alloy show the change of ultrasonic longitudinal wave velocities in a quenched specimen and in the same specimen after reversion, that is the specimen aged for 1600 h at 20 °C, then heated 10 min at 100 °C [3]. V_L in the just reverted specimen is the same as for the as-quenched one, though increasing more slowly with ageing.

Analogous measurements have been carried out using 2 MHz ultrasonic shear waves. The kinetics are the same for V_S as for V_L but $\Delta V_S/V_S$ is about twice $\Delta V_L/V_L$.

An attempt has been made to investigate the frequency dependence of these results; in that, Young's modulus measurements have been made using the resonant rod technique in the same alloys during ageing at 20 °C. The frequency is 70 kHz for cylindrical specimens of 10 mm diameter and 40 mm length.

These results are plotted in Fig. 3 and show that the relative variations of Young's modulus are identical to the variations obtained from the previous ultrasonic measurements. The experimental points from curve 2(Al–12.5% Mg) agree very well with the ultrasonic points, although the frequency ranges are quite different.

4.2 Dependence on the ageing temperature

The 12.5% Mg alloy was aged at different temperatures (Fig. 4). During ageing at 0, 20, and 40 °C, V_L increases from the very first hours, earlier as the temperature is higher. The final increase, however, seems to be higher when the temperature is lower, although the 0 °C ageing was carried out for 800 h only. Ageing at

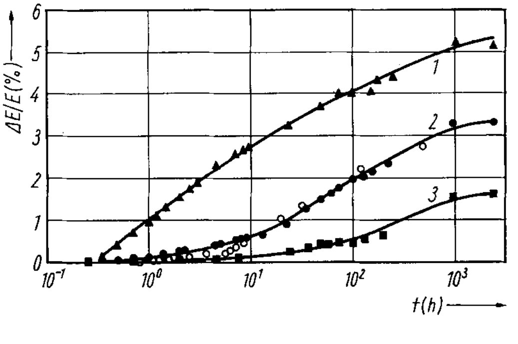

Fig. 3. Relative change of Young's modulus with ageing time at 20 °C for Al–Mg 15 wt % (curve 1), 12.5 wt % (curve 2), 11 wt % (curve 3) measured by resonant rod technique at 70 kHz. Light points in curve 2 are from ultrasonic measurements in the same specimen

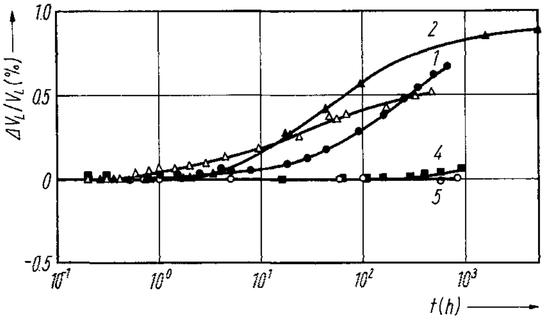

Fig. 4. Relative change of ultrasonic longitudinal wave velocity with ageing time for Al–Mg 12.5 wt % at five ageing temperatures: 0 °C (●, curve 1), 20 °C (▲, curve 2), 40 °C (△, curve 3), 60 °C (■, curve 4), and 80 °C (○, curve 5)

60 °C produces only a small increase of V_L after 600 h, and at 80 °C ageings, no variation at all is observed after 800 h. The existence of such an incubation period for temperatures higher than 40 °C has previously been shown by electron microscopy and X-ray high angle scattering experiments [1, 4].

The variations of electrical resistivity in the same alloys during isothermal ageing (Fig. 5) show the same two different domains; for ageings temperatures lower than 40 °C there is a maximum on the resistivity curves, but for temperatures higher than 40 °C, there is no maximum. These results may be compared with those of Junqua et al. [10] for aluminium–zinc solid solution decomposition; following them, the resistivity maximum should be due to a spinodal decomposition mode, and in the temperature range where the main decomposition mode is nucleation and growth, there is no resistivity maximum, but an incubation period.

Furthermore, the interpretation of high angle X-ray scattering [10] and of neutron small angle scattering experiments [2] have shown that Guinier-Preston zones in Al–Mg aged at room temperature are not randomly located in the depleted matrix; a spatial pair correlation function is necessary to explain the observed intensity curves.

In agreement with these different experimental features, we may assume that in Al–12.5% Mg alloy, the decomposition mode of the supersaturated solid solution is a spinodal one for temperatures lower than about 40 °C, and a nucleation and growth mode for upper temperatures.

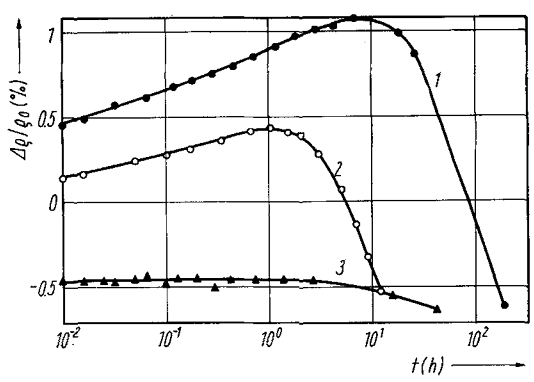

Fig. 5. Relative change of electrical resistivity $\Delta\varrho/\varrho_0$ with ageing time for Al–Mg 12.5 wt % at three ageing temperatures: 0 °C (curve 1), 20 °C (curve 2), and 40 °C (curve 3)

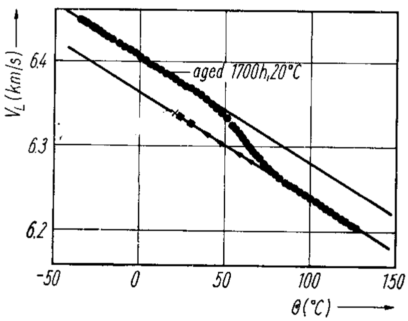

Fig. 6. Ultrasonic longitudinal wave velocity versus temperature for a specimen of Al–Mg 12.5 wt % aged 1700 h at 20 °C. × as-quenched

4.3 Reversion

In a temperature range sufficiently distant from 0 °K and also from the melting point, the elastic moduli vary linearly with temperature if no structural changes take place. Hence, the investigation of the elastic moduli of aluminium–magnesium alloys in the temperature range −50 °C to +150 °C permits the characterization of G.P. zones reversion by departure from linearity. In Fig. 6, an Al–12.5% Mg specimen aged 1700 h at 20 °C, has been cooled to −35 °C, then heated to +130 °C at a rate of 30 °C/h. G.P. zone reversion seems to be complete above 80 °C.

From −35 °C to +40 °C, V_L versus temperature is found to be linear. This corresponds to the stage in the ageing process which has not had time to change during the measurements. Above 80 °C, V_L is again linear with temperature, and this corresponds to the fully reverted stage. If the specimen is now quickly cooled down to 20 °C, the new value of V_L is the same as for the as-quenched stage (cf. Fig. 2).

The reversion of the G.P. zones seems to take place continuously from 40 to 80 °C. This belongs to the ageing of the specimen and to the rate of heating which is an important parameter for these experiments. However, the measurements confirm that G.P. zones formed in the spinodal decomposition domain are not stable when the temperature increases, particularly in the nucleation and growth domain, before the total reversion occurs.

5. Conclusion

The variations of the elastic moduli observed depend simultaneously on two factors.

Firstly the effect due to the existence of precipitates or G.P. zones in a matrix having particular values of elastic constants [12].

Then, there is the extrinsic effect due to lattice parameter and concentration, of ionic interaction etc., in the solid solution which becomes modified by the separation of the phases. This is related to another study in this laboratory [6] and requires measurements to be carried out in monocrystalline specimens at high pressure. This would enable anisotropic effects due to the texture of the polycrystalline materials to be separated and phenomena analysis to be simplified when considering C, C', and B elastic constants in monocrystals. For this reason, no attempt is made here to interprete the result quantitatively since only polycrystalline specimens have been used.

However, it has been shown that the study of the relative changes of the elastic moduli is suitable for the investigation of precipitation phenomena, especially in the case of Al–Mg alloys. It is possible to separate the different precipitation stages. By comparison with electrical resistivity measurement, the interpretation of which is still under discussion and with X-rays and neutrons scattering experiments, two different formation modes for the G.P. zones seem to appear: spinodal decomposition and nucleation and growth.

Since the technique is non-destructive and uses massive specimens, it may be employed to control the ageing stages of specimen used in other experiments, such as X-ray large angle scattering [11] or neutron scattering. Finally the method is particularly well suited to the study of the partial and total reversion phenomena.

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