EFFECT OF MICRO-ADDITION OF MAGNESIUM ON SIDE-BAND FORMATION IN ALUMINIUM-ZINC ALLOYS

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ABSTRACT

The effect of micro-addition of magnesium on the decomposition characteristics of an Al-30 at.% Zn alloy has been investigated with the help of X-ray diffraction and hardness measurements. The ternary alloy has been found to develop side bands after very long ageing at room temperature. The results have been explained on the basis of Cahn's theory of spinodal decomposition.

INTRODUCTION

IT has been known for more than two decades that some solid solution alloys exhibit special X-ray diffraction effects in the early stages of their decomposition into two phases.[1] The effect consists in the appearance of diffuse reflections, commonly known as 'side bands' on either side of the matrix Debye-Scherrer reflections. Such alloys in fact have come to be known as 'side-band alloys'.[2] Among the various models proposed to explain this phenomenon in terms of the structure of these alloys, the one proposed many years ago by Daniel and Lipson,[1] suggesting a sinusoidal variation in composition of the alloy in three dimensions having a characteristic wavelength (λ), has been supported by the recent theoretical studies of Hillert,[3,4] Cahn and Hilliard[5,6] and Cahn.[7-10]

According to Cahn's theory of 'spinodal transformation', an alloy whose composition lies between the inflection or spinodal points of chemical free energy *versus* composition curve for the alloy system (*i.e.*, points at which $\partial^2 F / \partial^2 C = 0$) tends to decompose spontaneously into solute-depleted and solute-rich regions, giving rise to a sinusoidal variation in its composition from the mean value. It has also been shown by Cahn[7,10] that because of the continuous variation in its composition in space, the alloy is elastically strained during this transformation. The elastic strain free energy associated with the alloy may then effectively stabilize it against any such composition variation until the driving force for the transformation is increased to balance the same. In other words, a certain minimum degree of under-cooling below the spinodal point is necessary before the alloy can undergo the spinodal transformation. A review of recent experimental work on side-band alloys in the light of Cahn's theory has recently been made by Wahi and Anantharaman.[11]

Considerable interest has naturally been aroused in recent times in the study of this mode of transformation. Apart from the theoretical interest, there is the expectation that this type of transformation will result in a significant improvement in properties like hardness, strength, resistance to grain boundary corrosion and particle coarsening as well as in the development of the property of super-plasticity in such alloys.

Experimental work confirming the existence of a spinodal transformation in Al-Zn alloys has been conducted by a number of investigators.[12-15] There has, however, been some discrepancy in the results. Rundman and Hilliard[12] have reported, on the basis of small-angle X-ray scattering measurements, a decomposition wavelength of 40 Å in a 22 at.% Zn alloy transformed at 60° C. Wahi and Anantharaman[13] could not, however, detect side bands in a similar alloy at any temperature below 140° C. Douglass and Barbee[14] have reported a wavelength of 100–300 Å in alloys containing 15–40 at.% Zn on transformation at room temperature and 100° C. Nuttal and Nicholson[15] have shown that such a transformation occurs only in alloys of eutectoid composition, *i.e.*, 60 at.% Zn.

The present investigations, which form part of a detailed programme of study on precipitation hardening in aluminium alloys are concerned with the influence of trace additions of magnesium (0·35 at.%) on the decomposition kinetics and side-band formation in an Al-30 at.% Zn alloy. It is relevant to recall in this connection that magnesium has been known to have a remarkable influence[16-19] on the precipitation kinetics in Al-Zn alloys and that the strongest commercial aluminium alloys are

based on the Al-Zn-Mg ternary system. An attempt is also made here to explain the absence of side bands in Debye-Scherrer patterns of high purity binary Al-Zn alloys transformed below 140° C.[13]

EXPERIMENTAL PROCEDURE

Alloy Preparation.—The binary and ternary alloys w e r e prepared from super-purity aluminium (99·999 + %) and high-purity B.D.H. zinc (99·99 + %) and magnesium (99·99 + %). Weighed quantities of aluminium were melted in a graphite crucible in an electric furnace. Required amounts of zinc or magnesium and zinc wrapped separately in aluminium foils were added to liquid aluminium. Each alloy was kept molten for 15–20 mins. at 750° C. for homogenization before pouring into cylindrical graphite moulds of 2 cm. inside dia. and 10 cm. length. The ingots were hot-forged to 0·5 cm. thick plates which were then homogenized and stress-relieved at 300° C. for 3 days. For hardness measurements, samples of 2 × 1 × 0·5 cm. were cut from the sheets. A strip was cut from the forged sheet of each alloy and rolled in several stages, with intermediate annealing at 300° C. to thin rods of 2–3 mm. dia. These were finally hot-drawn to wires of 0·25 mm. dia. for X-ray diffraction work. A careful chemical analysis showed the alloys to be within ± 0·2 at.% of the desired zinc content. No chemical analysis for magnesium content was done. However, since loss in weight of the alloy after casting was negligible, all the added magnesium was assumed to be present in the alloy.

Heat Treatment and Hardness Measurement. —The bulk specimens as well as the wire samples were solution-treated at 380° C. for one hour in an electric muffle furnace controlled to ± 2° C. and then quenched in water. Ageing treatment was carried out at room temperature (~ 30° C.).

Hardness values were determined on a Vickers Pyramid Hardness Testing Machine using a load of 5 kg., an average of 5 readings on each specimen constituting a single measurement.

X-ray Diffraction Experiments.—The wire samples were subjected to X-ray examination after the above-referred quenching and ageing treatments. An 11·4 cm. dia. Debye-Scherrer camera and nickel filtered CuK_α radiation from a Philips X-ray Generator were employed, with an average exposure time of 1½ hr. at 35 kV and 15 mA. Some X-ray investigation was also carried out, in a Philips (PW 1051) Diffracto-

meter, on bulk specimens heat-treated to show side band effects.

EXPERIMENTAL RESULTS

Figure 1 shows the room temperature (~ 30° C.) ageing curves of the binary alloy,
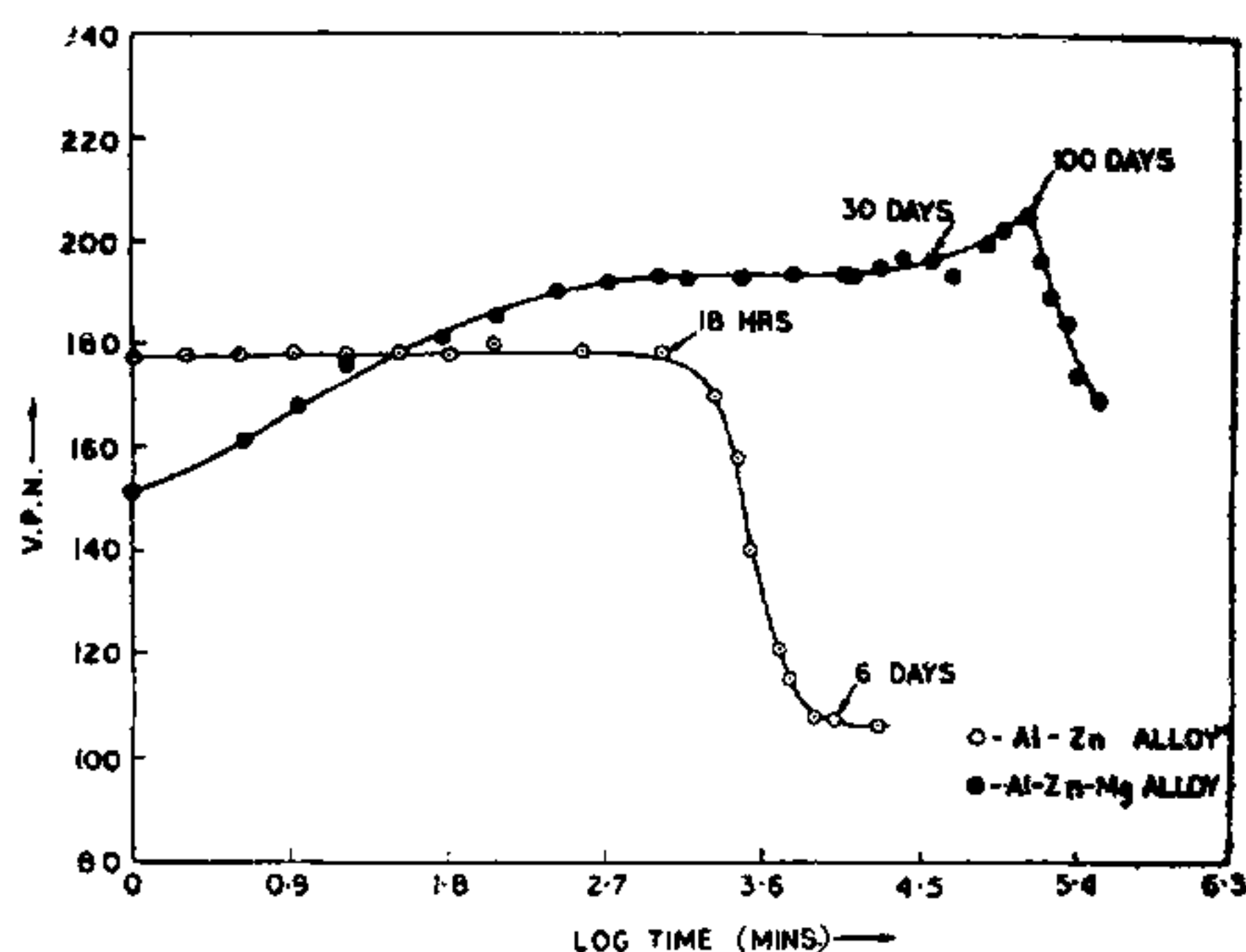

FIG. 1. Room temperature ageing curves of Al-30 at.% Zn and Al-30 at.% Zn + 0·35 at.% Mg alloys after quenching from 380° C.

viz., Al-30 at.% Zn alloy and the ternary alloy, *viz.*, Al-30 at.% Zn alloy containing 0·35 at.% Mg. The following important points are obvious :

The Ternary Alloy.—(i) The hardness of the ternary alloy increases rapidly from the as-quenched value of 150 VPN to a peak value of 190 VPN in about 24 hours. (ii) A second but much slower increase in hardness is observed in the ternary alloy after 24 hours for a period of 15 days. (iii) The hardness of the ternary alloy finally decreases slowly from the second peak value of 205 VPN.

The Binary Alloy.—The binary alloy, on the other hand, does not show any initial rapid increase in hardness. Instead, the hardness remains constant at as-quenched value of 178 VPN upto 18 hours and then falls continuously to a very low value of 105 VPN in 6 days.

The X-ray diffraction patterns taken at regular time intervals revealed the following features :

The Ternary Alloy.—(i) Reflections corresponding to f.c.c. matrix only were present for ageing times upto 4 days. (ii) Some faint zinc reflections appeared after about 5 days and increased both in number and intensity over a period of several days of ageing. (iii) Very faint side bands appeared after about 30 days of ageing and continued to be present for about 120 days. Since the bands were very

faint their photographic reproduction was not easy. A schematic representation of a typical Debye-Scherre pattern showing side bands is shown in Fig. 2. A diffractometric record of a bulk sample heat-treated to develop side bands is shown in Fig. 3. The thick curve shows
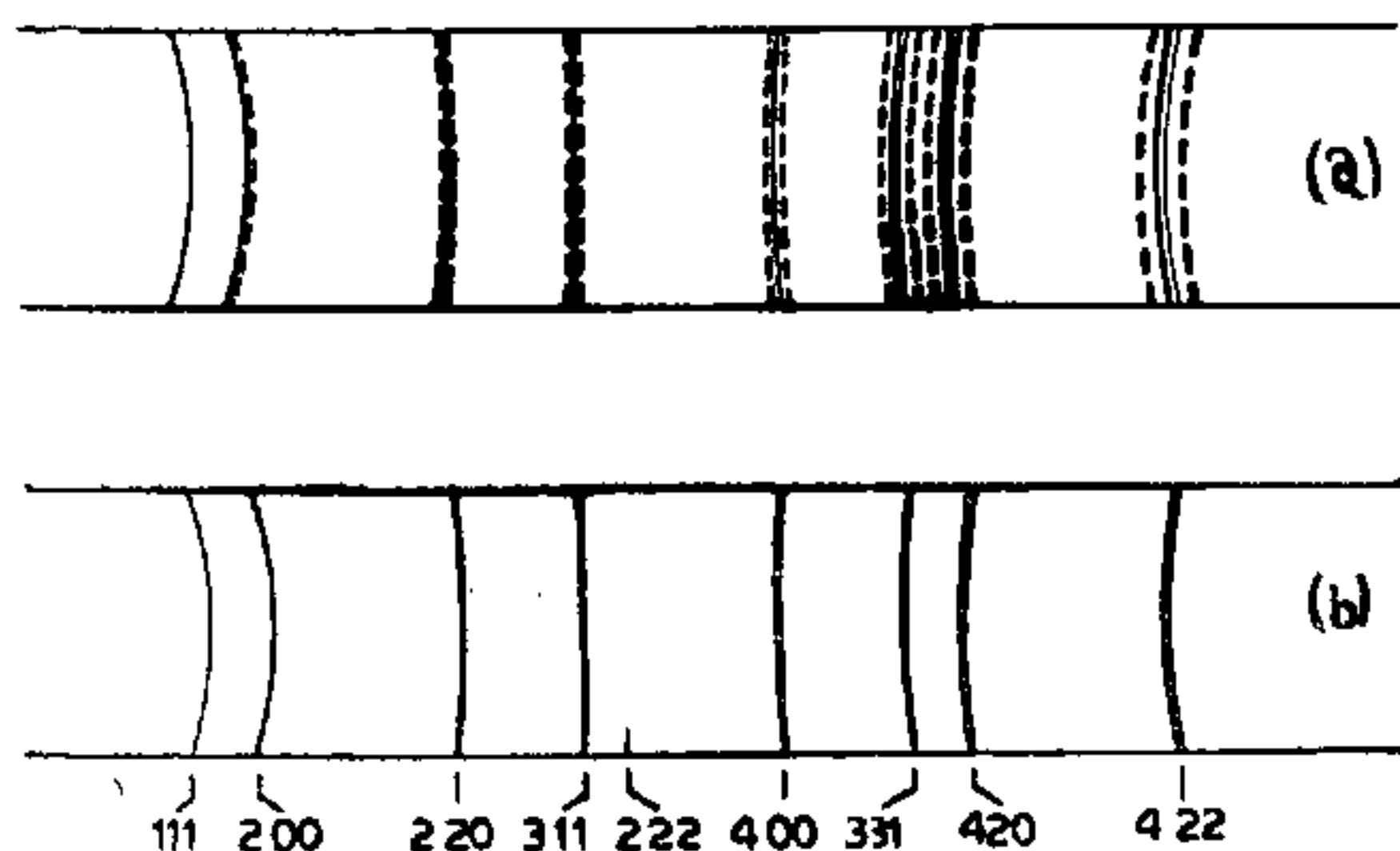

FIG. 2. A schematic representation of typical Debye Scherrer patterns : (*a*) with and (*b*) without side bands (- - - -).
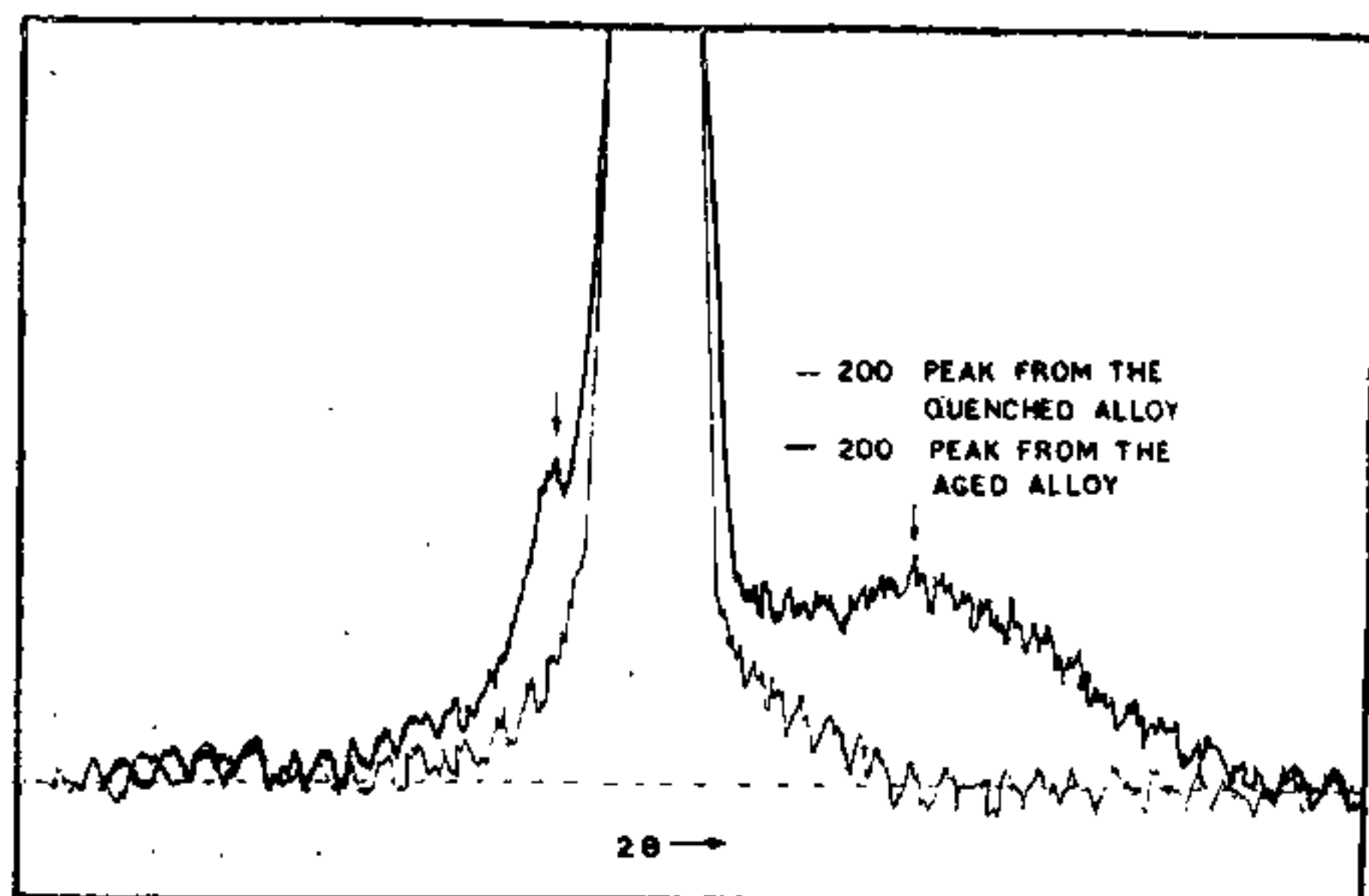

FIG. 3. Superimposition of diffractometric records from the bulk sample of the ternary alloy in the as-quenched (thin curve) and aged (thick curve) conditions. The positions of the side-band peaks are indicated by arrows.

the (200) diffraction peak from the matrix with a broad, small peak (side band) on either side. The thin curve shows the position of the (200) peak before the appearance of side bands, i.e., for ageing periods of less than 30 days. (*iv*) Matrix lattice parameter remained unchanged upto about 30 days after which it showed a gradual increase.

The Binary Alloy.— (*i*) Reflections corresponding to the f.c.c. zinc-rich matrix only were present for ageing times upto about 4-5 hours.

(*ii*) A few faint zinc reflections appeared between 6-18 hours of ageing.

(*iii*) Many intense zinc reflections made their appearance at time interval corresponding to the start of hardness fall in the corresponding hardness curve (Fig. 1).

(*iv*) No side bands were detected at any stage of ageing in the binary alloy.

DISCUSSION

It has been shown by Cahn[20] that the strength of a spinodally decomposed alloy is proportional to the wavelength of the transforming structure. For each transformation temperature, there is a characteristic wavelength which decreases with increasing undercooling and solute concentration. Once the transformation is complete, a process of competitive growth of the characteristic wavelength sets in to reduce the interfacial energy between the solute-rich and solute-depleted regions. This process is controlled by diffusion. In concentrated Al-Zn alloys, quenched from a high temperature to room temperature, the diffusion coefficient has been shown[12] to fall to the extremely low equilibrium value within 1-2 mins. of quenching. In such a case, the growth of the decomposition wavelength is expected to be negligible at room temperature. Hence the hardness, according to Cahn's model,[20] should remain constant. Further, because of the relatively fast diffusion rate of aluminium and zinc atoms in binary Al-Zn alloys and so a faster rate of spinodal transformation, the quenched alloy at room temperature may not have a single characteristic decomposition wavelength, but a spectrum of wavelengths formed at various higher temperatures during quenching. The hardness of such an alloy would, therefore, be proportional to an average wavelength which will be larger than the wavelength characteristic of room temperature. The ageing curve of the binary alloy shown in Fig. 1 is in accordance with the above reasoning.

The existence of a spinodal structure of extremely small wavelengths (40–100 Å) is also the reason why side bands could not at all be detected by Wahi and Anantharaman[13] in the Debye-Scherrer patterns of an Al-30 at.% Zn alloy aged at and around room temperature. Solute-rich and solute-depleted regions of the size of the orders of 20–50 Å cannot be expected to give rise to significant diffraction effects in Debye-Scherrer patterns.

The presence of an element like magnesium with a large binding energy[18,19] with vacancies is expected to have the following effects on vacancy distribution and migration in the ternary alloy :

(*i*) A large fraction of vacancies will be tied up with magnesium atoms in the form of Mg-Vac couples,[19] with the result that the rate of spinodal decomposition, which depends on the diffusion of aluminium and zinc, will be slower.

(ii) The fraction of excess vacancies associated with magnesium atoms will remain in solution for a long time in the form of mobile Mag-Vac couples.[10] Presence of such couples, which are, however, much less mobile than single vacancies, may be expected to cause a slow but steady and continuous growth of decomposition wavelength at room temperature.

It follows from the above argument that the ternary alloy will have a lower as-quenched hardness since only a negligible spinodal decomposition is likely to take place in it during the process of quenching. The average decomposition wavelength at room temperature immediately after quenching will then be nearer to that characteristic of room temperature and hence smaller as compared to that in the binary alloy. Because of the presence of some excess vacancies in the form of mobile Mag-Vac couples, the diffusion coefficient of zinc atoms will, however, remain a little higher than the equilibrium room temperature value for a much longer time, resulting in a continued competitive growth of the wavelength. This has been confirmed in the present work by the appearance of side bands in the ternary alloy after 30 days of ageing at room temperature. For the same reason, i.e., the continued growth of the decomposition wavelength over a period of several days the peak hardness of the ternary alloy is expected to be higher than that of the binary alloy.

One point which is very interesting and for which we are unable to offer proper explanation at present, is the much larger incubation period for the precipitation of zinc and, therefore, much longer time over which hardness remains constant at a high value in the ternary alloy than in the binary alloy. This appears to be associated with the difficulty in the nucleation of zinc in the ternary alloy. Although no definite reason can be given at present for such a behaviour, it may be related to a change in the equilibrium structure of the alloy with the addition of magnesium. According to the ternary Al-Zn-Mg equilibrium diagram,[21] the present ternary alloy lies in the phase region having the α-solid solution, zinc and MgZn$_5$ in equilibrium. Such a change in equilibrium state from a two-phase to a three-phase equilibrium is expected to change the solid solubility limit of zinc in aluminium. If the limit is extended to higher zinc content the ternary alloy will be less supersaturated with respect to zinc as compared to the binary alloy and therefore the kinetics of zinc precipitation in it will be slower.

ACKNOWLEDGMENT

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