

# STUDY OF REVERSION IN ALUMINIUM-ZINC ALLOYS CONTAINING 20 AND 30 AT.% ZINC

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## ABSTRACT

A metastable miscibility gap for G.P. zones in aluminium-zinc alloys has been established on the basis of hardness reversion studies. X-ray examination of the sequence of precipitation in these alloys has revealed the presence of a zinc-rich rhombohedral intermediate phase on ageing the alloys in the range of 200–310° C. A second high-temperature metastable miscibility loop is postulated to explain the experimental observations satisfactorily.

## INTRODUCTION

**M**ANY attempts have been made in recent years to establish the metastable equilibrium between Guinier-Preston Zones (to be referred to as zones hereafter) and their matrix in Al-Zn alloys. The results of Borelius,<sup>1</sup> Johnson *et al.*<sup>2</sup> and very recently Strongin<sup>3</sup> indicate that the metastable phase boundary lies well below the monotectoid temperature (275° C.). On the other hand, the work of Carpenter and Garwood,<sup>4</sup> Larsson<sup>5</sup> and Lasek<sup>6</sup> suggests that the boundary is obtained almost by extrapolation of the high temperature  $\alpha$ - $\alpha'$  miscibility gap (Fig. 1) to lower temperatures.

The present investigations which form part of a detailed study of the precipitation phenomena in Al-Zn alloys were undertaken by us to determine the above-referred metastable phase boundary independently through a study of hardness reversion. This technique was originally employed by Beton and Rollason<sup>7</sup> to determine G.P. zone solvus in Al-Cu alloys. The X-ray and optical metallographic techniques were also employed, wherever possible, to support the findings. Since the controversy over the position of the boundary is mainly in the composition range of concentrated alloys, we shall discuss here primarily the results on alloys containing 20 and 30 at.% Zn, although our studies were extended to alloys containing 5 and 10 at.% Zn.

## EXPERIMENTAL PROCEDURE

The alloys were prepared from super-purity aluminium (99.999 + %) and high-purity B.D.H. zinc (99.99 + %). Weighed quantities of aluminium were melted in graphite crucibles heated in an electric muffle furnace. Required amounts of zinc wrapped in aluminium foil were added to liquid aluminium and the molten alloy homogenised for 15 minutes before pouring into cylindrical graphite moulds of 2 cm. inside diameter and 10 cm.

length. The ingots were hot-forged to 0.5 cm. thick plates which were then homogenised and stress-relieved at 350° C. for 4 days. Samples (2 × 1 × 0.5 cm.) cut from these sheets were employed for hardness measurements. For X-ray diffraction studies wires of 0.25 mm. diameter were drawn from thin strips cut from the forged sheets. A careful chemical analysis showed the alloys to be within  $\pm 0.2$  at.% of the desired composition. The grain size of the alloys prior to the reversion studies was in the range of 90–120 microns.

A common treatment of quenching from 400° C. in water and ageing at room temperature (30° C.) for 30 minutes was given to every alloy specimen before studying hardness reversion at various temperatures upto the monotectoid temperature. This was done, on the basis of preliminary ageing studies, to enable the alloys to attain a constant hardness at room temperature before starting the reversion treatment. After each reversion treatment the samples were quenched in water and the change in hardness at room temperature followed for some time. The extrapolated value of hardness corresponding to zero ageing time at room temperature was used for plotting the reversion curves. All the hardness measurements were made on a Vickers-Armstrong Hardness Testing Machine using a 5 kg. load.

Wire samples for X-ray diffraction studies were directly quenched to and aged at different temperatures, as well as water-quenched and then aged at respective elevated temperatures. An 11.4 cm. dia. Debye-Scherrer camera and nickel-filtered  $\text{Cu K}_\alpha$  radiation were employed for getting the diffraction patterns. All the samples were given an exposure of 1½ hours at 35 kV and 15 mA.

The optical metallographic studies were conducted on the same samples as used for the hardness reversion studies. All the samples were electropolished and examined under a Leitz Panphot Metallograph.

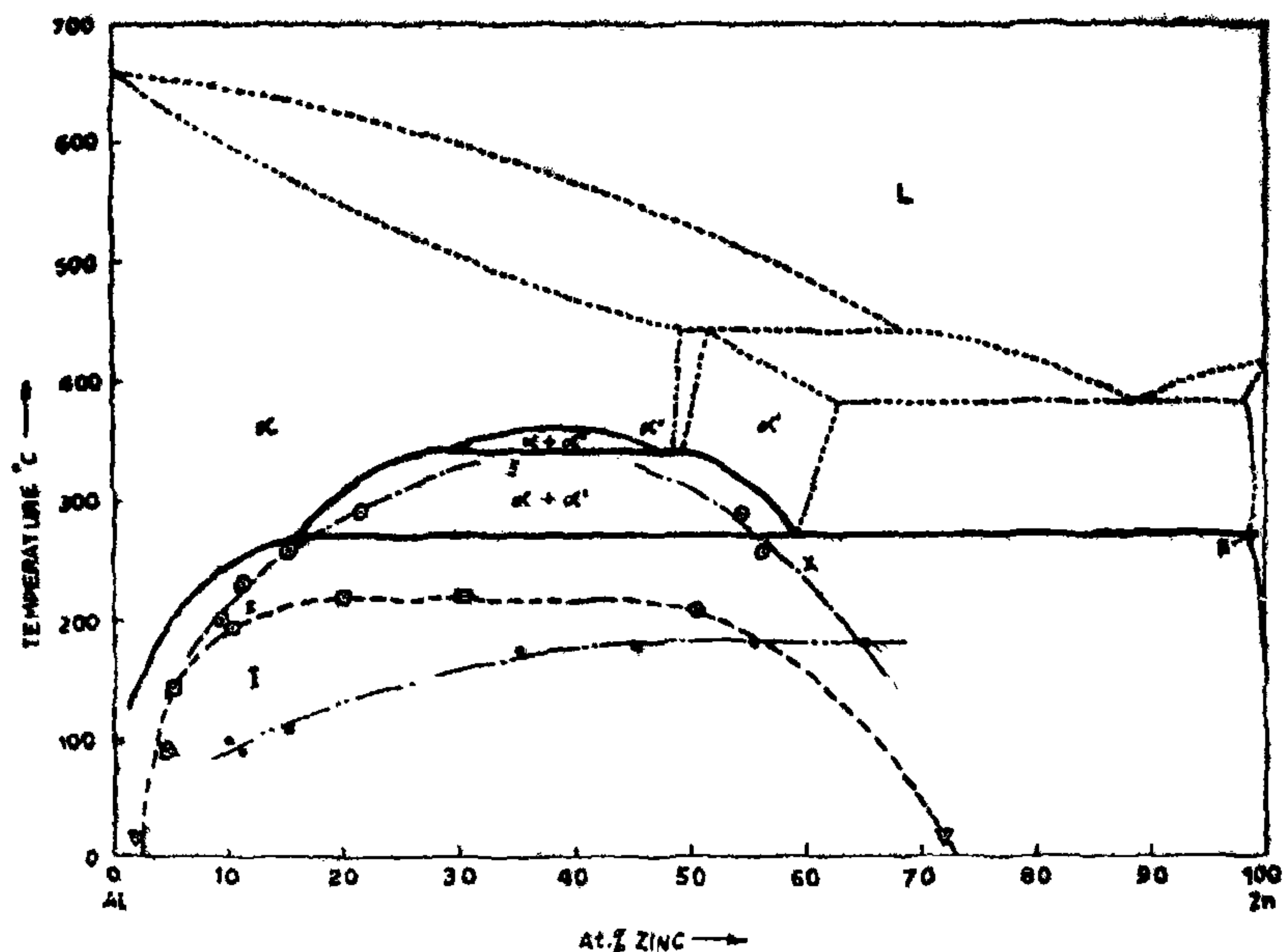


FIG. 1. Al-Zn equilibrium diagram (according to Goldak and Parr<sup>18</sup>) showing the proposed metastable miscibility loops for G.P. zones (---) and the rhombohedral transition phase (-.-.-). □ Present hardness reversion studies, ⊙ present X-ray studies, ● Borelius<sup>1</sup>, ⊗ Johnson *et al.*<sup>2</sup>, | Strongin<sup>3</sup>, ▽ Gerold and Schweizer<sup>8</sup>, Δ Panseri and Federighi<sup>9</sup>, x Simerska and Synecek<sup>13</sup>.

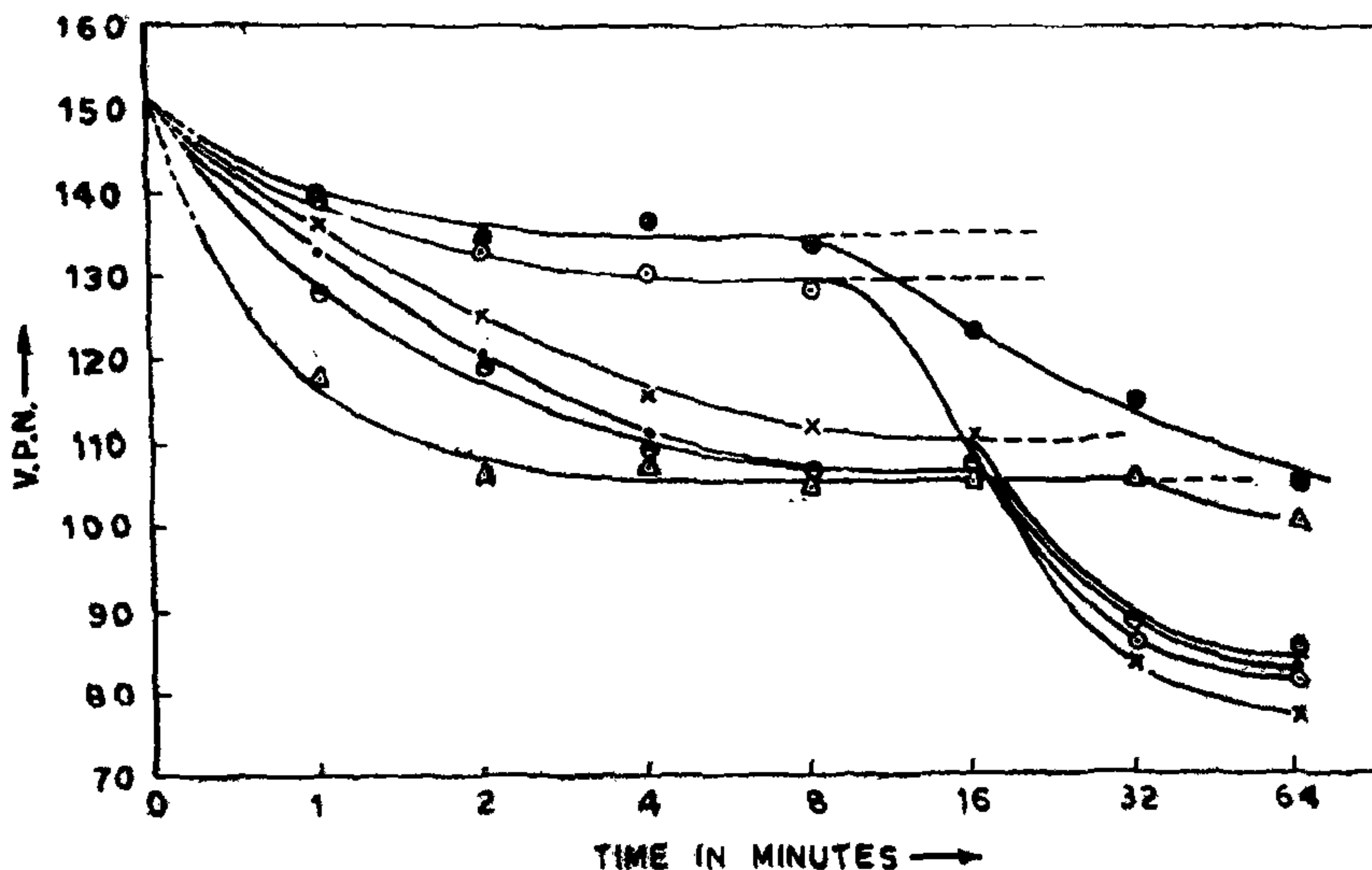


FIG. 2. Reversion curves obtained from an Al-20 at.% Zn alloy at 170° (●), 200° (⊙), 210° (x), 220° (.), 230° (◻) and 250° C (Δ).

## EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the reversion curves obtained for the 20 at.% Zn alloy at 170°, 200°, 210°, 220°, 230° and 260° C. Similar curves were obtained for the 30 at.% Zn alloy also. For both compositions, the hardness falls at a given reversion temperature in two different stages and at two different rates. An initial fast rate of fall which decreases with time (Stage 1) is generally followed by a relatively slower rate of fall (Stage 2). The former is obviously caused by the dissolution of zones formed at room temperature, while the latter is due, on the evidence of X-ray data, to heavy precipitation of the equilibrium zinc phase. Towards the end of Stage 1 the two processes seem to overlap. The value of hardness at the end of Stage 1 remains the same for reversion temperatures above 220° C. for both the alloys. This temperature is, therefore, taken to represent the upper limit of zone stability in both the alloys. Figure 1 shows the metastable miscibility loop on the basis of present investigations as well as those on 5 and 10 at.% Zn alloys (not described here) and also the work of some earlier investigators.<sup>1-3,8,9</sup> The following additional information was obtained from X-ray and optical metallographic studies on structural changes in these alloys during and after reversion at various temperatures between room temperature and the monotectoid temperature.

(1) Discontinuous precipitation of zinc at grain boundaries was found to be the major mode of decomposition in both alloys at and below 170° C. Sequential transformation of the zones to equilibrium zinc through intermediate phases, as reported by earlier investigators,<sup>10-12-14</sup> was found to be absent or negligible in this temperature range.

(2) On reversion at 200° C. and above, a zinc-rich rhombohedral transition phase was detected at time intervals roughly corresponding to Stage 1. This phase could be identified as the 'R' phase reported by earlier investigators.<sup>10-14</sup> It is relevant to note here that a considerable fall in hardness was always recorded at all temperatures in the 200-275° C. range before this transition phase made its appearance.

(3) The rhombohedral transition phase was found to form also on ageing the alloys directly quenched to temperatures in the range of 200-310° C. Zinc concentrations in the matrix and the transition phase, obtained on

direct quenching, were calculated using Ellwood's data for lattice parameters of Al-Zn alloys.<sup>15</sup> When plotted on the Al-Zn equilibrium diagram, these values seem to give rise to a second metastable miscibility loop (Fig. 1) extending well into the high temperature  $\alpha$ - $\alpha'$  miscibility gap.

(4) At time intervals corresponding to Stage 2 it was observed that the transition phase disappeared completely and heavy precipitation of zinc followed. In the alloy richer in zinc, such precipitation started much earlier and overlapped appreciably on the other two processes in Stage 1, viz., dissolution of zones and formation of the transition phase.

Considered along with the hardness data, the above results strongly suggest the existence of two metastable miscibility loops in the Al-Zn system as shown in Fig. 1. The first extending from lower temperatures to about 220° C., represents the metastable equilibrium between zones and the matrix and is in good agreement with the results of Johnson,<sup>2</sup> Gerold and Schweizer<sup>8</sup> and Panseri and Federighi.<sup>9</sup> It is also in qualitative accord with the data of Borelius<sup>1</sup> and Strongin,<sup>3</sup> although lying at temperatures appreciably higher than those suggested by their results. The second, extending into the high temperature  $\alpha$ - $\alpha'$  miscibility loop and in partial agreement with the conclusions of Carpenter and Garwood,<sup>4</sup> Larsson,<sup>5</sup> Lasek,<sup>6</sup> Cahn<sup>16</sup> and Rundman and Hilliard,<sup>17</sup> represents the metastable equilibrium between the rhombohedral transition phase and the matrix. The two loops overlap around 170-220° C. contributing to the observed greater complexity of the precipitation process in this temperature range, as also its sensitivity to the thermal history of the samples under investigation.

We believe that it is possible to explain all our observations and most of those of earlier investigators on reversion in Al-Zn alloys more satisfactorily than hitherto on the basis of the above-mentioned two metastable miscibility loops. It is worth recording in this connection that the investigations of Strongin<sup>3</sup> on an Al-12 at.% Zn alloy have also shown the existence of two different metastable phases. One, identified as a transition phase, has been shown to form around 210-215° C., while the other, identified as zones, exists upto around 146-157° C. These temperatures are slightly lower than those obtained in the present investigations, but definitely suggest the existence of two metastable miscibility loops.

On re-heating alloys, quenched to room temperature and aged at that temperature to produce zones, to temperatures in the range of 170–220° C., some of the zones get dissolved in accordance with the low-temperature miscibility loop. The remaining zones grow further and are able to nucleate the transition phase in accordance with the high-temperature miscibility loop. The expected shift in equilibrium also occurs on reverting the alloys at temperatures above the lower miscibility loop, i.e., at temperatures above 220° C. However, the question still remains open whether at these high temperatures dissolution of all the zones takes place or the larger zones transform to the rhombohedral phase. Further, there is no certainty about the mode of precipitation of zinc in these concentrated alloys on reversion above 170° C. It may form sequentially as suggested by some earlier investigators<sup>10,12–14</sup> and/or by discontinuous and continuous precipitation at grain boundaries and lattice defects.

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## RADIOCARBON DATES OF SOME CHALCOLITHIC SAMPLES

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### ABSTRACT

Radiocarbon dates, given here, were measured by counting methane in gas proportional counters. The  $C^{14}$  dates place the beginning of the Black-and-red Ware of Chirand (Bihar) to 8th-9th century B.C., the West Bengal Black-and-red Ware being still earlier. Kayatha Culture has been dated to ca. 1900 B.C.

**R**ADIOCARBON dates of some samples from the excavated Chalcolithic sites of Chirand, Eran, Mahisdal, Kayatha and Sonagaon, are presented in this report.

The samples were given the usual pretreatment, wherever possible, for the removal of extraneous carbonates and humic acid. Visible rootlets were picked manually. The samples were counted in the form of methane in gas proportional counters. For modern reference standard 95% activity of the N.B.S. oxalic acid was used. Detailed procedures have been described by us in earlier papers (Kusumgar *et al.*, 1963; Agrawal *et al.*, 1965).

All dates given below are in years B.P. To convert them to A.D./B.C. scale, 1950 should be used as the reference year. Each sample has two dates: the first one is based on the half-life value of  $5568 \pm 30$  yrs.; the second date, given within brackets, on  $5730 \pm 40$  yrs. For all intercomparison dates based on the same half-life value should be used.

### GENERAL COMMENT ON DATES\*

From Chirand, the date TF-444,  $2665 \pm 105$ , presented here, is in the series of TF-334,  $2795 \pm 125$  and TF-336,  $2715 \pm 100$  (Agrawal *et al.*, 1966)—all internally consistent within one standard deviation. These dates place the beginning of Black-and-red ware in Chirand to 8th-9th century B.C. The Black-and-red ware of Bengal antedates that of Bihar, as indicated by Mahisdal dates TF-390, -391 and -392, given below. TF-445 from Chirand is a wood sample from a natural pit from which a large number of microliths, unassociated with any ware, were reported and hence this date should not be used to date the Black-and-red ware of Chirand.

The  $C^{14}$  dates from the earlier excavations from Kayatha had shown some scatter. Therefore more samples were collected under

\* For discussions the dates based on the half-life value of 5730 yrs. have been used.