Metastable solvus curves in Al–Zn alloys

Part 1 The Guinier–Preston zones

K. G. SATYANARAYANA
Materials, Glass and Ceramics Division, Regional Research Laboratory, (CSIR), Trivandrum 695 019, Kerala, India

Reversion studies have been carried out on Al–4, 8 and 12 at % Zn* alloys through electrical resistivity measurements. The critical reversion temperatures were determined as 103, 162 and 183° C, respectively. Using these values along with earlier results, the solvus for Guinier–Preston (G–P) zones has been arrived at. The results hitherto obtained on the metastable equilibrium between G–P zones and the matrix in Al–Zn alloys have been discussed in the light of the new solvus.

1. Introduction

It is now generally accepted that decomposition of supersaturated solid solutions may occur in stages and be influenced by factors such as heat-treatment, ageing temperature (T_a), ageing time (t_a), alloy composition and the nature of the decomposition products [1]. During the last two decades, the aluminium–zinc (Al–Zn) system has aroused considerable interest among metallurgists and materials scientists because of the complexities of the precipitation process in its aluminium rich alloys and also because of its importance in developing high strength light alloys. Further, the possible existence of more than one miscibility gap (Fig. 1) in the Al–Zn system has rendered unequivocal interpretation of experimental data in this system extremely difficult. It is therefore not surprising that Al–Zn alloys have been the subject of frequent and intensive study in recent years [2–55]. It is also well known that metastable equilibrium studies in alloy systems are important in selecting heat treatment steps to develop alloys needed for specific usage. Thus, for example, in the case of Al–Zn it has been found [11] that with a small addition of copper, Al–40 to 60 wt % Zn alloys can be used as bearing materials if they are heat treated in such a way that the alloy undergoes spinodal decomposition.

Considerable confusion existed concerning the location of the peak of metastable solvus for Guinier–Preston (G–P) zones in the Al–Zn alloy system as is evident from Fig. 1. This has been critical reviewed elsewhere [12–14]. However, it was Anantharaman and Satyanarayana [12] who established for the first time that two metastable solvus curves exist in the Al–Zn system; one for the G–P zones and the other for the transition (R) phase. They also explained the possible formation of G–P zones and the R phase by spinodal decomposition. Since then, a number of investigations have been carried out [14–35] including those based on liquid quenched alloys to study the structural changes in the Al–Zn system. Some of these studies [17, 20, 28, 33, 35] deal with the position of the metastable solvus curve for G–P zones and the location of its peak conforming to the one established by Anantharaman and Satyanarayana [12]. Similarly, the existence of two metastable solvus curves has been convincingly confirmed through transmission electron microscopy (TEM) studies [14].

There is another recent investigation [35] on the metastable phase boundary for G–P zones in Al–Zn alloys through a hardness reversion technique using pure, commercial aluminium. It has been concluded that the impurities do not affect the solvus of the G–P zones and the stability of zones is governed by the metastable phase boundary much below the monotectoid temperature. There are also some investigations on the reversion

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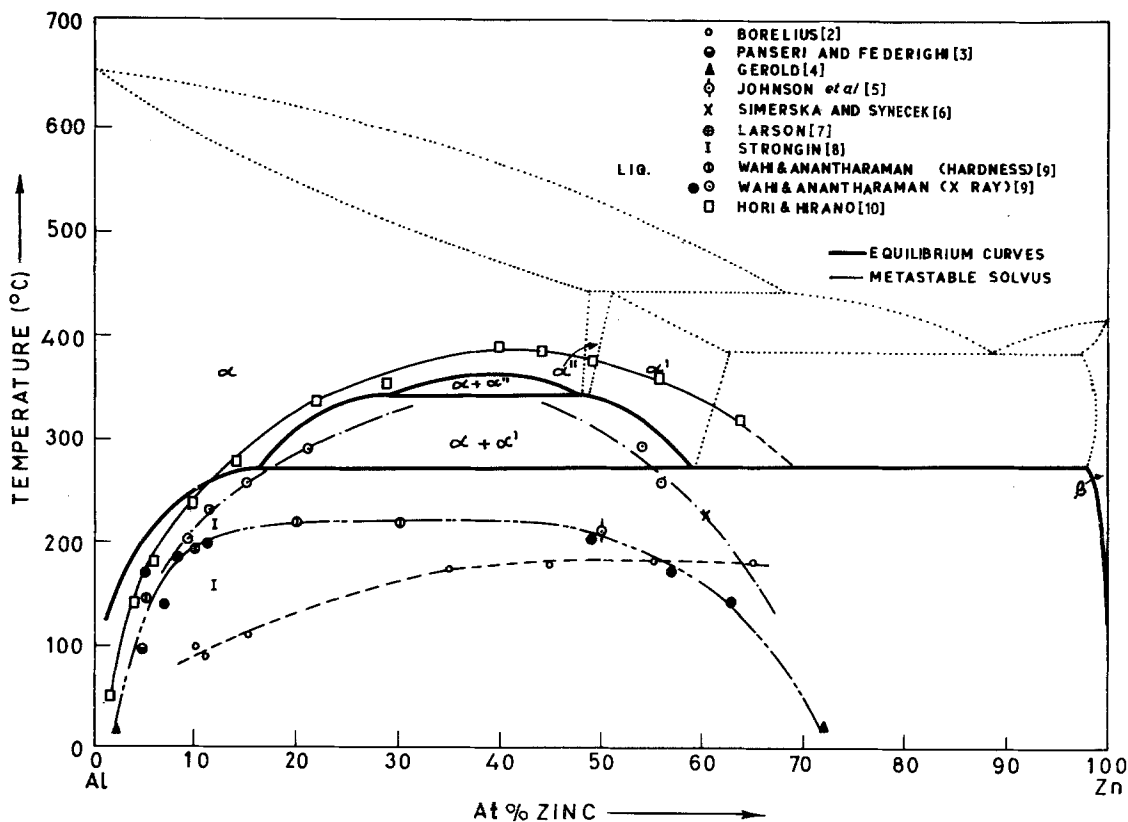*Composition is always expressed in atom percent unless otherwise stated.

TEMPERATURE (°C) →

700

600

500

400

300

200

100

0

○ BORELIUS [2]
◑ PANSERI AND FEDERIGHI [3]
▲ GEROLD [4]
◊ JOHNSON *et al* [5]
X SIMERSKA AND SYNECEK [6]
⊕ LARSON [7]
I STRONGIN [8]
◐ WAHI & ANANTHARAMAN (HARDNESS) [9]
●◉ WAHI & ANANTHARAMAN (X RAY) [9]
□ HORI & HIRANO [10]

LIQ.

━━ EQUILIBRIUM CURVES
── METASTABLE SOLVUS

α

α + α"

α"

α'

α + α'

β

I

I

0   10   20   30   40   50   60   70   80   90   100
Al   Zn

At % ZINC →

Figure 1 Phase diagram of Al–Zn system showing single metastable solvus curve for both G–P zones and the transition phases obtained by various investigations.

phenomenon through resistivity measurements [2, 3, 7, 36–38, 56], but all these studies have concentrated mainly on the influence of either prior ageing temperature or ageing time on the re-ageing process. None of these investigations has attempted to arrive at the solvus for the G–P zones. Also, not more than one or two techniques have been used in many cases and further attention has been confined to limited composition ranges. Obviously, results of any research group can be considered reliable only when several techniques are employed leading to the same conclusions. It is the purpose of the present investigation to re-examine the reversion phenomenon in the polycrystalline specimens of Al–Zn alloys to throw more light on the phenomenon and to resolve the conflicts about the location of the miscibility gaps thereby leading to a more satisfactory explanation of the observed facts than hitherto available. Three techniques, namely small angle X-ray scattering (SAXS), TEM and electrical resisitivity measurements have been utilized in the investigation of Al–4 to 35 at % Zn alloys in the present study. Results obtained by the first two techniques have already been

published elsewhere [12, 14, 32]. The present paper reports the results of the resistivity study. Based on the present study an attempt has also been made to analyse the results of earlier investigations.

2. Experimental procedure
2.1. Preparation of alloys
Alloys of composition 4, 8 and 12 at % Zn were prepared as described elsewhere [39] using super purity aluminium (99.999+%) and high purity zinc (99.99+%). They were homogeneized at 400° C for one week. After forging and rolling, wires of 0.70 mm diameter were prepared from each alloy as described earlier [40]. In order to relieve the rolling and forging stresses, the wires were homogeneized for a few hours at 300° C before electrical resistance measurements were made.

2.2. Heat treatment and resistance measurement
The wire samples of length 25 cm, were prepared as described earlier for the measurement of electrical resistance [40]. They were solution heat treated for 1 h at 400° C (each time before rever-
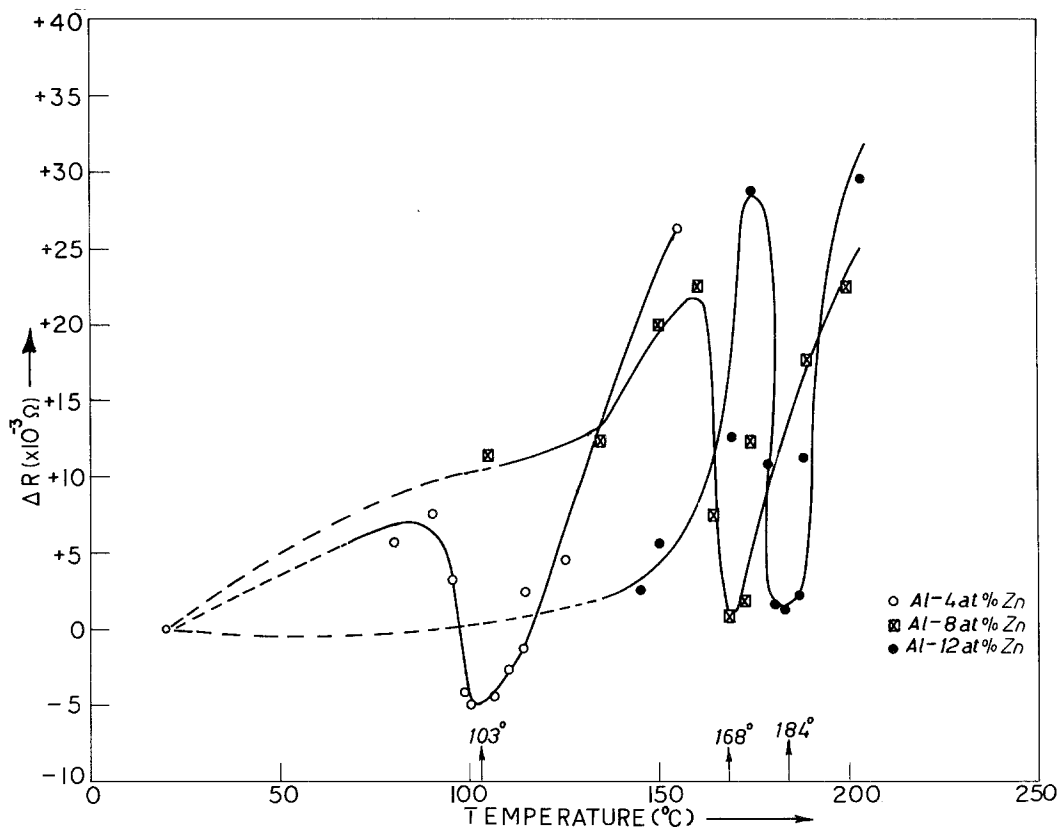
Figure 2 Plots of change in electrical resistivity for alloys Al–4, 8 and 12 at % Zn against reversion temperature.

sion treatment was given) in an electrically heated muffle furnace controlled to ± 2° C. The specimens were then quenched into water, aged at room temperature for 30 min. This time of 30 min was found to be sufficient for the zones to grow to a size showing constant hardness [9] and constant resistance from the present investigations. The stabilization of the specimens was ensured as described earlier [40]. Then the samples were heat treated in the temperature range 80 to 220° C in steps of 10° C in high temperature oil/salt baths whose temperatures were controlled to ± 1° C. The reversion treatment was for 5 min at each of the above temperatures. The samples were finally quenched in water and kept in a bath maintained at 0° C with intermediate dips in acetone.

Measurement of resistance was carried out at 0° C using Kelvin's double bridge before and after reversion treatment. The difference between these values is designated as ΔR.

3. Results and discussion
3.1. Resistivity study
Fig. 2 shows the reversion characteristics for the binary Al–Zn alloys studied in this investigation.

This constitutes ΔR (on an arbitrary scale) against reversion temperature. The following are the salient features:

(1) An increase in resistance upto a certain reversion temperature (i.e. 90, 160 and 175° C for the alloys containing 4, 8 and 12 at % Zn, respectively) was observed in all cases.

(2) In each case, a marked, sharp fall in resistance was observed above these temperatures thus resulting in critical reversion temperatures i.e. 103, 168 and 182° C for the three alloys, respectively.

(3) Above these critical temperatures, a continuous steep increase in the value of resistance was observed in each case.

The results described above can be understood in terms of current ideas on reversion. The G–P zones formed in alloys at room temperature attain a certain size. After reversion at various temperatures, the solute atoms are dispersed as after quenching, but with a new rate of formation of zones which is slow due to rapid annealing out of vacancies at the reversion temperature. Now, with the rise in temperature, the size of zones increases until it reaches a critical size, while the number of zones decreases. Above a certain temperature,

the zones which have reached a critical size either begin to grow or dissolve, depending on the reversion temperature, with fast diffusion of solute atoms from the zones to the matrix. The number of zones at the beginning and the rate of their dissolution beyond the critical size depends on the concentration of the alloy i.e. the higher the solute content of the alloy, the more will be the number of zones and the more rapid will be their growth or dissolution at higher temperatures once the zones reach a critical size.

According to Gerold [41], the resistivity of an alloy at any ageing temperature consists of two terms; one of which is due to structural changes taking place in the alloy and the other due to the scattering effect of conduction electrons at the zone boundaries. The first term included resistivities of both zones and depleted matrix. While this is a function of long-range order, it is independent of zone size. The second term is a function of the size of the zones. With increasing temperature, the zinc content in the zones will also increase. All these factors may contribute independently to the increase in resistivity upto a certain temperature at which the zones reach a critical size in the alloy. At temperatures above these, at which the zones reach a critical size, the zones grow larger in size or dissolve, thus resulting in a decrease in the contribution to resistivity from the zones. Finally, at the critical reversion temperatures, the zones dissolve completely resulting in a resistivity minimum.

Thus, the observed temperature 103, 168 and 182° C are the upper limits of stability of the zones in the alloys under investigation and constitute the point of intersection of the composition vertical with the metastable phase boundary.

Negative values obtained in the above cases may be explained as follows: After the complete dissolution of zones at the indicated temperatures, the value of resistance is lower than that of the initial value (which represents the resistance offered by G–P zones which have grown up to their critical size at room temperature). After reversion at these temperatures, there will not be any contribution to resistance from zones. This makes the value of resistance lower than that for the stabilised G–P zones, hence the negative values of ΔR.

Further increase can be attributed to the formation of a transition phase or precipitation of zinc.

3.2. Metastable solvus for G–P zones

Fig. 1 shows the single miscibility gap hitherto used extending upto $\sim 340^{\circ}$ C. The critical temperatures obtained in the present investigations including those obtained from SAXS and TEM work [12, 32] along with those obtained by earlier workers based on hardness, electrical resistivity and SAXS studies, are used to derive the new metastable solvus for the G–P zones and is shown in Fig. 3. More data for the new solvus curve has been obtained from the SAXS intensities measured by Zuern [43] as well as by Bonfiglioli and Guinier [44] for the fresh calculations. Also the data obtained from the resistivity reversion technique on Al–20 at% [42] and the recent hardness reversion technique [35] have also been included. As can be seen from Fig. 3, this new solvus extends from as low a temperature -50° C to $\sim 225^{\circ}$ C, but there is sufficient data between room temperature and 200° C. In all these cases evidence for G–P zones is available from direct quenching. However, there are only a limited number of investigations above 200° C locating the gap around 225° C [5, 9, 17, 35, 49]. As already pointed out [49], no side bands were observed above 230° C in Al–20 and 30 at% Zn alloys even for the shortest ageing times of a few seconds. Let us now see why some of the earlier results [2, 5, 8, 50, 51] are omitted in the present calculations. Values obtained by Borelius [2] are omitted in accordance with earlier investigations [2, 9, 11, 38, 47, 52]. Lasek's [50, 51] values, in our considered view, pertain to the formation of the partly coherent R phase and not to the fully coherent G–P zones as pointed out earlier [12]. The tensile property study [5] is inconclusive due to the fact that it is based only on one alloy and gives a range of temperatures over which the complete dissolution takes place. Also, for the latter reason, the results of Stongin [8] can be neglected. Further, reversion studies on zinc alloys [12] also concluded that the peak of the solvus is around $\sim 225^{\circ}$ C. Some recent results [17–21, 28] obtained on G–P zone solvus in Al–Zn alloys through SAXS, magnetic susceptibility measurements and calorimetric studies, conform with the new solvus arrived at in the present investigations. However, some data obtained by the hardness reversion technique [35] do not fall on this new curve. The difference may be due to the impurities (silicon and iron) present in the commercial aluminium used for the investigation.
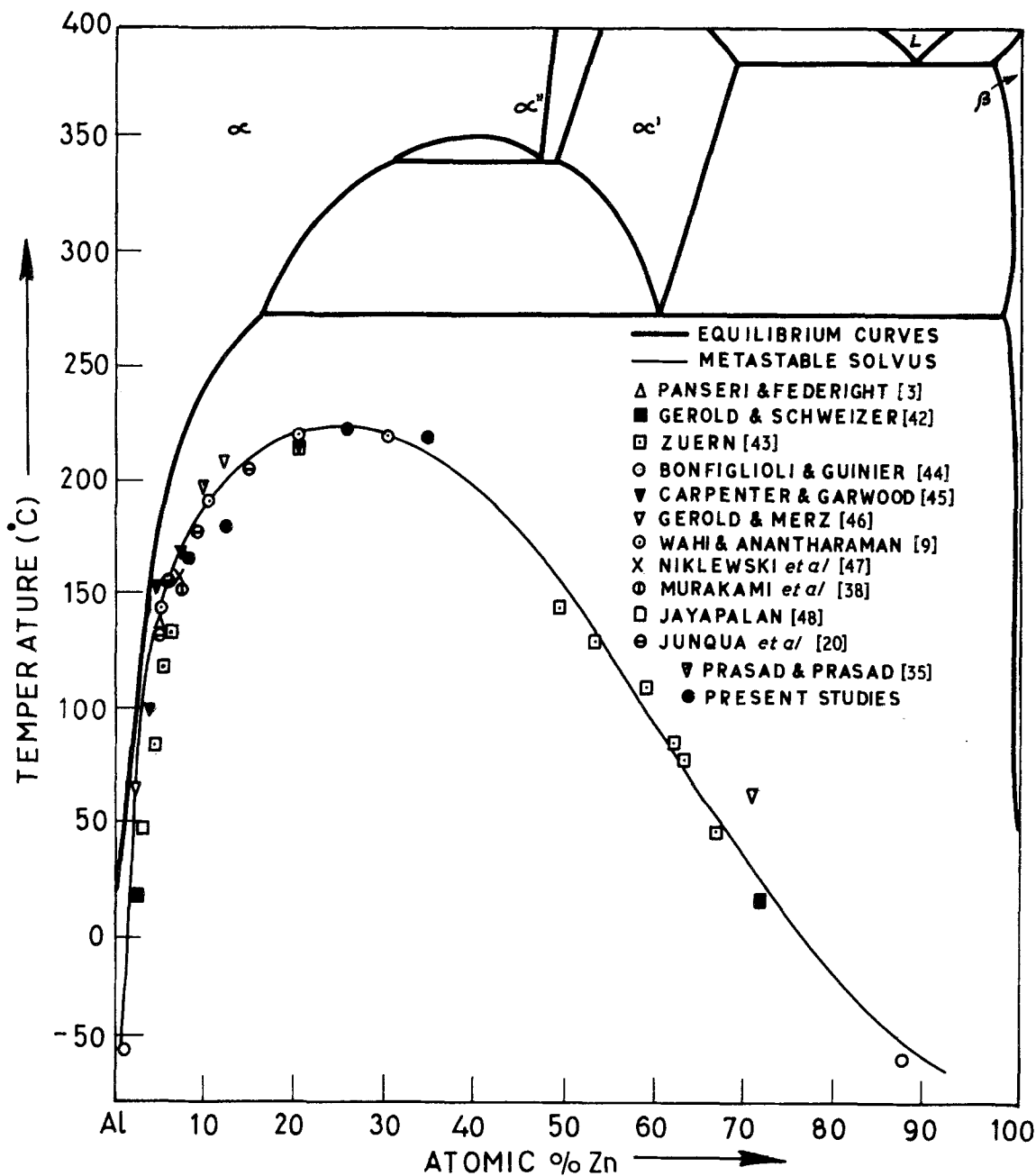
Figure 3 Metastable miscibility gap for G–P zones in the Al–Zn system.

Another point to be noted is that the curves flatten around ∼ 220° C above ∼ 1 at% Zn content over a certain range (Fig. 3). This has also been observed by other investigators [9, 35]. This may perhaps be due to the fact that above a certain percentage of zinc (∼ 18 at% Zn) whatever the composition of the alloy may be, the excess zinc precipitates out simply on quenching from high temperature. Such a conclusion is in accordance with earlier X-ray studies [34, 53, 54] made

on concentrated Al–Zn alloys. Thus, zinc content above this critical value does not contribute significantly to further changes in the mechanical and physical properties of the system. This is clear from the present work and also from earlier investigations [9, 37, 49, 52]. It is also in agreement with Larsson's observations [7].

Finally, it can be seen that the new solvus slopes towards the Zn-rich side of the diagram between its maximum at 225° C and low tempera-

tures. This may be due to free energy at these temperatures more closely approaching that of the terminal solid solution [1]. The spinodal mode of transformation observed in the Al–Zn system can be explained in the light of the new solvus curves (see Part 2, [55]).

4. Conclusions

Critical reversion temperatures for Al–4, 8 and 12 at % Zn alloys are found to be ~ 103, 168 and 182° C, respectively. These values along with those obtained by other investigators have been plotted to arrive at a new metastable solvus curve for G–P zones in the Al–Zn alloy system. This solvus satisfactorily explains many of the observations made so far concerning G–P zones in the Al–Zn system.

Acknowledgement

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