

Metastable solvus curves in Al-Zn alloys

Part 2 *The transition phase*

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Variation of the lattice parameter with zinc content in the Al-Zn system has been investigated using Al-4 to 30 at % Zn alloys. These data, along with earlier data have been fitted into a curve using the least square method. Lattice constant data on the transition (R) phase observed in Al-30 at% Zn alloy have been obtained. From these and the earlier work, zinc content in the R phase and the matrix have been evaluated and new metastable solvus curves for the R phase has been arrived at. On the basis of this, a critical analysis of all the data so far available on the solvus curves has been made. Finally, different modes of precipitation and reversion phenomenon in the Al-Zn system observed hitherto has been discussed in the light of the new metastable solvus curves.

1. Introduction

A number of investigations have been made from time to time on the aluminium-zinc (Al-Zn) system through measurements of hardness, electrical resistivity, X-ray diffraction, small angle scattering X-ray (SAXS), transmission electron microscopy (TEM) and other techniques to find the probable modes and sequence of precipitation [1]. These have been reviewed critically elsewhere [1, 2]. These studies have led to the discovery of two transition phases whose existence and role in property changes in this alloy system have been confirmed from time to time. Zinc contents in these transition phases have been calculated from X-ray diffraction studies using the data of Ellwood [3]. On the basis of these some analytical studies [4-7] have also been made. Many of these studies have assumed only a single miscibility gap for Guinier-Preston (G-P) zones and the transition phases (see Fig. 1 of [8]), until a second miscibility gap was postulated [7] for the transition phase. However, in all these calculations, there seems to be a lack of proper lattice constant data for these phases and an inaccurate plot of variation of lattice parameter with zinc content, as pointed out earlier [7]. So, there seems to be some controversy about the composition of the transition phases.

Further, appearance of side bands in some Al-Zn alloys [9, 11] with higher zinc content and their formation being attributed to spinodal

decomposition [11] has been criticized [12, 13]. The interpretation of side bands of $(200)_{Al}$ as $01\bar{1}2$ reflections of the R phase has been made in the later investigation. Also, some of these investigators [9-20] have reported the occurrence of transition phases when the alloys were quenched directly from temperatures greater than $160^{\circ}C$.

From the above, it becomes clear that in spite of the extensive work done in various laboratories considerable confusion still exists concerning the possible existence of a second miscibility gap and hence on the mode of decomposition and the stability of the transition phases. Therefore, it was decided to resolve some of these ambiguities and to throw light on the proper understanding of the metastable equilibrium in the Al-Zn system. The present investigation which forms the second part of the study was undertaken to resolve some of these ambiguities and to throw light on the proper understanding of the metastable equilibrium in the Al-Zn system. X-ray diffraction results obtained on a number of Al-Zn alloys are reported.

2. Experimental procedure

2.1. Preparation of alloys

The composition of the alloys used in the present study are listed in Table I. The procedure for the preparation of alloys was the same as described earlier [8]. Alloys were homogenized at $400^{\circ}C$ for

TABLE I Composition of the alloys used in the present investigations

Number	Alloy composition (at%)
1	Al-4 Zn*
2	Al-8 Zn*
3	Al-10 Zn†
4	Al-12 Zn*
5	Al-16 Zn†
6	Al-20 Zn†
7	Al-25 Zn†,‡
8	Al-30 Zn†
9	Al-35 Zn†,‡

* Use for both lattice constant data and resistivity measurements [8].

† Used only for lattice constant data and TEM [1].

‡ Used for SAXS work [1, 51].

one week after forging and the final process of wire drawing.

2.2. Heat treatment

Wire samples of binary alloys used for lattice constant data evaluation were solution heat treated for three weeks at 400°C to establish equilibrium as reported by Ellwood [3]. They were then quenched into water.

Wire samples of Al-30at% Zn alloy were solution heat treated at 400°C for 1 h and directly quenched to 200 and 245°C and aged for 16 and 10 min, respectively. They were then finally quenched into water before using for X-ray diffraction work.

2.3. X-ray diffraction studies

Debye-Scherrer patterns were obtained of all the alloys using a 11.46 cm diameter camera and filtered CuK α radiation. Three patterns were obtained using each sample under identical exposure conditions for 1.5 h at 35 kV and 15 mA.

3. Results and discussion

The Debye-Scherrer patterns of the binary alloys in the as-quenched condition showed only reflec-

tions due to matrix. From these measurements accurate lattice parameters were obtained using the Nelson-Reley method (Table II). A lattice parameters against zinc content plot was then prepared using the least square method from both the present investigations and previous data [3, 21-23] and this is shown in Fig. 1.

Extra reflections were observed in the powder patterns at low angles near the matrix reflections in Al-30at% Zn alloy. These seem to correspond to the transition rhombohedral phase. The d values and accurate lattice parameters were evaluated for both the matrix and the R-phase at 200 and 245°C and are shown in Table III.

Taking all the data available for the R-phase, calculations have been carried out to give accurate lattice parameters. On the basis of the plot of lattice parameter against zinc content (Fig. 1), the zinc content both in the matrix and and R-phase has been evaluated from the present study as well as from earlier work. These values are listed in Tables IV and V. In the case of the R-phase, the lattice parameter of an fcc cell equal in volume to the triple hexagonal cell of the R phase is calculated in accordance with earlier work [7]. These zinc contents were then plotted on the Al-Zn equilibrium diagram of Goldak and Parr [24] to represent the metastable phase boundary for the R phase and is shown in Fig. 2. Also, the data of Lasek [32-35], which were earlier considered as that of G-P zones, as well as those of Ardell *et al.* [19] have also been included in the present study. These conform to the new solvus curve. It can be seen from the figure that the values listed A in Table V and some of those listed B are used in arriving at the new solvus. The values of Wahi and Anantharaman [10] and those of Carpenter and Garwood [17, 18] deviate very much. Omission of some of the values in list B (table V) can be accounted for as follows.

In some cases [17, 18, 30, 36] the lattice parameters for both the R phase and the matrix have been taken to be the same, contrary to the real situation as can be seen from the deviation of the axial ratios due to greater rhombohedral distortion [7]. In some other cases [26-29], a range of temperatures but not the correct ageing temperature is mentioned. Also, as pointed out by Anantharaman [7], 75°C can not be taken as the temperature of formation [4, 5] of the R-phase because it might have formed during the quenching operation itself. There is also evidence [25-

TABLE II Lattice parameters of Al-Zn solid solutions (at 25°C)

Composition (at%)	a (Å)
4.5	4.0460
8.0	4.0432
10.0	4.0420
12.0	4.0398
16.0	4.0358
20.0	4.0320
30.0	4.0290

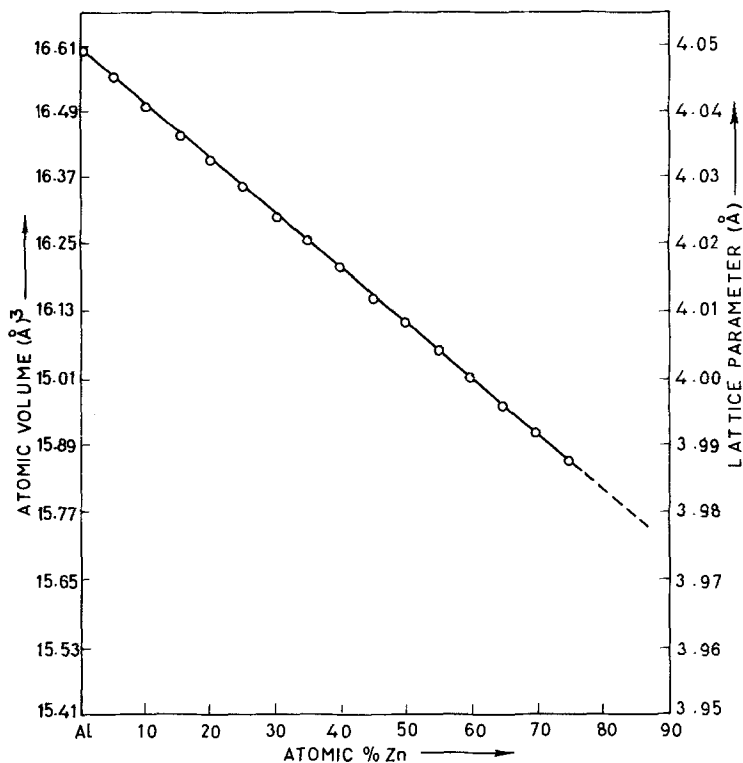


Figure 1 A plot of lattice parameter against zinc content in the Al-Zn system.

29] for the formation of this phase during slow cooling. Thus, consideration of 75° C as a temperature of formation of this phase may be ruled out but it may, however, refer to the temperature of decomposition. Moreover, from Fig. 2, it can be

seen that the new solvus from the transition phase extends to as high a temperature as ~ 340° C and turns towards the Al-rich side of the phase diagram at lower temperatures, in accordance with earlier suggestions [7]. For comparison, it may be

TABLE III *d* values (in Angstroms) of the R-phase reflections calculated from the X-ray diffraction patterns in the present investigations and those of Carpenter and Garwood [17, 18] and Wahi [25]

Indices of the reflections on the basis of a triple hexagonal cell	Present investigations Al-30 at% Zn		Wahi [25] (iso-ageing for 4 min)			Carpenter and Garwood [17, 18] (ageing for 2 to 20 h after water quenching from 475° C) Al-11.5 at% Zn
	200° C	245° C	Al-20 at% Zn		Al-30 at% Zn	
			260° C	260° C	290° C	
10 $\bar{1}$ 1	2.2953	—	—	—	—	—
0003	—	—	—	2.2550	2.2690	2.2700
01 $\bar{1}$ 2	1.9893	2.0054	1.9890	1.9890	1.9910	1.9980
11 $\bar{2}$ 0	—	—	—	—	—	—
10 $\bar{1}$ 4	1.4008	1.4053	1.3990	1.3970	1.4000	1.4000
02 $\bar{2}$ 1	—	—	—	—	—	—
11 $\bar{2}$ 3	1.2084	1.2060	—	1.2050	1.2040	1.2080
01 $\bar{1}$ 5	—	—	—	1.1900	1.1880	—
20 $\bar{2}$ 2	1.1582	—	—	—	—	—
20 $\bar{2}$ 4	1.0001	0.9986	0.9987	0.9988	0.9988	1.0000
20 $\bar{2}$ 5	—	—	—	0.9145	0.9156	—
10 $\bar{1}$ 7	0.9041	—	—	—	—	—
12 $\bar{3}$ 2	0.9003	—	—	0.8880	0.8869	—
11 $\bar{2}$ 6	—	—	—	—	—	—
30 $\bar{3}$ 0	—	—	—	—	—	—
21 $\bar{3}$ 4	—	—	—	0.8785	0.8177	—

TABLE IV Calculation of atomic volume (AV) and zinc contents of the rhombohedral transition phase (R-phase) and the matrix in Al-Zn alloys aged at different temperatures (data on α' -phase are also given in the available cases (Anantharaman [7])

Reference	Ageing temperature ($^{\circ}$ C)	Alloy composition (at% Zn)	R-phase				α -matrix*				α' -phase			
			a_h (Å)	c_h (Å)	$(c/a)_h$	AV (Å^3)	Zn (at%)	a_c (Å)	a_h (Å)	c_h (Å)	AV (Å^3)	Zn (at%)	a_c (Å)	Zn (at%)
Simerska and Syneck [26]	175	12 and 15	2.873	6.725	2.341	16.03	50	4.045	2.861	7.005	16.54	5	3.998	55
Carpenter and Garwood [18]	200	11	2.859	6.804	2.380	16.06	48	4.043	2.859	7.001	16.52	7	3.992	60
Simerska and Syneck [26]	225	12 and 15	2.867	6.736	2.350	15.99	54	4.041	2.858	6.998	16.50	9	3.995	58
Wahi and Anantharaman [10]	260	30	2.859	6.769	2.368	15.97	55	4.034	2.852	6.985	16.41	16	3.992	60
Wahi and Anantharaman [10]	290	30	2.850	6.822	2.394	16.00	53	4.028	2.848	6.976	16.34	22	3.995	58

* (c/a) for fcc matrix is 2.450.

TABLE V Calculation of atomic volumes (AV) and zinc contents of the rhombohedral transition phase (R-phase) and the matrix (α) in Al-Zn alloys aged at different temperatures (lattice constants and atomic volumes are in Angstrom and cubic Angstrom units respectively. Zinc contents are given in atom per cent)

Reference	Ageing temperature ($^{\circ}$ C)	Alloy composition (at% Zn)	R-phase					α -matrix*				
			a_h (Å)	c_h (Å)	$(c/a)_h$	AV (Å^3)	Zn (at%)	a_c (Å)	a_h (Å)	c_h (Å)	AV (Å^3)	Zn (at%)
Simerska and Synecek [26]	175	12 and 15	2.873	6.725	2.341	16.03	58	4.045	2.861	7.005	16.55	5
Present studies	200	30	2.856	6.800	2.380	16.01	60	4.043	2.859	7.001	16.52	8
Simerska and Synecek [26]	225	12 and 15	2.867	6.736	2.349	15.99	61	4.041	2.858	6.998	16.50	10
Present studies	245	30	2.854	6.821	2.390	15.99	61	4.037	2.853	6.993	16.45	15
Wahi and Anantharaman [10]	260	30	2.859	6.769	2.368	15.97	64	4.034	2.852	6.987	16.41	19
Wahi and Anantharaman [10]	290	30	2.851	6.822	2.394	16.00	61	4.028	2.848	6.976	16.34	26
Krishna Rao <i>et al.</i> [27-29]	75	29	2.852	6.785	2.379	15.93	67	4.025	2.845	6.971	16.30	31
Merz and Gerold [30]	130	9	2.855	6.717	2.353	15.81	80	4.037	2.855	6.993	16.45	15
Simerska and Synecek [26]	150-200	15	2.863	6.718	2.355	15.91	70	4.041	2.858	7.071	16.50	10
Carpenter and Garwood [18]	200	11	2.859	6.804	2.381	16.06	55	4.043	2.859	7.001	16.52	8
Graf and Lenormand [31]	275	21.5	2.800	6.770	2.418	15.327	100?	4.020	2.843	6.963	16.24	41?

* c/a for f c c matrix is 2.450.

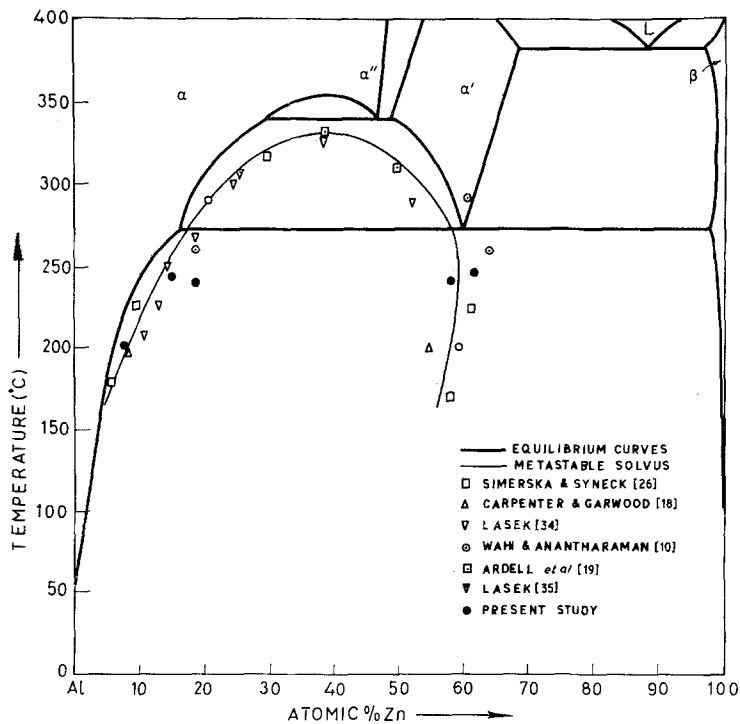


Figure 2 Metastable miscibility gap for R-phase in Al-Zn system.

relevant here to recall that the solvus for G-P zones [8], slopes towards the Zn-rich side of the diagram between its maximum at $\sim 225^\circ\text{C}$ and low temperatures (Fig. 3).

In the light of the new metastable solvus from the present work, further critical analysis of all the data available so far on the metastable equilibrium can be made. As can be seen from Fig. 3, the R-phase and the α' -phase can be obtained directly by quenching to temperatures above the metastable solvus curves for G-P zones, depending on the alloy composition. The R-phase is stable only over a short period of time, again depending on the alloy composition and heat treatment. Further, evidence for the formation of R-phase after direct quenching below 220°C is also available [10, 19, 25]. This is so because, by the time the observation is made, zones formed might have led to the formation of this phase. Further, formation of this phase seems to depend on the type of specimen used [4, 5]. Thus in single crystals it forms at and above 130°C [26, 30, 37] and above 170°C in the case of polycrystals [1, 10, 17, 18, 31].

It is now possible to formulate the sequence of precipitation depending on the heat treatment (up- or down-quenching), in the light of the new solvus curves (Fig. 3). For any alloy up to the

eutectoid composition, the following sequence can be postulated.

(a) When quenched directly to room temperature or below, the G-P zones, with a size characteristic of the ageing temperature, will be formed from a cluster of solute atoms. If the alloy is then aged at that temperature, the most probable mode of decomposition will be discontinuous precipitation [25, 38-44]. When the ageing temperature is higher than room temperature, zones characteristic to that temperature may form. But, due to fast reaction at higher temperatures, it may not be possible to observe these. However, the transition phase which transforms to equilibrium zinc, may next be observed [17, 20].

(b) If such a zone containing alloy is then reheated to higher temperatures at or below the G-P zone solvus, the smaller zones dissolve making way for the larger ones, characteristic of that temperature. Partial coherency sets in when they grow to a size of 30 to 35 Å after which the R-phase may start forming [1, 10, 25-31, 36-40, 46-52]. These platelets of R-phase may then transform into α' -phase which finally decomposes resulting in equilibrium zinc. This explanation is in accordance with all the earlier observations, and also with recent *in situ* observations of cellular precipitation in an Al-28 at% Zn alloy [43].

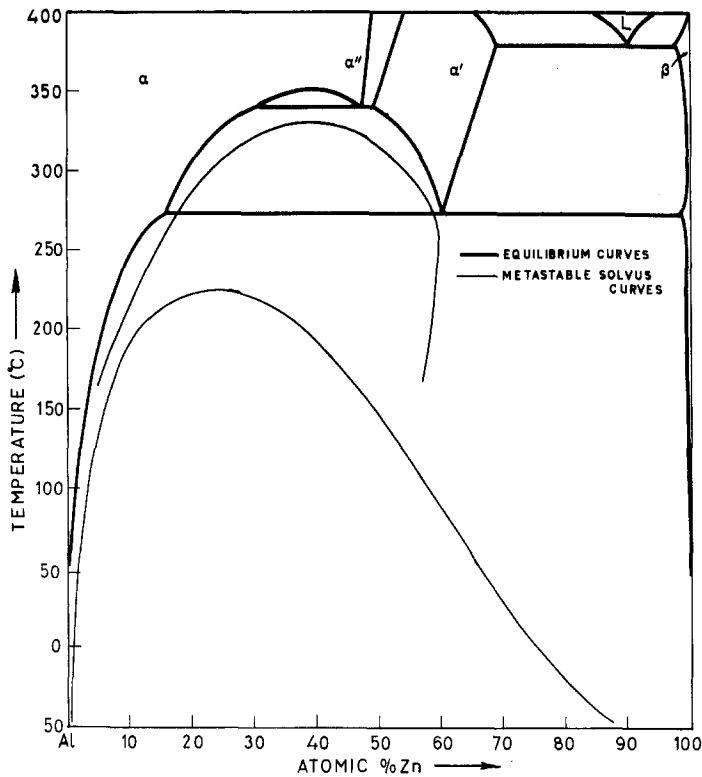


Figure 3 Metastable miscibility gaps in the Al-Zn system.

(c) On the other hand, when a zone containing alloy is reheated above solvus I (Fig. 3), the initial product is either R-phase or α' -phase, depending on the quenching conditions [10, 17, 18, 26, 47-49] in accordance with the earlier observations [10, 27-30]. Finally, equilibrium zinc will be precipitated out.

(d) Further, when the alloy is directly quenched to temperatures above solvus I but below solvus II (Fig. 3), the product is R-phase and/or α' -phase. The stability of these depends on composition of the alloy and heat treatment as observed by Ardell *et al.* [19] and Wahi and Anantharaman [10]. The final product is once again equilibrium zinc phase as a result of either continuous or discontinuous precipitation or a combination of the two processes.

Another relevant point to record at this juncture, as already pointed out [52], is that the precipitation and reversion behaviour of polycrystalline Al-Zn alloys is quite complex in the range 160 to 230° C as can be seen from the overlapping of the two solvus curves. Thus, the possible co-existence of matrix and one or more of three different phases, namely G-P zones, R-phase/ α' -phase and equilibrium zinc, brings about this

complication in the metastable equilibrium studies on concentrated Al-Zn alloys.

It may now be possible to explain the structural changes taking place in Al-Zn alloys in the whole composition range. It may also be possible to understand the appearance of side bands as well as the possible spinodal mode of decomposition in this alloy system in the light of the new solvus curves for the G-P zones and the transition phase. It is relevant at this point to dwell on the possible spinodal decomposition observed in this alloy system. From Fig. 3 it is evident that in the alloys quenched to as low a temperature as -45° C and aged up to 220° C, formation of the G-P zones may well be too quick to be detected at higher temperatures (say above 150° C), although the mode leading to the R-phase may possibly be detected in the lower regions of the solvus. This may well explain the results and the ambiguities which arose in some of the earlier investigations [9, 11-13]. However, in the superposed region of the two solvus curves (i.e. between 160 and 230° C) the dominating process will dictate the kinetics. There is some convincing experimental evidence for such a proposition [12, 13, 19, 41, 43-45, 53].

Although it appears that the concept of two miscibility gaps explains the modes of precipitation and hence the structural changes occurring in the Al–Zn system with more certainty, this system still seems to be a potential area for research not only to resolve the confusion that exists from some recent studies [53–59] but also to understand the competitive mechanism that may occur in other alloy systems.

4. Conclusions

(1) A plot of lattice constant against zinc content in Al–Zn alloy has been arrived at.

(2) Using the above plot and data on zinc content in the transition phase, a new metastable solvus curve for the transition phase has been established.

(3) Based on the new solvus curves a critical analysis of all the available data on the solvus curves in the Al–Zn system has been made. Also the sequence of precipitation in the system has been explained satisfactorily.

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