

# Splat cooling of aluminium-manganese alloys

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The gun technique of splat cooling is utilized to extend the solid solubility of manganese in aluminium by a factor of four above that at the eutectic temperature. The supersaturated solid solutions can be retained up to 250°C without any significant decomposition. Isochronal and isothermal studies of the variation of the lattice parameter of the 6.4 wt % manganese solid solution yield a value for the activation energy of 30 kcal mol<sup>-1</sup> which is considerably higher than that for the splat cooled aluminium-silicon alloys. The decomposition of the supersaturated solid solution leads to the precipitation of the equilibrium Al<sub>6</sub>Mn phase.

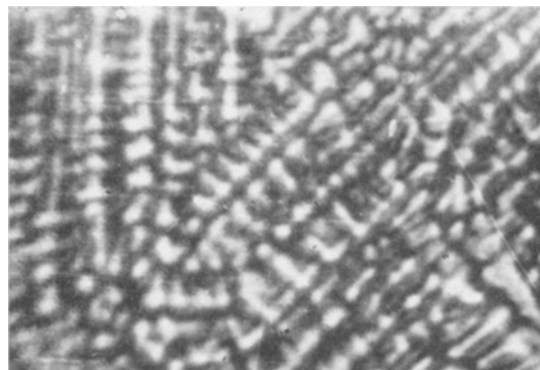
## 1. Introduction

The high degree of supersaturation of solute atoms and point defects obtainable by splat cooling is conducive to precipitation studies. Such studies have so far been made on the splat cooled supersaturated solid solutions of Cu-Ag [1], Al-Si [2], Al-Fe [3], Al-Ni [4] and Al-Ge [5]. The solid solutions of Cu-Ag, Al-Si and Al-Ge decompose at low temperatures of ~ 100 to 200°C while the Al-Fe and Al-Ni solid solutions need higher temperatures of the order of 200 to 300°C for decomposition. There appears to be a correlation between the temperature at which the splat cooled solid solution decomposes and the activation energy for solute diffusion. For example, Si and Ge diffuse in Al with an activation energy about the same as that for self diffusion in Al while Fe and Ni diffuse with substantially higher activation energies [6]. Mn resembles Cr and Fe in its diffusion behaviour in Al [7]. Recent solid state quenching studies indicate that the kinetics of decomposition of the supersaturated solid solutions of Mn in Al are sluggish even at temperatures of the order of 400°C [8]. In the present investigation, the splat cooling technique has been utilized to obtain highly supersaturated solid solutions of Mn in Al and the decomposition of the most concentrated solid solution has been followed by lattice parameter measurements.

## 2. Experimental procedure

Four alloys containing 0.9, 1.5, 4.5 and 6.4 wt %

Mn were made by melting 4 N pure Al and a master alloy containing 20% Mn under an argon atmosphere in an induction furnace. The alloys were homogenized at 450°C for 30 h. About 30 to 50 mg of the material (pure Al or alloy) were quenched from the liquid state (50 to 100°C above the liquidus) on to a copper substrate with the help of a modified gun apparatus [9, 10]. The Debye-Scherrer patterns of thin samples of splats were obtained in a 57.3 mm diameter camera using Ni filtered CuK $\alpha$  radiation. The measurements of the Bragg angles were made at least four times in order to minimize the random errors. The calculated values of lattice parameter ( $a$ ) were extrapolated to  $\theta = 90^\circ$  using the Nelson-Riley function. The error in the extrapolated value of  $a$  is estimated to be  $\pm 0.0005 \text{ \AA}$ .



*Figure 1* Dendritic structure in splat cooled Al-6.4% Mn alloy,  $\times 2400$ .

### 3. Results and discussion

#### 3.1. Microstructure

Thermal etching accompanying splat cooling allows direct optical observation of the splats. The cellular structure was very common in both pure Al and Al-Mn splats. In the alloy splats the cells were sometimes elongated in one direction leading to lineage structure. Dendritic structures were also observed in the alloy splats, an example of which is shown in Fig. 1. These have been utilized to estimate the cooling rates. The secondary dendrite arm spacings were calculated from measurements on the photomicrograph using the formula [11]

$$S = \frac{L \times 10^4}{(N - 1)M}$$

where  $S$  = secondary dendrite arm spacing ( $\mu\text{m}$ );  $L$  = length of the section line (cm);  $N$  = number of secondary dendrite arms cut by the section line;  $M$  = magnification of the photomicrograph. The cooling rates were calculated from the  $S$  values of 0.63 to 0.95  $\mu\text{m}$  and the master curve for Al alloys established by Matyaja *et al.* [12] to be in the range 1.8 to  $5.6 \times 10^5 \text{ }^\circ\text{C sec}^{-1}$ , with an average value of  $\sim 3 \times 10^5 \text{ }^\circ\text{C sec}^{-1}$ .

#### 3.2. Splat cooling of pure aluminium

The lattice parameters of pure Al in the as-splat

and well-annealed (500 $^\circ\text{C}$ , 10 h) conditions were measured at 35 $^\circ\text{C}$  to be 4.0501 and 4.0506  $\text{\AA}$  respectively. The difference of 0.0005  $\text{\AA}$  in these values is only marginally larger than the experimental error of 0.00035  $\text{\AA}$ . However, the splat cooled sample is expected to contain an appreciable concentration of quenched-in vacancies which would tend to decrease the lattice parameter. If the observed difference is assumed to arise entirely from quenched-in vacancies, the excess vacancy concentration can be calculated by employing the relationship due to Eshelby [13] to be  $\sim 1.2 \times 10^{-3}$ . This value compares well with that obtained from electron microscopic studies [14]. A decrease in the lattice parameter of 0.002  $\text{\AA}$  of splat cooled Al reported by Kirin *et al.* [15] is considerably higher than that observed by us.

#### 3.3. Formation of supersaturated solid solutions

The diffraction patterns of all the four alloys in the as-splat condition showed only the single phase solid solution. In Fig. 2, the change in lattice parameter,  $\Delta a = (a_{\text{Al}} - a_{\text{splat cooled alloy}})$  is plotted as a function of composition for these alloys. The data of Hofmann [16] for the equilibrium composition range and of Falkenhagen and Hofmann [17] and of Obinata *et al.* [18] for the splat cooled alloys are also included in the figure.

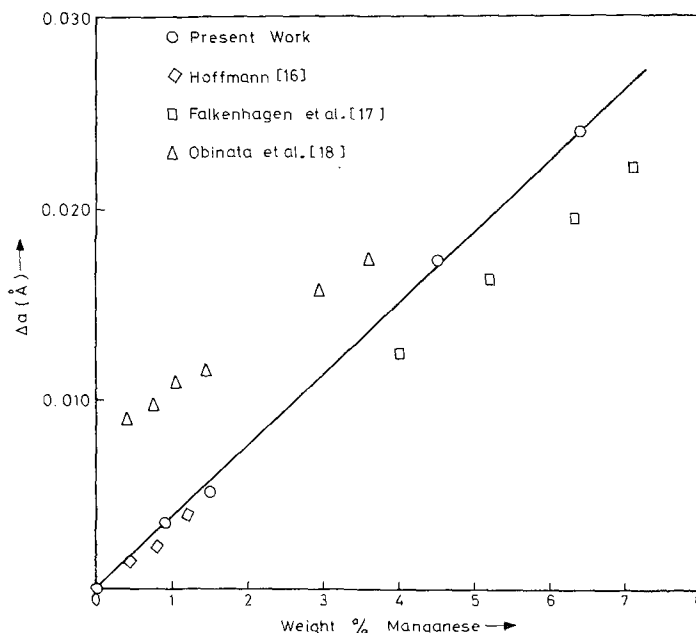


Figure 2 Change in lattice parameter as a function of composition for Al-Mn solid solutions.

While the data of Falkenhagen and Hofmann are close to ours, the data of Obinata *et al.* show considerable deviation. It is particularly noted that on extrapolating this set of data to zero Mn,  $\Delta a$  remains finite ( $\sim 0.08 \text{ \AA}$ ).

From Fig. 2, it is seen that the lattice parameter continues to decrease even beyond the maximum equilibrium value (1.6 wt % Mn), indicating the formation of supersaturated solid solutions. This trend continues even beyond the eutectic composition (2 wt % Mn). In many of the eutectic systems, like Al-Si, Al-Ge, etc. [2, 5], the extension of the solid solubility is limited to their respective eutectic composition. However, under non-equilibrium solidification conditions, eutectic composition may not have much significance and the cooling rate may determine the degree of supersaturation. Ichikawa *et al.* [19] have shown that a cooling rate of  $\sim 115^\circ\text{C sec}^{-1}$  is enough to obtain a solid solution beyond the equilibrium limit in Al-Mn alloys. They point out a marked increase in supersaturation with cooling rate up to  $\sim 400^\circ\text{C sec}^{-1}$  (4.2 wt % Mn), but further increase in cooling rate is shown to have negligible effect. While no attempt has been made in the present study to establish the limit of solid solubility it can be extended up to 6.4 wt % Mn at an estimated cooling rate of

$\sim 3 \times 10^5^\circ\text{C sec}^{-1}$ . This is about four times the equilibrium solubility limit.

Extrapolating the straight line of Fig. 2 to 100% solute, the apparent spacing of Mn in Al matrix is calculated to be  $3.677 \text{ \AA}$ . The apparent effective atomic volume of  $12.427 \text{ \AA}^3$  is higher than the value of  $12.21 \text{ \AA}^3$  for the atomic volume of Mn [20]. The fact that the atoms of Mn undergo dilatation when introduced in Al can be brought out by calculating the deviation from Vegard's law. Following Klement [21], the distortion parameter,  $\delta(c)$ , has been calculated to be  $-1.08\%$  for the Al-6.4% Mn alloy. This can be compared with the value of  $-0.68\%$  computed by Tonejc and Bonefačić [22] using the data of Falkenhagen and Hofmann [17].

#### 3.4. Isochronal annealing of Al-6.4% Mn solid solution

The Al-6.4% Mn alloy splat were annealed at a series of temperatures up to  $500^\circ\text{C}$ , for 1 h at each temperature. The  $a$  values obtained are plotted as a function of annealing temperatures in Fig. 3. It is seen that the supersaturated solid solution is retainable up to fairly high temperatures ( $\sim 250^\circ\text{C}$ ), decomposition being rapid only about  $350^\circ\text{C}$ ; it is complete within an hour at and above  $400^\circ\text{C}$ . Thus the Al-Mn supersaturated solid solution resembles that of Al-Fe

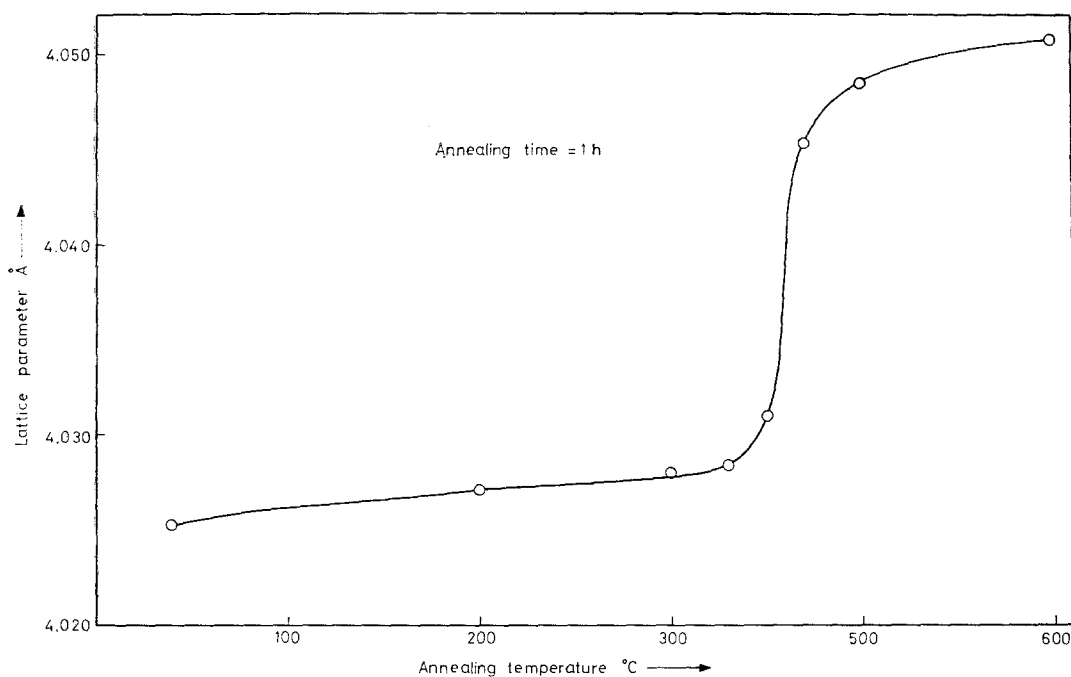


Figure 3 Isochronal annealing curve for Al-6.4% Mn alloy splat.

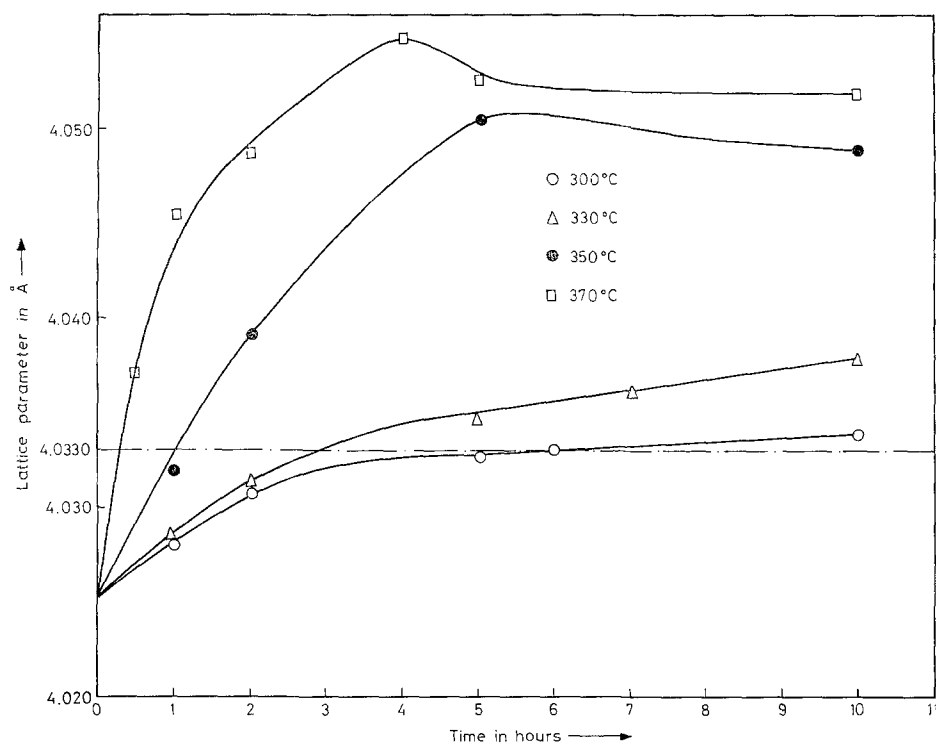


Figure 4 Isothermal annealing curves for Al-6.4% Mn alloy splat.

in its decomposition behaviour. With a view to identifying the precipitating phase, the Al-6.4% Mn alloy splat was annealed for 10 h at 500°C. The diffraction pattern of this sample could be satisfactorily indexed on the basis of the equilibrium  $Al_6Mn$  phase, rather than the metastable G, G', or G'' phases which are known to form on high temperature decomposition of Al-Mn solid solutions [23-25]. The previous studies [24, 25] indicate that the transformation  $G \rightarrow Al_6Mn$  is very sluggish and that the G phase can be detected even after annealing for a week at 550°C (G' and G'' phases behave in a similar way). Thus if any of these metastable phases were to form in the Al-6.4% Mn alloy, it could have been detected. Therefore, it is concluded, that in this concentrated alloy, annealing at high temperatures ( $\sim 500^\circ C$ ) leads to the precipitation of the equilibrium  $Al_6Mn$  phase.

### 3.5. Isothermal annealing of Al-6.4% Mn solid solution

The specimens were isothermally annealed at 300, 330, 350 and 370°C for various lengths of time. The lattice parameters of annealed specimens are plotted as a function of annealing time

in Fig. 4. An interesting feature is the observation of abnormal humps in the high temperature annealing curves (350 and 370°C). These effects are considerably larger than the possible experimental errors. Similar humps have been reported in the annealing of Al-11% Si alloy splats. Although it is difficult to explain this hump, it may be due to the strain accompanying precipitation. Using the method of cross-cut, the activation energy for the decomposition of the supersaturated solid solution has been calculated to be  $30 \pm 4.5 \text{ kcal mol}^{-1}$ . This is in contrast to the much lower value of 14 to 20  $\text{kcal mol}^{-1}$  reported for the decomposition of Al-Si solid solutions [2].

### 4. Conclusions

1. At a cooling rate of  $\sim 3 \times 10^5 \text{ }^\circ C \text{ sec}^{-1}$ , the solid solubility of Mn in Al can be extended at least up to 6.4 wt% Mn which is about four times the maximum equilibrium solubility.
2. Mn atoms assume an effective atomic volume of  $12.427 \text{ \AA}^3$  in Al matrix and the distortion introduced in the lattice for a 6.4% Mn alloy is  $\sim -1\%$ .
3. The supersaturated Al-6.4% Mn solid

solution can be retained up to fairly high temperatures ( $\sim 250^\circ\text{C}$ ). The decomposition becomes rapid only about  $350^\circ\text{C}$  and is characterized by an activation energy of  $\sim 30$  kcal  $\text{mol}^{-1}$ . The high temperature annealing leads to the precipitation of the equilibrium  $\text{Al}_6\text{Mn}$  phase.

## References

1. R. K. LINDE, *Trans. Met. Soc. AIME* **236** (1966) 58.
2. M. ITAGAKI, B. C. GIESSEN and N. J. GRANT, *Trans. ASM Quart.* **61** (1968) 330.
3. A. TONEJC, *Met. Trans.* **2** (1971) 437.
4. A. TONEJC, D. ROČÁK and A. BONEFAČIĆ, *Acta Met.* **19** (1971) 311.
5. B. PREDEL and G. SCHLUCKEBIER, *Z. Metalk.* **63** (1972) 198.
6. G. M. HOOD, *Phil. Mag.* **21** (1970) 305.
7. G. M. HOOD and R. J. SCHULTZ, *ibid* **23** (1971) 1479.
8. D. P. LAHIRI, T. R. RAMACHANDRAN and A. K. JENA, to be published.
9. P. RAMACHANDRARAO, P. RAMA RAO and T. R. ANANTHARAMAN, *Z. Metalk.* **61** (1970) 471.
10. S. P. BHAT, T. R. RAMACHANDRAN and A. K. JENA, DAE Conference on 'Electrical, Electronic and Magnetic Materials' held at I.I.T. Madras, (December 1972).
11. S. A. LAVY, R. E. HUGHES and A. I. KEMPINEN, *AFS Cast Metals Res. J.* **5** (1969) 93.
12. H. MATYAJA, B. C. GIESSEN and N. J. GRANT, *J. Inst. Metals* **96** (1968) 30.
13. J. D. ESHELBY, *J. Appl. Phys.* **25** (1954) 255.
14. G. THOMAS and R. H. WILLENS, *Acta Met.* **12** (1964) 191.
15. A. KIRIN, A. TONEJC and A. BONEFAČIĆ, *Scripta Met.* **3** (1969) 943.
16. W. HOFMANN, *Abhandl. Braunschweig Wiss. Ges.* **1** (1949) 83.
17. G. FALKENHAGEN and W. HOFMANN, *Z. Metalk.* **43** (1952) 69.
18. I. OBINATA, E. HATA and K. YAMAGI, *J. Japan Inst. Met.* **17** (1953) 496.
19. R. ICHIKAWA, T. OHAJI and T. IKEDA, *Trans. JIM* **12** (1971) 280.
20. C. S. BARRETT and T. B. MASSALASKI, "Structure of Metals" (McGraw Hill, New York, 1968).
21. W. KLEMENT, *Trans. Met. Soc. AIME* **227** (1963) 965.
22. A. TONEJC and A. BONEFAČIĆ, *Fizika* **2** (1970) 81.
23. K. LITTLE, G. V. RAYNOR and W. HUMEROTHERY, *J. Inst. Metals* **73** (1946) 83.
24. E. NES, S. E. NAESS and R. HOIER, *Z. Metalk.* **63** (1972) 248.
25. O. IZUMI, D. OESCHLAGEL and A. NAGATA, *Trans. JIM* **9** (1968) 227.

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