

The CsCl-type Order-Disorder Transition Temperature in VMn Alloys

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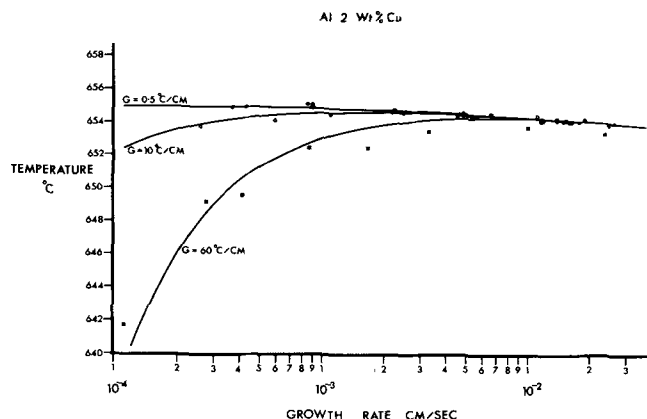


Fig. 1—An experimental plot of dendrite tip temperature against growth rate at three different temperature gradients 0.5°C/cm, 10°C/cm, and 60°C/cm for an Al 2 wt pct Cu alloy.¹

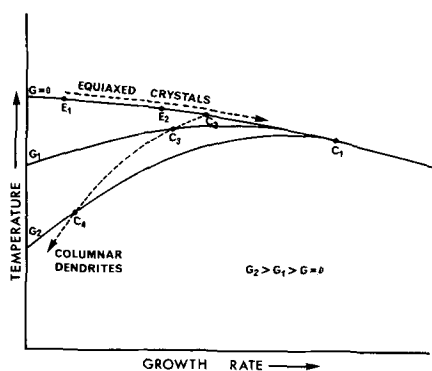


Fig. 2—Schematic diagram of dendrite tip temperature plotted against growth rate for different temperature gradients (G) showing the variation in temperatures of the columnar dendrites and equiaxed crystals.

of the greater rate of heat extraction from the bulk liquid (position E_2 on Fig. 2). This in turn will still further decrease the growth rate of the columnar interface and increase the temperature gradient and hence decrease the temperature of the columnar front (position C_4 , Fig. 2). The rates of growth and temperatures of the columnar and equiaxed crystals will therefore follow the arrows shown on Fig. 2. The growth rate of the equiaxed crystals rapidly increases and the growth rate of the columnar interface decreases. Eventually a condition is reached where the columnar front has almost stopped but where the equiaxed crystals are growing rapidly. This phenomena leads to the very abrupt change in structure observed in many castings and ingots. It is much more difficult to envisage such an abrupt change if the effect of gradient ahead of the columnar front is neglected.

A CsCl-type ordered structure in an equiatomic VMn alloy has been observed by Waterstrat¹ and Darby, Jr.,² on the basis of the X-ray diffraction using the $\text{CrK}\alpha$ radiation whose frequency is close to the absorption edge of one of the elements. This structure has also been confirmed by Doroshenko *et al.*³ and Kuchin *et al.*⁴ using the neutron diffraction technique. The purpose of the present study is to determine the CsCl-type order-disorder transition temperature in VMn alloys containing 30 ~ 55 at. pct Mn by means of the differential thermal analysis and specific heat measurement.

The alloys were prepared by arc-melting vanadium flakes 99.8 pct in purity and electrolytic manganese 99.9 pct in purity under an argon atmosphere. The composition of each alloy was calculated by assuming that the total weight loss during the melting was due to the vaporization of manganese. These calculated values agreed reasonably well with the results of chemical analyses which were done on some of the alloys. All the ingots were wrapped with molybdenum foil and encapsulated in a quartz tube in a vacuum and then homogenized at 1300°C for 2 h. Specimens for the DTA and specific heat measurement were made by grinding off the surface of the ingots, held at 1050°C *in vacuo*, and then either cooled at a rate of 50°C/day or quenched directly into iced brine. Before the thermal experiments, all the specimens were confirmed to be of a single phase, the bcc or CsCl structure, by the optical microscopy and X-ray examination with $\text{CrK}\alpha$ radiation.

Fig. 1 shows DTA curves at a heating rate of 10°C/min of equiatomic VMn alloy specimens quenched and annealed. On the curve of the quenched specimen, two distinct reactions, exothermic and endothermic, are observed. On the curve of the annealed specimen, however, only an endothermic reaction is observed. These results show that the disordered state can be quenched to room temperature, and that the exothermic reaction of the quenched specimen in the temperature range of 600 to 750°C is due to ordering and the endothermic reaction on both the cases is due to disordering. The peak temperature in the endothermic reaction exists at 845°C; this is the CsCl type order-disorder transition temperature in an equiatomic VMn alloy. In the case of the annealed specimen, however, an anomaly in the disordering process is observed; the curve does not fall down monotonously. The anomaly is also found in the specific heat curve of an annealed equiatomic alloy specimen at a heating rate of 2.5°C/min. As shown in Fig. 2, besides the main sharp peak owing to the order-disorder transition at 845°C, there is a broad peak at about 730°C. The peak at 760°C in the DTA corresponds to the 730°C peak in the specific heat.

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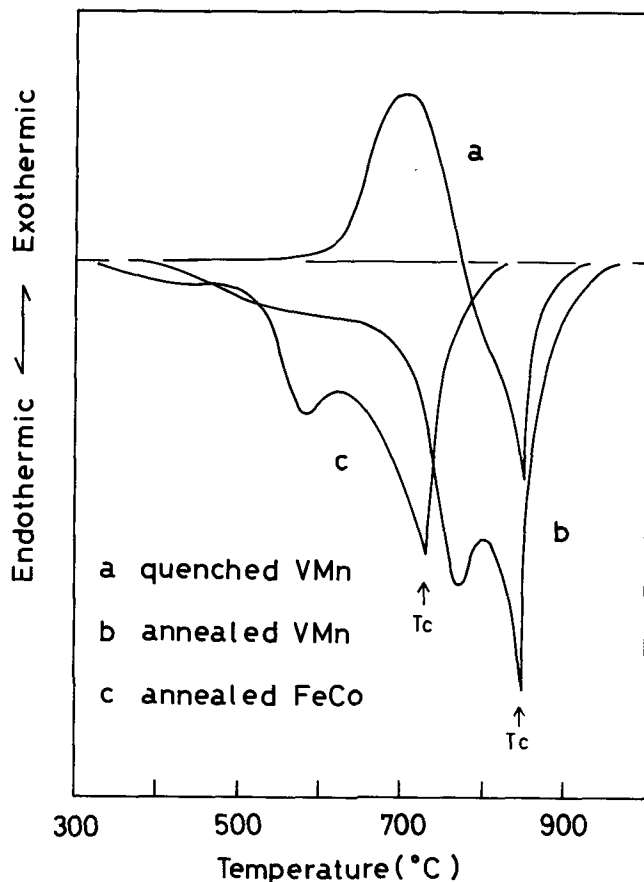


Fig. 1—Differential thermal analysis curves of equiatomic VMn and FeCo alloys.

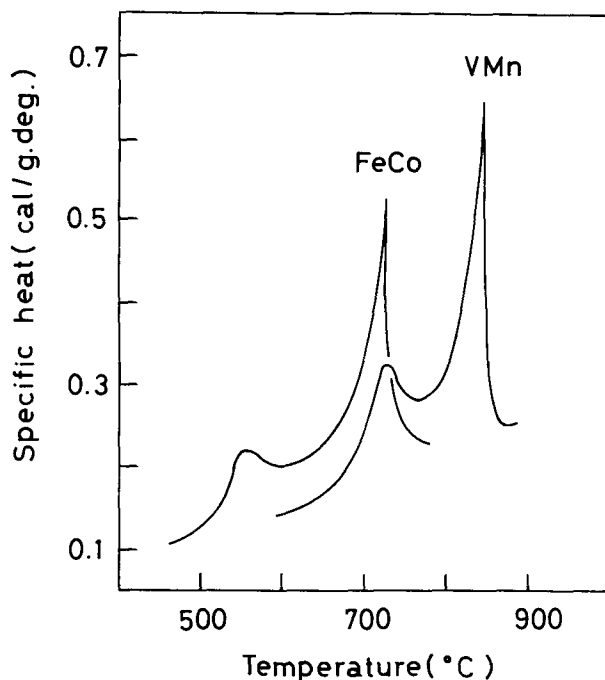


Fig. 2—Specific heat curves of annealed equiatomic VMn and FeCo⁸ alloys.

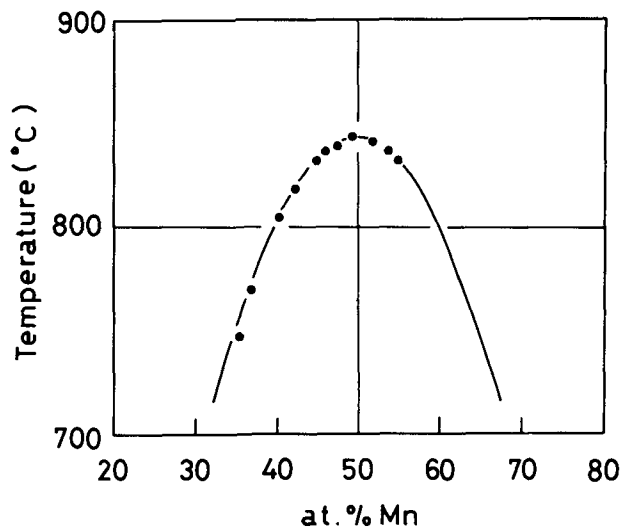


Fig. 3—Order-disorder transition temperatures in VMn alloys.

Thus, the heating rate markedly affects the 730°C peak, but not the transition temperature. An extra peak called “550°C anomaly” in the specific heat curve has been reported in the disordering process of the CsCl-type ordered FeCo alloy.⁵⁻⁸ In Figs. 1 and 2 the results of the DTA and the specific heat measurement of an annealed FeCo alloy are included for comparison with the VMn alloy. It is reasonable to consider that “730°C anomaly” in VMn alloy is equivalent to “550°C anomaly” in FeCo alloy and that both the anomalies originate from the same mechanism.

The order-disorder transition temperature in VMn alloys determined by the DTA are shown in Fig. 3. The solid line in the figure is a theoretical one based on Bragg-Williams approximation, *i.e.*, $T = 4T_c x(1-x)$, where x is the atomic fraction of the component and T_c is the transition temperature at equiatomic composition. In the composition range studied, a good agreement is obtained between the experimental and theoretical values.

The details of the X-ray diffraction, thermal analyses, dilatometric study, and other physical and mechanical properties of VMn alloys will be published elsewhere.⁹

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