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Abstract

Full Text

Physical Chemistry

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Some Features of the Crystallization of Eutectic-Type Alloys at a High Cooling Rate

(Presented by Academician G. V. Kurdyumov, 17 II 1960)

The few data available in the literature on the solidification of alloys at high cooling rates ($^{1-5}$) show that, both in the case of crystallization from the melt and in the case of obtaining alloys by electrodeposition or by vacuum deposition, highly supersaturated solid solutions can be obtained*. Analysis of these works shows that systems in which intermediate phases are present, as a rule, have a tendency toward the formation of highly supersaturated primary solid solutions.

Fig. 1. State diagram and dependence of the composition of the α-solid solution on alloy concentration for two degrees of supercooling: ΔT_1 (curve) and ΔT_2 (curve)

In some works ($^{6-8}$) the possibility of the formation of highly supersaturated solid solutions is associated with diffusionless crystallization, which, in the authors' opinion, can occur in alloys at high cooling rates.

Below are presented experimental studies of the formation of the structure of alloys cooled at a high rate by the method described in (^{9}). According to this method, a drop of melt flying out of a furnace solidifies in the form of a thin film between two copper plates moving toward one another. The use of this method makes it possible to obtain cooling rates of $\sim 10^5$ degrees/sec. In this case, small supercoolings are attained in the thin layer of melt directly adjacent to the interface between the melt and the cooling element. In layers farther away, the supercooling decreases somewhat. This circumstance makes it possible to trace the features of crystallization at different degrees of supercooling.

* In the present work, highly supersaturated solid solutions are considered to be solutions with a concentration exceeding the maximum solubility at the eutectic

Fig. 2

Figure 2: Fig. 2

(peritectic) temperature (C_M).

For the study of films 0.05-0.2 mm thick, metallographic and X-ray structural methods of investigation were used, as well as quantitative phase analysis by the Scheil–Saltykov method. Alloys with concentrations from C_m (Fig. 1) to the eutectic were investigated. The composition of the primary solid solution was determined from measurements of the lattice period; the composition of the alloy, by chemical analysis of the films. The results of the investigation may be summarized as follows.

I. In Al–Si, Pb–Sn, and Bi–Sn alloys, which belong to binary eutectic systems not forming intermediate phases, primary solid solutions arise with concentrations less than C_m. Figure 1 shows the change in composition of the primary solid solution with change in alloy composition for two undercoolings: ΔT_1 and ΔT_2. Thus, with increasing cooling rate, the concentration of the primary solid solution does not increase, as should follow from the theory of diffusionless crystallization, but, on the contrary, decreases.

II. In systems forming intermediate phases, at a high cooling rate primary solid solutions may arise with concentrations greatly exceeding C_m. In the systems studied, Al–Mn and Al–Cr form substitutional solid solutions with maximum solubility of Mn up to 9.8 wt.% and Cr up to 5.5 wt.%. In the systems Ni–C and Co–C, interstitial solid solutions are formed with maximum carbon solubility of 1.8 and 1.6%, respectively. In alloys of this system there is also observed a certain maximum solubility, above which the primary solid solution is not supersaturated, and melts with concentrations exceeding C_m crystallize with the formation of two phases. Moreover, the second phase in these cases is a metastable phase: $MnAl_4$ in Al–Mn alloys, Cr_2Al_{11} in Al–Cr alloys, Ni_3C and Co_3C in Ni–C and Co–C alloys, respectively. In Fe–C alloys, even at high cooling rates, it is likewise impossible to obtain a solubility of C in γ-Fe exceeding the maximum solubility at the eutectic temperature. On the contrary, the carbon content in rapidly cooled austenite is always less than the maximum solubility at the eutectic temperature.

Fig. 2. Two principal types of phase diagrams with intermediate phases and the dependence of the composition of the α-solid solution on alloy concentration in systems with intermediate phases for two degrees of undercooling: ΔT_1 (curve) and ΔT_2 (curve)

Changing the cooling rate over a fairly wide range practically does not change the maximum solubility C_m, if one disregards a certain decrease in the maximum solubility with increasing undercooling, similar to that observed in alloys without interme-

Fig. 3. Schematic arrangement of free-energy curves in a system with an intermediate phase

Figure 3: Fig. 3. Schematic arrangement of free-energy curves in a system with an intermediate phase

intermediate phases. It is possible that with a further increase in the cooling rate in systems with several intermediate phases one can again obtain an increase in solubility due to crystallization of a less stable intermediate phase.

With simultaneous crystallization of the stable and metastable phases, two solid solutions also arise in the alloys: one with concentration C_m, the other, strongly supersaturated, with concentration C'_m. In such cases the X-ray diffraction patterns show, respectively, two systems of lines.

On the basis of these data, a large number of phase diagrams with intermediate phases can be represented in the form of double phase diagrams with solid lines (stable equilibrium) and dashed lines (metastable equilibrium). In Fig. 2 two types of such diagrams are shown schematically. The same figure shows the dependence of the composition of the primary solid solution on concentration for two values of supercooling. When the cooling rate of the melt is insufficient to ensure crystallization according to the metastable diagram, alloy formation will proceed according to the stable phase diagram, and the change in the composition of the primary solid solution with change in alloy concentration will occur as shown in Fig. 1.

Fig. 3. Schematic arrangement of free-energy curves in a system with an intermediate phase

The eutectic point for the equilibrium primary solid solution—metastable phase shifts toward the metastable phase, and its melting temperature decreases by an amount that is greater the less stable the intermediate phase is. Thus, in Co—C alloys the eutectic point shifts more than in Fe—C, and in Ni—C more than in Co—C. The experimental data presented in the present work show that, in the alloys investigated, diffusion processes of component separation in the liquid have time to occur even at cooling rates of $\sim 10^5$ deg/sec. The results obtained are in agreement with the basic propositions of the diffusion theory of crystallization of binary systems. Crystallization in the system of a metastable phase is always associated with an increase in the solubility of the primary solid solution that is in equilibrium with this metastable phase. And the less stable the intermediate phase that forms, the greater the solubility the primary solid solution will have.

The precipitation of metastable phases is usually explained by more favorable kinetic conditions for their formation, by a smaller value of the surface tension at the interface between the parent and precipitating phases ([10], [11]). However, in the case where the metastable phase is more remote in composition from the matrix phase than the stable phase, a significant role may be played by the change in the free energy of the system per atom of the precipitating substance $\left(\frac{\Delta F}{N}\right)$ (^{12}, ^{13}). The value of $\frac{\Delta F}{N}$ for the stable and metastable phases is shown in Fig. 3 by the segments ab and a_1b_1. With a large difference in the concentrations of the stable and metastable phases and with considerable supersaturations of the matrix phase, the value of $\frac{\Delta F}{N}$ for the metastable phase may prove to be greater than for the stable phase ($a_1b_1 > ab$). In this case the conditions for formation of the metastable phase will be thermodynamically more favorable. However, after completion of the precipitation process the free energy of the system will be greater than in the case of precipitation of the stable phase, since the amount of metastable phase in the case under consideration is always smaller than the amount of stable phase. Further

the reduction of the free energy of the system is associated with the formation of a stable phase through the decomposition of a metastable one, which under conditions of high cooling rates may prove kinetically unfavorable.

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