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Abstract

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ON THE POSSIBILITY OF OBTAINING FINE-DISPERSED STRUCTURES IN ALLOYS BY QUENCHING THEIR EMULSIONS

The production of metallic alloys with specified mechanical and physicochemical properties is closely connected with the scientific substantiation of various methods for controlling the processes of structure formation in these alloys. Thus, the solution of one of the basic problems of physical metallurgy—raising the strength of metals and alloys—is achieved in most cases by creating an extremely fine-dispersed structure with a high density of uniformly distributed ultramicroscopic defects (block and grain boundaries, phase inclusions, etc.). In this case, structure formation is always carried out in that region of the phase diagram of the substance where a solid phase is already present—below the liquidus, and in most cases below the solidus. At the same time, the large body of experimental material available to colloid chemistry in the field of preparing fine-dispersed quasi-spontaneous emulsions indicates the possibility of using this new approach for controlling the properties of metallic alloys already at the melt stage. This question has arisen in part before as well: along with ultrasonic methods of refining the structure during crystallization, attempts were made to obtain emulsions in immiscible melts under the intensive action of ultrasound ([1]). However, from general thermodynamic considerations it follows that, using only such a route, it is impossible to obtain extremely highly dispersed emulsions: for this it is necessary, first of all, that the specific free energy of the interface between the liquid phases (the value of the interfacial tension) be very small. If this quantity is reduced to tenths of an erg/cm^2 or lower, then, as shown in works ([2], [3]), the spontaneous formation of thermodynamically stable fine-dispersed colloidal systems with particle sizes on the order of 10^{-6} cm is possible. If the interfacial tension is not reduced so strongly (for example, to units of erg/cm^2), an emulsion does not arise spontaneously, but under these conditions mechanical emulsification is already very effective and can lead to the formation of a sufficiently highly dispersed emulsion.

It is known that if substances A and B possess partial immiscibility in the liquid

Fig. 1

Figure 1: Fig. 1

state, then near the critical mixing point M of such a binary system (see Fig. 1) the surface tension between liquid phases approaching each other in composition can be arbitrarily small (and equal to zero at the point M). Consequently, in principle it is possible, by cooling a homogeneous melt of composition C_M to the temperature T_M, near which a critical emulsion forms (or to lower-lying points, where the interfacial tension is still not very large and a sufficiently fine emulsion can be produced by vibrational action), then to preserve by rapid quenching the structure of this emulsion in the crystallizing system; one may expect that the dispersity of the structure of the solid will be as high as the dispersity of the initial emulsion, or even exceed it owing to the decomposition of the emulsion droplets into various solid phases during crystallization. However, the practical realization

such a possibility is made extremely difficult by the fact that the quenching rate is always finite, while the temperature interval from M to the liquidus line is large. The droplets of the emulsion have time to coalesce, since the viscosity of any metallic melt is very low and ultrasonic vibrations prove insufficient to prevent this coalescence.

Fig. 1

The temperature at which a critical emulsion arises can, however, be substantially lowered in a ternary system—for example, in a system in which components A and B are only partially miscible, whereas each of them, with the third, more fusible component C, mixes in all proportions. In this case the dome bounding from above the region of coexistence of two liquid phases has a critical "ridge" descending from point M to point K, which already lies on the liquidus surface (^{4}) (Fig. 1). As such a most convenient low-melting model system, we chose in our work the zinc–lead–tin system. The melting diagram of this system, studied by us in detail in the region of interest, is shown schematically in Fig. 1: point K lies at about 38% zinc, 28% lead, and 34% tin at a temperature of 380°, whereas point M is no lower than 800°.

The experiments were carried out as follows. Charges of zinc, lead, and tin of purity not less than 99.99%, with a total mass of 40 g, were placed in tightly closing steel cylindrical molds–crucibles (height 70 mm, internal diameter 20 mm, wall thickness 1.5 mm). The mold was fastened to rods connected to a low-frequency mechanical vibrator (about 50 Hz), or to the conical concentrator of a PMS-15A ultrasonic vibrator powered by a UZG-6.3M unit (about 20 kHz). A cylindrical furnace with a chromel-alumel thermocouple made it possible to maintain the temperature to an accuracy of up to ±3°; in a number of control experiments an additional thermocouple was introduced into the melt inside the mold. The furnace was mounted in vertical guides, along which it could be rapidly removed during quenching. The temperature in the mold with the metal charge was first raised to a point lying 50-100° above the region of separation of the liquid phases; in this homogeneous region intensive vibrational stirring was carried out. The temperature was then lowered to the selected point T_1 (usually within the region of separation, at some distance from the surface of the separation dome); here a half-hour holding time was given to establish equilibrium in the system. Two minutes before the end of this holding time, in most of the experiments vibration was switched on. The furnace was then removed and the mold was cooled by means of a circular water shower or bath at a rate of about $15^\circ \cdot \mathrm{sec}^{-1}$. The cooled mold was sawn along the generatrices of the cylinder, and metallographic sections were prepared from the halves of the casting; after electrolytic etching, these were examined under a MIM-8 microscope (electrolyte composition: hydrochloric acid, sp. gr. 1.48—1 part; acetic acid 98% —4 parts; current density 9-15 A/dm^2; etching time 1-2 min; cathode—tinned iron).

Various series of experiments were carried out at a constant temperature T_1, a constant concentration ratio $C_{\mathrm{Zn}} : C_{\mathrm{Pb}}$, and a varied tin content; or at a chosen concentration of all three components and a varied value of T_1; or at $T_1 = \mathrm{const}$, $C_{\mathrm{Sn}} = \mathrm{const}$, and a variable ratio $C_{\mathrm{Zn}} : C_{\mathrm{Pb}}$; in this way, the structures arising were observed.

during quenching of emulsions over a wide range of concentrations and temperatures inside the miscibility gap, near its surface, and also during quenching of melts with an initial point T_1 lying outside this gap.

Fig. 2 gives microphotographs of structures arising upon quenching emulsions from a temperature $T_1 = 450^\circ$ (with low-frequency vibration), for a series of compositions with a constant ratio $C_{\mathrm{Zn}} : C_{\mathrm{Pb}} = 2.5 : 1$. As the tin content increases, the initial point approaches point K, and, correspondingly, the magnitude of the free energy at the boundary of the coexisting liquid phases decreases. In Fig. 2 it is clearly seen how sharply the emulsion structure is refined in this case (see the insert to p. 1333).

Fig. 3 (see the insert to p. 1333) corresponds to a vertical straight line on the phase diagram: constant alloy concentration (38% zinc, 29% lead, 33% tin) and different initial temperatures T_1. In the case of Fig. 3a, the point $T_1 = 375^\circ$ lay 5° below the liquidus surface; large dendrites of the zinc-rich phase are visible. In the case of Fig. 3b, quenching was carried out from a liquid two-phase region ($T_1 = 400^\circ$, which is approximately 10-15° below the miscibility surface), under the action of low-frequency vibration. Fig. 3c corresponds to the point $T_1 = 600^\circ$ (above the miscibility gap). The quenching rate used did not make it possible to preserve, during passage through the two-phase liquid region (from 415 to 380°), either the spontaneous colloidal emulsion that could arise when crossing the "ridge" of the miscibility gap, or, still less, the initial homogeneous structure. Together with the series of microphotographs in Fig. 2, this result emphasizes that, in order to obtain and preserve extremely fine emulsion structures, along with increasing the quenching rate,* it is especially important and necessary to choose the initial point T_1 as close as possible to point K in the miscibility region.

Fig. 4 (see the insert to p. 1333) corresponds to the horizontal straight line $T_1 = 550^\circ$, $C_{\mathrm{Sn}} = 20\%$; the points were chosen relatively far from the "ridge" of the gap, and the emulsions obtained were coarsely dispersed. In these photographs, the characteristic phenomenon of phase inversion of the emulsion as the concentration of one of the components increases is of interest (in the microphotographs shown, the light droplets are the zinc-rich phase, the dark ones the lead-rich phase).

The experiments carried out thus confirm the fundamental possibility of transferring the indicated concepts of colloid chemistry into the field of physical metallurgy—the possibility of controlling the disperse structure of the future solid body even before the onset of crystallization, in the emulsion state, under conditions of low interfacial tensions. The results we obtained relate to the low-melting "model" system zinc—lead—tin; it is evidently of considerable interest to develop similar studies for analogous compositions of more refractory metals used in technology, for example for the systems: cobalt—copper, molybdenum—copper, chromium—copper with nickel or iron as the third component.

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* A very sharp increase in the quenching rate is practically extremely difficult for massive specimens, but quite feasible, for example, for thin films, coatings, and filaments.

Note: Figure translations are in progress. See original paper for figures.

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