PHASE $T - C - P$ DIAGRAM OF BISMUTH-TIN ALLOYS

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Abstract

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PHASE $T-C-P$ DIAGRAM OF BISMUTH-TIN ALLOYS

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Phase equilibria in pure elements at high pressures have by now been studied rather well. For most elements, $P-T$ diagrams have been constructed, and in some cases even the crystal structure of polymorphic modifications formed at high pressures has been established. The study of the influence of hydrostatic pressure on phase equilibria in multicomponent metallic systems and, in particular, in binary alloys is, however, practically only beginning (see, for example, $^{(1-6)}$). Nevertheless, even the first thermodynamic calculations and experimental investigations in this direction have shown that in some systems even comparatively low pressures can lead to significant effects. Thus, for example, in the iron-carbon system $^{(4)}$ at a temperature of 1000° a pressure of only 3-5 kbar shifts the transformation $Fe_3C \rightarrow 3Fe + C$ (graphite) in the reverse direction, which leads to a sharp change in the processes of phase formation during annealing of white and gray cast irons.

Most works on the influence of pressure on phase transformations in alloys are devoted to studying the behavior of iron-based alloys. But for these alloys the melting temperatures are relatively high, reliable thermodynamic data for calculating the influence of pressure on the liquidus lines are insufficient, and experimental study of pressure effects is associated with great methodological difficulties. Therefore, in published works the action of pressure has usually been considered for particular regions of phase diagrams corresponding to phase equilibria in the solid state.

It was of interest to construct a more or less complete phase diagram for a suitable model system in the coordinates temperature—concentration—pressure.

The present work presents the results of a study of the influence of pressure on a simple eutectic diagram, using bismuth-tin alloys as an example.

The Bi—Sn system was chosen as the object of study for the following reasons:

1. Bi—Sn alloys are low-melting, which provides the methodological possibility of carrying out an investigation of phase transformations up to the liquidus line under conditions of hydrostatic pressures with sufficiently accurate measurement of temperatures and pressures.

Fig. 1. P–T diagram of Bi-Sn alloys containing Sn $\geq$ 50 at.%; *a*—alloy with 50 at.% Sn, *b*—alloy with 55 at.% Sn

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2. The melting temperature of one of the components (tin) increases with increasing pressure, whereas that of the other component (bismuth) decreases. This circumstance should lead to a strong deformation of the phase diagram with pressure.
3. As was established earlier by Bridgman (7,8), in the Bi–Sn system a new phase arises at high pressures (apparently the intermetallic compound BiSn). On the basis of Bridgman' s data and our earlier preliminary investigation of the $T - P$ diagram of an equiatomic Bi–Sn alloy (9), it could be assumed that, beginning with the pressures at which the new phase becomes thermodynamically stable (7000 atm), the type of the T–C diagram changes.

The investigations were carried out by the method of differential thermal analysis with photographic recording on an HTP-62M pyrometer. Hydrostatic pressure was produced in a multiplier with a working-chamber diameter of 16 mm. Isopentane served as the pressure-transmitting medium. Heating of the specimen of the alloy under study and of the standard (nickel) was performed by means of a nichrome heater placed in the working channel of the high-pressure vessel. The standard rates of temperature change were taken as 2.5 and 4.0 deg/min. The temperature of the specimen was measured with a chromel-alumel thermocouple with an accuracy of $±$2°, and the pressure with a manganin manometer with an accuracy of $±$200 atm. The effect of pressure on the thermocouple emf was not taken into account.

Alloys of the required composition were obtained by fusing the components Bi 99.99% and Sn 99.999% with thorough stirring and subsequent rapid cooling of the melt in order to avoid segregation. The weight of the specimen for thermal analysis was ~1 g.

Fig. 1. P–T diagram of Bi-Sn alloys containing Sn $\geq$ 50 at.%; *a*—alloy with 50 at.% Sn, *b*—alloy with 55 at.% Sn

From the thermograms obtained, T–P diagrams were constructed for alloys of various compositions, from which isobaric sections of the T–C–P diagram were constructed. Figure 1 shows the T–P diagrams of tin-rich alloys (100, 94, 90, 70, 55, and 50 at.% Sn), and Fig. 2 shows the T–P diagrams of bismuth-rich alloys (50, 55, 70, 80, 90, 100 at.% Bi). Figure 3 shows the most characteristic isobaric sections of the T–C–P diagram, corresponding to pressures of 1, 7000, 12 000, and 18 000 atm. In Figs. 1 and 2, for phase transformations occurring with the participation of the liquid phase, only the points recorded on heating of the specimens are plotted. The alloys are prone to supercooling; therefore

Fig. 2 and Fig. 3 diagrams

Figure 2: Fig. 2 and Fig. 3 diagrams

the positions of analogous points taken on cooling differ noticeably from the equilibrium positions and depend on the cooling rate. At the same time, for phase transformations in the solid state the diagrams show both the curves of formation of the new phase

$$\mathrm{Bi} + \mathrm{Sn} \rightarrow \mathrm{BiSn}$$

on heating of the alloys (or on increasing the pressure), and the curves of decomposition of the compound BiSn into its constituents:

$$\mathrm{BiSn} \rightarrow \mathrm{Bi} + \mathrm{Sn}$$

on lowering the temperature (or pressure).

At the heating and cooling rates used, the processes of formation and decomposition of the solid solution of bismuth in tin were not observed on the thermograms. Therefore the question of the effect of pressure on the solubility of bismuth in solid tin was not studied by us.*

Let us consider the results obtained. On the thermograms of the alloys studied, both arrests corresponding to the crossing of the eutectic line Bi + Sn—liq and points corresponding to the crossing of the liquidus line Sn—liq for tin-rich alloys and Bi—liq for bismuth-rich alloys were clearly visible. As can be seen from Figs. 1 and 2, the eutectic equilibrium temperature Bi + Sn—liq decreases with increasing pressure up to 7000 atm. At pressures above 7000 atm a new phase BiSn is formed, and on the T–P sections there appear solidus lines corresponding to the eutectic transformations BiSn+Sn—liq and BiSn+Bi—liq, depending–

···on the composition of the alloy. Arrests associated with these transformations are also clearly recorded on thermograms of alloys of different composition. The liquidus lines Bi–liq and Sn–liq intersect, respectively, with the eutectic lines BiSn + Bi–liq and BiSn + Sn–liq. The intersection points of these lines are the eutectic points BiSn + Bi–liq for bismuth-rich alloys and BiSn + Sn–liq for tin-rich alloys. The eutectic point BiSn + Bi–liq for the alloy with 70 at.% Bi corresponds to a temperature of 151° and a pressure of 11 500 atm. At pressures exceeding the eutectic crystallization pressure involving the BiSn phase,

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* In what follows in the article, the solid solution based on tin is denoted simply by the symbol Sn.

Fig. 2. P–T diagram of Bi–Sn alloys containing Sn $\geqslant$ 50 at.%: a—alloy with 50 at.% Bi, b—alloy with 55 at.% Bi

Fig. 3. Isobaric sections of the phase diagram of Bi–Sn alloys for pressures of 1; 7000; 12 000 and 18 000 atm

the liquidus lines BiSn–liq must be observed. The temperatures at which BiSn crystallization from the melt begins in all the alloys studied (with the exception of alloys close in composition to 50 at.% Bi + 50 at.% Sn) are not noticeable on the thermograms; therefore the liquidus lines BiSn–liq in the sections of the diagrams shown (see Fig. 3) were constructed from three points—the melting point of BiSn at the given pressure and the two eutectic points BiSn + Bi–liq and BiSn + Sn–liq.

The melting line of the BiSn compound is approximately straight, and the tangent of the angle of its inclination to the pressure axis is $6 \cdot 10^{-3}$ deg/atm. The position of the curve corresponding to formation of the intermetallic compound in the solid state,

$$\mathrm{Bi} + \mathrm{Sn} \to \mathrm{BiSn},$$

is practically independent of the composition of the alloy. The alloy composition affects only the magnitude of the heat effect of compound formation observed on the thermograms. Apparently, this indicates the low solubility of bismuth and tin in the BiSn compound. The curve of the reverse transformation,

$$\mathrm{BiSn} \to \mathrm{Bi} + \mathrm{Sn},$$

shifts noticeably with a change in composition; this can be explained by kinetic causes: by the accelerating influence of excess bismuth crystals on the decomposition process of the BiSn compound. In bismuth-rich alloys, at pressures above 18 000 atm, heat effects associated with polymorphic transformations of bismuth are noticeable. In Fig. 2 some points corresponding to the I–II and II –III transformations of bismuth in an alloy with 90 at.% Bi are plotted, and the I–II and II–III equilibrium lines for pure bismuth are drawn (^{10}). Polymorphic transformations

the excess bismuth in the alloys proceed more sluggishly than in pure bismuth, and as a result, after several heating-cooling cycles in the solid state, they become smeared over a considerable temperature (pressure) interval. The transformation points of bismuth in the alloys fall fairly well on the transformation lines of pure bismuth.

On the basis of the data obtained, the following conclusions may be drawn concerning the effect of pressure on the form of the T-C diagrams of Bi–Sn alloys: in the phase diagram of Bi–Sn alloys at pressures of 1-7000 atm there occurs a shift of the eutectic point in composition toward bismuth and a slight lowering of the eutectic temperature. At pressures above 7000 atm the diagram is divided into two eutectic diagrams, Bi—BiSn and BiSn—Sn. The liquidus line for BiSn forms a rather flat dome, as is also observed in the case of other similar state diagrams, for example InSb. With increasing pressure, the eutectic point BiSn + Sn—liq shifts strongly toward tin, while BiSn + Bi—liq shifts toward bismuth. At a pressure of 18,300 atm the temperature of the eutectic transformation BiSn + Bi—liq becomes equal to the melting temperature of pure bismuth. At pressures above 18,300 atm the BiSn—Bi phase diagram apparently becomes a diagram of the peritectic type, and the eutectic line BiSn + Bi—liq above 18,000 atm passes into a peritectic line.

In the pressure range 7000-15,000 atm, the BiSn compound obtained upon crystallization of the melt decomposes into the components during cooling to room temperature. At higher pressures this compound is thermodynamically stable over the entire investigated range of compositions and temperatures. The equilibrium line Bi + Sn $\rightleftarrows$ BiSn on the T-P diagrams apparently passes somewhere between the lines of direct and reverse transformation and can be determined in experiments with prolonged annealing.

In parallel with the thermographic investigation, a metallographic study was also carried out of Bi—Sn alloys after heat treatments at various pressures. The microstructural features of the samples crystallized at different pressures are in good agreement with the phase diagram obtained.

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