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Abstract**Full Text***Chemistry*

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CONSTRUCTION OF TIE-LINES IN TWO-PHASE REGIONS OF PHASE DIAGRAMS OF METALLIC SYSTEMS BY THE MICROHARDNESS METHOD*(Presented by Academician A. A. Bochvar, February 8, 1958)*

Determining the position of tie-lines in two-phase regions of phase diagrams is one of the most laborious operations of physicochemical analysis, especially in the study of metallic systems in the solid state. In this case it is necessary to know the chemical composition of the individual phases, which constitutes the main difficulty. However, by using the microhardness method, it is possible to cope with the solution of such a problem.

In previously performed studies ^(1,2) it was shown that the character of experimentally constructed microhardness isotherms for various sections of ternary phase diagrams depends substantially on the orientation of the sections studied with respect to the tie-lines. The present communication aims to show the possibility of using microhardness-measurement data to determine the fixed position of tie-lines.

In most cases, when binary solid solutions of metallic systems are formed, the increase in microhardness of the solid solution is proportional to its concentration*. Without any noticeable deviations, an analogous dependence is often also manifested for ternary solid solutions (Fig. 1a). In confirmation of the propositions that were set forth in ⁽³⁾, the increase in microhardness of the ternary solid solution in the copper–aluminum–titanium system** also proves to be an additive property with respect to the increases

Fig. 1. Additivity of the increase in microhardness of a ternary solid solution from the increase in microhardness in the corresponding binary solid solutions. Geometrical constructions emphasize the fact that the change in microhardness with composition for sections of the copper–aluminum–titanium phase diagram at constant titanium content takes place parallel to its change in the copper–aluminum system and is shifted by a certain amount corresponding to the quantity of titanium contained in the alloys.

of microhardness in the binary systems included in it. Thus, the addition of titanium to copper or aluminum affects the microhardness in approximately the

Fig. 2. Construction of tie-lines in the $\alpha + \text{Cu}_3\text{Ti}$ region of the copper–aluminum–titanium phase diagram at temperatures of 500 and 850° from microhardness measurement data.

Figure 1: Fig. 2. Construction of tie-lines in the $\alpha + \text{Cu}_3\text{Ti}$ region of the copper–aluminum–titanium phase diagram at temperatures of 500 and 850° from microhardness measurement data.

same way; when aluminum and titanium are introduced simultaneously into copper, their hardening action is summed.

* Generally speaking, the indicated dependence of microhardness for solid solutions is expressed by a curve convex to the concentration axis. However, at not very high concentrations the curvature of this curve is slight. Therefore, in the case of limited solubility—especially if it is small—the assumption made is fulfilled quite well, and linearity is preserved up to the attainment of the limiting concentration.

** Experimental data on this system are given here as an example.

microhardness values in the corresponding binary solid solutions. An illustration of this property on the basis of experimental data obtained by a specially developed method ⁽⁴⁾ is given in Figs. 1a and b.

To determine the position of the tie-lines, one may make use of the indicated dependence of the microhardness of a solid solution on its concentration. Since any given microhardness value will be possessed by a series of solid solutions, it is additionally necessary to use one of the characteristics of the conjugate points of a tie-line. These points must lie on the surface of limited solubility. Consequently, taking this circumstance into account, it will be easy, from the known value of the microhardness of the solid solution in the alloy, to find its concentration. The simplest way for this purpose is to use the method of geometrical constructions.

Fig. 2. Construction of tie-lines in the $\alpha + \text{Cu}_3\text{Ti}$ region of the copper–aluminum–titanium phase diagram at temperatures of 500 and 850° from microhardness measurement data. 1 –isosclers, 2 –solubility isotherms; I–500°, II –850°.

In Fig. 2 the necessary constructions have been carried out and, by way of example, the position of the tie-lines in the $\alpha + \text{Cu}_3\text{Ti}$ region of the copper–aluminum–titanium phase diagram has been determined at temperatures of 500 and 850°.

The following data should serve as the starting point for carrying out such constructions.

First, the dependence of the microhardness of the solid solution on concentration in the corresponding two-component systems must be known. If these depen-

dences are linear and there is experimental confirmation of the additivity of the increment in microhardness of the three-component solid solution, then the dependence of its microhardness on concentration will be expressed geometrically by a plane of general position, which passes through straight lines expressing the dependence of microhardness in the corresponding two-component systems, and whose inclination to the concentration axes of both alloying components will be determined by the magnitude of the strengthening caused by one or the other component upon dissolution. In this connection, one may confine oneself to knowing the dependence of microhardness on concentration for one of the two-component systems (in this case either of the two variants is possible), as well as knowing the ratio of the strengthening of the solid solution observed upon dissolution of one component to the strengthening of the solid solution upon dissolution of the other component.

Second, the joint solubility of both com-

ponents at the temperatures for which the position of the tie-lines is determined*.

Third, it is necessary to have data on measurements of the microhardness of the solid solution in that two-phase region for which the position of the tie-lines is being investigated. The investigation is carried out on quenched specimens. The results of the measurements must correspond to such a component content in the alloy at which the magnitude of the microhardness is not affected by microheterogeneity of the solid-solution crystals (^{1,5-10}). For this purpose an alloy is selected through which the constructed tie-line must pass and which is located, as far as possible, close to the solubility isotherm. This limitation may be dispensed with if, before the microhardness is investigated, the alloys have been subjected to prolonged homogenization sufficient to eliminate microheterogeneity of the solid-solution crystals (^{1,10,11}). In the case where the position of tie-lines is determined in two-phase regions located between the liquidus and solidus surfaces, quenching of alloys is possible only from the region of the solid-liquid state bounded by the surface of the onset of linear shrinkage (¹¹⁻¹³).

Next, from the known measured value of the microhardness of the solid solution of an alloy in the two-phase region, a line of equal microhardness values (an isoscler) is drawn. Obviously, the direction of all isosclers in the given ternary system will be parallel. Therefore, in order to draw the isosclers, it is first of all necessary to determine this direction. For this, in the case of the copper–aluminum–titanium system, for example, one may use the known values of strengthening associated with the formation of solid solutions in the copper–titanium and copper–aluminum systems. Dissolution of titanium in copper causes greater strengthening than dissolution of aluminum in copper. Experience shows that the microhardness increases by 33 kg/mm² upon the introduction of 1% titanium into the solid solution and by 12.4 kg/mm² upon the introduction of 1% aluminum. Therefore, with the same scale along the axes, isosclers in the copper–aluminum–titanium system cut off on the concentration axis in the copper–aluminum system segments that are 2.66 times larger

than the segments cut off by isosclers on the concentration axis in the copper–titanium system ($33.0 : 12.4 = 2.66$). After the direction of the isosclers has been established, to draw isosclers from the given microhardness values one may use the dependence of microhardness on concentration in either of the binary systems. Figure 2 shows the construction of tie-lines at 500° from the known dependence of microhardness on concentration in the copper–titanium system and at 850° from the same dependence in the copper–aluminum system.

The isoscler is drawn until it intersects the corresponding solubility isotherm. The point of intersection represents a point on the concentration triangle which corresponds to a limiting saturated solid solution having a microhardness, and consequently also a concentration, the same as that of the solid solution of the selected alloy in the two-phase region.

Then, by connecting the point of intersection of the isoscler with the corresponding solubility isotherm and the point representing the composition of the alloy for which the microhardness of the solid solution was measured, we obtain the direction of one of the tie-lines at the given temperature. Both points are marked in Fig. 2 by circles.

If the isoscler meets the solubility isotherm at several points, it becomes necessary to choose one of several alternatives. In that case one should be guided by data obtained in those geometrical constructions which lead to unambiguous solutions. In addition,

* It should be noted that not all points of the plane of general position reflecting the dependence of the microhardness of a solid solution on its concentration will correspond to actually realizable values. In projection onto the plane of the concentration triangle, the region of points corresponding to a definite physical meaning for equilibrium solid solutions will be bounded by the solubility isotherm.

Sometimes the known data on the possible position of the second conjugate point of a tie-line facilitate the solution of such a problem. Thus, for example, in the copper–aluminum–titanium system, limited solid solutions apparently form on the basis of the binary intermetallic compound Cu_3Ti , and the continuations of the constructed tie-lines intersect near the ordinate of this compound.

Under favorable conditions, the position of tie-lines can be outlined very accurately. For example, accuracy in constructing a tie-line is ensured when the specific volume of the second phase, which heterogenizes the solid solution, is small in comparison with the specific volume of the solid solution, when it is possible to select for measurement of microhardness an alloy lying in the two-phase region far from the solubility isotherm¹⁰. Also favorable is the case when the angle at which the isoscler crosses the solubility isotherm is close to a right angle. If, moreover, in the direction of the tie-line there are other alloys whose solid solution has not undergone microheterogenization affecting the microhardness,

then it is possible to refine and check the constructions carried out.

All the enumerated data necessary for determining the position of tie-lines are usually available after carrying out an investigation of the microhardness of the solid solution as a function of composition*, and the construction of tie-lines in this case may be only the final operation.

In conclusion, it should be pointed out that it is possible to use the microhardness method for constructing tie-lines in ternary systems whose solid solutions do not possess the indicated properties of linearity and additivity. For this purpose it is first necessary to establish the dependence of microhardness along the entire length, or on a separate region of interest, of the solubility isotherm by directly measuring it, if possible on a larger number of alloys. Then, from the known value of the microhardness of an alloy in the two-phase region and from the established dependence, the position on the solubility isotherm of an alloy with equal microhardness is determined by interpolation. The position of this alloy corresponds to the position on the diagram of one of the conjugate points of the tie-line. Further, to construct the tie-line, it remains to connect the point obtained with the point of the alloy of the two-phase region for which the microhardness measurement was made.

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* The results of an investigation of the copper–aluminum–titanium system were reported in works ^{14,15}.

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