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T-x-y Diagrams of Pd-Cu-{Ag,Ni,Pt} systems for membrane material

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Abstract

The features of the formation of surfaces in Pd-Cu-based T-x-y diagrams, given by order and disorder curves in boundary binary systems are discussed. The geometric structure of the Cu-Pd-Ag T-x-y diagram is discussed in detail; its 3D computer model has been designed.

Keywords: Phase diagrams; 3D simulation; Copper - Palladium - Silver - Nickel □Platinum.

Properties of metal alloys, applied for membranes, are contradictory. For instance, in spite of Pd-Ag alloys have been good studied and are widely applied in practice, they have such advantages (possible congestion of capillaries and membranes, Pd-Ag alloys are poisoned in gas mixtures even small amount of hydrogen sulfide) that necessity in elaboration of Ag-free Pd-based alloys is generated.

The Pd-Cu-based alloys have the most appropriate characteristics. The quality of two-component alloys may be improved by addition of third component, for instance, Pt, Ni, In or rare earth metals. In this case three-dimensional (3D) computer models of T-x-y diagrams become very convenient tool for selection of materials characteristics.

Ternary systems Pd-Cu-R (R=Ag, Ni, Pt) have similar geometric construction. Liquidus and solidus of systems with Ni and Pt are borders of continuous solid solution crystallization two-phase region (Gupta, 2004) and (Potekaev et al., 2013). Liquidus of the analogous system with Ag includes the univariant curve, given by eutectic solubility gap in

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the binary system Ag-Cu (Chang et al., 1977). Solubility gap in solid state has a place in systems Pd-Cu and Cu-Pt as a result of solid solution ordering. Order and disorder curves form in the ternary system with Pt as individual surfaces as uninterrupted surface extending from one binary system to another. This 3D diagram of the structural states in the Cu-Pd-Pt system, has been designed by both literature data and by geometric construction of multicomponent phase diagrams from topological principles (Potekaev et al., 2013). As for the system with Ni, it possess continuous ternary solid solution region.

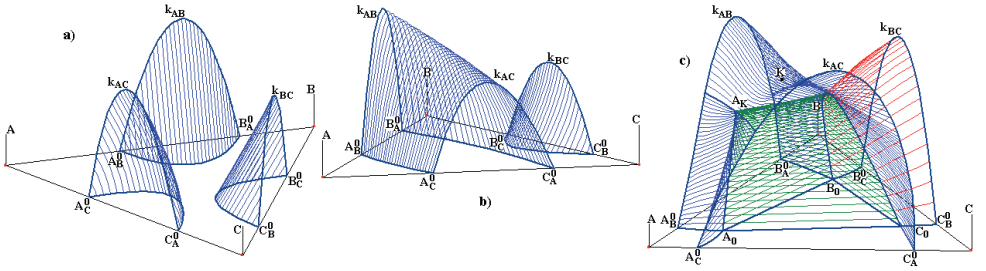

Fig. 1. Miscibility gaps in three binary systems.

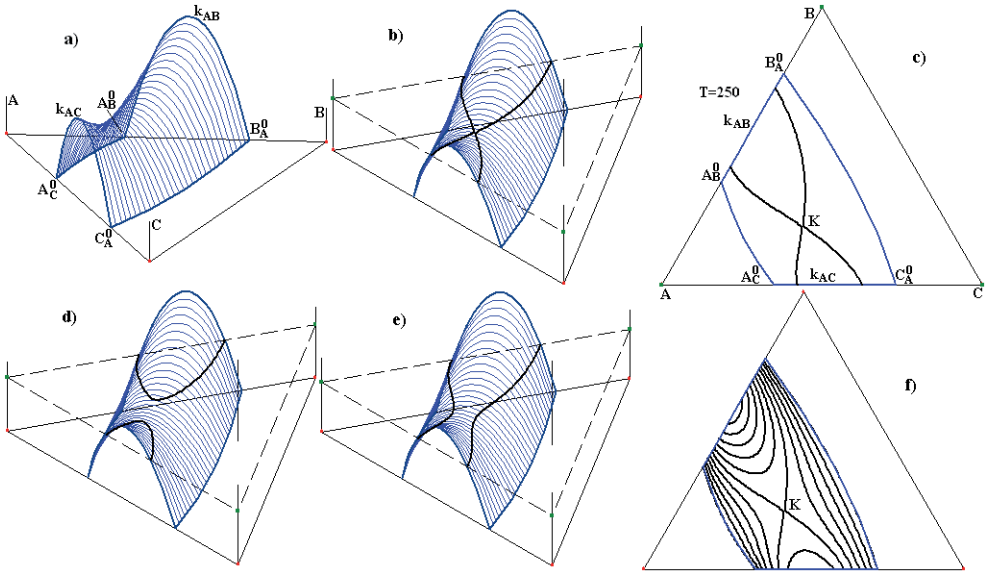

Fig. 2. Miscibility gaps in two binary systems (a), isothermal sections of the surface with the saddle critical point (b)-(e).

Detail analysis of features of phase regions of continuous solid solutions and surfaces, being boundaries around them, may be seen in the monograph by the outstanding Russian scientist Dmitry Petrov (Petrov, 1986).

In the simplest case the two-phase regions of the break of solubility are locked in the ternary system separately from each other (Fig. 1a). Two of them can merge, and the surface of solubility in this case becomes continuous and is extended from one binary system to another (Fig. 1b). Solubility curves in the binary systems are the boundaries of this surface. The curve $k_{AB}k_{AC}$ on the solubility surface is the critical one; its end points are

critical points in binary systems. If the ternary solid solution is unstable in the temperature range of higher than critical points in the binary systems, maximum point appears at the surface of solubility. It coincides with the ternary critical point K (Fig. 1c).

If the ternary critical point K lies below both critical points at the binary systems, then in that case it coincides with the saddle point on the surface of the solubility (Fig. 2). It is traditionally assumed that the isotherms, which correspond to the critical temperature, concern in the point K (Petrov, 1986, Fig. 84), and direction of the tie-lines (more precise, the tie-line, degenerated into the point), which correspond to the ternary critical point, connects them with the general tangent of these isotherms. Represented in Fig. 2 results refute this opinion. Intersected separatrices appear in the computer models of such surfaces instead of the isotherms being concerned at the point K (Fig. 2) (Fedorov et al., 1996). Two branches of curves in the environment of the hyperbolic (saddle) point K and in the tangential plane to the point K are the sections of surface by tangential plane to the point K and the asymptotic directions of surface in K. Surface intersects the tangential plane in the point K, main curvatures k_1 and k_2 have opposite signs, since the Gaussian curvature is negative: $K=k_1k_2<0$.

However if the shaping of continuous surfaces is dismantled in detail, then information about the formation of the separate surfaces and phase fields as a result of solid solution ordering is presented in the literature insufficient. For instance, it is necessary to examine the geometry structure of Cu-Pd-Ag T-x-y diagram in more detail.

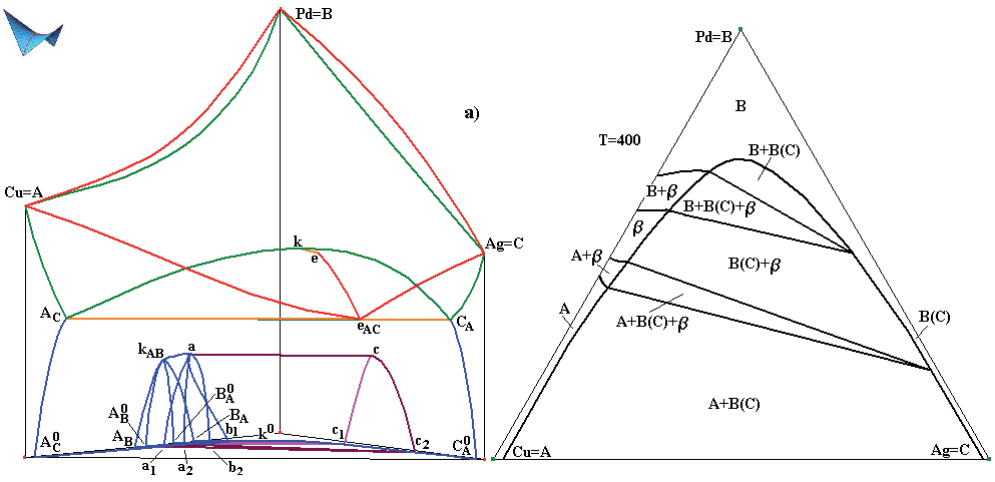

Fig. 3. T-x-y diagram 3D computer model of Cu-Pd-Ag=A-B-D (a) and isothermal section T=400°C (b).

Eutectic solubility gap in the binary system Cu-Ag=A-C gives the fold $e_{AC}e$ on the liquidus surface and the three-phase region L+Cu+Pd(Ag)=L+A+B(C). Ruled surfaces with directing lines $e_{AC}e$, A_Ck, C_Ak serve as the boundaries of the latter (Fig. 3). Solvus surface $A_CkC_AC^0{}_Ak_0A^0{}_C$ is intersected with surfaces, which are formed by order and disorder curves $A_Bk_{AB}B_A$ and $A^0{}_Bk_{AB}B^0{}_A$ in the binary system Cu-Pd=A-B. The solid solution Cu(Pd) in this system below 800°C is decomposed to Cu and Pd, and the solid solution β with another crystal structure is formed (Chang et al., 1977).

As a result, six new surfaces of solvus ($k_{AB}aa_1A_B$ and $k_{AB}aa_2A^0{}_B$, $k_{AB}ab_1B_A$ and $k_{AB}ab_2B^0{}_A$, aa_2b_2 and cc_1c_2) appear in the T-x-y diagram. They serve, correspondingly, as borders of two-phase regions A+β and B+β (Fig. 3b). Besides them, two three-phase

regions A+B(C)+β and B+B(C)+β are formed inside the eutectic solubility gap. Their boundaries are ruled surfaces, given by directing lines aa_1, aa_2, cc_2 and ab_1, ab_2, cc_1, correspondingly.

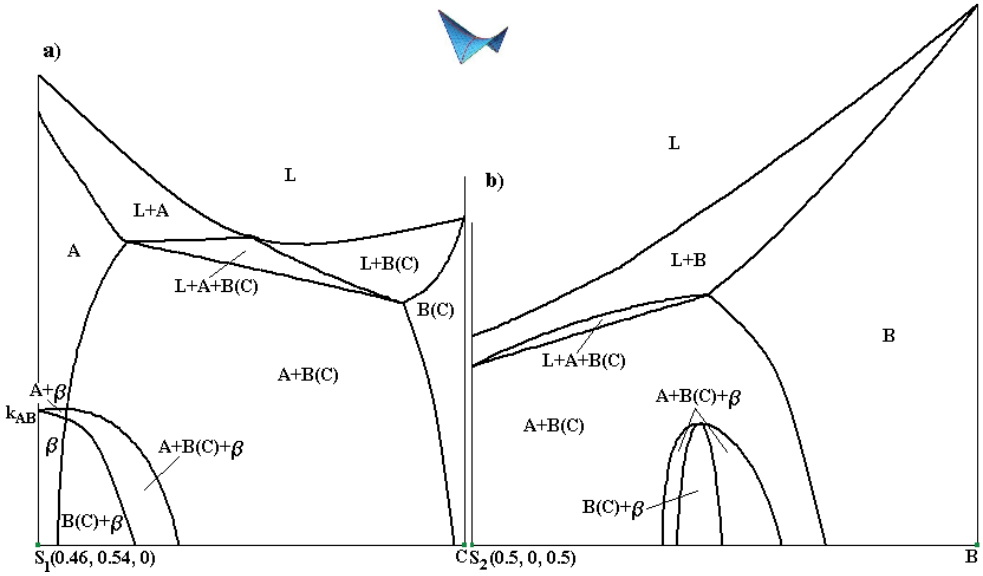

Fig. 4. Isopleths of the Cu-Pd-Ag=A-B-C T-x-y diagram 3D computer model (wt %): $S_1(0.46, 0.54, 0)=k_{AB}$-C=Ag (a), $S_2(0.5, 0, 0.5)$-B=Pd (b).

The very detailed study of the T-x-y diagram geometric structure is necessary for constructing 3D computer model. Such sort models make possible to investigate surfaces by vertical (Fig. 4) and horizontal (Fig. 3b) sections, to compare the 3D model sections with experimental ones, to calculate and to design so called mass balances diagrams, which demonstrate crystallizations of any initial composition, beginning from the liquid up to the final sets of microstructure elements.

Acknowledgements

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