INTERACTION OF SILVER AND PHOSPHORUS WITH ZIRCONIUM, NIOBIUM, AND MOLYBDENUM

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Interaction of components in the systems (Zr, Nb, Mo)—Ag—P is studied by X-ray analysis and phase diagrams are constructed at different temperatures for various phosphorus contents. Ternary compounds are not found in the systems studied. In the Zr—Ag—P system silver dissolves in phosphide Zr14P9 up to the limiting composition Zr0.8Ag3.2P. Comparative analysis is performed for interaction of components in (Zr, Nb, Mo)—(Cu, Ag)—P systems.

The interaction of components in M—Cu—P systems has been studied for a number of transition metals (M). In particular, formation of compounds in the system Ti—Cu—P system and also their structure have been studied [1]. Phase equilibria have been established at 1070 K in systems with refractory metals: (Zr, Nb, Cr, Mo)—Cu—P [2-4]. At the same time there is no information about interaction of components in M—Ag—P systems.

The aim of this work is to study ternary phosphorus-containing systems of refractory metals with silver, and in fact (Zr, Nb, Mo)—Ag—P.

Specimens were prepared from finely-ground zirconium, niobium, molybdenum, red phosphorus and silver powder. The original components contained not less than 0.999 weight fraction of the main component. A sample weighing 1-1.5 g mixed to a uniform charge was pressed into a briquette. With a phosphorus content in specimens of less than 0.33 atomic fraction a briquetted charge was melted in an electric-arc furnace on a copper water-cooled hearth in an atmosphere of purified argon. Specimens with a higher phosphorus content were sintered in evacuated quartz ampules in a muffle furnace with a gradual increase in temperature (100 deg/day) up to the temperature of the subsequent anneal. A feature of sintering specimens in systems containing Nb and Mo was the fact that these refractory metals were added to the charge in the form of phosphides of the composition M3P. If niobium or molybdenum is added in the form of metal powders, then during subsequent sintering they do not interact with the rest of the components and nonequilibrium specimens are obtained containing refractory metal (Nb, Mo) and silver phosphides (AgP2, Ag2P11).

All of the specimens were homogenized by annealing for 800 h after which the equilibrium condition was fixed by quenching in cold water. The interaction of components in the systems was studied at different temperatures depending on the phosphorus content in specimens. Those with 0.66-0.80 atomic fraction of P were annealed at 670 K with the aim of obtaining the phase Ag3P11 (it breaks down above 731 K [5]), specimens with 0.45-0.66 atomic fraction of P were annealed at 870 K since AgP2 breaks down (according not entirely reliable data) above ~827 K [6], and specimens with a lower phosphorus content were annealed at 1070 K.

Specimens were studied by X-ray structural analysis (RKD camera with a diameter of 57.3 mm, CrKα-radiation). Cell parameters for the phases were determined from diffraction pictures (DRON-3M diffractometer, CuKα-radiation) recorded in a stepwise regime in the range 2θ = 10-90° through each 0.05 degree with exposure at each point for 10 sec. The required calculations were carried out by the CSD set of programs [7].

X-ray phase analysis of annealed specimens of binary systems confirm known published [8] compounds: Ag3P11 (structure type Ag3P11), AgP2 (CuP2), ZrP2 (PbCl2), β-ZrP (TiAs), α-ZrP (NaCl), Zr14P9 (Zr14P9), Zr7P4 (Nb7P4), Zr2P3 (Zr2P3), Zr2P (Ti3P); NbP (NbAs), Nb2P3, Nb3P3, NbP4, Nb2P (inherent type of structure), Nb2P (Ti3P); MoP2 (MoP2), MoP (WC), Mo3P3 (Mo3P3), Mo3P (α-V3S). The existence of binary intermetallics is confirmed for the Zr—Ag system: ZrAg (TiCu), Zr2Ag (non-MoS2) [8, 9]. In the Mo—Ag system we have confirmed [10] at 1070 K the solubility of molybdenum in silver up to 0.06 atomic fraction; here the lattice spacing for the solid solution is reduced to a = 0.4057(1) nm compared with pure silver (a = 0.4076(3) nm). In the Nb—Ag system insignificant (not more than 0.05 atomic fraction) solubility of niobium in silver is established causing an increase in the solid solution lattice spacing (a = 0.4087(1) nm) compared with pure silver.

Fig. 1. Phase equilibria diagram in the Zr—Ag—P system. Here and in Figs. 2 and 3: (1), (2), (3) one-, two-, and three-phase specimens respectively.

Fig. 2. Phase equilibria diagram in the Nb—Ag—P system.

Fig. 3. Phase equilibria diagram in the Mo—Ag—P system.

X-ray phase analysis of specimens made it possible to establish phase equilibria in the ternary systems (Zr, Mo)—Ag—P in the range 0-0.80 atomic fraction of P, and in the Nb—Ag—P system in the range 0-0.67 atomic fraction of P, and also to construct isothermal sections at 670, 870, and 1070 K for regions with a phosphorus content of 0.66-0.80, 0.45-0.66, 0-0.45 atomic fraction respectively (Figs. 1-3).

A common factor for all three systems is the absence of ternary phosphides and marked solubility of the third component in binary compounds. Silver is in equilibrium with the majority of binary transition metal phosphides containing from 0.25 to 0.50 atomic fraction of P. Of the binary phosphides only Zr$_{14}$P$_9$ dissolves silver up to the limiting composition Zr$_{10.8}$Ag$_{3.2}$P$_5$; here lattice spacings decrease to $a = 1.6432(7)$, $b = 2.705(2)$, $c = 0.3600(2)$ nm. According to our data the lattice spacings for the Zr$_{14}$P$_9$ phase are: $c = 1.6726(9)$, $b = 2.758(1)$, $c = 0.3677(2)$ nm.

The results obtained make it possible to provide a comparative characteristic for interaction in the systems (Zr, Nb, Mo)—(Cu, Ag)—P. The greatest difference is observed between the systems Zr—Cu—P [2] and Zr—Ag—P. In the first of them two compounds form (ZrCu$_2$P$_2$ and Zr$_4$CuP), but in the second no compounds are detected. In our view formation of compounds in the Zr—Cu—P system and absence of them from the Zr—Ag—P system are due to the greater difference in