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PHYSICAL-CHEMICAL INVESTIGATION OF PHASE EQUILIBRIUM IN THE $Cu_3As_4Te_9$-$CrAsTe_3$ SYSTEM

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Abstract

The phase equilibrium in the $Cu_3As_4Te_9$-$CrAsTe_3$ system was studied by methods of physicochemical analysis: differential thermal analysis (DTA), X-ray diffraction analysis (XRD), microstructural analysis (MSA), determination of density and microhardness, and a T-x phase diagram of the system was constructed. As a result, it was established that the phase diagram of the $Cu_3As_4Te_9$-$CrAsTe_3$ system is a non-quasi-binary section of the quasi-ternary Cr_2Te_3-As_2Te_3-CuTe system. In the system at room temperature, solid solutions based on the $Cu_3As_4Te_9$ compound extends to 5 mol % $CrAsTe_3$. The peritectic compound $CrAsTe_3$ decomposes as follows: $CrAsTe \leftrightarrow M + Cr_2Te_3$.

Keywords: system, phase equilibrium, non-quasi-binary, diagram, density.

The components of the $Cu_3As_4Te_9$-$CrAsTe_3$ system consist of As_2Te_3, Cr_2Te_3 and CuTe compounds. Now let's look at each component. The As_2Te_3 compound and solid solutions based on it are thermoelectric and photosensitive materials [1-5]. A number of ternary and quaternary systems involving the As_2Te_3 compound have been studied [6-10]. Alloys based on chromium chalcogenides are magnetic materials. Ternary chromium and copper chalcogenides are being studied as materials with ferromagnetic properties [11-14]. Superionic semiconductors based on copper chalcogenides are energy generators, and at the same time, electrochemical sensors, recorders and selective ion electrodes are widely used in optical ion devices as a source of chemical electricity based on them [15-19]. From this point of view, obtaining composite phases of complex composition by studying the phase equilibrium of $Cu_3As_4Te_9$-$CrAsTe_3$ is of scientific and practical importance.

The purpose of the work is a physicochemical study of phase equilibrium in the $Cu_3As_4Te_9$-$CrAsTe_3$ system and its alloys.

Experimental part

Before the synthesis of alloys of the $Cu_3As_4Te_9$-$CrAsTe_3$ system, the $Cu_3As_4Te_9$ compound was synthesized from CuTe and As_2Te_3 compounds. The $CrAsTe_3$ compound is synthesized from high purity elements. Since the $CrAsTe_3$ compound is peritectic in nature, it was heat treated for 240 hours below the peritectic temperature to homogenize after synthesis. Equilibrium alloys were studied using methods (DTA, XRF, MSA, as well as microhardness and density assessment) of physicochemical analysis.

Differential thermal analysis (DTA) of the alloys was carried out on a TERMOSCAN-2 pyrometer. Chromel-alumel was used as a thermocouple; heating rate was 5ºC/min.

X-ray phase analysis (XPA) was carried out on a D2 PHASER X-ray diffractometer. In this case, CuKα radiation and a Ni filter were used. The microstructure of the samples was analyzed using a MIM-8 microscope. In well-polished samples, a chromium solution was used as a mordant to separate the phases. The microhardness of the alloys was measured using a PMT-3 metallographic microscope. The density of the samples was determined by the pycnometric method; Toluene was used as a working solution.

Results and its discussion

After obtaining the complete composition of the main components, the alloys of the $Cu_3As_4Te_9$-$CrAsTe_3$ system were synthesized by the ampoule method from the $Cu_3As_4Te_9$ and CrAsTe3 components in a wide range of concentrations. Rich in $Cu_3As_4Te_9$, they looked like a compact mass and were bright gray substances. With an increase in the amount of $CrAsTe_3$ compound, the alloys acquire a silvery color.

The alloys of the system are resistant to air, water and organic solvents. It dissolves well in strong mineral acids (HNO_3, H_2SO_4). After homogenization of the samples was completed, a physical and chemical analysis of the alloys of the system was carried out. The results of differential thermal analysis of alloys of the $Cu_3As_4Te_9$-$CrAsTe_3$ system show that up to four endothermic effects are observed in the thermograms of the alloys of the system. A large number of thermal effects in the system indicates a multiphase, complex interaction of components.

After heat treatment, the microstructure of the alloys of the system was analyzed and it was found that the system contains single-phase, two- and three-phase regions. The solid solution region in the system was determined based on the $Cu_3As_4Te_9$ compound.

To confirm the results of DTA and microstructural analysis used in constructing the state diagram of the $Cu_3As_4Te_9$-$CrAsTe_3$ system, X-ray phase analysis of alloys from different parts of the system was carried out (Fig. 1).

As a result of X-ray phase analysis of alloys with compositions of 30 and 80 mol. % CrAsTe3 it was established that in the diffraction patterns of these alloys of the system, in addition to the diffraction lines of the main components, there are diffraction lines of other phases. Based on the results, we can say that there are three phases in the system.

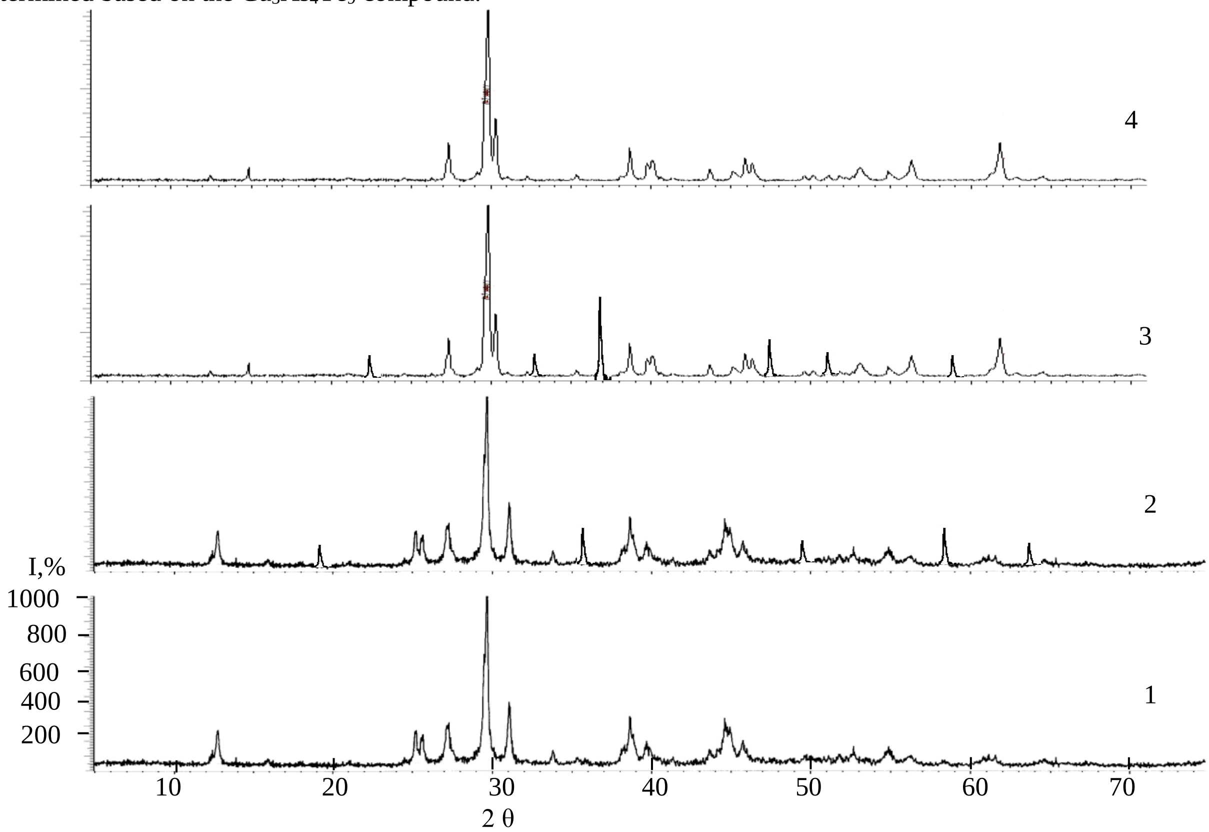

Fig. 1. Diffraction patterns of alloys of the $Cu_3As_4Te_9$-$CrAsTe_3$ system.
1- $Cu_3As_4Te_9$, 2-30 mol %, 3-80 mol %, 4-100 mol % $CrAsTe_3$.

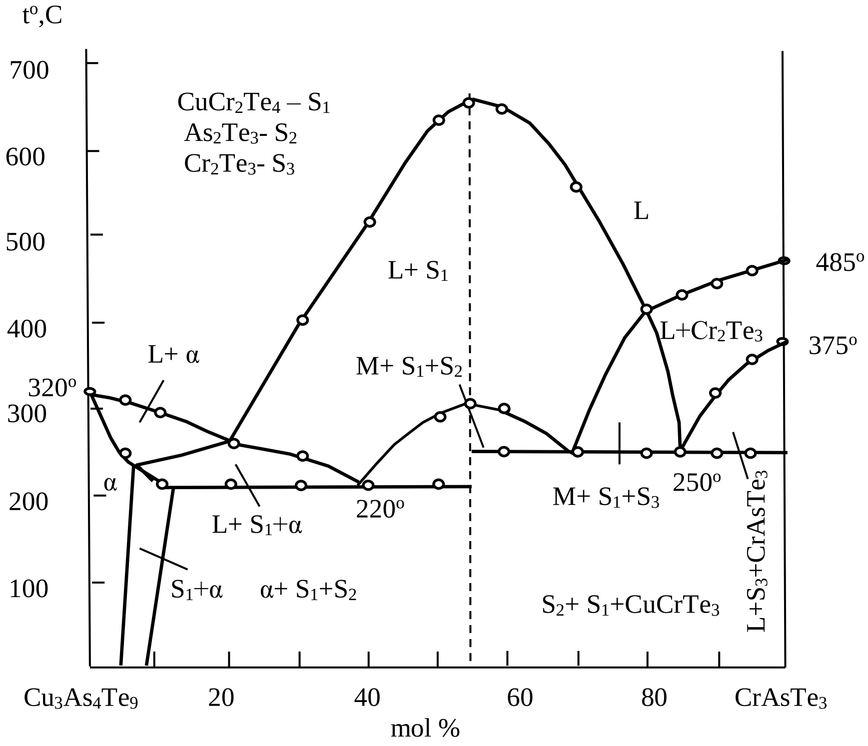

Fig.2. Phase diagram of the $Cu_3As_4Te_9$-$CrAsTe_3$ system/

The phase diagram of the $Cu_3As_4Te_9$-$CrAsTe_3$ system was constructed based on the results of the indicated methods of physicochemical analysis (Fig. 2). The phase diagram of the $Cu_3As_4Te_9$-$CrAsTe_3$ system is a non-quasi-binary section of the quasi-ternary As_2Te_3-Cr_2Te_3-CuTe system. The $Cu_3As_4Te_9$-$CrAsTe_3$ section, since it passes through the region of independent triangles As_2Te_3-$CuCr_2Te_4$-$Cu_3As_4Te_9$ and As_2Te_3-$CuCr_2Te_4$-$CrAsTe_3$, therefore the section is nonquasibinary. At the liquidus intersection point it is in the range of 0–55 mol. % $CrAsTe_3$ is surrounded by monovariant liquidus curves of an α-solid solution based on $Cu_3As_4Te_9$ and the $CuCr_2Te_4$ and As_2Te_3 phases. The liquidus cross section of the α phase and the $CuCr_2Te_4$ compound is 20 mol. % $CrAsTe_3$, temperature 260°C. At this moment, a three-phase equilibrium L↔ α+ $CuCr_2Te_4$ is formed. When the temperature reaches 220°C, a ternary eutectic and a four-phase equilibrium L↔ α+$CuCr_2Te_4$+As_2Te_3 are formed. In the concentration range in the system 55-100 mol % $CrAsTe_3$ is limited by the monovariant equilibrium curves of the $CuCr_2Te_4$ and Cr_2Te_3 phases. The liquidus intersection of the $CuCr_2Te_4$ and Cr_2Te_3 phases is 20 mol %, temperature 325°C. At this moment, there is a three-phase equilibrium L↔$CuCr_2Te_4$+Cr_2Te_3. Four-phase equilibrium occurs at the triple point of peritectic L+Cr_2Te_3↔As_2Te_3+$CrAsTe_3$. Contents 25 mol %, temperature 250°C.

Table 1.

Composition, DTA, density and microhardness of alloys of the $Cu_3As_4Te_9$-$CrAsTe_3$ system depending on the composition

Composition, mol %		Thermal effects, °C	Density, q/sm^3	Microhardness, MPa			
$Cu_3As_4Te_9$	CrAsTe			α	As_2Te_3	$CuCr_2Te_4$	$CrAsTe_3$
				P=0,15 N			P=0,10 N
100	0,0	320	6,96	1960		-	-
95	5,0	250,320	6,98	1980	-	-	-
90	10	225, 295	6,90	1990	-	-	-
80	20	220,265	6,88	1990	1650	1850	-
70	30	220,245,400	6,84	1990	1650	1860	-
60	40	220,515	6,80	1990	1650	1870	-
50	50	220,280,635	6,76	-	1650	1870	-
45	55	220,290,650	6,74	-	1650	1870	
40	60	250,285,640	6,70	-	-	1870	-
30	70	250,555	6,69	-	-	1880	-
20	80	250,430	6,67	-	-	-	-
15	85	250,440	6,65	-	-	-	880
10	90	250,290,450	6,62	-	-	-	880
5,0	95	250,360,475	6,59	-	-	-	870
0,0	100	375,485	6,57	-	-	-	850

Three-phase alloys, consisting of single-phase α, two-phase α+$CuCr_2Te_4$ and three-phase α+$CuCr_2Te_4$+As_2Te_3, crystallize below the solidus line in the range of 0–55 mol % $CrAsTe_3$. Below the solidus line in the range of 55–100 mol % $CrAsTe_3$ three-phase alloys As_2Te_3+$CuCr_2Te_4$+$CrAsTe_3$ are present. The results of measuring the microhardness of alloys of the $Cu_3As_4Te_9$-$CrAsTe_3$ system are given in Table 1. As can be seen from the table, four microhardness values were obtained. The microhardness value (1960-1990) MPa corresponds to the microhardness of the α-solid solution formed on the basis of $Cu_3As_4Te_9$, the microhardness value of 1650 MPa corresponds to As_2Te_3, the value of 1850 MPa corresponds to $CuAs_2Te_4$, and the value (850 -880) MPa corresponds to the microhardness of the $CrAsTe_3$ compound.

Conclusion

Thus, the chemical interaction in the $Cu_3As_4Te_9$-$CrAsTe_3$ system was studied and its phase diagram was constructed. It has been established that the phase diagram of the system is nonquasibinary. The $Cu_3As_4Te_9$-$CrAsTe_3$ cross section passes through the region of independent triangles As_2Te_3-$CuCr_2Te_4$-$Cu_3As_4Te_9$ and As_2Te_3-$CuCr_2Te_4$-$CrAsTe_3$, so the system is nonquasibinary. Liquidus of the $Cu_3As_4Te_9$-$CrAsTe_3$ system in the concentration range of 0-55 mol % $CrAsTe_3$ consists of monovariant equilibrium curves of an α-solid solution based on the $Cu_3As_4Te_9$ compound, $CuCr_2Te_4$ and As_2Te_3 phases. The joint intersection of the liquidus of the α-phase and the $CuCr_2Te_4$ compound is 20 mol % $CrAsTe_3$, temperature 260°C and is accompanied by a three-phase equilibrium reaction L↔α+$CuCr_2Te_4$. A ternary eutectic is formed in the system and a four-phase equilibrium L↔α+$CuCr_2Te_4$+As_2Te_3 is established. The system has 5 mol. % $CrAsTe_3$ are soluble at room temperature based on the $Cu_3As_4Te_9$ compound. The dependences of microhardness and density of alloys of the $Cu_3As_4Te_9$-$CrAsTe_3$ system on composition have been studied.

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