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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Phase Equilibria in the Cu–Cu_2S–As System

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Abstract—Phase equilibria in the Cu–Cu_2S–Assystem have been studied by DTA and X-ray powder diffraction. $Cu_{0.667}S_{0.333}$–As, $Cu_{0.667}S_{0.333}$–$Cu_{0.735}As_{0.265}$, and $Cu_{0.8}S_{0.2}$–As polythermal sections, an isothermal section at 300 K, and the liquidus projection have been constructed. Our data differ from reported data in the extents of primary crystallization phase fields and the coordinates of some invariant equilibrium points.

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The Cu–As–S system has long kept the attention of researches for the following two reasons. First, almost all of the hitherto known ternary compounds of this system are naturally occurring as minerals [1, 2]: Cu_3AsS_4 (enargite and luzonite), $Cu_{12}As_4S_{31}$ or Cu_3AsS_4 (tennantite), $Cu_6As_4S_9$ (sinnerite), CuAsS (lautite), and $Cu_3As_2S_4$ (pearceite), and they are of great interest for the geochemistry of the Earth.

Second, ternary compounds and vitreous alloys of this system are valuable functional materials, which have semiconductor, photoelectric, and other important properties [3–5].

Numerous reported data on phase equilibria in the Cu–As–S system and the properties of its ternary phases are compiled in the survey [5]. However, an inspection of these data shows that, although some polythermal sections have been studied, there is yet no comprehensive idea of phase equilibria in the system. The schematic liquidus-surface projection constructed in [5] using data taken from [6–9] suffers from serious drawbacks: because of the insufficiency of experimental data, primary crystallization fields for most phases are demarcated only conventionally, isotherms are not shown on them, nor are exact coordinates of invariant equilibrium points, and so on. The schematic and controversial character of this diagram was also mentioned by Müller and Blachnik [10, 11].

In the context of the foregoing, we have undertaken a new, detailed study of phase equilibria in the Cu–As–S system. Here, we report on the Cu–Cu_2S–As subsystem.

The boundary constituents and binary phases of the Cu–Cu_2S–As subsystem have been studied in a detailed way.

The Cu–As system [12,13] is characterized by the formation of three intermediate phases: Cu_8As, Cu_3As, and Cu_5As_2. The first phase is stable below 653 K, a temperature at which it decomposes by the peritectoid reaction $Cu_8As \rightarrow \alpha + \beta$ (where α and β are solid solutions based on copper and Cu_3As, respectively). The other two copper arsenides are phases of variable composition with homogeneity ranges of 25.6–27.4 at % As (β phase) and 30.31 at % As γ phase). The β phase melts congruently at 1100 K (the dystectic point has the composition 26.5 at % As). The γ phase is stable within a range of 573–982 K. At 573 K, it decomposes by the solid-phase reaction $\gamma \rightarrow \beta + As$, and at 982 K,

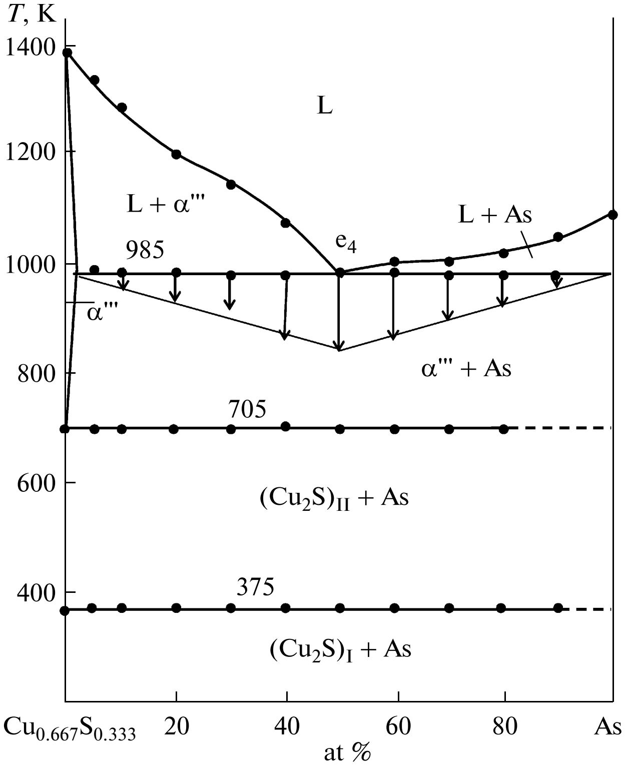

Fig. 1. $Cu_{0.677}S_{0.333}$–As quasi-binary system.

by the peritectoid reaction $\gamma \rightarrow L + \beta$. Two eutectics in the Cu–As system crystallize at 958 and 873 K; they contain 18.4 and 46 at % As, respectively.

The Cu–Cu_2S subsystem has a *T*–*x* diagram with monotectic equilibrium and eutectic equilibrium. At the monotectic temperature (1378 K), the immiscibility region extends from 3 to 32.9 at % S. The eutectic contains 1.5 at % S and solidifies at 1300 K [12, 13].

The crystallographic parameters of copper arsenides and Cu_2S polymorphs are found in [12, 13].

The Cu_2S–As system is quasi-binary and the eutectic type[7]. The eutectic contains 80 at % As and solidifies at 982 K. In [8, 9] there are different versions of the *T*–*x* diagram for the Cu_2S–Cu_3As inner section. According to Kopylov et al. [8], the Cu_2S–Cu_3As system is quasi-binary and is characterized by monotectic equilibrium and eutectic equilibrium at 1298 and 1098 K, respectively. According to Kurz and Blachnik [9], this is a non-quasi-binary system. The eutectic contains 95 mol % $Cu_{0.75}As_{0.25}$ and solidifies at 1073 K, and monotectic equilibrium is monovariant.

Elementary copper melts at 1357 K, and As sublimes at 889 K and melts under a pressure of 3.6 MPa at 1090 K [14].

EXPERIMENTAL

The compound Cu_2S and the β phase of composition $Cu_{0.735}As_{0.265}$ have been prepared by alloying the high-purity constituent elements in required proportions in quartz ampoules that were degassed to ~10^{-2} Pa and sealed. Cu_2S was prepared in a tilted two-zone furnace. The lower hot zone was maintained at 1420 K, and the upper cold zone at 650 K, a temperature is slightly below the sulfur boiling point (718 K [14]).

In order to obtain homogeneous stoichiometric Cu_2S, we followed the recommendation [15] that the synthesis be followed by quenching from 1300 K in cold water. The identity of both phases was verified by DTA and X-ray powder diffraction.

Alloys of the Cu–Cu_2S–As system were prepared by alloying the binary phases and elementary copper and arsenic in evacuated quartz ampoules. Annealing temperatures (~30–50 K below solidus) for exposing alloys for 600–800 h were determined using DTA data for selected nonhomogenized cast alloys.

Experiments were carried out using DTA (an NTR-72 pyrometer and an *xy* self-recorder; chromel–alumel thermocouples) and X-ray powder diffraction (DRON-3, CuK_α radiation).

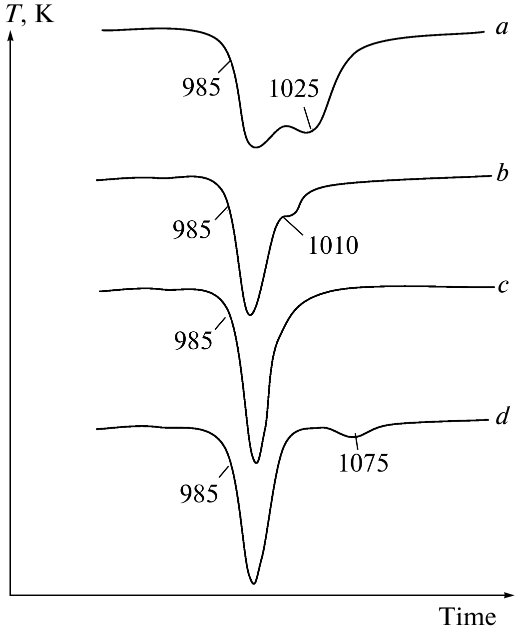

Fig. 2. DTA heating curves for selected alloys of the $Cu_{0.677}S_{0.333}$–As system: (*a*) 80, (*b*) 60, (*c*) 50, and (*d*) 40 at % As.

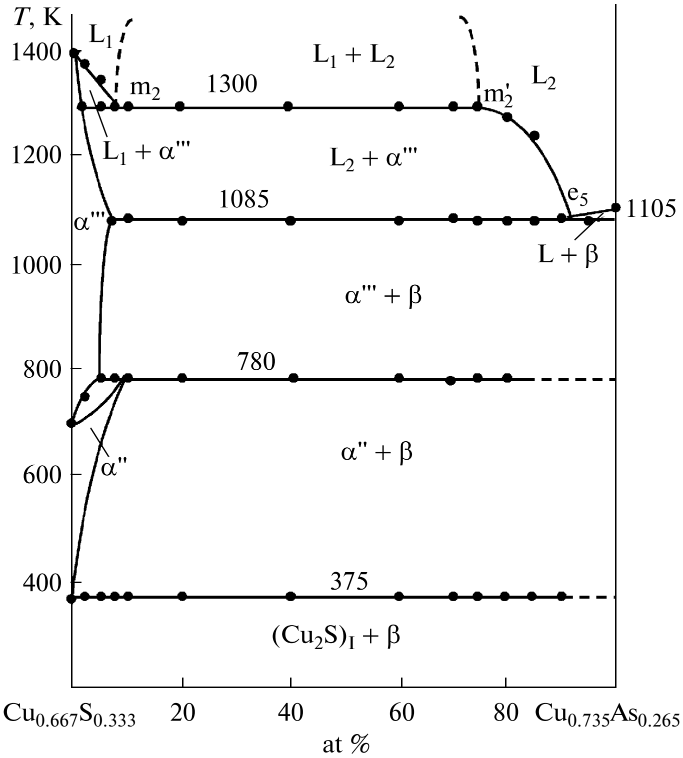

Fig. 3. $Cu_{0.677}S_{0.333}$–$Cu_{0.735}As_{0.265}$ quasi-binary system.

RESULTS AND DISCUSSION

$Cu_{0.677}S_{0.333}$–As system. Our results support the earlier reported [7] eutectic character of phase equilibria in this system (Fig. 1). According to our data, the eutectic coordinates are 50 at % As and 985 K. The Tammann's triangle shows that the intensity of the eutectic melting peak is maximal for this composition (Fig. 1).

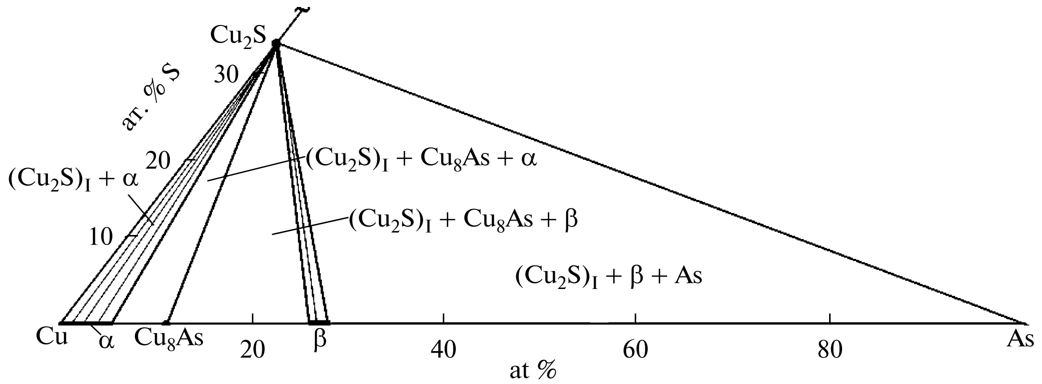

Fig. 4. Equilibrium solid-phase diagram for the $Cu-Cu_2S-As$ system.

The DTA curves in Fig. 2 clearly demonstrate the isothermal character of the only thermal event for the alloy of composition 50 at % As and the occurrence of two peaks for alloys of neighboring compositions, specifically the alloy containing 80 at % As, which corresponds to the eutectic mixture [7].

The 375 and 705 K horizontals in the $Cu_{0.677}S_{0.333}$–As phase diagram correspond to polymorphic transitions in the compound $Cu_{0.677}S_{0.333}$. Their coincidence with data for pure copper(I) sulfide [12, 13] provides an indirect indication of the insignificance of its homogeneity region in this system.

$Cu_{0.677}S_{0.333}$–$Cu_{0.735}As_{0.265}$ system. Studying the Cu_2S-Cu_3As section, we found that DTA curves for stoichiometric Cu_3As feature peaks at 960 K, which correspond to the α + β eutectic (where α and β are solid solutions based on copper and Cu_3As, respectively) [12, 13]. These peaks were also observed on DTA curves for Cu_2S-Cu_3As alloys. This observation suggests that the Cu_2S-Cu_3As section is non-quasi-binary and, below the solidus, its alloys consist of three-phase mixtures: $\alpha + \beta + Cu_2S$. Keeping this in mind, we did not use $Cu_{0.75}As_{0.25}$ (Cu_3As) as the initial constituent to study this section; rather, we used an alloy of composition $Cu_{0.735}As_{0.265}$, which is within the homogeneity region of the β phase and corresponds to the dystectic point in the Cu–As phase diagram [12, 13].

Invariant equilibria in the $Cu-Cu_2S-As$ system

Point in Fig. 5	Equilibrium	Composition, at %		T, K
		Cu	As	
D_1	$L \leftrightarrow \beta$	73.5	26.5	1105
D_2	$L \leftrightarrow \alpha'''$	66.7	–	1402
P	$L + \beta \leftrightarrow \gamma$	66	34	982
U	$L + \beta \leftrightarrow \alpha''' + \gamma$	54	46	970
e_1	$L \leftrightarrow \alpha + \beta$	82	18	958
e_2	$L \leftrightarrow \gamma + As$	54	46	873
e_3	$L \leftrightarrow \alpha + \alpha'''$	98.3	–	1340
e_4	$L \leftrightarrow \alpha''' + As$	33.3	50	985
e_5	$L \leftrightarrow \alpha''' + \beta$	73	24.5	1085
E_1	$L \leftrightarrow \alpha + \alpha''' + \beta$	81	17.5	945
E_2	$L \leftrightarrow \alpha''' + \gamma + As$	52	45.5	860
$m_1(m'_1)$	$L_1 \leftrightarrow L_2 + \alpha'''$	67.1(97)	–	1378
$m_2(m'_2)$	$L_1 \leftrightarrow L_2 + \alpha'''$	67.5(72)	2.1(20)	1300

Note: α and α''' are solid solutions based on the high-temperature Cu_2S phase; β and γ are phases of variable composition based on Cu_3As and Cu_5As_2, respectively.

Our study of the $Cu_{0.677}S_{0.333}$–$Cu_{0.735}As_{0.265}$ sections gave the results displayed in Fig. 3. One can see that this is a quasi-binary system. The eutectic contains 90 at % $Cu_{0.735}As_{0.265}$ and solidifies at 1070 K; to monotectic equilibrium, there corresponds a temperature 1295 K, at which the immiscibility region extends from 10 to 75 at % $Cu_{0.74}As_{0.26}$.

An isothermal section of the $Cu-Cu_2S-As$ phase diagram (Fig. 4) consists of three three-phase regions, which are demarcated by $(Cu_2S)_I$-Cu_8As and $(Cu_2S)_I$-β tie-lines. The occurrence of up to 6 at % As solid solutions based on Cu(α) in the Cu–As binary system [12, 13] leads to the formation of an extensive two-phase region $\alpha + (Cu_2S)_I$.

The liquidus surface (Fig. 5) is comprised of five primary crystallization fields. The most extensive liquidus surfaces are those of the α''' phase, which is based on the high-temperature Cu_2S polymorph, and elementary arsenic. There is an extensive immiscibility region, which occupies a considerable part of the liquidus surface of the α''' phase.

The types and coordinates of invariant equilibria in $Cu-Cu_2S-As$ system, including the boundary binaries, are listed in the table.

Comparing Fig. 5 with the schematic phase diagram reported in [5], we find that our eutectic curve e_4E_2 is strongly displaced toward the Cu–S subsystem compared to its position in [5], which considerably

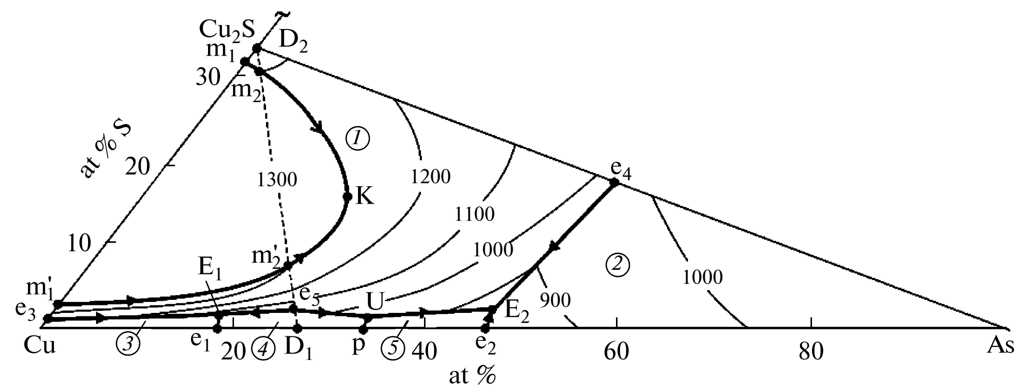

Fig. 5. Liquidus surface projection for the Cu–Cu_2S–As system. Primary crystallization fields: (*1*) α''', (*2*) As, (*3*) α, (*4*) β, and (*5*) γ. The dashed line shows the $Cu_{0.677}S_{0.333}$–$Cu_{0.735}As_{0.265}$ quasi-binary section.

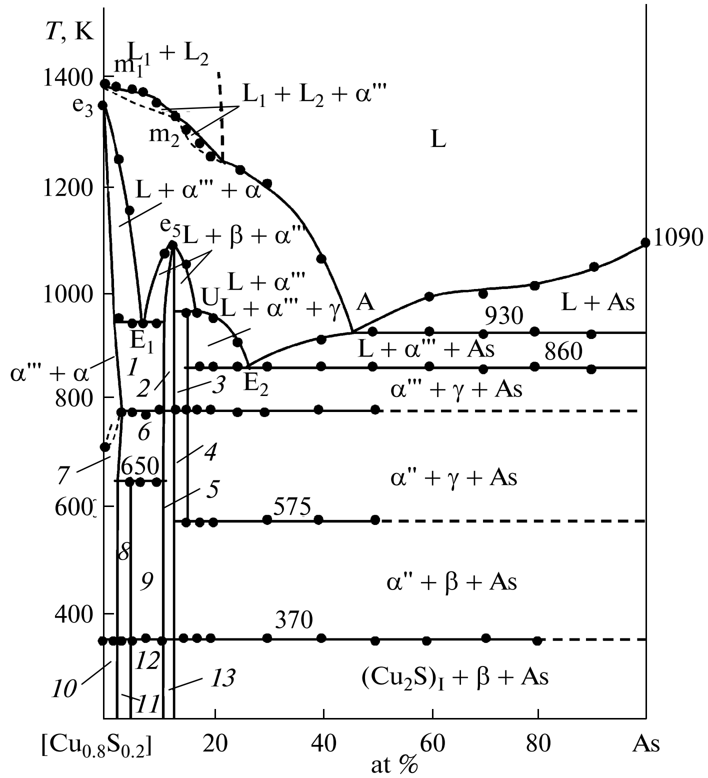

Fig. 6. $[Cu_{0.8}S_{0.2}]$–As polythermal section of the Cu–Cu_2S–As phase diagram. Phase fields: (*1*) α + α''' + β, (*2*) α''' + β, (*3*) α''' + β + γ, (*4*) α'' + β + γ, (*5*) α'' + β; (6) α + α'' + β, (*7*) α + α'', (*8*) α + α'' + Cu_8As, (*9*) α'' + Cu_8As + β, (*10*) α + $(Cu_2S)_I$, (*11*) α + $(Cu_2S)_I$ + Cu_8As, (*12*) $(Cu_2S)_I$ + Cu_8As + β, and (*13*) $(Cu_2S)_I$ + β.

expands the primary crystallization field of elementary arsenic and narrows the liquidus surface of the α''' phase. Further, we determined the temperatures and compositions of the alloys that correspond to invariant points E_1, E_2, and U (Fig. 5, table); in [5], these points were positioned proceeding from the general pattern of phase equilibria in the Cu–As system without appropriate experimental data.

$[Cu_{0.8}S_{0.2}]$–As polythermal section reflects many invariant and monovariant equilibria in the Cu–Cu_2S–As system and allows us to more exactly determine the coordinates of points and cures on the *T–x–y* diagram. The liquidus is comprised of two branches, which correspond to the primary crystallization of the α''' phase based on the high-temperature Cu_2S polymorph and elementary arsenic. In the range of compositions up to 22 at % As, the α''' phase crystallizes from two immiscible melts by the monotectic reaction $L_I \leftrightarrow L + \alpha'''$. The liquidus curves converge at 930 K and 47% As, which verifies the run of the eutectic curve e_4E_2 (Fig. 5). The 930 K horizontal and curve E_2A correspond to the joint crystallization of the α''' phase and arsenic by the monovariant eutectic reaction $L \leftrightarrow \alpha''' + As$. Curves e_3E_1, E_1e_5U, and UE_2 reflect monovariant eutectic equilibria (Fig. 5):

$$L_{e_3E_1} \leftrightarrow \alpha''' + \alpha \ (1340\text{–}945 \text{ K}),$$

$$L_{E_1e_5U} \leftrightarrow \alpha''' + \beta \ (945\text{–}1085\text{–}970 \text{ K}),$$

$$L_{UE_2} \leftrightarrow \alpha''' + \gamma \ (970\text{–}860 \text{ K}).$$

The 945, 970, and 860 K horizontals correspond to invariant eutectic equilibria (E_1 and E_2) and peritectic equilibrium (U) (see table).

The 650 and 575 K peaks, respectively, correspond to the eutectoid and peritectoid decomposition of intermetallic phases Cu_8As and Cu_5As_2 (γ phase) [12, 13].

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