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One-dimensional solidification of the $CuFe_2S_3$ melt

E. F. Sinyakova[1], V. I. Kosyakov.[2]
[1]V. S. Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk
[2]A. V. Nikolaev Institute of Inorganic Chemistry of the SB RAS, Novosibirsk

efsin@igm.nsc.ru

To elucidation the mechanisms of cubanite formation, a sample composed of Fe 33.3, Cu 16.7, S 50.0 at.% is subjected to quasi-equilibrium directional crystallization. The crystallized ingot consisted of three parts: (1) a pyrrhotine solid solution (*poss*), (2) a cubanite (*cb*), and (3) *poss* + *cb*? Curves of the component distribution in the sample are plotted; their partition coefficients between solid and sulfide melt are measured, the change of microstructures in the sample at cooling is defined. The obtained data indicate the existence of the primary crystallization field of cubanite on Cu-Fe-S phase diagram.

Key words: *Cu–Fe–S system, cubanite, pyrrhotite, one-dimensional solidification*

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Introduction

Cubanite (*cb* – $CuFe_2S_3$) is one of the main minerals of massive ore bodies at copper-nickel deposits. It occurs as tabular and grained inclusions [*Genkin et al., 1981; Distler et al., 1998*], large crystals [*Sereda, 2004*] and solid polycrystalline aggregates [*Distler et al., 1996*]. Among the massive ores of the Norilsk deposits there occur varieties with the relative content of cubanite up to 60 – 70% [*Genkin et al., 1966; Distler, 1994; Distler et al., 1998*]. In these ores orthorhombic cubanite is often associated with cubic cubanite or cubic chalcopyrite [*Genkin et al., 1966*].

Liquidus surface of the Cu–Fe–S system was plotted by Greig [*Greig et al.,1955*] but the primary crystallization field of cubanite from sulfide melt was absent on this surface. On the high-temperature isothermal cross-sections on the solid-liquid diagram one can observe the crystallization field of *iss* in its middle part and no signs of equilibrium sulfide melt with other intermediate phases [*Kullerud et al., 1969; Tsujimura, Kitakaze, 2004*]. On the other hand, *Kullerud* (*1963-1964*) and *Dutrizac* (*1976*) report results of thermal analysis of $CuFe_2S_3$, which evidence that this substance melts with decomposition. These data suggest the presence of a two-phase cubanite – liquid equilibrium in the Cu–Fe–S system. Some researchers also suggest the probability of formation of cubanite directly from sulfide magma [*Distler et al., 1996; Distler et al., 1988*]. This opinion agrees with the above experimental results [*Kullerud, 1963-1964; Dutrizac, 1976*] and conflicts with the traditional notion of the phase diagram of the Cu–Fe–S system [*Kosyakov, 2008*].

Elimination of this contradiction requires additional studies of phase relationships with participation of melts in the middle part of the Cu-Fe-S system. To reveal the mechanisms of cubanite formation in this work, we used the method of directional crystallization, which allows determination of the sequence and composition of phases formed from melt [*Kosyakov, Sinyakova, 2005*].

Experimental methods

One-dimensional crystallization of the melt with composition of Fe 33.3, Cu 16.7, S 50.0 at.% was carried out by vertical Bridgman method. The ampoule with homogenous melt had been dropped from the hot zone to the cold one with 2.3×10^{-8} m/s rate. The process occured in quasi-equilibrium regime under these conditions [*Kosyakov, Sinyakova, 2005*]. Length of cylindrical specimen was 90 mm and its diameter was 7 mm. It was cut into 17 samples perpendicular to the longitudinal axis, and each one was weighed. The samples were examined with microscopic, electron microprobe analyses, and X-ray diffraction. The melt composition and partition coefficient of the components were calculated from material balance of components.

Results

Distribution cuves and distribution coefficients of components. Distribution curves Fe and Cu, reflecting the crystallization process of sulfide melt up to g ≈ 0.83, are shown in Fig. 1. The same figure shows the curves of variations in melt composition during crystallization. The starting zone of ingot (I) ($0 \le g \approx 0.06$) is formed of pyrrhotite solid solution (*poss*) with impurity of Cu. Melt composition during crystallization of *poss* changes slightly from Fe 33.3, Cu 16.7, and S 50.0 to Fe 32.5, Cu 17.61, and S 49.88 at.%. Because of the short crystallization range of *poss*, its composition within the limits of error can be considered constant and equal to Fe 44.77 ±0.15, Cu 2.65 ± 0.18, S 52.58 ± 0.17 at.%.

In zone II ($\sim 0.06 \le g \le \sim 0.83$) cubanite crystallizes from melt. At the point of the phase reaction related to the termination of *poss* crystallization and the beginning of *cb* crystallization, the pathway of solid phase composition is broken while the pathway of the melt composition is subjected to bending (Fig. 1). The transition from one segment to another may be interpreted as a monovariant phase reaction: $L + poss \rightarrow cb$. The *cb* composition (Fe 33.25 ±0.18, Cu 16.64 ± 0.27, S 50.09 ± 0.21 at.%) within the limits of error is identical to the stoichiometric composition $CuFe_2S_3$. During *cb* crystallization the melt becomes depleted in iron (k Fe = 1.02 ÷ 1.14) and sulfur (k S = 1.00 ÷ 1.02) and enriched in copper (k Cu = 0.94 ÷ 0.78). Crystallization of cubanite is finished when melt composition is equal to Fe 29.20, Cu 21.88, S 48.92 at.%. The finite part of ingot ($0.83 \le g < 1$) consists of multiphase mixture, the composition and structure of which was not studied by us in detail.

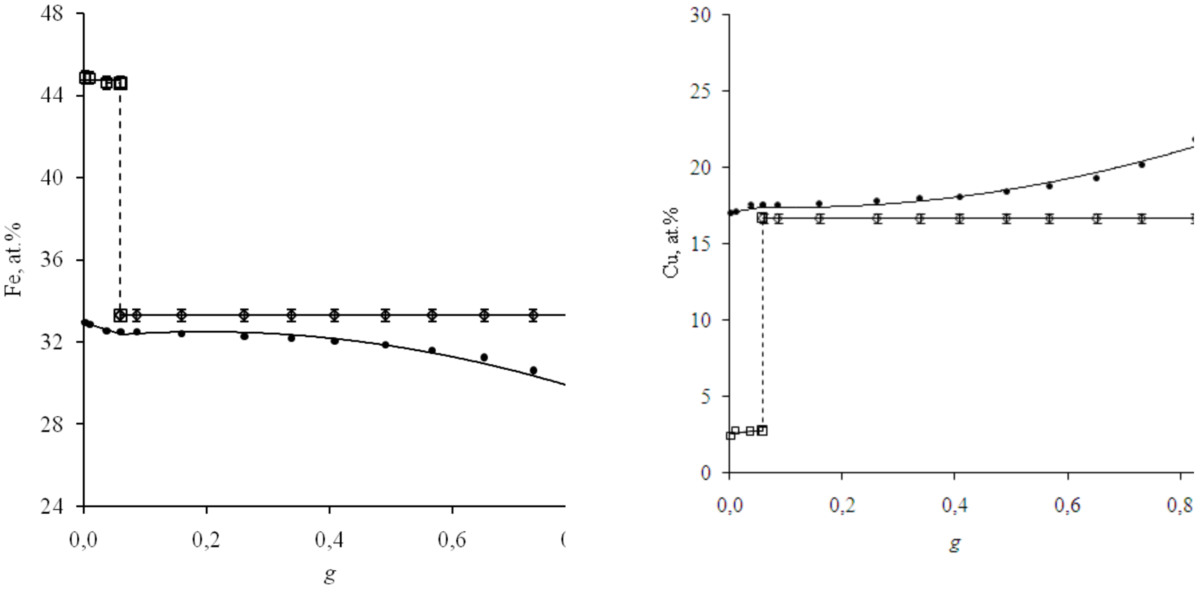

Fig. 1. Distribution of Fe and Cu in *poss* (square), *cb* (rhombus), and in the melt (close circle)

Microscopic description of the sample. The first part of the sample represented a low-temperature monoclinic modification of pyrrhotite solid solution. Lamellar inclusions of cubanite present in the *poss* matrix (Fig. 2a). The composition of inclusions is close to $Cu_{1.1}Fe_{1.9}S_3$, that is somewhat different from the stoichiometric $CuFe_2S_3$ formula. According to the data of X-ray analysis the lattice parameter "a" of the $Cu_{1.1}Fe_{1.9}S_3$ is 5.280 (3) Å, which coincides with the data for synthetic cubanite [*Caye et al., 1988*].

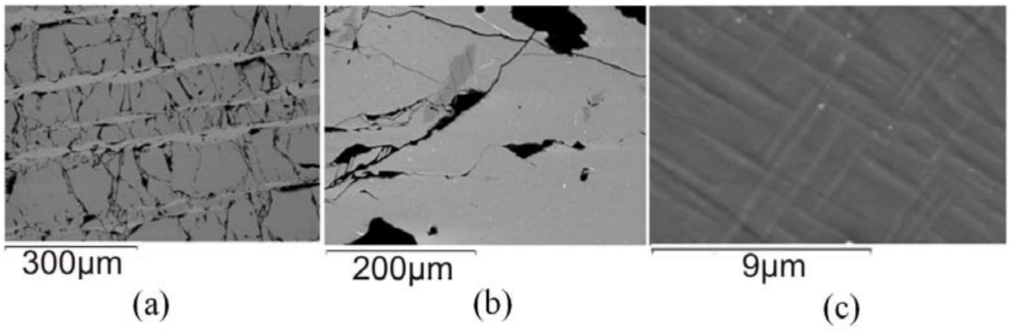

Fig. 2. Microstructure of the sample after one-dimensional solidification and following cooling

to room temperature. Back-scattered electron images: (a) zone I, (g = 0.01): in the gray pyrrhotite matrix are light grey lamellar inclusions of cubanite; (b, c) zone II, (g = 0.09): (b) in light grey cubanite matrix are dark grey inclusions of pyrrhotite; (c) heterogeneous structure of the matrix from figure (b). Black sites are cracks and pores in the sample

Fig. 2b demonstrates a cubanite matrix with inclusions of slightly depleted in iron pyrrhotite with 0.4–0.6 at.% Cu. These inclusions are result of partial breakdown of primary CuFe$_2$S$_3$. It should be formed the phase with composition near to cubanite, but with less iron content. Fig. 2c shows that the cubanite matrix is two-phase. One of the phases are present in the form of thin bars (≤ 1–2 µm in width and 4–8 µm in length), oriented at right angles to each other. It has a composition of Cu$_{1.1}$Fe$_{1.9}$S$_3$ and cubic lattice with parameter 5.280(3) Å. The matrix phase corresponds to stoichiometric cubanite CuFe$_2$S$_3$ with parameter 5.303(3) Å.

Results of our work confirm the data of *Kullerud* (*1963-1964*) and *Dutrizak* (*1976)* on possibility of cubanite crystallization from sulfide melt. It means that an area of cubanite primary crystallization should be on the phase diagram of Cu-Fe-S system. From Fig. 1 follows that this area borders with field of primary crystallization of pyrrhotite solid solution. Thus revision of the liquid-solid phase diagram of Cu–Fe–S system is need in the region of *poss* and *iss* crystallization.

The obtained data confirm possibility of formation coarse-crystalline cubanite in sulfide ores during fractional crystallization sulfide melt. On the other hand, presence of lamellar inclusions of cubanite in association with other Cu-Fe sulfide minerals is possible to explain by solid phase decay of primary phases at their cooling.

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Referenses

Caye, R., B. Cervelle, F. Cesbron et al. (1988). Isocubanite, a new definition of the cubic polymorph of cubanite CuFe$_2$S$_3$, *Mineral. Magazine*, *vol. 52*, pp. 509–514.

Distler, V.V. (1994). *Platinum mineralization the Noril'sk deposits, Geology and Genesis of PGE deposits, Laverov N.P., Distler V.V. eds.* Izdatelstvo Nauka, pp. 7–35 (in Russ.).

Distler, V.V., T.L.Grokhovskaia, T.L. Evstigneyeva et al. (1988). *Petrology of the sulphide magmatic ore-formation.* Izdatelstvo Nauka, p. 230 (in Russ.).

Distler, V.V., E.A. Kulagov, S.F. Sluzhenikin, I.P. Laputina (1996). Quenched sulfide solid solutions in the ores of Noril`sk deposit, *Geology of ore deposits, vol. 38*, pp. 41–53.

Dutrizac, J.E. (1976). Reactions in cubanite and chalcopyrite, *Canad. Mineral*., *vol. 14*, pp. 172–181.

Genkin, A.D, A.A. Filimonova, T.N. Shadlun et al. (1966). On cubic cubanite and cubic chalcopyrite, *Geology of ore deposit, vol. 1*, pp. 41–54.

Genkin, A. D., V. V. Distler, G. D. Gladyshev et al. (1981). *Copper–Nickel Sulfide Ores of the Norilsk Deposit.* Izdatelstvo Nauka, p. 234 (in Russ.).

Greig, J.W., E. Jensen, H.E. Mervin (1955). The system Cu–Fe–S, *Carnegie Inst. Washington Year Book, vol. 54*. pp. 129–134.

Kosyakov, V. I. (2008). Topological analysis of the melting diagram of the Cu–Fe–S system, *Russ. J. Inorg. Chem*, *vol. 53*, No 6, pp. 946–951.

Kosyakov, V.I., E.F. Sinyakova (2005). Directional crystallization of Fe–Ni sulfide melts within the crystallization field of monosulfide solid solution, *Geochem Intern*., *vol. 43*, pp. 372–385.

Kullerud, G. (1963-1964). The Cu–Fe–S system, *Carnegie Inst. Washington Year Book 63*, pp. 200–202.

Kullerud, G., R.A. Yund, G.H. Moh (1969). Phase relations in the Cu–Fe–S, Cu–Ni–S and Fe–Ni–S systems, *Econ. Geol. Monograph*., *vol. 4*, pp. 323–343.

Sereda, E.V. (2004). *Standart collection of the rocks, ores and minerals of Noril'sk deposits. Bowels of Taimyr. A Selection of Scientific Papers*. *Simonov O.N. ed.* Issue 2, Dudinka, pp. 306–309 (in Russ.).

Tsujimura, T., A. Kitakaze (2004). New phase relation in the Cu–Fe–S system at 800 °C; constraint of fractional crystallization of a sulfide liquid, *N. Jb. Miner. Mh*., *vol. 10*, pp. 433–444.