

PLATINUM AND PALLADIUM SULFIDES IN THE CRYSTALLIZATION PRODUCTS OF MELTS IN THE Cu-Fe-S SYSTEM

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To facilitate understanding conditions under which Pt and Pd sulfides were formed in Cu-Fe ores at magmatic Cu-Ni deposits of the Norilsk type, the crystallization of these minerals was experimentally modeled by cooling (from 1200–1100°C to room temperature) melts corresponding to the central portion of the Cu-Fe-S system doped with Pt and Pd (1 wt.%). The synthesized Pt and Pd sulfides are analogues of naturally occurring minerals: malanite $\text{Cu}(\text{Pt},\text{Fe})_2\text{S}_4$, cooperite PtS, vysotskite PdS and braggite (Pt,Pd)S. Their crystallization field in the examined portion of the Cu-Fe-S system (50 at.% S, Cu/Fe = 1.22–0.25 and 45 at.% S, Cu/Fe = 1.44–0.69) corresponds to the crystallization field of phase associations with chalcopyrite CuFeS_2 (Cu/Fe = 0.99–0.67), isocubanite CuFe_2S_3 (Cu/Fe = 0.61–0.48) and mooihoeikite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ (Cu/Fe = 1–0.95). The line of the bornite Cu_5FeS_4 – mooihoeikite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ – isocubanite CuFe_2S_3 separates the crystallization fields of Pt-Pd sulfides and Pt-Pd metallides. 2 tables, 1 figure, 18 references.

Keywords: Cu-Fe-S system, platinum, palladium, melt crystallization, Pt sulfides, Pd sulfides.

Introduction

Averaged data on the mineralogy of the Cu-Ni Norilsk ores indicate that their Pt and Pd amounts contained in minerals of these metals increase with increasing Cu content of the ores from their pyrrhotite to cubanite and then to chalcopyrite types (Dodin, 2002). It is currently generally believed that Pt-Pd minerals were formed in magmatic ores of the Norilsk type by their crystallization from magmatic fluid after the ore-forming sulfides (Genkin, 1968; Genkin *et al.*, 1981; Distler *et al.*, 1979, 1988, 1999). Thereby all researchers emphasized that the crystallization temperatures of several Pt-Pd minerals, such as isoferroplatinum Pt_3Fe , rustenburgite Pt_3Sn , atokite Pd_3Sn , cooperite PtS, vysotskite PdS and others, is higher than the crystallization temperatures of major ore-forming sulfides (chalcopyrite and pyrrhotite) and hence, they could have crystallized immediately from the melt. The behavior of Pt and Pd during crystallization of Pt-Pd sulfide melt is understood still inadequately poorly, largely because of our poor knowledge of the Cu-Fe-S system, whose central part corresponds to the compositions of the Norilsk Cu-Fe sulfide ores. Experimental data on the Pt and Pd speciation in the crystallization products of the central part of the Cu-Fe-S system at corresponding sulfur fugacity and 600°C (Kravchenko, Fedorova, 1996; Kravchenko, Kolonin, 1998) are consistent with data in (Evstigneeva *et al.*, 1989; Evstigneeva, 1996) on isoferroplatinum and cooperite crystallization in hydrothermal systems. Similar to naturally occurring ores, the crystallization fields of Pt-Pd and Pd-Pt sulfides are separated in the phase associations of the

Cu-Fe-S system (Kravchenko, 2009) and the boundary between these regions is so far uncertain. Our study was focused on experimental determining the stability field of Pt-Pd sulfides during the crystallization of the central part of the Cu-Fe-S system at 50 at.% S and Cu/Fe = 1.22–0.43 and 45 at.% S, Cu/Fe = 1.44. Provisional information has been obtained on phase equilibria in the central part of the Cu-Fe-S system at 50 at.% S, Cu/Fe = 1.22–0.25 and 45 at.% S, Cu/Fe = 1.44–0.69 (Fig. 1) and the composition of the respective phases: chalcopyrite CuFeS_2 , isocubanite (cubic *fcc* cubanite) CuFe_2S_3 , talnakhine $\text{Cu}_9\text{Fe}_8\text{S}_{16}$, mooihoeikite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ and cubic *pc* haycockite $\text{Cu}_4\text{Fe}_5\text{S}$ (Kravchenko *et al.*, 2012).

Experimental

The starting materials were carbonyl iron A-2, copper B3, reagent-grade sulfur, which had been additionally dehydrated by fusing in vacuum, metallic platinum and palladium. Pt and Pd were added separately (1 wt.% each) or simultaneously (0.5 wt.% each) to the starting mixtures of the preparatorily synthesized samples and to the preparatorily synthesized Ce-Fe-S phase associations. The melts with Pt and Pd admixtures were cooled in the same regimes as the melts without these admixtures. The synthesis was carried out in vacuumized quartz ampoules by cooling the melt from 1200–1150°C to room temperature. The cooling regimes of the melts have been adjusted experimentally in order to obtain phase equilibria stable at room temperature (Kravchenko, 2011; Kravchenko *et al.*, 2012; see the fig. 1). After synthesis, all crystallization

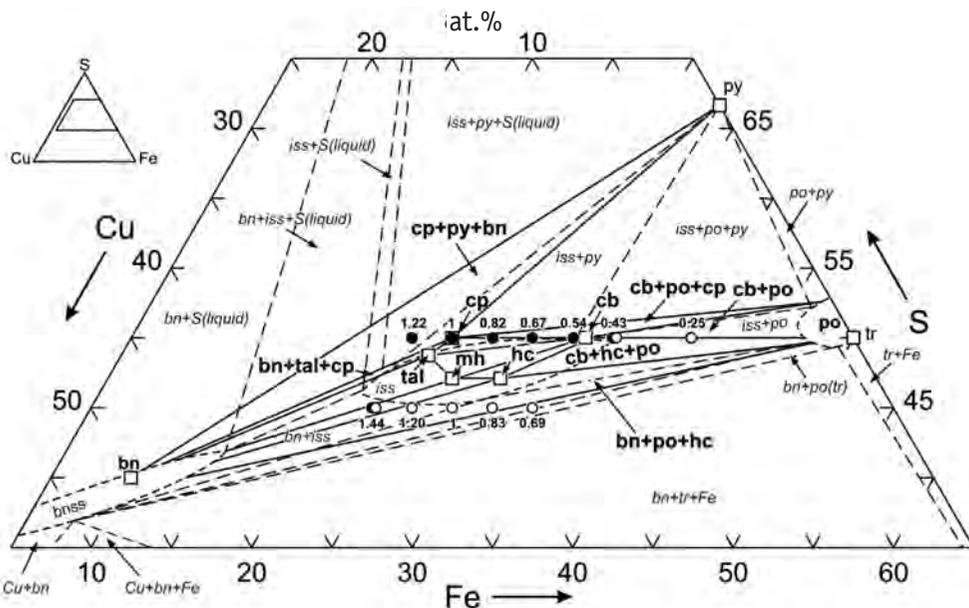


Fig. 1. Schematic representation of phase relations (solid lines according to Kravchenko, 2011, 2012) in the central part of the Cu-Fe-S system at 600°C (dashed lines according to Cabri, 1973).

□ – Stoichiometric compositions of chalcocopyrite CuFeS_2 (cp), bornite Cu_5FeS_4 (bn), pyrite FeS_2 (py), troilite FeS , talnakhite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ (tal), isocubanite CuFe_2S_3 (cb), mooihoekite $\text{Cu}_3\text{Fe}_2\text{S}_{16}$ (mh) and haycockite $\text{Cu}_4\text{Fe}_3\text{S}_8$ (hc). Solid solutions: iss – chalcocopyrite, bnss – bornite and po – pyrrhotite. Initial compositions of the synthesized samples: 50 wt.% S, Cu/Fe = 1.22–0.25 and 45 at.% S, Cu/Fe = 1.44–0.69. ● – Pt-Pd sulfides, ○ – Pt-Pd metallides.

products were examined under an optical microscope and by X-ray diffraction techniques. The polished sections were prepared from portions of each of the samples (which were cut along their vertical axes). The phases were analyzed for major elements and for distribution of admixtures over the whole volume of the samples on a Camebax-Micro microprobe, using the universal program (Lavrent'ev and Usova, 1991). Analysis was conducted based on the $\text{FeK}\alpha$, $\text{CuK}\alpha$, $\text{SK}\alpha$, $\text{PtM}\alpha$, $\text{PdL}\alpha$ X-ray reflections, which do not overlap. The standards were CuFeS_2 , Pt and Pd. The operating conditions were as follows: 20 kV accelerating voltage, 40 nA absorbed electron current, 40° angle, 10 s counting time on each analytical line and 2–3 μm beam diameter. The analytical errors for all elements were within 2%. The detection limits C_{min} in compliance with the 2 δ criterion at 99% confidence level were (in wt.%) 0.05 for Cu, 0.03 for Fe, 0.02 for S, 0.06 for Pt and 0.05 for Pd.

Results

As in our earlier publications (Kravchenko, 2011; Kravchenko *et al.*, 2012), the composition of the synthesized samples in the Cu-Fe-S system and the compositions of the corresponding Cu-Fe sulfides are expressed in the form of Cu/Fe ratios. The synthesized phases are named

according to their naturally occurring mineral analogues. We also report their generalized formulas, including elements whose concentrations in the synthetic phases are no lower than 5 at.%. The structures of the synthetic phases are mentioned when (and if) they differ from those of the natural mineral analogues. The synthesized phases of the haycockite composition $\text{Cu}_4\text{Fe}_3\text{S}_8$ have a cubic pc structure and thus differ from naturally occurring orthorhombic haycockite.

Generalized information on the accommodation of Pt, Pd and Pt together with Pd in the phase associations of the central part of the Cu-Fe-S system (50 at.% S, Cu/Fe = 1.22–0.25 and 45 at.% S, Cu/Fe = 1.44–0.69) are graphically represented in the figure and reported in Table 1. Solid circles in the figure show the composition of the samples with Pt-Pd sulfides examined in this publication and open circles display the composition of Pt-Pd metallides studied earlier (Kravchenko, 2009). The composition of phases in the region of Pt-Pd metallides that have been obtained previously and are necessary for discussing our results herein are printed in Table 1 in italics. Neither Pt nor Pd are major elements in the phases synthesized in the Cu-Fe-S system. As can be seen in Fig. 1, when the melts crystallize, Pt and Pd admixtures are contained in the same phases that crystallize from melts with admixtures of either Pt alone or Pd alone. The Pt-

Table 1. Phase composition of the synthesized crystallization products of Cu-Fe-S melts with admixtures of Pt (1 wt.%), Pd (1 wt.%) and Pt + Pd (0.5 wt.% each)

Starting composition (at.%) of Cu-Fe-S melts and their Cu/Fe ratios			Crystallization products of Cu-Fe-S melts with Pt, Pd and Pt + Pd admixtures				
S	Cu	Fe	Cu/Fe	Cu-Fe-S	Pt	Pd	Pt + Pd
	27.5–25	22.5–25	1.22–1	cp + bn + py	Cu(Fe,Pt) ₄ S ₄	PdS	Cu(Fe,Pt) ₄ S ₄ ; (Pt,Pd)S
	25–17.5	25–32.5	1–0.54	cp + icb, 0.61–0.52*	PtS	PdS	(Pt,Pd)S
50	15	35	0.43 ₁	icb, 0.52–0.48*			
			0.43 ₂	mh + bn, 0.95*			
			0.43 ₃	hc + bn, 0.90*			
45	32.5	22.5	1.44 ₁	mh + bn, 1.00*	Pt ₃ Fe	(Pd,Cu) ₁₆ S ₇	Pt ₃ Fe; (Pd,Cu) ₁₆ S ₇
			1.44 ₂	mh + bn, 0.95*	PtS		(Pt,Pd)S; (Pd,Cu) ₁₆ S ₇
	30–25	25–30	1.20–0.83	hc + bn, hc + bn + po, 0.90–0.68*	Pt ₃ Fe	Pd(Cu,Fe)	Pt ₃ Fe; (Pd,Cu) ₁₆ S ₇
						Pd(Cu,Fe)	Pd(Cu,Fe)

Note: bn – bornite Cu₃FeS₄; py – pyrite FeS₂; po – pyrrhotite Fe_{1–3}S; cp – chalcopyrite CuFeS₂ (Cu/Fe = 0.99–0.67); cb – isocubanite CuFe₂S₃ (Cu/Fe = 0.61–0.39); mh – mooihokite Cu₉Fe₉S₁₆ (Cu/Fe = 1.04–0.93); hc – haycockite Cu₄Fe₃S₈ (Cu/Fe = 0.90–0.68); Cu(Pt,Fe)₂S₄ – malanite, PdS – vysotskite, PtS – cooperite, (Pt,Pd)S – braggite, (Pd,Cu)₁₆S₇ – unnamed Pd sulfide, Pt₃Fe – isoferroplatinum, Pd(Cu,Fe) – unnamed Pd metallide. * – Cu/Fe isocubanite, mooihokite, or haycockite. Phase compositions compiled from (Kravchenko *et al.*, 2012) are printed in italics.

bearing melts in samples with 50 at.% S and Cu/Fe = 1.22–1 crystallized the association chalcopyrite + bornite + pyrite and malanite Cu(Pt,Fe)₂S₄. The Pd-bearing melts crystallized cooperite PtS and the melts that contained both Pt and Pd crystallized malanite and braggite (Pt, Pd)S. In samples with 50 at.% S and Cu/Fe = 1–0.54, cooperite, vysotskite PdS and braggite were synthesized in association with chalcopyrite and isocubanite (Cu/Fe = 0.61–0.52) from melts with Pt, Pd and Pt + Pd admixtures, respectively. Isocubanite of variable composition and various Cu-Fe sulfide associations were synthesized in samples with 50 at.% S and Cu/Fe = 0.43 (see Table 1, lines 0.43₁, 0.43₂ and 0.43₃). This is explained by certain specifics of isocubanite crystallization and related traits in establishing phase equilibria during the crystallization of melts corresponding to the central part of the Cu-Fe-S system. If the cooling rate of the melt was increased, the field of Fe-enriched (Cu/Fe < 0.5) isocubanite CuFe₂S₃, shrank, as also did the crystallization field of Fe-enriched chalcopyrite CuFeS₂ (Kravchenko *et al.*, 2012). The samples with 50 at.% S and Cu/Fe = 0.43₁ obtained at different cooling rates of the melts contained isocubanite (Cu/Fe = 0.52–0.48) whose composition is closely similar to the stoichiometric one CuFe₂S₃ (Cu/Fe = 0.5) and corresponds to the bornite Cu₃FeS₄ (bn) – mooihokite Cu₉Fe₉S₁₆ (mh) – isocubanite CuFe₂S₃ (cb) equilibrium (Fig. 1). The composition of the mooihokite Cu/Fe = 1.04–0.93 corresponding to this equilibrium is also close to the stoichiometric composition (Cu/Fe = 1). Moreover, an increase in the cooling rate of the melt resulted in that phase associations of isocuba-

nite, chalcopyrite and pyrrhotite (figure) gave way to phase associations of mooihokite and haycockite with bornite and pyrrhotite. In samples with 50 at.% S, Cu/Fe = 0.43₂ and 0.43₃ isocubanite (Cu/Fe = 0.52–0.48) and mooihokite (Cu/Fe = 0.95) with bornite respectively, occur in association with the same Pt-Pd sulfides (cooperite, vysotskite and braggite) as in samples with 50 at.% S and Cu/Fe = 1–0.54. In samples 0.43₃ with 50 at.% S and Cu/Fe = 0.43, the association haycockite (Cu/Fe = 0.90) + bornite contains synthesized isoferroplatinum Pt₃Fe and (Pd,Cu)₁₆S₇, which is Cu-enriched analogue of the Pd sulfide (which has no proper name) Pd₁₆S₇ in the Pd-S system, which crystallized at 639°C (Taylor, 1985). In samples with 45 at.% S and Cu/Fe = 1.44, the association of mooihokite + bornite (with mooihokite having Cu/Fe = 1) involves cooperite, (Pd, Cu)₁₆S₇ and braggite and this association with mooihokite having Cu/Fe = 0.95 contains isoferroplatinum and (Pd, Cu)₁₆S₇. Hence, Pt-Pd sulfides were synthesized from melt with 50 at.% S and Cu/Fe = 1.22–0.43 in association with chalcopyrite and isocubanite (Cu/Fe = 0.61–0.48), whereas from melt with 45 at.% S and Cu/Fe = 1.44 these sulfides crystallized in association with mooihokite (Cu/Fe = 1–0.95) and bornite.

Table 2 reports typical compositions of the synthesized crystallization products of Cu-Fe-S melts with admixtures of Pt and Pd sulfides. The following Pt and Pd sulfides crystallized from melts with Pt and Pd admixtures: malanite, cooperite and vysotskite as single grains and as zoned aggregates (Table 2). Thereby malanite and cooperite formed the cores of the grains and vysotskite made up their outer por-

Table 2. Composition of crystallization products of melts in the Cu-Fe-S system with admixtures of Pt (1 wt.%), Pd (1 wt.%) and Pt + Pd (0.5 wt.% each)

Initial composition: S, at.%, Cu/Fe ratios and admixtures	Phases	Composition (at.% / wt.%) of phases					Total, wt.%
		Cu	Fe	Pt	Pd	S	
50, 1.22 – 1	cp	24.59	25.90	0.00	0.00	49.11	99.80
		33.93	31.41	0.00	0.00	34.48	
	bn	48.70	10.38	0.00	0.00	40.92	99.63
		61.81	11.60	0.00	0.00	26.22	
	py	0.37	33.26	0.00	0.00	66.37	99.45
		0.59	46.08	0.00	0.00	52.78	
Pt + Pd (each 0.5 wt.%)	Cu(Pt,Fe)S ₄ *	15.21	11.20	17.40	0.00	56.19	100.17
		14.26	9.23	50.09	0.00	26.59	
Pt + Pd –//–	(Pd,Pt)S**	1.18	0.55	13.59	35.43	49.25	101.90
		0.94	0.39	33.33	47.39	19.85	
Pt + Pd –//–	PdS**	1.17	0.54	0.00	49.14	49.15	99.73
		1.08	0.44	0.00	75.46	22.75	
50, 0.82	cp	23.77	26.91	0.00	0.00	49.32	99.83
		32.82	32.66	0.00	0.00	34.35	
Pt	PtS	1.54	1.00	49.39	0.00	48.07	100.30
		0.87	0.49	85.30	0.00	13.64	
Pd	PdS	0.36	0.22	0.01	50.72	48.69	99.68
		0.33	0.18	0.04	76.89	22.24	
Pt + Pd (each 0.5 wt.%)	(Pt,Pd)S*	2.13	2.16	44.72	5.40	45.59	99.04
		1.22	1.09	78.42	5.17	13.14	
Pt + Pd –//–	(Pd,Pt)S**	1.34	1.10	5.84	43.38	48.34	101.53
		1.16	0.87	15.52	62.85	21.13	
50, 0.67	cp	22.89	27.50	0.00	0.00	49.61	99.50
		31.00	33.36	0.00	0.00	34.54	
cb	cb	18.15	32.48	0.00	0.00	49.37	99.40
		25.20	39.62	0.00	0.00	34.58	
Pt + Pd (each 0.5 wt.%)	PtS*	1.25	1.13	49.70	2.02	45.90	99.27
		0.69	0.54	83.51	1.85	12.67	
Pt + Pd –//–	PdS**	0.14	0.15	0.54	49.61	49.56	100.35
		0.12	1.12	1.49	75.42	22.20	
50, 0.54	cp + cb	22.12	28.73	0.00	0.00	49.15	98.96
		30.34	34.62	0.00	0.00	34.00	
Pt	PtS	0.99	0.64	50.74	0.00	47.63	100.36
		0.55	0.31	86.20	0.00	13.30	
Pt + Pd (each 0.5 wt.%)	(Pt,Pd)S*	1.93	3.06	44.11	6.50	44.40	99.60
		1.11	1.54	77.62	6.22	12.84	
Pt + Pd –//–	PdS**	0.42	0.68	0.06	49.62	49.21	99.33
		0.38	0.54	0.18	75.84	22.66	
50, 0.43 ₁	cb	16.33	34.07	0.00	0.00	49.60	99.80
		22.86	41.91	0.00	0.00	35.03	
Pt + Pd (each 0.5 wt.%)	(Pt,Pd)S*	1.22	1.92	45.88	5.33	45.65	99.75
		0.70	0.96	79.94	5.07	13.08	
Pt + Pd –//–	PdS**	0.29	0.52	0.04	50.32	48.83	99.73
		0.26	0.42	0.11	76.56	22.38	
50, 0.43 ₂	mh	25.84	27.18	0.00	0.00	46.98	99.02
		34.84	32.22	0.00	0.00	31.96	
Cu/Fe = 0.95	bn	46.37	13.55	0.00	0.00	40.08	99.29
		58.65	15.06	0.00	0.00	25.58	
Pt + Pd (each 0.5 wt.%)	(Pt,Pd)S*	0.52	0.78	47.64	4.16	46.90	100.17
		0.29	0.38	82.27	3.92	13.31	
Pt + Pd –//–	PdS**	0.35	0.48	0.11	49.48	49.58	99.15
		0.32	0.38	0.29	75.40	22.76	
50, 0.43 ₃	hc	24.96	27.78	0.00	0.00	47.26	98.80
		33.68	32.94	0.00	0.00	32.18	
bn	bn	46.37	13.55	0.00	0.00	40.08	99.29
		13.55	15.06	0.00	0.00	25.58	
Pt + Pd (each 0.5 wt.%)	Pt ₃ Fe	2.07	28.14	68.01	1.34	0.44	99.62
		0.86	10.35	87.38	0.94	0.09	
Pt + Pd –//–	(Pd,Cu) ₁₆ S ₇	12.21	4.31	0.00	53.50	29.98	98.76
		9.98	3.10	0.00	73.30	12.38	
1.44 ₁	mh	26.94	27.00	0.00	0.00	46.06	99.47
		36.26	31.94	0.00	0.00	31.27	
bn	bn	46.19	12.92	0.00	0.00	40.89	99.92
		59.04	14.51	0.00	0.00	26.37	
Pt + Pd (each 0.5 wt.%)	PtS	8.30	0.98	45.45	2.84	42.43	99.23
		4.71	0.49	79.18	2.70	12.15	
Pt + Pd –//–	(Pd,Cu) ₁₆ S ₇	17.02	0.97	0.00	52.67	29.34	99.91
		14.07	0.70	0.00	72.90	12.24	
1.44 ₂	mh	25.86	27.20	0.00	0.00	46.94	98.76
		34.78	32.14	0.00	0.00	31.84	
Cu/Fe = 0.95	bn	47.10	13.40	0.00	0.00	39.50	99.62
		59.542	14.18	0.00	0.00	25.19	
Pt + Pd (each 0.5 wt.%)	Pt ₃ Fe	2.38	27.18	69.10	0.82	0.52	99.64
		0.99	9.92	88.04	0.58	0.11	
Pt + Pd –//–	(Pd,Cu) ₁₆ S ₇	15.71	0.30	0.00	54.70	29.29	101.24
		13.00	0.22	0.00	75.80	12.22	

Note: cp – chalcopyrite CuFeS₂; bn – bornite Cu₅FeS₄; py – pyrite FeS₂; cb – isocubanite Cu₉Fe₂S₁₆; hc – haycockite Cu₂Fe₂S₅; Cu(Pt,Fe)S₄ – malanite, PdS – vysotskite, PtS – cooperite, (Pt,Pd)S – braggite; (Pd,Cu)₁₆S₇ – unnamed Pd sulfide, Pt₃Fe – isoferroplatinum.
* – cores of zoned grains, ** – margins of zoned grains.

tions. The synthesized Pt-Pd phases exhibit crystallization features and phase relations with sulfides in the central part of the Cu-Fe-S system analogous to those of Pt-Pd and Ag-Au phases synthesized and described in much detail earlier (Kravchenko and Nigmatulina; 2009 Kravchenko, 2009): the largest grains crystallized on the surface and cavities (fractures) of the synthetic samples, crystal faces are unequally developed, crystallizing grains were often zoned, a single sample may contain different modes of occurrence of the phases, a single grain may show uneven distribution of elements and Cu-Fe sulfides are found in fractures and cavities in larger grains. These features are typical of crystallization of Pt-Pd and Au-Ag phases immediately from melts of less refractory Cu-Fe sulfides with admixtures of Pt, Pd, Au and Ag and if encountered in naturally occurring ores, are commonly regarded as evidence that these minerals crystallized after the ore-forming sulfides.

Discussion

As seen in Table 1, Pd sulfide $(\text{Pd,Cu})_{16}\text{S}_7$ was synthesized with isoferroplatinum or with cooperite and braggite in samples whose compositions (50 at.% S, Cu/Fe = 0.43 and 45 at.% S, Cu/Fe = 1.44) are transitional from the crystallization field of Pt-Pd sulfides to that of Pt-Pd metallides. The composition point at 45 at.% S, Cu/Fe = 1.44 lies on the equilibrium line bornite (*bn*) – mooihoekite (*mh*) – isocubanite (*cb*) (Fig. 1). In sample with 45 at.% S and Cu/Fe = 1.441, Pt-Pd sulfides were synthesized with mooihoekite of stoichiometric composition $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ (Cu/Fe = 1). The composition with 50 at.% S and Cu/Fe = 0.43 corresponds to the Fe-rich end member of the chalcopyrite solid solution of cubic fcc structure (Fig. 1, *iss*; Cabri, 1973). Naturally occurring analogues of the cubic fcc solid solution (Caye *et al.*, 1988) are referred to as isocubanite to distinguish them from natural cubanite of the stoichiometric composition CuFe_2S_3 (Cu/Fe = 0.5) of orthorhombic structure. The composition of the synthetic isocubanite (Kravchenko *et al.*, 2012) is closely similar to its natural analogue and varies within the Cu/Fe range of 0.61 – 0.39. The Cu-enriched isocubanite (Cu/Fe = 0.61 – 0.52) crystallizes from melt in association with chalcopyrite, whereas Fe-enriched isocubanite (Cu/Fe = 0.49 – 0.39) is formed in association with pyrrhotite and haycockite. As was mentioned above, isocubanite in association with Pt-Pd sulfides (sample 0.43₁, Table 1) has the composition (Cu/Fe = 0.52 – 0.48) close to the stoichiometric

composition CuFe_2S_3 and corresponds to the equilibrium line bornite – mooihoekite – isocubanite. We have previously proved (Kravchenko, 2009) that melt with 50 at.% S and Cu/Fe = 0.25 crystallizes, in association with isocubanite (Cu/Fe = 0.43) + pyrrhotite, Pt_3Fe and Pd_3Fe or, in associations haycockite + bornite and haycockite + bornite + pyrrhotite (Table 1), Pt-Pd metallides: Pt_3Fe and $\text{Pd}(\text{Cu,Fe})$. Hence, the equilibrium line bornite Cu_5FeS_4 – mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ – isocubanite CuFe_2S_3 is the boundary line between the crystallization fields of Pt-Pd sulfides (malanite, cooperite, vysotskite and braggite) and Pt-Pd metallides (Pt_3Fe and $\text{Pd}(\text{Cu,Fe})$).

Our data indicate (Tables 1 and 2) that in samples 0.43₂ of the composition 50 at.% S, Cu/Fe = 0.43, Pt-Pd sulfides were synthesized (cooperite PtS, vysotskite PdS and braggite (Pt,Pd)S) in association with bornite and mooihoekite. In samples 1.44₂ of the composition 45 at.% S and Cu/Fe = 1.44, bornite and mooihoekite were synthesized with isoferroplatinum and sulfide $(\text{Pd,Cu})_{16}\text{S}_7$, which were also synthesized in samples 0.43₃ of the composition 50 at.% S, Cu/Fe = 0.43, in association with haycockite and bornite. This testifies that the modes in which Pt and Pd are contained in the crystallization products of melts in the Cu-Fe-S system are controlled by the initial composition of the melt. These modes are independent of variations in the phase associations: isocubanite → mooihoekite + bornite and isocubanite + pyrrhotite → haycockite + bornite, which crystallized at different cooling rates of the melt.

Conclusions

1. The crystallization field of Pt and Pd sulfides, which are analogues to those of natural minerals, such as malanite $\text{Cu}(\text{Pt,Fe})_2\text{S}_4$, cooperite PtS, vysotskite PdS and braggite (Pt, Pd)S, in the crystallization products of melts in the Cu-Fe-S system at 50 at.% S, Cu/Fe = 1.22 – 0.25 and 45 at.% S, Cu/Fe = 1.44 – 0.69 with Pt and Pd admixtures 1 wt.%) corresponds to the crystallization field of associations with chalcopyrite CuFeS_2 (Cu/Fe = 0.99 – 0.67), isocubanite CuFe_2S_3 (Cu/Fe = 0.61 – 0.48) and mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ (Cu/Fe = 1 – 0.95). The bornite Cu_5FeS_4 – mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ – isocubanite CuFe_2S_3 equilibrium line separates the crystallization fields of Pt-Pd sulfides and Pt-Pd metallides.

2. The Pt-Pd sulfides synthesized in association with less refractory sulfides in the central part of the Cu-Fe-S system typically occur in grains similar to natural minerals and show

phase relations analogous to those of the corresponding natural minerals. This testifies that malanite, cooperite, vysotskite and braggite could have crystallized immediately from Pt- and Pd-bearing Cu-Fe-S melts of the Norilsk type before ore-forming sulfides (isocubanite, chalcopyrite and mooihoekite) crystallized from these melts.

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