

## Pt-Pd-Sn INTERMETALLIC COMPOUNDS CRYSTALLIZED FROM Cu-Fe SULFIDE MELT

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To understand the formation conditions of Pt-Pd-Fe-Sn minerals in the Noril'sk magmatic Cu-Fe ore they were synthesized by cooling of Fe-Sn-S and Cu-Fe-S melts containing admixtures of Pt, Pd, and Sn (1–2 wt.%) from 1200°C to room temperature. Crystallization of the Fe-Sn-S melts with Fe/Sn 3/1, 1/1 и 1/3 and 50 at.% S leads to the formation of PtSn and PtSn<sub>2</sub>, which involve the whole Pt (1 wt.%) containing in the melts. The relationship between Pt-Pd phases (by 1 wt.%) and crystallized products of the Cu-Fe-S melts with 50 at.% S and Cu/Fe 1.22–0.25, and 45 at.% S and Cu/Fe 1.44–0.38 has been determined. Isoferroplatinum, Pt<sub>3</sub>Fe, has been synthesized in association with cubanite CuFe<sub>2</sub>S<sub>3</sub> + pyrrhotite Fe<sub>1-x</sub>S, mooihoekite Cu<sub>9</sub>Fe<sub>9</sub>S<sub>16</sub> + bornite Cu<sub>5</sub>FeS<sub>4</sub>, haycockite Cu<sub>4</sub>Fe<sub>5</sub>S<sub>8</sub> + bornite + pyrrhotite, and bornite + pyrrhotite. Pd analogue of isoferroplatinum, Pd<sub>3</sub>Fe, has been synthesized in association with cubanite + pyrrhotite. Rustenburgite, Pt<sub>3</sub>Sn, atokite, Pd<sub>3</sub>Sn, Pd-bearing rustenburgite, (Pt,Pd)<sub>3</sub>Sn, Fe-bearing niggliite Pt(Sn,Fe), and Sn-bearing solid solutions of the hongshite series (Pt,Pd)(Fe,Cu,Sn) have been synthesized in the crystallization field of isoferroplatinum (50 at.% S, Cu/Fe = 0.25 and 45 at.% S, 1.44 > Cu/Fe ≥ 0.69). Thus, the presence of Sn in the field of stability of Pt-Pd-Fe intermetallic compounds determines the crystallization of their Pt-Pd-Sn analogues. The deficiency of Sn to form Pt-Pd-Sn phases is balanced by Fe and Pt-Pd-Sn-Fe phases crystallize simultaneously. The habit of synthesized phases and phase relationships in the crystallized products studied here are consistent with available published data for relevant natural assemblages.

3 tables, 3 figures, 17 references.

Keywords: chalcopyrite, mooihoekite, haycockite, talnakhite, intermetallic compounds of Pt and Pd.

### Introduction

Pt and Pd minerals with Sn from chalcopyrite and chalcopyrite-pyrrhotite ores are unique assemblage at the Noril'sk Cu-Ni deposits. The Sn-bearing Cu-Fe assemblage, in which Sn incorporates into intermetallic compounds with PGE rather than into cassiterite or sulfides, was identified only at the Noril'sk deposits (Nekrasov, 1984). At the other deposits, Pt-Fe alloys, isoferroplatinum, Pt<sub>3</sub>Fe and tetraferroplatinum, PtFe are the most abundant, whereas their Pt-Pd-Sn analogues – maslenitskovite, (Pt,Pd)<sub>3</sub>Sn, rustenburgite Pt<sub>3</sub>Sn, atokite, Pd<sub>3</sub>Sn, and niggliite, PtSn characteristic of the Noril'sk Cu-Fe ore (Genkin *et al.*, 1981) are sporadic.

The problem of the genesis of Pt-Pd-Sn minerals is attractive due to controversial conclusion of their formation after magmatic crystallization of the major ore-forming sulfides, chalcopyrite, pyrrhotite, and pentlandite (Genkin, 1968; Genkin *et al.*, 1981; Distler *et al.*, 1979, 1988, 1999). Solution of the crystallization sequence problem is primary important because this determines mechanism of accumulation of rare elements. High melting temperature of most Pt-Pd-Sn minerals (> 1200°C) and their close intergrowths with Pt-Fe alloys combined with the data of potential Sn content in the upper mantle (Barsukov & Dmitriev,

1972; Nekrasov, 1984) indicate a probable direct crystallization of Pt-Pd-Fe-Sn intermetallic compounds simultaneously with Cu-Fe sulfides from magmatic melt. However, such crystallization is not studied.

The aim of this study is an experimental modeling of the formation of Pt-Pd-Sn intermetallic compounds during cooling of Cu-Fe sulfide melts relevant to Cu-Fe ores from the Noril'sk Cu-Ni deposits.

### Experimental

The Cu-Fe-S and Fe-Sn-S systems are used as model macrosystems, where PGE and also Sn in the Cu-Fe-S system are traces but their amount (not less than 1 wt.%) is sufficient to be detected by optical methods and electron microprobe. In this case, crystallized phases of trace elements are suggested to be determined by physicochemical conditions of crystallization of equilibrium Cu-Fe and Sn-Fe sulfides (macrocomponents). Three runs were carried out.

1. The samples of the Fe-Sn-S system containing 1 wt.% Pt were synthesized. Platinum phases depending on Fe and Sn in initial Fe-Sn sulfide melt were established.

2. The samples of the central Cu-Fe-S system (Fig. 1) corresponding to the composition of the Noril'sk Cu-Fe ores, with which Pt-Pd-

Fe-Sn intermetallic compounds are formed, were synthesized. The relationship between Pt and Pd phases (initial amount 1 wt.%) and assemblages of Cu-Fe sulfides was established and field of stability of the Pt-Fe and Pd-Fe intermetallic compounds was determined.

3. Pt-Pd-Sn intermetallic compounds associated with Cu-Fe sulfides corresponding to the established (item 2) field of stability of Pt-Fe and Pd-Fe intermetallic compounds were synthesized.

Samples (0.2–1 g) of the Fe-Sn-S system were prepared from synthetic FeS and SnS, whereas those of the Cu-Fe-S system, from elements. Carbonyl iron A-2, copper B3, ultrapure sulfur additionally dehydrated by melting in vacuum, ultrapure tin, and metallic platinum and palladium were raw material.

All samples of both systems were synthesized in vacuum quartz vials by cooling of melt from 1200–1150°C to room temperature. The Cu-Fe-S cooled samples were kept at 600°C for couple weeks and at 400°C, for three months. The samples were cooled from 600 and 400°C to room temperature in cold water.

After synthesis, the crystallized products were studied with optical microscope and X-ray diffraction. Polished sections were prepared from half of each sample (cut through the centre from the top down). The chemical composition of phases and distribution of trace elements in the sample bodies were detected by a Camebax-Micro electron microprobe according to the RMA-96 universal program (Lavrent'ev & Usova, 1991). The following analytical lines were used: Fe  $K_{\alpha}$ , Cu  $K_{\alpha}$ , S  $K_{\alpha}$ , Pt  $M_{\alpha}$ , Pd  $L_{\alpha}$ , Sn  $L_{\alpha}$ . In this set, lines are not superposed. The following standards were used: FeS, SnS, CuFeS<sub>2</sub>, Pt и Pd. Operating conditions are 20 kV, 40 nA, counting time 10 s, and beam diameter 2–3 microns. All components were detected with accuracy of 2 relative percents. The detection limit calculated according to the 2 $\delta$  test at 99% significance level is as follows, wt. %: 0.05 Cu, 0.03 Fe, 0.02 S, 0.06 Pt, 0.05 Pd, 0.05 Sn.

The conventional names of mineral analogues and generalized chemical formulas taking into account elements whose content is not less than 5 at.% were used to denote synthesized phases.

### Platinum phases (1 wt.%) in crystallized products of the Fe-Sn-S melts

The results of investigation of crystallized products of the Fe-Sn-S melts with 50 at.% S and Fe/Sn 3/1, 1/1, and 1/3 containing 1 wt.%

Pt are given in Table 1 and in Fig. 2. Most synthesized samples are composed of pyrrhotite, Fe<sub>1-x</sub>S and herzenbergite that is consistent with experimental study (Moh, 1974). As seen from Table 1, Pt does not incorporate into pyrrhotite and herzenbergite. The isolated Pt-bearing phases were indentified in all synthesized phases. In samples 1 and 2 (Fe/Sn = 3/1 и 1/1), niggliite PtSn was found and PtSn<sub>2</sub> was identified in sample 3 (Fe/Sn = 1/3). Thus, in the crystallized products of the Fe-Sn sulfide melts studied here, PtFe compounds were not identified and Pt is associated with Sn.

### Platinum and palladium phases in the crystallization products of the Cu-Fe-S melts

The samples of the Cu-Fe-S system 50 at.% S, Cu/Fe 1.22–0.25 and 45 at.% S, Cu/Fe 1.44–0.38 with Pt and Pd (1 wt.%) were synthesized. The identical phase composition was established at room temperature in the samples synthesized with different regime of cooling (quenched from 600 or 400°C) (Table 2). The phase relations of Cu-Fe sulfides in the synthesized samples are consistent with experimental data of the Cu-Fe-S system at 600°C (Cabri, 1973) and 400°C (Vaughan & Craig, 1978) (Fig. 1). The primary compositions of the synthesized samples are shown in Fig. 1 as black circles 1–14. The iss field in Fig. 1 corresponds to high-temperature cubic solid solution with face-centered (fcc) unit cell. Cubanite, CuFe<sub>2</sub>S<sub>3</sub>, talnakhite, Cu<sub>9</sub>Fe<sub>8</sub>S<sub>16</sub>, mooihoekite, Cu<sub>9</sub>Fe<sub>9</sub>S<sub>16</sub>, and haycockite, Cu<sub>4</sub>Fe<sub>5</sub>S<sub>8</sub> pertain to the compositional field of this solid solution. Together with chalcopyrite, these minerals compose the Noril'sk ore enriched in copper, during deposition of which Pt-Pd-Fe-Sn intermetallic compounds were formed. The synthesized crystallized products of iss are shown in Fig 1b in parentheses. These are cubic (fcc) cubanite (samples 3–7) and cubic (pc) phases, which are close in composition to mooihoekite (samples 8 and 9) and haycockite (samples 10 and 11). The synthesized assemblages of Cu-Fe sulfides are given in Table 2. These are chalcopyrite + pyrite + bornite (samples 1 and 2), chalcopyrite + cubanite (samples 3 and 4), chalcopyrite + cubanite + pyrrhotite (samples 5 and 6), cubanite + pyrrhotite (sample 7), mooihoekite + bornite (samples 8 and 9), haycockite + bornite (sample 10), haycockite + bornite + pyrrhotite (sample 11), bornite + pyrrhotite (sample 12), and bornite + pyrrhotite + Cu (samples 13 and 14).

Table 1. Phases crystallized from the FeS-SnS melts containing 1 wt.% Pt

№	Initial composition, at.%		Synthesized phases	Composition of synthesized phases, at.% / wt.%				
	FeS	SnS		Fe	Sn	S	Pt	Σ
1	75	25	Fe <sub>1-x</sub> S	48.50	0.16	51.34	0.00	
				62.05	0.42	37.71	0.00	100.18
				0.21	49.75	50.03	0.00	
				0.16	78.14	21.23	0.00	99.53
				0.05	49.31	0.25	50.39	
			0.02	37.04	0.05	62.21	99.32	
2	50	50	Fe <sub>1-x</sub> S	49.12	0.04	50.84	0.00	
				62.95	0.12	37.41	0.00	100.48
				0.17	49.89	49.94	0.00	
				0.13	78.52	21.22	0.00	99.87
				0.44	49.47	0.24	49.85	
			0.16	37.32	0.05	61.82	99.35	
3	25	75	Fe <sub>1-x</sub> S	48.85	0.06	51.09	0.00	
				62.52	0.17	37.54	0.00	100.23
				0.14	49.92	49.94	0.00	
				0.10	78.50	21.22	0.00	99.82
				0.68	65.99	0.02	33.31	
			0.26	53.73	0.01	44.57	98.57	

Table 2. Phase composition of crystallized products of the Cu-Fe-S melts containing Pt or Pd (1 wt.%)

№ о́бр.	Initial composition, at.%			Synthesized phases		
	S	Cu	Fe	Cu-Fe-S	Pt	Pd
1	50.0	27.5	22.5	cp + bn + py	Cu(Fe,Pt)S <sub>4</sub>	PdS
2		25.0	25.0		PtS	
3		22.5	27.5	cb + cp		
4		20.0	30.0			
5		17.5	32.5	cb + cp + po		
6		15.0	35.0			
7		10.0	40.0	cb + po	Pt <sub>3</sub> Fe	Pd <sub>3</sub> Fe
8	45.0	32.5	22.5	mh + bn	Pt <sub>3</sub> Fe + PtS	PdS
9		30.0	25.0		Pt <sub>3</sub> Fe	
10		27.5	27.5	hc + bn		Pd(Cu,Fe)
11		25.0	30.0	hc + bn + po		
12		22.5	32.5	bn + po		
13		20.0	35.0	bn + po + Cu		
14		15.0	40.0		PtFe	

Notes: (cp) chalcopyrite  $CuFeS_2$ , (bn) bornite  $(Cu_3FeS_4)$ , (py) pyrite  $FeS_2$ , (cb) cubanite  $CuFe_2S_9$ , (po) pyrrhotite  $Fe_{1-x}S$ , (mh) mooihoekite  $Cu_9Fe_9S_{16}$ , and (hc) haycockite  $Cu_4Fe_3S_8$ .

Platinum and palladium were not detected in sulfides of this macrosystem. In all synthesized samples, they occur as proper phases. According to the results obtained, along section 50 at.% S, Pt and Pd sulfides, malanite, (Pt,Cu,Fe)S<sub>4</sub>, cooperite, PtS, and vysotskite,

PdS were identified in samples 1–6 (Cu/Fe 1.22–0.43), whereas in sample 7 (Cu/Fe 0.25), Pt-Pd-Fe alloys, isoferroplatinum Pt<sub>3</sub>Fe and unnamed palladium analogue of isoferroplatinum Pd<sub>3</sub>Fe were found. Palladium mineral vysotskite and platinum minerals cooperite

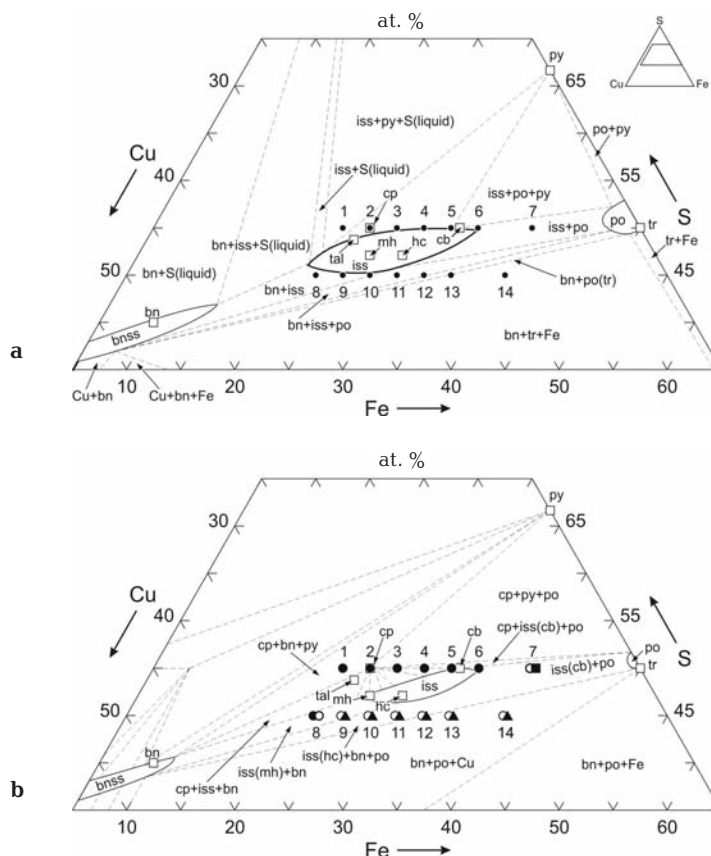


Fig. 1. Phase relations in the central part of the Cu-Fe-S system. (a) at 600°C (Cabri, 1973), (b) at 400°C (Vaughan, Craig, 1978). (iss, bnss, and po) fields of chalcopyrite, bornite, and pyrrhotite solid solutions, respectively. □ – stoichiometric chemical composition of minerals: (cp) tetragonal chalcopyrite  $\text{CuFeS}_2$ , (bn) bornite  $\text{Cu}_5\text{FeS}_4$ , (py) pyrite  $\text{FeS}_2$ , troilite FeS, and crystallization products of iss: (tal) talnakhite  $\text{Cu}_9\text{Fe}_8\text{S}_{16}$ , (cb) cubic cubanite  $\text{CuFe}_2\text{S}_3$ , (mh) mooihoekite  $\text{Cu}_9\text{Fe}_8\text{S}_{16}$ , and (hc) haycockite  $\text{Cu}_4\text{Fe}_3\text{S}_8$ . (1–14) Initial compositions of synthesized samples with admixtures (Fig. 1b) of Pt-Pd phases: ● –  $(\text{Cu, Fe, Pt})\text{S}_9$ , PtS and PdS; ○ –  $\text{Pt}_3\text{Fe}$ , PtFe; ■ –  $\text{Pd}_3\text{Fe}$ ; ▲ – Pd(Cu, Fe).

and isoferroplatinum were identified in sample 8 (45 at.% S, Cu/Fe 1.44). The latter minerals crystallize simultaneously. In Pd-bearing samples 9–14 (45 at.% S, Cu/Fe 1.20–0.38), unnamed Pd-Fe-Cu alloys, Pd(Cu, Fe), considered (Nekrasov, 1994) as palladium analogues of hongshite, PtCu, and isoferroplatinum and tetraferroplatinum, PtFe were found in Pt-bearing samples. The same phases were synthesized with both Pt and Pd in primary melt (Kravchenko, 2002, 2006).

Thus, Pt-Fe intermetallic compounds corresponding to the Pt-Fe natural alloys, isoferroplatinum and tetraferroplatinum synthesized in the central Cu-Fe-S system (50 at.% S, Cu/Fe 0.25 and 45 at.% S,  $1.44 \geq \text{Cu/Fe} \geq 0.40$ ) are associated with cubanite, pyrrhotite, bornite and depleted in S crystallized products of chalcopyrite solid solution – mooihoekite and

haycockite. Palladium analogue of isoferroplatinum,  $\text{Pd}_3\text{Fe}$  associated with cubanite and pyrrhotite was synthesized in the same field.

### Synthesis of Pt-Pd-Sn intermetallic compounds in the field of stability of their Pt-Pd-Fe analogues in the Cu-Fe-S system

Pt-Pd-Sn intermetallic compounds were synthesized in the Cu-Fe-S system corresponding to the field of crystallization of  $\text{Pt}_3\text{Fe}$  and  $\text{Pd}_3\text{Fe}$  (Table 2, sample 7–12). Electron microprobe data of the synthesized phases, of samples of the macrosystem and of Pt-Pd-Fe phases described above (samples 7–1, 9–1, 11–1, 12–1) are given in Table 3. Samples 7–3, 9–2, 11–2, and 12–2 with admixture of Pt and Sn (Pt/Sn = 3/1), sample 7–4 with admix-

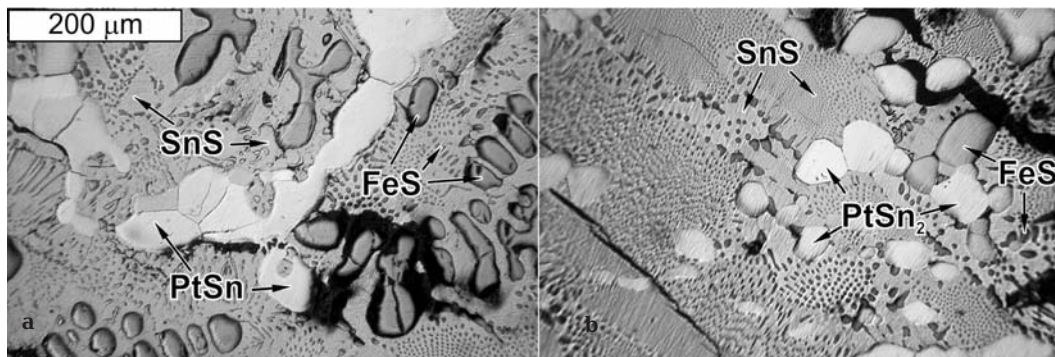


Fig. 2. Platinum phases (1 wt.%) in synthesized samples of the FeS-SnS system. (a) PtSn (Fe/Sn = 3/1), (b) PtSn<sub>2</sub> (FeS/SnS = 1/3).

ture of Pd and Sn (Pd/Sn = 3/1) as well as samples 7–5 and 9–3 with Pt, Pd, and Sn (Pt,Pd/Sn = 3/1) were synthesized. In addition, samples 11 and 12 with Pt/Sn = 3/1 and with 1 wt.% Pd were synthesized again (samples 11–3 and 12–3 in the Table 3). The composition of Cu-Fe sulfides and phase relations in the synthesized samples are identical to those in aforementioned Sn-free samples. Both Sn and Pt and Pd are not detected in sulfides of the macrosystem. To estimate the effect of Sn on Pt and Pd species in the synthesized samples, Cu was combined with Pt and Pd in formulas of the Pt-Pd phases with the exception of Sn-bearing solid solution (Pt,Pd)(Fe,Cu,Sn) in sample 12–3. The comparison of results of crystallized Sn-free melts indicates that in all Sn-bearing samples, Pt-Pd-Sn phases, which are analogues of Pt-Pd-Fe phases, were synthesized. In the samples with Pt,Pd/Sn = 3/1, these are rustenburgite, Pt<sub>3</sub>Sn, atokite, Pd<sub>3</sub>Sn, and palladium rustenburgite, (Pt,Pd)<sub>3</sub>Sn containing up to 1 wt.% and 2.5 wt.% Cu. In samples 11–3 and 12–3 with Pt,Pd/Sn > 3/1 (due to Pd in initial samples), Pt-Pd-Sn intermetallic compounds of variable composition were synthesized. These compounds are characterized by zoned grains enriched in Sn and Pt in cores and Pd and Fe, in margins. In sample 11–3, Fe-bearing (up to 3 wt.%) analogues of palladium rustenburgite (Pt,Pd)<sub>3</sub>Sn were identified and in sample 12–3, Fe-bearing (up to 4 wt.%) analogues of niggliite PtSn and Sn-bearing (up to 7 wt.%) analogues of the (Pt,Pd)(Fe,Cu) natural solid solutions of hypothetical (Nekrasov, 1994) hongshinite series Pt(Fe,Cu) – Pd(Cu,Fe).

The phase relations in the synthesized samples are shown in Fig. 3. Location of the largest grains on the surface of the samples, in interstices between host sulfide minerals, and in pores and fractures is characteristic feature of

the Pt-Pd-Sn synthesized phases. The inclusions of host Cu-Fe sulfides and grains of various shape (well-shaped crystals and crystals with irregularly grown faces, skeletons, veinlets, and irregular shaped grains) are observed within single sample. Similar morphological features are suggested to be features of metacrystals (Genkin, 1968, Genkin *et al.*, 1981). The same phase relations were established for Au and Ag behavior in the studied field of the Cu-Fe-S system (Kravchenko *et al.*, 2005, 2007; Kravchenko & Nigmatulina, this issue).

Thus, in the crystallization field of isoferroplatinum Pt<sub>3</sub>Fe in the Cu-Fe-S system (50 at.% S, Cu/Fe 0.25 and 45 at.% S, 1.44 ≥ Cu/Fe ≥ 0.69, Pt,Pd/Sn 3/1), rustenburgite Pt<sub>3</sub>Sn, atokite Pd<sub>3</sub>Sn, and palladium rustenburgite (Pt,Pd)<sub>3</sub>Sn were synthesized and at Pd + Pt/Sn > 3/1, Fe-bearing niggliite Pt(Sn,Fe) and Sn-bearing solid solutions of the hongshinite series.

## Conclusions

1. The results obtained indicate that formation of proper phases is mechanism of accumulation of PGE (admixture of Pt and Pd 1–2 wt.%) in the crystallized products of melt in the central Cu-Fe-S system (50 at.% S, Cu/Fe 1.22–0.25 and 45 at.% S, Cu/Fe 1.44–0.38). This results in the absence of PGE admixture in Cu-Fe sulfides. PGE move to the boundaries of crystallized Cu-Fe sulfide grains or cavities, fractures, and sample surface during melt crystallization.

2. The presence of Sn in the field of stability of the Pt-Pd-Fe intermetallic compounds (50 at.% S, Cu/Fe 0.25 and 45 at.% S, 1.44 > Cu/Fe ≥ 0.69) determines crystallization of their Pt-Pd-Sn analogues. In this case, the deficiency of Sn to form Pt-Pd-Sn phases is ba-

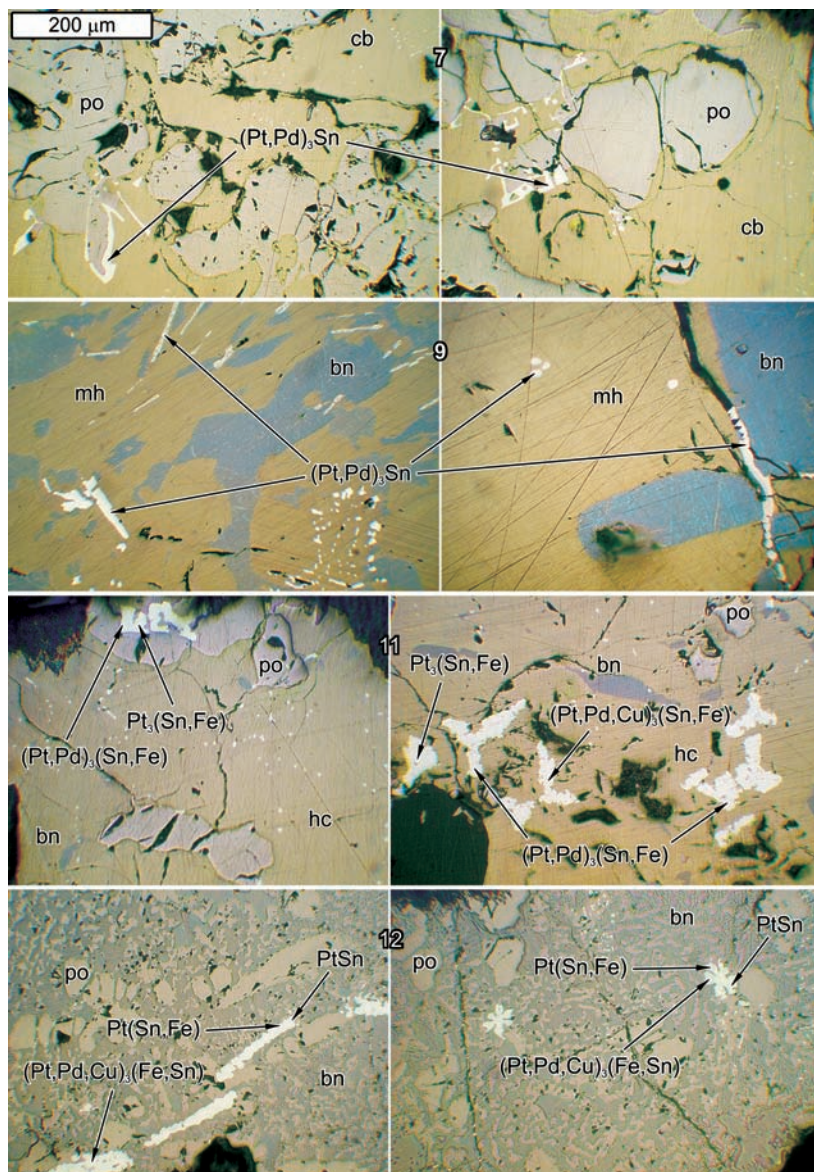


Fig. 3. Pt-Pd-Sn intermetallic compounds (bright white) associated with cubanite (cb), pyrrhotite (po) in sample 7–5, bornite (bn), mooihoeite (mh) in sample 9–3, and haycockite (hc), bornite, and pyrrhotite in sample 11–3, bornite, and pyrrhotite in sample 12–3.

lanced by Fe and Pt-Pd-Sn-Fe phases crystallize simultaneously.

3. Pt-Pd-Fe-Sn intermetallic compounds synthesized from melt along with Cu-Fe sulfides have the same phase relations as typical metacrystals. Thus the phase relations of their natural analogues could not tell us about their formation before or after Cu-Fe sulfides crystallization.

## References

- Barsukov V.P. & Dmitriev L.V. Upper mantle of the Earth as probable source of ore matter // *Geokhimiya*. **1972**. No 12. P. 1459–1461. (In Russian).
- Cabri L.J. New Data on phase relations in the Cu-Fe-S system. // *Econ. Geol.* **1973**. 68. P. 443–454.
- Distler V.V., Grokhovskaya T.L., Evstigneeva T.L., et al. Petrology of sulfide magmatic ore formation. Moscow: Nauka, **1988**. 232 pp. (In Russian).
- Distler V.V., Sluzhenikin S.F., Cabri L.J., et al. Platinum ores of the Noril'sk layered intrusions: magmatic and fluid concentration of noble metals // *Geol. Ore Dep.* **1999**. 41. P. 214–237.

**Table 3. Phases crystallized from the FeS-SnS melts containing Pt, Pd и Sn**

№	Admixture	Synthesized phase	Composition of phase, at.% / wt.%					Σ, wt.%	
			Cu	Fe	Pt	Pd	Sn		S
7		cb	15.25	35.76	0.00	0.00	0.00	48.38	
			21.28	43.84	0.00	0.00	0.00	34.47	
		po	3.60	45.66	0.00	0.00	0.00	50.74	
			5.20	57.96	0.00	0.00	0.00	36.97	
7-1	Pt	Pt <sub>3</sub> Fe	1.84	26.17	71.50	0.00	0.00	0.49	100.06
			0.85	9.40	89.71	0.00	0.00	0.10	
7-2	Pd	(Pd,Cu) <sub>3</sub> Fe	6.56	22.47	0.00	70.85	0.00	0.12	100.42
			4.54	13.68	0.00	82.16	0.00	0.04	
7-3	Pt/Sn = 3/1	Pt <sub>3</sub> Sn	2.10	2.69	72.81	0.00	21.98	0.42	100.04
			0.78	0.88	83.05	0.00	15.25	0.08	
7-4	Pd/Sn = 3/1	Pd <sub>3</sub> Sn	4.11	2.55	0.00	70.89	22.14	0.31	99.97
			2.47	1.34	0.00	71.24	24.82	0.10	
7-5	(Pt + Pd)/Sn = 3/1	(Pt,Pd) <sub>3</sub> Sn	2.69	2.91	50.80	19.29	24.00	0.31	100.35
			1.12	1.08	65.63	13.60	18.86	0.06	
9		bn	48.39	12.49	0.00	0.00	0.00	39.11	99.52
			60.88	13.81	0.00	0.00	0.00	24.83	
		mh	25.32	28.39	0.00	0.00	0.00	46.30	99.60
			34.25	33.75	0.00	0.00	31.60		
9-1	Pt	(Pt,Cu) <sub>3</sub> Fe	5.08	27.19	67.16	0.00	0.00	0.58	100.94
			2.18	10.24	88.40	0.00	0.00	0.12	
9-2	Pt/Sn = 3/1	Pt <sub>3</sub> Sn	3.62	2.70	71.79	0.00	21.89	0.00	100.28
			1.36	0.89	82.69	0.00	15.34	0.00	
9-3	(Pt + Pd)/Sn = 3/1	(Pt,Pd) <sub>3</sub> Sn	2.70	2.44	51.66	18.90	24.02	0.28	99.84
			1.12	0.90	65.94	13.16	18.66	0.06	
11		bn	56.68	6.85	0.00	0.00	0.00	36.47	100.07
			69.94	7.43	0.00	0.00	0.00	22.70	
		hc	24.15	29.87	0.00	0.00	0.00	45.98	100.30
		32.91	35.78	0.00	0.00	0.00	31.61		
		po	0.67	48.99	0.00	0.00	0.00	50.34	
			0.96	61.95	0.00	0.00	36.54	99.45	
11-1	Pt	(Pt,Cu) <sub>3</sub> Fe	5.05	27.60	66.72	0.00	0.00	0.64	100.24
			2.16	10.37	87.57	0.00	0.00	0.14	
11-2	Pt/Sn = 3/1	Pt <sub>3</sub> Sn	3.42	2.70	71.64	0.00	22.04	0.20	100.90
			1.29	0.90	83.11	0.00	15.56	0.04	
11-3	Pd + Pt/Sn = 3/1	Pt <sub>3</sub> (Sn,Fe)	3.28	7.53	67.00	2.45	19.46	0.29	99.64
			1.27	2.57	80.01	1.59	14.14	0.06	
		(Pt,Pd) <sub>3</sub> (Sn,Fe)	3.64	6.77	58.67	10.96	19.67	0.29	100.32
		1.49	2.44	73.77	7.51	15.05	0.06		
		(Pt,Pd,Cu) <sub>3</sub> (Sn,Fe)	5.57	8.09	46.22	20.46	19.17	0.49	
			2.49	3.18	63.39	15.30	15.99	0.11	100.46
12		bn	54.17	7.14	0.00	0.00	0.00	38.69	100.52
			68.10	7.88	0.00	0.00	0.00	24.54	
		po	2.37	47.59	0.00	0.00	0.00	50.04	99.52
			3.40	59.94	0.00	0.00	36.18		
12-1	Pt	Pt <sub>3</sub> Fe	3.45	29.45	66.65	0.00	0.00	0.45	100.28
			1.48	11.08	87.62	0.00	0.00	0.10	
12-2	Pt/Sn = 3/1	Pt <sub>3</sub> Sn	3.35	2.70	71.58	0.00	22.09	0.27	101.10
			1.27	0.90	83.25	0.00	15.63	0.05	
12-3	Pd + Pt/Sn = 3/1	PtSn	1.60	2.04	43.94	3.50	47.80	1.11	99.87
			0.68	0.77	57.58	2.50	38.10	0.24	
		Pt(Sn,Fe)	2.23	10.37	44.89	3.02	39.37	0.13	99.79
		0.98	3.99	60.37	2.21	32.21	0.03		
		(Pt,Pd)(Fe,Cu,Sn)	8.44	33.04	42.32	8.33	7.66	0.20	
		4.30	14.78	66.11	7.09	7.28	0.05		
(Pt,Pd,Cu) <sub>3</sub> (Sn,Fe)	8.66	9.64	49.20	11.90	20.37	0.22	100.35		
			3.76	3.84	66.99	8.84		16.87	0.05

Notes: See Table 2 for abbreviations. Only trace phases are given in the synthesized phase column for samples 7-1 – 7-5, 9-1 – 9-3, 11-1 – 11-3, 12-1 – 12-3. The major phases in these samples are identical to those in sample of corresponding number, i.e., 7, 9, 11, 12

- Distler V.V., Smirnov A.V., Grokhovskaya T.L., et al.* Stratification and subtle layering of differentiated trap intrusions and formation conditions of sulfide mineralization // Conditions of formations of magmatic ore deposits. Moscow: Nauka, **1979**. P. 211 – 269 (In Russian).
- Genkin A.D.* Minerals of platinum-group metals and their associations in Cu-Ni ores of the Noril'sk deposit. Moscow: Nauka, **1968**. 106 pp. (In Russian).
- Genkin A.D., Distler V.V., Gladyshev G.D., et al.* Sulfide Cu-Ni ores of the Noril'sk deposits. Moscow: Nauka, **1981**. 233 pp. (In Russian).
- Kravchenko T.A.* Experimental study of the Sn role in case of the formation of Pt-Pd phases during crystallization of Cu-Fe sulfide melt // Bull. Earth Sciences. Russian Academy of Sciences. **2002**. No 1. [www.scgis.ru/russian/cp1251/h\\_dgggms/1-2002/informbul-1.htm#term\\_10](http://www.scgis.ru/russian/cp1251/h_dgggms/1-2002/informbul-1.htm#term_10). (In Russian).
- Kravchenko T.A.* Experimental study of crystallization features of Pt-Pd intermetallic compounds from Cu-Fe sulfide melt // Bull. Earth Sciences. Russian Academy of Sciences. **2006**. No 1. [www.scgis.ru/russian/cp1251/h\\_dgggms/1-2006/informbul-1\\_2006/term-44.pdf](http://www.scgis.ru/russian/cp1251/h_dgggms/1-2006/informbul-1_2006/term-44.pdf) (In Russian).
- Kravchenko T.A., Nigmatulina E.N.* Experimental study of fine-dispersed Au and Ag formation in the crystallization products of Cu-Fe sulfide melt // Bull. Earth Sciences. Russian Academy of Sciences. **2007**. No 1. [http://www.scgis.ru/russian/cp1251/h\\_dgggms/1-2007/informbul-1-2007](http://www.scgis.ru/russian/cp1251/h_dgggms/1-2007/informbul-1-2007) (In Russian).
- Kravchenko T.A., Pavlyuchenko V.S., Sluzhe-nikin S.F. & Mokhov A.V.* Au and Ag behavior during crystallization from melt of phase assemblages of the Cu-Fe-S system with chalcopyrite and pyrrhotite // XV Russian Conference on Experimental Mineralogy. Syktyvkar. Abstr. **2005**. P. 57 – 59 (In Russian).
- Lavrent'ev Yu.G. & Usova L.V.* The RMA-89 program for a Camebax-Micro electron microprobe // J. Analyt. Chem. **1991**. 46(1). P. 67 – 75 (In Russian).
- Mihalik P., Hiemstra S.A. & de Villiers J.P.R.* Rustenburgite and atokite, two new platinum-group minerals from the Merensky Reef, Bushveld Igneous Complex // Can. Mineral. **1975**. No 13. P. 146 – 150.
- Moh G.H.* Tin-containing mineral system I: The Sn-Fe-S-O system and mineral assemblages in ores // Chemie der Erde. **1974**. 33. P. 243 – 275.
- Nekrasov I.Ya.* Petrology and platinum content of ring alkali-ultrabasic massifs. Moscow: Nauka, **1994**. 379 pp.
- Nekrasov I.Ya.* Tin in magmatic and postmagmatic processes. Moscow: Nauka, **1984**. 235 pp. (In Russian).
- Vaughan D.J. & Craig J.R.* Mineral Chemistry of Metal Sulfides. London: Cambridge University Press. **1978**.