

## THE Pt-Pd-Sn ALLOYS IN THE Pt-Pd SULFIDES CRYSTALLIZATION FIELD IN THE Cu-Fe-S SYSTEM

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To understand conditions under which the unique Cu-Fe association was formed at the Norilsk Cu-Ni deposits, crystallization products of melts were studied in the Cu-Fe-S system with Pt, Pd, and Sn admixtures (1 wt.%). Pt-Pd-Sn alloys — analogues of rustenburgite  $Pt_3Sn$ , atokite  $Pd_3Fe$  and palladium rustenburgite were synthesized in phase associations with chalcopyrite, isocubanite, and mooihoekite corresponding to the stability field of Pt-Pd sulfides analogues of the naturally occurring minerals malanite  $(Pt,Cu,Fe)_S$ , cooperite PtS, vysotskite PdS, and braggite  $(Pt,Pd)_S$ . The results thus obtained testify that the presence of Sn, together with Pt and Pd, in the melts of the central part of the Cu-Fe-S system corresponding to the compositions of magmatic Cu-Fe sulfide ores of the Norilsk Cu-Ni deposits predetermines the preferable crystallization of Pt-Pd-Sn alloys.  
1 figure, 2 tables, 8 references.

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

Most Pt and Pd minerals with Sn were discovered in Cu-Fe sulfide ores of the Norilsk Cu-Ni deposits (Genkin *et al.*, 1968) and were later distinguished as a unique Sn-bearing Cu-Fe association (Nekrasov, 1984). Following the first publications and later experimental studies at temperatures corresponding to postmagmatic crystallization, most researchers connects the formation of the Pt-Pd-Sn minerals with Pt-bearing fluids after the crystallization of the ore-forming Cu-Fe sulfides. Experimental studies the features of melt crystallization in the central part of the Cu-Fe-S system corresponding to the composition of Norilsk magmatic Cu-Fe sulfide ores (50 at.% S, Cu/Fe = 1.22–0.25 and 45 at.% S, Cu/Fe = 1.44–0.69 with Pt and Pd admixtures or Pt, Pd, and Sn admixtures; Kravchenko, 2009) suggest that Pt-Pd minerals can crystallize before the ore-forming sulfides and that Pt-Pd-Sn minerals preferably crystallize in the stability field of Pt-Pd-Fe alloys. Materials presented in this paper demonstrate that Pt-Pd-Sn alloys also predominantly crystallize in the stability field of Pt-Pd sulfides.

### Methods

The starting materials were carbonyl iron A-2, copper V-3, reagent-grade sulfur (additionally dehydrated by fusing in vacuum), metallic platinum, palladium, and tin. Pt, Pd, and Sn ((Pt, Pd)/Sn = 3/1, total concentration 1 wt.%) were added to the phase associations that were preliminarily synthesized in the Cu-Fe-S system and corresponded to the crystallization field of Pt-Pd sulfides, and to samples that have been studied previously and contained Pt-Pd sulfides (Pt + Pd = 1 wt.%, Kravchenko, 2013). The Cu/Fe ratios

(0.25, 0.43, 0.54, 0.69, 1.20, and 1.44) of these samples are not labeled by indexes in the tables. The total concentrations of admixtures in the synthesized samples were either 1 wt.% or > 1 wt.% because of a certain concentrations of Pt-Pd sulfides in the starting material. Synthesis was conducted in evacuated quartz ampoules by cooling the melt from 1200°C to room temperature. Similar to the synthesis of Pt-Pd-Sn alloys in the crystallization field of Pt-Pd-Fe-Cu alloys in the Cu-Fe-S system (Kravchenko, 2009), when cooled, all samples were held at a temperature of 600°C for two weeks and then (upon remelting) at 400°C for three months. In view of certain crystallization specifics of the Cu-Fe-S phases (Kravchenko, 2011), some of the samples were also held when cooled at 800°C for 1–10 days and/or cooled at various rates within the temperature range of 1200–850°C. The samples were cooled from 600 or 400°C to room temperature in cold water. The synthesized crystallization products were examined under an optical microscope and by X-ray diffraction techniques. Polished sections were manufactured of the halves of the samples (cut through their central parts from tops to bottoms). The chemical compositions of the samples and the distribution of minor elements in them were analyzed on a Camebax-Micro microprobe, using the RMA-96 universal computer code (Lavrent'ev and Usova, 1991), by the  $FeK_{\alpha}$ ,  $CuK_{\alpha}$ ,  $SK_{\alpha}$ ,  $PtM_{\alpha}$ ,  $PdL_{\alpha}$ ,  $SnL_{\alpha}$ . X-ray diffraction lines, in which no overlaps occur. The standards were FeS, SnS,  $CuFeS_2$ , Pt, and Pd. The accelerating voltage was 20 kV, the absorbed-electron current was 40 nA, the take-off angle was 40°, the counting time was 10 s on each analytical line, and the beam diameter was 2–3  $\mu m$ . The analytical errors were within  $\pm 2\%$  for each

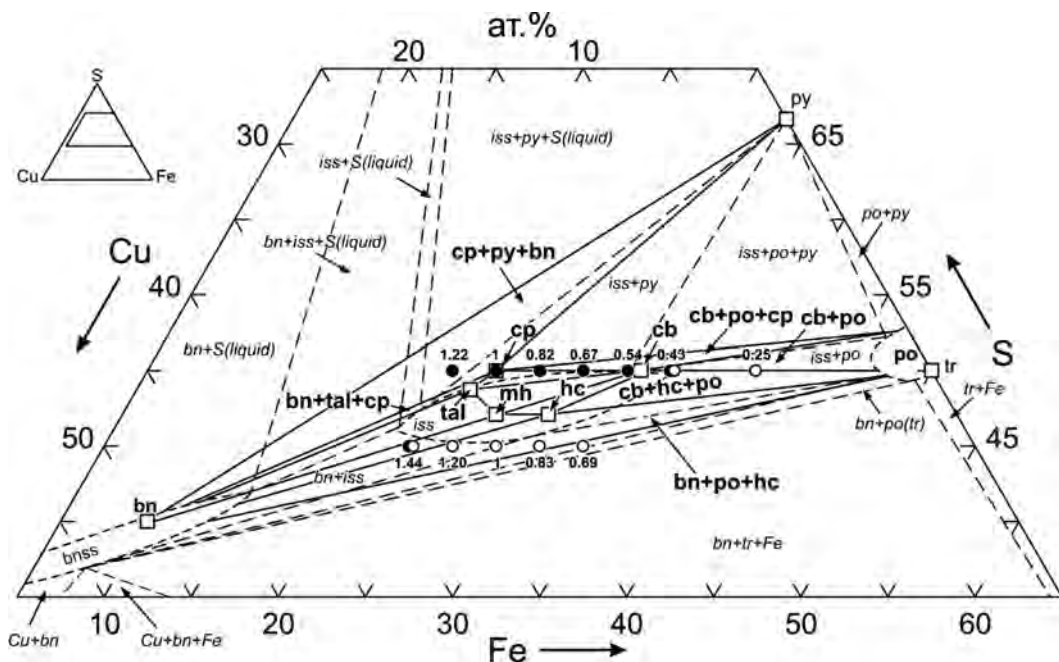


Fig. 1. Phase relations of synthesized phases (solid lines) (Kravchenko, 2011, 2012) in the central part of the Cu-Fe-S system at 600°C (dashed lines) (Cabri, 1973).

□ – stoichiometric compositions: chalcopyrite  $\text{CuFeS}_2$  (cp), bornite  $\text{Cu}_3\text{FeS}_3$  (bn), pyrite  $\text{FeS}_2$  (py), troilite  $\text{FeS}$  (tr), talnakhite  $\text{Cu}_9\text{Fe}_8\text{S}_{16}$  (tal), isocubanite  $\text{CuFe}_2\text{S}_3$  (cb), mooihoeikite  $\text{Cu}_9\text{Fe}_9\text{S}_{16}$  (mh) and haycockite  $\text{Cu}_4\text{Fe}_5\text{S}_8$  (hc), iss, bns and po are the chalcopyrite, bornite and pyrrhotite solid solutions. Starting compositions of the synthesized samples: 50 at. % S, Cu/Fe = 1.22–0.25; 45 at. % S, Cu/Fe = 1.44–0.69. • – Pt-Pd sulfides; ○ – Pt-Pd-Fe-alloys.

element. The detection limits  $C_{\min}$  were calculated using the 2 $\delta$ -criterion at 99% confidence level and were as follows: Cu – 0.05, Fe – 0.03, S – 0.02, Pt – 0.06, Pd – 0.05, and Sn – 0.05. The composition of the synthesized phases was expressed in the form of chemical formulas involving all elements whose concentrations in these phases were no lower than 5 at.%; the phases were named accordingly to their analogues naturally occurring as minerals. The exceptions were the phases of haycockite composition  $\text{Cu}_4\text{Fe}_5\text{S}_8$ , which have a cubic *pc* structure in contrast to natural orthorhombic haycockite. In describing our results, we expressed the starting compositions of the samples synthesized in the Cu-Fe-S system and the compositions of the synthetic Cu-Fe-S sulfides in the form of the Cu/Fe ratio (in at.%) because all sulfides in the central part of the Cu-Fe-S system have variable Cu and Fe concentrations (Kravchenko *et al.*, 2012).

## Results and discussion

Tables and figures below summarize the results of our experiments on the synthesis of Pt-Pd and Pt-Pd-Sn phases in the phase associations in the central part of the Cu-Fe-S system when

either Pt or Pd (alternatively) or both elements were added to the system are printed in the tables in ordinary type. The Cu/Fe ratios of the starting compositions of the synthesized samples presented of this research and their Pt-Pd phases are printed in bold type. Samples whose Cu-Fe-S are labeled with the subscript index 1 (for example, 0.43<sub>1</sub>, 0.54<sub>1</sub> etc.) were cooled within the temperature range of 1200–850°C at a higher rate than samples labeled with the subscript index 2 (0.43<sub>2</sub>, 0.54<sub>2</sub>, etc.). The sulfides synthesized in the Cu-Fe-S system do not contain Pt, Pd, and Sn admixtures. Their compositions and phase relations are consistent with experimental data (Kravchenko, 2011; Kravchenko *et al.*, 2012; Fig. 1). The figure shows the stoichiometric compositions of chalcopyrite  $\text{CuFeS}_2$ , isocubanite  $\text{CuFe}_2\text{S}_3$ , mooihoeikite  $\text{Cu}_9\text{Fe}_9\text{S}_{16}$  and haycockite  $\text{Cu}_4\text{Fe}_5\text{S}_8$ . The ranges of the Cu/Fe ratio for these phases are specified in the note to Table 1. Solid circles in the figure correspond to the starting compositions of samples with Pt-Pd sulfides, and open circles show the compositions of the Pt-Pd-Fe alloys (Kravchenko, 2013). As can be seen in the figure and Table 1, the crystallization fields Pt-Pd sulfides are 50 at. % S, Cu/Fe = 1.22–0.43 and 45 at. % S, Cu/Fe = 1.44, the crystallization

**Table 1. Phase composition of synthesized crystallization products of Cu-Fe-S melts with Pt, Pd, and Sn admixtures**

S	Starting composition, at.%, Cu/Fe			Synthesized phases		
	Cu	Fe	Cu/Fe	Cu-Fe-S, Cu/Fe*	Pt, Pd <b>Pt(Pd)+Sn</b>	Pt + Pd <b>Pt+Pd+Sn</b>
50	27.5–25	22.5–25	1.22–1	cp + bn + py	Cu(Pt,Fe) <sub>2</sub> S <sub>4</sub> , PdS <b>Pt<sub>3</sub>Sn</b>	Cu(Pt,Fe) <sub>2</sub> S <sub>4</sub> , (Pt,Pd)S <b>(Pt,Pd)<sub>3</sub>Sn+PdS</b>
	25–17.5	25–32.5	1–0.54	cp + cb, 0.61–0.52*	PtS, PdS <b>Pt<sub>3</sub>Sn</b>	(Pt,Pd)S <b>(Pt,Pd)<sub>3</sub>Sn+PdS</b>
	15	35	0.43 <sub>1</sub>	cb + cp 0.52–0.48*		
	15	35	0.43 <sub>2</sub>	mh(hc) + bn	PtS или Pt <sub>3</sub> Fe, (Pd,Cu) <sub>16</sub> S <sub>7</sub> <b>Pt<sub>3</sub>Sn, Pd<sub>3</sub>Sn</b>	(Pt,Pd) <sub>3</sub> Fe, (Pt,Pd) <sub>16</sub> S <sub>7</sub> <b>(Pt,Pd)<sub>3</sub>Sn+PdS</b>
15	35	0.43 <sub>2</sub>	cb + po, 0.49–0.43* mh(hc) + bn			
45	32.5–30	22.5–25	1.44–1.20	mh(hc) + bn		
50	10	40	0.25–0.43	cb + po	Pt <sub>3</sub> Fe, Pd <sub>3</sub> Fe	(Pt,Pd) <sub>3</sub> Fe
				0.43	Pt <sub>3</sub> Sn, Pd <sub>3</sub> Sn	(Pt,Pd) <sub>3</sub> Sn
45	30–25	25–30	1.20–0.69	hc + bn	Pt <sub>3</sub> Fe, PtFe	(Pt,Pd) <sub>3</sub> Fe,
				hc + bn + po	Pd(Cu,Fe)	Pd(Cu,Fe),
				bn + po	Pt <sub>3</sub> Sn, PtSn, Pt(Sn,Fe)	(Pt,Pd) <sub>3</sub> (Cu,Fe) (Pt,Pd) <sub>3</sub> (Sn,Fe) (Pt,Pd,Cu) <sub>3</sub> (Sn,Fe)

Note: \* – Cu/Fe of isocubanite, cp – chalcopyrite CuFeS<sub>2</sub> (Cu/Fe = 0.99–0.67), bn – bornite Cu<sub>3</sub>FeS<sub>4</sub>, py – pyrite FeS<sub>2</sub>, cb – isocubanite CuFe<sub>2</sub>S<sub>3</sub> (Cu/Fe = 0.61–0.43), mh – mooihoekite Cu<sub>9</sub>Fe<sub>9</sub>S<sub>16</sub> (Cu/Fe = 1.04–0.93), hc – cubic (pc) haycockite Cu<sub>4</sub>Fe<sub>5</sub>S<sub>8</sub> (Cu/Fe = 0.92–0.68), and po – pyrrhotite Fe<sub>1-x</sub>S.

field of the Pt-Pd-Fe alloys is 50 at.% S, Cu/Fe = 0.43–0.25 and 45 at.% S, Cu/Fe = 1.20–0.69, and they are separated by the equilibrium line bornite Cu<sub>3</sub>FeS<sub>4</sub> (bn) – mooihoekite Cu<sub>9</sub>Fe<sub>9</sub>S<sub>16</sub> (mh) – isocubanite CuFe<sub>2</sub>S<sub>3</sub> (cb). The region of phase associations with isocubanite and pyrrhotite Fe<sub>1-x</sub>S: cb + po, 50 at.% S, Cu/Fe = 0.49–0.43, and mooihoekite (or haycockite) and bornite Cu<sub>3</sub>FeS<sub>4</sub>: mh(hc) + bn, 45 at.% S, Cu/Fe = 1.44–1.20, occur between the crystallization fields of Pt-Pd sulfides and Pt-Pd-Fe alloys. In this transitional field, PtS or Pt<sub>3</sub>Fe were synthesized together with Pd sulfides (Pd,Cu)<sub>16</sub>S<sub>7</sub> and (Pt,Pd)<sub>3</sub>Fe was synthesized if the melt contained both Pt and Pd. As can be seen in Table 1, the Pt<sub>3</sub>Sn, Pd<sub>3</sub>Sn, and (Pt, Pd)<sub>3</sub>Sn alloys were synthesized in both the crystallization fields of Pt-Pd sulfides and the aforementioned transitional field. PdS was synthesized, together with (Pt,Pd)<sub>3</sub>Sn, in samples containing both Pt and Pd. The compositions of the Pt<sub>3</sub>Sn and Pd<sub>3</sub>Sn are closely similar to the compositions of the phases synthesized previously in the crystallization field of Pt-Pd-Fe-Cu alloys, and the compositions of (Pt,Pd)<sub>3</sub>Sn in association with PdS have lower Pd concentrations. Similar to the crystallization field of Pt-Pd-Fe alloys, the compositions of all of the synthesized Pt-Pd-Fe alloys did not vary when the samples were held at 600 and 400°C in the course of their cooling.

Table 2 presents the compositions of some samples with (Pt,Pd)<sub>3</sub>Sn in association with PdS and samples with Pt-Pd sulfides with

Cu/Fe (0.54, 0.43, and 1.44) that were used as starting materials for the synthesis. As in Table 1, the Cu/Fe ratio of the starting samples synthesized in the course of this research and the Pt-Pd phases in them are printed in Table 2 in bold type. It can be seen in Table 2 that (Pt,Pd)<sub>3</sub>Sn was synthesized in all Sn-bearing samples and has similar Pt and Pd ratios (Pt: 56.37–65.49 at.%, Pd: 13.48–6.36 at.%). Lower Pd concentrations (6.36 at.%) were detected in (Pt,Pd)<sub>3</sub>Sn of sample 2 (Cu/Fe 0.54<sub>1</sub>), which was cooled at a higher rate from 1200 to 850°C, than sample 3 (Cu/Fe 0.54<sub>2</sub>) and other Sn-bearing samples. Samples 3 (Cu/Fe 0.54<sub>2</sub>), sample 6 (Cu/Fe 0.43<sub>2</sub>) and sample 8 (Cu/Fe 1.44<sub>1</sub>), which were cooled at similar rate from 1200 to 850°C, contain (Pt,Pd)<sub>3</sub>Sn with Pd concentrations of 9.35–13.48 at.%. This means that the Pt and Pd concentrations in (Pt,Pd)<sub>3</sub>Sn are independent of the starting Cu-Fe-S composition of the samples. As follows from Table 2, in samples of the same starting composition, 50 at.% S, Cu/Fe = 0.43, (Cu/Fe = 0.52–0.48\*; Table 1), associations of Cu-Fe sulfides of different composition were synthesized: these were isocubanite + chalcopyrite in sample 5 (Cu/Fe = 0.43<sub>1</sub>) and mooihoekite + bornite in sample 6 (Cu/Fe = 0.43<sub>2</sub>). Similar compositions of (Pt,Pd)<sub>3</sub>Sn in these samples testify that the compositions of the synthesized Pt-Pd-Fe phases do not vary when the composition of the associations of Cu-Fe sulfides change during cooling.

**Table 2. Chemical composition of synthesized crystallization products of Cu-Fe-S melts with Pt, Pd, and Sn admixtures**

Sample	Cu/Fe, at.%, Cu-Fe-S association, admixtures, wt.%	Pt-Pd phases	Composition of Pt-Pd phases, at.%/wt.%						$\Sigma$ , wt.%
			Cu	Fe	Pt	Pd	S	Sn	
1	0.54, cb + cp, Pt + Pd, $\Sigma = 1$	(Pt,Pd)S	1.93	3.06	44.11	6.50	44.40	0.00	99.60
			1.11	1.54	77.62	6.22	12.84	0.00	
		PdS	0.42	0.68	0.06	49.62	49.21	0.00	99.33
			0.38	0.54	0.18	75.84	22.66	0.00	
2	<b>0.54<sub>1</sub></b> , cb + cp, (Pt,Pd)/Sn > 3/1, $\Sigma > 1$	<b>(Pt,Pd)<sub>3</sub>Sn</b>	3.25	0.56	65.49	6.36	0.24	24.10	100.87
			1.26	0.19	77.83	4.12	0.04	17.43	
		PdS	1.96	0.34	0.00	48.42	49.28	0.00	99.92
			1.80	0.28	0.00	74.88	22.96	0.00	
3	<b>0.54<sub>2</sub></b> , cb + cp, Pt,Pd/Sn > 3/1, $\Sigma > 1$	<b>(Pt,Pd)<sub>3</sub>Sn</b>	3.06	2.13	56.37	13.48	1.45	23.51	99.93
			1.25	0.76	70.53	9.20	0.30	17.90	
		PdS	2.33	0.05	0.00	49.98	47.64	0.00	99.79
			2.11	0.04	0.00	75.85	21.79	0.00	
4	0.43, cb + po, Pt + Pd, $\Sigma = 1$	(Pt,Pd)S	1.22	1.92	45.88	5.33	45.65	0.00	99.75
			0.70	0.96	79.94	5.07	13.08	0.00	
		PdS	0.29	0.52	0.04	50.32	48.83	0.00	99.73
			0.26	0.42	0.11	76.56	22.38	0.00	
5	<b>0.43<sub>1</sub></b> , cb + po, Pt,Pd/Sn > 3/1, $\Sigma > 1$	<b>(Pt,Pd)<sub>3</sub>Sn</b>	3.71	1.55	62.12	10.23	0.03	22.36	99.65
			1.46	0.53	74.60	6.71	0.01	16.34	
		PdS	3.57	0.50	0.00	47.28	48.65	0.00	100.68
			3.36	0.41	0.00	73.99	22.92	0.00	
6	<b>0.43<sub>2</sub></b> , mh + bn, (Pt,Pd)/Sn > 3/1, $\Sigma > 1$	<b>(Pt,Pd)<sub>3</sub>Sn</b>	3.82	1.64	62.68	9.35	0.17	22.34	99.73
			1.50	0.56	75.20	6.13	0.04	16.30	
		PdS	2.42	0.12	0.00	49.58	47.88	0.00	100.52
			2.21	0.14	0.00	76.08	22.14	0.00	
7	1.44, mh + bn, Pt + Pd, $\Sigma = 1$	PtS	8.30	0.98	45.45	2.84	42.43	0.00	99.23
			4.71	0.49	79.18	2.70	12.15	0.00	
		(Pd,Cu) <sub>16</sub> S <sub>7</sub>	17.02	0.97	0.00	52.67	29.34	0.00	99.91
			14.07	0.70	0.00	72.90	12.24	0.00	
8	<b>1.44<sub>1</sub></b> , mh + bn (Pt,Pd)/Sn > 3/1, $\Sigma > 1$	<b>(Pt,Pd)<sub>3</sub>Sn</b>	4.43	3.16	57.52	12.46	0.81	21.62	99.28
			1.80	1.13	71.75	8.43	0.16	16.36	
		PdS	2.14	0.27	0.00	48.26	49.33	0.00	100.48
			1.99	0.22	0.00	75.14	23.13	0.00	

Note: cb – isocubanite, CuFe<sub>2</sub>S<sub>3</sub>, cp – chalcopyrite CuFeS<sub>2</sub>, po – pyrrhotite Fe<sub>1-x</sub>S, mh – mooihoeite Cu<sub>9</sub>Fe<sub>9</sub>S<sub>16</sub>, hc – cubic (pc) haycockite Cu<sub>4</sub>Fe<sub>2</sub>S<sub>9</sub>, bn – bornite Cu<sub>5</sub>FeS<sub>4</sub>.

Our results indicate that the simultaneous crystallization of Pt, Pd, and Sn, all Pt and partly Pd generates (Pt,Pd)<sub>3</sub>Sn, and the remaining Pd crystallizes as sulfide PdS. The Pt and Pd concentrations in (Pt,Pd)<sub>3</sub>Sn are independent of the starting Cu, Fe, and S concentrations of the samples and do not vary either when the composition of the association of Cu-Fe sulfides is varied at the crystallization temperatures of the Cu-Fe-S melts (1070–854°C) (Kravchenko, 2011) or when they are held at temperatures of 600 and 400°C in the course of cooling. This indicates that the synthesized Pt-Pd-Sn phases crystallized earlier than the Cu-Fe sulfides did.

All of the synthesized Pt-Pd-Sn alloys and all Pt-Pd phases synthesized in melts of this composition but containing no Sn (Table 1) have the same morphological features and show the same phase relations in the crystallization products of Cu-Fe-S melts as those of

corresponding natural minerals in Cu-Fe sulfide ores of the Norilsk Cu-Ni deposits.

## Conclusion

Pt-Pd-Sn alloys analogous to rustenburgite Pt<sub>3</sub>Sn, atokite Pd<sub>3</sub>Sn, and Pd-rustenburgite (Pt,Pd)<sub>3</sub>Sn were synthesized in phase associations with chalcopyrite, isocubanite, and mooihoeite corresponding to the stability field of Pt-Pd sulfides that are analogues of naturally occurring minerals: malanite Cu(Pt,Fe)<sub>2</sub>S<sub>4</sub>, cooperite PtS, vysotskite PdS, braggite (Pt,Pd)S and an unnamed compound of the composition (Pd,Cu)<sub>16</sub>S<sub>7</sub>. Our results and the results of synthesis in the crystallization field of Pt-Pd-Fe-Cu alloys that are analogues of isoferroplatinum Pt<sub>3</sub>Fe, Pd analogue of isoferroplatinum Pd<sub>3</sub>Fe, tetraferroplatinum PtFe, and the unnamed compound Pd(Cu,Fe) testify to the dominant crystallization of Pt-Pd-Sn alloys when

the melts crystallize in the central part of the Cu-Fe-S system with 50 at.% S, Cu/Fe = 1.22–0.25 and 45 at.% S, Cu/Fe = 1.44–0.69 and with Pt, Pd, and Sn admixtures. Similarities in the composition, morphological features, and phase relations of the Pt-Pd-Sn alloys in the crystallization products of the Cu-Fe-S melts and the corresponding natural minerals in Cu-Fe sulfide ores of the Norilsk Cu-Ni deposits testify that these compounds and natural minerals were formed under similar conditions.

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