EXPERIMENTAL STUDY OF CRYSTALLIZATION PECULIARITIES OF Pt-Pd ALLOYS FROM Cu-Fe SULFIDE MELT

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Pt-Pd alloys represent a unique mineral association of Norilsk magmatic Cu-Ni deposits. The inferences [1] about its formation from the fluids after crystallization of the basic ore-forming sulfides chalcopyrite and pyrrhotite at the temperatures below 600°C are ambiguous [2] and inconsistent with the data on the temperatures (above 1200°C) of the majority of Pt-Pd minerals. Due to above mentioned, the experimental study of the peculiarities of their direct crystallization from Cu-Fe sulfide melt is necessary for understanding of the Pt-Pd alloys formation conditions.

The methodical peculiarity of the given study is that tin like platinum and palladium is introduced into the samples of Cu-Fe-S system as a micro component (not more than 1 wt%). This study allowed us to synthesize tin-containing phases in the frames of three-component Cu-Fe-S system and to demonstrate that tin together with platinum and palladium found in Cu-Fe sulfide solution define the crystallization of Pt-Pd-Sn phases - analogs of Pt-Pd-Fe alloys, where tin partially or completely replaces Fe [3]. Pt-Pd-Sn alloys were synthesized in association with chalcopyrite and pyrrhotite by the melt cooling method in the vacuumed quartz ampoules.

Microscopic and X-ray study has been used to diagnose the synthesized phases. Microprobe analysis has been used to determine the chemical composition. The morphology and phase relations of crystallization products against the initial melt composition and cooling regime have been studied.

The table below demonstrates the results. The sulfides of Cu-Fe-S system do not contain any Pt, Pd and S admixtures. Their compositions and phase relations correspond to the experimental data [4] except that cubic chalcopyrite solid solution at room temperature is characterized not by fcc but by pc [5] cell.

Table

smpl №	Initial compositions of melt, at. %			Synthesized phases	Composition of Pt-Pd-Sn phases, at. %					
	Cu	Fe	S		Cu	Fe	Pt	Pd	S	Sn
31	10	40	50	Cp_{ss}+Po						
				$(Pt,Pd)_3Sn$	2,69	2,91	50,80	19,29	0,31	24,00
49	30	25	45	Cp_{ss}+Bn_{ss}						
				$(Pt,Pd)_3Sn$	2,70	2,44	51,66	18,90	0,28	24,02
51	25	30	45	Cp_{ss}+Bn_{ss}+ Po						
				$Pt_3(Sn,Fe)$	3,28	7,53	67,00	2,45	0,29	19,46
				$(Pt,Pd)_3(SnFe)$	3,64	6,77	58,67	10,96	0,29	19,67
				$(Pt,Pd,Cu)_3(Sn,Fe)$	5,57	8,09	46,22	20,46	0,49	19,17
52	22,5	32,5	45	Bn_{ss} + Po+Cu						
				PtSn	1,60	2,04	43,94	3,50	1,11	47,80
				Pt(Sn,Fe)	2,23	10,37	44,89	3,02	0,13	39,37
				(Pt,Pd)(Fe,Cu,Sn)	8,44	33,04	42,32	8,33	0,20	7,66
				$(Pt,Pd,Cu)_3(Sn,Fe)$	8,66	9,64	49,20	11,90	0,22	20,37

Cp_{ss} – cubic chalcopyrite solid solution (enriched in Fe and depleted in S as compared to $CuFeS_2$), Po – pyrrhotite FeS, Bn_{ss} – bornite solid solution (enriched in Fe as compared to Cu_5FeS_4. Formulae of Pt-Pd-Sn phases do not show the elements, which contain less than 5 at%.

Pt-Pd phase compositions are defined by the composition of the initial melt. $(Pt,Pd)_3Sn$ – analogs of palladium rustenburgite and platinum attocite crystallized in the associations Cp_{ss}+Po and Cp_{ss}+Bn_{ss} (samples 31 and 49). The formation of the phases with the irregular distribution of elements forming during one cooling process is characteristic of the associations Cpss+Bn_{ss}+Po and Bn_{ss}+Po+Cu (samples 51 and 52). The phases compositions represented in table are specified both for different and single grain as well (fig).

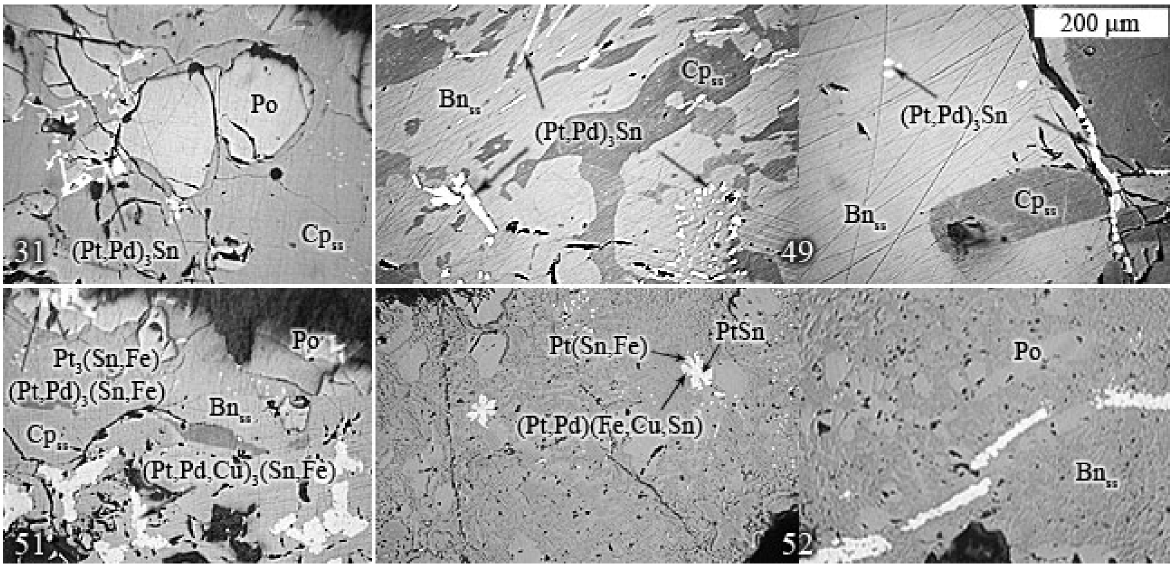

Fig. Pt-Pd-Sn alloys in associations with c chalcopyrite (Cp_{ss}), pyrrhotite (Po), and bornite (Bn_{ss}).

The size and form of the synthesized Pt-Pd grains alloys do not depend on their composition and the composition of the initial melt. Different forms (well-formed crystals, crystals with irregular and step faces, skeleton crystals, rounded grains and the irregular form grains etc.) can be simultaneously observed in all samples.

The main factor, which defines the relationships of the crystallized phases, is the export of microelements to the crystallization front of the melt. Pt-Pd phases are located between the grains of the less high-melting sulfides, in the cracks and cavities of the samples and on the surface and even beyond the boundaries of the samples. The veins cutting sulfides and the largest grains along the surface of the samples are peculiar to the melt crystallization. The chalcopyrite, pyrrohtite and bornite inclusions are met in the Pt-Pd phase's grains.

The obtained results correlate with literature data [1, 2] on the composition, grain morphology and phase relations in the corresponding natural associations of Norilsk Cu-Ni deposits. The obtained data allow concluding that direct crystallization of Pt-Pd alloys from the melt of basic ore-forming sulfides of chalcopyrite and pyrrhotite is possible.

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