EXPERIMENTAL STUDY OF THE ROLE OF TIN AT THE FORMATION OF PLATINUM-PALLADIUM PHASES DURING THE CRYSTALLIZATION OF CU-FE-S MELT

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The interest in the role of tin at crystallization of sulfide melt, which contains platinum and palladium, is related the fact that tin minerals with platinum and palladium (analogs of the corresponding Fe minerals) are the most common in sulfide ores from Norilsk deposits. Despite a large body of research the conclusions about their possible crystallization immediately from magmatic melt at high temperatures are ambiguous [1,2]. Cu-Fe-S system is chosen as a model, its central part according to composition corresponds to the most common natural associations of copper-pyrite ores. The methodical peculiarity of the given study is that tin like platinum with palladium is introduced into the samples of the studied system as a micro component (not more than 1wt %). This study allows us to synthesize tin-containing phases within the framework of Cu-Fe-S three component system and to compare them with the results of crystallization of Pt-Pd-bearing melt of the same composition, but without tin.

The platinum behavior depending on the change of the iron and tin content in the crystallizing sulfide melt (it contains 1wt % of Pt) of FeS-SnS binary system has been preliminary evaluated. Platinum-ferrous phases have not been distinguished in all synthesized samples. The whole of platinum is bound with tin forming phases of PtSn or $PtSn_2$ composition; they are synthetic analogs of natural niggliite and paolovite.

Pt and Pt with Pd have been introduced in amounts of 1wt % into the samples of the central part of Cu-Fe-S system with cross-sections 45 and 50 at %. Mineral forms of separations of platinoids depending on the composition of phase associations of system have been studied. The crystallization areas of sulfides and intermatallic compounds have been established [3]. To investigate the influence of tin on the formation of Pt-Pd phases the samples in which intermetallic compounds of platinum and palladium have been synthesized, are selected as initial. Synthesis has been carried out at cooling of the melt to 600°C and 400°C and subsequent annealing at 600°C during two weeks and at 400°C – during three months. The composition of the synthesized phases is defined by micro-x-ray-spectrometry. The obtained results are given in the table 1.

Table 1

Initial compositions of samples, at. %			Pt-Pd Phase	Pt-Pd-Sn Phase	Composition of Pt-Pd-Sn phase, at. %					
Cu	Fe	S			Cu	Fe	Pt	Pd	S	Sn
15,2	35,5	49,3 I_{ss}+Po	$(Pt,Pd)_3Fe$	$(Pt,Pd)_3Sn$	2,7	2,9	50,8	19,3	0,3	24,0
32,5	22,5	45,0 I_{ss}+Bn_{ss}	Pt_3Fe	Pt_3Sn	2,1	2,7	72,8	0,0	0,4	22,0
30,0	25,0	45,0 I_{ss}+Bn_{ss}	Pt_3Fe Pd(Cu,Fe)	$(Pt,Pd,Cu)_3(Sn,Fe)$	6,2	6,3	51,4	9,8	0,3	20,0
25,0	30,0	45,0 I_{ss}+Bn_{ss}+ Po	Pt_3Fe Pd(Cu,Fe)	$(Pt,Pd,Cu)_3(Sn,Fe)$	4,8	6,9	62,2	6,1	0,3	19,7
22,5	32,5	45,0 Bn_{ss}+ Po+ Cu	(Pt,Pd)(Fe,Cu)	Pt (Sn,Fe) (Pt,Pd)(Sn,Cu)	2,0 20,7	6,8 4,8	44,6 38,6	3,2 13,8	0,5 0,0	42,8 22,0

I_{ss}- intermediate solid solution $(Cu,Fe)S_2$ (it differs form chalcopyrite by cubic structure [5], in the given paper the structure is not defined), Po-pyrrhotite FeS, Bn_{ss} – bornite solid solution (more rich in Fe and S as compared to stoichiometric bornite (Cu_5FeS_4). The elements the contents of which are lower than 5 at. % are not indicated in the formulae of Pt-Pd-Sn phases.

The phase relations in the synthesized samples are in accordance with the data of experimental study of Cu-Fe-S system [4]. Tin is not found in the sulfides of macro system. Pt-Pd-Sn alloys are formed in all phase associations. In the area of crystallization of synthetic analog of Pt_3Fe isoferropllatinum the phases of $(Pt,Pd)_3Sn$ composition are synthesized. They correspond to the rustenburgite-atokite field [6] but contain iron and copper. In Bnss association with pyrrhotite and copper the crystallization forms vary Pt_3Fe – Pt_2Fe – PtFe as the iron content increases in the presence of platinum only, and platinum together with palladium form alloys (Pt,Pd)(Fe,Cu). If tin is found in this association together with platinum and palladium, then (Pt,Pd(Sn,Cu) and Pt,(Sn,Fe) alloys crystallize. The latter can be considered both as an iron-bearing analog of niggliite PtSn and tetraferroplatinum PtFe in which iron is almost completely substituted by tin. The availability of iron in sythesized Pt-Pd-Sn alloys is related to minor quantity of tin in the initial melt. This fact is supported by the results of crystallization from the melt of Pt-containing samples of FeS-SnS system. Only Pt-Sn alloys without iron are formed in Pt-containing samples of FeS-SnS system.

In the process of crystallization of melts without palladium the analog of rustenburgaite Pt_3Sn, containing up to 8,5 at% of iron, has been synthesized in all samples typical for isoferroplatinum formation.

The peculiarity of Pt-Pd phases synthesized from melt by cooling is formation of complex grains. Their composition varies depending on the majority of possible variants of synthesis regime. Zonal grains, the central part of which is filled in with a platinum phase (always with Pd), and the periphery – by palladium (with Pt and without Pt) are typical [3]. During the process of annealing the composition of these grains is redistributed up to complete homogenization. These grains are formed in the samples with similar crystallization form of platinum and palladium phase (Pt_3Fe and Pd_3Fe). The grains, which are visually homogenous but heterogeneous according to the content of the elements of platinum group, are also characteristic. The composition of these grains can vary in the process of annealing, but as a rule they preserve irregular distribution of platinum and palladium. These grains are characteristic for Pt_3Fe and Pd (Cu,Fe) crystallization area. Besides, the grains of like composition but different form similar to the described [2] for natural minerals of platinum group are found. They are metacrysts and the formation of the same phases of irregular form within one sample. Their formation is probably related to a step-by-step character of melt crystallization. The comparison of the results of crystallization of the melts both, with or without tin shows that the character of phase relations, the morphology of synthesized phases and the peculiarities of the distribution of platinum and palladium in joint compounds does not depend on tin presence.

Thus, the presence of tin together with platinum and palladium in the copper-iron sulfide melt of the central part of Cu-Fe-S system defines the crystallization of Pt-Pd-Sn phases-analogs of Pt-Pd-Fe alloys, in which iron partly or completely replaced by tin.

References

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