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Arsenic influence on noble metals behavior during fractional crystallization of the Cu-Fe-Ni-S melts

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It is well known that Fe, Cu, Ni sulfide magma containing platinum-group elements (PGE), Ag, Au forms ore deposits of the Norilsk, Bushveld, and Sudbury type. The impurities of As, Se, Te, Sb, Bi, and Sn are also typically in the magma. They may present in the form of isomorphic impurities in main ore-forming minerals, or be in either own mineral: alloys, intermetallic phases, sulfarsenides, arsenides, sulfides, tellurides, etc. [*Distler, et al.*, 1988; *Cabri*, 2002]. The published mineralogical information gives evidence for specific role of arsenic in a behavior of PGE in the deposits [D*istler, et al.,* 1988; *Cabri*, 2002; *Dare, et al.*, 2010]. Besides immiscibility between arsenide and sulfide melts was experimentally established and arsenide globules were detected in As-rich sulfide ores [*Makovicky,* 2002; *Helmy, et al.*, 2010; *Gervilla, et al.*, 1996]. These data suggest that Pt, Pd, Au, Bi, Te, Sb, Pb, Zn, Ag, and Sn have a stronger affinity for arsenide melts than for sulfide and silicate liquids. It is important that arsenic accumulates in the melt during crystallization of pyrrhotite solid solution [*Helmy, et al.*, 2010].

Currently prevalent concept on the formation of copper-nickel ores by fractional crystallization of sulfide melts [*Naldrett*, 2010]. It is a cause of primary, secondary and impurities zonality of orebodies [*Kosyakov and Sinyakova,* 2010].

One-dimensional solidification of the sulfide melt has been carried out to clarify an arsenic influence on impurities behavior at the fractional crystallization. The melt composition was Fe 35.5, Ni 4.9, Cu 10.4, S 48.3 (at.%) with an additive on Pt, Pd, Rh, Ru, Ir, Au, Ag, As and Co (0.1 at.%). It roughly imitates of average copper content in massive ore of Norilsk deposits [*Naldrett,* 2010].

Experimental.

One-dimensional crystallization of the melt was carried out by Bridgman method. The ampoule with homogenous melt has been dropped from the hot zone to the cold one with 2.3Ч10^{-8} m/s rate. The process occurs in quasi-equilibrium regime under these conditions [*Kosyakov and Sinyakova*, 2005]. Length of cylindrical specimen was 75 mm and its diameter was 7 mm (fig.1). It was cut into 20 samples perpendicular to the longitudinal axis, and each one was weighed. The samples were examined with optical and electronic microscopic, X-ray diffraction and electron microprobe analyses. The melt composition and partition coefficient of the components were calculated from material balance of components.

Results.

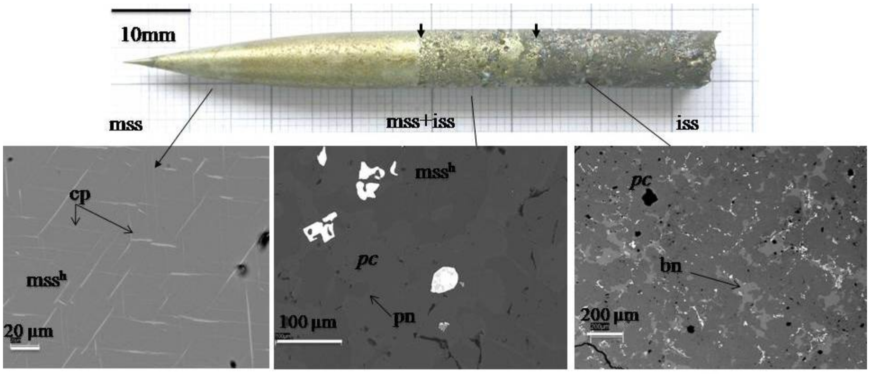
Microscopic description of the sample.

The specimen and typical microstructure of its different sites are shown in fig. 1. You can see visually that the sample is divided into three primary zones with sharp interface between them. According to the chemical analysis the first zone ($0 \le g \le \sim 0.5$) consists of Fe-rich monosulfide solid solution (Fe-mss), the second zone ($\sim 0.5 \le g \le \sim 0.7$ is composed of Fe-mss and an intermediate solid solution (iss) mixture, and the third zone ($\sim 0.7 \le g \le 1$) includes of iss.

The primary mss and iss are decomposed on low-temperature phases at further cooling. As a result an additional division of the specimen on sub-zones is realized. Subzone Ia ($0 \leq g \leq \sim 0.4$) consists of hexagonal mss^h (sp. gr. $P6_3/mmc$) matrix with tetragonal chalcopyrite lamellar inclusions. Subzone Ib ($\sim 0.4 \leq g \leq \sim 0.5$) contains also on pentlandite micro particles. Subzone IIa ($\sim 0.5 \leq g \leq \sim 0.6$) consisted of Fe-mss, pentlandite, and cubic pc-phase with haycockite composition [*Cabri*, 1973]. These phases and rich copper bornite present in subzone IIb ($\sim 0.6 \leq g \leq \sim 0.7$). The third zone of the ingot ($\sim 0.7 \leq g \leq 1$) is formed from pc-phase, bornite and pentlandite. These phases appear at iss decay.

Distribution of base components during mss crystallization.

The distribution curves of Fe and Cu are shown in fig 2. This data show that Fe and S with $k > 1$ are concentrated in mss while the melt is enriched in Cu and Ni with $k < 1$.



$g = 0.02$ $g = 0.49$ $g = 0.89$

Fig. 1. A crystallized sample (above) and its typical microstructure (below). *g* is a weight fraction of the specimen.

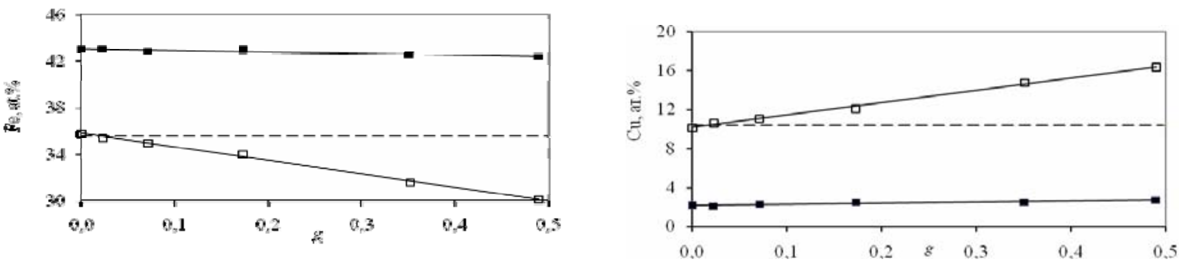


Fig. 2. Distribution of Fe and Cu in Fe-mss (close square) and in the melt (open square) in the crystallized specimen. The horizontal dashed line shows the concentration of the component in the initial melt

Impurities in primary mss. Microprobe analysis of initial part of the specimen showed that impurities (at.%): Co (~ 0.12), Rh (0.14), Ru (up to 0.38) , and Ir (up to 0.1) pass partly into the mss matrix. Ru distribution in mss and the melt is shown in fig. 3. The *k* values increase during mss crystallization in the range: 1.2 ч 1.4 for Co, 4 ч 8 for Ru, 1.2 ч 1.7 for Rh. The content of remaining impurities in mss is on the sensitivity level of the analysis: Pd ≤ 0.03, Pt ≤ 0.06, Ag, Au, As < 0.01 at.%.

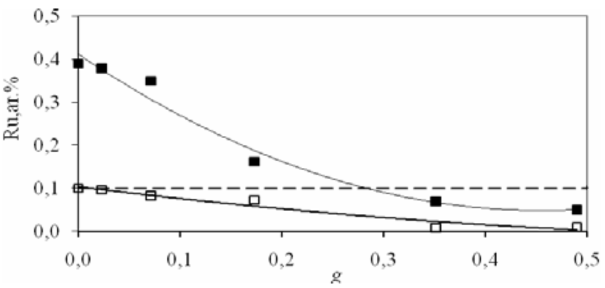
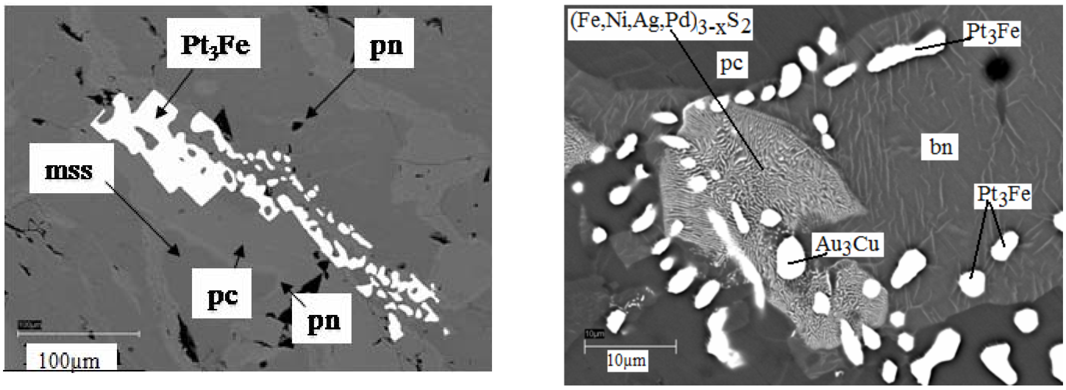


Fig. 3. Ru distribution in Fe-mss (close square) and in the melt (open square). The horizontal dashed line shows Ru concentration in the initial melt

Impurities solid solutions in subsolidus phases. A solubility of impurities in subsolidus mss is 0.13 Co, 0.38 Ru, 0.13Rh, 0.07Ir, and up to 0.02 at.% Pd. Chalcopyrite lamellas contain 0.47 Ru, 0.09 Ir, and 0.12 at.% Rh. The composition of grains, rims and lamellas of pentlandite varies slightly along the specimen from $Fe_{29.73}Co_{0.28}Ni_{20.17}Cu_{2.42}Rh_{0.10}Pd_{0.07}Ag_{0.04}S_{47.19}$ to $Fe_{28.78}Co_{0.24}Ni_{22.36}Cu_{1.57}Rh_{0.14}Pd_{0.52}S_{46.39}$. Distribution coefficients mss/cp are 0.3 ч0.9 for Ru, 0.5ч1.2 for Ir, and 0.9ч1.6 for Rh, and mss/pn are 0.4 - 0.5 for Co, Rh, and 0.05 - 0.1 for Pd.

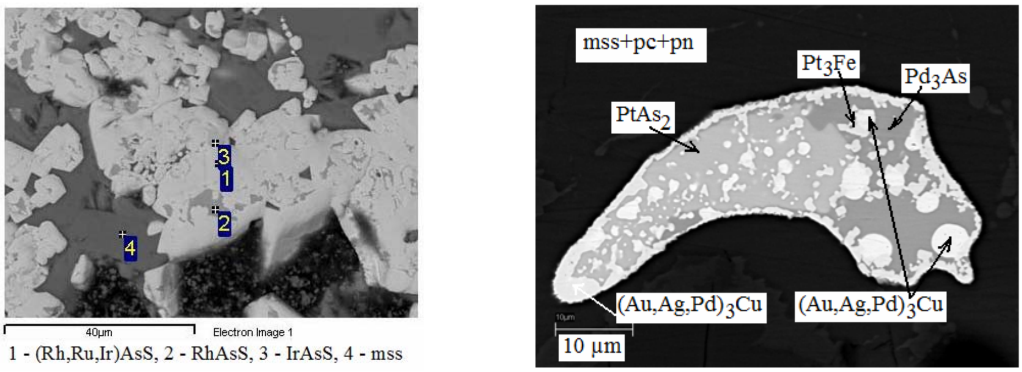
Microphases without As. Excess impurities of precious metals forms own phases in the sulfide matrix. (Ag, Pd), (Au, Cu), (Au, Pt), and (Pt,Fe) alloys present at the first part of the ingot. Alloys on the base on Au_3Cu, isoferroplatinum Pt_3Fe, $(Fe,Ni,Ag)_3S_{2-x}$, and Ag attend at the second and third parts. Note that these minerals may be in the form of isolated inclusions (fig. 4a), colonies of inclusions, or aggregates of microphase (fig. 4b).

Microphases with As. An impurity of precious metals are also present as sulfarsenides irarsite-hollingworthite series RhAsS, IrAsS, (Ir,Rh)AsS. They may contain an admixture of Ru. Note that sulfarsenides are allocated at the very beginning of the ingot (fig. 5a).



(a) (b)

Fig. 4. (a) Euhedral crystals of isoferroplatinum in sulfide matrix (subzone IIb, *g* ~ 0.49). (b) Pt_3Fe colonies and aggregates of Pt_3Fe, Au_3Cu, and $(Fe,Ni,Ag)_3S_{2-x}$ (zone III, *g* ~ 0.89)



(a) (b)

Fig. 5. (a) Aggregates of sulfarsenides in mss matrix (subzone Ia, *g* ~ 0.02). (b) Drop-like inclusion in sulfide matrix consists with two parts. As_2Pt matrix with $(Au,Ag,Pd)_3Cu$ drops in the light left part. Pd_3As matrix with Pt_3Fe crystals and (Au, Ag, Pd)$_3$Cu spherical inclusions in the dark right part

Drop-shaped inclusions based on the precious metals arsenide. These inclusions appear in the second zone. Their composition is presented in the table. Likely metallic-arsenic liquid drops appear inside the sulfide melt and then they solidify. Pt_2As or Pd_3As are the main components of the melt. These compounds can form a matrix phase or to present as euhedral crystals or cammed inclusions (fig. 5b).

Table. Average composition of two metal-arsenide inclusions in the sample at *g* ~ 1 (at.%).

Fe	Co	Ni	Cu	As	S	Ru	Rh	Pd	Ag	Au	Pt	Ir
23.60	0.10	2.70	3.23	2.73	0.08	0.00	0.05	17.71	0.00	1.78	47.82	0.19
19.95	0.11	2.73	2.89	6.46	0.10	0.00	0.09	28.88	0.00	1.36	37.10	0.33

A sequence of As-bearing phases formation during crystallization

A mass crystallization of high-melting minerals of irarsite-hollingworthite series (Ir,Rh)AsS occur early in the process of crystallization (g ~ 0). Then these phases are observed as rare single microcrystalls in the mss. Their deposition results in depletion of arsenic from the sulfide melt. On the other hand, As partition coefficient between mss and melt << 1, i.e. arsenic predominately remains in the melt during crystallization. In addition, mss concentrates Rh, Ru, Ir, while Ag, Au, Pt and Pd mainly pass into the melt. In the second zone the inclusions of fusible Pt-$PtAs_2$ eutectic ($T_{liq} = 597^oC$) with the addition of Fe, Pd and other impurities are formed. Excess of metallic impurities are found inside those inclusions in the forms of sperrylite and intermetallic phases. Similar phases were observed in natural samples of copper–nickel sulfide ores and their synthetic analogues [*Gervilla, et al.*, 1996; *Helmy, et al.*, 2010].

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