AN EXPERIMENTAL MODELLING OF PRIMARY, SECONDARY AND IMPURITY ZONING DURING FRACTIONAL CRYSTALLIZATION OF THE Cu-Fe-Ni-S-(Pt, Pd) MELTS Sinyakova E.F. (IGM SB RAS), Kosyakov V.I. (Nikolaev IICh SB RAS) efsin@uiggm.nsc.ru; fax: (383) 333-27-90; phone: (383) 333-30-26 kosyakov@che.nsk.su; fax: (383) 330-94-89; phone: (383) 330-92-59

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Ore bodies of magmatogene Platinum-Copper-Nickel Deposits of Noril'sk-type are divided into zones with a different mineral and chemical composition [1 - 3]. The theoretical and experimental substantiation of possibility of laboratory modeling of fractional melt crystallization, simulating on natural sulfide magma is revealed in [4, 5]. In the present work the quasi-equilibrium one-dimensional solidification of melt with composition (Fe 38,40, Cu 9,65, Ni 2.50, S 49.35, Pt = Pd = 0.05 at.%), similar to pyrrhotite-cubanite type of massive sulfide ores of the Talnakh deposit, is carried by a technique described in [6]. The ampoule with homogenous melt has been dropped from the hot zone to the cold one with 2.3 410^{-8} m/s rate. The process occurs in quasi-equilibrium regime under these conditions. The temperature in the bottom end of the quartz container in the beginning of crystallization was 1097°C. The length of cylindrical specimen was ~75 mm and its diameter was of ~ 7 mm. It was cut along sections perpendicular to the longitudinal axis into 24 pieces, and each piece was weighed. They were examined with optical and electronic microscopic, X-ray diffraction and electron microprobe analyses.

The monosulfide solid solution (mss) was formed at the first stage of the process, and after that the intermediate solid solution (iss) was crystallized. Final part of an ingot consisted of a mix of sulfide phases. The sequence of primary sulfide phases mss/iss simulates spatial differentiation of components in an ore body and reflects of primary mineral zoning. Redistribution of macrocomponents between crystal and melt during crystallization results in change of solid solutions composition, i.e. primary chemical zoning of an ore body. The melt composition at random instant has been determined according to the equations of material balance of components [7]. Experimental distribution curves of Cu and Ni in the sample are shown in fig. 1. Obtained data make it possible to calculate the distribution coefficients (*k*) for components between solid and liquid. So, *k* (mss/L) varies in following limits: Fe 1.2 – 1.5, Ni 0.7 – 1.2, Cu 0.15 – 0.3, S 1.05 – 1.1, and *k* (iss/L): Fe 0.84-1.03, Ni = 0.45 – 0.7, Cu 0.96 – 1.47, S 0.95 – 1.02.

The mss and iss is decomposed at further cooling. Consequently the phase composition of the sample is changed. Character solid-phase decay depends on composition of solid solution. The primary mss zone breaks on two subzones (Ia) and (Ib), where Ni-poor and Ni-rich mss decay, correspondingly (fig. 1). Subzone Ia occupies about 60 % of the ingot. A matrix of hexagonal po (7C type) includes of lamellar isocubanite (cub) of $Fe_{34.2}Cu_{14.9}Ni_{0.8}S_{50.1}$ composition. Its quantity increases to the end of subzone, where the grains of cub present along with lamellar phase. The subzone Ib (about 10 % of an ingot) corresponds a matrix of hexagonal pyrrhotite with lamellar cubanite and Fe-pentlandite inclusions (Fe-pn), containing up to 6.0 at. % Cu. Zone IIa (about 20 % of an ingot) represented a multiphase mix of decay products of high-temperature iss ($Cu_{27.5}Fe_{25.6}Ni_{1.6}S_{45.3}$). It consists of: (i) matrix of Fe-rich phase of haycockite (Fe_{29.7}Cu_{22.9}S_{47.4}) (hc); (ii) lamellar bornite I (bn I) Fe_{14.1}Cu_{45.0}S_{40.9}; (iii) grains of bornite II (bn II) Fe_{5.4}Cu_{59.5}S_{35.1} close to digenite composition; (iv) thin lamellar Fe-pn (Fe_{29.8}Ni_{22.7}Cu_{1.4}Pd_{0.3}S_{45.9}); and (v) the grains of average composition Fe_{23.4}Cu_{17.9}Ni_{14.0}S_{43.7} consisting from Fe-pn (Fe_{31.5}Ni_{15.9}Cu_{6.0}Pd_{0.1}S_{46.5}) and Cu-rich bn II. Thus, poor in Ni and Cu iss is formed as a result of solid-phase decay. Excess of Ni mainly passes in lamellar and granular pentlandite, and excess of Cu basically concentrates in lamellar and granular bornite.

Thus, variation of a chemical composition of the sample reflects primary zoning, what dictates the composition of the minerals crystallized directly from melt. Mineral zoning in the sample reflects results of solid-phase decay of primary minerals, i.e. secondary mineral zoning of the sample. It simulates mineral zoning in ore bodies.



Fig.1. The scheme of the crystallized sample (a), its microstructure (b) and distribution of Cu and Ni (c). *g* is the fraction of the crystallized melt.

Open squares and rhombuses show concentration of elements in the melt, closed – in solid phases.

The dashed lines show the concentrations of elements in the starting melt. po – hexagonal pyrrrhotite (7*C* type), cub – izocubanite, pn – Fe-rich pentlandite, hchaycockite, bn I – bornite I, bn II – bornite II

Chemical zoninig of Pt and Pd also is observed. These impurities may present in mss and iss as well they are able to form own minerals such as: hongshiite ($Pd_{50}Cu_{38}Fe_{12}$), vasilite ($Pd_{51.9}Cu_{17.8}Fe_{1.2}Ni_{0.3}S_{28.9}$), isoferroplatinum (Pt_3Fe), etc. Solid-phase decay leads to redistribution of these impurities between solid phases. For example Pd is concentrates in pentlandite. Final impurity distribution, including their own minerals, forms impurity zoning of an ore body.

Fractional crystallization is thought to have been a major mechanism of components concentration in the generation of sulfide ores. Early we have demonstrated physicochemical similarity between processes of the one-dimensional solidification in laboratory and nature [4]. It results from scale invariance of the progressive crystallization. Therefore the obtained results should reflect the basic features of a structure of ore bodies. Chemical heterogeneity of the ore bodies describes in [2, 8]. It reflects chemical zoning. These data allow drawing a conclusion of a generic aspect of sulfide magmatic melt solidification. In addition these data reflect heterogeneity of distribution of minerals in massive ores, i.e. secondary zoning. The mineralogical data testified two types of mineral zoning of massive ores: (i) pyrrhotite–chalcopyrite and (ii) pyrrhotite – cubanite – poor in S minerals of chalcopyrite group (haycockite, mooihoekite, talnakhite). Transition from pyrrhotite to cubanite and haycockite is observed in our sample. It confirms the features of distribution of ores in the second type of zoning.

Primary and secondary processes of mineral formation are accompanied by redistribution PGE between the basic ore-forming sulfides, and also their deposition as own minerals. Thus, their behavior reflects as primary so secondary zoning. Apparently a chemical originality of each impurity has an influence on their distribution in ore bodies.

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2

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