Sinyakova E.F.¹, Kosyakov V.I.² Investigation on the distribution of platinum metals in the system Fe-FeS-NiS-Ni at 900°C in the region of primary crystallization of a monosulfide solid solution.

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The compositions of equilibrium liquid solution (L) and monosulfide solid solution (mss) have been carried out at 900°C, interphase distribution of platinum group elements (Pt, Pd, Rh, Ru, Ir) has been studied at the concentration of each of the above elements in the sample 0.5 wt%.

To determine the composition of equilibrium phases the sample containing 50 at% sulfur with the given Ni(Ni+Fe) ratio has been burnt at 900°C during 10 days, then quenched in icy water and investigated by the methods of microstructural and micro X-ray spectral analyses. The ratio x = Ni(Ni+Fe) in the starting samples varied



within 0.3 - 1. The positions of conodes have been determined from the experimental results and liquidus (line A) and solidus (line B) isotherms have been plotted (fig.1).



Fig.1. High temperature part of the join of the system Fe-Ni-S at 900°C with sulfur content 50 at% based on the present work data.

The diagrams of the dependence of Ni and Fe concentration in mss on the concentration of these elements in the melt (at%) have been plotted (fig.2 a,b), the qualitative description of the phase diagram has been done. Fig.2 shows that the melt is getting enriched in Ni and depleted in Fe in the course of crystallization. The relationship between the concentrations can be described by the equations:

$$C(Ni)_{mss} = -5.284 - 0.0825 * C(Ni)_{L} + 0.0205 * C(Ni)_{L}^{2}$$

$$C(Fe)_{mss} = -3.1938 + 2.5361 * C(Fe)_{L} - 0.033 * C(Fe)_{L}^{2}$$



Fig.2. Dependence of Ni (a) and Fe (b) concentration in mss on their concentration in the melt (at%).



Fig.3. Dependence of k_d (mss/L) of Ni, Pd, and Rh on the starting Ni(Ni+Fe) ratio.

The distribution coefficients of the elements between mss and melt were determined by the traditional ratio

 $K_d = C_{mss}/C_L$

Experimental values of the distribution coefficients of Ni, Pd, and Ph between coexisting mss and a melt are

shown in fig.3. For nickel k_d <1 and varies from 0.44 to 0.92. The values of k_d for palladium are much less than a unit (0.01-0.07), and for rhodium markedly more than a unit (2.2 – 7.3). Therefore at the crystallization of mss palladium is accumulated in the melt and rhodium concentrates in mss. Rh and Ir content in the melt is close to zero, therefore k_d of these elements between mss and a melt is >1. Pt practically whole moves into the melt and its k_d (mss/L) is<1. The dependences of $k_d^{Ni,Pd,Rh}$ (mss/L) on the Ni(Ni+Fe) ratio are described by the following equations:

$$k_d^{Ni} = 0.2121 + 0.7922 * x - 0.0925 * x^2$$

$$k_d^{Pd} = -0.0711 + 0.3567 * x + 0.0052 - 0.2295 * x^2$$

$k_d^{Rh} = -4.284 + 26.678 * x - -15.049 * x^2$

One should note that the isolations of Pt₃₋₈Fe intermetallic compound including some amount of platinum group elements is observed in the iron-rich samples, whereas in Ni-rich samples some singles crystals of the sulfide phase of RuS_2 composition similar to daurite mineral were detected.

The data obtained on the distribution coefficients can be used for the estimation of the behavior of platinum elements at the crystallization of iron-nickel melts and the interpretation of the research results on the fractionation of PGE in copper-nickel magmatic deposits.

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