

# STUDYING OF RHODIUM DISTRIBUTION BETWEEN FE-NI SULFIDE MELT AND MONOSULFIDE SOLID SOLUTION BY THE ONE-DIMENSIONAL SOLIDIFICATION

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**Key words:** Fe-Ni-S system, one-dimensional solidification, rhodium, partition coefficient, monosulfide solid solution, sulfide melt.

According to literature data the measured values of rhodium partition coefficients ( $k_{Rh}$ ) in Cu-Fe-Ni-S system are in the range from 0.2 to 21, i.e. on the data of different authors this impurity can concentrate both, in the melt and in monosulfide solid solution (mss) during crystallization [1-7]. Consequently the  $k_{Rh}$  value may be either greater or smaller than 1. In review [8] experimental points of  $k_{Rh}$  dependence on S concentration in the melt form a diffuse field. It means that metallic components of the melt essentially influence  $k_{Rh}$  value, and it is necessary to define functional dependence of  $k_{Rh}$  on Cu, Ni, and S concentration in the field of mss primary crystallization for understanding the peculiarities of behavior of this admixture. In the present report we restrict our consideration to the study of rhodium fractionation at crystallization of Fe-Ni sulfide melt.

Earlier isothermal annealing of samples has been conducted and after quenching of the samples the chemical composition of phases has been studied to measure partition coefficients. A great number of samples are needed to solve the above problem using this method. More appropriate method to obtain data on the partition coefficients of components is one-dimensional solidification, which allows measuring the compositions of the coexisting phases along a trajectory on the liquidus surface [9]. It makes possible to construct the required dependence according to the data on the distribution of macro- and micro-components along several directly crystallized samples. For this purpose the one-dimensional solidification of six samples has been carried out. The composition of these samples and the experimental conditions are given in the table:

**Table**

Sample	Starting composition, at.%				Temperature °C	
	S	Fe	Ni	Rh	T <sub>1</sub>	T <sub>2</sub>
I	45.000	42.475	12.475	0.050	1010	680
II	43.000	28.400	28.400	0.200	860	636
III	46.700	26.550	26.550	0.200	970	724
IV	47.000	17.900	34.900	0.200	962	727
V	48.000	9.900	41.900	0.200	967	633
VI	48.000	0	51.800	0.200	943	672

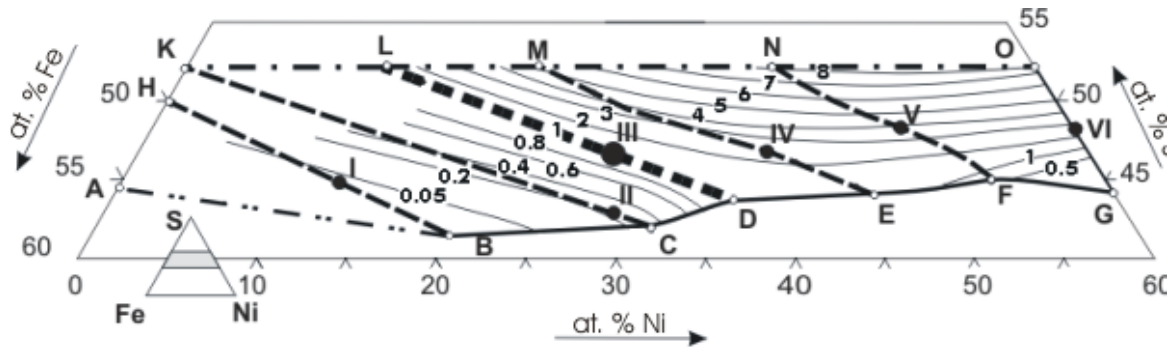
**Note.** T<sub>1</sub> and T<sub>2</sub> – the temperature in the lower end of the quartz container at the beginning and the end of crystallization

The technique of samples preparation and experimental procedure is described in [10]. Contrary to [10] we have put rhodium admixture of 99.99% pure into the initial mixture of macro-components. To carry out one-dimensional solidification the ampoule with homogenous melt has been dropped from the hot zone to the cold one with  $2.3 \times 10^{-8}$  m/s rate. The process occurs in quasi-equilibrium regime under these conditions [9].

A bar of near 70 mm long and 7 mm in diameter is cut into 20 sections perpendicular to the longitudinal axis. The fragments of the bar have been used to make polished sections, studied by microscopic, microprobe and x-ray phase analysis. The first part of all the bars is formed by monosulfide solid solution ( $\text{Fe}_z\text{Ni}_{1-z}\text{S}_{1+\delta}$ ). The second part corresponds to crystallization of heazlewoodite solid solution ( $\text{Ni}_z\text{Fe}_{1-z}\text{S}_{2}$ ). The mixture of phases formed at quenching of residual melt is situated at the end of the bar. The present work is devoted to the rhodium behavior at crystallization of mss only.

It is known that solubility of S in mss reduces when temperature drops [11]. This fact leads to partial decay of solid solution. As a result, taenite (sample I) and pentlandite (samples II-IV) are found

in the mss mono-crystalline matrix. In samples V and VI inclusions are not found. To measure the mss chemical composition, which forms from the melt, we use defocused probe. The probe allows us to average the composition of heterogeneous samples. The material balance of the chemical analysis has been made with the accuracy of 2%.



**Fig.** The field of mss primary crystallization in Fe-Ni-S system with isolines of  $R_h$  distribution coefficients.

Points I-VI correspond to the compositions of the initial samples, AB – cotectic line L-mss+tn(y-Fe, Ni solid solution), BCDEFG – mono-variant peritectic line L+mss-hzss. Line HKLMNO limits a part of the liquidus surface, where the experimental data are extrapolated to construct  $k_{Rh}$  isolines. Lines IB, IIC, IIID, IVE, VF, VIG demonstrate the change in the melt compositions during the crystallization of the corresponding samples. Lines IH, IIK, IIL, IVM, VN, VIO – extrapolated segments of the trajectory of the change in the melt composition during directed crystallization. Numbers mark the  $k_{Rh}$  isolines

The melt composition at random instant has been determined according to the equations of material balance of component [9]. According to these data the  $k_{Rh}(x_{Ni}, x_S)$  dependence on fraction of solidified melt was calculated for all samples. These relationships for Ni and Fe for all bars are rectangular segments. Therefore we suppose that the experimental results can be extrapolated to the area of large S concentrations (up to  $x_S \sim 0.50 - 0.52$ ). As a result the trajectories of the melt and mss composition during crystallization were represented in the field of mss primary crystallization.

The data of directed crystallization supplemented by our own results for the samples annealed at 900°C (for  $x_{Rh} = 0.0045$ ) and by the information from [1, 5, 6] have been used to make the  $k_{Rh}(x_{Ni}, x_S)$  relationship. This function is presented in the figure as  $k_{Rh}$  isolines in the area of mss primary crystallization.

The obtained results demonstrate complicated character of  $k_{Rh}$  dependence on the melt composition. It is seen that Rh can concentrate at crystallization both in the melt ( $k_{Rh} < 1$ ) and in mss ( $k_{Rh} > 1$ ). The boundary between these sections corresponding to  $k_{Rh} = 1$  coincides with a rectangular trajectory of change of the melt composition for sample III and fits  $\text{Fe}_{0.4525}\text{S}_{0.5475} - \text{Ni}_{0.6477}\text{S}_{0.3523}$  direction. It has been shown in [10] that the section of the phase diagram along this trajectory is quasi-binary, i.e. the tie lines are in the plane of this section. At the left of the boundary is the area of liquidus surface, where Rh concentrates in the melt, in this case  $k_{Rh}$  value drastically decreases in a direction away from  $k_{Rh} = 1$  line. In the area to the right of this line, Rh concentrates in mss except a small section near the Ni-S boundary of the concentration triangle in the vicinity of the point of three-phase equilibrium between the melt,  $\text{NiS}_{1-x}$  and  $\text{Ni}_{3\pm x}\text{S}_2$ . It is seen that  $k_{Rh}$  increases as S content grows in the melt to the given value Ni/(Ni+Fe), this fact corresponds to the conclusions in [8].

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