
Pd and Rh Distribution in Fe-Ni Sulfide Melt by the One-Dimensional Solidification Method

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Knowledge of PGE partition coefficients between solid and liquid in the Fe-Ni-S system is important to model PGE concentration processes in deposits and the distribution of PGE in zoned ore bodies. Experiments on one-dimensional solidification of PGE-bearing Fe-Ni-S melts were carried out to determine the behavior of PGE at the onset of monosulfide solid solution (mss) crystallization. All the initial compositions of the melts lie within the field of primary crystallization of mss. The experimental conditions correspond to quasi-equilibrium crystallization, where the composition of the melt is homogeneous, and thermodynamic equilibrium is obtained at the solid-melt interface. A model of the liquid surface (Sinyakova et al., 1999) was used to follow the liquid line of descent of sulfide melts.

Experimental procedure

The initial composition of the two samples investigated is as follows (in at. %): sample 1, Fe–9.7, Ni–41.7, S–48.0, Pt, Pd, and Rh –0.2 each; sample 2, Fe–26.55, Ni–26.55, S–46.7, Rh–0.2. The samples were synthesized from pure elements in evacuated silica glass tubes. Nearly 12 g of these samples were put into a quartz ampoule having an inner diameter of 7 mm, and evacuated to $1.5 \cdot 10^{-2}$ Pa. The ampoule was placed in a sealed evacuated quartz container to protect the sample in case the ampoule broke. The container was put into a vertical double-zone furnace with a diaphragm and was heated until the sample melted. Then the container was lowered into a cold zone at a rate of 0.081 mm/h to carry out one-dimensional solidification of the melt. The crystallized rods were cut into sections perpendicular to their axis. The polished sections were observed optically and *in situ* phase analyses were obtained using a Camebax SX-50 microprobe. Additional determination of phases was completed through X-ray diffraction of samples.

The solidified rods consist of two phases: monosulfide solid solution (mss) located at the bottom of the rod, and heazlewoodite solid solution (hzss) at the top. In sample 1 mss is homogenous,

whereas hzss was exsolved and consists now of a mixture of different phases. In sample 2 both early formed mss and hzss are heterogeneous. The assemblages observed result from subsolidus recrystallization of the primary phases formed at higher temperatures from the melt. The chemical composition of primary phases was determined by a defocused electron beam of 50 - 170 μm in diameter.

The mass balance equation of the i -th component during conservative directional solidification of multicomponent melt can be written as (Kosyakov, 1998):

$$C_{i0} - \int_0^g C_i^S dg = \frac{C_i^L}{(1-g)} \quad (1)$$

where g is the mass fraction of crystallized melt, C_{i0} is the concentration of the i -th component in the initial ingot (wt%), C_i^S is wt% of the i -th component in the solid sample at a distance related to g from the lower end of the ingot, C_i^L is the average concentration of the i -th component in the melt (wt%) at the same time. This equation connects the melt and solid composition to any arbitrary g . It allows one to determine effective partition coefficients of components $k_i = C_{Si}/C_{Li}$ and their variation during the process of one-dimensional solidification. One-dimensional solidification ended at $g \sim 0.8$.

Results and discussion

According to the equilibrium phase diagram relevant of the Fe-Ni-S system, mss crystallized at the colder extremity of the rod in both samples. Crystallization of mss decreases S and Fe and increases Ni in the melt. Variation of melt and solid phase composition during crystallization of sample 1 is shown in Fig. 1. Partition coefficients of components as mss crystallizes in equilibrium conditions can be calculated as follows:

$$k^{\text{Ni}} = 0.8694 - 0.0988 * g \quad (2)$$

$$k^{\text{Fe}} = 1.32 + 0.741 * g \quad (3)$$

$$k^{\text{S}} = 1.033 + 0.124 * g \quad (4)$$

Tie lines between mss and liquid are closely spaced and the slope of the tangent of these tie lines to the Fe-Ni side of the Fe-Ni-S triangle is equal to 0.44.

Hrss solid solution crystallizes at the other extremity of the rod. Partition coefficients of Fe, Ni and S are close to 1. Unfortunately, the volume of the rod where hrss crystallized is too small, and consequently, the behavior of components during its crystallization cannot be determined. Crystallization of hrss should begin when the liquid composition reaches the monovariant line, corresponding to reaction between mss and liquid to give hrss. However, in the present experiment the melt did not reach the reaction line, thus indicating that the process of solidification departed slightly from pure equilibrium conditions.

Similar results were obtained for sample 2. The values of Fe, Ni and S partition coefficients as mss was crystallizing can be described by the following equations:

$$k^{\text{Ni}} = 0.5057 - 0.2723 * g \quad (5)$$

$$k^{\text{Fe}} = 1.3329 + 0.7547 * g \quad (6)$$

$$k^{\text{S}} = 1.0738 + 0.2086 * g \quad (7)$$

The trajectory relating the changes in melt composition is a straight line. Therefore the projections of tie lines between mss and liquid on the concentration triangle coincides with the trajectory of melt, shown in Figure 2, i.e., and lie in the same plane. This implies that the section of the Fe-Ni-S system including this plane is a pseudo-binary system. The tangent of the slope between tie lines and the Fe-Ni side is equal to 0.34.

In sample 2 mss and hrss crystallize at the two extremities of the rod, as for sample 1. The measured partition coefficients for hrss are close to one. These results are quite compatible with the previous ones obtained during the study of a section at 0.51 at.% S within the Fe-Ni-S system (Sinyakova et al., 2001).

Partition coefficients between mss and liquid for Pt, Pd and Rh in sample 1 and for Rh in sample 2 were calculated using equation (1). Equations, which describe the $k^{\text{PGE}}(\text{mss/L})$ - dependence of g are as follows:

$$k^{\text{Pt}} = 0.0998 - 0.1133 * g \quad (8)$$

$$k^{\text{Pd}} = 0.1415 - 0.2926 * g \quad (9)$$

$$k^{\text{Rh}} = 3.7892 - 0.8903 * g - 8.0481 * g^2 \quad (10)$$

According to these equations, Pt and Pd are concentrated in the melt and Rh in mss during solidification of sample 1. The behavior of these elements differs and their variation should be correlated to that of the major elements within mss and melt. During solidification of sample 2 the partition coefficient of Rh is about 1, and this element cannot be used as a geochemical marker during solidification of Fe-Ni sulfide melts in the part of the phase diagram involved.

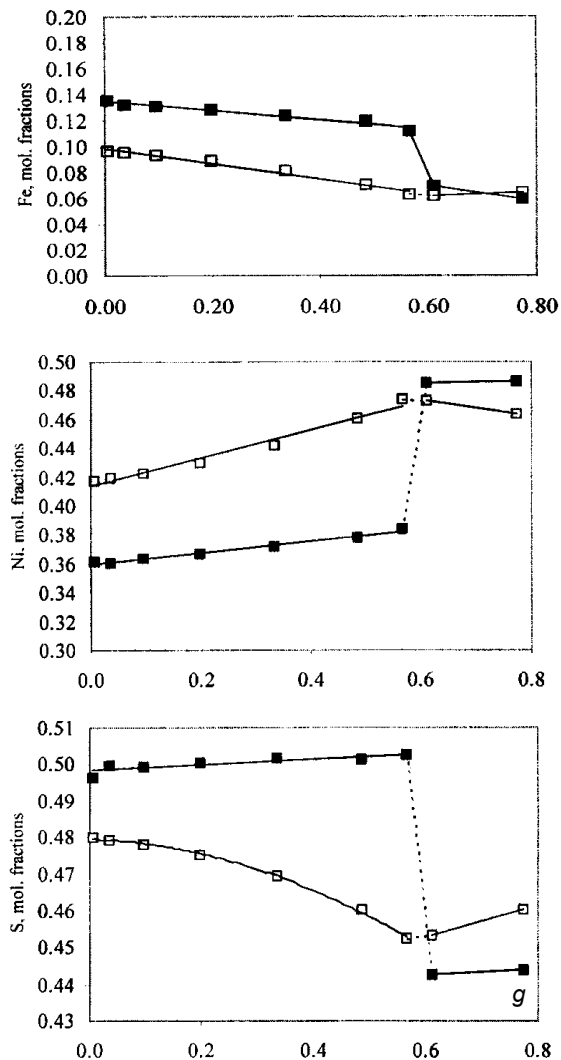


Figure 1. Distribution of elements in rod sample 1 after one-dimensional solidification of the melt. Open and black squares correspond to concentration of elements in the melt and solid, respectively.

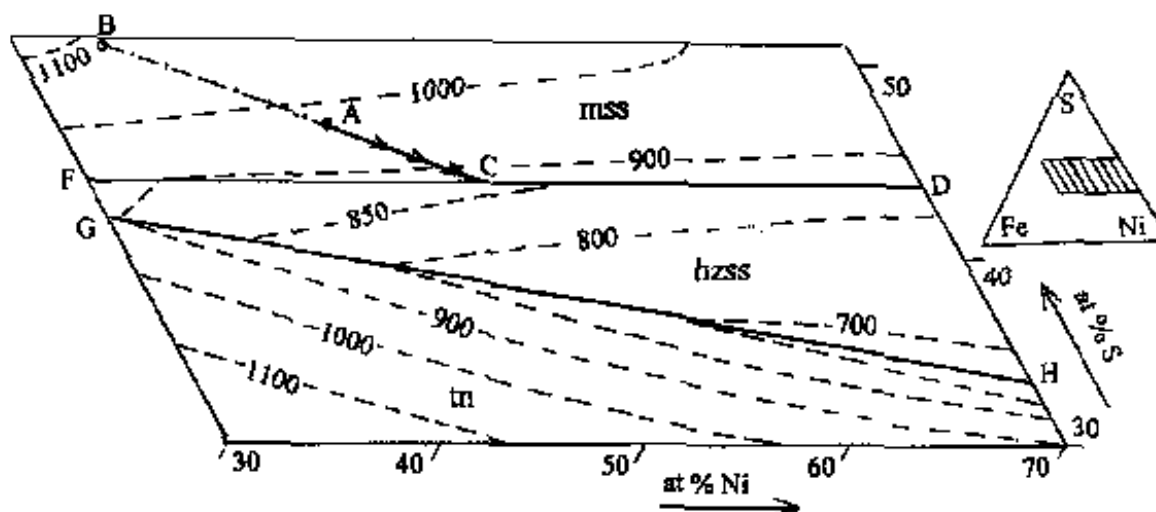


Figure 2. Portion of the liquidus surface in the Fe-Ni-S system in which one-dimensional solidification was performed. AB - tie line at the beginning of solidification; A - initial melt composition; B - solid phase composition; C - melt composition when mss ceases to crystallize; GH - monovariant eutectic line [L + taenite (tn) + hzss]; FD - monovariant peritectic line (L + mss + hzss); dashed lines correspond to isotherms ($^{\circ}\text{C}$) (Sinyakova et al., 1999).

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