Kosyakov V.I.[1], Sinyakova E.F.[2], Nenashev B.G.[2] Method of the directed crystallization of sulfide iron-nickel melts applied for the study of the system Fe-Ni-S

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The purpose of the present study is a working out of the method of investigation of phase diagrams in ternary sulfide systems by the method of thermal analysis and directed crystallization. The thermal analysis allows to reliably determine the liquidus temperature, while the directed crystallization gives an information on a composition of coexisting liquid and solids within the arbitrary moment of the process. Their combination allows to construct a liquidus and a solidus along the trajectory of changing of a melt composition at the directed crystallization.

A sample of composition (at. %) Fe – 26.65, Ni – 26.65, S – 46.7 was produced from the melt by heating of elements in the given ratio in vacuum in quartz capsules. After the run, the sample was crystallized in the vertical two-zone electrical stove with a diaphragm by means of sinking of the capsule into the cool zone with a rate of 0.2 cm per day. Preliminary estimations of the effectiveness of the diffusion migration in the melt allowed to suggest, that in such conditions the results of crystallization should be defined by an equilibrium phase diagram.

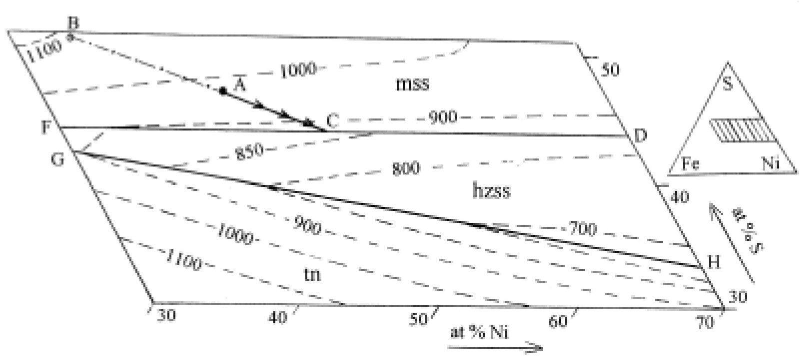

Fig. 1. The fragment of the liquidus surface in the system Fe-Ni-S, in which the directed crystallization was carried out. AB – the tie-line in the beginning of the process of the directed crystallization; A – composition of the starting melt; B – solid phase composition; C – melt composition, corresponding to the mss crystallization from the melt; GH – eutectic monovariant line (L + tn + hzss), where tn – Fe-Ni solid solution with the γ-Fe structure; FD – peritectic monovariant line (L + mss + hzss); dashed lines correspond to isotherms (^{O}C) [1].

The crystallized ingot of 80 mm long consisted of two adjusted portions: the frontal conical portion and the main cylindrical portion. The ingot produced by the directed crystallization was cut to cross sections perpendicular to the lengthwise axis. The samples were studied microscopically, by x-ray diffraction, and thermal analysis. Besides, additional samples for the DTA analysis were produced by the quenching method.

As a result of the directed crystallization, the ingot consisting of two monophase portions was produced: monosulfide solid solution $(Fe_zNi_{1-z})S_{1+\delta}$ (mss) in the frontal portion of the ingot and heazlewoodite solid solution $(Fe_zNi_{1-z})_{3\pm\delta}S_2$ (hzss) in the rear of the ingot. The first portion of the ingot is found to be of constant composition (at. %): Fe = 35.83±0.47, Ni = 13.52±0.22, S = 50.65±0.38, while a composition of the sulfide melt (L) becomes richer in nickel and poorer in iron (Fig. 1). The trajectory of changing of the melt composition on the triangle is surely approximated by straight line, whereas projections of tie-lines at the directed crystallization coincide by direction with the melt trajectory (Fig. 1), i.e. lie on the same plane. As a result, the cross section of the phase diagram in the region (mss+L) by the plane, which includes the trajectory of the melt composition, is quasibinary. The cross section along this direction is shown in Fig. 2. It is constructed from our experiments on the directed crystallization and six additional samples, which lie in this cross section. All tie-lines lie in the plane of this figure. The upper portion is situated beyond the experiment. However, it is evident, that the liquidus in the given cross section has a maximum, whose coordinates (T = 1120^{O}C, X_S = 0.52) were estimated from our data and published data [1-3]. Accounting for it, our experimental data on the liquidus were approximated by equation

$$T = -19568.96x^3 - 14925.43x^2 + 31396.79x - 8418.995,$$

where T – temperature, ^{O}C, x – sulfur mole fraction in the sample.

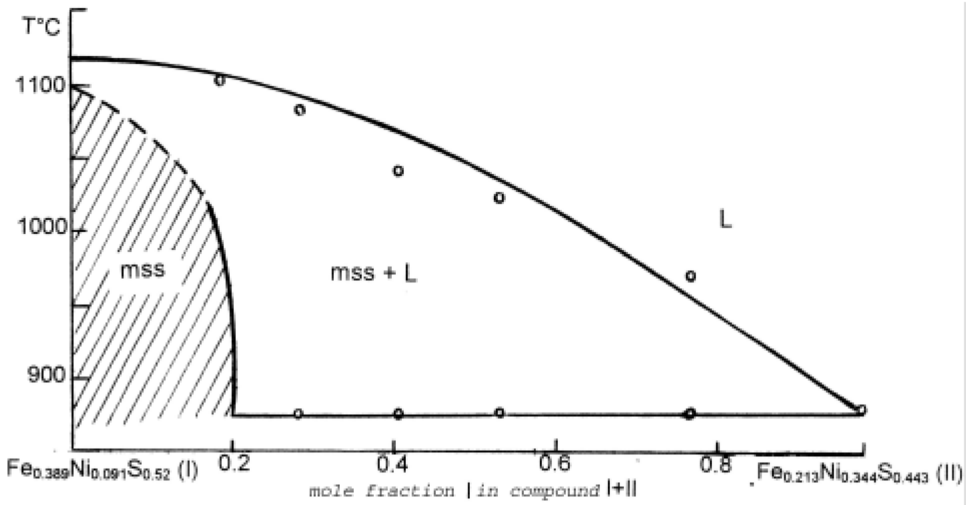

Fig. 2. Polythermal crosssection of the Fe-Ni-S phase diagram along the direction $Fe_xNi_{0.6477-1.4314x}S_{0.3523+0.4314x}$ in the region of mss crystallization.

The solidus line in this portion is drown tentatively by dashed line. The liquidus and the solidus in the region of the primary crystallization mss are confined below by points, corresponding to reaction mss + L $\rightarrow$ hzss. Crossing the corresponding monovariant line on the liquidus surface, the trajectory of the melt composition has an inflection. Therefore, below the corresponding temperature, the cross section of the diagram is not quasi-binary, since in this region the tie-lines do not lie in the cross section plane.

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