INVESTIGATION OF $Fe_{0.4525}S_{0.5475}$-$Fe_{0.18}Ni_{0.39}S_{0.43}$ SECTION OF THE Fe-Ni-S PHASE DIAGRAM (ONE-DIMENSIONAL SOLIDIFICATION, DERIVATIVE THERMAL ANALYSIS, MICROSCOPY, X-RAY DIFFRACTION)

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Derivative thermal analysis (DrTA) allows determining the coordinates of points on the liquidus surface. The one-dimensional quasi-equilibrium solidification of multi-component melts permits to define the position of tie lines and the coordinates of points on the monovariant lines. Optical microscopy, X-ray diffraction and thermal analysis methods are used to identify the reactions with participation of the melt as well as subsolidus phase reactions. Combination of these methods gives information for building a multi-component phase diagram.

There are two versions for mechanism of the pentlandite $(Fe_zNi_{1-z})_{9+\delta}S_8$ (pn) formation in the Fe-Ni-S system. The mineral is produced in subsolidus region of the phase diagram following the first version [1], but the second version speculates the peritectic reaction with the melt participation [2]. An investigation of the $Fe_{0.4525}S_{0.5475}$-$Fe_{0.18}Ni_{0.39}S_{0.43}$ section permits in our view to discriminate these versions.

The $Fe_{0.4525}S_{0.5475}$-$Fe_{0.18}Ni_{0.39}S_{0.43}$ section was studied by a combination of above-mentioned methods. Firstly, we carried out an one-dimensional solidification of the pentlandite melt with $Fe_{0.2665}Ni_{0.2665}S_{0.467}$ composition at a rate of $2.25*10^{-8}$ m/s. Secondly, the produced rod was divided into 10 parts by flat sections that were examined by optical microscopy and X-ray diffraction methods. Concentration of the components was also measured by microprobe analysis. The composition of the melt at one point in time was deduced from the composition of a solid, using the material balance equations. Thirdly, liquidus temperature along crystallization path was measured by DrTA method for specifically prepared samples.

The solidified rod consisted from two homogeneous areas [3]. At first the monosulfide solid solution (mss) deposited from the melt. The heazlewoodite solid solution (hzss) crystallized from the melt in the second stage of the one-dimensional solidification. The observed order of phase formation is consistent with the liquidus scheme in [4]. It is interesting that mss composition was constant. This is possible when crystallization path on the liquidus surface is a straight line. It corresponded to $Fe_{0.4525}S_{0.5475}$-$Fe_{0.18}Ni_{0.39}S_{0.43}$ quasi-binary section of the Fe-Ni-S phase diagram.

The obtained data allowed plotting the $Fe_{0.4525}S_{0.5475}$-$Fe_{0.18}Ni_{0.39}S_{0.43}$ section in the region of primary crystallization of monosulfide solid solution [5]. Cooling of the mss samples below solidus temperature yielded lamellar pentlandite inclusion in the mss matrix. To interpret the data, it is necessary not only to plot the section of solid-liquid diagram along crystallization path, but it is also to study subsolidus section of the ternary phase diagram. For this purpose, we carried out thermographic studies of the samples cut out of two parts of the rod and synthesized six samples with intermediate composition. The effects were interpreted using the previous results of topological analysis of phase diagram Fe-FeS-NiS-Ni [6-8]. For quantitative description studied section we used data on isothermal sections of phase diagram Fe-Ni-S at 1100°C [9], 900°C [6, 10], 820°C [6], 725°C [11], 600°C [12].

The section under studying contains monophase fields: L, mss, hzss, and pn. The liquidus line in the section was obtained just as from the data of the present work, so from the model of the liquidus surface [4]. Both methods yielded nearly the same results. The boundaries of the mss region at temperature above 870°C were determined using data of one-dimensional solidification, and at ≤ 600°C, using literature data and X-ray studies of mss samples after one-dimensional solidification. The existence of regions of hzss and pentlandite are contoured according to own and literature data. Fig. 1 shows that pentlandite is stable at 600°C in the range of compositions from 0.59 Q to 0.75 Q (Q is mol. fraction $Fe_{0.18}Ni_{0.39}S_{0.5475}$ in mixture $Fe_{0.4525}S_{0.5475}$ + $Fe_{0.18}Ni_{0.39}S_{0.5475}$. Data on the boundaries of one-phase regions are sufficient for interpretation of two-phase equilibria.

Three-phase monovariant equilibria in the section under discussion were determined from thermoanalytical data. It is shown in [6] that hzss appears on cooling at first inside the concentration triangle. Data of this work imply that hzss is generated by the monovariant reaction L + mss → hzss at 870°C. Doubled thermal effect between 612 and 632°C allowed outlining of two three-phase regions mss + hzss + pn. It was established in [13, 6] that at these temperatures pentlandite is formed by peritectoid reaction mss + hzss → pn. The boundaries of three-phase regions hzss + hz + pn, hzss + pn + tn, and pn + hz + tn were constructed on the basis of phase reactions proceeding in the Ni-rich part of the section, thermal events and microstructure of hzss sample, taken from the end top part of a rod

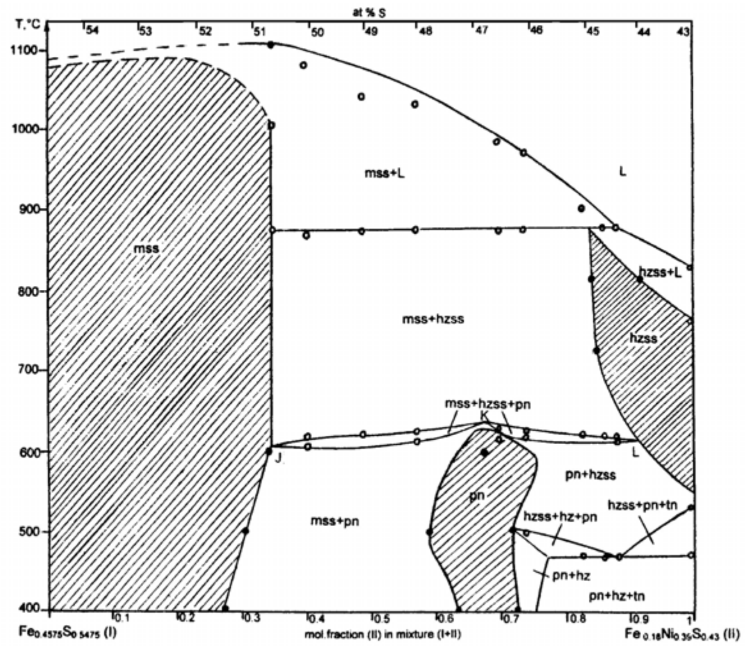

Fig.1 The section $Fe_{0.4525}S_{0.5475}$ – $Fe_{0.18}Ni_{0.39}S_{0.43}$ of the Fe-Ni-S phase diagram. Light circles correspond to temperatures of thermal events, dark circles relate to the composition of mss and pn on the literature and own experimental data. The fields of mss, hzss and pn phases are hatched.

Results of this work provide possibility for assumption about probable mechanisms for mineral formation in the Fe-Ni-S system. The mss forms, most likely, during crystallization of melt. Pentlandite may arise as a result of several solid phase reactions in the section $Fe_{0.4525}S_{0.5475}$-$Fe_{0.18}Ni_{0.39}S_{0.43}$. At $0.28 < Q < 0.35$ pentlandite evolves during decomposition of mss by the reaction:
mss (Fe) → pn + mss (Ni) (1). On cooling of samples in the region $0.35 < Q < 0.92$, pentlandite produces from mixture (mss + hzss) along the line JKL by the monovariant reaction: mss + hzss → pn (2). Because of the intricate shape of existence field pentlandite may decompose by reaction (1) proceeding in an inverse direction at decreasing temperature and also by the reactions pn (Ni) → pn (Fe) + hzss (3) and pn (Ni) → pn (Fe) + hz (4).

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