THE SHEME OF PHASE REACTIONS IN THE Fe-FeS-NiS-Ni SYSTEM

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Two variants of Fe-Ni-S phase diagram, corresponding to two versions of pentlandite formation mechanism are recently presented. According to the first variant, pentlandite is formed by a peritectic reaction with participation of melt [1-4]. According to the second variant it occurs as a result of solid phase reaction [5-7]. Therefore, there is a problem to choose the only one variant, which is best suited to the whole set of the available experimental data on the study of the phase relations in the Fe-FeS-NiS-Ni system. We have critically analyzed the literature information and our own unpublished experimental data, referred to the temperature interval from 1200 to 430°C. It is stated that the occurrence of two versions is related to different interpretations of the data of microscopic study of the structure of the quenched samples, including the phases enriched in Ni: heazlewoodite, pentlandite, godlevskite, Ni-monosulfide solid solution. These phases appear as a result of the decay reactions of heazlewoodite and godlevskite solid solutions, which are not preserved at quenching. This factor makes the reconstruction of the phase composition of the initial high-temperature sampled difficult. Therefore, the results of microscopic studies of the samples, combined with the DTA and high-temperature X-ray data should be taken into account. Besides, to make the results of the analyses more reliable, it is worthwhile to make the system analysis of the whole set of experimental data and to construct the temperature sequence of the phase reactions in the Fe-FeS-NiS-Ni system.

It is shown that the first version of the pentlandite formation mechanism is based on the interpretation of small amount of the experimental information, related to the limited range of the compositions of the initial samples. The results, obtained by the authors of this version, allow, in our opinion, ambiguous interpretation and there is no sharply defined contradiction between them and the assumption on the solid phase mechanism of pentlandite formation. On the other hand, both the majority of the published data on isothermal sections and polythermal cross sections of the phase diagram and on physicochemical study of separate samples are in accordance with the second version of the pentlandite formation mechanism.

The scheme of the phase reactions in the Fe-FeS-NiS-Ni system is made using the data of Kullerud [5] on 9 isothermal sections of the phase diagram, our own previously published results, and also separate data from [1, 3]. To simplify this scheme we do not demonstrate the reactions with awaruite participation, which exists below 530°C. It should be noted that there are two versions of the phase diagram of Ni-S system. According to Rau [8], the existence area of $(Fe_xNi_{1-x})_{3\pm y}S_2$ high temperature solid solution on the diagram is supposed to be single- phase. According to Lin [9], two solid solutions on the base of Ni_3S_2 and Ni_4S_3 are observed. More simple Rau's version of the phase diagram of the Ni-S system is used in the given study. Using the obtained results, the scheme of phase reactions, which considers the presence of two heazlewoodite solid solutions in this system, is not difficult to create. Fig. 1 demonstrates the scheme of phase reactions. We use the following designations of phases to write the reactions: melt (L), monosulfide solid solution $(Fe_xNi_{1-x})S_{1+y}$ (mss), Fe-Ni solid solution with the structure of γ-FeNi - taenite, FeNi - solid solution with the structure of α-Fe (α), triple heazlewoodite solid solution $(Fe_xNi_{1-x})_{3\pm y}S_2$ (hzss), heazlewoodite Ni_3S_2 (hz), pentlandite solid solution $(Fe_xNi_{1-x})_{9+y}S_8$ (pnss), godlevskite solid solution $Ni_{7+z}S_6$ (gdss), godlevskite Ni_9S_8 (gd). The equations of the phase reactions in the studied system are written in the rectangular area of the scheme. The temperatures of these reactions (°C) are given in parentheses. Phase associations disappear or appear on the phase diagram as a result of the reaction. The associations, which appear or disappear in binary boundary systems, are given in hexagonal areas. Similar associations, which appear or disappear in triple system, are framed by ovals. The lines demonstrate the bonds between the phase reactions. If the represented scheme is supplemented by the schemes of the phase reactions in binary systems, the complete topological pattern of the phase diagram of the Fe-FeS-NiS-Ni system will be obtained. This type of schemes is widely used in reference books and data bases on the phase diagrams of the systems, formed from three chemical elements.

The represented version of the Fe-FeS-NiS-Ni system phase diagram correlates with all isothermal sections, plotted by Kullerud [5], besides the section at a temperature not much below 500°C. According to our data, the pnss+mss+gdss phase association, which is absent in Kullerud work, exists in this section. Besides, we have used the data to refine Ni-S phase diagram in the area, where gdss converts into gd [10]. According to these data, at 500°C both phases are stable, whereas the diagram of Kullerud demonstrates the only one gd-phase. Finally, according to Kullerud, at T>500°C, mss decays into two phases. We do not take into account this phenomenon as a two-phase $mss_1 + mss_2$ area is small.

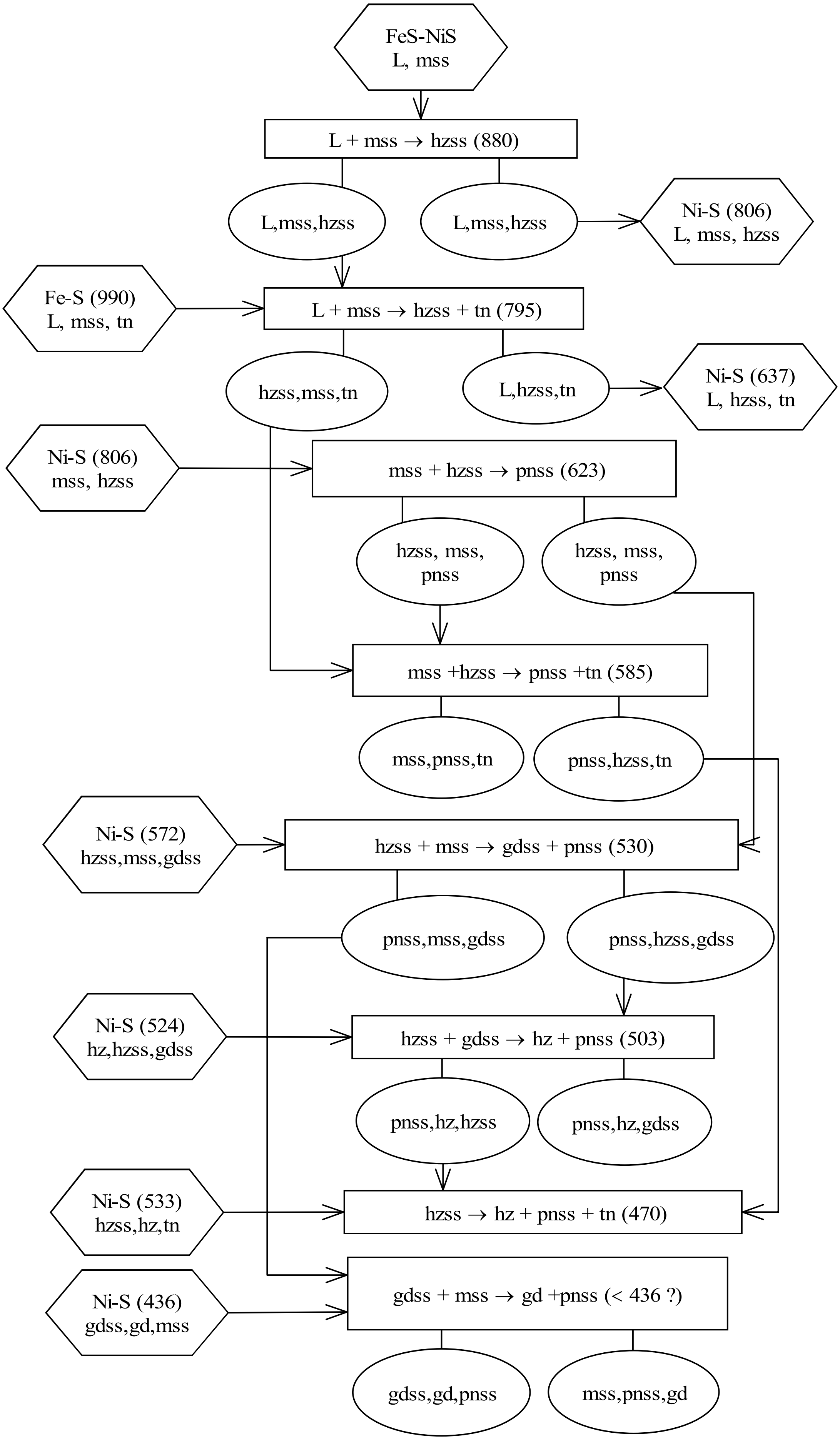

Fig. 1. The scheme of phase reactions in Fe-FeS-NiS-Ni system

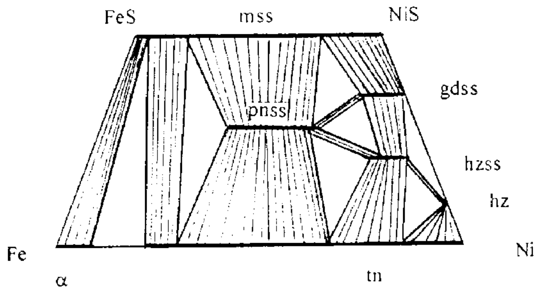

Fig.2. Scheme of phase ratios in isothermal cross section at 520°C

Basing on the phase diagram of binary boundary systems the scheme (Fig. 1) can be used to define phase relations in the studied interval. The topological scheme of isothermal section of the diagram at 520°C is given in Fig.2 as an example.

The performed analysis of the phase relations in the Fe-FeS-NiS-Ni system evidences for solid phase mechanism of pentlandite formation. This conclusion is of vital importance to interpret the results of the study of natural samples of granular pentlandite and to describe its formation in the mostly Cu-depleted pyrrhotite ores.

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