# Kosyakov V.I.[1], Sinyakova E F.[2], Shestakov V.A.[1] Sulfur fugacity in the system Fe-FeS-NiS-Ni at 600°C.

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The study of the system Fe-Ni-S is essential to the solution of some problems of mineral genesis in copper-nickel magmatogenic deposits as well as to the modeling of fractionation elements in the course of mineral formation. Besides the phase diagram the data on other thermodynamic properties of this system including the dependence of sulfur fugacity ($f_{S2}$) on composition and temperature are of major interest. The dependence of sulfur fugacity on composition in the coexisting region of monosulfide solid solution and pentlandite at 600°C was determined in [1]. This work presents the results of such dependences for other regions of the isothermal join of the diagram at 600°C based on the obtained and literature data.

The samples with S content of 48 and 51 at% were synthesized from melt using the capsule method. They were additionally annealed at 600°C after which $F_{S2}$ of the samples was measured by the pyrrhotine method. Phase compositions were determined by micro X-ray spectral analysis.

Isothermal join of the system Fe-FeS-NiS-Ni (figure) has been plotted based on the literature data on phase equilibria in the binary systems Fe-FeS, Ni-NiS, Fe-Ni and obtained experimental results on the boundaries of stability regions of the associations and compositions of the coexisting phases in the three-component system [2-4]. The characteristics of nonvariant points is given in the table.

The join consists of the following phase associations: five monophase – hzss $(Fe_zNi_{1-z})_{3\pm\delta}S_2$, mss $(Fe_zNi_{1-z})S_{1+\delta}$, pn $(Fe_zNi_{1-z})_{9+\delta}S_8$, ka- kamacite (Fe-Ni of the solid solution with α-Fe structure), tn- tenite (Fe-Ni of the solid solution with γ-Fe structure); seven two-phase – hzss + mss (two regions), hzss+pn, hzss+tn, mss+pn, mss+tn, ka+mss; three three-phase – hzss+mss+pn, hzss+mss+tn, ka+mss+tn. To describe the dependence of sulfur fugacity on composition the analytical expressions were derived for the boundaries of monophase solid solutions. The quantitative description of the boundaries of homogenous regions of mss and pentlandite and experimental results on the $f_{S2}$ on composition dependence were earlier presented in [1]. Note that the description of sulfur fugacity in the mss region was done on the basis of an additive model in which $f_{S2}$ within the mss region is related to the sulfur fugacity in the corresponding regions of the binary systems Fe-S and Ni-S. Sulfur fugacity at the boundary of the coexisting region of pentlandite from the side of mss has been determined from the date of chemical phase composition in the two-phase samples (pn+mss) and the log $f_{S2}$ values for mss.

**Table. Estimation of the coordinates of nonvariant points in the system Fe-FeS-NiS-Ni at 600°C**

| Point | Composition in mole fractions | | | Source |
|---|---|---|---|---|
| | Fe | Ni | S | |
| I | 0.9494 | 0.0006 | 0.5000 | Our data |
| II | 0.4649 | 0.0344 | 0.5006 | Our data |
| III | 0.4474 | 0.0516 | 0.5010 | -"- |
| IV | 0.2018 | 0.2928 | 0.5054 | -"- |
| V | 0.2998 | 0.2252 | 0.4750 | -"- |
| VI | 0.2107 | 0.3201 | 0.4692 | -"- |
| VII | 0.2600 | 0.2970 | 0.4430 | -"- |
| VIII | 0.1491 | 0.3930 | 0.4579 | -"- |
| IX | 0.2400 | 0.3600 | 0.4000 | -"- |
| A | 0.0000 | 0.5600 | 0.4400 | [5] |
| B | 0.0000 | 0.6300 | 0.3700 | -"- |
| C | 0.9470 | 0.0530 | $< 10^{-4}$ | [7] |
| D | 0.8000 | 0.2000 | $< 10^{-4}$ | -"- |
| E | 0.3740 | 0.6260 | $< 10^{-4}$ | Our data |

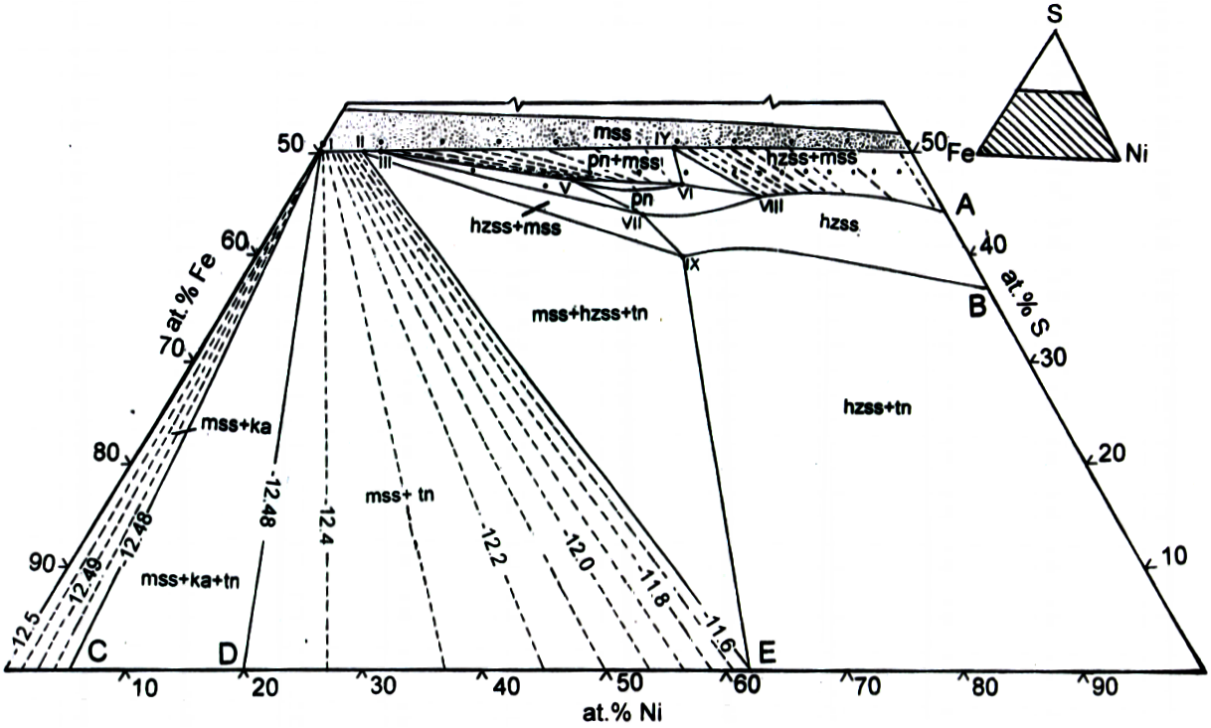


Fig. Isothermal section of the phase diagram Fe-FeS-NiS-Ni at 600°C. Solid lines – boundaries of phase fields, dashed lines – isobars $S_2$in two-phase regions

The boundaries between hzss and hzss+mss (II) regions were determined using the data on chemical phase composition in two-phase samples. These data were approximated by the equation:

$$y = -0.459653\ x^2 + 0.730033\ x + 0.17022 \quad (1)$$

where y- mole fraction of S, x- mole fraction of Ni/(mole fraction of Ni+ mole fraction of Fe).

The line hzss (pn+hzss) is situated between points YII and YIII (table). Moreover, the coordinate of one point more has been determined on this boundary from the polythermal join FeS-$Ni_3S_2$. These data allowed to approximate the position of the above boundary by the parabola:

$$y = 1.26196\ x^2 - 1.33391\ x + 0.814487 \quad (2)$$

The boundary hzss/(tn+hzss) was plotted using three experimental points situated within the studied system [4] and the fourth point B belonging to the Ni-S side [5]. It was described by the equation :

$$Y = 1.93602\ x^2 - 5.0468\ x^2 + 4.20779\ x - 0.726004 \quad (3)$$

To complete the description of the coexisting region of hzss one should plot the missing section hzss/hzss + mss(I) between points YII and IX. This section is approximated by the straight line because of the lack of data:

$$y = -0.682539\ x + 0.645714 \quad (4)$$

The dependence of sulfur fugacity on the composition of hzss samples on the boundary hzss/(hzss+mss)(II) has been determined by the method described for pentlandite on the boundary pn/(pn+mss) [2]. For this purpose the data on chemical phase composition in two-phase samples (hzss+mss) and values log $f_{S2}$ for mss were used. We suggested that phase mss and hzss in the sample at 600°C were in thermodynamic equilibrium with each other. That is why sulfur fugacity above them is the same. The dependence $f_{S2}$ along the studied boundary is as follows:

$$\log f_{S2} = -15.5538\ x2 + 28.82288\ x - 19.9984 \quad (5)$$

There are no enough data to derive an approximating expression, which could describe the dependence of sulfur fugacity on the composition within the hzss region. The contradictory ideas on the structure of the binary solid solution $Ni_{3\pm\delta}S_2$ [5, b] suggest that the structure must be complex. The lack of data did not allow us to describe the analogous dependence for the two=phase equilibria with hzss: hzss+pn, hzss+mss(I), hzss+tn.

The estimated data on sulfur solubility in iron and nickel at 600°C showed that it is rather low, probably less than 0.01 mol%. About the same sulfur solubility should be expected in the solid solutions of Fe-Ni – tenite and kamacite. As the value of sulfur solubility is inessential the concentration of one of the metallic components is quite enough to characterize the saturation of solid solutions with sulfur. Nowadays there are no data on measuring sulfur fugacity over two-phase samples in the region tn+mss, the positions of five conodes are, however, given in [4]. The values of sulfur fugacity over mss calculated from the equations are accepted for log $f_{S2}$ over tn. The obtained data on the dependence of sulfur fugacity on Ni(Ni+Fe) in the samples of tenite saturated with sulfur were approximated by the equation:

$$\log f_{S2} = 22.116\ x^2 - 23.2535\ x^2 + 9.08963\ x - 13.5994 \quad (6)$$

Since the minimal content of nickel in tenite is 0.20 of mole fraction [7] and the data on sulfur fugacity in the two-phase region mss+tn within the range of 0.20-0.31 mole fractions of Ni are absent, the dependence of log $f_{S2}$ in tenite in this region was approximated by the line with the slope coefficient equal to the tangent to the point on the curve of equation (6) with the coordinates (in mole fractions): Fe- 0.69, Ni- 0.31 and is as follows:

$$\log f_{S2} = 1.0485\ x - 12.685 \quad (7)$$

The positions of neither conodes nor corresponding isolines log $f_{S2}$ are known in the mss + cm region. Since the region of kamacite coexistence at 600°C (0-5.3 at% Ni) is not large the dependence of log $f_{S2}$ on nickel concentration in the melt are approximated by the line:

**log $f_{S2}$ = 03774 x –12** **(8)**

Based on the equations the fugacity isolines have been calculated in the two-phase regions mss+hzss, mss+tn and mss+cm (figure).

The obtained results may be used to construct the thermodynamic models of the system Fe-Ni-S within the medium temperatures region, to establish the correlation between the regions of phase stability in the system and sulfur fugacity. The data are supposed to be used to establish the relationship between sulfur fugacity and the form of the existence of platinum metals in different phases and phase associations of the considered system.

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