*Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 925-929*

# THE Fe–Ni DISTRIBUTION BETWEEN PENTLANDITE AND MONOSULFIDE SOLID SOLUTION EQUALIZED AT LOW TEMPERATURE

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## Abstract

Two mixtures of pentlandite and the monosulfide solid solution (mss) have been synthesized. The bulk compositions of the samples are $Fe_6Ni_3S_8$ and $Fe_3Ni_6S_8$. Differential scanning calorimetry detected exothermic process in the samples under heating. The process takes place in temperature range between phase transition in the mss (near 400 K) and 690 K and is governed by diffusion.

X-ray powder diffraction has showed that equilibrium Fe–Ni distribution between pentlandite and the mss is achieved after short-time heating up to 670 K.

**Keywords:** DSC, equilibrium, Fe–Ni distribution, monosulfide solid solution, pentlandite

## Introduction

The phase relations in the central part of the Fe–Ni–S system were investigated intensively to establish the temperature which defines an equilibrium in the natural mineral assemblages. To solve the problem, the charges of various chemical compositions are heated up to the preset temperature and then quenched. The resulting samples are inferred to represent the phase relations at the quenching temperature.

This procedure was used to investigate the phase relations at different temperatures: between 600 and 250°C [1]; 600, 500, and 400°C [2]; 600, 500, 400, 300, and 230°C [3]; 300, 275, 250, 225, 200, 175, and 150°C [4]. The result of the investigations is information of two types: i) phase assemblages (how many and what phases coexist) and ii) chemical compositions of the phases (tie-lines on the phase diagram).

Decay of the monosulfide solid solution (mss) was investigated by differential scanning calorimetry [5]. This solid-state chemical reaction was found to proceed at unusually low temperatures (below 200°C). One would expect that the compositions of the phases can reach equilibrium at even lower temperatures.

The objective of this work was to elucidate the question whether the Fe–Ni distribution between pentlandite and the mss is the result of ion-exchange reaction governed by diffusion.

1418–2874/99/ $ 5.00

*Akadémiai Kiadó, Budapest*
*Kluwer Academic Publishers, Dordrecht*

## Experimental

High purity Fe, Ni and S were used to synthesize the samples of $Fe_6Ni_3S_8$ and $Fe_3Ni_6S_8$ composition. After synthesis, the samples were cooled slowly down to room temperature, without being quenched. The synthesis and the samples synthesized are described in [6]. The $Fe_6Ni_3S_8$ consists of pentlandite $Fe_{5.78}Ni_{3.33}S_8$ (90%) and the mss $Fe_{0.98}Ni_{0.03}S$ (10%), the $Fe_3Ni_6S_8$ consists of pentlandite $Fe_{3.06}Ni_{6.07}S_8$ (92%) and the mss $Fe_{0.30}Ni_{0.67}S$ (8%).

Calorimetric measurements were carried out in standard aluminum crucibles with a DSC-111 (SETARAM). All the samples were crushed to powder. The $Fe_6Ni_3S_8$ (518.1 mg) and the $Fe_3Ni_6S_8$ (526.0 mg) were analyzed in the temperature range from 300 to 690 K in two steps. From 300 to 460 K, the samples were measured with a heating rate 1 K $min^{-1}$. After heating had ended, the isothermal calorimetric signal was measured. Thereafter the temperature was lowered down to 445 K. From 445 to 690 K, the samples were measured with a heating rate 1.5 K $min^{-1}$. At 690 K, the isothermal measurements were carried out again. The baseline for the scanning heating was measured and the results of the experiments were evaluated as heat capacity.

Equal parts of the $Fe_6Ni_3S_8$ and the $Fe_3Ni_6S_8$ were mixed in a mortar and crushed to powder. The mixture was used in calorimetric and X-ray powder diffraction experiments. Part of the mixture of 428.7 mg in mass was measured in the calorimeter from 300 to 920 K with a heating rate 6 K $min^{-1}$. Two other specimens were used in X-ray powder diffraction analyses. One sample was analyzed immediately and the other one after a short-time heating to 670 K.

X ray powder diffraction patterns were taken at room temperature by using $CuK_\alpha$.

## Results

Heat capacities of the $Fe_6Ni_3S_8$ and $Fe_3Ni_6S_8$ are in Figs 1 and 2. Both samples show an endothermic peak in the temperature range from 300 to 460 K. This is the phase transition in the mss [5]. The peaks of the $Fe_6Ni_3S_8$ and $Fe_3Ni_6S_8$ differ in temperature by 40 K. There is an exothermic peak in the temperature range from 445 to 690 K. The results of the measurements in the low-temperature part do not interface to those in the high-temperature one. Heat capacity at the end of the first curve is less

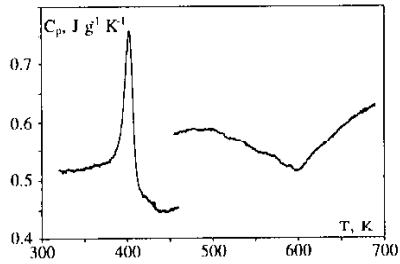


**Fig. 1** Heat capacity of the $Fe_6Ni_3S_8$

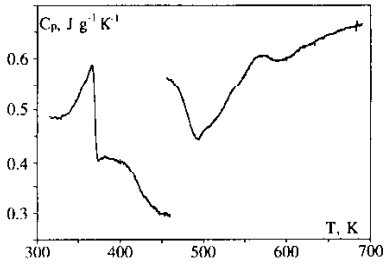


**Fig. 2** Heat capacity of the $Fe_3Ni_6S_8$

han that at the beginning of the second curve. The difference is caused by a heat release in the samples.

This heat release was observed directly in isothermal measurements (Figs 3 and 4). At the very beginning of the measurements of the $Fe_3Ni_6S_8$ at 460 K the signal was out of scale and the data had been in part lost. The first 200 s is the time when the heat flows in the calorimeter change from scanning heating to isothermal state. These data are to be ignored. The isothermal signal at 690 K is nearly constant. At 460 K, the signal changes in time like decreasing exponential function. The heat release relaxes. A differential scanning calorimeter is not a suitable device to investigate prolonged isothermal process. The baseline is hard to be measured and an amplitude value of the heat release is out of discussion. For 1500 s, i.e. from 500 to 2000, the heat release decreases by 0.35 mW for the $Fe_6Ni_3S_8$ and by 0.6 mW for the $Fe_3Ni_6S_8$. Heat capacity at scanning heating is $C_p=\Delta W/m\beta$. Here $\Delta W$ is the calorimetric signal, $m$ is the mass of the sample and $\beta$ is the heating rate. The values 0.35 and 0.6 mW for calorimetric signal correspond to the decreases in heat capacity by 0.04 and 0.07 J g$^{-1}$ K$^{-1}$. Low- and high-temperature curves of heat capacity differ by approximately 0.12 and 0.25 J g$^{-1}$ K$^{-1}$ for the $Fe_6Ni_3S_8$ and $Fe_3Ni_6S_8$, respectively. So, the scanning and isothermal measurements agree with each other.

X-ray powder diffraction patterns of the mixture $Fe_6Ni_3S_8$+$Fe_3Ni_6S_8$ are shown in Figs 5a (initial) and 5b (heated). The unit cell parameters both of pentlandite and of the mss depend on composition and they are different for the samples in question [6]. This is a reason why the reflections of pentlandite in the initial mixture are split.

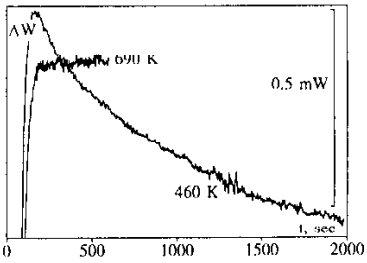


**Fig. 3** Isothermal calorimetric measurements of the $Fe_6Ni_3S_8$

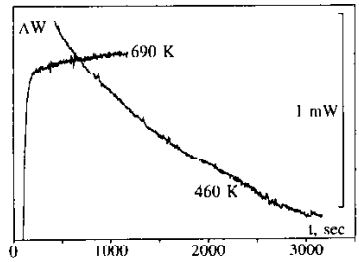


**Fig. 4** Isothermal calorimetric measurements of the $Fe_3Ni_6S_8$

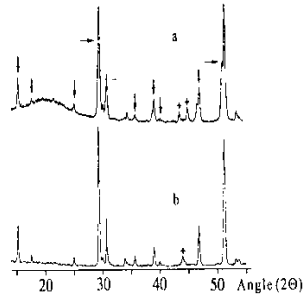


**Fig. 5** X-ray powder diffraction patterns of the mixture $Fe_6Ni_3S_8$+$Fe_3Ni_6S_8$ (a) before and (b) after short-time heating up to 690 K. The arrows indicate the reflections of pentlandite. The sign '+' shows reflection (022) of the mss

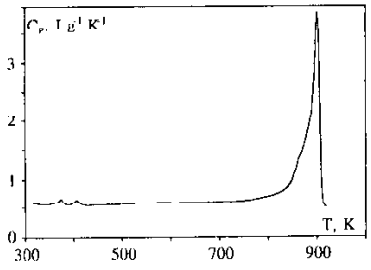


**Fig. 6** Heat capacity of the mixture $Fe_6Ni_3S_8$+$Fe_3Ni_6S_8$

Those of the mss differ more significantly but are weak in amplitude. The reflections become single and sharp after heating to 690 K. All the compositions have been equalized.

The results of calorimetric measurements of the mixture are shown in Fig. 6. One can see two peaks one by one below 460 K and no others up to 900 K. The compositions of the phases in the $Fe_6Ni_3S_8$+$Fe_3Ni_6S_8$ mixture were equalized without endothermic transformations.

## Discussion

We have investigated the changes in Fe–Ni distribution between pentlandite and the mss by means of calorimetry. X-ray powder diffraction is useless here because it does not distinguish the phase transition from the change in composition. The phase transition does take place near 400 K. X-ray powder diffraction is applicable to the mixture containing two pentlandites and two species of mss that differ in composition. The Fe–Ni distribution is equalized between various sorts of the phase and between different phases as well. All the changes in composition begin just after the phase transition in the mss and last for some time that depends on the temperature. This is typical of diffusion process.

The changes in the Fe–Ni distribution between pentlandite and the mss under heating start after the phase transition in the mss. One would expect that the distribution at room temperature is governed by the phenomenon related with the phase transition as well.

The heat release is much more intensive in the $Fe_3Ni_6S_8$ as compared to that in the $Fe_6Ni_3S_8$. The crystalline structure of the mss is not known but ought to be similar to that of hexagonal pyrrhotite [7]. Iron atoms in pyrrhotite occupy octahedral positions. Atomic radii of $Ni^{2+}$ and $Fe^{2+}$ in octahedral coordination are 0.069 and 0.0778 nm (iron in high-spin state) [8]. Small $Ni^{2+}$ atoms diffuse through crystal structure faster than $Fe^{2+}$ atoms. The $Fe_3Ni_6S_8$ contains less iron atoms than the $Fe_6Ni_3S_8$. This makes the process in the $Fe_3Ni_6S_8$ more active.

## Conclusions

1. Exothermic process was detected in the mixture of pentlandite and the mss under heating. It takes place in the temperature range between the point of the phase transition in the mss (near 400 K) and 690 K. The process is controlled by diffusion.

2. The Fe–Ni distribution between pentlandite and the mss was found to equalize in the temperature range where the exothermic process takes place.

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This work was supported by the Russian Foundation for Basic Researches (Project N.96-05-66100).

## References

1 A. J. Naldrett, J. R. Craig and G. Kullerud, Econ. Geol., 62 (1967) 826.
2 R. W. Shewman and L. A. Clark, Canadian J. Earth Sci., 7 (1970) 67.
3 K. C. Misra and M. E. Fleet, Econ. Geol., 68 (1973) 518.
4 J. R. Craig, Am. J. Sci., 273A (1973) 496.
5 V. A. Drebushchak, Zh. N. Fedorova and E. F. Sinyakova, J. Thermal Anal., 48 (1997) 727.
6 V. A. Drebushchak, T. A. Kravchenko and V. S. Pavlyuchenko, J. Crystal Growth, 193 (1998) 728.
7 N. Morimoto, A. Gyobu, K. Tsukuma and K. Koto, Amer. Mineral., 60 (1975) 240.
8 D. J. Vaughan and J. R. Craig, Mineral Chemistry of Metal Sulfides, Cambridge University Press, Cambridge 1978.