Journal of Thermal Analysis, Vol. 48 (1997) 727-734

DECAY OF $(Fe_{1-x}Ni_x)_{0.96}S$
DSC investigation

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(Received May 6, 1996)

Abstract

The decay of a monosulphide solid solution (*mss*) with the composition $(Fe_{1-x}Ni_x)_{0.96}S$ was investigated by means of differential scanning calorimetry in the temperature range, from 20 to 305°C. Thermal effects of various natures were detected:

i) Ordering-disordering in the Fe–Ni sublattice near 100°C.

ii) Pentlandite exsolution (exothermal peak); the peak temperature varies from 180 to 240°C and depends on the initial composition; the higher the Ni content, the lower the exsolution temperature.

iii) Magnetic-paramagnetic transition. The transition temperature decreases down to 220°C as the Fe:Ni ratio is decreased from 10:0 to 4:6.

Ni atoms are the defects in the magnetic ordering of the *mss* generated by the Fe atoms in the metal sublattice. Thus, the driving force for pentlandite exsolution is the removal of Ni atoms from the magnetic *mss* into the nonmagnetic pentlandite. This is the reason why the Fe:Ni ratio in the generated pentlandite is much higher than that in the initial *mss*.

Keywords: DSC, monosulfide solid solution, system Fe–Ni–S

Introduction

The homogeneous phase, termed the monosulphide solid solution or *mss*, varies from $Fe_{1-x}S$ to $Ni_{1-x}S$ and predominates in a wide range of composition in the system Fe–Ni–S. It is stable in the temperature range from 900 down to 270°C [1]: synthesized from a melt, the *mss* does not break down after annealing at 300°C for 40 days [2].

Unstable sulphides of this composition are capable of reacting at moderate temperatures. Thermal analysis can provide new information about the relations between the phases under transformation. This study deals with the results of an investigation of the system Fe–Ni–S across the section $(Fe_{1-x}Ni_x)_{0.96}S$.

Experiment

High-purity Fe, Ni and S were used to synthesize the samples of composition $(Fe_{1-x}Ni_x)_{0.96}S$ with $x=0, 0.1, \ldots, 1$. The mixtures were heated up to melting and

0368–4466/97/ $ 5.00

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Table 1 Data on synthesis and investigation of the samples with the $Fe_{0.96}S$–$Ni_{0.96}S$ composition

Fe : Ni	Phase transition temp./°C		ΔH_{exo}/ J g^{-1}	Quenched samples		Phases after slow cooling from 1070°C
	1st run	2nd run		a/Å	c/Å	
10 : 0	>305	>305	–	3.444(1)	5.817(4)	$Fe_{0.96}S$
9 : 1	>305	>305	–	3.449(2)	5.746(6)	mss
8 : 2	291±1	291±1	–	3.4465(12)	5.7204(36)	mss+10% pn
7 : 3	266±2	261±3	10.3	3.4451(6)	5.6881(18)	mss+23% pn
6 : 4		(253)	12.3	3.4425(14)	5.647(4)	mss+23% pn
5 : 5		238±4	25.4	3.443(2)	5.615(7)	mss+25% pn
4 : 6		220±4	35.7	3.448(2)	5.575(4)	mss+20% pn
3 : 7				3.4456(26)	5.5390(45)	mss+ 9% pn
2 : 8				3.442(4)	5.497(6)	mss
1 : 9				3.437(2)	5.370(6)	mss
0 :10				3.4366(18)	5.3405(46)	$Ni_{0.96}S$

then cooled down to room temperature in two ways. In the first way, the hot silica tube with the homogeneous melt was dropped into water at room temperature; in the second way, it was cooled down by switching the furnace off. In the first case, the samples were homogeneous crystalline solid solutions with a hexagonal unit cell. In the second case, the same solid solution was found, but the samples with Fe:Ni ratio ~1 contained exsolved pentlandite $(Fe,Ni)_9S_8$. The samples were analysed by means of X-ray powder diffraction and optical microscopy. The unit cell parameters of the investigated samples are listed in Table 1.

Calorimetric measurements were carried out in sealed aluminum crucibles (40 μl) with a DSC-30 of the Mettler TA-3000 System. The sample mass varied from 65 to 85 mg. Only samples quenched in water were investigated. Preliminary measurements on the sample were carried out in the temperature range from 20 to 150°C at 3°C min^{-1} for both heating and cooling. After heating, the crucibles were unsealed, and the samples were investigated by X-ray powder diffraction and optical microscopy.

Two heating runs up to 305°C were carried out at a heating rate of 5°C min^{-1}. Between the runs, the samples were cooled down at the highest rate attainable in the DSC-30; the time of cooling was about 5 min. After the measurements were complete, the crucibles were unsealed and the contents were examined visually for corrosion markings. No markings were found. The samples were then investigated by means of X-ray powder diffraction and optical microscopy.

Results

The unit cell parameters of pentlandite and of the *mss* depend critically on the chemical composition (e.g. [2]). The X-ray reflections of our samples are sharp, which means that the compositions of the individual grains vary in a narrow range. Just after heating to a temperature higher than 100°C, the reflections become

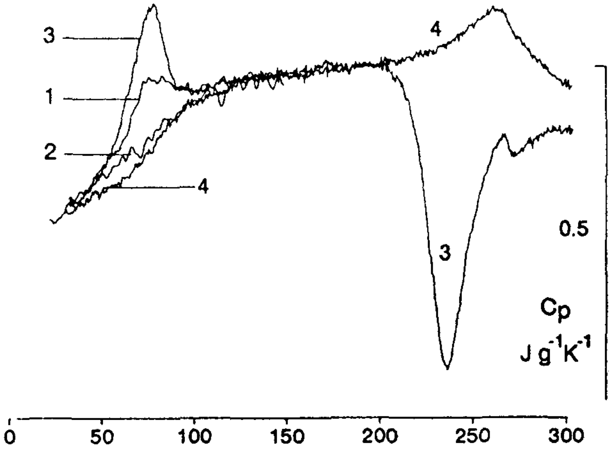

Fig. 1 Measurements on sample with composition $(Fe_{0.7}Ni_{0.3})_{0.96}S$: (1) heating up to 150°C and (2) cooling down to 20°C; first (3) and second (4) runs up to 305°C

broader. This is due to the ordering-disordering processes taking place near 100°C in the metal sub-lattice [3].

No phase changes were found in the cooled samples after preliminary measurements (up to 150°C). All samples except $Ni_{0.96}S$ gave an endothermic peak near 100°C. This peak was absent under cooling. The results on the sample with composition $(Fe_{0.7}Ni_{0.3})_{0.96}S$ are shown in Fig. 1. In the measurements up to 305°C, the peak near 100°C was detected only during the first run. These results are also given in Fig. 1.

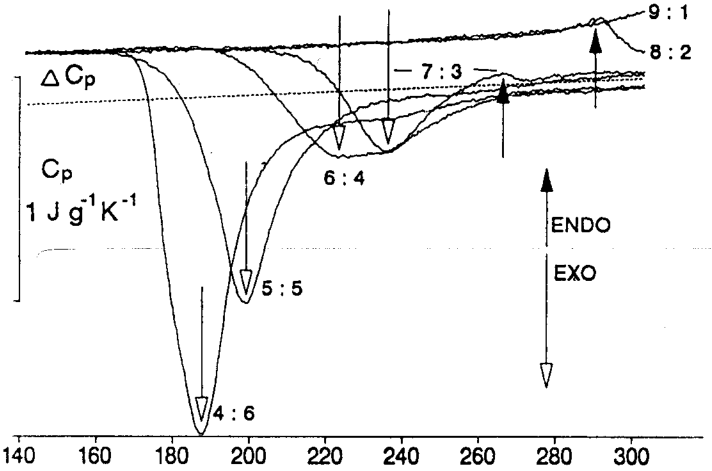

Fig. 2 Results of first run. ΔC_p indicates difference in heat capacity between magnetic and paramagnetic phases

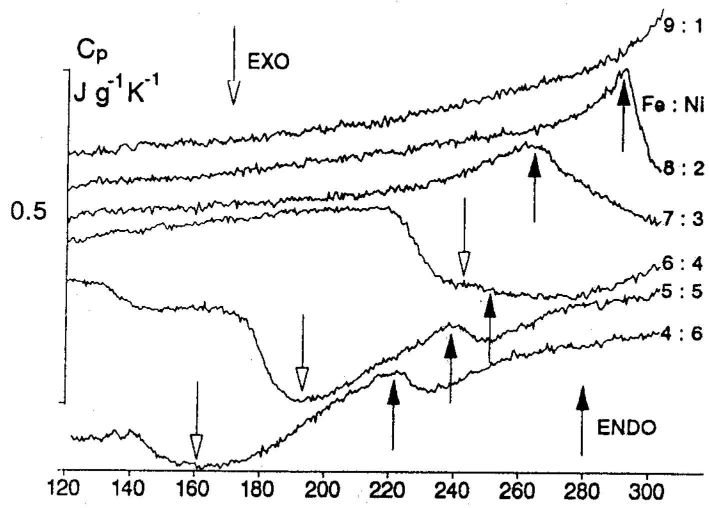

Fig. 3 Results of second run

During the first run, the exothermic peak was detected in the samples with Fe:Ni ratios of 7:3, 6:4, 5:5 and 4:6 (Fig. 2). The heat release was high enough to heat up the samples with Fe:Ni ratios of 5:5 and 4:6 ($C_p<0$). During the second run, the exothermal effect was again detected for the samples with Fe:Ni ratios of 6:4, 5:5 and 4:6. The heat release was much lower than during the first run (Fig. 3). Pentlandite was found in the samples exhibiting heat release.

The samples with Fe:Ni ratios of 8:2 and 7:3 underwent a magnetic phase transition during the first run (Fig. 2), as did those with Fe:Ni ratios of 8:2, 7:3, 6:4, 5:5 and 4:6 during the second run. The endothermal effect of the phase transition was masked by the exothermal effect of pentlandite exsolution from the *mss*. The peak temperature decreased together with the Fe:Ni ratio (Table 1). For the sample with an Fe:Ni ratio of 9:1, the increase in heat capacity was detected only at the beginning of the phase transition. The peak itself was outside the temperature range of the measurements.

Discussion

Both $Fe_{1-x}S$ and $Ni_{1-x}S$ are magnetic materials. $Fe_{1-x}S$ is antiferromagnetic, with the antiferromagnetic → paramagnetic phase transition temperature (the Neel point) near 320°C. The direction of easy magnetization is in the plane perpendicular to the *c* axis [4]. $Ni_{1-x}S$ is antiferromagnetic, with the Neel point near −10°C. The direction of easy magnetization is parallel to the *c* axis [5]. It is evident that the composition change from $Fe_{1-x}S$ to $Ni_{1-x}S$ must go through at least one point of discontinuity in the relationship between the electron spin structure and the Fe:Ni ratio.

Antiferromagnetism in $Fe_{1-x}S$ is replaced by ferrimagnetism as x increases. It is known with certainty that troilite (FeS) and hexagonal pyrrhotite ($Fe_{1-x}S$, $x\leq 0.1$) are antiferromagnetic, but monoclinic pyrrhotite (Fe_7S_8) is ferrimagnetic [3]. The experimentally derived phase transition temperatures for natural samples with the composition $Fe_{1-x}S$ vary from 308 to 320°C [6]. It is conventional to use 'the Neel point' for antiferromagnets, but 'the Curie point' for ferrimagnets. We are not sure what the type of long-range magnetic order is in the sample in question. To avoid any misunderstanding, the term 'transition temperature' will be used below.

As concerns the phase transition in pyrrhotites, it is surprising that the temperature hardly depends on the metal:sulphur ratio. The change in the transition temperature together with the change in sample composition deduced in this work is perfectly legitimate: the energy of the superexchange interaction changes on substitution of one *d*-metal for another. All the energetic parameters, i.e. the transition temperature, the exothermal peak temperature, and the heat release, change monotonously with decreasing Fe:Ni ratio. This suggests that down to an Fe:Ni ratio of 4:6 the long-range magnetic order changes in quantity, but not in quality. The discontinuity in $Fe_{1-x}S$–$Ni_{1-x}S$ mixing was earlier suggested at a Ni content between 25 and 33 at.% (between 5:5 and 3:7 for the Fe:Ni ratio) at 300°C [7]. The present work proves the existence of the discontinuity between 4:6 and 3:7 and at a metal:sulphur ratio of 0.96. The superexchange interaction is responsible for the discontinuity. The electron spin system is capable of creating the long-range magnetic order of the same type as that for FeS. The interaction Fe–S–Fe is must greater than the interaction Ni–S–Ni: the effective magnetic polarization is 5.22 μ_B for FeS and 2.35 μ_B for NiS [8] (it should be remembered that the Neel point for FeS is two times greater than the Neel point for NiS). Thus, the Fe minority in $(Fe_{0.4}Ni_{0.6})_{0.96}S$ creates the intrinsic magnetic field that governs the total electron spin system.

During the first run up to 305°C, the decrease in heat capacity occurs after the transition temperature: $\Delta C_p/R \sim 2$. This is the magnetic part of the heat capacity of the initial samples, i.e. two degrees of freedom per molecule $(M_{0.96}S)$.

Analysis of the bulk compositions of the sulphide fractions of many sulphide nickel ore bodies shows that the sulphides in these ores initially crystallized as *mss*. Pentlandite was produced after ore cooling [9, 10].

This scheme of the origin of the sulphide ores is in accordance with the results of the present work. The reaction of the low-temperature evolution of the *mss* is

$$(Fe_{1-x}Ni_x)_{0.96}S \rightarrow (Fe_{1-a}Ni_a)_9S_8 + (Fe_{1-y}Ni_y)_{0.96-z}S \qquad (1)$$

The *mss* is enriched with sulphur after pentlandite exsolution. The pentlandite in its turn concentrates Ni: $a/x > 1$. This concentration was deduced in experiments involving a wide range of initial *mss* composition. For example, $a \sim 0.3$ for $x \sim 0.05$, and $a \sim 0.57$ for $x \sim 0.35$ [7]. Reaction (1) relates to the decay of unstable solid solution into stable pentlandite and stabilized (less unstable, but not yet stable) *mss*. Pentlandite exsolution lasts until the Ni concentration in the *mss* falls to zero $(y \rightarrow 0)$.

Chemical composition of reagents

Equation (1) describes the transformation that lasts for a long time. The chemical composition of the *mss* undergoing decay changes during the reaction. The composition of the generated pentlandite must change as well. While growing the grains of pentlandite ought to be different in composition both from each other and between different parts of a grain. This can readily be detected, for the unit cell parameters of the reagents depend critically on the chemical composition. As mentioned above, the samples in this study were homogeneous.

The chemical composition of pentlandite exsolved from the *mss* was investigated in [1, 7, 11]. The composition was found to be unexpectedly homogeneous. Compositional zoning and significant grain-to-grain variations in composition were not observed for any phase that occurred in grains large enough for accurate electron probe analysis.

The phase transitions in sulphides are classified into two types. The first type involves change in the metal sublattice, whereas the anion framework of sulphur atoms remains constant. This type of transformation is responsible for ordering-disordering in pyrrhotites [12]. In the present work it is manifested as the peak near 100°C. The second type is the usual recrystallization; this changes the anion framework. This is the type responsible for pentlandite exsolution. The breaking of sulphur bonds requires high energy. This transformation is a slow reaction. The metal atoms diffuse through the sample much more quickly than sulphur atoms transit from the *mss* lattice to the pentlandite lattice on a boundary between them. The sample cooled down to room temperature has the texture that was frozen up at any stage. During cooling and just after it, the anion framework reconstruction vanished, whereas metal diffusion still continued. As a result, each grain of pentlandite was in equilibrium with the *mss* that surrounded the grain and the *mss* in turn was homogeneous.

Kinetics of pentlandite exsolution

The exothermal decay of the *mss* with Fe:Ni ratios of 5:5 and 4:6 occurs as a violent reaction. The heat release proceeds rapidly and then falls away in the same way. During the first run, the rate of reaction decreases with increasing temperature. The shape of the peak is usual for a reaction proceeding to completion. The reaction ceases when the initial reagent has disappeared:

$$dX/dt = f(x) \to 0 \text{ at } x \to 0 \qquad (2)$$

It is not valid here. The amount of exsolved pentlandite after the second run is slightly less than that after slow cooling (Table 1). The reaction must continue. It is evident from the results of the second run that the reaction does continue, but its rate is much less. The second fact to be explained is the approximately constant content of exsolved pentlandite after the slow cooling in the samples with Fe:Ni ratios of from 3:7 to 6:4.

There are two rate-determining factors that reduce pentlandite exsolution at elevated temperatures:

1. Reaction (1) takes place only outside the area of *mss* stability. The *mss* is undoubtedly stable at $T \geq 400°C$ [1, 2].

2. The rate of the reaction *mss* → pn+*mss'* depends on the M:S ratio in the initial *mss*. For example, on reaction at 400°C for 10 h in the *mss* containing 3.7 at.% of Ni, 65% of pentlandite exsolved at an M:S ratio of 1.000, 35% at a ratio of 0.981, and 15% at a ratio of 0.965. The reaction does not occur at all at a ratio of 0.955 [1].

These reasons explain why the reaction does not go to completion. They do not explain why the reaction is so violent during the first run, but not during the second one. Pentlandite exsolution passes through two stages: the nucleation of pentlandite particles, and then the growth of these particles. Pentlandite nucleation was studied in [1]. Natural processes were simulated by cooling from elevated temperatures down to room temperature. Exsolution of pentlandite from the very beginning takes place as heterogeneous nucleation at the *mss* grain boundaries. Subsequent growth results in the impingement of these particles and the formation of continuous rims of pentlandite along the *mss* grain boundaries. During the first run, DSC detects the nucleation as a violent exothermal reaction. The heat released decreases as the nucleation ceases, and all the subsequent measurements detect only the diffuse expansion of pentlandite particles.

Conclusions

1. Monosulphide solid solutions within the range of composition $(Fe_{1-x}Ni_x)_{0.96}S$ ($x=0$, 0.1,..., 0.6) are capable of forming magnetic structures like $Fe_{0.96}S$.
2. Ni atoms create defects in the magnetic structure. The temperature of the magnetic-paramagnetic transition decreases with decreasing Fe:Ni ratio.
3. The changes in the initial monosulphide solid solution are directed toward moving Ni from the magnetic *mss* into the nonmagnetic pentlandite.

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This work was supported in part by the Russian Foundation for Basic Researches (Project N.94-05-16780).

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