Observations of transformation behavior in Ni_7S_6 by transmission electron microscopy

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Abstract

Millerite (β-NiS) has been examined by transmission electron microscopy and found to lose sulfur on beam heating. The product of this sulfur loss is α-Ni_7S_6 which undergoes a series of reversible polymorphic transformations on cooling. These involve the formation of super-structures based on the high temperature body-centered structure.

Low temperature β-Ni_7S_6 forms on rapid cooling of α-Ni_7S_6 and is invariably poly-synthetically twinned normal to the (011) plane.

Introduction

The Ni–S system appears to be one of the few sulfide systems in which the phase equilibria are relatively well understood and compatible with the known mineralogy. In the course of a transmission electron microscope (TEM) study of sulfides, a part of this system has been reexamined to determine the nature of phase transformations in the NiS-Ni_7S_6 region. Transmission electron microscopy allows the direct observation of such processes and can provide information not obtainable by other means.

Transitory phenomena associated with structural phase transformations and compositional changes in nickel sulfides can be observed by *in situ* TEM experiments. This paper outlines the effects of beam heating on millerite (β-NiS) and its subsequent transformation to α-Ni_7S_6. The behaviour of α-Ni_7S_6 with decreasing temperature is described in terms of a series of superstructures based on the high temperature cell prior to the transformation to the low temperature β-Ni_7S_6 form.

Previous work

A comprehensive study of the Ni–S system by Kullerud and Yund (1962) indicates the existence of two structural modifications of both NiS and Ni_7S_6. Below 390°C β-NiS has the millerite structure (Grice and Ferguson, 1974; Rajamani and Prewitt, 1974), whereas the high temperature α-NiS has the nickel arsenide structure. α-Ni_7S_6 is stable between 400°C and 573°C, and the randomly disordered structure has been described by Fleet (1972). α-Ni_7S_6 is orthorhombic with a body centered cell. The low temperature β-Ni_7S_6 form has a primitive orthorhombic cell and occurs as the mineral godlevskite (Kulagov *et al.*, 1969; Naldrett *et al.*, 1972). The structural details of β-Ni_7S_6 are not yet known.

Method

Naturally occuring millerite crystals from Wissen, Germany, were crushed and the finest grains collected from a suspension in absolute alcohol and mounted on a carbon-coated copper grid for observations in an AEI EM6G electron microscope operating at 100 kV. The heating effect of the electron beam was used to induce transformations in the millerite. This heating effect can be partially controlled by the use of various condenser aperture sizes and by beam focussing, although the temperature in an individual grain depends on such factors as the size of the grain, its conductivity, whether it is in contact with other grains or the copper grid, etc. In suitable grains, transformations on heating and cooling can be observed, although the temperatures involved cannot be determined in this way. A "suitable grain" in this context means that the edge must be thin enough to be transparent to the electron beam while the bulk of the grain is thick enough to absorb enough heat to give the required temperature increase.

The phases present in the electron microscope were identified from electron diffraction patterns indexed from the following data: for α- and β-NiS, Kullerud

and Yund (1962); for α-Ni₇S₆, Fleet (1972); for β-Ni₇S₆, Naldrett *et al.* (1972).

Results

Beam heating of millerite (β-NiS) produces an abrupt transformation to the high temperature α-NiS form. Details of this transformation and the orientational relationships between these two polymorphs are being published elsewhere (Kennedy and Putnis, in preparation). Sulfur loss occurs at temperatures above this transformation and is generally spontaneous, transforming the whole grain to a new more nickel-rich structure. Careful beam heating of suitable grains shows that the sulfur loss is initiated at edges of grains or at defects, and a curved boundary separates the α-NiS from the metal enriched phase. Such a boundary can be seen in Figure 2a. Once this
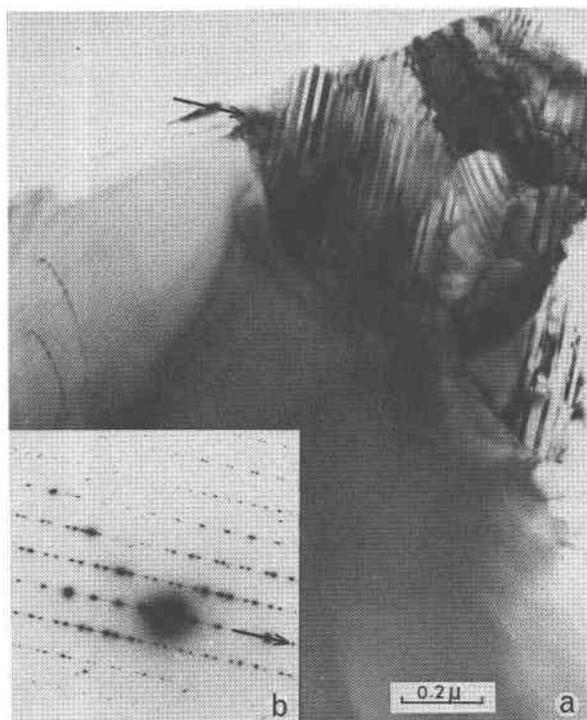

FIG. 2(a) Bright field image showing twinned β-Ni₇S₆ coexisting with α-NiS (untwinned phase). (b) A [21$\bar{1}$] zone-axis diffraction pattern from the twinned region of β-Ni₇S₆ in the same orientation as Fig. 2a. The arrows indicate the direction $\mathbf{g} = (011)$.
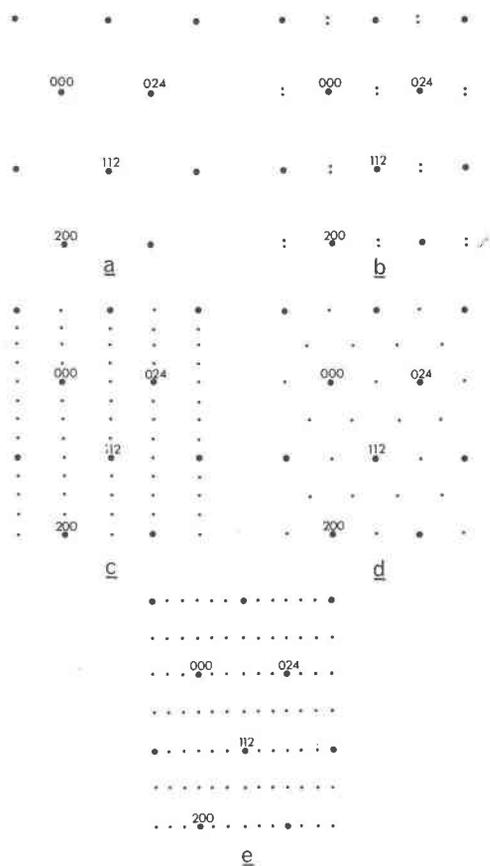

FIG. 1. A series of [012] zone-axis diffraction patterns of α-Ni₇S₆ illustrating successive transformations with decreasing temperature. (a) The high temperature body-centered cell. (b) Satellite pairs about the $h+k+l$ = odd positions. (c) The $4a, 1b, 1c$ superstructure. (d) The $2a, 2b, 2c$ superstructure. (e) The $2a, 3b, 3c$ superstructure.

'frozen in' boundary has been formed, it is relatively stable, but beam heating below the temperature of sulfur loss permits observation of polymorphic transformations in the more metal-rich phase without further decomposition.

Electron diffraction patterns of this metal-rich region can generally be indexed on the basis of the lattice parameters for α-Ni₇S₆ (Fleet 1972). The body-centered disordered structure of Fleet (1972) is only observed at the highest temperatures, and on cooling α-Ni₇S₆ rapidly passes through a series of transitory states which are described in terms of superstructures of this high temperature disordered structure.

Figure 1 shows diagrams illustrating a series of diffraction patterns observed in an [012] zone-axis section of α-Ni₇S₆ undergoing successive transformations with decreasing temperature. Figure 1b shows the first of these states. Slow cooling by defocussing the beam produces satellite pairs about the absent $h+k+l$=odd positions, with the separation of the pairs in the a^* direction. This indicates the existence of periodic antiphase domains of primitive α-Ni₇S₆ with periodicity about 50A and domain boundaries

normal to a^*. Such antiphase domains arise as a consequence of the two possibilities for the origin of the primitive structure in the transformation from the body-centered structure. The antiphase vector is thus $\frac{1}{2}\langle 111\rangle$

Further cooling produces a transitory $4a,1b,1c$ superstructure (Figure 1c)—where a, b, and c are the parameters of the high temperature disordered state—before transformation to a $2a,2b,2c$ superstructure (Figure 1d). This state involves a slight contraction of the lattice and is generally associated with a certain amount of disorder shown as streaking of superstructure reflections parallel to b^*. Defocussing the beam further produces a $2a,3b,3c$ superstructure (Fig. 1e) which appears to be the lowest temperature state of α-Ni_7S_6 in this case. The above transformations are fully reversible.

In some grains, the $2a,2b,2c$ superstructure transforms with cooling to a $2a,2b,4c$ superstructure, in others to a $2a,2b,3c$ superstructure for low temperature α-Ni_7S_6. Variation in nickel content may account for this behavior, but at present the limits of solid solution in α-Ni_7S_6 are unknown.

To produce the low temperature β-Ni_7S_6 form, it is necessary to reheat the grain and reduce the temperature quickly, thereby avoiding the production of the superstructure states of α-Ni_7S_6. The β-Ni_7S_6 is polysynthetically twinned with composition plane (011) and twin axis normal to the composition plane. A twin law for β-Ni_7S_6 has not been previously reported. Figure 2a shows twinned β-Ni_7S_6 coexisting with α-NiS. The diffraction pattern (Figure 2b) is from the twinned region and is indexed from the lattice parameters of Naldrett *et al.* (1972).

The reverse transformation from β- to α-Ni_7S_6 results in the direct formation of the high temperature disordered form of α-Ni_7Si_6 without the production of the superstructure states.

An attempt was made to reproduce the sulfur loss observed in the microscope by heating experiments in a high vacuum furnace. The vacuum in this furnace was similar to that in the microscope at 10^{-5}mm. The millerite was prepared in the same way as for electron microscopy, and a number of runs were made on 50 mg samples heated in platinum crucibles. The sulfur loss was determined by accurate weighing of the sample in the crucible before and after heating. Although sulfur loss occurred at temperatures above 400°C, the rate of the process was such that after 5 hours at 650°C only 2.6 percent of the total weight of the sample was lost, compared with the 5.0 percent which is lost when NiS is converted to Ni_7S_6. In the

electron beam this sulfur loss is spontaneous. One possibility for this difference is that the effective sulfur pressure in the 50 mg sample in the vacuum furnace may be relatively high despite the vacuum. Analyses of the products after heating in the furnace were not made.

Discussion

In α-Ni_7S_6 there are 5 non-equivalent Ni sites of which 3 have occupancy factors of about 0.5 in the disordered body-centered structure (Fleet, 1972). Fleet discusses the possibility of Ni ordering and reports the existence of diffuse non-integral superstructure reflections indicating the development of long range order. The superstructures described above may be attributable to the development of various ordering schemes in α-Ni_7S_6. If this is so, then the different low temperature superstructures in α-Ni_7S_6 could be due to variation in nickel content. Such a variation can be accommodated by the structure, and Haugsten and Rost (1969) report a composition of $Ni_{5.87}S_5$ for this phase. On the basis of the present work it would be reasonable to assume that above the α–β transformation in Ni_7S_6, there exists a range of compositions which can be described in terms of superstructures of the α-Ni_7S_6 cell, and that these superstructures are due to the ordering of Ni atoms.

The low temperature transformation product is in all cases twinned β-Ni_7S_6. Such twinning has been reported for natural β-Ni_7S_6 (Naldrett *et al.*, 1972) and may be evidence that it had transformed from the high-temperature form.

A further outcome of this work concerns the effects of the electron beam on sulfides. Sulfur loss has been observed on beam heating chalcopyrite (McConnell, personal communication) although no loss was observed in similar experiments on troilite (Putnis, 1974). The fact that the sulfur loss could not be reproduced by heating experiments in a high vacuum furnace suggests that radiation effects may play a significant role in controlling the rate of the process, and the possibility of sulfur loss must be taken into account in any electron microscopic study of sulfides.

References

FLEET, M. E. (1972) The crystal structure of α-Ni_7S_6. *Acta Crystallogr.* **B28,** 1237–1241.

GRICE, J. D., AND R. B. FERGUSON (1974) Crystal structure refinement of millerite (β NiS). *Can. Mineral.* **12,** 248–252.

HAUGSTEN, K., AND E. ROST (1969) Phase relations in the system Ni–S–Se at 500°C. *Acta Chem. Scand.* **23,** 3599–3600.

KULAGOV, E. A., T. L. ERSTIGNEEVA, AND O. E. YASHKO-ZAKHAROVA (1969) The new nickel sulfide godlevskite. *Geol. Rud. Mestorozhd.* **11,** 115-121.

KULLERUD, G., AND R. A. YUND (1962) The Ni–S system and related minerals. *J. Petrol.* **3,** 126–175.

NALDRETT, A. J., E. GASPARRINI, R. BUCHAN, AND J. E. MUIR (1972) Godlevskite (β-Ni_7S_6) from the Texmont Mine, Ontario. *Can. Mineral.* **11,** 879-885.

PUTNIS, A. (1974) Electron optical observations on the α transformation in troilite. *Science,* **186,** 439-440.

RAJAMANI, V., AND C.T. PREWITT (1974) The crystal structure of millerite. *Can. Mineral.* **12,** 253–257.