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VARIATION IN PROPERTIES OF SYNTHETIC "PYRRHOTITES" OF COMPOSITION $Fe_{1-x}S$ $(0 \leq x \leq 0.14)$

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A series of eight synthetic "pyrrhotites" containing from 50.0 to 46.0 atomic percent iron have been examined for systematic variation in three properties : Vickers microhardness, reflectivity, and breakdown temperature in air. The samples were homogenised, annealed and quenched from 701 ± 7°C. Details of the method of preparation, together with structural, magnetic, Mossbauer and compositional data are given elsewhere (Vaughan 1971 ; Schwarz & Vaughan 1971). Polished sections of the samples, mounted in cold setting plastic and polished on lead laps, were used to study the systematic variation in reflectivity and microhardness. Some of the powdered material was used in differential thermal analysis in an air atmosphere. Samples quenched from high temperature were used in an attempt to avoid inhomogeneities. Although not observable under the microscope, the *x*-ray and magnetic data suggested that the samples of bulk composition 49.0 and 47.0 at, % iron were two-phase intergrowths.

A Leitz Durimet microscope fitted with a Vickers diamond indenter was used in the determination of indentation microhardness. The results of the measurements are given in Figure 1 and show a linear trend of increasing microhardness with decreasing metal content. The indentations were made using a 25 g load which minimized errors due to large scale fracturing of the small grains of synthetic pyrrhotite. The use of a small load explains any discrepancies between these values and other absolute values reported in the literature. The increase in microhardness follows the decrease in the *a* and *c* parameters of the basic NiAs-type unit cell of the structure (or "substructure").

The variation in reflectivity was determined using a Leitz Ortholux Pol microscope fitted with a Leitz MPE microscope photometer and a continuous band interference filter. This instrument (at the Mines Branch, Ottawa) has been described in detail by Nickel (1970). Reflectivities were measured relative to silicon standard N2538.42 calibrated by the National Physical Laboratory. Maxima and minima of the reflectivity values were determined for numbers of grains at a wave length of 589 nm. The data, illustrated in Figure 2, show an increase in reflectivity with decreasing metal content. This result agrees with reports by Arnold (1969) and Naldrett & Simpson (1970).

DTA studies of synthetic "pyrrhotites" in a nitrogen atmosphere were made by Roberts (1935) and similar work on the present samples is report-

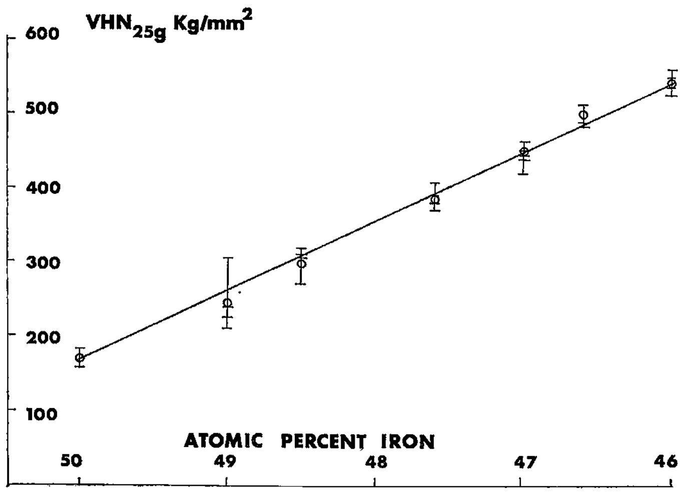

FIG. 1. Variation in microhardness with composition in synthetic pyrrhotites (annealed at 701°C).

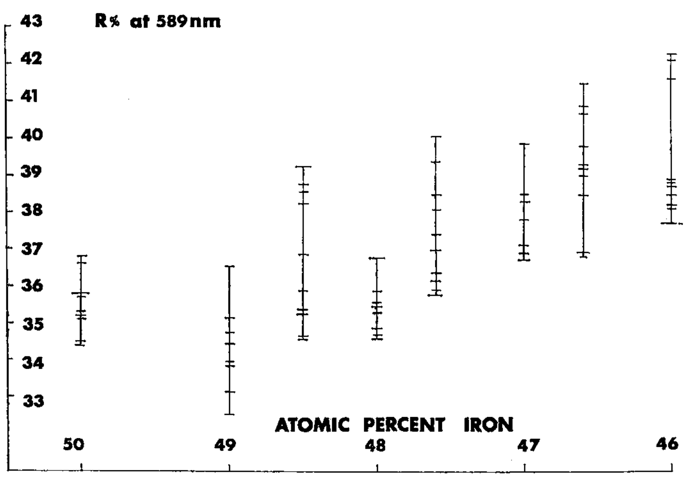

FIG. 2. Variation in reflectivity with composition of synthetic pyrrhotite (annealed at 701°C).

ed elsewhere (Schwarz & Vaughan 1971). However, samples of approximately 20 mg weight were also heated in a vertical tube furnace at a constant rate of 6° C/minute in an atmosphere of air. These samples were held on a platinum foil disc and temperature differences were recorded using a thermocouple of Pt/87% Pt + 13% Rh. The results are presented as traces in the form of a phase diagram in Figure 3. A number of the same endothermic transitions as observed in a nitrogen atmosphere occur, and a series of large exothermic oxidation reactions. These reactions took place over the temperature range 520-570° C for stoichiometric FeS but dropped to the range 417-500° C in the most metal-deficient composition.

The limited, although clearly significant variations in microhardness and reflectivity in this series of compounds could perhaps not be used as indicators of composition. They are of interest, however, when the crystal chemistry of the pyrrhotites is being considered. The increase in micro-

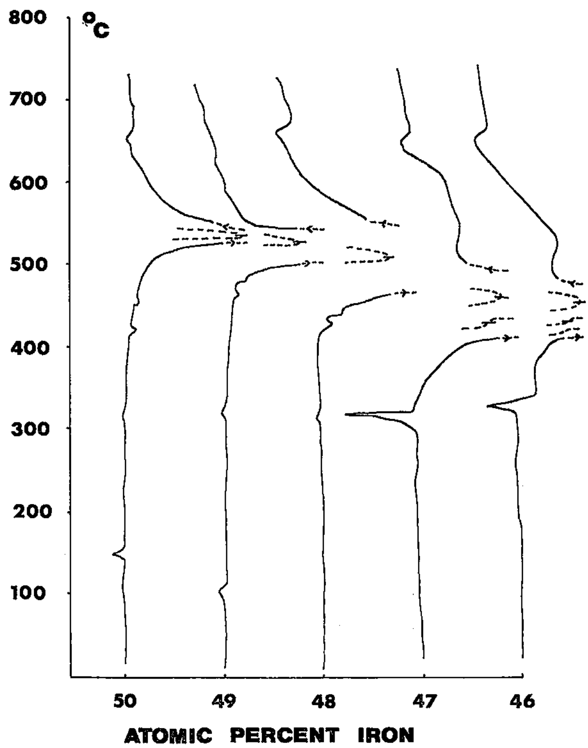

FIG. 3. Differential thermal analysis curves for synthetic pyrrhotites (in air). Pyrrhotite samples which had been annealed at 701°C were used in the determinations.

hardness with decreasing iron content, which corresponds to the reduction in cell parameters, is probably the consequence of some collapse of the atoms around the vacancies created by metal depletion. Crystal structure studies of "monoclinic" and "hexagonal" pyrrhotite suggest such collapse (pers. comm. B. J. Wuensch). Reflectivity variations are difficult to interpret in such a complex system. However, Burns & Vaughan (1970) have shown that a linear relationship exists between percent reflectivity and the "effective number of free electrons" suggesting increasing free electron behavior with metal depletion in this system.

The decreasing temperature range of the oxidation breakdown of "pyrrhotite" with increasing vacancy concentration might intuitively be predicted, although the rapid tarnishing of troilite (FeS) polished surfaces in air remains unexplained.

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