TWO-PHASE HEXAGONAL PYRRHOTITES

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ABSTRACT

Microscopic and *x*-ray diffraction studies on two natural specimens of two-phase hexagonal pyrrhotites show that the two unmixed phases have a common crystallographic orientation. In polished section, the common *c*-axis is in the same plane as the short diagonals of the rhombic sections formed by the intersection of the exsolution lamellae. The superstructures of the intermediate hexagonal pyrrhotite in the two samples are different from one another and have not been reported previously from natural material, being hexagonal $2A,6C$ and hexagonal $2A,4C$, where A and C refer to the a and c parameters of the subcell.

INTRODUCTION

Two-phase hexagonal pyrrhotites have been reported by several investigators in recent years (Kouvo, Vuorelainen & Long, 1963; Carpenter & Desborough, 1964; Rao & Rao, 1968). The two co-existing phases are troilite, of near-stoichiometric FeS composition, and a hexagonal pyrrhotite whose composition is within the range 47.0 to 47.9 atomic % iron: the one phase, generally troilite, being present as exsolution lamellae within the other. The resulting texture is distinguished quite readily from that produced by lamellae of monoclinic pyrrhotite within hexagonal pyrrhotite (Naldrett & Kullerud, 1967), since the birefringence of the two hexagonal phases differs sufficiently for them to be resolved with crossed-nicols, whereas the latter are resolved only after etching with a suitable solvent. It has been shown that the exsolution occurs at some temperature less than 300°C with synthetic pyrrhotite of the appropriate bulk composition (von Gehlen, 1963), and natural two-phase pyrrhotites can be homogenised by heating under vacuum at 320°C for 20 minutes (Rao & Rao, 1968). After investigating several hexagonal pyrrhotites of intermediate composition, Carpenter & Desborough concluded that all natural pyrrhotites of this type have a supercell with $a = 2A$, $c = 5C$, where A and C are the equivalent a and c parameters of the simple NiAs-type subcell. Hexagonal pyrrhotites, co-existing with troilite, have not been investigated for superstructure type, although it has been suggested that the hexagonal $2A,5C$ supercell is common to these also (Desborough & Carpenter, 1965).

This study was directed to examining the orientation of the co-existing phases and the nature of the superstructure in the intermediate hexagonal pyrrhotite in two specimens of two-phase pyrrhotites available to the authors.

OBSERVATIONS

Specimen 500

This specimen was obtained from a pit in a mineralized sulphide zone at the contact between a basalt flow and a diabase dike, in Beatty Township, District of Cochrane, Ontario. The sulphides in the sample consist essentially of pyrrhotite with approximately 15% pentlandite and minor amounts of chalcopyrite, cubanite and mackinawite. The pentlandite is found associated with euhedral spinel grains, along pyrrhotite grain boundaries and as "blebs" within the pyrrhotite.

The pyrrhotite contains exsolution lamellae (Fig. 1); both phases were shown by *x*-ray diffraction analysis to be hexagonal, being troilite and intermediate hexagonal pyrrhotite. Electron microprobe studies confirmed that the more reflectant and more anisotropic phase is troilite. The apparent proportions of the two phases vary from grain to grain but, generally, troilite is the more abundant. Both flame-like and more regular, parallel-sided lamellae are apparent but, in either case, the lamellae are oriented in two directions, within each grain, and intersect to form a diamond pattern. When examined under crossed-nicols the two phases extinguish together (Carpenter & Desborough). In addition, the extinction

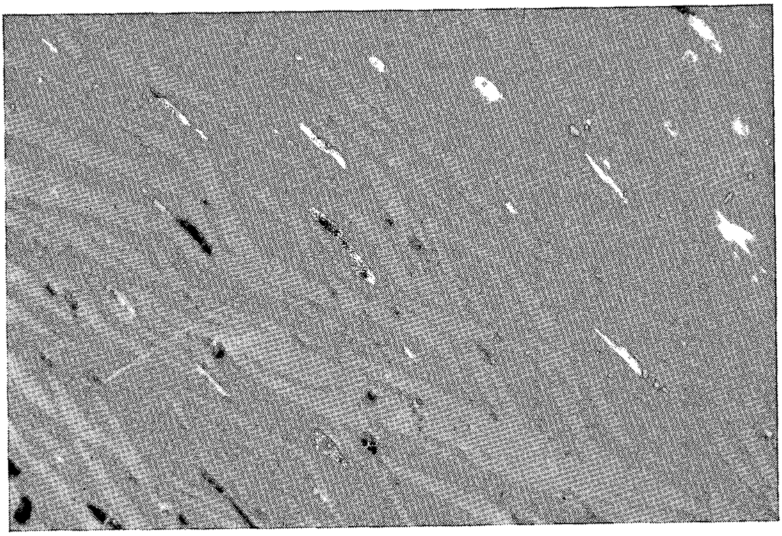

FIG. 1. Specimen 500, two-phase hexagonal pyrrhotite showing pentlandite blebs. X-nicols, ×200.

is symmetrical with the diamond pattern, being parallel to the diagonals of the rhombic sections. In some grains, blebs of pentlandite lie within the pyrrhotite. These blebs are elongated and are always oriented with their long axes parallel to the long axes of the rhombic sections (Fig. 1). If the pentlandite is exsolved in the basal plane of the pyrrhotite (as is commonly the case) then, for those grains sectioned normal to the basal plane, the short axes of the rhombic sections are parallel to the *c* axes of the two phases. Interference figures obtained on some grains (although somewhat anomalous because of the presence of the two phases) give evidence in support of this assumption. Naldrett & Kullerud reported a similar orientation for lamellae of monoclinic pyrrhotite within hexagonal pyrrhotite. In basal sections the lamellae are very irregular, are always flame-like and intersect at an angle approaching 90° (Rao & Rao).

Small fragments of the pyrrhotite were examined on the Buerger precession camera. Precession photographs show that the two phases have a common *a* axis in addition to a common *c* axis, and that, to within the precision of the method, there is no displacement between the common axes (Fig. 2). The variation in the *c* parameters is much greater than in the

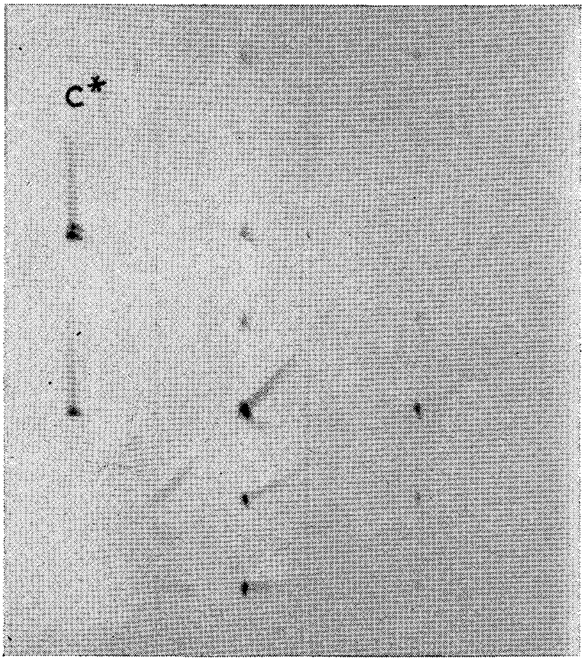

FIG. 2. Part of a zero level, *a* axis precession photograph of specimen 500, showing crystallographic continuity of the two phases: Mo Kα radiation, 35 Kv, 20 Ma, 24 hour exposure: c^* is vertical, a^* is horizontal.

a parameters, so that for the three lattice rows shown ($00l$, $10l$, $20l$), resolution between equivalent reflections of the two phases becomes greater with higher values of l; the troilite phase having the smaller reciprocal lattice spacing in the c^* direction. In addition to superstructure reflections characteristic of the troilite phase, there were other superstructure reflections which were correlated with the intermediate hexagonal phase. These reflections suggested a supercell with $a = 2A$ and $c = 6C$. The superstructure, designated hexagonal $2A,6C$, has not been reported previously. It is an addition to the series of hexagonal superstructures $2A,\mathrm{n}C$ reported for pyrrhotites of intermediate and more sulphur-rich composition. The known representatives of this series are $2A,3C$ (Corlett, 1968 and Fleet, 1968); $2A,4C$ (Fleet, 1968); $2A,5C$ (Carpenter & Desborough); $2A,6C$; $2A,7C$ (Desborough & Carpenter). The superstructure reflections were too weak to allow for meaningful reproduction for the purpose of presentation, largely because of the abundance of troilite in the fragments examined, although, on films exposed for several days, there was sufficient information to make a positive identification of the supercell. The distribution of the reflections was similar to the distributions of the superstructure reflections in the other representatives of the series (Fleet).

The lattice parameters, d_{102} spacings and probable compositions for the two phases are as follows: troilite, $a = 3.446$ Å, $c = 5.876$ Å, $d_{102} = 2.0933$ Å, 50.0 atomic % iron; hexagonal pyrrhotite, $a = 3.446$ Å, $c = 5.746$ Å, $d_{102} = 2.0705$ Å, 47.7 atomic % iron. The lattice parameters and d_{102} spacings were determined with a Jagodzinski focussing powder camera and these values and those for specimen 1351 (below) refer to the subcell to facilitate comparison: the compositions were determined from the d_{102}, composition curve of Toulmin and Barton (1964).

Specimen 1351

Specimen 1351 is from the Great Lakes Nickel intrusion in Pardee Township, Thunder Bay District, Ontario, and was sampled from within a chromite horizon which is approximately 500 feet from the intrusion floor. The mineralogy of the sulphides is similar to that of the previous specimen, except that troilite makes up only 10 to 15% of the pyrrhotite (Fig. 3).

Precession photographs of fragments of the pyrrhotite confirm the common crystallographic orientation of the two phases (Fig. 4). The superstructure of the intermediate hexagonal phase is the hexagonal $2A,4C$ one previously reported from synthetic pyrrhotites (Fleet): some of the characteristic reflections of the supercell are evident in Fig. 4.

The lattice parameters, d_{102} spacings, and composition for these two phases are: troilite, $a = 3.449$ Å, $c = 5.864$ Å, $d_{102} = 2.0942$ Å, 49.9

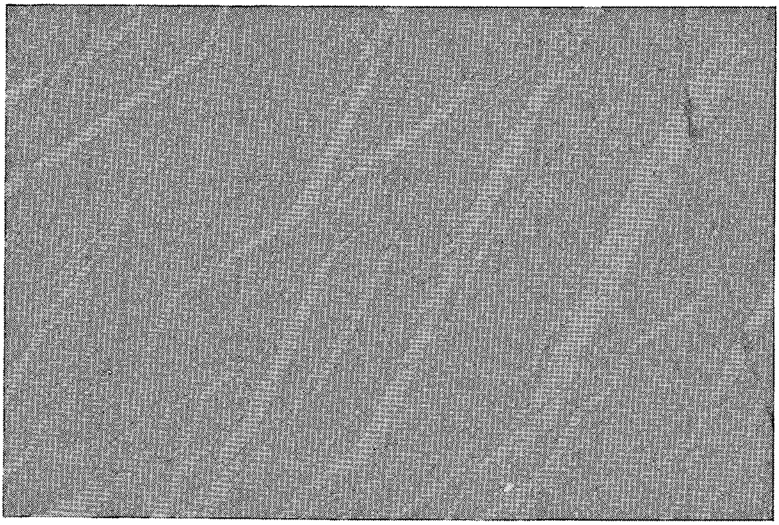

FIG. 3. Specimen 1351, two-phase hexagonal pyrrhotite. X-nicols, ×200.

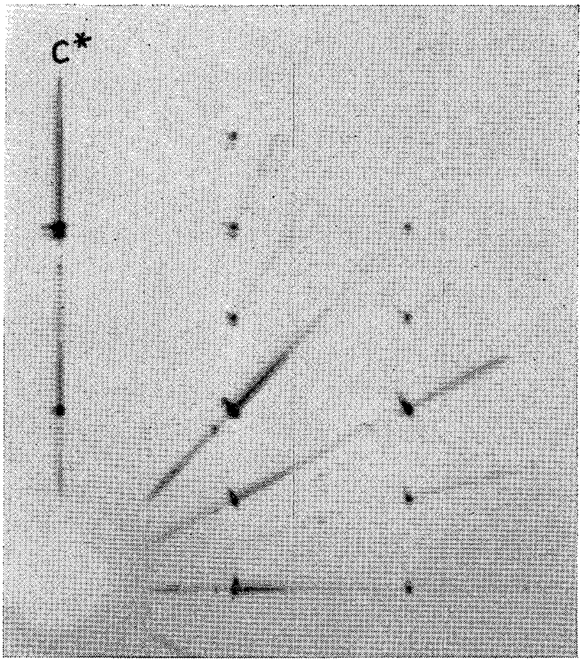

FIG. 4. Part of a zero level, *a* axis precession photograph of specimen 1351, showing crystallographic continuity of the two phases and reflections characteristic of the hexagonal 2*A*,4*C* superstructure: Mo Kα radiation, 35 Kv, 20 Ma, 29 hour exposure: *c** is vertical, *a** is horizontal.

atomic % iron; hexagonal pyrrhotite, $a = 3.437$ Å, $c = 5.734$ Å, $d_{102} = 2.0649$ Å, 47.3 atomic % iron. The parameters were determined from the precession photographs since there was insufficient material for a powder analysis.

SUMMARY

That the two phases in the pyrrhotites examined in this study have a common crystallographic orientation, within each grain, is consistent with them having been formed by exsolution. The rapidity with which the two phases are homogenised at a relatively low temperature suggests that the structural reorganisation involved is minimal and it seems probable that the unmixing occurs merely by migration of the iron atoms within the layers normal to the *c*-axis. Also, it is unlikely that one can use the interrelation of lamellae at twin boundaries to chronicle the period of deformation in those pyrrhotites which have undergone deformation, since the orientation of the lamellae is controlled solely by the orientation of the host.

The nature of the superstructure to be expected in the intermediate hexagonal pyrrhotite, co-existing with the troilite, is not restricted to the hexagonal $2A,5C$ type, and probably is not restricted to the three types now known to exist. For this reason, the genetic significance of individual superstructures in these pyrrhotites is doubtful and, clearly, much work remains to be done in this area.

Finally, the compositions of the hexagonal pyrrhotite in the two specimens examined are in agreement with the values reported by other workers for hexagonal pyrrhotite in equilibrium with troilite.

ACKNOWLEDGMENT

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