THE COMPOSITION AND MICROTEXTURE OF AN ULVÖSPINEL-MAGNETITE INTERGROWTH[1]

ERNEST H. NICKEL[2]

Mines Branch, Ottawa, Canada

ABSTRACT

Chemical analysis, x-ray diffraction, and electron microscopy have been used to determine the composition and microtexture of an ulvöspinel-magnetite intergrowth in titaniferous iron ore from Rouville County, Quebec. The composition of the ulvöspinel is estimated to be $(Mg_{0.42}Fe_{0.58})$ $(Fe_{1.03}Ti_{0.71}Al_{0.26})O_{3.90}$. It has a spinel-type structure with $a = 8.460$ Å. Electron micrographs show an exsolution texture consisting of pleonaste lamellae and magnetite cubes in an ulvöspinel matrix.

Introduction

During the course of routine ore microscopy, a shipment of titaniferous iron ore from Yamaska Mountain, Rouville County, Quebec, was examined. According to this examination the principal metallic mineral appeared to be magnetite, with ilmenite as a minor constituent. Gangue minerals were identified as apatite, augite, and biotite. Since the magnetite and ilmenite were not closely intergrown, it was inferred that they should be easily separated, and therefore that a titanium-free magnetite concentrate should be practicable. A series of ore dressing tests, however, failed to produce a low-titanium magnetic concentrate, the best one containing about 18% TiO_2. It was evident, therefore, that the mineralogy was not as simple as had at first appeared.

X-Ray Diffraction

Debye-Scherrer x-ray diffraction patterns were obtained from the magnetic concentrate and from magnetite grains gouged from the polished sections. Iron-filtered cobalt radiation ($K\alpha = 1.78890$ Å) and a large camera (114.6 mm. diameter) were used. The x-ray diffraction patterns confirmed the presence of magnetite, but they also revealed doubling of the lines in the middle and back reflection regions (Fig. 1), indicating the presence of two phases, each with a spinel-type structure. The lattice constants of the two phases, $a = 8.401$ Å and 8.460 Å, were calculated from the powder patterns using Straumanis' method of
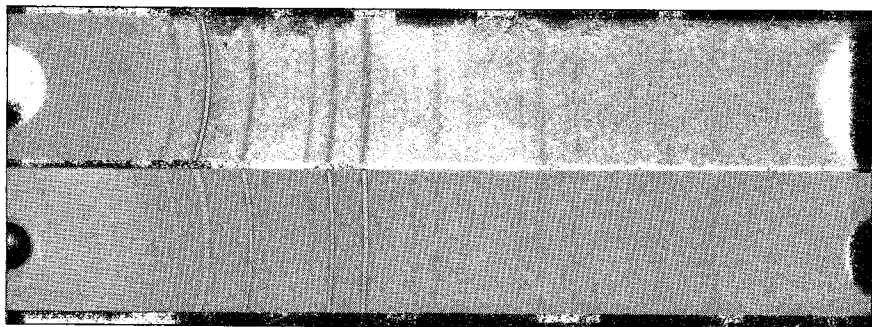
Fig. 1. Prints made from a portion of the x-ray diffraction powder patterns of the magnetic concentrate (*above*) and pure magnetite (*below*). The forward reflection region is to the left of the print. All the strong lines in the middle and back reflection region in the upper pattern exhibit doubling, indicating the presence of the two spinels—ulvöspinel and magnetite.

shrinkage correction and Bradley and Jay's extrapolation procedure for increased precision. The smaller value (8.401 Å) corresponds to the lattice constant of magnetite, while the larger value (8.460 Å) must be regarded as that of a titanium-bearing spinel.

The existence of a naturally-occurring titanium-bearing spinel was first reported by F. Mogensen (1946) in iron ore from the Ulvö Islands in northern Sweden, and he gave the lattice constant of this spinel as 8.47 Å. Ramdohr (1953) designated this mineral as ulvöspinel and assigned this name to $TiFe_2O_4$ and "mixtures of similar composition". Pouillard (1950) synthesized $TiFe_2O_4$ and found that it had a spinel-type structure with a lattice constant of $a = 8.534$ Å. He also succeeded in producing intermediate compounds between magnetite ($FeFe_2O_4$) and $TiFe_2O_4$ and concluded that a complete solid solution existed between the two end members. It seems reasonable to assign the name ulvöspinel to the titanium-bearing spinel described in this paper, and this name will be used hereafter although as is shown below, the composition of the mineral departs appreciably from $TiFe_2O_4$.

Ore Microscopy

In an attempt to distinguish the magnetite and ulvöspinel in the polished section, photomicrographs of what appeared to be magnetite grains were taken at a high magnification (Fig. 2). These showed that the grains consist of a fine intergrowth of two phases, giving the photomicrograph a mottled appearance. Enclosed in the fine intergrowth are relatively large pleonaste ($MgAl_2O_4$ spinel) lamellae rimmed by magnetite and ulvöspinel.
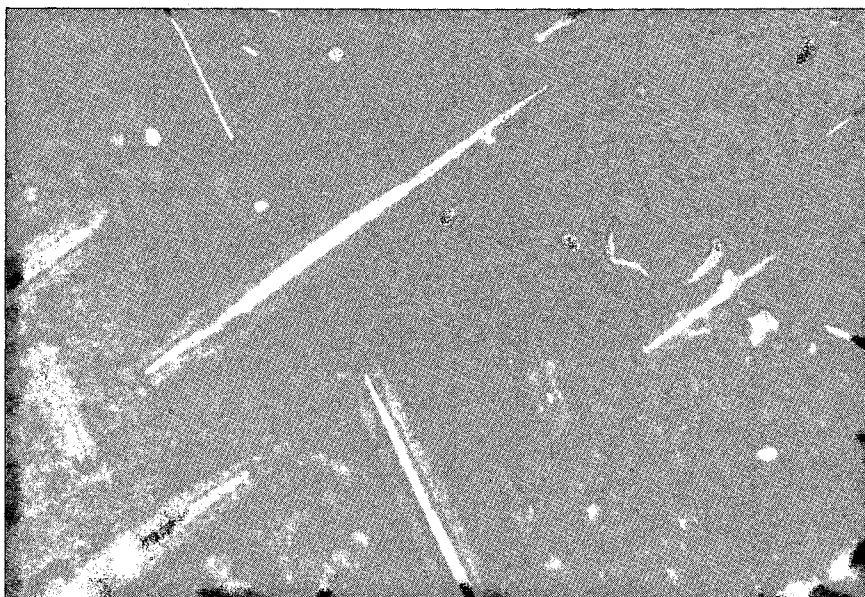
Fig. 2. Photomicrograph of polished section under oil immersion showing a ground-mass composed of barely resolved magnetite and ulvöspinel (mottled white and grey) with large oriented pleonaste lamellae (black). Magnified 2650X.

Since, at this magnification, the photomicrographs are at the limit of resolution of the optical equipment, it was decided to resort to electron microscopy to further resolve the components.

Electron Microscopy

Etching with several reagents was attempted in an effort to provide surface relief for an electron replica micrograph, and it was found that a 90-second etch with concentrated HBr was satisfactory, since the magnetite was attacked by the reagent while the ulvöspinel and pleonaste were relatively unaffected. Some of the resultant micrographs are shown in Figs. 3 to 5. The central portions of the long lamellae in Fig. 3 probably consist of pleonaste, since they are quite similar in size and shape to the recognizable pleonaste in Fig. 2. The magnetite occurs as oriented cubes in the ulvöspinel groundmass, as shown in Fig. 4 (the triangular sections in Figs. 3 and 5 are sections cutting across the cube corners), and as envelopes around the pleonaste lamellae (Fig. 3). The magnetite envelopes are broken into small oriented blocks with their sides parallel to the pleonaste lamellae and to the magnetite crystals in the intergrowth. The magnetite-ulvöspinel intergrowth continues in a uniform fashion to the edges of the intergrowth grains (Fig. 5).
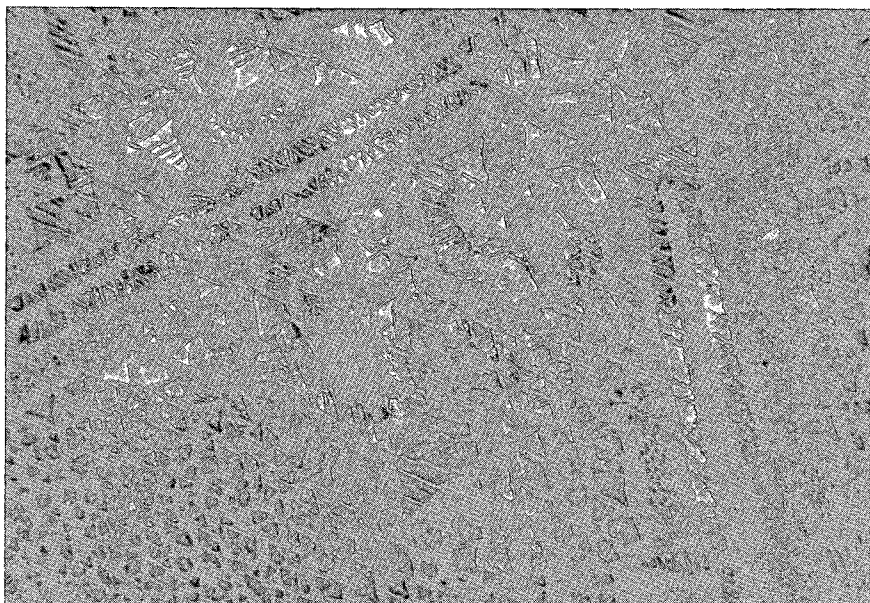
FIG. 3. Electron replica micrograph of a similar field to that in Fig. 2, etched with HBr. The grey raised portions with triangular outlines are magnetite crystals. The central portions of the long lamellae consist of pleonaste, and the rest of the light grey groundmass is ulvöspinel. Note the envelope of magnetite around the pleonaste and the larger magnetite crystals in the vicinity of the pleonaste. Magnified 6000X.

Composition of Ulvöspinel

It would, of course, be desirable to isolate the ulvöspinel from the accompanying minerals and determine its chemical composition by analysis. Mechanical separation of the ulvöspinel from magnetite is a practical impossibility, however, as the electron micrographs have indicated. A number of solvents were used in attempts to dissolve selectively either the ulvöspinel or the other minerals, using the following solvents at different strengths and for varying lengths of time: HCl, HBr, HF, H_2SO_4, $SnCl_2$, and mixtures of n-amyl alcohol and bromine. Unfortunately none of the attempts was successful.

Because of the failure to isolate the ulvöspinel, its composition had to be determined indirectly. The procedure used was as follows:

A high-grade magnetic concentrate was made from minus 200 mesh ore using Crockett and Ball-Norton magnetic separators. The chemical analysis of this concentrate is shown in column a of Table 1. The minerals present in the concentrate, in addition to magnetite and ulvöspinel, are augite, apatite, ilmenite, and pleonaste. The amount of augite present,
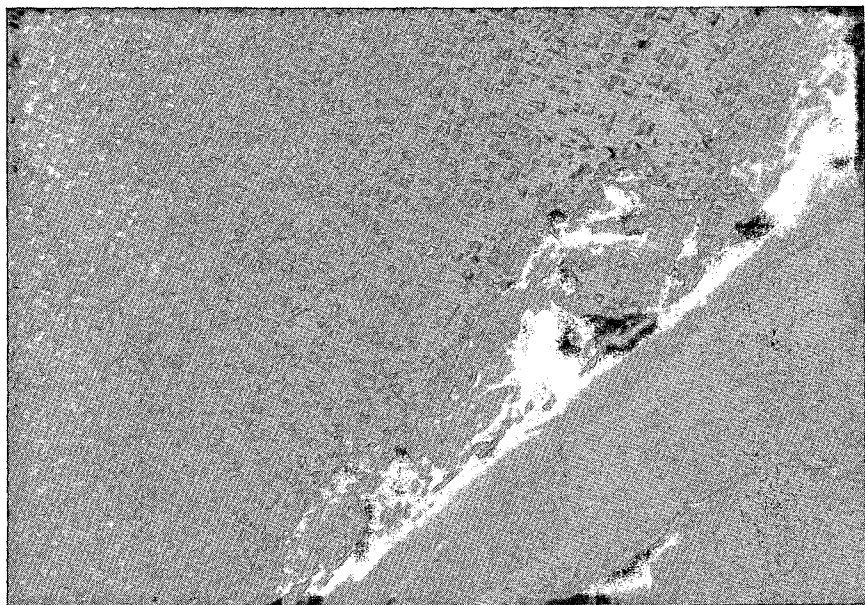
FIG. 4. Electron replica micrograph of magnetite-ulvöspinel intergrowth showing magnetite·cubes in ulvöspinel. Magnified 6000X.

calculated from the silica content, is 2.2%. The amount of apatite, cal- culated from the P_2O_5 value, is 0.7%. The content of ilmenite and pleon- aste could not be determined directly from the analysis since they have components in common with the magnetite and ulvöspinel, but their percentages can be determined by selective leaching. This was accom- plished by refluxing the concentrate with $1:2$ H_2SO_4 for varying periods of time and analyzing the liquor and x-raying the residue. It was found that after 3 hours all the magnetite and ulvöspinel were dissolved, leaving a residue of 3.0%, consisting of ilmenite and pleonaste. Further refluxing slowly dissolved the ilmenite until, after 10 hours, only pleonaste was left, to the extent of 1.8%. The residue remained unchanged even after 40 hours of refluxing. The ilmenite and pleonaste are estimated from this to be 1.2 and 1.8% respectively. The impurities (augite, apatite, ilmenite, and pleonaste) therefore total 5.9%, and the magnetite and ulvöspinel make up 94.1% of the sample.

The amounts of iron and titanium in the ilmenite, the magnesium and aluminum in the pleonaste, and the iron, magnesium, aluminum, and titanium in the augite (determined spectrographically from augite concentrated from the ore) were subtracted from the analyzed values shown in column a of Table 1. The resulting values were then multiplied
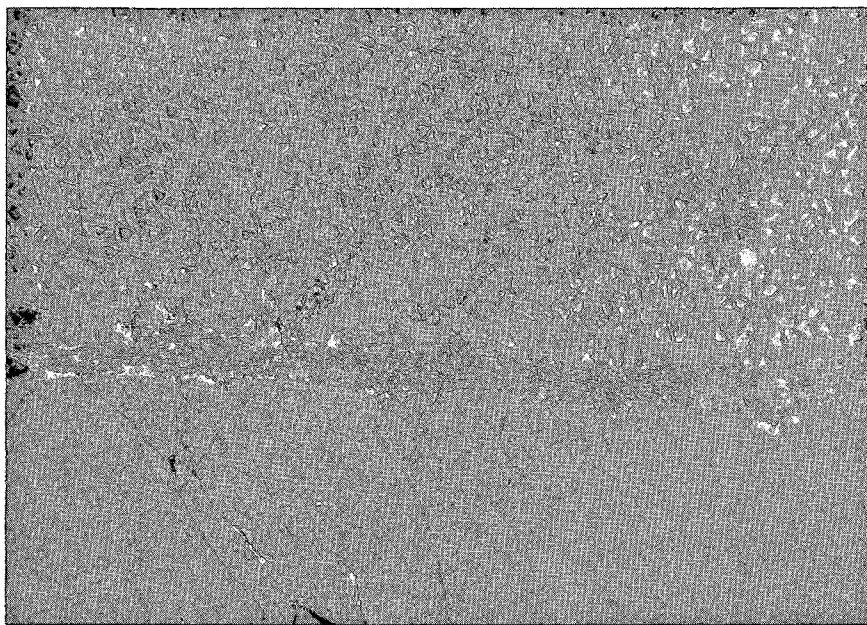
FIG. 5. Electron replica micrograph of magnetite-ulvöspinel grain boundary showing the presence of magnetite crystals in ulvöspinel up to the grain boundary. Magnified 6000X.

by the factor 100/94.1 to bring the total to 100%. The final figures, corresponding to the composition of magnetite and ulvöspinel, are listed in column b of Table 1.

TABLE 1. CHEMICAL ANALYSIS OF −200 MESH MAGNETIC CON-
TRATE AND CALCULATED COMPOSITION OF MAGNETITE-ULVÖSPINEL
INTERGROWTH

	a	b
Fe (+Mn)*	51.8%	54.3%
Ti	10.7	10.8
Al₂O₃	5.4	4.1
MgO	5.8	5.3
SiO₂	1.00	—
P₂O₅	0.29	—

a. Chemical analysis of −200 mesh magnetic concentrate.
b. Composition of magnetite-ulvöspinel mixture calculated from the analysis by adjusting for the presence of 2.2% augite, 0.7% apatite, 1.2% ilmenite, and 1.8% pleonaste.
*The iron percentage includes 0.5% manganese, which is com-combined with the iron in all subsequent calculations.

To determine the composition of the ulvöspinel alone from the composition of the magnetite-ulvöspinel intergrowth it is necessary to know the proportion by weight of the two components. Since this could not be established directly, the volume proportion was determined by a point-counting procedure carried out on electron micrographs, and this value was converted to a weight proportion by multiplying each volume by the corresponding specific gravity. The magnetite-ulvöspinel volume ratio was found to be 31.6:68.4, which is the average value of three point-counting determinations, viz. 33:67, 32:68, and 30:70. (The number of points counted on each electron micrograph was at least 700). The specific gravity of the concentrate, as determined by the pycnometer, is 4.56. When corrected for the augite, apatite, ilmenite, and pleonaste present, the value for the magnetite and ulvöspinel together is increased to 4.61. Assuming the specific gravity of pure magnetite to be 5.20, and knowing the volume percentage of the two components, a simple arithmetical calculation shows that the specific gravity of the ulvöspinel is 4.34, and that magnetite and ulvöspinel are present in the weight ratio of 35.6:64.4.

Assuming the magnetite to be pure Fe_3O_4, i.e. with an iron content of 72.4%, the amount of iron as magnetite in the intergrowth is 0.356×72.4 = 25.8% Fe. The composition of the ulvöspinel alone, therefore, is that shown in column b of Table 1 minus the 25.8% Fe, with each value divided by 0.644, the decimal fraction of ulvöspinel in the intergrowth. The resultant ulvöspinel composition, in terms of metal percentages, is given in the first column of Table 2.

TABLE 2. COMPOSITION AND UNIT CELL CONTENTS OF ULVÖSPINEL

	Wt. %	At. wt.	At. prop.	Unit cell contents	Weight of unit cell contents
Fe (+Mn)	44.3	55.85	0.793	12.92 ⎫	721.6
Ti	16.8	47.90	0.351	5.71 ⎪ 24.00	273.6
Al	3.4	26.98	0.126	2.05 ⎬	55.4
Mg	4.9	24.32	0.203	3.32 ⎭	80.6
O (by diff.)	30.6	16.00	1.912	31.15	498.5
	100.0				1629.7

Table 2 also includes the figures used in calculating the "molecular weight" or, more correctly, the weight of matter contained in a unit cell. The atomic proportions are obtained by dividing the weight percentage of an element by its atomic weight. The unit cell contents are derived by multiplying the atomic proportions by a factor to bring the

total number of metal atoms to 24, the number of di-and trivalent atoms in the unit cell of a spinel-type compound. The weight of the unit cell is obtained by multiplying the number of atoms of each element (unit cell contents) by the atomic weight of the elements and adding these products, resulting in a value of 1629.7.

The preceding calculations can be checked by determining the weight of the unit cell by another method, using the volume of the unit cell and the specific gravity of the mineral. The formula used is $M = V\rho/1.6604$ where V is the volume of the unit cell in Ångstrom units and ρ is the density of the mineral. The cell edge of the ulvöspinel has been noted previously as being 8.460, so the volume of the unit cell is simply $(8.460)^3$. The density of ulvöspinel, as noted earlier, is 4.34 g/cc. Using these figures, M is calculated to be 1583. This value is about 3% lower than that given in Table 2, but the agreement is considered to be satisfactory, in view of the assumptions made in calculating the composition.

It is not known how the 24 metal atoms are distributed among the A and B positions in the spinel unit cell $A_8B_{16}O_{32}$. In the case of divalent and trivalent atoms, the distribution of the metals appears to be $A^{+2}B_2^{+3}O_4$, as in $MgAl_2O_4$. If, in the case of ulvöspinel, magnesium is considered to be divalent, aluminum and titanium trivalent, and the iron is distributed between the A and B positions to yield the required 1:2 ratio of divalent to trivalent atoms, the formula of the ulvöspinel is $(Mg_{3.32}Fe_{4.68})(Fe_{8.24}Ti_{5.71}Al_{2.05})O_{31.15}$. By dividing through by 8 to obtain the AB_2O_4 formula, it becomes $(Mg_{0.42}Fe_{0.58})(Fe_{1.03}Ti_{0.71}—Al_{0.26})O_{3.90}$. An alternative way of considering the composition is as a solid solution between two end members: $A^{+2}(Ti^{+4}A^{+2})O_4$, where an electron transfer between two adjacent B^{+3} ions results in a $(Ti^{+4}A^{+2})$ combination without structural change, and $A^{+2}B_2^{+3}O_4$. The A positions would be occupied by divalent magnesium and iron, and the B positions by trivalent aluminum and iron. This assumes that the titanium in the mineral has a valency of 4 and requires most of the iron to be divalent rather than trivalent. The coordination of the cations would be the same as expressed by the chemical formula given above, however.

This formula is offered as a solution to the ulvöspinel composition, but the final evaluation of the valence states of the ions is outside the scope of this paper.

Discussion

The magnetite-ulvöspinel-pleonaste intergrowth is very likely the result of exsolution from an original spinel solid solution. That this intergrowth is not the result of replacement is evident from the uniformity of the intergrowth up to the margins of the grains (Fig. 6). The pleonaste

probably exsolved first since the exsolution bodies are in general much larger than those of the magnetite. A possible reason for this is that the cell constant of the pleonaste (8.080 Å) is quite different from those of magnetite (8.401 Å) and ulvöspinel (8.460 Å), which may make this component the least stable one in a solid solution of these three members. The pleonaste lamellae probably served as nucleii for the crystallization of the magnetite, and triggered the formation of magnetite crystals nearby, giving rise to the magnetite rim around the lamellae and the coarse magnetite crystals in the immediate vicinity of the lamellae, in contrast to the finer-grained crystals a short distance away (Fig. 3).

Homogenization of the intergrowth is readily achieved by heating it to about 1000°C. A powder pattern of a sample heated in vacuum to this temperature revealed only one spinel-type compound with a lattice constant of 8.438Å, which is intermediate between that of the magnetite (8.401 Å) and ulvöspinel (8.460 Å).

The occurrence of ulvöspinel as a matrix for exsolved magnetite crystals as described in this paper, appears to be rather unusual, as Ramdohr (1955) finds that the most common occurrence of this mineral is as extremely fine networks in magnetite parallel to (100). The amount of titanium present in the original spinel solid solution probably determines which mineral forms the matrix and which one the crystallites. When the titanium content is high, the ulvöspinel would be more likely to form the matrix, as in the present case, whereas with a low titanium content, magnetite would be more likely to form the matrix and ulvöspinel, the crystallites.

Acknowledgments

REFERENCES

MOGENSEN, F. (1946): A Ferro-ortho-titanate ore from Södra Ulvön, *Geol. Fören. Förhandl.*, **68**, 578–588.

POUILLARD, E. (1950): Sur le Comportement de L'Alumine et de L'Oxyde de Titane vis-a-vis des Oxydes de Fer. II. Etude du System TiO_2-Fe_2O_3-FeO, *Ann. de Chimie*, **5**, 190–214.

RAMDOHR, P. (1953): Ulvöspinel and its significance in iron ores, *Ec. Geol.*, **48**, 677–688.

———— (1955): *Die Erzmineralien und ihre Verwachsungen*, Akademie-Verlag, Berlin, 875 pp.