

SOME CHROMITE-ILMENITE ASSOCIATIONS IN THE MERENSKY REEF, TRANSVAAL¹

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ABSTRACT

Microscopy showed five types of relation of ilmenite to chromite in the Merensky platiniferous horizon of the Bushveld Complex: (1) irregular grains of ilmenite in pyroxenite without chromite, (2) ilmenite-rutile grains enclosed in chromite, (3) Lamellae of ilmenite in chromite with a selvage of low-ferric chromite with low reflectivity, (4) Skeletal and pseudographic intergrowths of ilmenite with chromite, again with low-iron borders, and (5) Massive aggregates of large grains of ilmenite and chromite. As the ferric oxide content (and reflectivity) of the chromite increases, rutile is superceded by ilmenite as the titanium-bearing phase.

The ilmenite lamellae may have formed by oxidation of ulvospinel, and the ferric-poor chromite was segregated at the contact. Conditions of high temperature, low oxygen fugacity, and very slow cooling were required.

INTRODUCTION

During a mineralogical study of chromite from the chrome bands of the Merensky Reef, the platiniferous horizon in the upper part of the Critical Zone of the Bushveld Igneous Complex of the Transvaal, described by Beath, Cousins and Westwood (1961), some interesting occurrences of ilmenite in association with chromite were observed. The samples were studied in reflected light, and by X-ray diffraction and electron-probe micro analysis. All reflectivity measurements quoted were made using the method of Santokh Singh (1965) on a Reichert photomultiplier fitted to a Reichert Zetopan ore microscope. Measurements were made at a wavelength of 520 nanometers against a carborundum standard.

THE OCCURRENCE OF ILMENITE

Ilmenite was observed to occur in five different types of association with chromite.

1. As discrete irregularly shaped grains enclosed in pyroxenite. Ilmenite in this form was observed in samples from all levels of the Merensky Reef, as well as from lower chrome seams, and appears to be interstitial to pyroxene, occurring in a very similar manner to the abundant associated sulphides. The ilmenite is never seen in contact with chromite, and its occurrence bears no relationship to chromite composition.

2. Composite grains of ilmenite with rutile, enclosed in chromite, are

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common in the basal chrome band of the Reef. They are usually sub-spherical in shape, and show no preferred orientation in the host chromite, although a few examples are lamellar in form and appear to be orientated parallel to the (111) planes of the chromite. Ilmenite and rutile show sharp margins against each other, and the surrounding chromite is unaltered. Grains of this type are found in chromite having a reflectivity of between 14.0 and 14.5 percent in air at 520 nm.

3. Lamellae and minute equant grains of ilmenite occur in samples from all three chrome bands of the Reef. In chromites with a reflectivity of about 14.5 percent they are associated with lamellae of rutile, both types of lamellae showing an orientation parallel to the (111) planes of the host. In chromites of higher reflectivity rutile is absent, and the ilmenite lamellae may be associated with other types of ilmenite occurrence. Small equant grains show margins which are parallel with the principal directions of the lamellae. Lamellae of ilmenite vary in size from those just visible under the highest magnification available (x2000) to laths up to 0.25 mm in length. In many cases the chromite immediately adjacent to ilmenite has a lower reflectivity than the main part of the chromite grain, the low reflectivity chromite grading into normal chromite. In some samples two distinct generations of ilmenite lamellae can be seen. Large lamellae orientated in the (111) directions with distinctly darkened contact zones are surrounded by chromite containing large numbers of minute ilmenite lamellae orientated in a single direction which is not parallel with the directions of the large lamellae. The presence of darkened chromite around each minute lamella gives a mottled or rippled appearance to the chromite (Fig. 1). Zones of darkened chromite

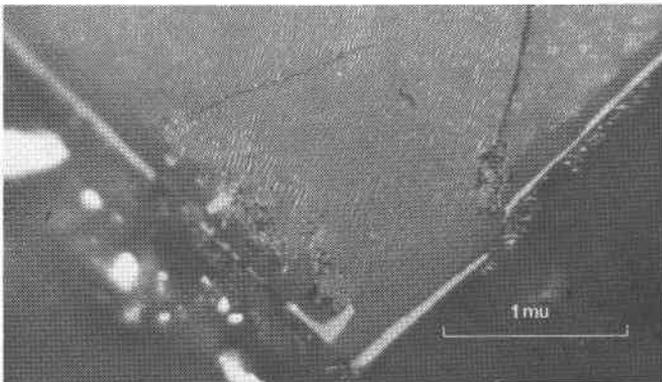


FIG. 1. Chromite (gray) containing large numbers of lamellae of ilmenite (light gray) orientated in a single direction. Note rims of ilmenite around the chromite grain and darkening of chromite adjacent to ilmenite.

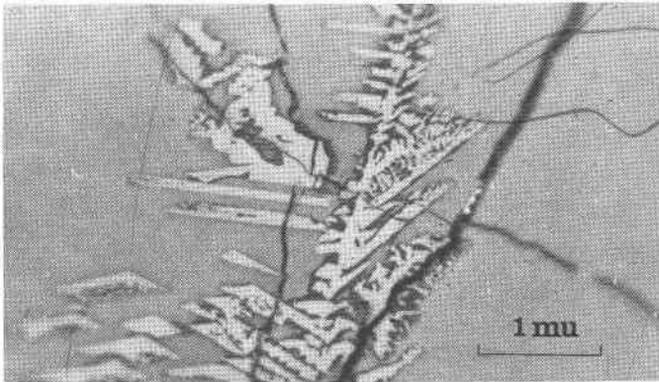


FIG. 2. Skeletal ilmenite (light gray) in chromite. Note the presence of the dark iron-poor chromite phase at chromite-ilmenite contacts. Irregular black lines are cracks in the surface of the sample.

around large ilmenite lamellae are free from the smaller lamellae. The large lamellae sometimes form rims around grains of chromite.

4. In some samples from the upper chrome band at Union Platinum Mine, large lamellae of ilmenite pass laterally into skeletal intergrowths of ilmenite with chromite (Fig. 2), which can in turn grade into disorientated pseudographic intergrowths (Fig. 3). In all cases there is a sharply defined zone of lower-reflectivity material adjacent to ilmenite, as well as numerous inclusions of the darker material within ilmenite. In a few cases the darker material grades into normal chromite, but more commonly the contact is sharp. The contact between the dark material and ilmenite is often fractured and infilled with later silicates, but the contact with chromite is never fractured and is microscopically crenulate. The

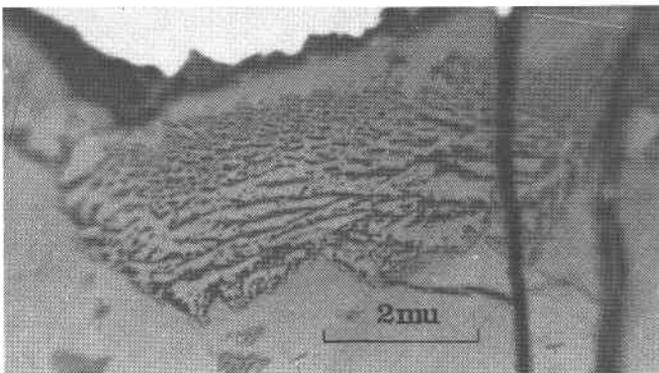


FIG. 3. Pseudographically intergrown ilmenite and iron-poor chromite with iron-rich chromite in the lower part of the picture. White is sulphide.

reflectivity of chromite containing ilmenite in this form is between 15.5 and 16.5 percent. No rutile is present in these samples.

5. Large grains of ilmenite occur with chromite, forming a massive aggregate in two samples from Union Mine. The grains show mutual boundaries with chromite, a rim of the dark phase being always present at the contacts. (Fig. 4). Lamellae and skeletal crystals of ilmenite sometimes project from the large grains into the surrounding chromite, and are in optical continuity with the large ilmenite grains. Some smaller euhedral ilmenite grains contain inclusions of the dark phase arranged in a pseudographic fashion (Fig. 5).

THE IDENTITY OF THE DARK PHASE

The identity of the dark phase has been established from its optical properties, relative hardness, X-ray diffraction pattern and approximate chemical composition. The reflectivity was measured in twelve places, giving an average value of 12.0 percent in air at 520 nm. Using a Nomarski interference contrast device, the dark phase was found to be harder than both ilmenite and the iron-rich "normal" chromite. The mineral is always isotropic and in some cases shows dark-green internal reflections. An X-ray diffractometer trace from a sample containing this mineral showed in addition to peaks of iron-rich chromite and ilmenite some peaks which could be assigned to an iron-poor chrome-aluminum spinel. Examination of one sample with a Cambridge electron-probe micro-analyzer showed that the dark phase is richer in chromium and poorer in iron and titanium than the surrounding iron-rich chromite. The dark

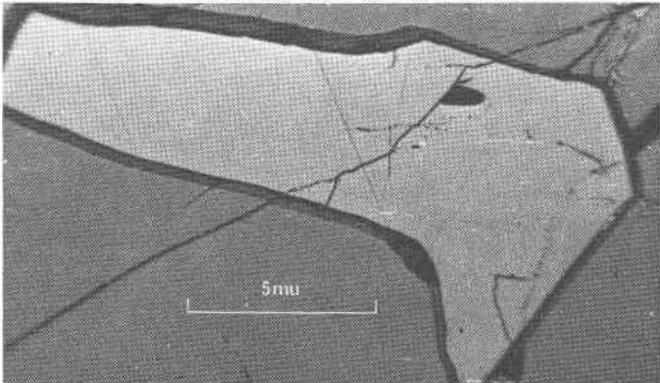


FIG. 4. An ilmenite grain (light gray) enclosed in chromite (gray) Note the presence and uniform thickness of iron-poor chromite (dark gray) at the chromite-ilmenite contact, and the fracturing (black) along the contact of ilmenite with iron-poor chromite but rarely along the contact between iron-poor and iron-rich chromite.

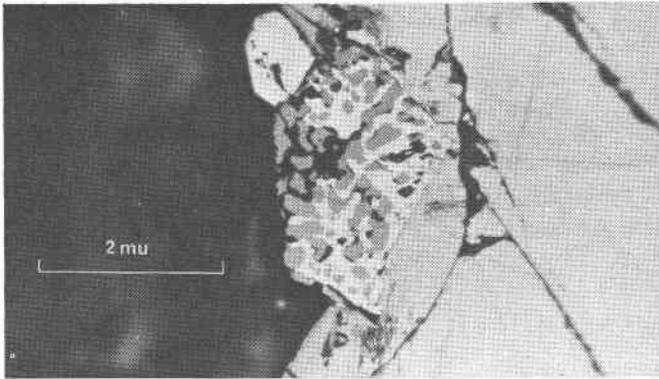


FIG. 5. Euhedral grain of ilmenite partially surrounded by iron-rich chromite and intergrown in a random fashion with iron-poor chromite.

phase is thus an iron-poor chromite, probably containing substantial amounts of magnesium and aluminum in addition to chromium and iron.

COMPOSITION OF THE CHROMITE

Some of the chromites examined during the course of this study were partially analyzed on the electron probe. Partial analyses for two typical chromites with their reflectivities and mineral association are given in Table 1. It was found that chromite reflectivity increased with increasing ferric iron content (Legg, In prep.), and reflectivity can thus be used as a guide to the approximate ferric iron content of the specimens studied.

DISCUSSION

As the ferric iron content of the chromite increases as indicated by increasing chromite reflectivity, rutile appears to be superseded by ilmenite

TABLE 1. COMPOSITIONS OF TYPICAL MERENSKY-REEF CHROMITES^a

Description	Fe ₂ O ₃	Cr ₂ O ₃	Al ₂ O ₃	R% at 520 nm	Mineral associations
Lower chrome band Rustenburg Mine	16.0	43.0	10.5	13.9	Rutile only
Upper chrome band Union Mine	39.4	16.8	12.3	15.8	Ilmenite and iron-poor chromite

^a Analysed for Fe, Cr and Al only against pure element standards on Cambridge Geoscan Electron Probe Microanalyzer. Analyses corrected for atomic number, fluorescence and absorption using IBM computer. Fe₂O₃ is approximate only, being calculated from total Fe, assuming 68.50% by weight of trivalent oxides.

as the titanium-bearing phase present. Increasing amounts of ferric iron in the chromite may favor the formation of an iron-titanium oxide (ilmenite) in preference to a titanium oxide (rutile). Wittke (1967) has shown that the solubility of ferric iron in rutile does not exceed three cation percent even at high temperatures. As pointed out by Lindsley (1962), ilmenite lamellae can be present in spinels with a minimum of deformation of the host spinel lattice, while rutile shows no close structural fit in the lattice. Therefore it would appear that the formation of ilmenite in a spinel by whatever means would produce less lattice distortion and require less "energy" than the formation of rutile and in the presence of available ferric iron ilmenite would be formed preferentially.

The varied associations of ilmenite with chromite described above suggest that ilmenite or other titanium-bearing minerals must either have been soluble at high temperatures in iron-rich chromites and then have segregated on cooling, or a complex process of simultaneous crystallization of chromite and titanium-bearing minerals must have been operative. The large ilmenite grains observed in samples from the upper chrome band at Union Mine were almost certainly formed simultaneously with chromite, but in view of the orientation of ilmenite intergrowths with chromite, it seems unlikely that complex intergrowths of chromite, ilmenite and spinel could have formed by this process.

Ramdohr (1953) and others have suggested that ilmenite lamellae in titanomagnetite can form by oxidation of exsolved ulvospinel. Ilmenite lamellae formed by this process would show oblique extinction whereas lamellae formed by subsolidus oxidation of titanomagnetite solid solution would show straight extinction. Most of the ilmenite lamellae in chromite show oblique extinction indicating that they could have been produced by oxidation of a form of ulvospinel.

The iron-poor chromite which is almost always present at ilmenite-chromite boundaries could have been formed by reaction between the two minerals or by exsolution or similar segregation from one of them. The first possibility is ruled out by the fact that the iron-poor phase is not always in contact with chromite, but can be totally enclosed in ilmenite. Following the same reasoning, ilmenite must be the parent of any exsolution or breakdown process. The often close spatial relationship between iron-poor chromite and normal chromite is probably a result of the close structural similarity between the two spinel phases, which might favour segregation of iron-poor chromite at the contact between ilmenite and iron-rich chromite.

No data are available on the existence of a chrome-rich ulvospinel-type phase at high temperatures, or on the solid solution relationships between ulvospinel and members of the spinel series other than magnetite.

It is postulated that if a chrome-rich ulvospinel were exsolved from a titanium-rich ferrian chromite at high temperatures and was later oxidized to form ilmenite, a second phase incorporating the chromium from the ulvospinel would be formed as a by-product of this oxidation. This phase would be an iron-poor chromite. Slow oxidation could result in some segregation of the two phases into pseudographic and disordered intergrowths where the original ulvospinel grains were large, or could produce rims of the chromite phase at the margins of thin lamellar and dendritic intergrowths in iron-rich chromite. It is probable that the large ilmenite grains observed in some samples were formed as a primary phase from a titanium-rich magma, and that they either contained some chromiferous ulvospinel in solid solution or were rimmed with ulvospinel which oxidised to produce additional ilmenite with iron-poor chromite at the contacts with iron-rich chromite. The latter explanation seems the most likely as there is no evidence for solid solution between ilmenite and ulvospinel.

In the absence of sufficient available ferric iron in the primary chromite phase, early exsolution of ulvospinel would not occur; any titanium in the chromite exsolving as rutile without any intermediate phases. Composite grains of ilmenite and rutile observed in a few samples could have formed by the breakdown of exsolved pseudobrookite on cooling below 1140°C (Lindsley 1965).

Ramdohr (1963) describes associations of chromite, ilmenite and suspected rutile in meteoritic material. He describes textures indicating exsolution of ilmenite from chromite and spinel, and of rutile from chromite and ilmenite. Associations of rutile and ilmenite with chromite in meteorites are described by Buseck and Keil (1966). Rutile lamellae appear to have exsolved from chromite and from ilmenite while chromite appears to have exsolved from ilmenite and from rutile. Analyses of chromites sometimes show minor amounts of titanium (Palache *et al.*, 1944; Buseck and Keil, 1966), but in view of the very small size of titanium-bearing inclusions in chromite recognised in the course of this study, such results must be treated with caution. Similar reservations must be held about ilmenite analyses showing minor amounts of chromium.

The ilmenite-chromite associations described briefly above can only be satisfactorily accounted for by the postulation of high-temperature exsolution at low oxygen fugacity and with very slow cooling of a chromiferous ulvospinel from titanium-rich ferrian chromite, and by later breakdown of this exsolved phase by a process of oxidation to form ilmenite and iron-poor chromite. There is a need for experimental work on the relationships between titanium-bearing minerals and coexisting members

of the spinel group other than magnetite. The investigation of high-temperature phase equilibria in the system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2-\text{Cr}_2\text{O}_3$ could prove especially rewarding.

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