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Flux growth of Fe_2TiO_4 from BaO-B_2O_3 in an iron crucible

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Crystals of titanomagnetite have been grown from a barium borate flux in an iron crucible under an atmosphere of nitrogen following preliminary phase equilibrium and solubility studies. The crystals were octahedral, up to 4 mm in width, and their composition corresponded to the formula $Fe_{2.12}Ti_{0.88}O_4$. The Néel point was found to be 195 K.

1. Introduction

Titanomagnetite, Fe_2TiO_4, is of interest in rock magnetism and related earth sciences. It possesses the inverse spinel structure, with the Ti^{4+} ions in octahedral sites and the Fe^{2+} ions equally divided between the tetrahedral and octahedral sites. It is paramagnetic at room temperature, but weakly ferrimagnetic below 115 K. Magnetization of 0.36 μ_B per molecule at 2.4×10^6 A m^{-1} has been reported, although a simple model with anti-parallel spins would suggest antiferromagnetism [1, 2].

Fe_2TiO_4, which occurs in nature as the mineral ulvöspinel, is found only in the form of a fine intergrowth with magnetite in igneous rocks. Since ulvöspinel and magnetite are isostructural, they form a complete series of solid solutions of titanomagnetites, $Fe_{3-x}Ti_xO_4$, at high temperatures (above about 800°C). The middle members of the series tend to segregate into spinels which are, respectively, richer and poorer in iron, and this may account for the ulvöspinel-magnetite intergrowth.

Single crystals of titanomagnetites were first synthesized by Syono [3] by the Bridgman method. A special technique for the fast production of titanomagnetite crystals from the melt was subsequently devised by Hauptman and Stephenson [4] and further developed by Hauptman [5].

The growth of these crystals by a flux method, which has not previously been reported, is described below. This method was favoured since it was anticipated that the crystals would be of more uniform composition and of greater perfection. In addition, crystals with habit faces were desirable since these could be easily orientated.

The equilibrium oxygen fugacity for Fe_2TiO_4 at 1200°C is of the order of 10^{-12} atm, and the phase diagram constructed by Taylor [6] indicates that a composition very near to Fe_2TiO_4 should co-exist with iron in the temperature range between 1300°C and the melting point of Fe_2TiO_4 (1395 ± 5°C). This has been verified by the authors, who found that when a sintered tablet of Fe_2TiO_4 was placed in a sealed iron ampoule, with the mineralizer $TeCl_4$ [7] to promote crystallization, the spinel phase was still dominant after several days at 1300°C. EPMA showed that $FeTiO_3$ and iron were also present as minor phases.

Although the flux growth of oxide crystals is usually performed under oxidizing conditions, it may be extended to reducing conditions provided that both crucibles and fluxes are compatible with the oxygen fugacity of the surrounding atmosphere. For example, iridium has been used for the growth of MnO under N_2 [8], graphite for the growth of $CeAlO_3$ [9] and V_2O_3 [10], and graphite or tungsten for Ti_nO_{2n-1} [11]. In the case of Fe_2TiO_4, it appeared that an iron crucible would be suitable, since in an inert gas it would act as a natural oxygen buffer and precise control of the oxygen fugacity would be unnecessary.

2. Experimental

2.1. Chemicals

BDH Laboratory Reagent grade BaO, B_2O_3 and TiO_2, Koch Light 99.9% pure iron powder, and Mapico Products 99.8% pure Fe_2O_3 were used.

2.2. Flux

The flux system BaO-B_2O_3 has proved suitable for growing iron spinels and a composition of 78wt % BaO + 22wt % B_2O_3 [12] was chosen for this work.

2.3. Preparation of solute

Pressed tablets of Fe_2TiO_4 were prepared from a stoichiometric mixture of Fe, Fe_2O_3 and TiO_2 by sintering at 1300°C in a mullite tube which contained a CO_2-CO buffer.

2.4. Solubility determination

Preliminary solubility determinations were carried out in an iridium strip crucible [5]. A 100 mg melt, which consisted of 90 wt % flux and 10 wt % Fe_2TiO_4, was held at 1020°C in a 66% CO_2-34% CO atmosphere. A weighed crystal (60 mg) of approximate composition $Fe_{2.4}Ti_{0.6}O_4$, which had been previously grown from a melt on the tip of a 0.1 mm Ir wire, was then lowered into the melt. A viewing window in the apparatus enabled the dissolution-crystallization balance to be observed and controlled. When equilibrium had been attained, the undissolved part of the crystal was quickly withdrawn and weighed. The solubility at 1020°C was found to be 33 wt%.

Since the eutectic temperature is at about 950C° and Fe_2TiO_4 melts at 1395°C, the solubility at 1200° was expected to be about 50%. However, to be certain of complete solution in the flux, only 45 wt % solute was used in the crystal growth experiment.

2.5. Crystal growth

A 30 cm^3 iron crucible was used to contain the charge and was supported by refractory brick inside a mullite tube as shown in Fig. 1. The tube was placed on the hearth of a muffle furnace between two vertical arrays of horizontal crusilite elements. The temperature gradient inside the tube was such that the base of the crucible was about 5 K cooler than the top. The open end of the tube fitted into a water-cooled brass cylinder and the joint was made gas-tight by means of an "O" ring seal.

The tube was evacuated twice and flushed with nitrogen. The gas was then passed through the apparatus at 100 cm^3 min^{-1} and the internal pressure was maintained slightly above atmospheric for the duration of the experiment. The furnace was heated to 1200°C at 100 K h^{-1}, held at this temperature for 6 h, cooled to 900°C at 3 K h^{-1}, and finally cooled at 100 K h^{-1} to room temperature.

At the end of the experiment, the crystals were recovered by dissolving the flux (and the crucible) in hot 1:5 nitric acid.

3. Results

The crystals comprised shiny black octahedra with well developed {111} faces, up to 4 mm across, as shown in Fig. 2, and smaller, transparent, light yellow pseudocubes. The former were identified as titanomagnetite, the latter as barium titanate, $BaTiO_3$.

The titanomagnetitite crystals were characterized as follows.

1. Highly polished cross-sections of several

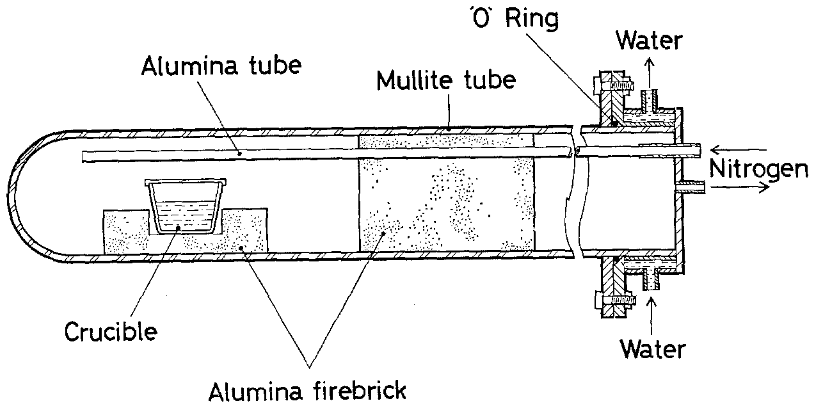

Figure 1 The apparatus.

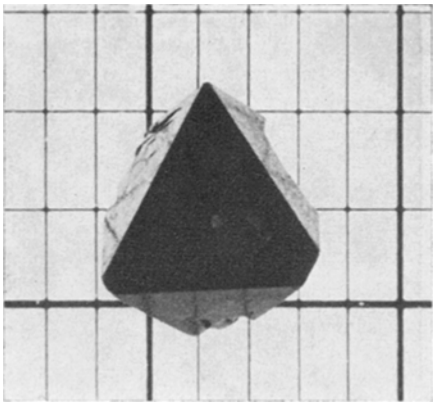

Figure 2 {111} face of Fe_2TiO_4 crystal (1 mm × 2 mm scale).

crystals were examined under an ore microscope and the crystals of more perfect appearance were found to be free or almost free of optically visible internal imperfections. The imperfections were of two types: an included greyish phase distinguishable in reflected light from the brown-black background of titanomagnetite, and trapped, overgrown small crystals of barium titanate, usually at the edges of the titanomagnetite crystals.

2. A cross-section was examined more closely by EPMA. The greyish inclusions were too small and shallow to allow a reliable quantitative analysis, but semi-quantitative analysis revealed the presence of about 45% Ba, 20% Fe and 2% Ti. The included phase was found to exhibit spontaneous magnetization at room temperature.

The intensitites of the spectral lines of Fe and Ti from different parts of several titanomagnetite crystals in the inclusion-free regions were very consistent, and EPMA indicated that these contained 52.4% Fe and 18.8% Ti. Assuming the balance to be oxygen, the calculated composition can be expressed by the formula $Fe_{2.12}Ti_{0.88}O_4$.

3. The concentration of Fe^{2+} ions was determined by titration against ceric sulphate. Analyses of three crystals yielded a value of 46.0 ± 0.1% Fe^{2+}. This result is in reasonable agreement with the above formula (which requires 46.7% Fe^{2+}).

4. The X-ray powder patterns of a selected, well formed crystal, taken with an ordinary 114 mm diameter camera and with a Guinier camera,

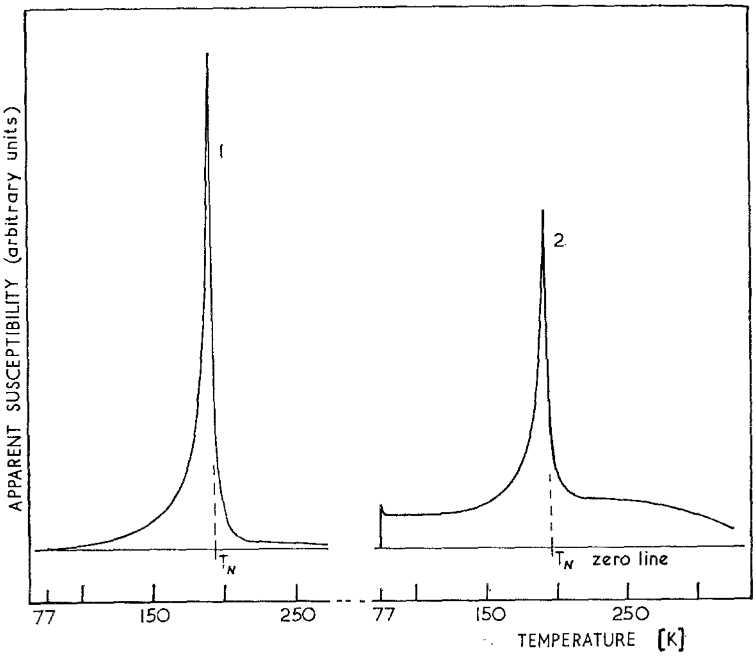

Figure 3 Facsimiles of curves of susceptibility versus temperature, from which the Néel points were determined. The peak values of susceptibility are of the order of 10^{-2} emu g^{-1}. Curve 1 is typical of an inclusion-free crystal, curve 2 shows a "background" susceptibility owing to inclusions.

using Fe$K\alpha$ radiation, showed lines of the spinel phase only. No traces of other phases were observed.

5. Graphs of apparent susceptibility versus temperature, which were determined by means of a low field susceptibility bridge [13], showed an extremely sharp drop in the susceptibility when the temperature of the magnetic transition was reached on slow heating from 77 K (see Fig. 3). The projections of the dropping sections of the Hopkinson peaks on the temperature abscissae were taken as the Néel temperatures.

The average Néel point for ten crystals was 195 K and the largest difference was 6 K. This indicated that there was little variation in the composition of the crystals, since a change $\Delta x = 0.1$ in composition corresponds to a change of about 70 K in the Néel temperature. The measurement of susceptibility also proved to be a useful, non-destructive method of detecting the magnetic, barium-containing inclusions, as is evident from Fig. 3. For "pure" crystals, the apparent susceptibility was nearly zero before and after the transition (curve 1), but crystals which contained inclusions showed some "background" susceptibility and this remained constant within the temperature interval which was studied (curve 2).

4. Conclusions

The experiment showed that crystals containing iron ions in a predominantly Fe^{2+} state can be grown by a flux method. Since titanomagnetite is an example of those compounds which contain transition metal ions in more than one valence state, it is evident that the method would need modification if strict adherence to the stoichiometry were required.

In titanomagnetites, the stoichiometry is defined by two parameters, x and γ, according to the formula:

$$Fe^{2+}{}_{1+x-2\gamma}\,Fe^{3+}{}_{2-2x+2\gamma}\,Ti_x{}^{4+}O_{4+\gamma}$$
$$(0 < x < 1, 0 \leqslant \gamma \leqslant \gamma_c(T))$$

where γ is a function of oxygen fugacity and temperature, and could be experimentally controlled by an appropriate gaseous buffer, such as CO/CO_2 in synchronism with the temperature programme. The maximum or critical value, $\gamma_c\,(T)$, for a given titanomagnetite is a function of temperature only, and at 1200°C is about 0.04. In this experiment x was slightly affected by a reaction between solute and flux, which resulted in $BaTiO_3$, and thus the TiO_2 content of the solute was reduced.

The observed change in composition from that of the initial solute can be explained by the following reaction:

$$Fe_2TiO_4 + \frac{1-x}{3-x}\,O_2 + \frac{3(1-x)}{3-x}\,BaO$$
$$\rightarrow \frac{2}{3-x}\,Fe_{3-x}\,Ti_xO_4 + \frac{3(1-x)}{3-x}\,BaTiO_3.$$

For the observed value of $x = 0.88$, the value of $(1 - x)/(3 - x)$ is 0.057. The extent of the reaction is clearly controlled by the availability of oxygen in the environment.

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