Solid solution of TiO$_2$ in mullite

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Titania is one of the most common impurities found in silico-aluminate minerals. Although various studies have been carried out on the solid solubility limit of titania in mullite, there is no agreement on the actual value. Green and White [1] fixed this limit at 4 wt % titania at 1720° C; Murthy and Hummel [2] found maximum solubilities of 2 to 4 wt % TiO$_2$ in synthetic mullites after firing at 1400, 1600 and 1700° C; Glesdorf *et al.* [3, 4] fixed the limit at 2 to 2.5 wt % TiO$_2$ at 1700° C and McGee and Wirkus [5] at 3 wt % TiO$_2$ at 1700° C. Caldwell *et al.* [6] found that in a bauxite that had been slowly cooled from 1700° C the mullite contained 3.3 wt % TiO$_2$, and Agrell and Smith [7] found natural mullites containing 0.55, 1.29 and 2.27 wt % TiO$_2$.

The titania solid solubility limit in mullite has been determined in this work by X-ray diffraction* and by X-ray dispersive energy (Kevex)† techniques.

A type of disordered mullite (premullite), very active, (72.80 wt % Al$_2$O$_3$, 26.92 wt % SiO$_2$, 99.9 purity) was used as the starting material. It was obtained on the basis of the theoretical and experimental researches carried out by Moya *et al.* [8, 9].

Titania and premullite mixtures with titania proportions running from 0 to 5 wt % have been studied. The mixtures were homogenized in an agate mortar with isopropyl alcohol, pressed at 30 MPa, and fired at 1600° C for 20 h with intermediate milling in order to achieve equilibrium faster.

For Kevex analysis, the samples were subsequently annealed for 16 h at 1600° C in order to obtain larger grain sizes (> 3 μm), improving the accuracy of the test as grain boundary discontinuities were avoided. The samples were then polished and sputtered with a gold–palladium alloy. The quantitative titanium analysis was made on several points on the centre of at least five grains larger than 3 μm (Fig. 1).

For the X-ray diffraction studies the samples were ground and homogenized. Eleven overlap-free reflections between 60° and 76° 2θ were analysed for each composition. The mullite lattice parameters, *d*, were refined by the least squares method and the error calculated according to:

$$d_i = (\sin^2 \theta_i)_{\text{calc}} - (\sin^2 \theta_i)_{\text{obs}}$$

The error level in the determination of the unit cell volume was < 0.1% in all cases.

Data from X-ray diffraction are shown in Fig. 2. The mullite unit cell volume increases gradually with TiO$_2$ content, reaching a maximum at about 2.9 wt % TiO$_2$. This value can be taken as the solid solubility limit of TiO$_2$ in mullite. For increasing quantities of TiO$_2$ the unit cell volume decreases. This is due to the fact that, when the limit of solubility is surpassed the TiO$_2$ is not compatible with mullite (SS) reacting by giving aluminium titanate. Consequently during this process the mullite composition does not remain constant.

X-ray dispersive energy analysis data are shown in Table I. It can be seen that for samples with 3 and 5 wt % TiO$_2$ added, no more than 2.9 ± 0.2 wt % TiO$_2$ is found inside the grains.

The close agreement between the results obtained by the two different techniques allows us to fix at 1600° C the solid solubility of TiO$_2$ in mullite at 2.9 ± 0.2 wt %.

TABLE I

TiO$_2$ added (wt %)	TiO$_2$ by Kevex (wt %)
0.5	0.3 ± 0.1
3	2.90 ± 0.14
5	2.99 ± 0.16

*Philips PW-11401 diffractometer with CuKα radiation.
†ISI Super-3A scanning electron microscope with incorporated Kevex. ZAF corrections computerized by the MAGIC V program have been used.
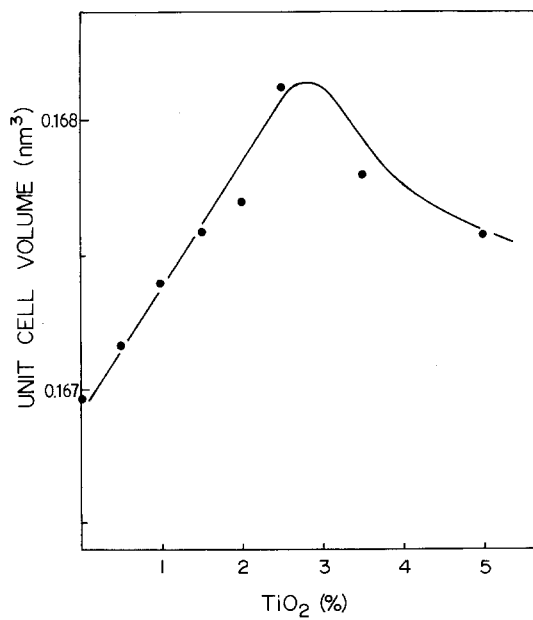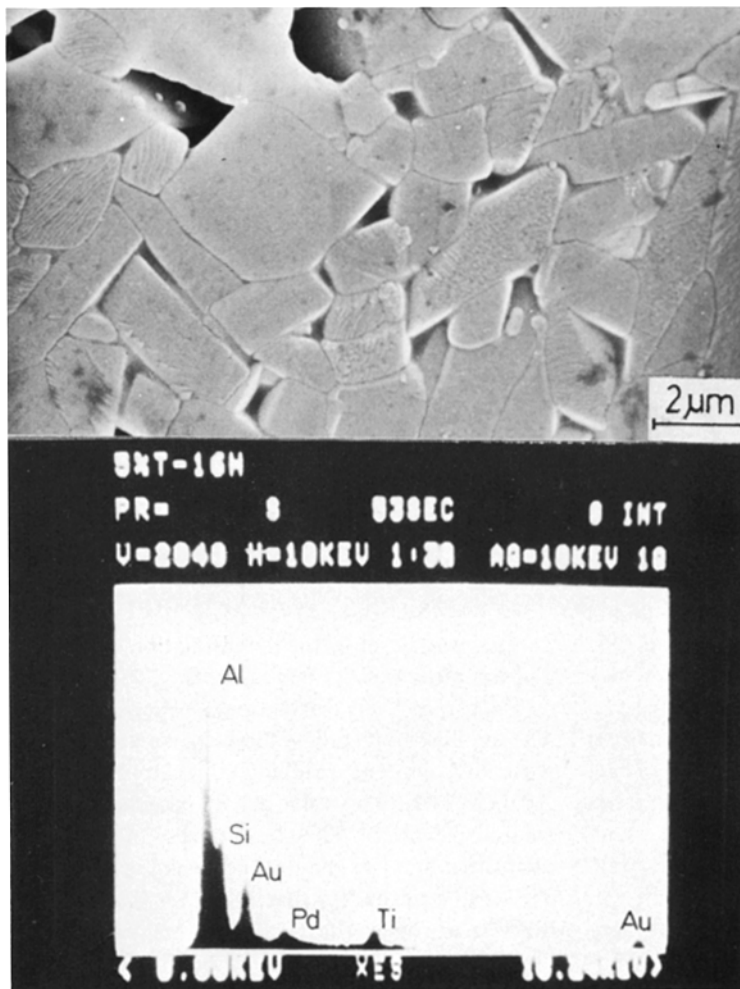
Figure 2 A plot of mullite unit cell volume against wt % TiO_2 added.

Acknowledgements

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