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Distribution of titanium and aluminium in sintered mullite

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The distribution of TiO_2 and Al_2O_3 in mullite and the glassy phase of samples obtained by sintering kaolin and Al_2O_3 with 0 to 3 wt% TiO_2 has been studied. Quantitative phase analysis was performed by means of X-ray diffraction and by successive dissolution of the glassy phase and mullite in HF. The microstructure and microanalyses of the samples were determined using scanning electron microscopy and by analytical electron microscopy. With samples containing >1 wt% TiO_2, not only two morphologically and compositionally different mullites have been determined (the large prismatic mullites and the small needle-shaped ones, embedded into the glassy matrix) but also rutile in the form of needle-shaped crystals embedded in the glassy matrix. In addition on the surface of prismatic mullites, an exsolution of the phase enriched in titanium and iron has been detected. However, the formation of tialite, Al_2TiO_5, has not been proved either by X-ray diffraction or by analytical electron microscopy. Using energy dispersive X-ray analysis a greater Al/Si ratio has been determined for needle-shaped mullites than for prismatic ones. Prismatic mullites have constant Al_2O_3 values, not dependent on the sintering temperature and on TiO_2 added. The solubility of TiO_2 in prismatic mullites is due to the decrease in SiO_2.

1. Introduction

It has been found that titania is one of the most frequently occurring impurities in the natural raw materials used for mullite synthesis (kaolins, bauxites, sillimanites, etc). Therefore, its influence on the sintering temperature, its solubility in the mullite lattice and the mechanism of solid solutions formation have been the subject of several studies [1–8]. According to Murphy and Hummel [4] and Ustitschenko *et al.* [5] the solubility limit of TiO_2 at 1600° C ranges between 2 and 4 wt % and decreases with temperature, while according to Baudin and Moya [6] at the same temperature its solubility ranges between a considerably narrower concentration region: 2.9 ± 0.2 wt %. Schneider [8] found that there are not only morphologically and compositionally distinguished mullites, but also that titanium in large mullite grains is not distributed uniformly. In all these papers the mullite solid solutions were obtained by sintering mullite and TiO_2. According to Davis and Pask [9], mullite obtained by solid state reaction has nominally 3:2 composition; however, needle-shaped mullite precipitated from the liquid phase on cooling has a higher Al_2O_3 content.

The aims of this work were: to determine the distribution of TiO_2 and Al_2O_3 in prismatic and needle-shaped mullites, and in the glassy phase with samples obtained by sintering kaolin and Al_2O_3; to determine the solubility of TiO_2 in the prismatic mullite crystals dependent on the sintering temperature and added TiO_2; and to determine the crystal form of TiO_2 when its quantity surpasses the solubility limit of TiO_2 in mullite.

2. Experimental procedure

For the synthesis of 3:2 mullite ($3Al_2O_3 \cdot 2SiO_2$), a homogenized and wet milled mixture of kaolin and reagent grade Al_2O_3 with Al_2O_3/SiO_2 ratio = 3:2 was used. The chemical composition of kaolin (wt %) was: 45.57 Al_2O_3, 51.27 SiO_2, 0.88 Fe_2O_3, 0.17 TiO_2, 0.90 CaO, 0.33 MgO, 0.85 K_2O and 0.02 Na_2O. Reagent grade TiO_2 in the form of anatase was added in the quantity of 0 to 3 wt %. Pellets were pressed at 100 MPa and fired in a Bickley gas furnace in an oxidizing atmosphere at 1600 and 1750° C. The samples were heated at a constant heating rate of $8° C\,min^{-1}$ up to the maximum temperature and kept there for 8 h and then cooled down at the rate of $1.2\,min\,°C^{-1}$.

The quantitative phase analysis was performed by means of X-ray diffraction analysis (XRD) with CaF_2 as an internal standard and by successive dissolution of the glassy phase and mullite in HF, according to GDR Standard TGL 23165. Each of the separated phases was subjected to chemical analysis using atomic absorption spectrometry (AAS).

The microstructure and composition of the samples were determined by scanning electron microscopy (SEM) and analytical electron microscopy (AEM). Microprobe analysis with an energy dispersive X-ray spectrometer (EDX) was performed on polished and HF-etched sections. Weight percentages of Al_2O_3,

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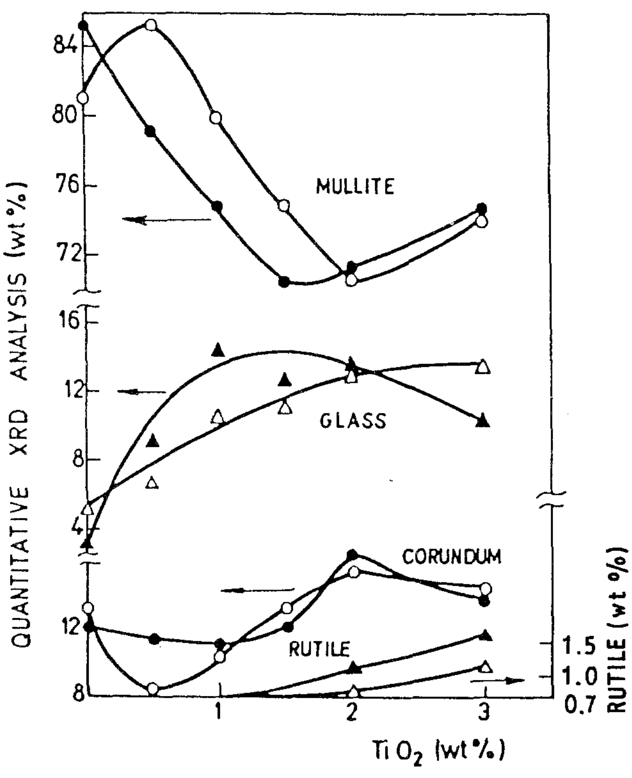


Figure 1 Variation in phase analysis with TiO_2 added, at (○, △) 1600° C, and (●, ▲) 1750° C.

SiO_2, TiO_2 and Fe_2O_3 were calculated from net intensities by means of a program correcting the influence of atomic number, absorption and degree of fluorescence (ZAF process). AEM analyses were performed on samples thinned by an ion-beam milling technique.

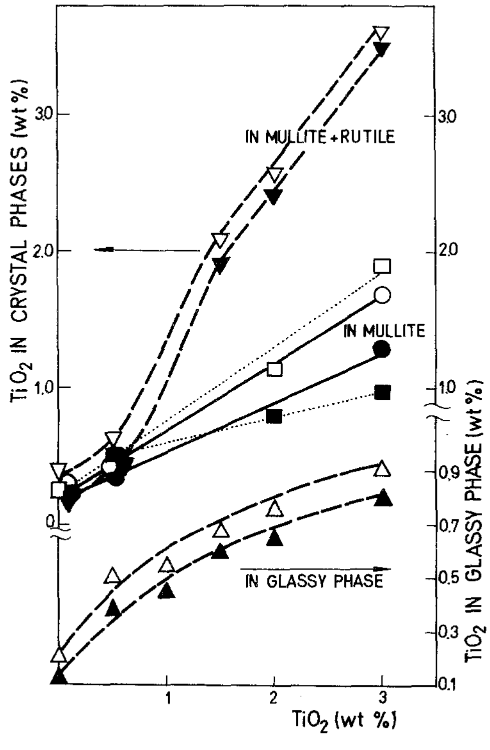


Figure 2 Variation of distribution of TiO_2 in mullites and glassy phases with TiO_2 added at (▽, □, ○, △) 1600° C, (▼, ■, ●, ▲) 1750° C. (- - -) TiO_2 in mullite + rutile and in the glassy phase determined by AAS. (· · · ·) TiO_2 calculated by substraction of rutile from the total TiO_2 determined by AAS. (——) TiO_2 in prismatic mullites determined by EDX.

3. Results and discussion

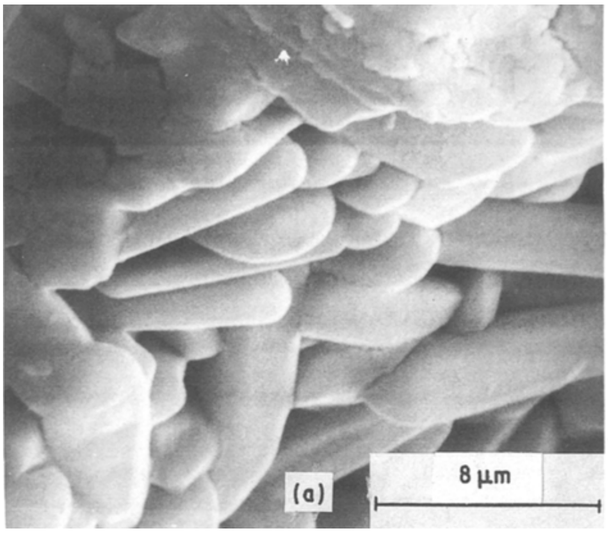
Quantitative XRD analysis (Fig. 1) shows that the maximum content of mullite at 1600° C is obtained when 0.5 wt % TiO_2 is added. The same quantity of mullite in the samples containing no TiO_2 is obtained only at 1750° C. With samples containing > 1 wt % TiO_2, rutile as an additional phase was determined by XRD. Its quantity increases with added TiO_2 and decreases with sintering temperature.

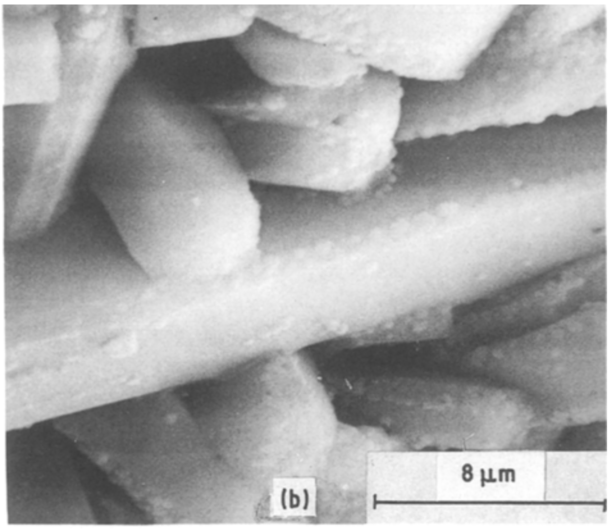
The quantity of TiO_2 in the mixture of mullite and rutile, as well as in the glassy phase depending on TiO_2 added, has been determined by AAS and is given in Fig. 2. During successive dissolution of phases in HF according to the GDR Standard TGL 23165, it was noticed that rutile, occurring in the samples with higher percentages of titania, was dissolved under conditions identical to those required for the dissolution of mullite. Therefore, mullite and rutile cannot be separated; consequently, TiO_2 in mullite itself cannot be determined by the AAS method. Because the quantity of rutile has already been determined by quantitative XRD, the solubility of titania in mullite can be calculated by substracting the quantity of rutile from titania determined in the solution of both phases. The calculated titania in mullite is shown in Fig. 2 by dotted curves.

Titania solubility in large prismatic mullite crystals has been determined by EDX and is also given in Fig. 2. These results are in accordance with the calculated ones. It can be seen that with 3 wt % TiO_2 added the solubility limit given by Baudin and Moya [6] is not yet achieved, because a larger amount of titania is dissolved in the glassy phase, and during the cooling process recrystallized as rutile. Scanning electron micrographs of samples with various quantities of TiO_2 are shown in Fig. 3. Morphologically, as well as compositionally, two different mullite crystals can be distinguished: the large prismatic mullites with a small quantity of TiO_2 in the cores of the crystals and with slightly more titanium at the crystals rims and the small needles embedded into the glassy matrix, which is in agreement with previous authors' results [9, 10]. Not only is the titanium at the rims of the prismatic mullite crystals increased, but also the exsolution of the phase rich in titanium and iron at the surface of prismatic mullites has been noticed (Figs 3b and 4). In the glassy matrix further from the mullite grain boundaries, TiO_2 recrystallizes in the form of rutile, with no iron content (Fig. 5b,C). The formation of tialite, Al_2TiO_5, which, according to some authors [5] appears at the grain boundaries of prismatic mullites, has not been proved, either by XRD or AEM. The exsoluted phase rich in titanium and iron, has not been detected by XRD, due to its small quantity.

Analytical electron micrographs of the sample with 3 wt % TiO_2 sintered at 1750° C and energy dispersive spectra of prismatic mullites, of relatively shorter needle-shaped rutile crystals embedded in the glassy matrix, as well as of the glassy phase itself, are given in Fig. 5, while the micrograph and X-ray spectrum of mullite needles, separated from the sample, are given in Fig. 6.

Using energy dispersive X-ray analysis, a greater





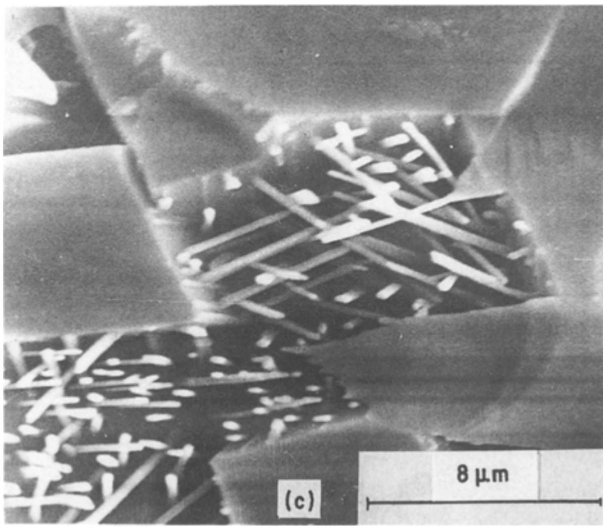


Figure 3 Scanning electron micrographs (SEI) of samples: (a) 0.5% TiO_2, 1600° C; (b) 3% TiO_2, 1600° C; (c) 3% TiO_2, 1750° C.

Al/Si ratio has been determined for needle-shaped mullite than for the prismatic ones.

The distribution of aluminium in prismatic mullite crystals dependent of titania in the system, as determined by EDX, is shown by curve C in Fig. 7. Curves A and B in Fig. 7 represent the total quantity of alumina found by the AAS method in the prismatic + needle-shaped mullite crystals. While Al_2O_3 in the prismatic crystals is constant and independent of the quantity of titania, the Al_2O_3 found by the AAS method is constant only up to 1.5 wt % added; with larger quantities of added titania, a significant increase in alumina content occurs.

The interpretation of the constant quantity of alumina in prismatic mullites over the whole testing range in terms of the structure position of titanium, turns out to be difficult. The similar cation radii of six-fold coordinated Al^{3+} (0.053 nm) and Ti^{4+} (0.0605 nm) suggests that titanium enters the octahedral position in mullite. But it could occur only under the supposition that Al^{3+} replaces tetrahedrally coordinated Si^{4+} in the same quantity in which Ti^{4+} replaces Al^{3+} in the octahedral position. This supposition, however, still ought to be proved. Microanalysis of large mullite crystals suggests such an explanation, because a decrease in silica at the expense of titania has been found (Table I).

On the other hand, an increase in Al_2O_3 up to ~ 75 wt % if > 1.5 wt % TiO_2 is added, could be explained by the increase in the quantity of the needle-shaped mullite containing an Al/Si ratio higher than that detected in prismatic crystals. The higher the TiO_2 content, the greater is the quantity of needle-shaped mullite detected to be embedded in the glassy phase (Fig. 3), which is in accordance with the results mentioned above.

4. Conclusions

1. Mullite appears in two, not only morphologically, but also compositionally distinguished crystals. The prismatic mullites have constant Al_2O_3 values, independent of the sintering temperature, and added TiO_2. The increase in TiO_2 in prismatic mullites is due to the decrease in SiO_2.
2. The solubility of TiO_2 in prismatic mullites decreases with sintering temperature and increases with TiO_2 added. With 3 wt % TiO_2 added it yields 1.7 and 1.36 wt % TiO_2 at 1600 and 1750° C, respectively.
3. If > 1 wt % TiO_2 is added, titania is not only

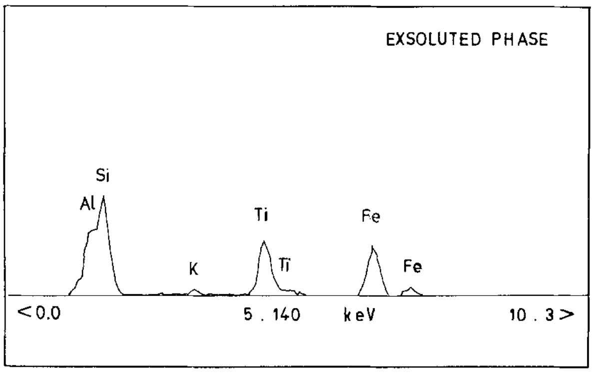
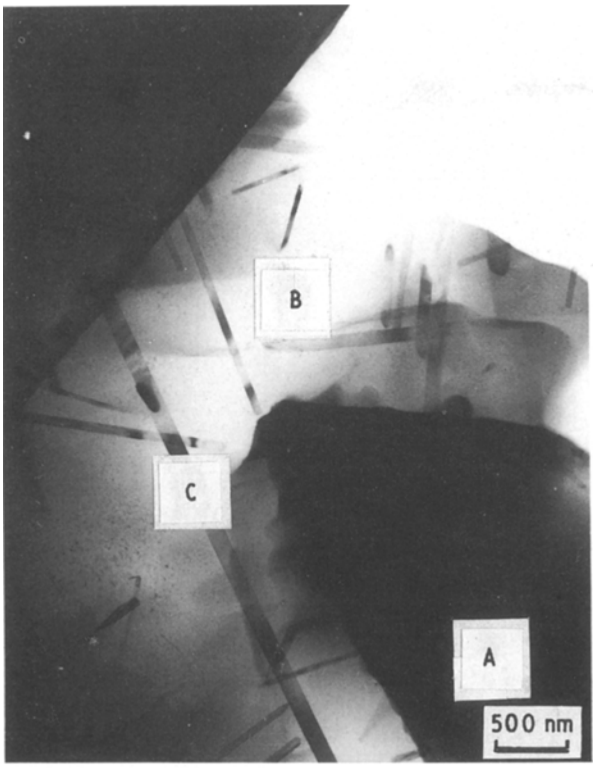


Figure 4 Energy dispersive X-ray spectrum of exsoluted phase rich in titanium and iron. The scanning electron micrograph of this sample is shown in Fig. 3b.



(a)

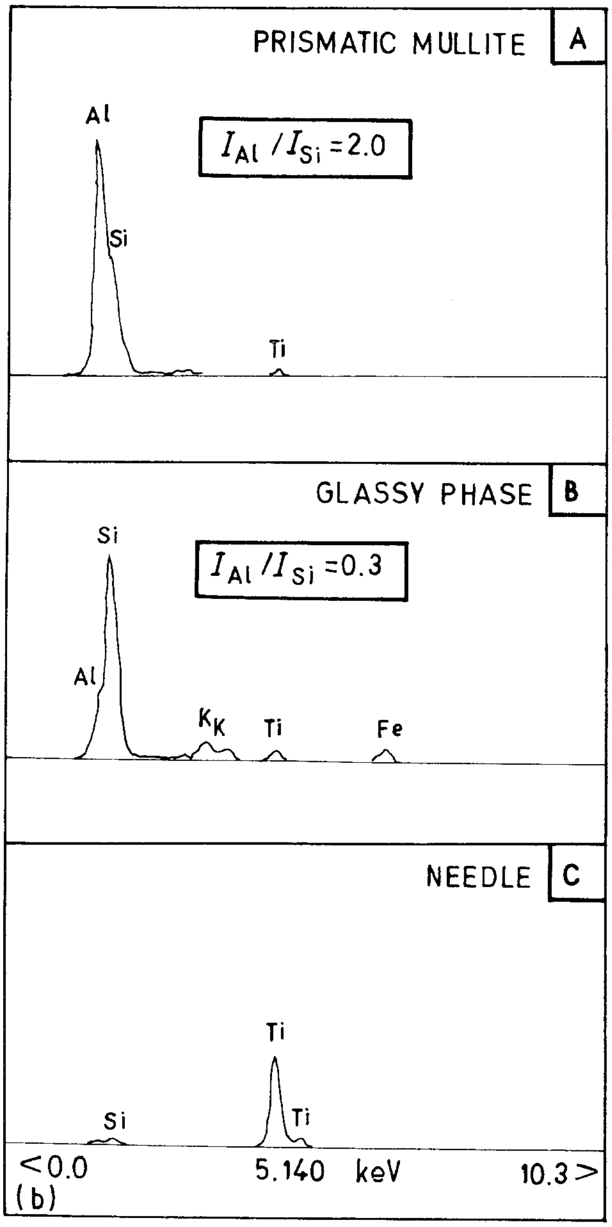
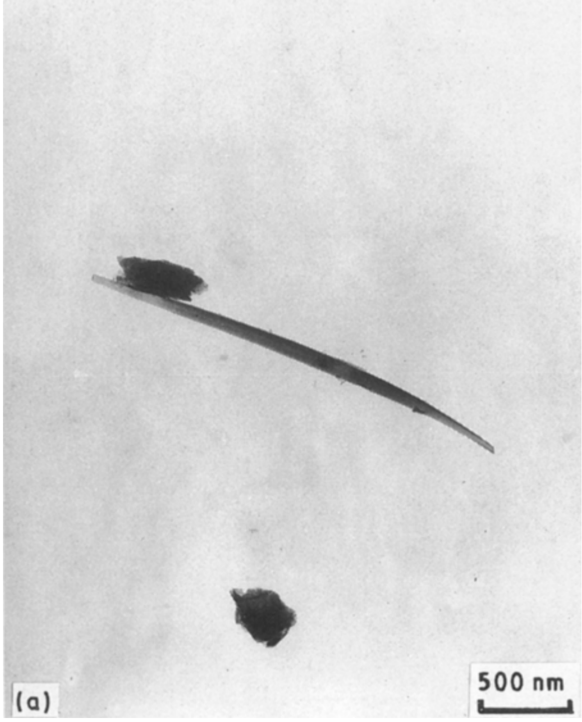


Figure 5 (a) Bright-field micrograph and (b) energy dispersive X-ray spectra of the sample with 3 wt% TiO_2 at 1750° C; A, prismatic mullite; B, glassy phase; C, acicular rutile.



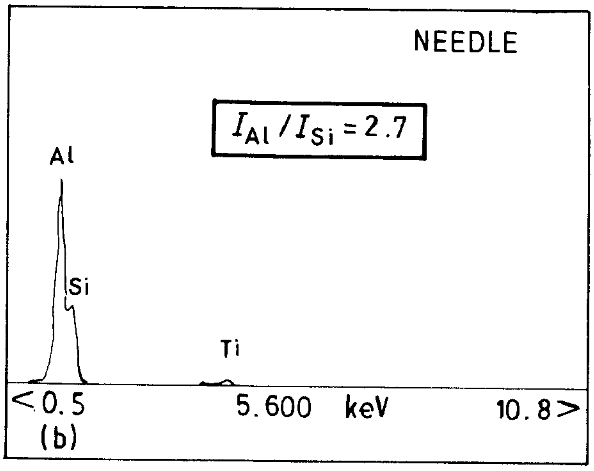


Figure 6 (a) Bright-field micrograph and (b) energy dispersive X-ray spectrum of needle-shaped mullite.

TABLE I Chemical composition of prismatic mullite determined by EDX, and of prismatic + needle-shaped mullite determined by AAS

Component	Prismatic mullites (EDX)				Prismatic + needle-shaped mullite (AAS)				
	TiO_2 (wt %) at 1600° C	TiO_2 (wt %) at 1750° C			TiO_2 (wt %) at 1600° C		TiO_2 (wt %) at 1750° C		
	3.0	0	0.5	3.0	0	3.0	0	0.5	3.0
Al_2O_3 (wt %)	66.84	67.09	66.82	66.59	68.30	75.99	67.52	69.63	75.04
SiO_2 (wt %)	31.45	32.68	32.48	32.05	31.38	22.10	32.35	29.49	23.98
TiO_2 (wt %)	1.71	0.23	0.34	1.36	0.32	1.91	0.13	0.88	0.98
Fe_2O_3 (wt %)	0.21	0	0.21	0.19	n.d.	n.d.	n.d.	n.d.	n.d.
Al_2O_3/SiO_2	2.13	2.05	2.06	2.07	2.18	3.44	2.09	2.36	3.13

n.d. = not detected.

distributed between mullite crystals and the glassy matrix, but also recrystallizes in the form of needle-shaped rutile crystals.

4. The presence of tialite, Al_2TiO_5, has not been proved, but the exsolution of the phase rich in titanium and iron on the grain boundaries of prismatic mullites has been detected.

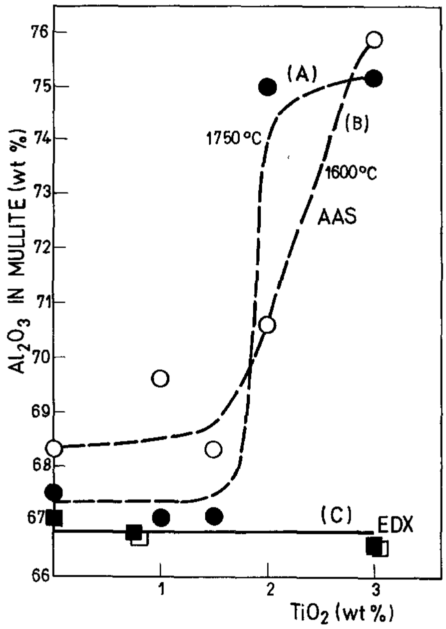


Figure 7 Variation of Al_2O_3 in mullite with TiO_2 added. (A) and (B) Al_2O_3 in prismatic + needle-shaped mullites determined by AAS. (C) Al_2O_3 in prismatic mullite determined by EDX.

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