Characterization of mullite/ZrO₂ toughness ceramic materials microstructure by medium voltage analytical electron microscopy

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Abstract

A series of mullite/ZrO₂ and mullite/alumina/ZrO₂ high-toughness ceramic materials have been examined by analytical electron microscopy (AEM) at 300 kV and by using the following techniques: energy dispersive X-ray (EDX) microanalysis, microdiffraction and convergent beam electron diffraction (CBED). The relative advantages and disadvantages for the analysis at higher voltages on the investigation of advanced ceramics are compared with results obtained at 120 kV.

Keywords: TEM/EDX; Medium voltage analytical electron microscopy; Ceramics; Mullite; Zirconia

1. Introduction

In order to explore the high-toughness properties of mullite/ZrO₂ ceramics, it is of great interest to determine the composition at grain boundaries and in the phases which constitute these composite materials. Therefore, analytical electron microscopy (AEM) experiments have been performed [1] and [2] to characterized the microstructure of mullite/ZrO₂ composites obtained by reaction sintering with CaO, MgO, or TiO₂ as sintering aids. These experiments were carried out in an AEM instrument operating in transmission electron microscopy (TEM)/energy dispersive X-ray (EDX) mode at 120 kV.

With the recent development of the conventional high and medium AEM instruments [3], a wide field of new analytical capabilities has been made available up to 400 kV. The medium and higher voltage AEMs are very useful for examining high-toughness ceramic materials which are difficult to thin. With conventional TEM methods, relatively thick (200 nm) foils of these materials are difficult to observe.

The aim of this research has been to compare the microanalysis results obtained at 300 kV with those obtained at 120 kV in some mullite/ZrO₂ ceramics evaluating in both cases the TEM and scanning transmission electron microscopy (STEM) microanalysis modes.

2. Materials and methods

The samples here considered were thin foils of the following high-toughness ceramic materials, viz:

- Mullite/ZrO₂
- Mullite/alumina/ZrO₂ heat-treated at 1570°C for 16 h.
- Mullite/ZrO₂ with 1% CaO as sintering aid and annealed at 1425°C for 65 h, with their processing reported previously by Miranzo et al. [2].

All these samples have been characterized before in an AEM Philips-400 instrument. The thin foils have been obtained as usual by conventional methods for TEM: Ion bombardment with Ar in a Gatan-Dual Ion Miller with 15° tilting angle after wafering, grinding and mechanical thinning.

Both Philips EM-420 and EM-430 instruments with EDX spectrometers have been used. The results shown here correspond to the EDX microanalysis obtained at 120 and 300 kV, respectively and convergent beam electron diffraction (CBED) diffractions have been registered under 60-nm beam diameter center properly exposed. The electron gun was LaB₆ and the STEM system was PW 6585 with remote focus control. EDX microanalyses were performed in an EDAX-ECON IV detector with 8° elevation angle, giving 0.014 sterad, solid angle of detection and analyser PV 9100.

3. Results and discussion

3.1. Ceramic materials of mullite/ZrO₂ and mullite/alumina/ZrO₂

The results obtained at 120 kV were reported elsewhere [4]. Fig. 1a shows the general microstructure obtained at 300 kV from the binary composite (mullite/ZrO₂). Likewise, Fig. 1b and c show the CBED patterns obtained at the intergranular ZrO₂ (indicated with the arrow) and at the grain boundary of the ZrO₂ with the mullite, respectively. The phases of ZrO₂ and of mullite, as well as the grain boundary and the contrast lines which show a high level of stress in the mullite crystals can be seen clearly. On the other hand, despite the opacity of the ZrO₂ with respect to the electron beam though using higher voltage, fine CBED patterns can be obtained such as those shown in Fig. 1b for the [001] zone axis orientation. Fig. 1c depicts the CBED obtained from the interphase, which includes Kikuchi lines from thicker mullite crystals.

Fig. 1d and e show the EDX spectra obtained at 300 kV by STEM mode in the ZrO₂ and at the ZrO₂/mullite grain boundary, respectively. These spectra have lower background than those obtained at 120 kV but in spite of the lower probe diameter by STEM mode (10 nm compared with the 100 nm by TEM mode), the Al₂O₃ and SiO₂ percentages obtained at the grain boundary are excessive compared to that prevented by phase diagramme as was shown by Rincón et al. [5]. As has been discussed by Zaluček et al. [6], radiation-induced segregation phenomena can take place at medium voltage AEM, giving rise to local changes in composition. Therefore, the STEM mode does not give analytical advantages even at higher voltages.

TEM microanalysis has been carried out at grain boundaries at 300 kV, showing that the Si and Al gradients are higher than those observed at 120 kV (Fig. 1f). Consequently, the solid solution effect at grain boundaries would be lower than expected; even more, these might not take place. Nevertheless, observations by HREM have shown that there is a coherent relation in (110) planes along the grain boundary between the zirconia and mullite crystals [7].

Fig. 1. (a) Transmission electron micrograph of the mullite/ZrO₂ tough ceramic composite annealed at 1570°C for 2 h, showing intergranular ZrO₂ (arrow) in a matrix of mullite crystals depicting high stress field contrast lines. (b) CBED pattern (Camera length: 450 mm and E.O. Cam. length: 180 mm) of the ZrO₂ in [001] axis zone as shown by the arrow in the former micrograph. (c) CBED pattern (same conditions as in b) obtained at the ZrO₂/mullite interphase, showing Kikuchi lines from mullite crystals in the high-order Laue zone. (d) EDX spectrum obtained at 300 kV in the center of the ZrO₂ crystal. (e) EDX spectrum obtained at 300 kV at the ZrO₂/mullite grain boundary. (f) Gradient microanalysis at 120 and 300 kV between mullite and ZrO₂ mullite.

Fig. 2a shows the microstructure observed at 300 kV in the ternary composite mullite/alumina/ZrO₂. The different phases which constitute this material can be clearly seen, as well as the different stress fields around the different phases. The Al₂O₃ grains do

not show contrast lines due to stress fields, while the mullite crystals show abundant “bundles” or clusters of dark lines due to stress fields. Otherwise, a glassy phase area can be distinguished between the mullite and the alumina, which is removed partly by the radiation damage produced at 300 kV [5]. Fig. 2b, c, and d show the EDX spectra obtained from different areas closer to the ZrO₂/Al₂O₃ and ZrO₂/mullite grain boundaries and inside the zircona grains.

Fig. 2. (a) Transmission electron micrograph of the mullite/alumina/ZrO₂ ternary tough ceramic composite, showing the intergranular ZrO₂ between the Al₂O₃ crystals (which do not show stress field contrast lines) and intergranular ZrO₂ showing twins close to the mullite crystals which depict high stress field contrast lines. (b–d) Corresponding spectra obtained in the alumina, ZrO₂, and mullite crystals, respectively (areas analyzed correspond to the same letters in the micrograph).

3.2. Ceramic material of mullite/Al₂O₃/ZrO₂ with 1% CaO

In order to form a transitory liquid that facilitates the sintering, as reported elsewhere [5], the mullite/ZrO₂ ceramic composites containing CaO as sintering aid are constituted by:

- A matrix of mullite crystals inter- and intra-granular ZrO₂ grains

- Alumina grains
- Anorthite feldspar crystals and
- A residual glassy phase.

Table 1 shows the microanalysis results obtained by TEM and STEM at 120 and 300 kV. The quantitative microanalysis was performed by using the well-known Cliff–Lorimer method [8] developed for thin foils. According to this method:

$$X_B / X_A = k_{BA} I_B / I_A$$

where X_B and X_A are the concentrations of B element and A element taken as reference (in this case Si); k_{BA} is the Cliff–Lorimer constant evaluated for each instrument with a series of standards, and I_B and I_A are the respective peak intensities. In this case, after calibration the following values were obtained:

$$k_{AlSi} = 1.17; k_{ZrSi} = 2.77 \text{ and } k_{CaSi} = 0.96$$

Table 1. Quantitative microanalysis (oxides, wt.%) at different acceleration voltages in mullite/ZrO₂ containing 1 (wt.%) CaO

Area	Mode	120 kV				300 kV			
		ZrO ₂	Al ₂ O ₃	SiO ₂	CaO	ZrO ₂	Al ₂ O ₃	SiO ₂	CaO
Mullite grain boundary ^a	TEM	5.8	64.3	29	0.3	–	67.3	27.8	4.8
	STEM	–	–	–	–	–	60.1	31.9	7.9
ZrO ₂ grain boundary	TEM	97.7	–	1.8	0.3	80.6	9.7	8.2	1.3
	STEM	96	1	2.3	0.6	78.6	8.8	10.2	2.2
Anorthite center ^a	TEM	3.9	32.9	46.5	16.6	–	37	44.7	18.2
	STEM	0.9	28.5	57.9	12.5	–	35.9	46.4	17.5
Anorthite grain boundary ^a	TEM	2.8	32	46.8	18.2	–	39.6	39.3	21.3
	STEM	0.9	29.4	54.9	14.7	b	36.5	46.2	17.2

^a Mullite and anorthite respectively have the following stoichiometric formula: 71.80Al₂O₃·28.20SiO₂ and 37.23Al₂O₃·21.90CaO·40.88SiO₂.

^b In some areas, more than 1.0 wt.% ZrO₂ has been detected.

These values are higher working at 120 kV than those obtained by Rincón et al. [1] while calibrating a similar AEM configuration (Philips TEM-400 with an EDX Kevex detector).

Table 1 gives the quantitative results obtained at different acceleration voltages in ZrO₂/mullite materials with addition of CaO as sintering aid.

By comparing different adquisition modes (TEM and STEM) and different voltages (120 and 300 kV here used), several experimental comments arise.

3.2.1. TEM and STEM mode analysis

At lower acceleration voltage (120 kV), the concentrations of Al₂O₃ and SiO₂ obtained by STEM mode are overstated, as previously shown in similar samples [4] and [5]. Likewise, though the anorthite is deficient in Al₂O₃ and CaO, the SiO₂ contents obtained by STEM are higher than those analysis expected in this case into the center and grain boundaries of crystals.

At higher acceleration voltage (300 kV), a similar effect takes place, i.e., an overvalue in the STEM results of SiO₂ and CaO in the zirconia grains, as well as CaO in mullite. Similarly, the SiO₂ values into the anorthite are higher in STEM than in TEM modes. On the other hand, the solid solution of ZrO₂ in mullite has not been detected operating at 300 kV.

It has been recognized by different authors [9], [10] and [11] that when operating an AEM in STEM mode, the beam and the non-collimated fluorescence can produce strange excitations which can produce errors in the analytical results. Therefore, though the STEM mode is more suitable for detecting the thin foils of interboundary glassy phase, it is not sufficiently adequate for the microanalysis at grain boundaries. Otherwise, an additional difficulty in STEM mode is that it is more difficult to locate the probe at the right place due to the loss of image resolution in this mode.

3.2.2. Different acceleration voltage analysis

When observing the microanalytical results at 300 kV (Table 1), it can be seen that different results are obtained with respect to the 120 kV results. Thus, at 300 kV the ZrO₂

is not detected either in mullite or into anorthite, but CaO values are higher than those obtained at 120 kV. At the zirconia grains, higher values of Al₂O₃, SiO₂ and CaO were obtained operating at 300 kV.

As is well-known, among other factors, the spatial resolution is different varying the voltage affecting the microanalytical results. Since the beam broadening is:

$$b = 625(Z / E_0)(\rho^{3/2} / A)t$$

where b (beam broadening) is expressed in centimeters (cm); Z is the atomic number; A is the atomic weight; E_0 is the acceleration voltage in kilovolts (kV); ρ is the density in grams per cubic centimeter (g/cm³) and t is the thickness in centimeters (cm) [12]. Therefore, when E_0 increases, a narrower beam can be obtained improving the analytical resolution. However, the heavier elements, such as CaO and ZrO₂ can produce a broadening of the beam. This effect is enhanced at higher voltages. It can be argued that in the results shown here, the absence of variation of the Cliff–Lorimer constants with the acceleration voltage has not been taken into account. Usually, these constants decrease their values for higher acceleration voltages only for heavy elements [13]. In any case, this fact could affect the larger values of the ZrO₂ expressed in Table 1, but cannot explain the absence of ZrO₂ in mullite or in anorthite, which must be more related to the beam broadening.

By using higher acceleration voltages in the AEM, the amount of ionization or X-ray production at the K level increases. Conventionally, it is possible to excite the K lines for heavy elements, though from the $Z=40$ elements, the conventional detector efficiency of Si (Li) is low [6]. The observation of EELS spectra in these samples at 120 kV has been attempted with no success. According also to Zaluček et al. [6], the effect of displacement rates exceeding the X-ray detection rate does not take place by EELS due to their higher collection efficiency. Therefore, the next step of this research will be to use the EELS spectroscopy at higher voltages, because in thick specimens (approximately 200 nm) such as the tough ceramic materials, an improvement of energy loss results could be obtained giving rise to new additional and valuable microanalytical data.

4. Conclusions

By EDX microanalysis experiments in TEM and STEM modes carried out at 300 kV at grain boundaries of several zirconia/mullite tough materials, large differences from those results obtained at 120 kV have been observed. With the 300 kV microanalysis, the peak/background ratio is improved, facilitating also the observation of thicker samples and providing a better X-ray excitation and better definition of the zero-order Laue zone by CBED. However, higher radiation damage can be produced at higher voltages, especially in the glassy phase, as well as ion displacement effects and decrease of the high-order Laue zone visibility

The solid solution effect at grain boundaries, previously detected at 120 kV, has been observed to a lesser extent at 300 kV. On the other hand, the microanalytical experiments carried out in the same materials by TEM and STEM have shown that the STEM analytical mode can produce large analytical errors, especially at grain boundaries. Hence, in the future, the higher voltage microanalysis (300 or 400 kV) carried out by TEM mode appears to be the more adequate procedure in solving the various microanalytical problems and microstructural observations involved in this type of advanced ceramic composites.

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