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Microstructural investigations in cordierite–mullite refractories

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Abstract

The influence of the mineralogical composition and phase distribution on crack initiation and propagation in cordierite–mullite refractory plates used as substrates in fast firing of porcelain whiteware is investigated. Two different refractory compositions (termed REFO and CONC), characterised by different silica to alumina ratios, were studied. Propagation of cracks introduced by Vickers' indentations was observed by scanning electron microscopy. Chemical analysis by EDS was used for phase identification together with X-ray diffraction analysis. Microstructural features and crack propagation behaviour were correlated and used to draw conclusions on the behaviour of the two different refractory compositions under thermal shock. It was found that the presence of α-quartz crystals and favourable residual stress field are responsible for room temperature fracture toughness in REFO samples. The CONC material contains a larger amount of residual glassy phase than REFO material, which should lead to better high-temperature mechanical properties and higher thermal shock resistance, as the glass phase may close (''heal'') propagating cracks.

Keywords: B. Microstructure; D. Mullite; D. Cordierite; E. Refractory; Crack propagation

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1. Introduction

A refractory microstructure is that of a typical polycrystalline ceramic where second phases, which are either intentionally or unintentionally incorporated into the microstructure, can act directly as crack impediments or produce internal strain fields that can indirectly alter the crack path [1].

It is well established that internal stresses result from thermal expansion mismatch of different phases within a ceramic body [2]. Since it is common practice for industrial refractory production to add quartz in order to reduce the overall thermal expansion coefficient, a mismatch of thermal expansion behaviour of the different crystalline phases present is expected, which should lead to the development of internal stresses. Although internal stresses in model 2-phase systems can be calculated by analytical equations [2–5], the stress distribution in ''real'' systems is complex because of anisotropy within individual grains and particle–particle interactions. Moreover, a second source of internal stresses is recognized to be anisotropic elastic moduli of the different phases, as discussed in the literature [6,7], adding complexity to the calculations. In the case of refractory materials, which work under conditions of heat flow, localised tensile and compressive thermal stresses arise also from mismatches in thermal conductivity [8].

Cordierite–mullite composites find increasing applications as refractory materials in the context of recent developments in fast-firing techniques of ceramic products. These refractories exhibit in general a complex microstructure characterized by crystalline phases of different thermal expansion coefficients and elastic moduli and a residual silicate glassy phase. There is a current lack of understanding about the effect of microstructural features, including residual thermal stresses, on the overall performance of the materials at high temperature and under thermal shock conditions. The aim of this work is to investigate the microstructure and microcrack propagation

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behaviour of two different commercial compositions of cordierite–mullite refractories, which are widely used to produce substrates for porcelain articles in fast-firing cycles. Moreover it was an interest of the authors to correlate the crack propagation at room temperature with the observed thermal shock behaviour when refractory plates are used in actual duty cycles, which has been studied elsewhere [9]. Two different types of refractory plates were chosen, one exhibiting a fast microcrack propagation behaviour and the second showing early microcrack formation, but delayed microcrack propagation. The microcrack propagation was studied by means of scanning electron microscopy after inducing crack formation by Vickers' indentations, with the intention to verify the presence and the effect of internal stresses.

2. Experimental

2.1. Refractory plates

The two commercial plates (hereafter indicated as REFO and CONC) used for this work are made of cordierite–mullite refractory mixtures. A chemical composition check was performed on powdered samples by ICP-AES (Model Liberty 200, VARIAN) since official data were not available from the manufacturers; the results are shown in Table 1. It is seen that the two materials present very similar chemical composition.

2.2. Mineralogical analysis

X-ray diffraction (XRD) analyses (Cu Kα, Ni-filtered radiation, Philips Model PW3710) were carried out on powdered samples to determine the mineralogical composition of the two refractory materials. ICCD files were used to identify the crystalline phases.

2.3. Microstructure and crack propagation observation

In order to evidence phase distribution, scanning electron microscopy (SEM) (PHILIPS XL 40) was performed on polished sections after gold coating. Energy Dispersion X-ray fluorescence Spectroscopy, EDS, (X_EDS INCA, Oxford Inst.) accompanied SEM observation to allow the identification of the crystalline phases and their distribution. An image elaboration software (Materials_Pro® Analyzer, Version 3.1, Media Cybernetics, Silver Spring, MD, USA) was employed to evaluate overall porosity on

Table 1
Chemical composition of the two refractory samples investigated (in wt.%)

Sample	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	Others	Total
REFO	54.98	31.71	0.05	6.28	0.05	0.57	1.2	0.72	4.44	100.00
CONC	46.86	37.91	0.00	7.89	0.00	0.58	1.38	0.61	4.77	100.00

Table 2
Semi-quantitative data of EDS spectra compared with theoretical compositions of the crystalline phases found in XRD patterns (in at.%)

Element in crystalline phase	Theoretical composition (in at.%)			Determined from EDS (in at.%)												
	Cordierite $Mg_2Al_4Si_5O_{18}$	Mullite $Al_6Si_2O_{13}$	Quartz SiO_2	Molochite	Fig. 3b	Fig. 4b	Fig. 4c	Fig. 4d	Fig. 5b	Fig. 5c	Fig. 5d	Fig. 6b	Fig. 7b	Fig. 7c	Fig. 8b	Fig. 8c
Mg	6.89	–	–	0.155	0.08	0.39	9.42	2.69	6.07	0.93	0.72	0.71	3.21	3.23	6.57	1.69
Al	13.79	28.57	–	16.8	0.31	1.26	22.95	5.59	14.53	16.23	18.59	15.91	15.01	15.03	14.46	25.55
Si	17.24	9.52	33.33	18.14	33.73	32.24	7.42	27.02	17.13	17.42	15.60	19.03	18.43	18.12	17.61	10.39
K	–	–	–	1.33	–	–	0.1	0.09	0.12	0.79	0.62	1.05	0.56	0.63	0.08	–
Fe	–	–	–	0.44	–	0.03	0.88	0.12	0.24	0.55	0.58	0.36	0.21	0.24	0.29	0.62
Ti	–	–	–	0.023	–	0.01	0.13	0.12	0.1	0.94	0.92	0.1	0.08	0.13	0.06	0.56
O	62.08	61.91	66.67	62.52	66.48	66.18	59.12	64.55	61.9	62.67	62.5	62.85	62.28	62.13	61.99	61.39

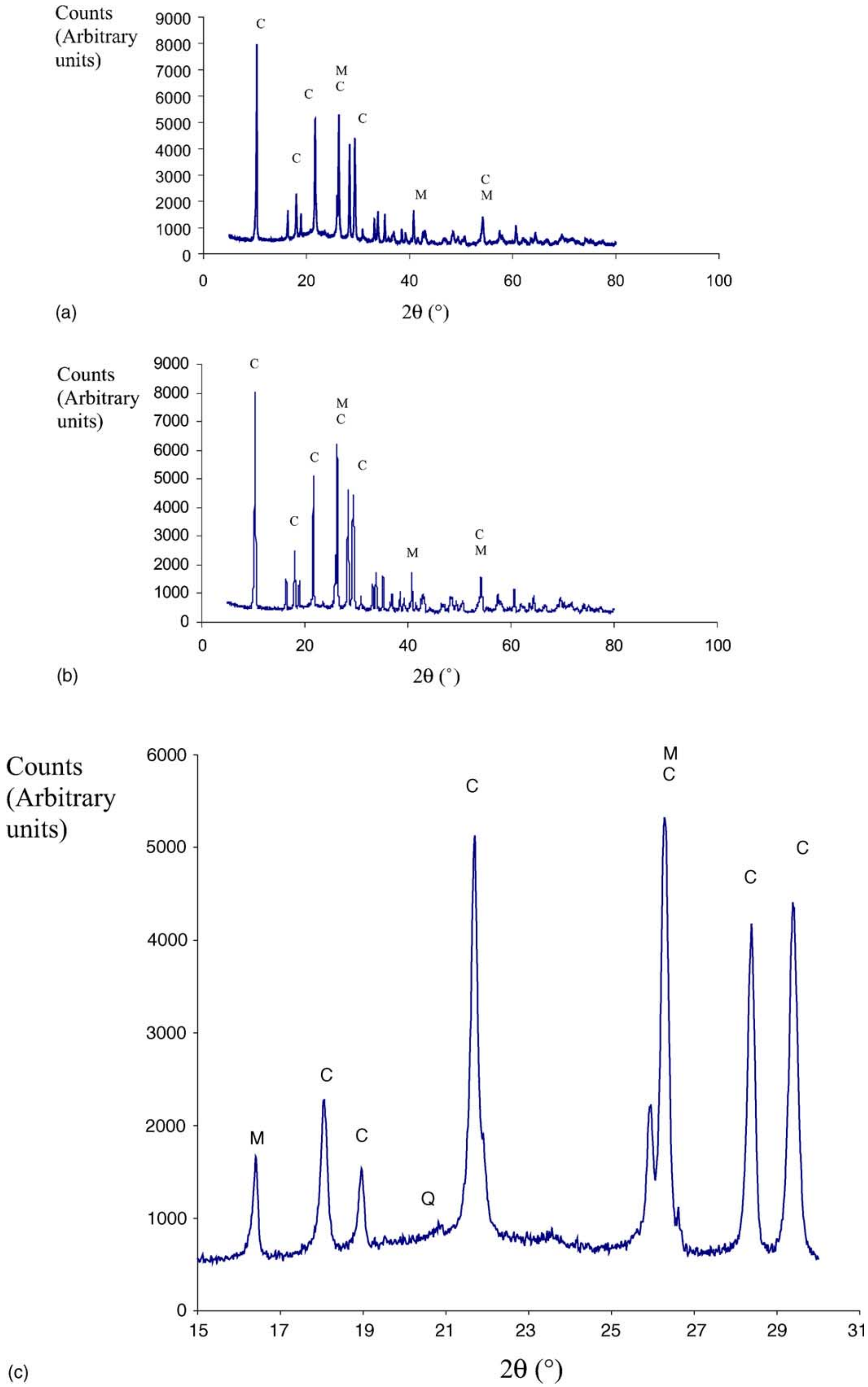


Fig. 1. XRD patterns of the two samples investigated: (a) REFO, (b) CONC, collected in the same 2θ range at room temperature, showing mullite (M) and cordierite (C) as main crystalline phases. The enlargement of (a) in the range $15^\circ < 2\theta < 30^\circ$ is shown in (c), evidencing the presence of quartz in the REFO material.

five different images collected on polished sections of the two samples.

Microcracks were created by means of Vickers' indentations (REMET HX 1000) on polished surfaces using loads in the range 500–1000 g. Indented samples were coated with gold for SEM observation.

3. Results

3.1. Mineralogical composition

The identification of the crystalline phases present in refractory plates REFO and CONC was performed by XRD. Typical XRD patterns, as shown in Fig. 1a and 1b, evidentiate the similarity between the two materials: as expected the major crystalline phases are cordierite and mullite. Some traces of α-quartz are present in composition REFO, as observed in the XRD pattern shown in Fig. 1c. From a compositional point of view (Table 1) the excess of SiO_2 in this material (REFO) is well evidenced since the cordierite to mullite weight ratio is equal to 50:45 in this material, with excess of 5 wt.% of SiO_2, while it is 50:50 in CONC material.

To better identify the crystalline or amorphous phases present in the two refractory materials, EDS spectra were collected on different samples of each composition at different magnifications. Quantitative data are reported in Table 2 and compared with theoretical compositions of the crystalline phases found by XRD, i.e. mullite, cordierite and quartz, as well as molochite, which is an aluminosilicate used as raw material in the refractory batch preparation.

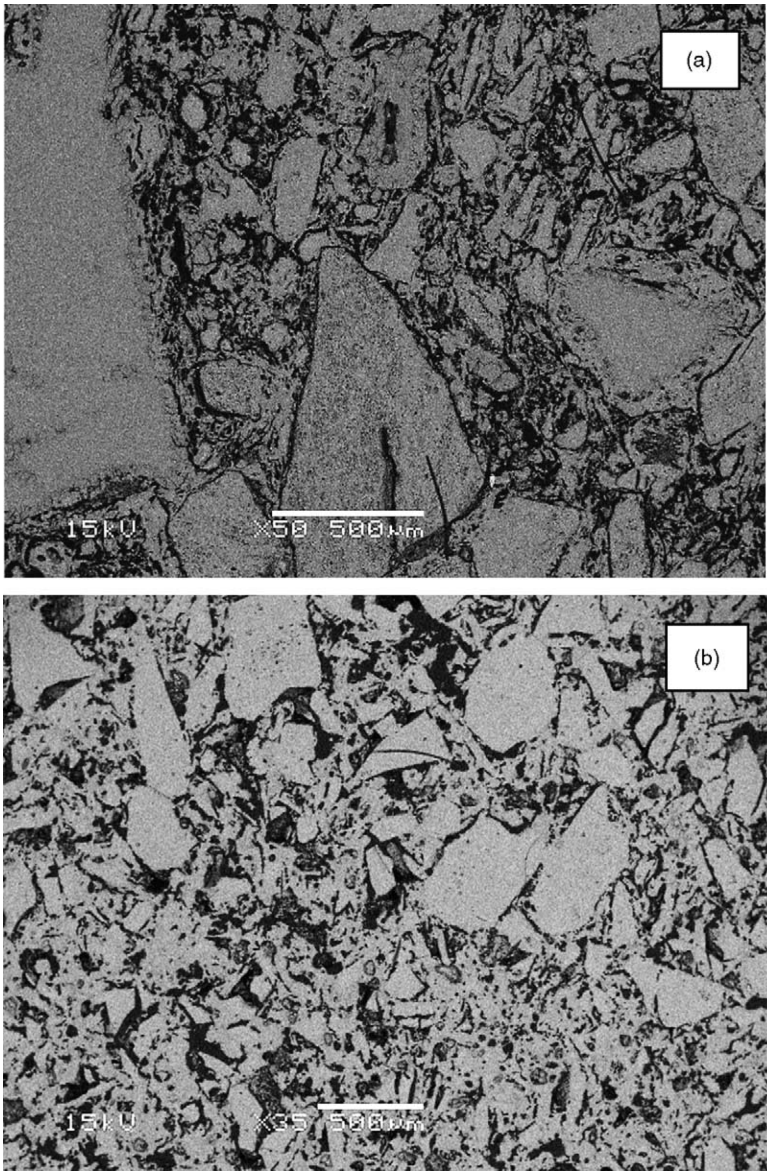


Fig. 2. SEM micrographs of polished sections of refractory samples at low magnification: (a) REFO, (b) CONC, showing different microstructural features.

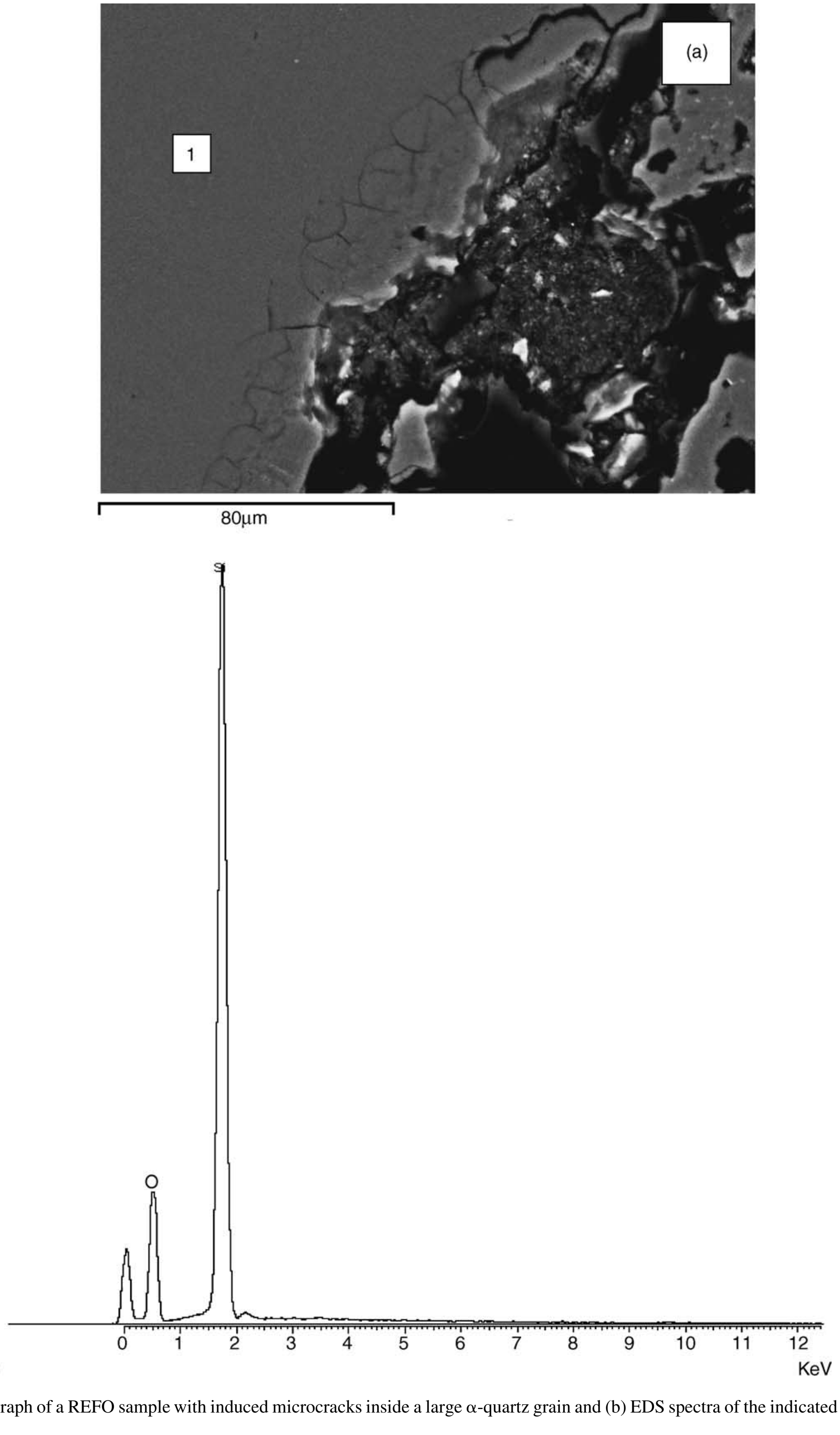


Fig. 3. (a) SEM micrograph of a REFO sample with induced microcracks inside a large α-quartz grain and (b) EDS spectra of the indicated area, labelled (1) in (a).

3.2. Microstructure and crack propagation behaviour

The microstructures of REFO and CONC materials were observed by SEM on polished cross sections. At first glance the microstructures of the two refractory samples appear very different, with REFO samples exhibiting a less dense and interconnected microstructure than CONC samples, as observed in the low magnification SEM images in Fig. 2a and b, respectively. REFO samples show a microstructure with large and well-defined grains not connected by any

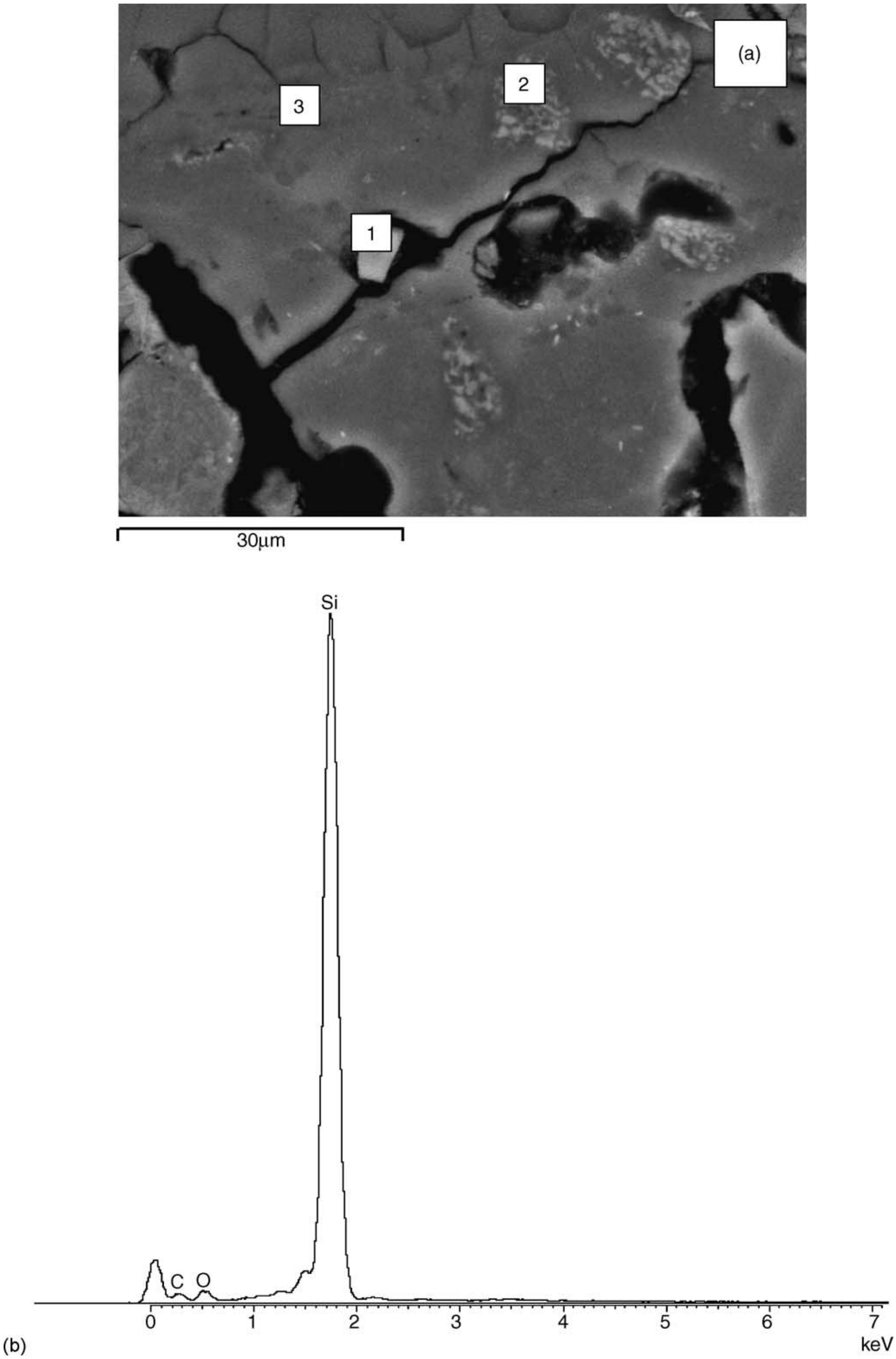


Fig. 4. (a) High-magnification SEM image of crack propagation in a REFO sample with (b)–(d) EDS spectra of the indicated areas, labelled (1), (2), and (3) in (a).

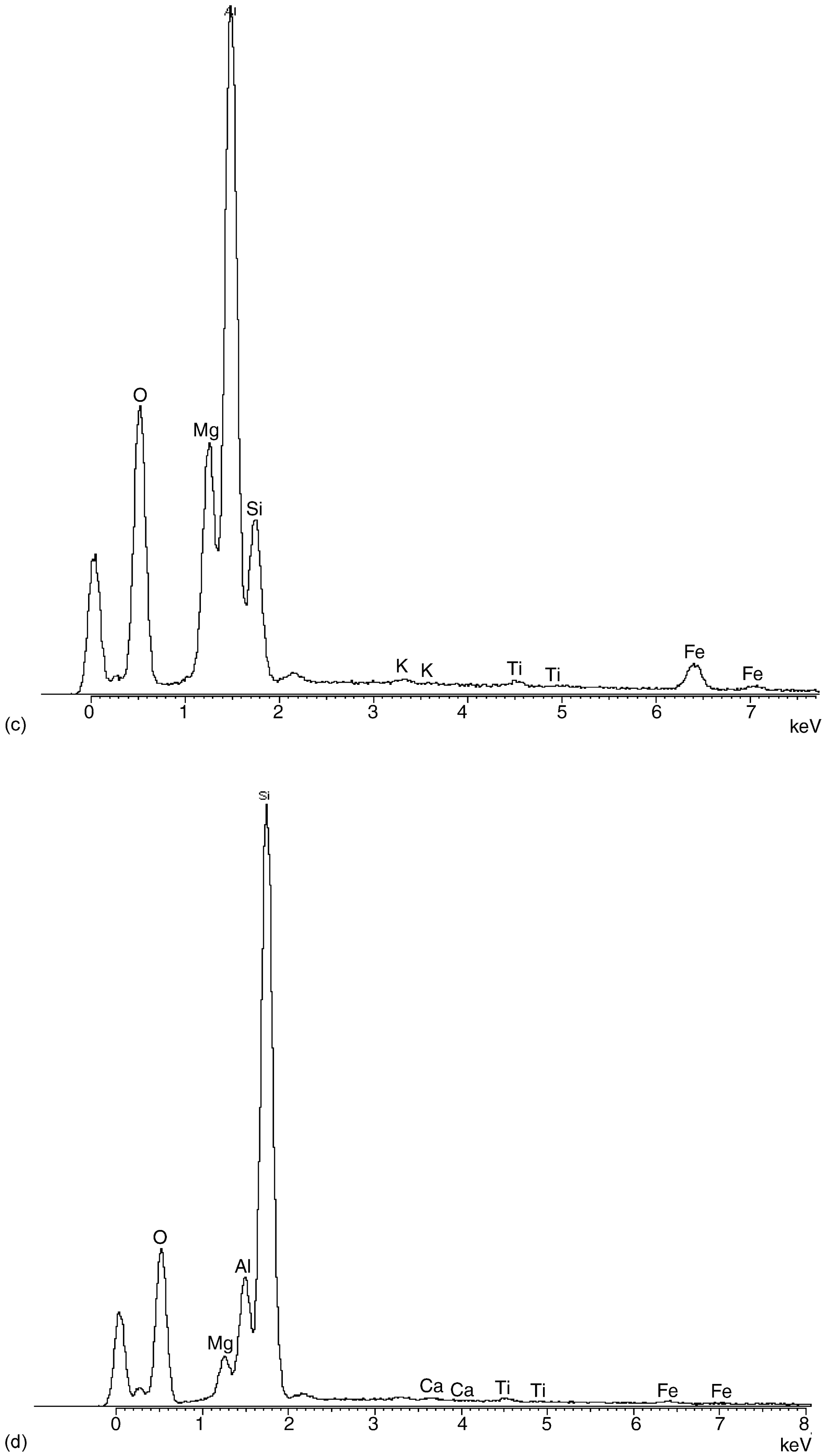


Fig. 4. (*Continued*).

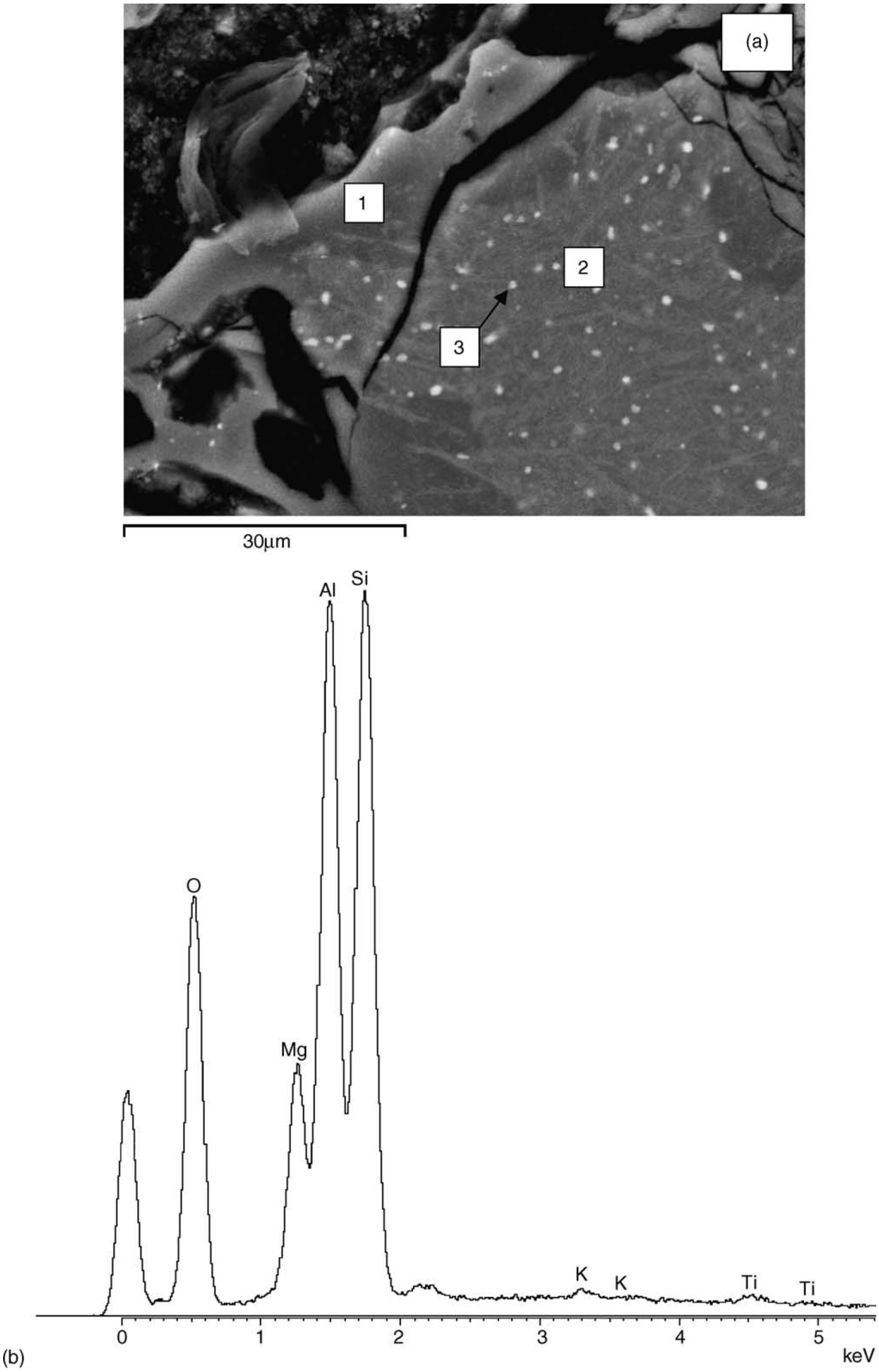


Fig. 5. (a) Detailed SEM image of crack propagation in the cordierite-rich area of a REFO sample with (b)–(d) EDS spectra of the indicated areas, labelled (1), (2), and (3) in (a).

amorphous continuous phase (Fig. 2a). In the REFO material the interconnected porosity amounts 26%, as evaluated by 2D image analysis, whilst for the CONC sample the porosity is 28%. In both materials pores are not spherical, indicating an early stage of sintering [10].

At increasing magnification, the SEM observation of induced microcracks allows the description of the fracture propagation mechanism in both samples, as discussed next.

Some large grains constituted of SiO_2 in the REFO sample (Fig. 3a and b), which can be ascribed to α-quartz

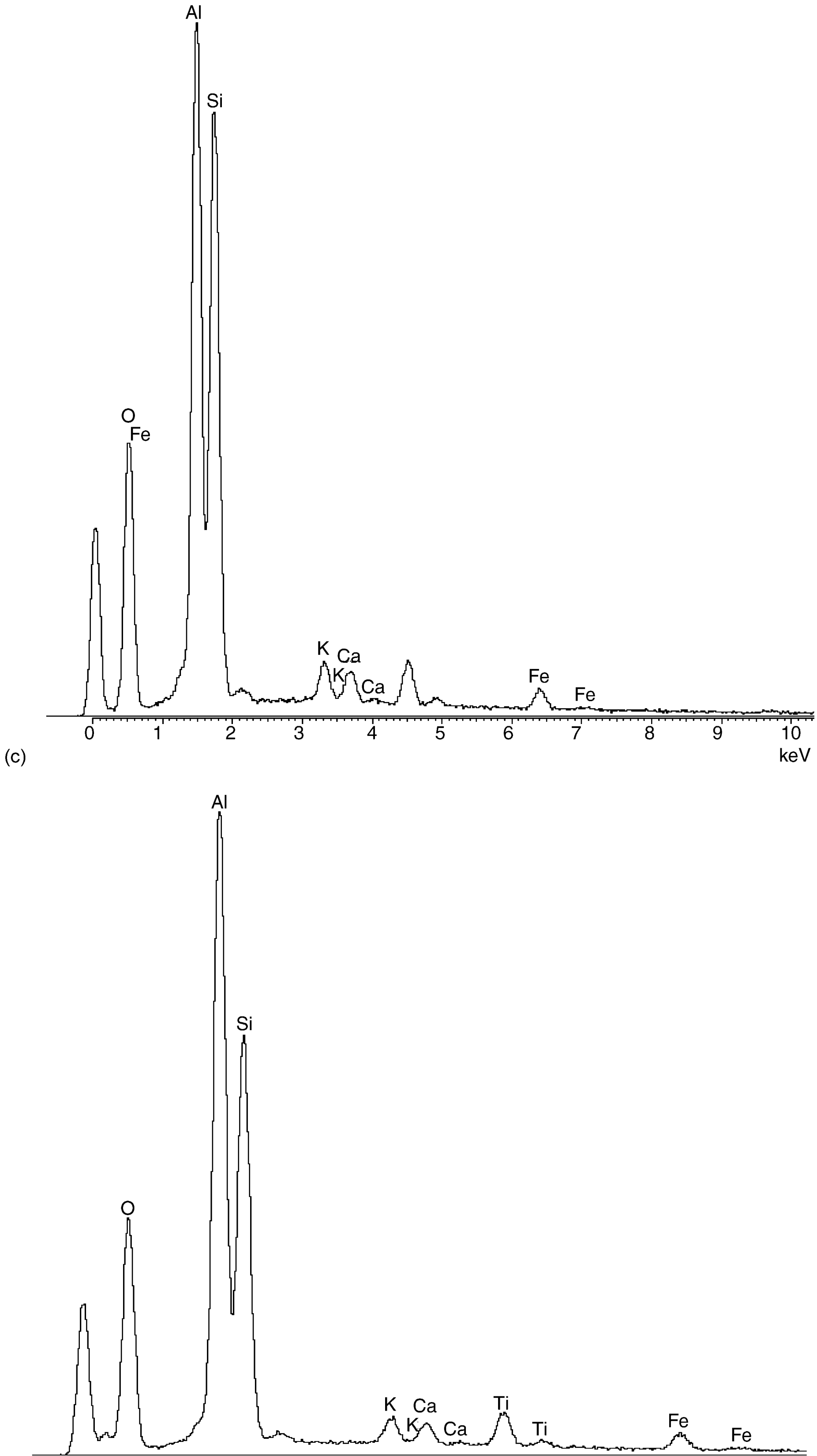


Fig. 5. (*Continued*).

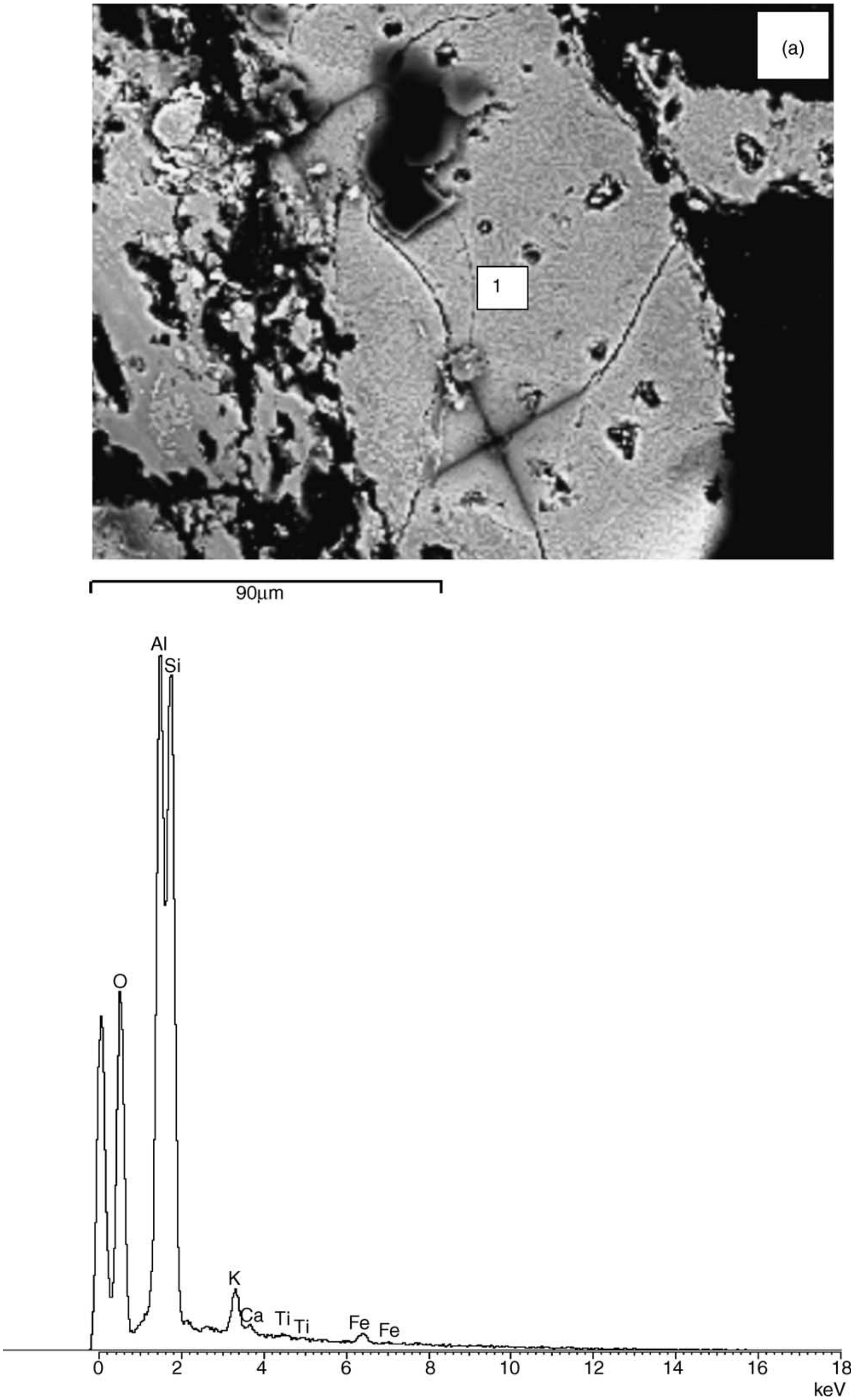


Fig. 6. (a) SEM image of a CONC sample with induced microcracks, (b) EDS spectra of the indicated area, labelled (1) in (a).

grains, exhibit diffuse crack branching. In agreement with the microcracking behaviour of other ceramics, e.g. porcelain stoneware tiles [11], the main crack is dispersed in numerous microcracks and it is finally stopped inside the quartz grains. This behaviour should contribute to toughening of the material, similarly to the microcracking toughening mechanism identified in several ceramic-ceramic and glass matrix composites [12,13].

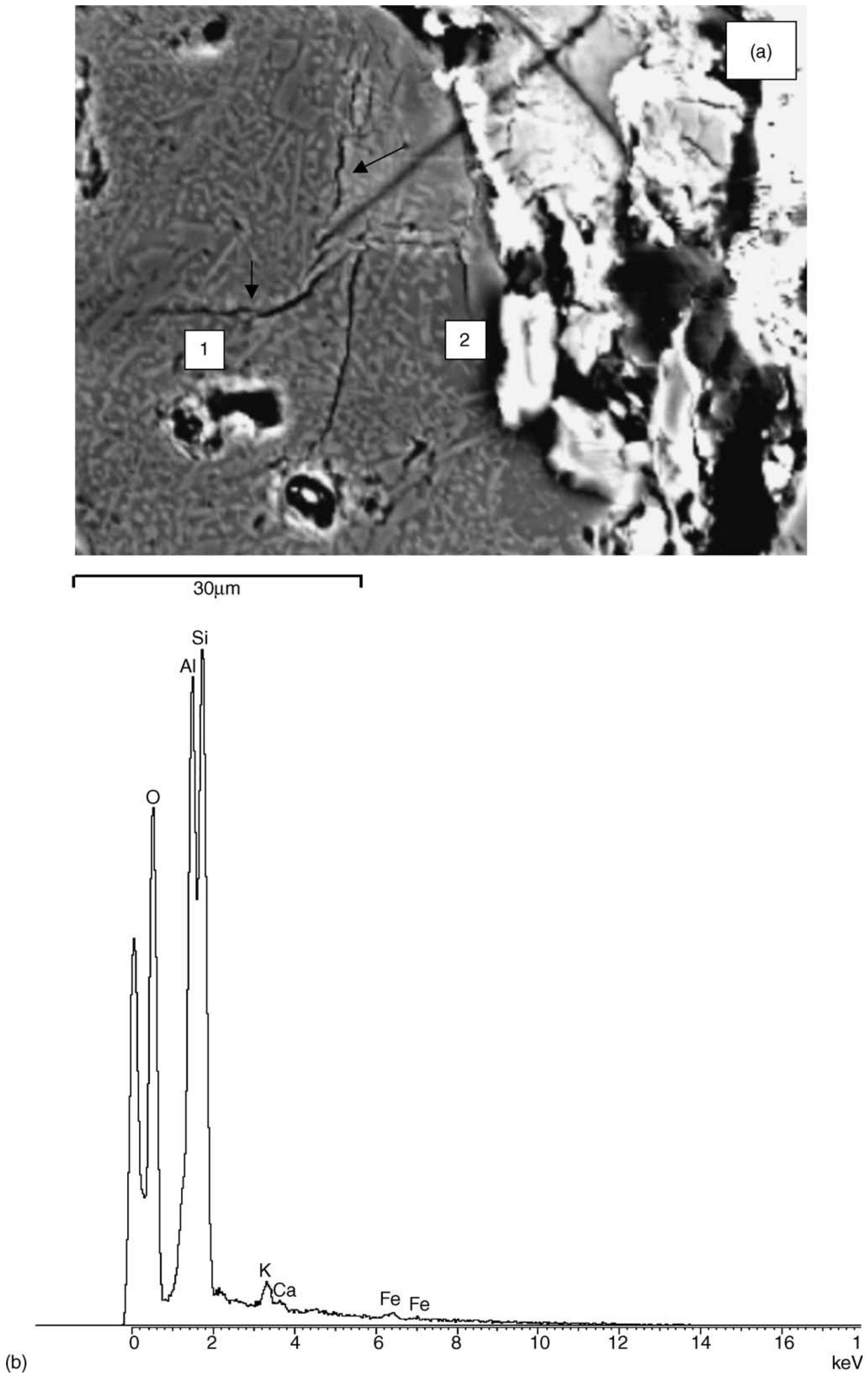


Fig. 7. (a) SEM images showing detail of crack propagation through a crystalline phase rich in Al and Si in a CONC sample, (b) and (c) EDS spectra of the indicated areas labelled (1) and (2) in (a).

Fig. 4a shows another SEM area of a REFO sample at high magnification, while Fig. 4b–d are the EDS spectra of selected areas. In Fig. 4a it is seen that the major crack is deviated by the small quartz grain, labelled (1) in Fig. 4a, which is weakly bonded to the glassy matrix, while areas presenting microcrystals of Mg-Al silicate, labelled (2) in Fig. 4a, induce only a slight deviation of the crack. These crystalline arrangements present higher alumina content

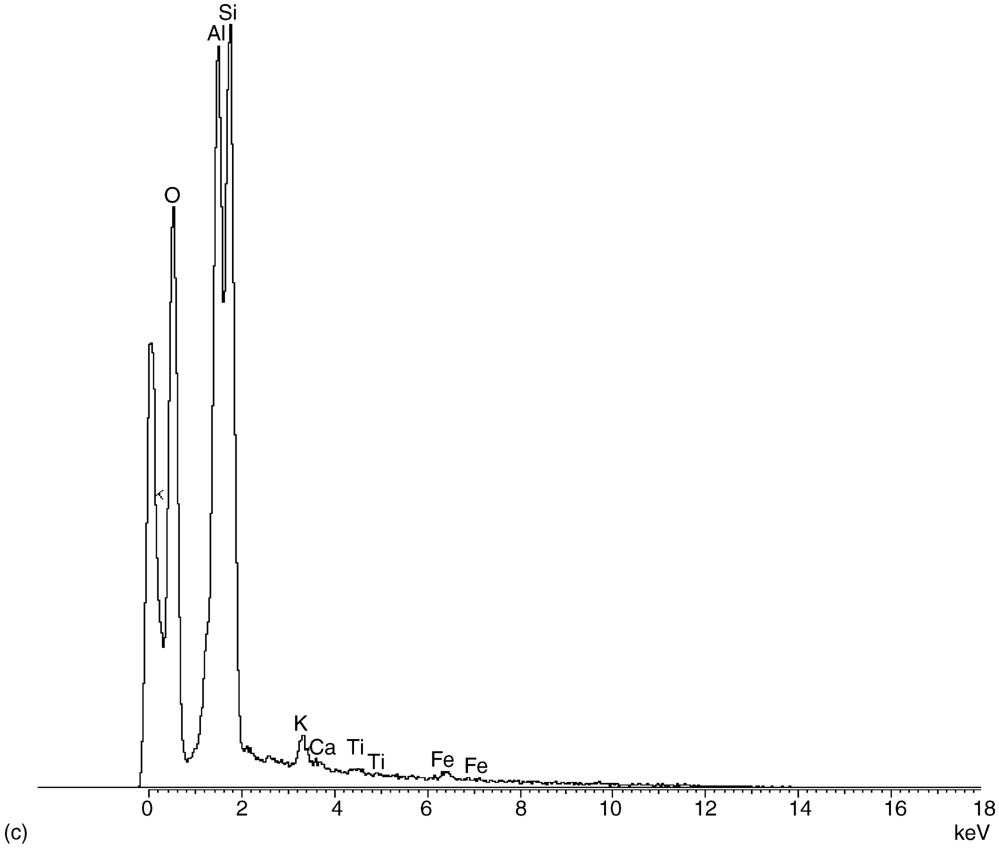


Fig. 7. (*Continued*).

than the area labelled (3) in Fig. 4a (compare also Fig. 4c and d), which can be considered very close to quartz (see comparison in Table 2). For crystals in the area labelled (2) the presence of a more adherent interface is thought to be responsible for the slight microcrack path deviation, contrarily to that encountered for small quartz crystals which seem to be weakly bonded to the matrix. Thus Fig. 4a shows that two mechanisms may be contributing to toughness in this material, particle debonding and crack deflection at small α-quartz grains, and to a lesser extent, crack deflection at Mg-Al silicate crystals.

Fig. 5a shows a crack which propagates in the centre of a cordierite rich area. The matrix, labelled (1) in Fig. 5a, is rich in Mg, Al and Si, as indicated in Fig. 5b, whilst the small needle-like crystals, labelled (2) and (3) in Fig. 5a, contain mainly Al and Si (Fig. 5c and d). The area labelled (1) in Fig. 5a has a cordierite composition whilst crystals in area (2) have a composition close to molochite, which is a compound mixture of amorphous SiO_2 (45 wt.%) and mullite (55 wt.%). Since molochite presents the same X-ray diffraction pattern as mullite, the investigation using EDS spectra appears to be a convenient method to identify the presence of molochite grains in the crystalline or amorphous phases present in refractory materials.

Regarding the microcrack propagation mechanism observed in this area of the REFO material, it is seen that the crack path is not locally deviated by the molochite small crystals. Thus, there should be no contribution of the presence of molochite crystal to toughening, at least at room temperature.

The microstructure of the CONC sample, as shown in Fig. 6a, presents a continuous phase in which small needle-like grains are embedded. As indicated by EDS spectra (Fig. 6b), the area labelled (1) is rich in Al and Si indicating possible formation of molochite crystals. The presence of this textured phase does not deviate the crack path to a great extent, in agreement with the finding in the REFO sample described above (Fig. 5a).

At higher SEM magnification, it is possible to observe some crack deflection from the small crystals, as indicated by arrows in Fig. 7a. Many of these crystals are embedded in the continuous matrix without any crack or sharp interface, indicating either an incipient solubilisation or uncompleted devitrification (Fig. 7a). The crystal composition shows less concentration of K and Ti than in the matrix, both being rich in Al and Si, indicating that mullite is the most possible crystalline phase. This is confirmed in Fig. 7b and c, which show EDS spectra of areas labelled (1) and (2) in Fig. 7a. Fig. 8a is a SEM image showing a crack path through an area

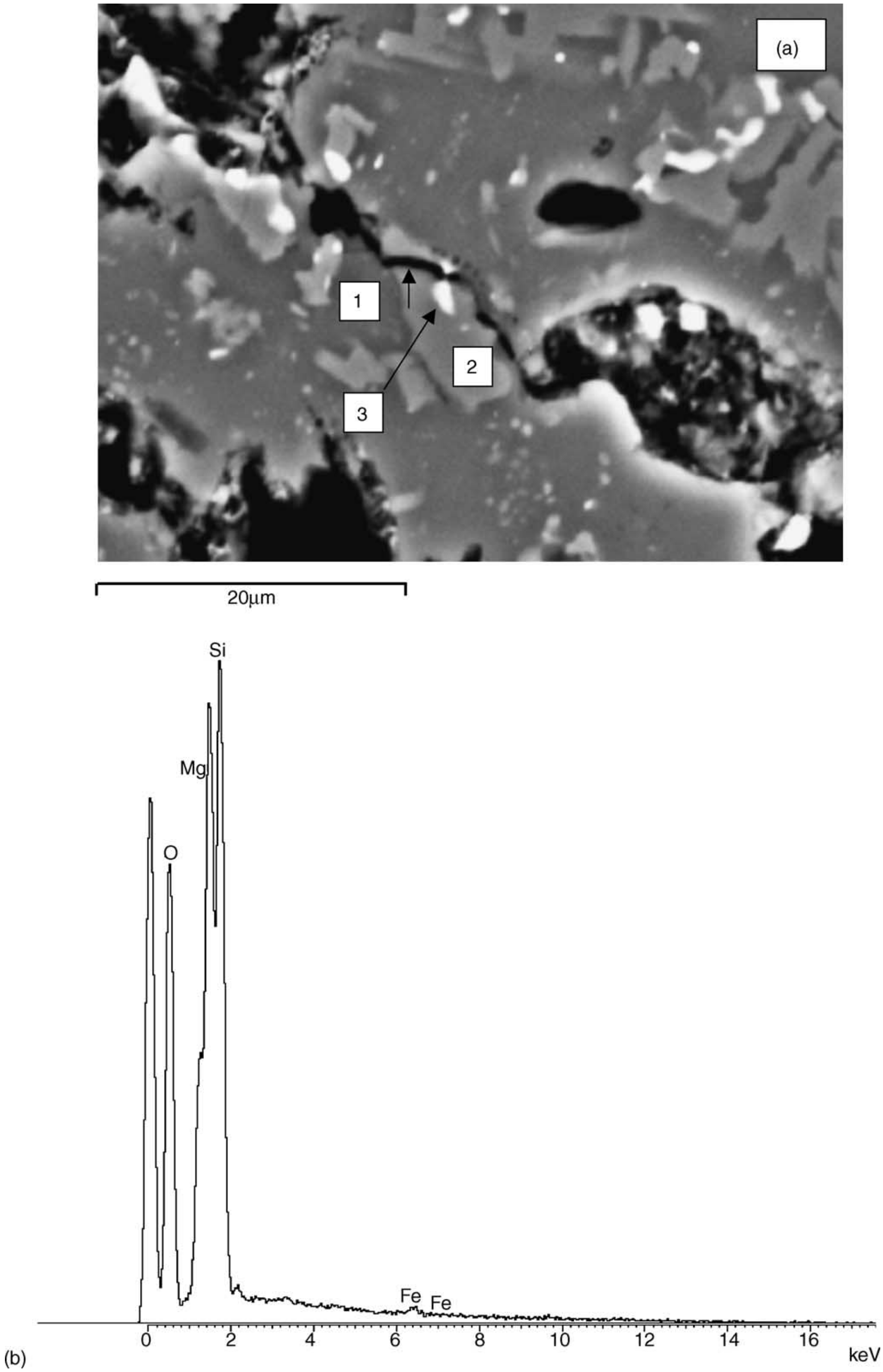
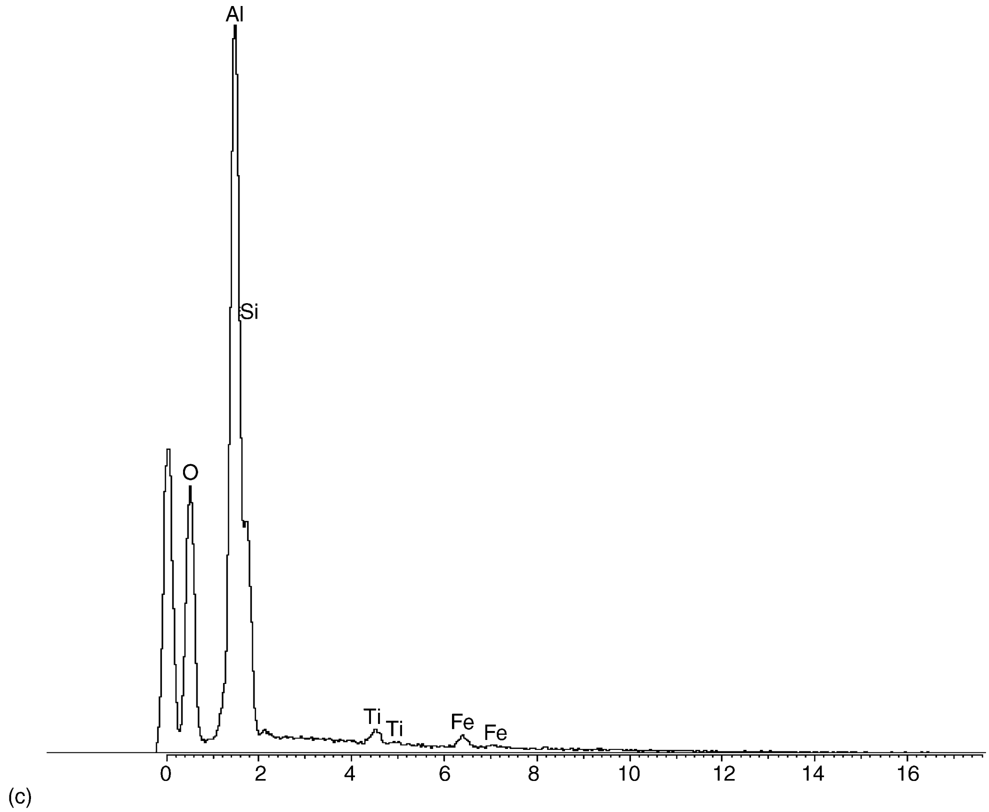


Fig. 8. (a) SEM image showing detail of crack propagation through an area rich in crystals of different shape and size in a CONC sample, (b)–(d) EDS spectra of the indicated areas labelled (1), (2), and (3) in (a).

rich of different crystals of very different shape and size in a CONC sample. The crack path is not deflected during propagation through the matrix, which has a stoichiometric cordierite composition (Fig. 8b and Table 2). Neither the light grey phase, rich in silica and alumina in mullite composition (Fig. 8c), nor the white crystal (Fig. 8d) rich in TiO_2 strongly affect the crack path since only a slight deviation is observed (see arrow in Fig. 8a). Mullite-rich



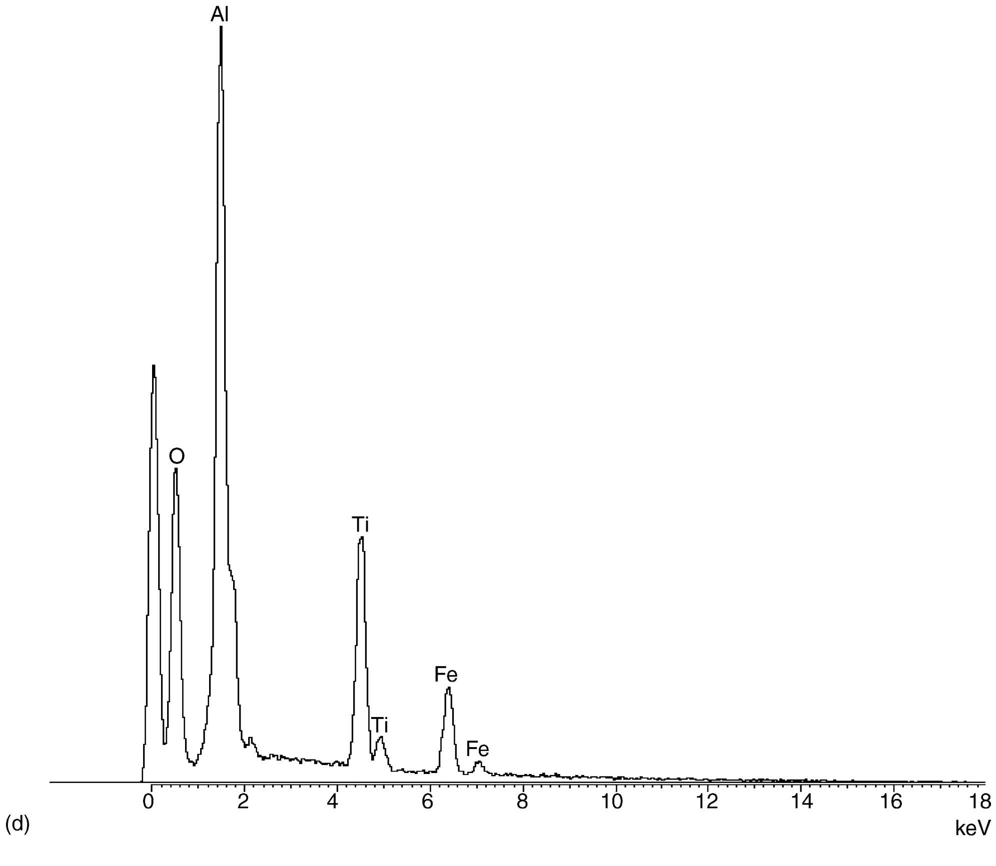


Fig. 8. (*Continued*).

crystals in the CONC sample are larger than in REFO samples, indicating the use of this crystalline component as raw material. Moreover there is a strong interface between the cordierite matrix and mullite crystals in the CONC material, leading to cracks propagating through both phases without major deflection.

4. Discussion

Flaw-crystallite interactions in glass-crystal systems have been studied in the past and detailed experimental [8] and theoretical [14] investigations are available for glass-ceramics, alumina and barium titanate ceramics. The nature of such interactions depends on [8]: (i) local stress distribution around the crystallites which can affect the local magnitude of stress, and (ii) the effect of the crystallites on the propagation behaviour of the flaws during mechanical or thermal loading. In the present study, these two aspects have been considered for cordierite–mullite refractories.

The observed crack propagation behaviour should have direct implications in the different room temperature mechanical behaviour and different thermal shock resistance exhibited by the REFO and CONC materials. The thermomechanical behaviour of one of the two refractory plates (REFO) has been studied recently [9]. Those preliminary results have indicated that REFO plate shows delayed crack initiation under thermal shock conditions. Preliminary investigations (not published) have shown that CONC plates exhibit early crack initiation and delayed crack propagation under actual in-service conditions resulting in a longer on-duty life.

The present results have shown that REFO samples show convenient crack propagation behaviour at room temperature because the diffuse microcracking of the α-quartz grains may act as an efficient toughening mechanism; whilst CONC samples show easier crack propagation due to the large glassy (structureless) phase present. However, at high temperature, this glassy phase in the CONC refractory microstructure should become viscous, and it could fill or blunt the propagating microcracks. This mechanism should explain the superior thermal shock behaviour of CONC refractories, as demonstrated and discussed in a separate investigation [15].

Other toughening mechanisms active in glass-crystal systems at room temperature, in particular crack deflection [2,3,8,11,12], seem to be minor contributors to toughness in the present refractory materials (see Figs. 4a, 5a and 7a). Toughness increases can also result from the interactions between propagating cracks and the localised stress field around inclusions [16]. However the quantification of the relative contribution of these mechanisms to toughness in the refractory materials of complex microstructure studied here is beyond the scope of the current investigation. The early studies by Morena et al. [8] and Cook et al. [14] present an in-depth investigation of these effects in glass-crystal systems of simple microstructure (model systems), e.g. aluminas, barium titanate and cordierite glass-ceramic.

5. Conclusion

Two refractory materials of commercial origin denominated REFO and CONC, which have wide industrial use in kilns for fast firing cycles of porcelain articles, were investigated in terms of microstructure and microcracking behaviour. The different microcrack propagation behaviour observed in the two materials can be explained on the basis of their different microstructure. The presence of α-quartz grains in the REFO samples, as confirmed by XRD diffraction patterns as well as by EDS spectra, should lead to better room temperature toughness of the REFO samples when compared to CONC samples. However the presence of the glassy phase in the CONC samples should result in better high-temperature fracture toughness of the CONC material. This different microcrack propagation behaviour of REFO and CONC materials should in turn explain their different thermal shock resistance.

In order to fully understand the thermal shock behaviour of these materials, further work should be carried out to measure properties which govern thermal shock resistance, i.e. Young's modulus, linear thermal expansion coefficient, fracture strength and fracture energy in order to determine their inter-relationship in thermal shock resistance parameters [17].

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