TEM AND AES STUDY OF MICROSTRUCTURE CHANGES DURING CREEP OF ALUMINA

FRANTIŠEK LOFAJ, JÁN DUSZA, BARBARA RICHARZ

Transmission electron microscopy (TEM), Auger electron spectroscopy (AES) and scanning electron microscopy (SEM) were used for the study of microstructure changes during creep of alumina in the temperature range of 1150–1300 °C. TEM revealed a presence of Si and Ca impurities in the intergranular phase between the Al_2O_3 grains. AES identified a very thin layer of secondary phase with Ca content on the fracture surface of the damaged specimens in the areas where microcrack formation between grains caused the failure. SEM revealed a cavity/micro-crack formation between the grains during the creep process on the tensile surface of the sample stressed in bending mode. Based on the detailed analysis, it seems that the main creep controlling mechanism in the studied material is cavity/microcrack formation influenced by the presence of impurities.

ŠTÚDIUM MIKROŠTRUKTÚRNYCH ZMIEN POČAS CREEPU Al_2O_3 KERAMIKY POMOCOU TEM A AES

Transmisnú elektrónovú mikroskopiu (TEM), Augerovu elektrónovú spektroskopiu (AES) a rastrovaciu elektrónovú mikroskopiu (REM) sme použili na štúdium mikroštruktúrnych zmien počas creepu Al_2O_3 keramiky v teplotnom intervale od 1150 do 1300 °C. Pomocou TEM sme zistili nečistoty Si a Ca v integranulárnej fáze medzi zrnami Al_2O_3. AES analýza potvrdila prítomnosť veľmi tenkej vrstvy s obsahom Ca na lomovej ploche v miestach, kde lom spôsobili mikrotrhliny medzi zrnami. Pomocou REM sme na ťahovom povrchu vzorky deformovanej v ohybe zistili vznik a rast kavít/mikrotrhlín medzi zrnami. Na základe analýzy možno predpokladať, že hlavným mechanizmom kontrolujúcim creep v študovanom systéme je vznik kavít/mikrotrhlín, ovplyvnený prítomnosťou nečistôt.

1. Introduction

The high temperature mechanical properties of engineering ceramics are controlled mainly by the properties of the grain boundary phases. These phases, arising

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from sintering additives and impurities, form usually continuous amorphous intergranular layers. Their physical and mechanical properties depend on the content of the additives and on the chemical composition: even a very low concentration of different impurities significantly affects high temperature properties [1–8]. The vitreous secondary phases can partially crystallize and/or change their local composition due to the heat treatment. The crystallization of the glassy phase was assumed to improve its mechanical characteristics and the concept of grain boundary engineering (GBE) was proposed to improve the properties of such materials [6]. Despite of a possible positive effect of crystallization, the simultaneous high temperature degradation of residual glassy phases can enhance the processes limiting the characteristics of these ceramics [7]. The other way to eliminate the deleterious influence of glassy phases at high temperatures is to reduce the contents of additives and impurities [8]. The analysis of the influence of the characteristics of extremely thin intergranular phases on the high temperature degradation processes in these "single" phase materials requires precise detection of the very low concentration of elements of additives and impurities in them. Transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) are usually used to reveal and characterize the microstructure boundary phases [8–10]. However, the determination of the composition with energy dispersive X-ray spectroscopy (EDS) is rather complicated due to their limited thickness and very low content of impurity elements. Auger electron spectroscopy (AES) allows to determine the presence of elements in very thin surface layers with the detection limit of 0.1–1%. Earlier AES studies of different two-phase ceramics showed that if the room temperature fracture occurred intergranularly, crack would propagate inside the glassy phase [12–17].

Single phase alumina with a small amount of additives (usually 0.1–0.25% MgO) is very suitable for a model study of basic high temperature fracture processes. Considerably lower Mg concentration than expected and the segregation of Ca as well as C impurities were observed in grain boundary phases on room-temperature fracture surfaces by different authors and methods including AES [10, 11, 15–19]. However, most of the above mentioned AES studies of alumina and other ceramics [12–15, 17] were related to room-temperature fracture surfaces of the as-received materials. Our recent studies of creep behaviour of commercial alumina [20–21] showed intensive cavitation and considerably lower values of secondary creep rates than those reported for vitreous bonded alumina at the same conditions. Detail information about the microstructure, intergranular phase compositions and their possible influence on the cavitation are required for better understanding of creep deformation and rupture processes in the studied model material.

The aim of this work is a detailed characterization of secondary phases and their role in microstructure changes during creep of commercial alumina by two analytical methods – TEM/EDS and AES.

2. Experimental methods

The commercial alumina (Feldmühle AG, Plochingen, Germany) containing 4% MgO and Al_2O_3 additives with the mean grain size $\sim$ 5.4 μm and about 4% porosity was studied after creep tests in 4-point bending tests with outer/inner rollers span of 40/20 mm (HTTF2, SFL Ltd., Scotland) in the temperature range of 1150–1300 ℃ in air. The results of the creep tests are reported elsewhere [20–21].

The specimens were cooled down under load and their tensile surfaces were examined by scanning electron microscope (SEM) to reveal creep cavities and micro-cracks. The substructure of the tensile stress zone was investigated by TEM (JEOL 2010) combined with windowless energy dispersive X-ray spectrometer (EDS) on thin foils prepared by grinding, dimpling, and ion thinning. Several different methods were used to reveal the presence of secondary phases – bright and dark field, lattice fringe, and defocusing imagining [9]. The room-temperature fracture of the crept specimens, similarly as the fracture of an undeformed one, can occur in brittle manner mainly intergranularly, fracturing the glassy phase between the grains and especially between the developed creep cavities on grain interfaces. The evidence of creep cavity formation was found in such a way by SEM in vitreous bonded alumina [1–3]. It is suggested that the AES study of inner surfaces of creep cavities should be possible on such fracture surfaces. The samples for the AES study were prepared from crept alumina specimens by cutting approximately 0.7 μm thin slice from the zone between the inner rollers, parallel to the tensile surface by a wire saw. This sample was broken inside the microscope (Scanning Auger Microscope, Microlab 310-D, MPI für Eisenforschung, Düsseldorf, Germany) under ultra high vacuum conditions to avoid surface contamination. The composition of surface layers from different local zones of transgranularly and intergranularly fractured grains (including cavities) was analyzed under the accelerating voltage of 5 kV. The fracture surface of the specimens was coated by Au after the AES study and studied by SEM.

3. Results

SEM study of the tensile surface of the crept specimens revealed the presence of the full facet crack-like cavities in relatively early stages of deformation and large creep cracks in later stages which propagated only intergranularly due to the crack tip linking with the isolated full facet cavities in front of it (Fig. 1). SEM observations of the fracture surfaces of crept specimens broken at room temperature (after the AES study) showed that fracture occurs mainly intergranularly, but transgranular fracture mode was also present, especially in the case of large grains (Fig. 2). In contrast to the tensile surface, the study of fracture surface of crept specimens did not reveal the traces of cavity growth on grain facets due to a glassy phase morphology change as it was reported in [2, 3]. However, the changes in the

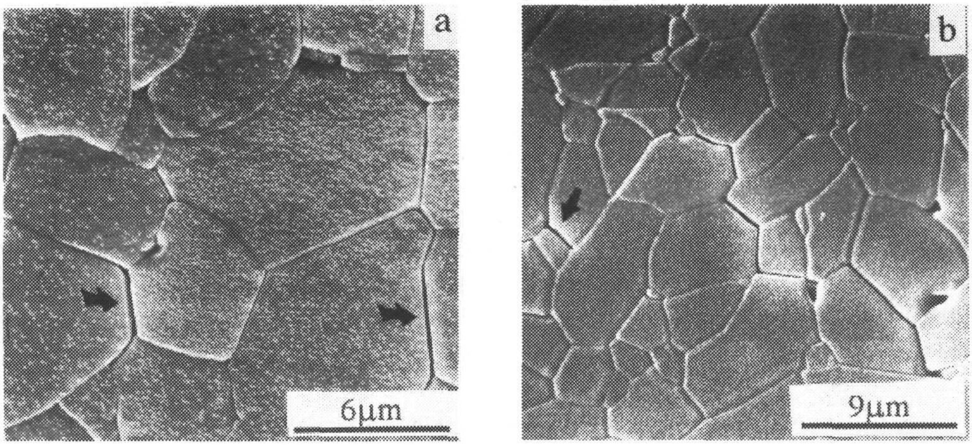


Fig. 1. Tensile surface of the studied alumina after relative creep strain of 1.1% (1300 °C, 98 MPa): a – full facet cavity; b – mechanism of creep-crack propagation by linking with the isolated cavities in front of the crack tip.

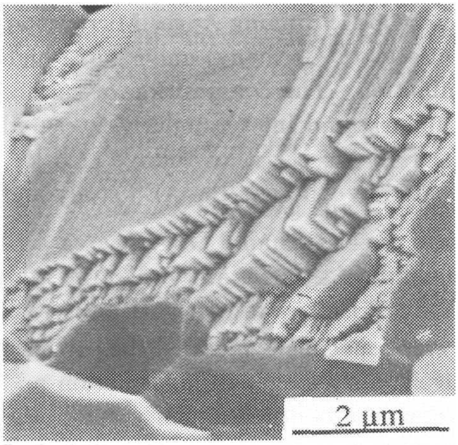


Fig. 2. Cleavage of a large alumina grain.

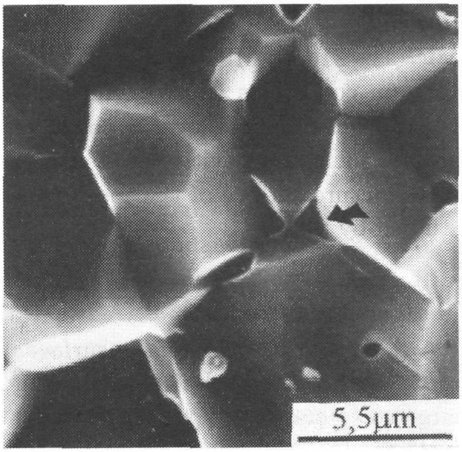
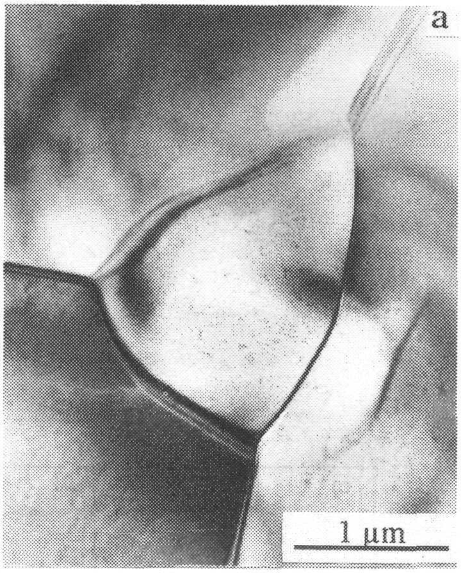


Fig. 3. Formation of a full-facet cavity due to the growth of crack-like cavities from two adjacent triple points (after creep at 1300 °C up to ~ 1% of outer fiber strain).

geometry of cavity-like pores in triple points and grain edges were identified (Fig. 3). These cavities grew from the triple points along the grain boundaries (see arrow). It should be noted that the identification of the origin of these cavities on grain facets is complicated due to the presence of the pores with a similar morphology.

TEM study of thin foils showed the presence of 3–10 μm large as well as approximately 1 μm small grains (Fig. 4a). EDS analysis revealed that large grains contained only Al and O (Fig. 4b) whereas also a considerable amount of Mg was present in small grains (Fig. 4c). Different types of triple points and grain boundaries were identified in the crept specimens: the most often observed ones are created by three alumina grains without the presence of a pore and without detectable amount of a secondary phase (Fig. 5a). The presence of glassy phase on the grain boundaries was not identified by HREM because of possible overlapping of grain lattices and lack of the wedge-on boundaries in the studied foils. However, the existence of a very thin layer of the the secondary phase is not



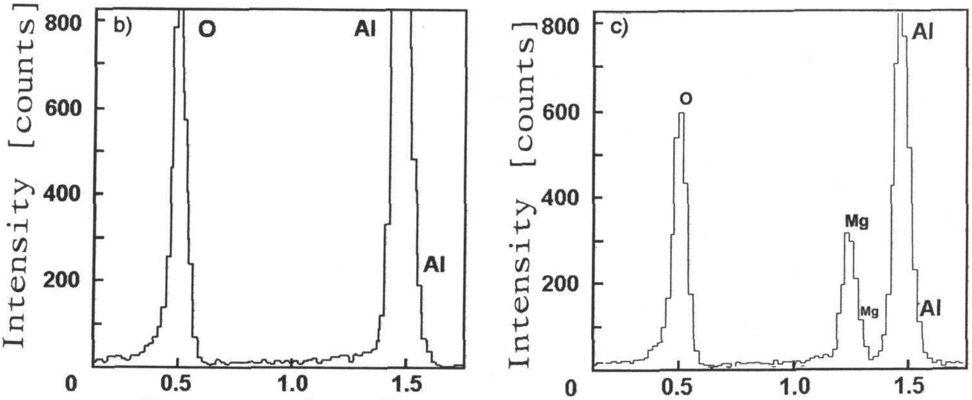
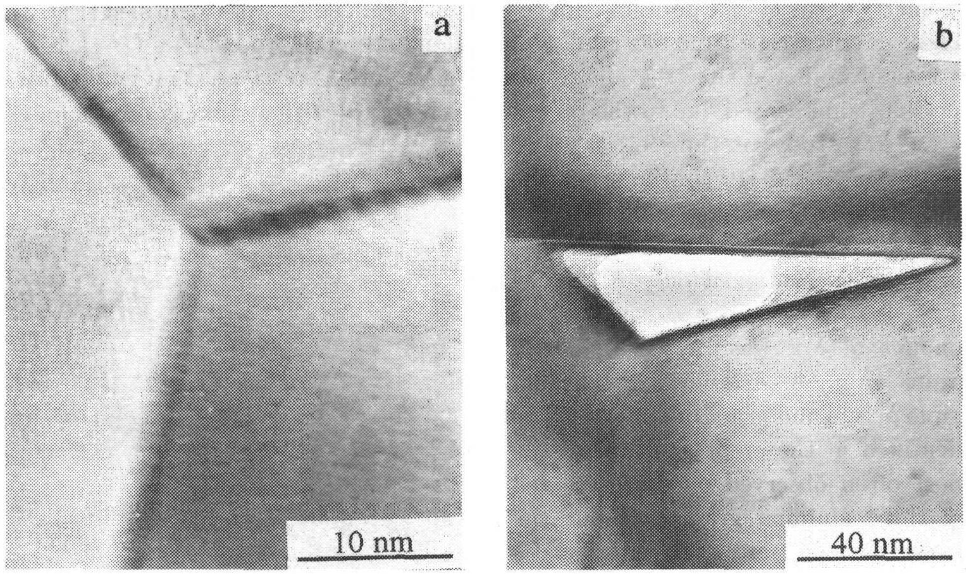


Fig. 4. a – characteristic microstructure of alumina, b – EDS spectrum of a large grain, c – EDS spectrum of a small grain.



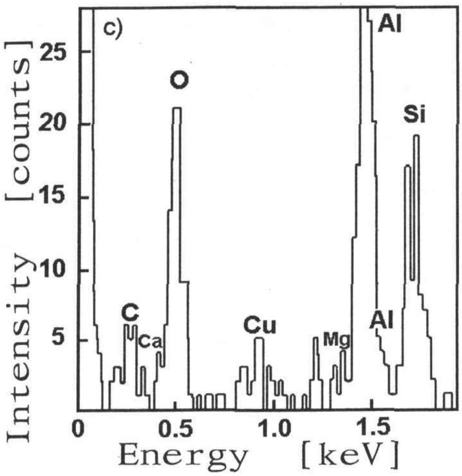


Fig. 5. Morphology of typical triple points and grain boundaries in the studied alumina: a – without detectable intergranular phase, b – triple point containing cavity-like pore and glassy phase, c – EDS spectrum of the glassy phase at a triple point.

excluded. The second type of triple point contained a pore (or cavity) between three rounded grains and the small amount of the glassy phase around it. Only a very limited number of triple points with pore-like creep cavities and glassy phase was found in the studied thin foils (Fig. 5b). The number of these cavities was low and comparable with the results of the fractography study. The composition of the secondary phase in such triple points was complex (Fig. 5c): they contained Si and Mg from sintering additives and Ca impurities were found there, as well (C was evaporated on thin foils to provide their electroconductivity and Cu was present because the specimen holder contained Cu).

AES spectra measured on fracture surfaces after creep showed two different compositions: the large, transgranularly fractured grains (see Fig. 2) revealed only the characteristic peaks at ~ 1378 and ~ 503 eV for Al and O, respectively (Fig. 6,a) [22]. AES spectra of different sites on grain facets after intergranular fracture (Fig. 6,b) revealed the presence of new peaks besides Al and O with the characteristic energies of approximately 75 and 270–300 eV. These peaks were identified as peaks of Si (76 eV in the form of oxide), Ca (the characteristic energies 291, 294 and 318 eV) and small amount of C (272 eV) [22]. The presence of Mg, expected on the base of EDS analysis, was almost not visible in the measured spectra and its concentration seemed to be less than 1%. The identical compositions of secondary phases were determined at different sites of grain facets – inside the pores and pore-like cavities and also from the areas between such pores.

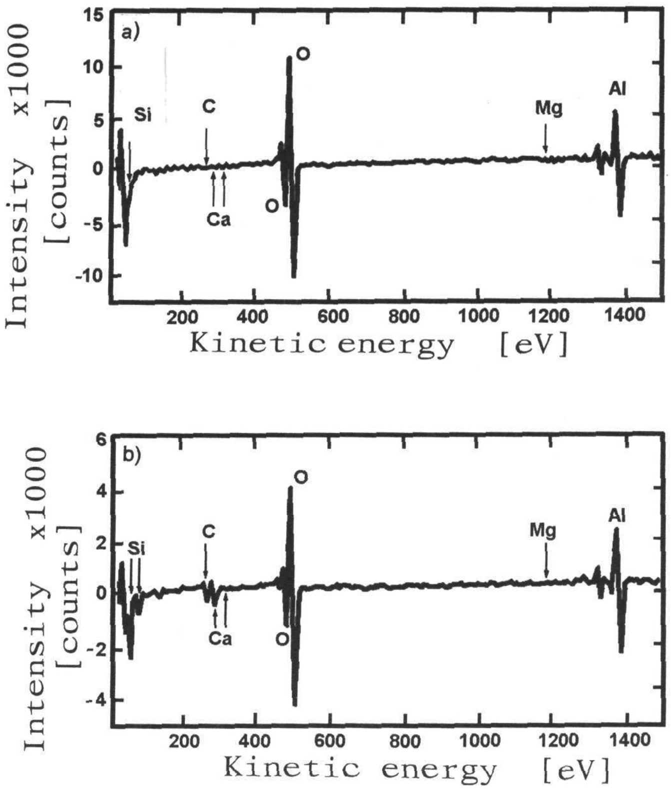


Fig. 6. AES spectra: a – of transgranularly fractured alumina grain, b – of grain facets after creep and room-temperature fracture.

4. Discussion

The TEM/EDS study of thin foils showed that the microstructure of the studied material is very similar to the single phase alumina. The additives of MgO are concentrated in small grains, Si and Ca impurity – in small glassy pockets at triple points. This observation is consistent with earlier studies on single phase alumina where the presence of Mg-rich particles, identified as $MgAl_2O_4$, and segregation of impurities in the glassy phase were determined [23]. The formation of magnesium spinel grains could explain the relatively low content of Mg in the glassy phase revealed by AES on the grain facets and its small thickness. The concentration of glassy phase at three grain junctions and formation of thin, continuous intergranular phase on the grain interfaces with constant thickness in equilibrium state was proposed by Clarke [24] and experimentally supported e.g. in [4].

Auger electron spectroscopy offers an exact evidence of the presence of a very thin glassy phase on the grain facets. The grain boundary phase contains a relative high amount of Ca and C impurities and practically no Mg is found there. The detection of high concentration of Ca in comparison with Mg is in very good agreement with the earlier studies on similar materials [10, 15–19], which reported Ca segregation on grain boundaries. The presence of carbon in the secondary phase was also reported in high purity alumina and its source was supposed to be the starting powder [16, 23]. It was shown in [16] that carbon was responsible for active cavitation during annealing at 1630 ℃ in air due to the CO/CO_2 formation. However, carbon could hardly cause the cavity formation observed in our experiments at considerably lower temperatures and under the bending stresses. We connect them only with creep damage development during deformation. The AES spectra from the zones inside the pore-like cavities indicate that the creep cavities had grown during high temperature creep deformation inside the glassy phase in the similar way as the fast cracks at the room temperature, although the thickness of the glassy phase layer is found to be only of several atom layers. It means that the surface energy of glass was considerably lower than the surface energy of the glass-alumina interface and/or alumina surface.

The segregation of Ca and C in grain boundary phase could also influence the ratio of surface energies on different interfaces, equilibrium secondary phase thickness [4] and contribute to easier grain boundary sliding, cavity nucleation, growth along the grain facets, development of creep cracks, and finally to creep rupture [2].

The SEM study confirmed the controlling role of grain boundary phase in creep cavitation. Cavities are nucleated mainly in three grain junctions and grew along the grain facets inside this secondary phase. Fig. 3 illustrates the mechanism of discontinuous creep-crack growth by its linking with damage (full facet cavities) ahead of the crack tip. Such creep-crack growth can be described by the model, assuming the cavity nucleation in triple points after grain boundary sliding, which was proposed in [1] for the ceramics, containing small amount of glassy phase.

5. Conclusion

The TEM study of the microstructure changes in the studied commercial alumina with the additives of MgO and Al_2O_3 showed that Mg was concentrated in small grains, which formed probably magnesium spinel, while Si and Ca impurities were segregated in boundary phase in triple point pockets. AES allowed to identify the presence of very thin secondary phase on grain facets and determine its composition. The segregation of Ca and the presence of C impurities was confirmed in this phase.

SEM observation showed the cavity formation after creep, and AES revealed approximately the same glassy phase composition inside the creep cavities, developed at high temperatures, as on the grain facets fractured intergranularly at room temperature. The growth of creep cracks inside the secondary phase indicated the controlling role of the secondary phase in creep cavitation and rupture. The segregation of the above mentioned impurities can significantly influence both the surface energy and mechanical properties of glassy phase and creep resistance of the studied material.

Auger electron spectroscopy in combination with TEM/EDS of thin foils showed to be a very powerful tool for the study of chemistry of the thin secondary phases in alumina and its influence on the high temperature mechanical properties.

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