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Properties of zirconia-toughened mullite ceramics improved by B_2O_3 additive

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Zirconia-toughened mullite (ZTM) ceramics has been prepared by using an electrically fused mullite as a raw material and its mechanical properties and microstructure as a function of impurities in the raw material were studied. These impurities led to a decrease in the mechanical properties of ZTM ceramics by changing the properties of the glassy phase in the ceramics, especially at high temperature. The mechanical properties of the ceramics were improved by adding B_2O_3, and the toughness at room temperature increased from 4.4 MPa $m^{1/2}$ to 5.9 MPa $m^{1/2}$ while that at 800 °C increased from 2.9 MPa $m^{1/2}$ to 4.4 MPa $m^{1/2}$. The toughness of the ceramics on the addition of B_2O_3 at room temperature was increased by 34% and that at 800 °C by 52%. The influence of the impurities on the ZTM ceramics and the improvement of the ceramic properties by the addition of B_2O_3 were studied and their mechanisms were discussed.

1. Introduction

Mullite is a potential candidate for high-temperature application because of its low thermal expansion coefficient ($\sim 5 \times 10^{-6}$ °C^{-1}), low thermal conductivity (~ 2 W m^{-1} °C^{-1}), chemical inertness, thermal stability, and mainly because of its high creep resistance [1]. Its oxidation product always contains an alumino-silicate plus mullite phase, which remains protective because of viscous flow relaxation of volume-change-induced stresses. Thus the ceramic provides fairly good long-term thermal stability. Mullite ceramics toughen on the addition of ZrO_2 particles. This toughening of mullite by ZrO_2 is understood to be a result of the transformation of t-ZrO_2 to m-ZrO_2 (transformation toughening) and microcrack formation around m-ZrO_2 (microcrack toughening) during crack propagation [2–4].

The zirconia-toughened mullite ceramics (ZTM) are prepared either by using electrically fused mullite as the raw material or a high-purity mullite. The latter is characterized by an evident increase in the ceramic mechanical properties (bending strength and fracture toughness) at high temperature, but the former shows the opposite trend because of the existence of some alkali-metal impurities (such as Na^+ and K^+) in the raw material used. In this work, electrically fused mullite was chosen as the starting material to prepare ZTM ceramics and B_2O_3 as an additive was added to the ceramics. The influence of the raw material on the properties of ZTM ceramics and the removal of the impurities from the matrix by the additive was investigated. The reason for this lies in the fact that the impurities exist mainly in the glassy phase and the grain boundaries in the ceramics, and the additive can absorb the impurities when it is added to the ceramics because of its loose network structure [5]. This research work is an important and meaningful project, which will promote improvement of the ceramic properties and the application of ceramics to high-temperature and abrasive situations.

2. Experimental procedure

The electrically fused mullite used in this experiment is an industrially pure product, which contains many impurities, such as Na^+, K^+, etc. Table I gives the contents of the main impurities obtained by atomic adsorption spectroscopy (AAS).

ZTM ceramics were prepared by using the electrically fused mullite and $Zr(OH)_4$, which was prepared by the coprecipitation method using zirconium oxychloride and yttrium oxide as starting materials. The mixture was heated at 800 °C. The average particle sizes of ZTM powder were about 1–3 μm. The composite powder was dry-pressed into a cuboid of edges 8.4 cm × 4.2 cm × 0.7 cm, isostatically pressed at 220 MPa and sintered at different temperatures for 4 h. The sample was machined into dimensions 0.25 cm × 0.50 cm × 36 cm.

Flexural strength of the specimens was determined by three-point flexure with a span of 2 cm at a loading rate of 0.017 cm min^{-1}. Fracture toughness was determined by the single-edge notched beam method for test bars of similar dimensions, with a 0.25 cm deep diameter swan V notch (90°), using a loading length and rate of 2 cm and 0.006 cm min^{-1}, respectively. Bulk density and apparent porosity were measured by using the water displacement method according to Archimedes' principle. Phase compositions of ZrO_2 in the samples were analysed by X-ray diffraction (XRD)

TABLE I Chemical compositions (wt %) of the electrically-fused mullite

Al_2O_3	SiO_2	Na_2O	K_2O	CaO	Others
76.66	21.54	0.17	0.02	0.26	1.35

and their contents calculated according to the formula proposed by Garvie and Nicholson [6]. ZTM powder was analysed by high-temperature microscopy. The microstructure of the ceramics was observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Influence of B_2O_3 additive on sinterability of ZTM ceramics

B_2O_3 additive was added to the ceramics after mixing of the mullite powder and $Zr(OH)_4$ powder. It was found that the additive obviously affected the sinterability of the samples. The linear shrinkage behaviour of two powders (one with 0.75 wt % B_2O_3 and one without the additive) was examined, as illustrated in Fig. 1.

As shown in Fig. 1, the powder with 0.75 wt % additive had larger shrinkage than that without the additive below 1200 °C. From the sinterability of the ceramic samples, it was found that bubbles formed in the surface of the specimens on the addition of B_2O_3. This resulted from some volatile substances which existed in the samples. These volatile substances formed a higher pressure inside the ceramics during sintering and thus affected its densification. The substances must be extruded from the ceramics in order to make it densify. The volatile substance was certainly the additive B_2O_3. Thus the additive suppressed the sinterability of the ceramics. In order to enable boron oxide to escape entirely before the sintering of the ceramics, a slow heating rate and a long hold time were used over a temperature range 900–1100 °C. As reported elsewhere [5], boron oxide evaporates during this temperatures range. Table II shows the variation of the sintering properties of the ceramics with B_2O_3 additive.

3.2. Relationship between the properties of ZTM ceramics and amount of B_2O_3 added

The determined mechanical properties of various ZTM samples are listed in Table III. The sample with addition of 0.75 wt % B_2O_3 had the worst properties, with a bending strength of only 195 MPa and a fracture toughness of 4.9 MPa m$^{1/2}$. The properties of samples were gradually enhanced when the amount of B_2O_3 added was increased (> 0.75 wt %).

ZrO_2 in the samples contributes to transformation toughening and microcrack toughening. However, the amount of ZrO_2 added was the same for all the samples in this experiment. Therefore, the function of B_2O_3 on the ceramics seems very obvious. As shown in Table I, the raw material used contained more alkali-metal ions, such as sodium ions (Na^+) and potassium ions (K^+), which were the dominant factors in deteriorating the ceramic properties. It is seen from Table III that the strength for the samples with more than 2.25 wt % B_2O_3 was slightly higher than that without B_2O_3 but the toughness was much increased. The toughness for the sample with 2.6 wt % B_2O_3 reached 5.9 MPa m$^{1/2}$, but that for the sample without B_2O_3 was only 4.4 MPa m$^{1/2}$. The former was 34% higher than the latter. It is reasonable to consider that the boron oxide cleared the grain boundaries in the ceramics because it removed the impurities introduced by the raw material.

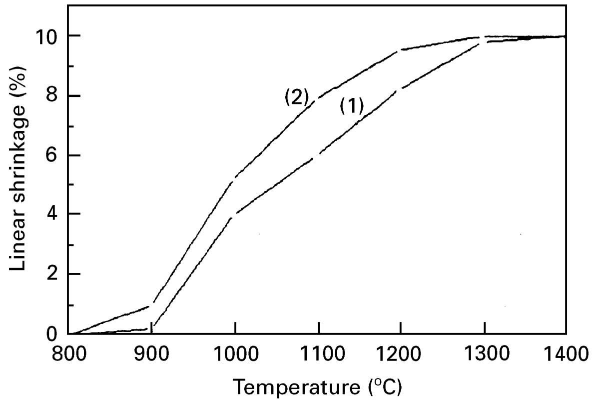

Figure 1 Linear shrinkage of the samples; (1) 0 wt % additive, (2) 0.75 wt % additive.

TABLE II Sinterability of ceramic samples

	B_2O_3 (wt %)				
	0	0.25	0.75	1.50	2.25
Linear shrinkage (%)	16.0	16.1	15.0	15.6	16.5
Relative density (%)	99.0	98.6	99.2	99.5	100
Porosity (%)	1.3	0.8	1.2	1.4	1.6

3.3. Mechanical properties of the ceramics at high temperature

The mechanical properties of the ceramic samples were determined at different temperatures. The strength and toughness of all the samples at 800 °C are listed in Table IV and the toughness of the samples as a function of temperatures is plotted in Fig. 2.

As shown in Table IV and Fig. 2, the toughness of all the samples decreased with temperature, but the extent to which it was lowered was different for each sample. At 800 °C, the toughness without the additive was the lowest. Table V gives the ratios of the properties of the samples at 800 °C to that at room temperature.

The ratios for the samples with the additive were higher than those for the sample without the additive. Thus, the extent by which properties are lowered with temperature is smaller for the samples with the additive. The addition of B_2O_3 contributed to the properties of the ceramic samples at high temperature. Under

TABLE III Influence of B_2O_3 additive on the properties of ZTM samples

	B_2O_3 (wt %)						
	0	0.25	0.75	1.50	2.25	2.60	3.00
Strength (MPa)	300	235	195	250	320	325	320
Toughness (MPa m$^{1/2}$)	4.4	5.5	4.9	5.4	5.8	5.9	5.7

TABLE IV Properties of ZTM ceramics at 800 °C

	B_2O_3 (wt %)						
	0	0.25	0.75	1.50	2.25	2.60	3.00
Strength (MPa)	205	205	195	230	275	280	280
Toughness (MPa m$^{1/2}$)	2.9	3.9	3.8	4.1	4.2	4.3	4.0

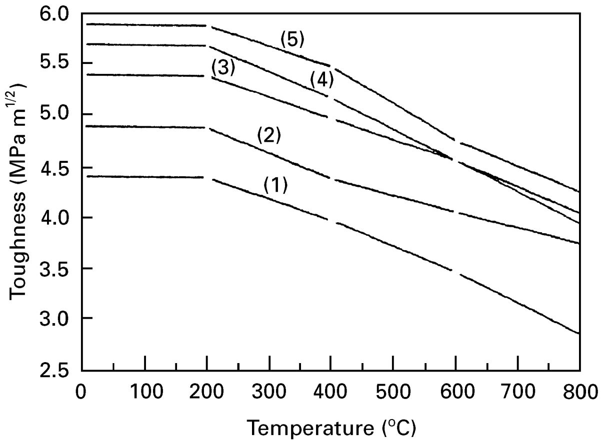

Figure 2 Variation of toughness with temperature. (1) 0 wt % additive; (2) 0.75 wt % additive; (3) 1.5 wt % additive; (4) 2.6 wt % additive; (5) 3.0 wt % additive.

TABLE V Comparison of the ratios of the ceramic properties

	B_2O_3 (wt %)				
	0	0.75	1.50	2.60	3.00
$\sigma_{f,800\,^\circ C}/\sigma_{f,RT}$	0.68	1.00	0.92	0.86	0.87
$K_{IC,800\,^\circ C}/K_{IC,RT}$	0.66	0.78	0.76	0.73	0.70

high temperature condition, the boron oxide will enter the grain boundary and glassy phase in the ceramics. Because alkali-metal ions exist in the matrix, they provide free oxygen and produce a change in the B_2O_3 structure from the B–O triangle (BO_3) to the B–O tetrahedron (BO_4). The change in the structure of B_2O_3 is dependent on alkali-metal ions and B_2O_3 content. By volatilizing at high temperature, the boron oxide, with the impurities, escape from the ceramic matrix, and the viscosity of the glassy phase is thus increased. The viscous glassy phase led to an enhancement of the ability to prevent cracks from propagating, and thus the properties of the ceramics were improved. Therefore, the properties of the ceramics were improved by adding B_2O_3, which restrained the function of these impurities in the raw material.

TABLE VI t-ZrO_2 content in the ceramic samples

	B_2O_3 (wt %)				
	0	0.75	1.50	2.60	3.00
t-ZrO_2 (vol %)	46.5	17.1	16.4	16.5	15.9
m-ZrO_2 (vol %)	53.5	82.9	83.6	83.5	84.1
Transformable (vol %)	24.6	3.5	2.8	2.7	2.4

3.4. Variation of zirconia phase compositions in the ceramics

Zirconia phase compositions in the ceramic samples with the addition of B_2O_3 varied because t-symmetry to m-symmetry transformation occurred in zirconia [7–9]. This transformation determines the toughening mechanism for the ceramics and leads to the change in the ceramic properties. Table VI shows t-ZrO_2 contents for the samples, where the transformable amounts were determined according to the difference between the t-ZrO_2 content in the natural surface of the sintered bodies and that in a fractured surface of the bodies.

Hence, the t-ZrO_2 content in the samples was decreased on addition of B_2O_3. It was found that the transformable amount for the samples with the additive was much lower than that for the sample without the additive. The addition of boron oxide was proved to suppress the phase transformation of the zirconia and decrease its transformation toughening function. The main contribution of the zirconia to the ceramics was thus only the microcrack toughening. The toughening mechanism of the ceramics is also attributed to the improvement of the glassy phase property resulting from the addition of B_2O_3.

3.5. Microstructure of ZTM ceramics

The microstructure of the ceramic sample with an addition of 0.75 wt % B_2O_3 was observed by SEM.

Fig. 3 shows the SEM microstructure of a sintered surface and a fracture surface of the sample and

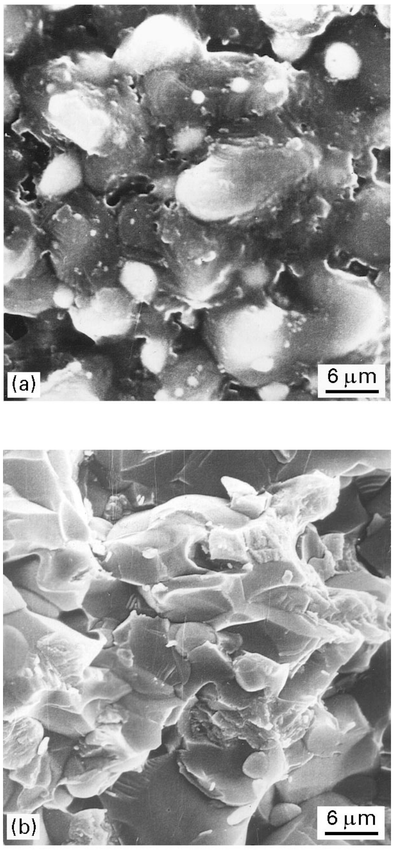

Figure 3 The scanning electron micrographs of (a) the sintered surface of the sample, and (b) the fracture surface of the sample.

reveals that ZrO_2 particles were homogeneously distributed in the sample. Mullite particles were larger than zirconia particles. It is seen from Fig. 3 that no abnormal grain particles exist but there are some holes in the fracture surface of the sample. This is most likely related to the pull-out of the particles. The pull-out process is a mechanism for the improvement of the ceramic properties.

4. Conclusion

Na^+ and K^+ ions in the raw material of mullite decreased the properties of ZTM ceramics, primarily due to the lowering of the viscosity of the glassy phase in the ceramics. B_2O_3 additive can clear the grain boundaries and improve the property of the glassy phase in the ceramics. The ZTM sample with an addition of 2.6 wt % B_2O_3 has the highest toughness reached 5.9 MPa $m^{1/2}$, 34% higher than that of the sample without the additive.

The addition of B_2O_3 evidently enhances the ceramic properties at high temperature by removal of the impurities in the raw material and improvement of the properties of the glassy phase in the ceramics. It also resulted in a decrease of the t-ZrO_2 content in the ceramics and so suppressed the transformation toughening function of zirconia.

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