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Assessment on mechanical properties controlling of alumina ceramics for harsh service conditions

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Abstract

Improvement of mechanical properties of alumina ceramics is investigated by addition of MgO and ZrO_2 starting from inorganic precursors. The doping of alumina ceramics is performed by infiltration of solutions of magnesium chloride and zirconium oxychloride into preformed samples. Two types of alumina powders were used. The impregnated samples were fired in 1550–1780 °C temperature range and characterised by bulk density, bending strengths and their microstructure are analysed. The dispersion and concentration of reinforcing particles is analysed by electron microprobe (energy dispersive analysis).

After firing the infiltration method leads the dopants concentrate especially at the surface of samples. The surface enrichment in dopants determines increased strengths with about 17–27% as function of sintering temperature.

Keywords: Al_2O_3; ZrO_2; MgO; Mechanical properties; Sintering

1. Introduction

The improvement of mechanical properties of alumina ceramics for harsh mechanical exploitation conditions is very challenging for the researchers in the last decades.[1–3] The fracture behaviour of alumina is strongly affected by microstructure due to crack deflection, secondary microcracking and crack bridging phenomena. The thermal expansion anisotropy of alumina is responsible for these behaviour.[4] A possible way of modify the mechanical strengths of an alumina matrix is to avoid abnormal grain growth during sintering. This can be achieved by addition of a dispersion of particles (as secondary phase) such as MgO, ZrO_2, Cr_2O_3, etc. The presence of secondary phase can have a role of inhibitor of alumina grains growth during sintering and consequently a favourable influence on bending strengths.[5–10] On the other hand, the discover of martensitic transformation t → m of ZrO_2 as toughening mechanism[5–8] which is responsible for the strength[5] and toughness[6] at room temperature of tetragonal zirconia polycrystals (TZP) has been receiving increasing attention in obtaining of so called zirconia toughened alumina (ZTA) ceramics containing several % of ZrO_2. It has been shown that tetragonal precipitates determine hardening in partially stabilised zirconia (PSZ) single crystals with respect to totally stabilised zirconia (TSZ)[7,8] at low temperatures.

In present paper, the mechanical strengths correlated with the microstructure and the densification degree determined by the MgO or/and ZrO_2 infiltrated as secondary phases in porous alumina ceramics, after sintering in air, in 1550–1780 °C temperature range were investigated.

2. Experimental procedure

2.1. Starting materials

As raw materials, the calcinated alumina powder (at 1550 °C, for 4 h, grade 17/1993-ICEM) with particles size (average values) of 0.8 μm (sample A1) and of 2.1 μm (sample A2) was used. The alumina powders have min. 99.5% α-Al_2O_3, max. 0.15% SiO_2, max. 0.20% Fe_2O_3, 0.15% alkali.

Magnesium chloride ($MgCl_2{\cdot}6H_2O$) and zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$) both of analytical grades—Chimopar and Merck were used as inorganic precursors for MgO and ZrO_2, respectively.

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2.2. Fabrication and sintering

The powders (A1 and A2) were deflocculated by 0.5 wt.% alkali-free polyelectrolyte (Dolapix CE64 Germany) which assures a minimum viscosity for alumina slips. Ceramic bars of dimensions of 5 mm × 5 mm × 50 mm were prepared by slip casting of aqueous slurry with 70% of solid phase into plaster moulds. The bars were dried and pre-fired at 1100 °C. After firing the samples have a water absorption of 18.5% and 19.8%. The secondary phase was added as vacuum infiltrated isopropyl alcohol solution of $MgCl_2{\cdot}6H_2O$ and of $ZrOCl_2{\cdot}8H_2O$ with a concentration of 15%. After five cycles of infiltration of each chloride solutions, the specimens were dried and cured at 1550, 1750 and 1780 °C (4 h hold time at maximum temperature) in a kiln with methane gas.

2.3. Characterisation methods

The alumina powders particles size was determined by laser granulometry (Fritsch). The bulk density of specimens after sintering was measured by the hydrostatic method followed by relative density calculation—considering 3898 the theoretical density of alumina. The three points bending strengths of sintered specimens were carried out on a MTS at 100KN testing machine. Non-infiltrated alumina bars were sintered in the same conditions as reference specimens in order to compare the mechanical characteristics. The dispersion and the grain size of the reinforcing particles were analysed on samples surfaces by a Hitachi S2600 S scanning electron microscope (SEM) with energy dispersive analysis (EDS).

3. Results and discussion

3.1. Densification and sintering

The influence of sintering temperature and of the additives nature (ZrO_2, MgO and ZrO_2 + MgO) on the relative density of alumina ceramic (A1) made from alumina powder with average particles size (0.8 μm) is shown in Fig. 1. The influence of sintering temperature and of additives nature on the relative density of alumina ceramic (A2) with higher particles size of initial powder (2.1 μm) is shown in Fig. 2. The increases of sintering temperature in 1550–1780 °C range has a linear positive effect on densification of both undoped alumina specimens as seen in Fig. 1—the specimen A1 at 1550 °C has a relative density of 95.4%, while at 1780 °C this is about 96.9%. In Fig. 2 are shown the evolution of the relative density for the specimen A2, which has a value of 94.6% at 1550 °C and 95.6% at 1780 °C, respectively.

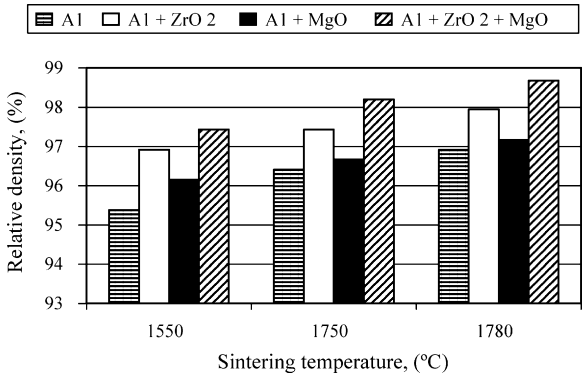

Fig. 1. Influence of sintering temperature and of various additives on relative density of alumina ceramic (A1) made from alumina powder with median particles size (0.8 μm).

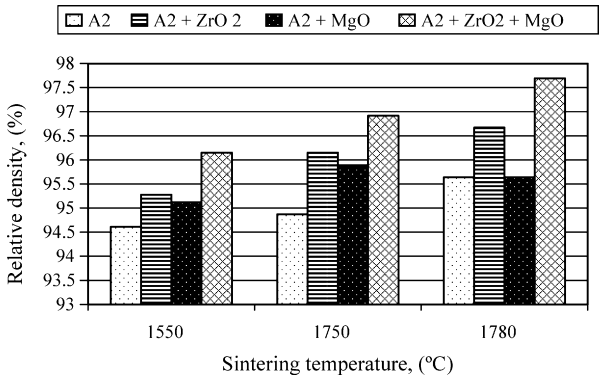

Fig. 2. Influence of sintering temperature and of various additives on relative density of alumina ceramic (A2) made from alumina powder with median particles size (2.1 μm).

The addition of 0.2% by weight of MgO and ZrO_2 or the 1:1 mixture of MgO + ZrO_2 leads to a different densification. Densification in the case of both alumina compositions (A1 and A2) is much more enhanced by the 1:1 mixture of MgO + ZrO_2 in the all investigated temperature range. However, the composition A1 + ZrO_2 + MgO present the best densification—97.4% from theoretical density at 1550 °C, 98.7% from theoretical density at 1780 °C, while the composition A2 + ZrO_2 + MgO (obtained with coarser alumina powder) has only 96.2% from theoretical density at 1550 °C and a relative density of 97.6% at 1780 °C.

Both alumina specimens A1 and A2 obtained only with ZrO_2 are more dense (i.e. for the composition A1 + ZrO_2, a relative density of 96.9% at 1550 °C and 97.9% at 1780 °C, respectively), comparatively with the samples realized with MgO (i.e. for the composition A1 + MgO_2, a relative density of 96.1% at 1550 °C and 97.2% at 1780 °C, respectively).

3.2. Microstructure

The separate or combined effect of MgO and/or ZrO_2 on the evolution of grain size and shape – on thermally etched polished sections of A1 alumina samples – after sintering at 1780 °C are presented in Figs. 3–5. For the composition A1 + ZrO_2 the average grain size is about 3–4 μm, for the composition A1 + MgO is about 4–6 μm and for the specimen A1 + MgO + ZrO_2 is much more fine, having around 1–2 μm. The microstructure of undoped A1 alumina sample prepared in the same way is shown in Fig. 6, where the average grain size determined by image analysis is about 6–8 μm.

The presence of MgO + ZrO_2 mixture as secondary phase can have a stronger inhibitor role for the alumina grains growth dur-

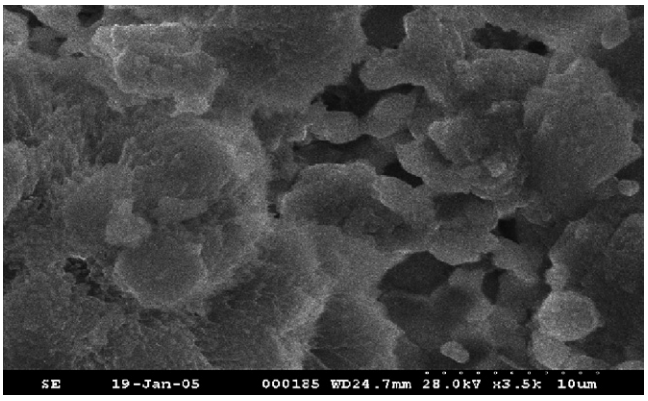

Fig. 3. SEM micrograph of A1 + ZrO_2 composite after firing at 1780 °C.

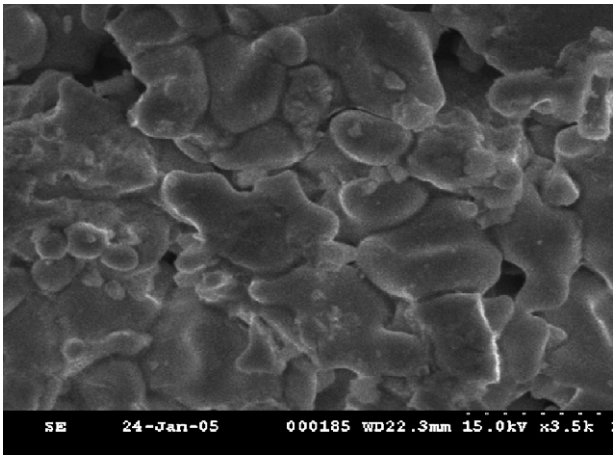

Fig. 4. SEM micrograph of A1 + MgO composite after firing at 1780 °C.

ing sintering, (comparatively with the effect of the same oxides considered alone) and consequently a favourable influence on bending strengths should be expected. The SEM and ESD surface analysis proves a finer grain size on surface layer which might be caused by a concentration gradient of the dopants. Seem to be obvious that infiltration usually leads to higher concentration mainly in the surface layer of sample, which develop an increased mechanical strength by about 17–27%.

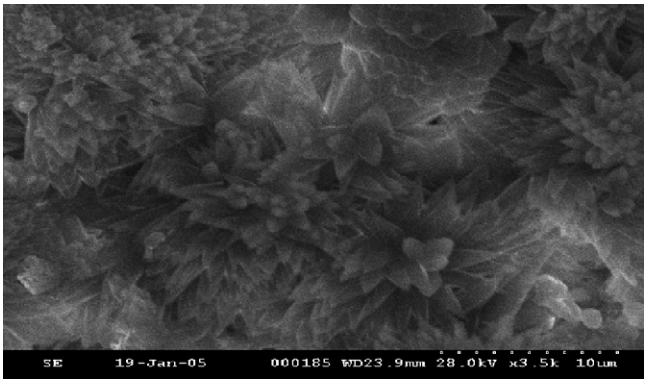

Fig. 5. SEM micrograph of A1 + ZrO_2 + MgO composite after firing at 1780 °C.

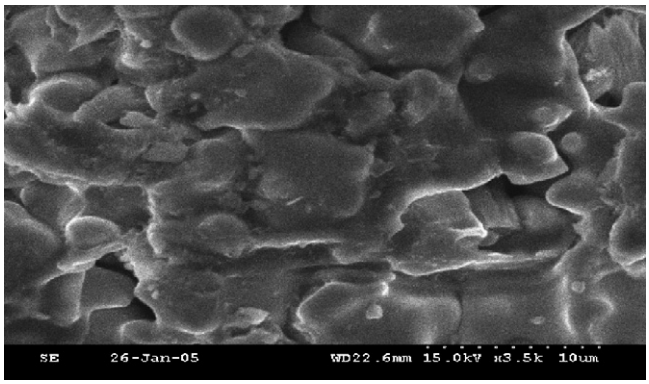

Fig. 6. SEM micrograph of A1 reference sample after firing at 1780 °C.

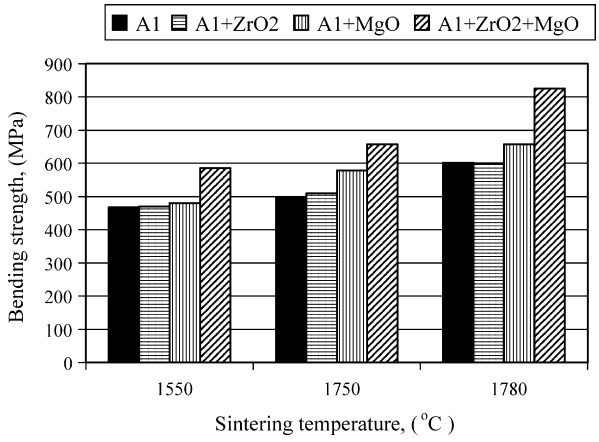

Fig. 7. Influence of sintering temperature and of various additives on bending strengths of alumina ceramic (A1) made from alumina powder with median particles size (0.8 μm).

3.3. Mechanical properties

The three points bending test measurement results of alumina specimens (A1 and A2) after sintering at 1550, 1750 and 1780 °C are summarised in Figs. 7 and 8.

The increase of sintering temperature from 1550 to 1780 °C leads to increased bending strengths for both types of alumina

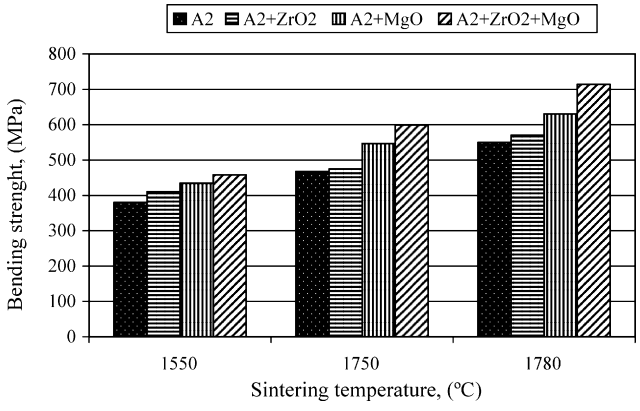

Fig. 8. Influence of sintering temperature and of various additives on bending strengths of alumina ceramic (A2) made from alumina powder with median particles size (2.1 μm).

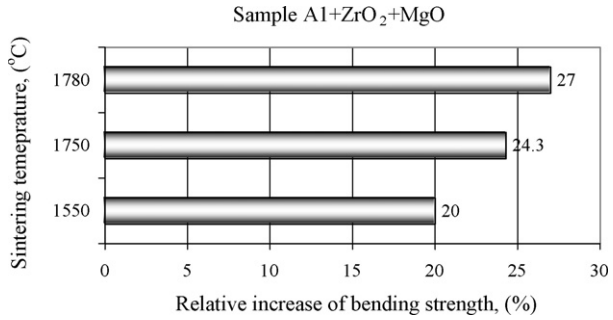

Fig. 9. The relative increase of bending strength of alumina ceramic A1 + ZrO_2 + MgO vs. the sintering temperature.

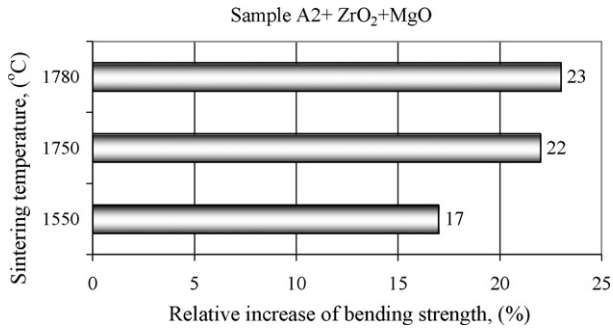

Fig. 10. The relative increase of bending strength of alumina ceramic A2 + ZrO_2 + MgO vs. the sintering temperature.

samples as seen in Fig. 7 (sample A1) and Fig. 8 (sample A2). Better mechanical strengths are obtained by using the finer grade (0.8 μm, average size) alumina powder A1.

The addition of MgO, ZrO_2 and their mixture has a different effect on bending strengths of alumina ceramics. It might be noticed that for alumina samples (A1 and A2) the combined influence of MgO + ZrO_2 is obvious. The relative increase of bending strength of A1 + ZrO_2 + MgO composition versus the sintering temperature is given in Fig. 9 and might be noticed, the improvement of mechanical properties with about 20% at 1550 °C and with 27% at 1780 °C, comparatively with the undoped samples. The relative increase of bending strength for the A2 + ZrO_2 + MgO ceramic versus the sintering temperature is given in Fig. 10 and might be observed the improvement of mechanical properties with 17% at 1550 °C and about 23% at 1780 °C.

The results proved that the improving of the bending strength of alumina matrices is possible by avoiding the abnormal grain growth during sintering, which can be achieved by the dispersion of MgO + ZrO_2 as secondary phase. On the other hand, the martensitic transformation t → m of ZrO_2 as toughening mechanism should be considered responsible for the enhanced strength[5–8,10] and toughness[6] at room temperature of zirconia polycrystals.

4. Conclusions

Apart from the well known role of ZrO_2 for enhancing fracture toughness, presence of zirconia and magnesia infiltrated as chlorides solutions in preformed alumina ceramic can act as growth inhibitors limiting the growth of alumina during sintering in 1550–1780 °C and thus have a positive influence on bending strength which develop an increased mechanical strength by about 17–27%.

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References

1. Yeomans, J., Improving performance in ceramic matrix composites. *Mater. World*, 1994, **l.2**(2), 63–64.
2. Houseman, J. E., 50 years of ceramics in the US—looking back, looking forward. *Interceram*, 2001, **50**(4), 310–316.
3. Baudin, C., Sanchez-Herencia, A. J. and Moreno, R., Possibilities of controlling mechanical properties of alumina ceramics by MgO and ZrO_2 addition. In *Sixth ECERS Proceedings, British Ceramic Proceedings, Vol 60*, 1999, p. 107.
4. Baudin, C., Sanchez-Herencia, A. J. and Moreno, R., Thermal mismatch effects on the mechanical behaviour of alumina based materials. In *Sixth ECERS Proceedings, British Ceramic Proceedings, Vol 60*, 1999, p. 23.
5. Swain, M. V., Grain size dependence of fracture toughness and transformability of 2% Y-TZP. *J. Mater. Sci. Lett.*, 1985, **5**, 1159.
6. Srdic, V. and Radonjic, L., Processing of the Alumina–Zirconia Composite and its Mechanical Properties. In *Third Euro-Ceramics*, *Vol 3*, ed. P. Duran and J.F. Fernandez. 1997, pp. 701–706.
7. Evans, A. G., Perspectives on the development of high toughness ceramics. *J. Am. Ceram. Soc.*, 1990, **73**(2), 187.
8. Neagu, R., Motoc, S., Abagiu, A. T. and Volceanov, E., Mechanical characteristics of the advanced alumina ceramics. In *Proceedings of the Ninth Conference on Science and Engineering of Oxide Materials—CONSILOX Sighisoara, Vol Ceramics*. 2004, pp. 121.
9. Motoc, S., Neagu, R., Volceanov, E., Abagiu, A. T. and Seitan, C., High toughness ceramic composites with Al_2O_3 oxide matrix for special applications. *Metall. New Mater. Res.*, 2005, **XIII**(1), 30–35.
10. Motoc, S., Volceanov, E., Neagu, R. and Apostol, A., Influence of forming condition on ZTA composites characteristics. *Br. Ceram. Trans.*, 2000, **99**(6), 280–283.