ALUMINUM TITANATE CERAMIC WITH MULLITE ADDITION

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The relation between the size of the thermal expansion hysteresis curves area and grain-boundary cracks presence of aluminum titanate ceramic with mullite addition were established. Ceramic samples from Al_2TiO_5 and mullite were obtained by a two-stage technology. To the sintered by solid state reaction at 1500°C aluminum titanate 5; 7,5; 10; 12,5; 15; 20; 25 and 30 wt.% mullite were added and then the compositions were wet milled in a ball mill. The samples with sizes $20\times10\times105$ mm^3 were cold isostatically pressed at 100 MPa and then fired at 1515°C in a chamber gas furnace with holding time 2 h at maximum temperature. The physico-mechanical and thermal properties as mechanical bending strength, water absorption, apparent density, porosity, thermal expansion coefficient (TEC) and thermal hysteresis curves of the ceramic samples with pure Al_2TiO_5 and of the Al_2TiO_5 ceramic with mullite addition were measured. With the increasing of the mullite quantity, the density is not significantly changed and the water absorption slightly decreases. The mechanical strength increases from 30 for pure AT up to 38.5 MPa in the sample with 30 wt.% mullite. The thermal expansion coefficient increases from $0.74\times10^{-6}K^{-1}$ for AT up to $2.45\times10^{-6}K^{-1}$ for ATM30. Simultaneously, mullite addition decreased the hysteresis curves area and the micro-crackcing of the tialite ceramic. The calculated hysteresis areas with increase of mullite content decreases from 82.13 cm^2 for pure AT to 52.74 cm^2 for ATM30. It is proved that the mullite, acts as a barrier against microcracks growth, as is in higher quantity, because part of him is dissolved in the lattice of aluminum titanate and form solid solution with him. The presence of mullite as second phase to Al_2TiO_5 limited the grain growth of aluminum titanate and effectively prevented microcracking and increased the bending strength and thermal expansion coefficient.

INTRODUCTION

The aluminum titanate is known for its excellent thermal shock resistance resulting from the low thermal expansion coefficient, low thermal conductivity, low Young's modulus and for its good chemical resistance. These properties allow the aluminum titanate ceramic materials to find an application as an insulating material in engines, e.g. portlainers, swirl chambers, valves, priston bottons, turbochargers and manifold insulations. Other important applications include thermocouple sleeves, burner nozzles and it is widely used as refractory crucibles for metal casting and flow regulation [1-3].

The disadvantage of this ceramic is the moderate mechanical strength and thermal instability in the temperature range between 750-1280°C. The decomposition of aluminum titanate can be controlled by the leading of additions as MgO, Fe_2O_3, SiO_2, ZrO_2, etc. [4-7]. Additions form solid solutions with aluminum titanate. Wither use of aluminum titanate is limited from very weak mechanical strength due to the thermal expansion anisotropy-induced microcracking. Many authors, such Huang Y. et al., Yano T. et al., Morishima H. et al. and Kim et al. work on the development of composites on the base of tialit and mullite to improving the mechanical strength of titanate and to keep low thermal expansion [8-13]. Ohya et al. and Teruaki et al. study by acoustic emission tialit–mullite composites microcracking mechanism and effect of crack volume on bending strength in aluminum titanat–mullite composites. They proved that aluminum titanate ceramic can be strengthened with mullite [13]. Ohya Y. et al. study the relation between thermal expansion coefficient and grain-boundary crack volume of aluminium titanate ceramic [14].

The aim of this work is to study the relation between the size of the thermal expansion hysteresis curves area and grain-boundary crack presence of aluminum titanate ceramic with mullite addition.

EXPERIMENTAL

Ceramic samples from Al_2TiO_5 and mullite addition were obtained by a two-stage technology. First Al_2TiO_5 was sintered by a solid-state reaction of mixture of a-Al_2O_3 (Nabaltec Gmbh, 99.00 %, X_{50} = 2 μm) and TiO_2 - anatase (KRONOS International INC, 99.00%, X_{50} = 0.43 μm) with addition of MgO (MAF, 99.00 %, X_{50} = 0.26 μm) for stabilization. The raw materials in a stehiometric ratio 1:1 and the MgO in quantity 2.5 wt. % were wet milled for 6 h in ball mill with corundum milling elements. After drying from the batch, cylinders with diameter 10 mm and high 10 mm were cold isostatically pressed, and fired at temperature 1500°C with a holding time 1 h at maximum temperature in a laboratory electrical furnace. To the sintered at 1500°C aluminum titanate 5; 7.5; 10; 12.5; 15; 20; 25 and 30 wt.% mullitte (Nabaltox M72, Germany) were added and then the compositions were wet milled in a ball mill. The samples with sizes 20×10×105 mm were cold isostatically pressed at 100 MPa. These were fired at 1515°C in a chamber gas furnace with holding time 2 h at maximum temperature. For comparison, samples with Al_2TiO_5 without mullite addition were fired. The phase composition of the fired ceramic samples after the synthesis and the second firing was determined by X-ray diffraction analyses using "TUR - M62" apparatus with Breg Brentano geometry and with a computer control on goniometer "HZG-3" Co-Kα ray. The content of the present phases was determined by the program "PowderCell". Phase identification is performed with the help of the base of data JCPDS (International Center for Diffraction Data, Alphabetical Indexes, Pennsylvania 19073-3273, sets 1-86, 1997). By program "UnitCell" [T. Holland and S. Redfern (1997) "Unit cell refinement from powder diffraction data: the use of regression diagnostics". Mineralogical Magazine, 61: 65-77] unit cell parameters were refined. The microstructure of the investigated compositions is settled using scanning electron microscope "JEOL JCXL-733 - Japan" coupled with scanning electron probe microanalyser "ESD LINK 10/85 – Japan". The physico-mechanical and thermal properties as mechanical bending strength, water absorption, apparent density, porosity, thermal expansion coefficient (TEC) and thermal hysteresis curves of the ceramic samples with pure Al_2TiO_5 and of the Al_2TiO_5 ceramic with mullite addition were measured. The bending strength at room temperature of samples with sizes 10×10×100 mm were tested on apparatus "Bimko" - B200T 211573 using the tree point bending method with a span length of 30 mm and a crosshead speed of 0.2 mm/min. The water absorption of sintered ceramics is tested after boiling of samples in water for 3 hours. The density of the sintered samples was measured using the Archimedes method in distilled water. The thermal expansion coefficient from room temperature to 1000°C were determined for a 6 mm × 6 mm × 30 mm samples in air using dilatometer "Linseis L75" at a heating rate of 10°C. The hysteresis area was calculated by program AutoCad 2005 for calculate of area.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction pattern for sintered aluminum titanate. The base phase is Al_2TiO_5 and the trace of corundum is found. The size of the aluminum titanate grains is between 5 and 15 microns. Unit cell parameters (a,b,c) of aluminum titanate in comparison with standard (a = 9.439; b = 9.647; c = 3.592 Å) are higher (a = 9.457; b = 9.667; c = 3.604 Å). This deflection is a result from the introducing of magnesium ions in the crystal lattice of aluminum titanate.

The result from measured properties of fired ceramic samples from pure Al_2TiO_5 and with mullite addition at 1515°C are given in Table 1.

With increasing the mullite quantity, the density of ceramic samples is not significantly changed and the water absorption slightly decreases. The mechanical bending strength increases up to 38.48 MPa at sample ATM30. Figure 2 shows the thermal hysteresis curves at heating and cooling of ceramic samples AT, ATM10, ATM20 and ATM30. The calculated hysteresis area, with the increase of mullite content, decreases from 82.13 cm^2 for AT to 52.74 cm^2 for ATM30. At ATM10 the hysteresis area is 77.72 cm^2 and at ATM20 it is 58.62 cm^2. Larger is the difference in the hysteresis areas between AT and ATM20 and ATM30. Composites with increasing of mullite content exhibit increased thermal

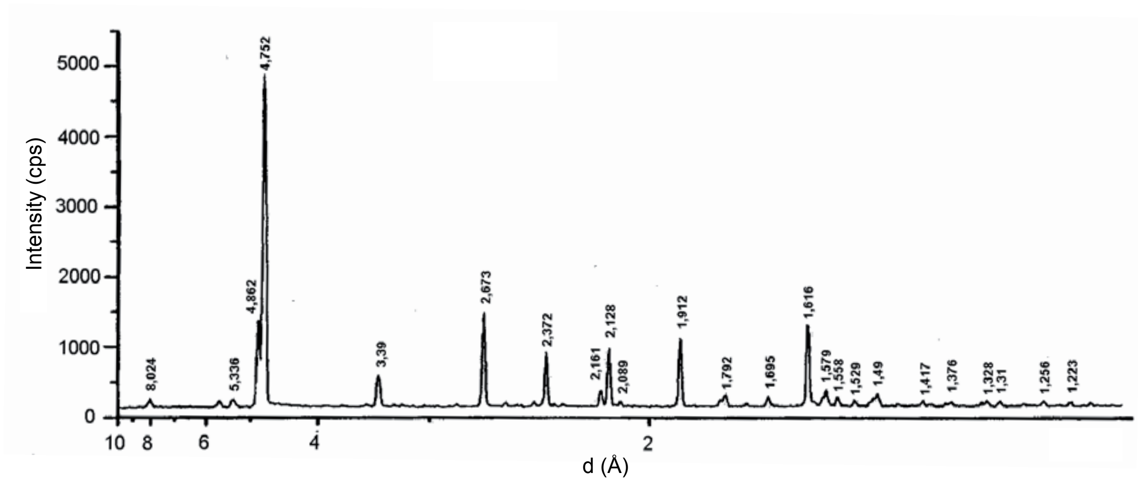


Figure 1. XRD of sintered at 1500°C aluminum titanate.

expansion coefficient accompanied by a pronounced small hysteresis area as the mullite content is increased, as shown in Figure 2. The thermal expansion coefficient increases from 0.74×10^{-6} K^{-1} for AT up to 2.45×10^{-6} K^{-1} for ATM30. These results are in good agreement with measured mechanical bending strength given in Table 1.

Figure 3 presents the X-ray diffraction patterns of compositions with 5, 15 and 30 wt.% mullite. The basic phase is Al_2TiO_5 and as secondary phase corundum is identify in ceramic samples with 5 and 15 wt.% mullite. At ATM30 as secondary phases corundum and mullite are found. Part of mullite probably is dissolved and silicon ions are introduced in lattice of aluminum titanate and solid solutions are formed. Corundum is remains as secondary phase. Proof for this is a changing of unit cell parameters with increasing of the mullite quantity (unit cell parameters of sample ATM5 are a = 9.489 Å, b = 9.707 Å and c = 3.605 Å and of sample ATM15 unit cell parameters are a = 9.481 Å, b = 9.671 Å and c = 3.599 Å) and displacing of the interplanar spaces, as seen from the Figure 3. Electron probe microanalysis (EPMA) of sample ATM15, shown on Figure 4, confirmed that in the sample is observed two phases - solid solution of aluminum titanate containing silicon ions and secondary phase corundum.

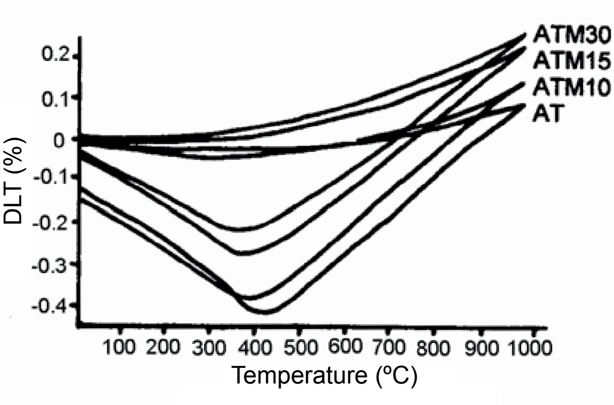


Figure 2. Thermal expansion curves of Al_2TiO_5-mullite ceramic materials.

Figure 5 shows the microstructures of AT, ATM15 and ATM30 ceramic samples. The microstructure is in accordance to the thermal characteristic. In sample AT many micro cracks on grain-boundary are observed. A tendency of decreasing of the micro-cracks in the samples with increased of mullite is observed. Microstructure results show that the thermal expansion behavior is due to the micro-crack system of tialit-mullite at the grain boundary. Decreasing of hysteresis area is related with improved strength and lower micro-cracking of aluminum titanate ceramic. This confirm that mullite addition improved mechanical strength and of aluminum titanate.

CONCLUSIONS

The relation between the size of the thermal expansion hysteresis curves area and grain-boundary crack presence of aluminum titanate ceramic with mullite addition are established. Mullite addition decreased the hysteresis curves area and the micro-crackcing of the tialite ceramic. The calculated hysteresis area with increase of mullite content decreases from 82.13 cm^2 for pure AT to 52.74 cm^2 for ATM30. Ceramic materials on the basis of aluminum titanate and mullite with improved mechanical strength and less presence of microcrack are obtained. It is proved that the mullite, acts as a barrier against microcrack growth as is in higher quantity, because part of him is dissolved in the lattice of aluminum titanate and formed solid solution. The presence of mullite as second phase to Al_2TiO_5 limited the grain growth of aluminum titanate and effectively prevented microcracking and increased strength and thermal expansion coefficient.

Table 1. Physical and thermal properties of Al_2TiO_5-mullite ceramic materials.

Ceramic sample	Water absorption (%)	Apparent density (g/cm^3)	Mechanical bending strength (Mpa)	Apparent porosity (%)	Coefficient of thermal expansion (CTE) $\alpha_{25\text{-}1000°C}$ (10^{-6} K^{-1})
AT	1.50	3.30	30.0	4.95	0.74
ATM5	1.68	3.31	33.0	5.56	1.00
ATM7.5	1.52	3.33	34.0	5.06	1.33
ATM10	1.48	3.32	34.0	4.91	1.22
ATM12.5	1.58	3.31	33.5	5.23	0.78
ATM15	1.42	3.32	36.0	4.71	0.78
ATM20	1.34	3.30	36.0	4.42	2.14
ATM25	1.29	3.31	37.0	4.27	2.45
ATM30	1.33	3.28	38.5	4.36	2.45

Key: AT – pure aluminum titanate; ATM5 - aluminum titanate with 5 wt.% mullite; ATM7.5 - aluminum titanate with 7.5 wt.% mullite; ATM10 - aluminum titanate with 10 wt.% mullite; ATM12.5 - aluminum titanate with 12.5 wt.% mullite; ATM15 - aluminum titanate with 15 wt.% mullite. ATM20 - aluminum titanate with 20 wt.% mullite; ATM25 - aluminum titanate with 25 wt.% mullite; ATM30 - aluminum titanate with 30 wt.% mullite.

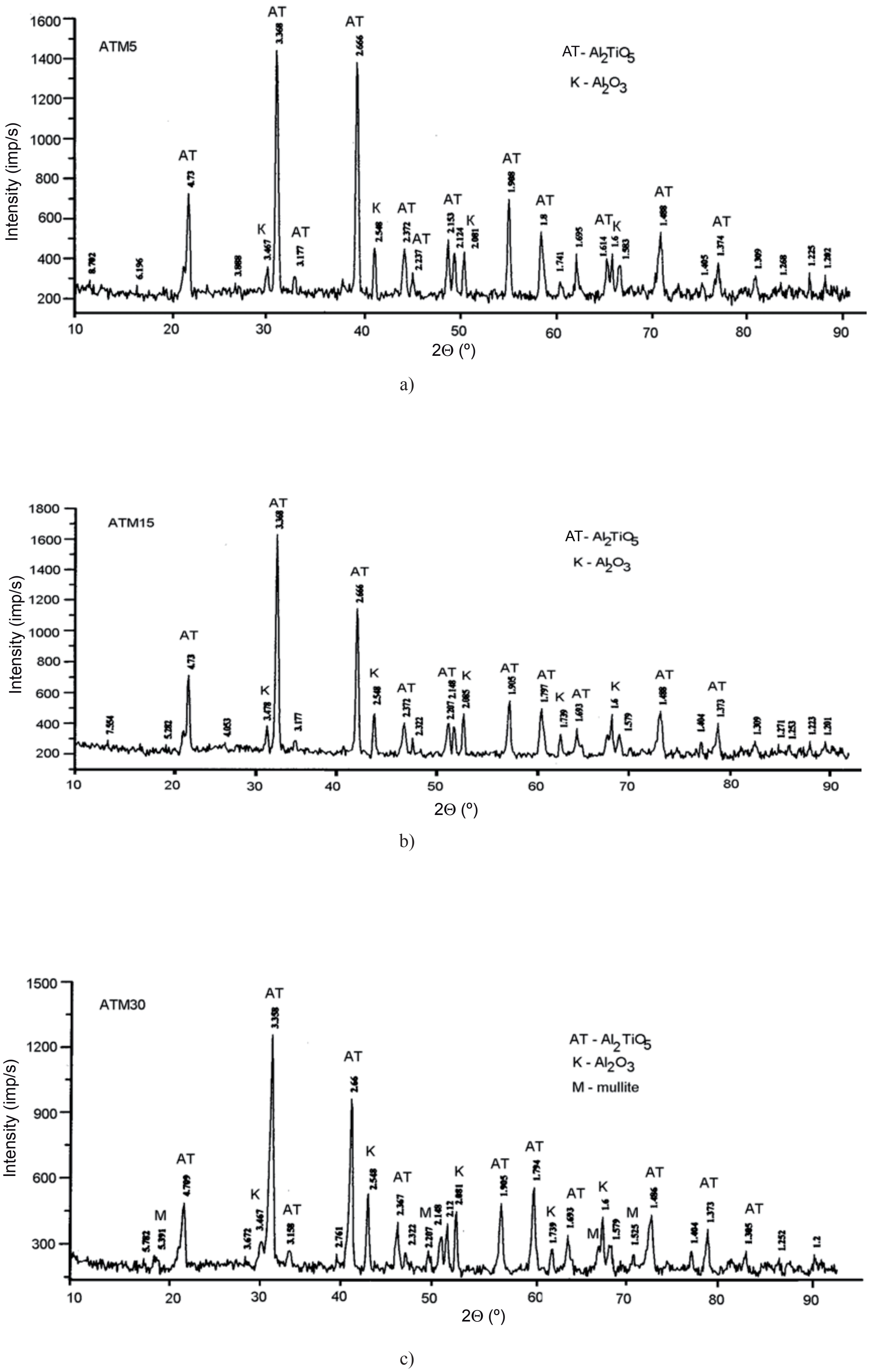


Figure 3. X-ray diffraction patterns of Al_2TiO_5-mullite ceramic materials.

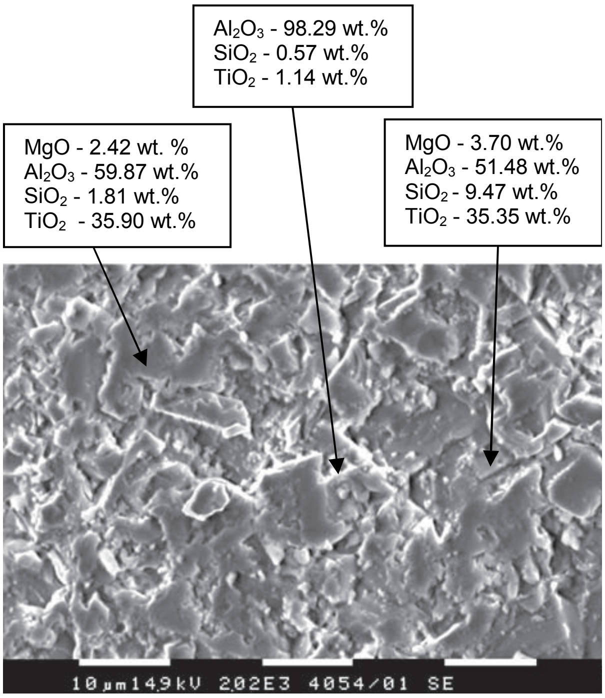
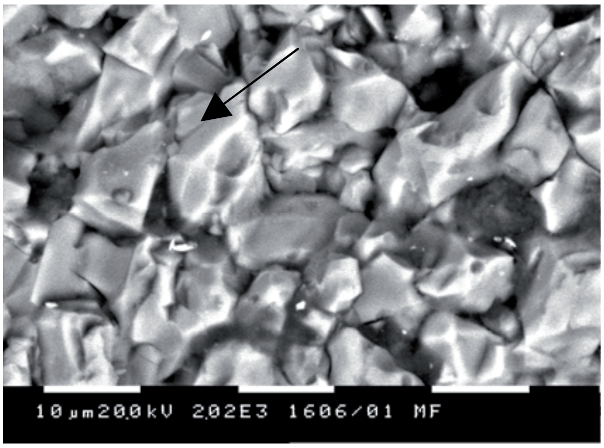


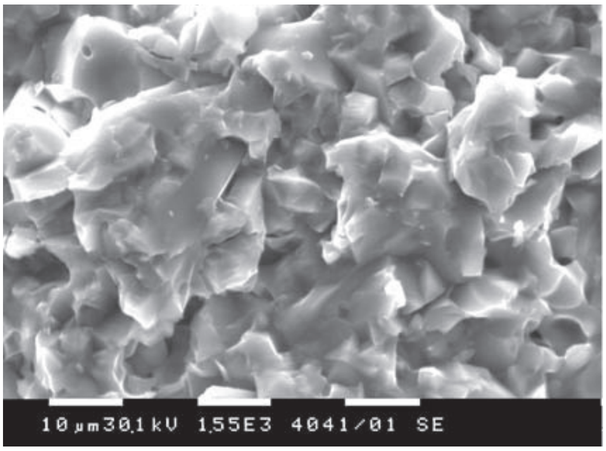
Figure 4. EPMA of sample ATM15.

References

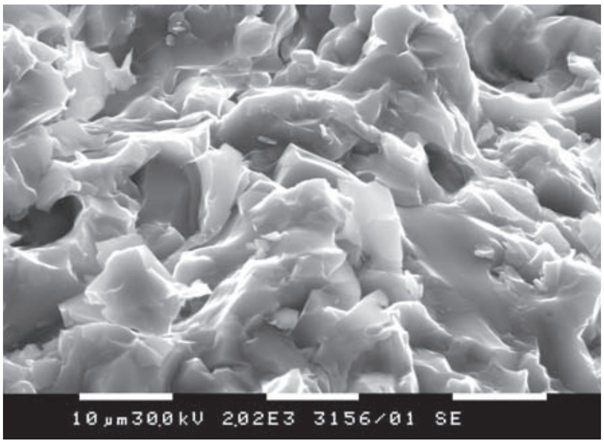
1. Stingl D., Heinrich J., Huber J.: Proceeding of 2nd International Symposium on Ceramic Materials & Components for Engines, Lübeck Travemünde, p.369, Ed.: Bunk W., Havsner H., DKG, Bad Honnef, 1986.
2. Gani M. S., McPherson R.: J.Mater.Sci. *15*, 195 (1980).
3. Pratapa S., Low J. M., O'Connor B. H.: J. Mater. Sci. *33*, 3037(1998).
4. Djambazov S., Lepkova D., Ivanov I.: J.Mater.Sci. *29*, 2521 (1994).
5. Buscaglia V., Nanni P., Leoni M.: Key Engineering Materials 132-136, 810 (1997).
6. Ishitsuka M. et al.: J. Am. Cer. Soc. *70* , 69 (1987).
7. Thomas H. A. J., Stevens R., Gilbert E.: J. Mater. Sci. *26*, 3613 (1991).
8. Huang Y., Senos A., Baptista J.: Ceramic International *24*, 223 (1998).
9. Kato E., Daimon K., Takahashi J.: J. Amer. Ceram. Soc. *63*, 355 (1980).
10. Yano T., Kiohara M., Otsuka N.: J. Ceram. Soc. Japan *100*, 482 (1998).
11. Kim I. J., Kwak H. S.: Canadian Metallugical Quarterly *39*, 387 (2000).
12. Morishima H., Kato Z., Saito K., Yano T., Ootsuka N.: J. Mater. Sci.Lett. *6*, 389 (1987).
13. Teruaki O., Yosuke S., Masayuki I., Seizo O., Osami S., Minori H.: Ceramic International *33*, 879 (2007).
14. Ohya Y., Takanashi Y., Nakagawa Z.: J. Mater. Sci. *31*, 1361 (1996).



SEM image of pure A_2TiO_5 ceramic (AT) sintered at 1515°C for 2 hours



SEM image of A_2TiO_5 – mullite ceramic (ATM15) sintered at 1515°C for 2 hours



SEM image of A_2TiO_5 – mullite ceramic (ATM30) sintered at 1515°C for 2 hours

Figure 5. Microstructure of Al_2TiO_5-mullite ceramic materials.