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Mullite-alumina functionally gradient ceramics

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ABSTRACT

Cracks free mullite-alumina Functionally Gradient Ceramics (FGC) have been obtained by sequential slip casting of Mullite-alumina slurries with different mullite/alumina ratios. These slurries were prepared with 65% solids content and viscosities ranging from 10 to 40 mPa.s. The presence of cracks perpendicular to the FGC layers have been attributed to residual stresses developed because of the mismatch in thermal expansion between layers. The microstructure of the different layers, and de residual stress value σ_R in each layer was also determined.

I.- INTRODUCTION

Very recently a new concept is being emerged to approach new materials requirements in advanced technologies. This is the case of Functionally Gradient Materials which are materials with a continuously varying property (i. e. hardness, κ , dielectric constant, etc.) from one surface to the other. Some reports have appeared in the literature by japanese researchers concerning metal/ceramic FGMs [1,2]. The first work dealing with Functionally Gradient Ceramics was recently published by Moya et al. [3] on $\text{Al}_2\text{O}_3/\text{YTZP}$ laminates obtained by sequential slip casting.

Mullite is a compound with very interesting properties [4] i.e. Young modulus of 200 GPa, $\kappa = 2 \text{ Wm}^{-1} \text{ K}^{-1}$, very low creep rate value at temperatures higher than 1200°C ($\dot{\epsilon} = 10^{-9} \text{ s}^{-1}$), thermal expansion coefficient $\alpha_{20-1000} = 4.5 \cdot 10^{-6} \text{ K}^{-1}$ close to Si, low permittivity value ($\epsilon=6$) and very high transmittance in the mid-infrared range. Conversely Al_2O_3 shows a Young modulus $E= 400 \text{ GPa}$, thermal expansion coefficient $\alpha_{20-1000} = 8.10^{-6} \text{ K}^{-1}$, thermal conductivity $\kappa= 30 \text{ Wm}^{-1} \text{ K}^{-1}$ and a permittivity of $\epsilon=9$ [5]. Because of this mullite based materials have attracted much attention for application such substrate in multilayers packaging, optical IR windows, etc.

It is clear that the feasibility to obtain mullite-alumina FGC has today scientific and technological interest for many functional high technological applications for instance electromagnetic lens, and broad band windows in the microwaves to IR range.

The aim of the present investigation is to obtain mullite-alumina FGC by sequential slip casting of both mullite and alumina slurries.

II. Experimental

Starting materials

Commercially available submicrometer powders were used as starting materials: a) alumina(1) with an average particle size of $0.5\ \mu\text{m}$, specific surface area of $8\ \text{m}^2\ \text{g}^{-1}$, chemical analysis (wt.%): Al_2O_3 (>99.6), Na_2O (0.1), SiO_2 (0.08), MgO (0.1), Fe_2O_3 (0.03), and b) mullite(2) with an average particle of $0.7\ \mu\text{m}$, specific surface area of $10\ \text{m}^2\ \text{g}^{-1}$, and chemical analysis: Al_2O_3 (72.6), SiO_2 (26.4), Na_2O (0.12), MgO (0.03), Fe_2O_3 (0.1), CaO (0.01).

Slip-casting process

Aqueous alumina + mullite suspensions with 65 wt.% solids contents and with different alumina relative content (ranging from 0 to 100%) were prepared using 1 wt.% addition of an alkali-free organic polyelectrolyte(3). A detailed description of deflocculant selection and optimization of rheological properties is given elsewhere [6,7].

The suspensions were homogenized in an alumina ball mill for 17 h. using high purity alumina balls. Before carrying out the measurement, bubbles were removed by smooth agitating. The temperature and pH were also determined.

The rheological behavior of suspensions with different Al_2O_3 contents were studied by means of a rotation viscosimeter(4). Viscosity and shear stress of the suspensions were determined for a range of shear rates between 0 and $1000\ \text{s}^{-1}$. All measurements were conducted at a constant temperature of 25°C .

Monolithic cylindrical bars of 10 mm diameter and 120 mm length were cast from each studied suspension. Two functionally gradient green layered compacts with a) six different layers (100wt% mullite, 80 mullite/20 Al_2O_3 , 60 mullite/40 Al_2O_3 , 40 mullite/60 Al_2O_3 , 20 mullite/80 Al_2O_3 , 100 Al_2O_3 and b) five different layers 100% mullite, 10 Al_2O_3 /90 mullite, 20 Al_2O_3 /80 mullite, 30 Al_2O_3 /70 mullite and 40 Al_2O_3 /60 mullite were obtained by alternately casting the corresponding mullite/alumina suspensions in plaster of Paris molds made with a 70/100 water to plaster ratio. Green densities were determined by the Archimedes method in liquid mercury.

Sintering process

The sintering behavior up to 1600°C of the different monolithic cast compacts were studied by dilatometry, using a constant heating rate of $2^\circ\text{C}\ \text{min}^{-1}$. The shrinkage behavior during heating was established in a dilatometer(5) with alumina support using green rods of 10 mm diameter and 10 mm height.

The selected heating schedule from monolithics as well as for FGC compacts were 1650°C 2h with a heating and cooling rates of $2^\circ\text{C}\ \text{min}^{-1}$. The microstructure of fired specimens were studied on cross-sectioned surfaces, cut perpendicularly to the different layers interface and diamond polished to $1\ \mu\text{m}$ finish and thermally etched, using reflected light optical microscopy (RLOM) and scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometry analyzer (EDS).

The thermal expansion behavior of different monolithic sintered compacts between room temperature and 1000°C during heating and cooling was established in a dilatometer(5) with vitreous

(1) Alcoa CT 3000 SG, Pittsburg, Pa, USA.

(2) Baikowsky, France.

(3) Dolapix PC 33, Zschimmer & Schwarz, Lahnstein, FRG.

(4) Haake Rotovisco RV 20, Karlsruhe, FRG

(5) Adamel Lhomargy, Ivry, France.

silica support. The experiments were run at $2^{\circ}\text{C min}^{-1}$ heating rate on specimens with 20 mm height. Toughness (K_{IC}) and residual stress field (σ_R) was determined by Vicker's indentation [8].

III. RESULTS AND DISCUSSION

In Fig.1 the viscosity of the different suspensions versus mullite content is plotted. As observed the viscosity increases linearly with mullite content.

Figure 1: Viscosity versus mullite content for the different studied suspensions.

The dynamic sintering curves at constant heating rate corresponding to the different monolithic green bars studied are shown in Fig 2. From this plot it can be deduced that the habit of the different curves is very similar.

Figure 2: Linear shrinkage versus temperature corresponding to the different monolithic green compacts. Constant heating rate $10^{\circ}\text{C min}^{-1}$.

The thermal expansion behavior in the different monolithic sintered compacts at 1650°C 2 h., is shown in Fig. 3. It can be observed from this plot that the thermal expansion coefficient increases with alumina content from $\alpha_{20-900} = 4.5 \cdot 10^{-6}$ (mullite compact) to $\alpha_{20-900} = 8.10^{\circ}\text{C}^{-1}$ (alumina compact) as expected.

The relative density of sintered monolithic FGC compacts were found to be 98%th. Fig. 4 show the SEM micrograph corresponding to polished cross sections of alumina-mullite FGC. A very intimate contact between the layers was observed over the whole interface area with a good interfacial adhesion between layers. As observed cracks perpendicular to the layers interfaces starting from the alumina layer

were formed in the six layer FGC, most likely due to the residual stress developed because of the thermal expansion mismatch between layers.

Figure. 3: Thermal expansion behavior of different monolithic mullite-alumina sintered compacts after sintering at 1650°C/2h.

Figure 4: Micrographs corresponding to the cross section of A) the six layers mullite-alumina FGC and B) the five layers mullite-alumina FGC.

Figure 5: SEM micrographs of mullite-alumina FGC showing layers with different grain size.

In Fig. 5 SEM micrographs of the FGC are shown. In these micrographs it can be clearly observed the drastic influence of the layers composition on the layer average grain size. Layers with a single phase have significant bigger grain size (alumina layer $d_{50} \approx 25 \mu\text{m}$ and mullite layer $d_{50} \approx 20 \mu\text{m}$) than the two phase layers ($d_{50} \approx 2 \mu\text{m}$). It is also important to notice that the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of mullite grains changes from 2:1 in the two phase layers to 3:2 in the single mullite layer.

The residual stress σ_R in the different layers was determined by indentation method according

Figure 6: Optical micrograph showing the effect of residual stress field on the indentation crack in mullite-alumina FGC. For comparison purpose the symmetric cracks pattern corresponding to a monolithic 80mullite-20alumina compact is shown.

to the equation:

$$K_c = \chi \frac{P}{\sqrt{c^3}} + \frac{2}{\sqrt{\pi}} \sigma_R \sqrt{c}$$

where P is the load, $\chi = 0.084$ is the proportionality constant, K_c is the toughness of the corresponding monolithic compact with the same composition of the layer and C is the indentation crack length in the FGC layer. As can be clearly observed from the crack patterns shown in Fig. 6, the alumina layer is subjected to tension with $\sigma_R = -105$ MPa and the mullite layer to compression with $\sigma_R = 60$ MPa.

In order to decrease the absolute value of σ_R and consequently avoid cracking, a new mullite/alumina FGC with five layers were designed. The processing flow chart followed in this case was similar to the one described before. As can be observed in the micrographs showing in Fig. 4B the new mullite-alumina FGC is free of cracks. The residual stress developed in mullite rich layer $\sigma_R = 38$ MPa is significantly smaller than the one measured in the previous FGC compact.

IV. CONCLUSIONS

- (i) Sequential slip-casting has been proved to be a simple and feasible route to obtain mullite-alumina free of cracks FGC with tailored thickness and layer composition
- (ii) The effect of the second phase on the grain size and mullite stoichiometry has also been point out.

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