

Al₂O₃/Y-TZP Continuous Functionally Graded Ceramics by Filtration-Sedimentation

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Abstract

The filtration-sedimentation method is applied as an alternative route to obtain functionally graded ceramics (FGCs) without defined interfaces. Using this technique a fully dense Al₂O₃/Y-TZP continuous functionally graded ceramic has been obtained after sintering at 1550°C. The concentration gradient shows a parabolic distribution of phases which depend on the starting slurry solid concentration. © 1997 Elsevier Science Limited.

1 Introduction

The functionally graded materials (FGMs) are characterized by continuously changing properties within the bulk material. An extensive review of this new family of materials is giving by Hirai.¹ This kind of material covers a wide range of applications like dental implants, energy conversion thermal barriers, joining and others reported in the three international symposiums^{2,3,4} held on this topic to date.

Powder processing techniques lead to FGMs with defined interfaces, where the gradient is obtained by varying the composition of the different layers.⁵ Using sequential slip casting, Moya *et al.*⁶ have made functionally graded ceramics (FGCs) with very sharp interfaces in the system Al₂O₃/Y-TZP. The main problem with this kind of FGM is the development of residual thermal stresses at the interface between the different layers as a consequence of the thermal expansion mismatch.⁷ Several techniques like CVD, PVD or plasma spray have been used to avoid the presence of these interfaces. Chu *et al.*⁸ have developed a colloidal method to obtain continuous ceramic-metal FGMs. Jüngling *et al.*⁹ have used a similar method in which the filtration was carried out after sedimentation. Marple and Boulanger¹⁰

used a continuous filtration technique to obtain continuous FGCs without defined interfaces, continuously changing the composition of the slurry during the cast process.

The aim of this investigation is to obtain continuous FGCs in the system Al₂O₃/Y-TZP using a slip casting technique.

2 Experimental procedure

The following starting powders were used: (i) α -alumina (99.99% purity AKP-50, Sumitomo, Japan) with 0.2 μ m average particle size and 10.5 m²/g specific surface area and (ii) Y-TZP (99.98% purity, TZ-3YS, Tosho, Japan) with 0.4 μ m average particle size and 6.7 m²/g specific surface area.

The zeta potential versus pH was measured by a mass transfer zetameter (micromeritics) using slurries with 25 wt% of solid content.

To obtain the continuously graded ceramic, a mixture of alumina and zirconia powders was prepared with a volume ratio of 2:8. With this mixture, two slurries with 5 and 10 vol% of powder were prepared by adding a fixed amount of powder (\approx 1.7 g) to the corresponding volume of distilled water. The pH was adjusted at 4.5 using HCl and 2 wt% of binder (FC-51 Nikken Fine Chemical Co. Ltd) was added in both cases. After 4 h of ball milling the pH was checked again and readjusted to 4.5 if necessary. The stable slurries were cast in a 5.2 mm \times 9.7 mm \times 100 mm mould with plastic walls and a plaster-of-Paris basement. The slurries were maintained inside the mould up to complete filtration and the green bodies were removed after one additional day of drying at room temperature. Samples were sintered at 1550°C for 2 h at a heating rate of 5°C/min. Green and sintered densities were determined by the Archimedes' method in kerosene.

For SEM observations and EDS analysis the sintered specimens were polished with diamond paste down to 1 μm and subsequently chemically etched in a 5% HF solution. The microstructural analysis was performed using SEM-EDS equipment (JEOL, JMS-6400) with image analyser.

3 Results and discussion

Figure 1 shows the zeta potential versus pH plot for the alumina and zirconia powders. As can be observed at the selected pH of 4.5, the slurries have a zeta potential value > 40 mV, thus enabling the preparation of well-dispersed slurries.

The filtration time required was 15 and 20 days for 10 and 5 vol% solid content slurries, respectively. At the end of the drying process, a thin layer of ≈ 1.3 mm with graded composition separates from the top of the green sample. This takes place due to the differential shrinkage during drying. According to Stokes law, $v = a^2(\rho_s - \rho_l)g/18\eta$, where v is the sedimentation rate, a is the diameter of the particle and ρ_s , ρ_l are the densities of the particle and the liquid, respectively, η is the viscosity of the liquid media and g is the gravitational force, the top layer must be constituted by the finer fraction of particles and therefore its green density is expected to be higher than that of the bulk. Consequently the shrinkage of the bulk during drying must be higher.

As reported in Table 1, the density after sintering is always lower for the graded layer than for the monolithic compact despite the fact that the total porosity is found to be zero in all the samples. This suggests that the alumina content is higher in the layer than in the bulk as can be expected from Stoke's law, taking into account the differences in density between alumina and zirconia particles ($\Delta\rho \approx 2$ g/cm³).

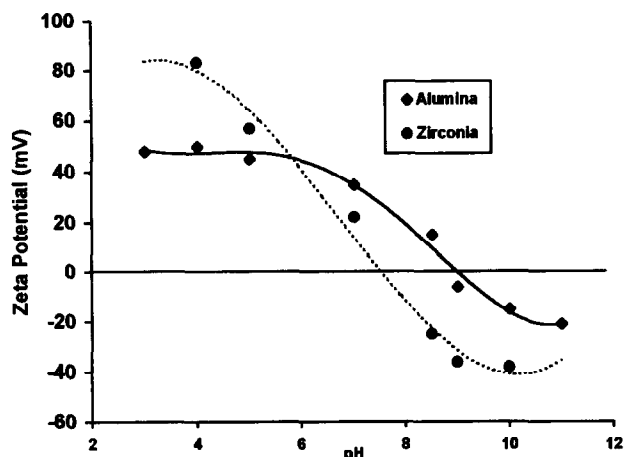


Fig. 1. Zeta potential versus pH curves corresponding to Al_2O_3 and Y-TZP powders.

Table 1. Sintered densities for the layer and monolithic compact obtained by filtration sedimentation

Solid content of the starting slurry (vol%)	Density (g/cm ³)	
	Graded	Monolithic
10	4.74	5.35
5	4.83	5.62

SEM and EDS analysis shows that the monolithic compacts of both samples have a similar composition and microstructure, i.e. the phase composition (20 vol% of Al_2O_3) is very close to that corresponding to the slurry.

This fact can be explained considering that at the beginning of the filtration process Stoke's law is not met owing to the strong suction force produced by the mold. Once a cake of about 1 mm is formed, the suction force is drastically reduced. Then the condition for the appropriate formation of a graded structure by sedimentation is established.

Figure 2 shows a general view of the FGC layer obtained with the 10 vol% slurry. As can be observed, a graded structure appears through the sample. Figure 3 shows a close-up view of this sample obtained at different distances from the bottom. No porosity and no agglomerates inside the graded material can be observed.

The limit composition of the gradient structure (Fig. 4), determined by EDS, are shown in Table 2. In both samples the composition of the bottom was similar to that observed in the monolithic compact.

Quantitative phase analysis of the graded layers was carried out on polished cross-sections using BSE (back-scattered electron image) micrographs combined with a linescan optical density technique. This technique is particularly indicated in

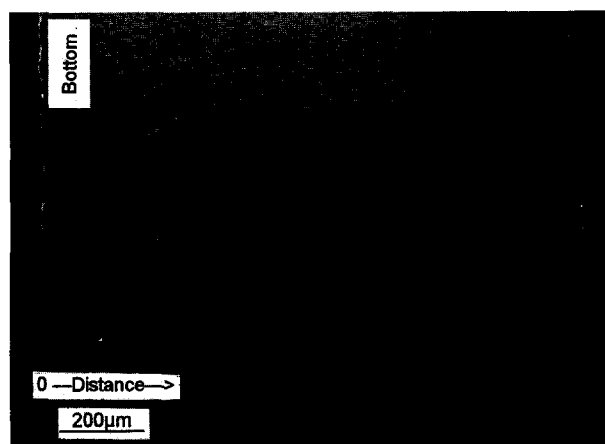


Fig. 2. SEM micrograph of polished cross-section of FGC layer corresponding to 10 vol% solid content slurry.

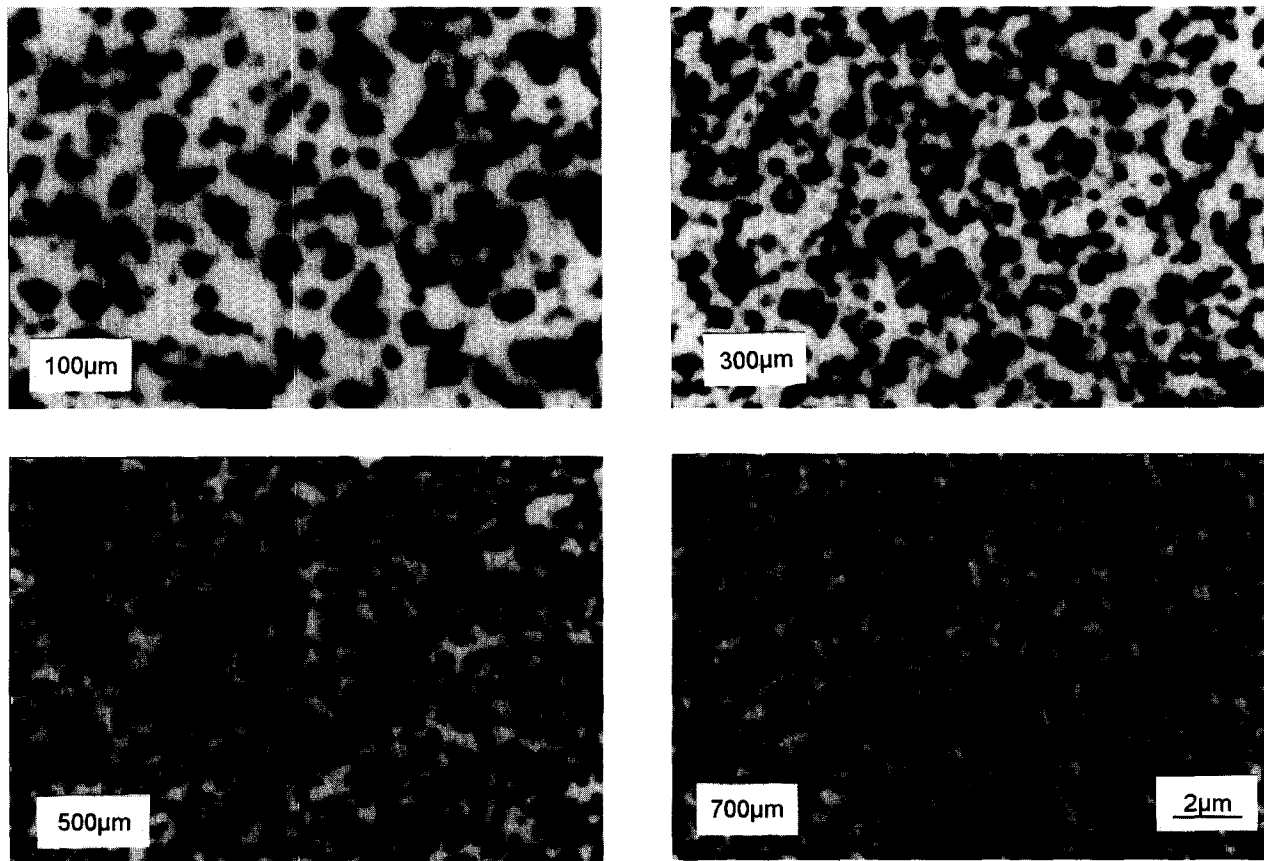


Fig. 3. SEM-BSE micrographs obtained at different distances from the bottom of the FGC layer corresponding to 10 vol% of solid content slurry.

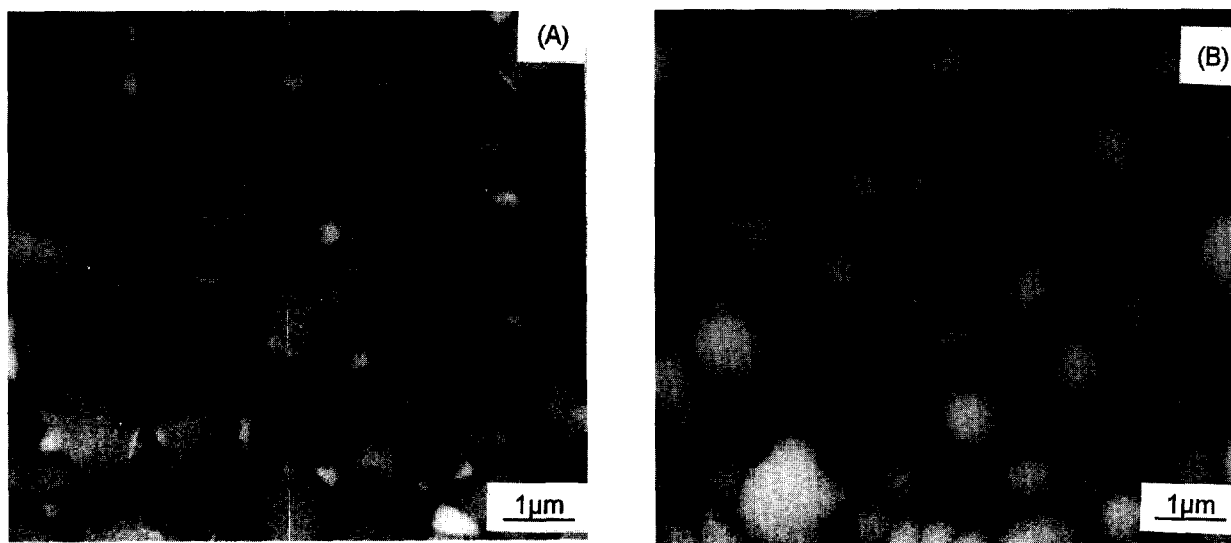


Fig. 4. SEM micrographs corresponding to top (A) and bottom (B) of polished cross-section of FGC 5 vol% solid content slurry after thermal etching at 1450°C for 1 h.

this case because, as observed in Fig. 3, the alumina grains appear black while the zirconia bright white.

Figure 5 shows the variation of phase composition versus distance in the FGC layers corresponding to a 5 and 10 vol% solid content in the starting slurries. It can be clearly observed that the composition profile of the graded layer is

Table 2. Alumina content on the top and bottom of the obtained FGC samples

Solid content of the starting slurry (vol%)	Al ₂ O ₃ content (vol%)	
	Top	Bottom
10	80	20
5	95	20

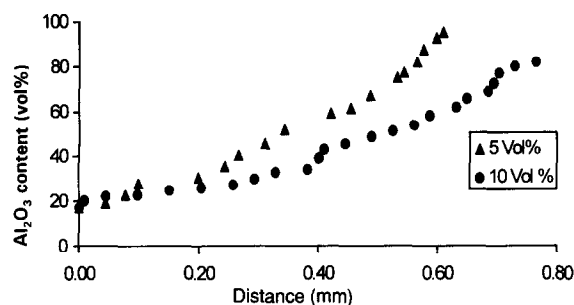


Fig. 5. Alumina vol% versus distance from bottom for the obtained FGC samples.

strongly dependent on the solid content of the starting slurry.

4 Conclusions

The following conclusions can be drawn:

- (1) With the combination of filtration and sedimentation methods it is possible to obtain fully dense and continuous functionally graded ceramics in the Al₂O₃/Y-TZP system.
- (2) It is also proved that the concentration gradient has a parabolic profile strongly depending on the solid concentration of the starting slurry.

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