JOURNAL OF MATERIALS SCIENCE **34** (1999) 2855 – 2857

The preparation of laminated ceramic composites by sedimentation and sieving

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Two simple methods have been developed to fabricate layered microcomposites, with alternative Al_2O_3 layers as thin as 20 μm in Ce-TZP matrix. One is sieving different dry powder into a die alternatively and pressed into greenbody, the other is realized by rapid particle sedimentation occurred in aqueous suspending systems of Al_2O_3 and ZrO_2 powder. These methods avoid the thermolamination step associated with tape casting and adoption of organic assistant. Finally the possibility of processing thin layers by xerox has been explored.

1. Introduction

Recently, in order to exploit the latent toughening effect in Tetragonal Zicornia Polycrystal (TZP) ceramic materials, many efforts have been employed to the optimization of the transformation zone in these materials [1]. Through the research on the transformation zone in ceria-partially-stabilized zirconia (Ce-TZP) and magnesia-partially-stabilized zirconia (Mg-PSZ), multilayered composites have been exploited to creat high toughness materials with exaggerated R-curve behavior, as in the case of a Ce-TZP/Al_2O_3 layered materials [2, 3].

Many methods have been reported for processing laminar composites [4–6]. Two main approaches are tape-casting and rolling method, both of which involves the suspension of ceramic powder in a solvent-resin vehicle which is suitable for subsequent casting and rolling. Paint technology has been described as an alternative method for preparing laminar ceramic composites [7]. All these manufacturing approaches derived from polymer technology and involved the incorporation and dispersion of ceramic powder in an organic vehicle. Although the introduction of organism acting as dispersant, binder, plasticizer and solvent makes the laminar have good working ability during greenbody processing, the removal of these organism before sintering makes the processing period too long and complex to be used effectively. So in this paper, on basis of colloidal theory, we have developed a simple and effective way to fabricate laminar composites by sedimentation. No organism is introduced into the slurries.

In this method, the stable suspending system is first acquired by mixing Al_2O_3 or Ce-ZrO_2 powder with a aqueous solvent so that heterogeneity within the as-received powder can be broken apart. The long-range electrostatic repulsive potential is produced at a pH between 2 and 3 by addition of HNO_3. Thus, the slurries in which long-range repulsive interparticle potentials dominate relative to the attractive Van der Waals potentials can be acquired. Second, by addition of electrolyte (NH_4NO_3) into the dispersed slurry, the interparticle potentials become attractive because of the diminished electrostatic potential as given by Derjaguin-Landau-Verwey-Overbeek (DVLO) theory [8, 9]. Thus the coagulation process can be expected to finish in a satisfactory short time. Through the alternative sedimentation of Ce-ZrO_2 and Al_2O_3/Ce-ZrO_2 suspention, multi-layered composites with thin Al_2O_3 layers (20–100 μm) can be fabricated.

This method can achieve high packing densities because of dominating repulsive forces which allowed particles to rearrange during sedimentation [9]. The dominating repulsive forces (the hydration forces in the case of coagulated slurries) that arise when particles are pushed together during coagulation plays a role as a lubricant to allow particles to rearrange during sedimentation. Moreover, this procedure can be even so simplified that the sedimentation is substituted by sieving dry powder into a die to form alternative layers without adoption of any aqueous vehicle. Compared to tape-casting for processing laminar composites, these two methods introduced no organic dispersant, binder and plastizer, thus considerably simplify the procedure and large areas of laminate can be expected. No subsequent lamination process is needed.

2. Experimental

Two slurries were needed, both the 12 mol % Ce-ZrO_2 (produced by chemical sedimentation, particle size about 200 nm) and the Al_2O_3/Ce-ZrO_2 (alumina powder supplied by DaHua Ceramic plant China, particle size about 1 μm) slurries were initially dispersed by stirring at pH value 2–3, which is adjusted by HNO_3. In the subsequent procedure, the slurries were coagulated with the addition of 3 mol % NH_4NO_3 solvent.

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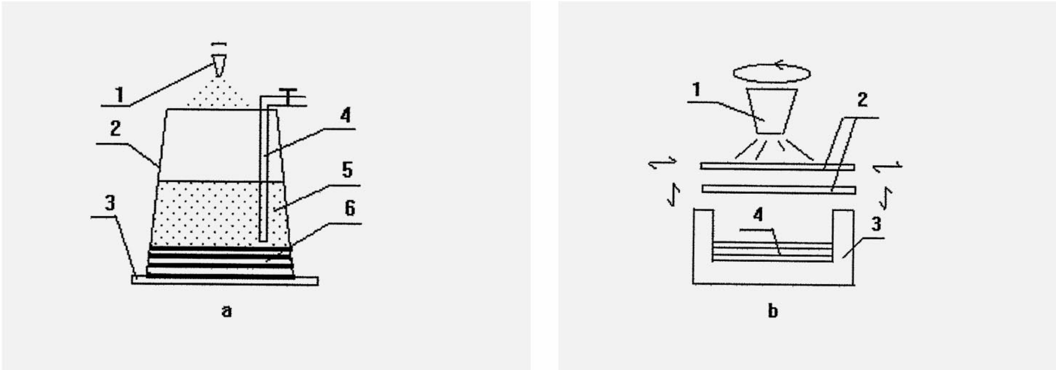

Figure 1 (a) Schematic device for sedimentation: 1. spray gun, 2. container, 3. glass substrate, 4. syphon tube, 5. suspension, 6. sedimentation layers. (b) schematic device for sieving: 1. distributing deviece, 2. screen mesh group, 3. die, 4. layered structure.

Once prepared, Ce-ZrO_2 slurry was added into a cone-shaped paper container (schematic device shown in Fig. 1a), which acted as a die and cone-shape was favor of die removing. The slurry volume was chosen according to the expected layer thickness. Then using a spray gun, certain amount 3 mol % NH_4NO_3 solvent was sprayed into the container to break stable suspending system. Within five minutes, the Ce-ZrO_2 particles were deposited, forming a certain thickness of deposition layer. Then the cleaning solution was siphoned out from the container. A multilayer Ce-TZP/Al_2O_3 composite greenbody can thus be processed by alternative sedimentation of Ce-ZrO_2 and Ce-ZrO_2/Al_2O_3 slurries, with final Al_2O_3 layer as thin as 20 μm. In this experiment, 14 Al_2O_3/Ce-ZrO_2 layers were introduced into the composite. After sedimentation, the container was placed in an oven at 50 °C for 48 hours. The melting of wax coat painted on the container wall at 50 °C can make the greenbody be separated from container wall easily during oven drying. After oven drying, a perfect greenbody with a density up to 45% can be obtained.

It was necessary that this dried greenbody be heated at 0.5 °C/min to 350 °C and held for 2 h to remove residual NH_4NO_3 prior to sintering, without which the abrupt decomposition of NH_4NO_3 during sintering would lead to etching morphology on the surface of sample. Then the greenbody was isocompressed at 70 MPa, having a density up to 70%. The processing mentioned above can also be simplified by sieving technique (schematic device shown in Fig. 1b). The preprilling process was needed to improve the powder fluidity. The powder was then pumped out from a rotating distributing device onto screen mesh group, which made powder deposit into the die homogeneously, thus the uniform multilayer structure can be obtained, with final Al_2O_3 layer as thin as 25 μm. The layer thickness can be controlled by powder batching. The green body processed by the techniques mentioned above was sintered at 1600 °C for 3 h in air. Reasonably uniform layers with thickness in the range of 20 to 100 μm were readily formed. SEM micrographs of typical layers of Al_2O_3/Ce-TZP within a matrix of Ce-TZP are shown in Fig. 2.

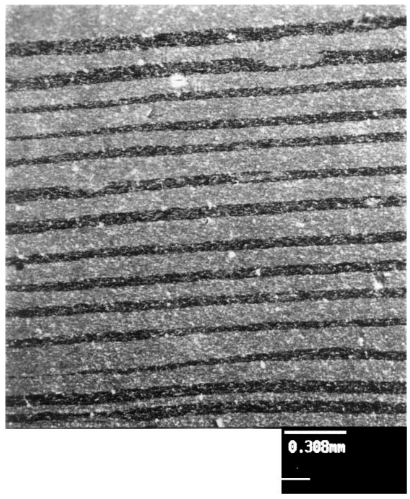

Figure 2 SEM micrograph showing alternative layers, with Al_2O_3 layer (dark) thickness of about 30 μm, in a matrix of Ce-TZP (light).

3. Results and discussion

The Ce-ZrO_2 and Al_2O_3/Ce-ZrO_2 (50 vol % Al_2O_3) suspensions were tested initially for sedimentation. When both suspensions maintained a pH value 3 (adjusted by HNO_3), only 15–20 vol % suspending particles deposited after two days stewing. This good stability assured that the particles in green body can keep the homogeneity in suspension. The amount of deposited particles increased with the addition of 3 mol % NH_4NO_3 solvent, which finally made the time needed for more than 80 vol % particles to deposit reduced to less than 5 minutes, which meaned the green body processing could be completed in a satisfactory short time. Fig. 3 showed the relationship between the time needed for 80 vol % particles to deposit and the amount of 3 mol % NH_4NO_3 solvent, which indicated that the Al_2O_3/Ce-ZrO_2 suspending system was less stable than Ce-ZrO_2.

The smooth glass substrate, wax coat on the container wall and pattern taper facilitated the green body shrinkage during oven-drying, otherwise the crack of green body was unavoidable. The high drying rate would inhibited the further water removal due to the NH_4NO_3 crystal film formed on the upper surface of green body, which was prevented by oven-drying under a high water content atmosphere. After oven-drying, the green density reached 45%. Although the long time oven-drying was not needed for sieving technique, density of greenbody processed by it only reached 60% after isocompressing at 70 MPa, compared to 70% for greenbody

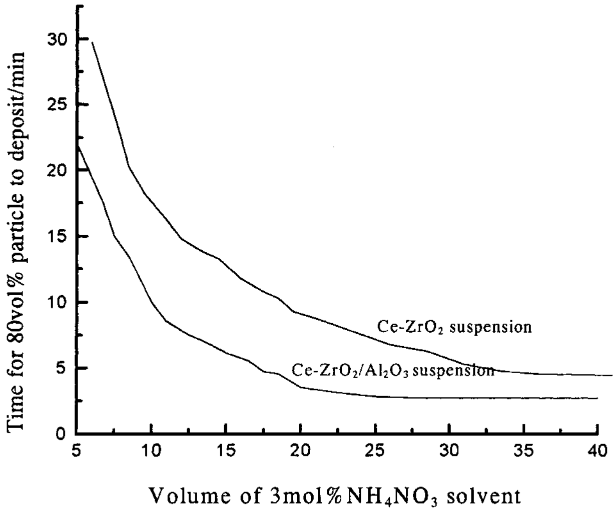

Figure 3 Curve of the time for 80 vol % particles to deposit vs the amount of 3 mol % NH_4NO_3 solvent.

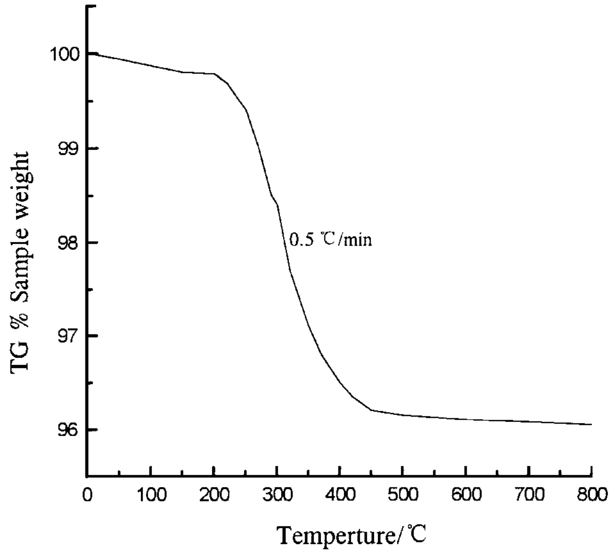

Figure 4 Thermogravimetric analysis of green body prepared by sedimentation.

processed by sedimentation technique, which proved that the colloidal technique was nessary for obtaining high packing density greenbody.

As mentioned before, the etching morphology on the surface of sample and crack between the layers were caused by the eruptive reaction during sintering as follows:

$$HNO_3 \xrightarrow{356\,K} 4NO_2 + 2H_2O + O_2$$

$$NH_4NO_3 \xrightarrow{473\,K} N_2O + 2H_2O$$

$$NH_4NO_3 \xrightarrow{573\,K} 2N_2 + O_2 + 4H_2O$$

Based on the equations above and thermogravimetric analysis of green body after over-drying (shown in Fig. 4), the greenbody stayed at 350 °C for 2 h. Then continuing isocompressing at 70 MPa and sintering at 1600 °C for 3 h. The final sintering sample had a density up to 97%.

Finally, we explored the possibility of processing layered materials by xerox technique. The pigment particles containing Ce-ZrO_2 and Ce-ZrO_2/Al_2O_3 suitable for xeroxing were first processed respectively, by alternatively xeroxing procedure using Ce-ZrO_2 and Ce-ZrO_2/Al_2O_3 pigment particles respectively, the layered greenbody can be obtained. The Ce-ZrO_2 tape processed by tape-casting can be adopted as 'copy-paper'. The thickness of layers can be controlled by the xeroxing times. So the films less than 10 μm can be expected. Moreover we should see the potential applications of this technique in smart materials, the embedded structures having special functions can thus be implanted by xeroxing, and fine and complex two dimensional structure can be expected. The experiment on this technique is undertaken by us.

4. Conclusions

The feasibility of processing laminated composite ceramics by sedimentation and sieving has been demonstrated. Compared to present popular processing techniques, these two methods are simple, effective and no introduction of organic additives during green body processing. The sample with layer thickness of 20–30 μm were produced. Moreover the possibility of processing thin layers by xerox has been explored, together with the application in smart materials, thus the layers less than 10 μm and fine structures can be expected.

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Received 17 June
and accepted 23 December 1998