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Fabrication of Functionally Graded SiAlON Ceramics by Tape Casting

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Functionally graded SiAlON ceramics (FG-SiAlONs) were successfully prepared by the tape casting and lamination approach. Non-aqueous SiAlON slurries with five different α to β-SiAlON ratios (85α:15β, 70α:30β, 55α:45β, 40α:60β, and 25α:75β) were prepared by a 66 methyl ethyl ketone/34 ethanol (vol%) mixture. Phase and microstructure analyses incorporation with hardness measurements clearly show that the FG-SiAlONs, prepared by tape casting, exhibit a continuous and gradual change in composition and hardness. Thus, the tape casting approach is a viable method to produce FG-SiAlONs with a precisely controlled composition, and subsequently properties, as a function of position.

I. Introduction

Functionally graded materials (FGMs) are an interesting and important class of materials in which material properties gradually change with position.[1–3] The property gradient is achieved by position-dependent chemical composition, microstructure or atomic order. Continuous changes in their microstructure distinguish FGMs from conventional composite materials. Fabrication of FGMs offers a technological challenge in extension of gradient to large scales, and requires elaborate processing facilities.[1,2]

SiAlON is a general name for a large family of ceramic alloys based on silicon nitride and alumina.[4] These ceramics are one of the commercially produced advanced ceramic materials because of their outstanding combination of thermal and mechanical properties.[5] There are two SiAlON phases that are usually used as engineering ceramics: α-SiAlON and β-SiAlON. While β-SiAlON has higher toughness (7–8 $MPa \cdot m^{1/2}$), strength, and thermal conductivity than α-SiAlON, α-SiAlON has excellent hardness (~20 GPa) but lower strength and toughness (3–4 $MPa \cdot m^{1/2}$) than β-SiAlON ceramics. Although α/β-SiAlON composites possess better mechanical properties with respect to monolithic phases of either α- or β-SiAlON, α→β SiAlON phase transformation limits the compositional design of α/β-SiAlON ceramics.[6,7] As a FG structure is ideal for smooth reduction of thermal stresses at interfaces, development of FG-SiAlON ceramics is expected to provide better mechanical properties than either monolithic α- or β-SiAlON and α-/β-SiAlON composites. There are a few studies to fabricate FG-SiAlON ceramics in the literature[8–14] via various techniques, including diffusion-controlled processes such as the powder bed technique, lamination, infiltration, as well as controlling the sintering condition. However, there is still need for a processing approach that will enable one to better control and extend the degree of gradient through the FG-SiAlONs.

Tape casting is a process for production of thin layers of materials to obtain single-layer or stacked and laminated multilayer structures where close control of thickness is critical.[15] When the variations in compositions between layers are relatively small, the material approaches a continuous composition and stress concentrations at interfaces can be decreased to practically insignificant values.[16] Consequently, the research objectives of this study were to produce FG-SiAlON ceramics by the tape casting approach and subsequently to understand the effect of processing parameters on compositional gradient development.

II. Experimental Procedure

In this study, commercially available powders of Si_3N_4 with a composition of 95% α, 5% β, and 1.4 wt% O (UBE SN E-10, Tokyo, Japan), AlN (1.6 wt% O content, H-Type Tokuyama Corp., Tokyo, Japan) and Y_2O_3 (H.C. Starck, 99.9 wt% pure, Berlin, Germany) were utilized to prepare SiAlON compositions. Methyl ethyl ketone (MEK, purity >99%, Merck, St. Louis, MO) and its binary combinations with ethanol (EtOH) (purity 99.8%, Merck) as azeotropic mixtures were tested as solvents for tape-casting slurries. In addition, polyvinyl butyral (PVB, Butvar B98, molecular weight: 40 000–70 000, Solutia) and STPP (MW 367.93 g/mol, Akca, Denizli, Turkey) were used as a binder and a dispersant, respectively. Polyethylene glycol (PEG) and dibutylphtalate (DBP) were tested as plasticizers.

Initially, polymeric tapes with no ceramic powder were cast on a glass substrate to investigate solvent, binder, and plasticizer compatibility. The quality of the tapes was evaluated based on their physical characteristics such as flexibility and sticking to the substrate. Once the polymeric carrier composition was determined, then slurries for tape casting were prepared. Five SiAlON compositions with different α- to β-SiAlON phase ratios were prepared for tape casting. These compositions were 85α:15β, 70α:30β, 55α:45β, 40α:60β, and 25α:75β. For the preparation of slurries, weighed amounts of Si_3N_4, AlN, Y_2O_3, and dispersant were ball milled for 6 h in an azeotropic solvent (i.e., 66 vol% MEK/34 vol% EtOH) with Si_3N_4 balls. After this first milling step, a plasticizer was added and the slurry was mixed for 1 h. Then, binder emulsion was added to the slurry and ball milled for 16 h. After a stable and homogeneous slurry was attained, the slurry was de-aired.

Tape casting was performed by a laboratory type tape caster on a glass substrate at a speed of 8 cm/s. The blade height was 400 μm. After drying at room temperature, tapes were cut into smaller pieces with 1 cm × 1 cm dimensions. Those pieces from

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tapes with different compositions were stacked on top each other in such a way that the α-SiAlON content was systematically reduced from top to bottom, while the β-SiAlON content was increased in that direction. Stacks with 25 layers (5 sheets × 5 composition) were prepared. These stacks were laminated by uni-axial pressing under various pressures, ranging from 5 to 15 MPa, at room temperature to investigate the effect of compaction pressure on binder burnout behavior via pore connectivity. In addition, to improve the contact between layers, some samples were cold isostatically pressed under 300 MPa after the binder burnout. As a result, two types of samples were prepared: 25-layer only uniaxially pressed (under ~15 MPa) samples and 25-layer uniaxially pressed (under ~7 MPa) and then cold isostatically pressed samples. These samples were designated as FGM-A and FGM-B, respectively.

Sintering of samples was carried out under 2.2 MPa nitrogen gas pressure at 1800°C for 1 h in a boron nitride crucible. The phase composition and relative amount of β-SiAlON from the top surface to the bottom of the samples were determined by using an X-ray diffractometer (XRD) by successive grinding of the surface at 100 μm intervals.[17] In addition, hardness change through the sample was measured by the Vickers indentation method under a 19.6 N (HV2) load. The microstructure of the sintered samples was analyzed by a scanning electron microscope (SEM).

III. Results and Discussions

A mixture of binder (12 vol%) and solvent was initially tested. As PVB is soluble in non-polar solutions, it was chosen as a binder.[18] The tape exhibited a very high degree of sticking to the glass substrate and poor flexibility. Similar observations were made previously by other researchers on different systems and the high degree of sticking was attributed to the binder, which increases wetting to the substrate as well as adhesiveness.[19] Accordingly, in this study, as the binder content decreased from 12 to 6.5 vol%, the sticking was reduced and flexibility was also improved. Then, an MEK+EtOH azeotropic mixture was tested as a solvent to improve the drying process and prevent differential volatilization.[18] Addition of EtOH to MEK reduced sticking but it did not eliminate the problem completely. An increase in the EtOH content from 10% to 34.4% in the MEK+EtOH azeotropic mixture eliminated the sticking problem. However, the flexibility of the tapes produced from this solvent–binder mixture was still insufficient. The flexibility of the tape was improved by addition of PEG as a plasticizer to the solvent–binder system. Consequently, based on the physical characteristics of the tape such as sticking to the substrate and the flexibility properties of polymer films, the following composition was chosen as a suitable polymeric carrier formulation for further tape casting studies: 95.6 vol% MEK (65.6 vol%) and EtOH (34.4 vol%) mixture, 2.5 vol% PEG, and 1.9 vol% PVB. The slurry composition with powders was determined based on the polymeric tape formulation studies. Thus, it was 49.7 wt% (20.9 vol%) SiAlON, 35.8 wt% (61.1 wt%) the mixture of MEK+EtOH, 0.4 wt% (0.6 vol%) dispersant, 7.7 wt% (9.8 vol%) PVB, and 6.4 wt% (7.7 vol%) PEG. After tape casting and drying, ~150 μm thick crack-free tapes were produced and readily removed from the substrate.

According to results of thermogravimetric analyses, a heating rate of 1°C/min was chosen between 175° and 425°C to prevent disruption of green ceramic parts due to evaporation of organic substances. The furnace was heated at a slow heating rate (i.e. 2°C/min) from 425° to 550°C and held at 550°C for 1 h. None of the samples exhibited cracks or delamination after the binder burnout process.

Figure 1 shows the change in α-SiAlON fraction and hardness values through an FGM-A sample. It is shown that phase transitions occur, and therefore, the continuous α-SiAlON content gradually changes from ~85% to ~20% through the thickness of the sample. Thus, composition and layer thickness

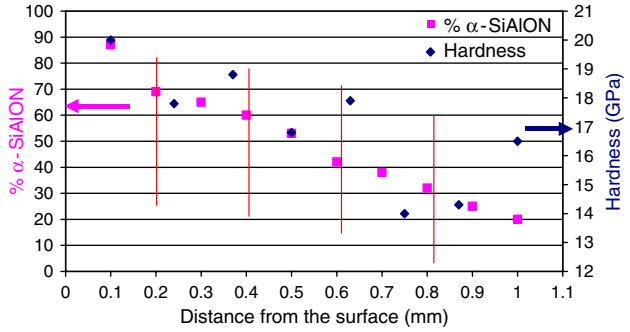

Fig. 1. Change in α-SiAlON fraction and hardness measurements of sintered functionally graded material-A, throughout the thickness of the sample (expected interface positions are shown in the figure, and the *x*-axis was normalized to 1).

can be easily adjusted in such a system. This is a critical parameter especially for designing FGMs for structural applications. In addition, FGM-A (with ~1.3 mm thickness) consisted of five different compositions. That is, each composition occupied ~0.2 mm thickness in the sample. In the figure, expected interface regions are marked as vertical lines. It is noteworthy that these lines match with the α-SiAlON fractions, predicted by XRD.

The hardness values indicate that a high hardness at the top and a relatively low hardness at the bottom were accomplished (Fig. 1). However, hardness values exhibit fluctuations throughout the thickness of the sample. When these results are closely examined, it is seen that lower hardness values are observed at about the interfaces of two compositions. In addition, microstructure analyses revealed the presence of some microstructural defects (i.e., pores) at the interfaces. One possible cause of these defects could be the weakening of interfaces during the binder burnout process. Density gradients in tapes could also result in such defects. To eliminate these defects, FGM-B samples were laminated under ~7 MPa and after the binder burnout, they were cold isostatically pressed under 300 MPa. Figure 2 shows hardness values and α-SiAlON fraction as a function of position in FGM-B. The hardness values exhibit a continuous and gradual decrease from top to bottom. The lack of fluctuations in hardness values and the SEM micrograph confirm that defect formation at interfaces can be prevented by controlling the lamination pressure and the cold isostatic pressing after binder burnout.

The cold isostatic pressing probably refurbishes weaknesses at the interfaces, and yield a homogeneous microstructure before sintering. XRD results reveal a continuous and gradual change in compositions in FGM-B samples (Fig. 2). Back-scattered SEM micrographs also confirm such a gradual and continuous change (Fig. 3). α-SiAlON grains that contain a small amount of rare-earth elements are gray and mainly equiaxed

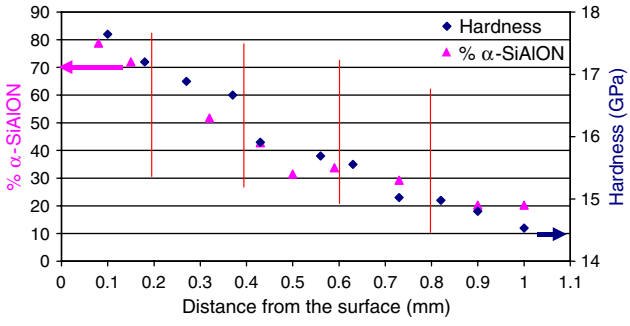

Fig. 2. Change in α-SiAlON fraction and hardness measurements of sintered functionally graded material-B, throughout the thickness of the sample (expected interface positions are shown in the figure, and the *x*-axis was normalized to 1).

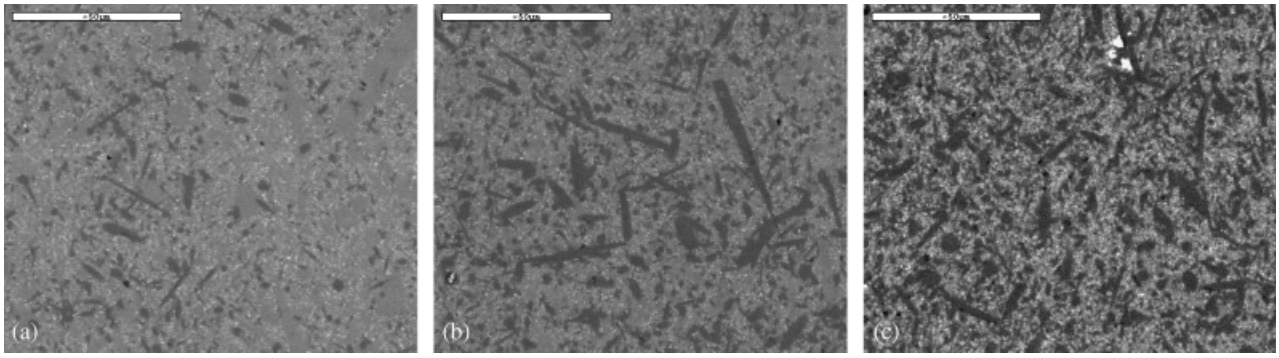

Fig. 3. BE-SEM images of functionally graded material-B (a) rich in α-SiAlON content, (b) intermediate region, (c) rich in β-SiAlON content.

with some elongated grains (Fig. 3(a)), whereas β-SiAlON grains containing no rare-earth elements are dark and more needle like (Figs. 3(b) and (c)). The glassy phase appears white because of the high cation content. This continuous change is one of the main advantages of the tape casting approach over the powder lamination approach where a relatively sharp transition zone is usually present between layers.[11] The presence of a sharp transition zone may affect the mechanical properties of FG-SiAlONs negatively.

IV. Conclusions

The results, presented above, clearly show that tape casting in combination with lamination is a viable method for fabrication of FG-SiAlONs. Although, in this study, only one type of microstructural configurations (i.e., five different compositions) is presented, high predictability of layer thickness, and composition as a function of position provides flexibility in microstructure design by this approach. As a result, FG-SiAlONs with a variety of microstructures can be designed and tested for specific applications by using this approach.

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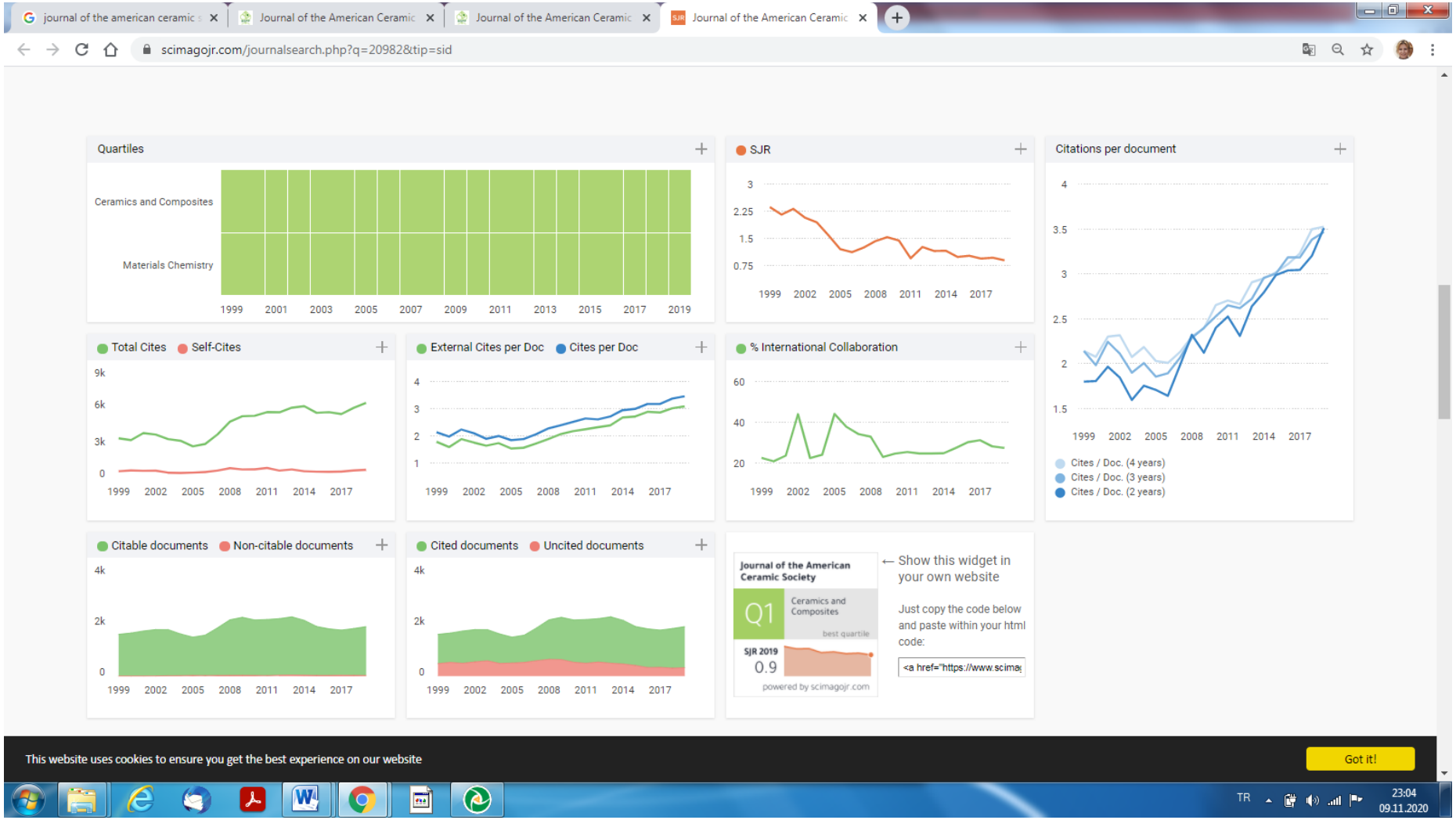
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