In situ Fabrication of a Dense/Porous Bi-layered Ceramic Composite using Freeze Casting of a Ceramic–Camphene Slurry

Young-Hag Koh,*† In-Kook Jun, Jong-Jae Sun, and Hyoun-Ee Kim*

School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

Dense/porous bi-layered ceramic composites were fabricated in situ by freeze casting a ceramic/camphene slurry with a low solid content (φ = 20 vol%). The warm slurry was prepared at 55°C by ball milling and cast into a mold at 25°C, where the top surface of the cast body was exposed to air to allow for the controlled evaporation of molten camphene. This simple method produced a high solid content with negligible camphene (φ > 50 vol%) on the top layer, while maintaining a low solid loading with solidified camphene (φ ~ 20 vol%) in the inner region. The sintered sample showed a dense 125-μm-thick ceramic layer on a highly porous layer with a thickness of ~1.7 mm and three-dimensionally interconnected pore channels that were representative of entangled dendritic growth of the solidified camphene.

1. Introduction

Porous ceramics have many industrial applications including liquid or gas filters, catalysis supports, gas burners, and implantable bioceramics.1–2 They are also basic components for porous electrodes in solid oxide fuel cells (SOFCs), e.g. Ni–yttria-stabilized zirconia (YSZ) cermet as an anode.3,4 For these applications, porous ceramics should have a three-dimensional (3-D) interconnected pore network with a high porosity.

To date, many techniques have been developed to fabricate porous ceramics.5–16 For example, tape casting using pore formers is one of the most commonly used methods, owing to its simple processability.10,11 In addition, this method allows the lamination of two different types of green tape, producing a dense/porous bi-layered composite, which is useful as a basic component as an electrolyte/anode layer in planar SOFCs.12,13

Another simple approach is to use aqueous freeze casting with a low solid content (φ).14,15 This method produces a porous ceramic with a 3-D pore network, which is representative of the entangled dendritic crystals of frozen ice. However, an extremely low operation temperature, e.g. ~40°C, is needed to freeze the aqueous slurry.

Recently, Araki and Halloran developed a novel way to produce porous ceramics at room temperature using freeze casting of a ceramic/camphene slurry.16 This method exploits the fact that a warm slurry prepared at 55°C solidifies with entangled dendritic crystals of frozen camphene at room temperature, resulting in a 3-D interconnected pore network.

This study demonstrates the possibility of using this freeze casting of a ceramic/camphene slurry to fabricate a dense/porous bi-layered ceramic in situ. To accomplish this, a cast body was exposed to the air at 25°C to produce a highly packed layer on the top by the controlled evaporation of the molten camphene, while at the same time preserving the 3-D dendritic growth of the camphene in the inner region (Fig. 1). This method allowed the in situ formation of a dense/porous bi-layered YSZ after sintering at 1400°C for 3 h. The processability of the freeze casting of the ceramic/camphene slurry is discussed.

II. Experimental Procedure

Commercially available YSZ doped with 8 mol% Y₂O₃ (TZ-8Y; Tosoh Co., Tokyo, Japan) was used as the ceramic material. Camphene (C₁₀H₁₆, Alfa Aesar/Avocado Organics, Ward Hill, MA) at a melting temperature of 44–48°C, was used as a vehicle without further purification. The 20 vol% YSZ powder, which contained a 3 wt% oligomeric polyester (Hypermer KD-4; UniQema, Everburg, Belgium) as a dispersant in the molten camphene was ball milled at 55°C for 24 h using zirconia balls as the media.

The warm slurry was then cast into a 2 × 10 × 50 mm mold at 25°C, where the top surface was exposed to the air, in order to control the rate of evaporation of the molten camphene. The weight change in the cast body was monitored using an electronic balance. After 30 min, the green sample was carefully removed from the mold and placed in a hood at room temperature in a flowing air atmosphere for 24 h, to remove the solidified camphene. The camphene-free sample was then sintered at 1400°C for 3 h. The macro- and microstructures of the green and sintered samples were examined using optical microscopy (PMG3, Olympus, Tokyo, Japan) and scanning electron microscopy (SEM, JSM-6330, JEOL Techniques, Tokyo, Japan), respectively.

III. Results and Discussion

The freeze casting of a ceramic/camphene slurry was used to fabricate a dense/porous bi-layered composite. To accomplish this, warm slurry was cast at 55°C, where the top surface of the cast body was exposed to air at 25°C. Camphene has a relatively high-vapor pressure of 2.0 × 10⁻¹³ Pa at 55°C.17 Therefore, the camphene near the surface in the cast body can evaporate readily until significant solidification has occurred, which can increase the solid content on the surface. On the other hand, the slurry solidifies in the inner region with entangled dendritic crystals of frozen camphene.

Such camphene evaporation during freeze casting was identified by monitoring the weight change in the cast body, as shown in Fig. 2. Two distinctive regions were observed for the weight loss of the sample. In the early stage (< 4 min), the level of weight loss increased linearly, suggesting that the rate of evaporation of molten camphene dominated the overall weight loss. Subsequently, the rate of weight loss was reduced, because the overall weight loss was determined by the amount of sublimation of the solidified camphene that had a lower vapor pressure than that of the molten camphene. This observation suggests that the thickness of the closely packed layer for a dense YSZ layer can be determined by controlling the evaporation rate of the molten camphene before significant solidification of the slurry has occurred.

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*Member, American Ceramic Society.
†Author to whom correspondence should be addressed. e-mail: kohyh@snu.ac.kr

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**Member, American Ceramic Society.
Figure 3(A) and (B) show the in situ formation of a dense/porous bi-layered YSZ. A 1.8-mm-thick sample was successfully fabricated after sintering at 1400°C for 3 h in air without any noticeable defects, e.g. interfacial cracking or distortion, as shown in Fig. 3(A). When the bi-layered composite is co-fired, bending of the sample frequently occurs because of the shrinkage mismatch between the two layers.\(^\text{18,19}\) Although the shrinkage mismatch between the dense and porous layers was not measured, the level of curling in the sample was quite small because the thickness of the dense layer was much smaller than that of the porous layer. Figure 3(B) shows the dense and porous layer at a higher magnification. A uniform and dense layer with a thickness of \(\approx 125\ \mu\text{m}\) was formed on the highly porous layer. Furthermore, the thickness of the dense layer could be reduced down to \(95\ \mu\text{m}\) by exposing the cast body at a lower temperature of \(18\ 1^\circ\text{C}\), because of the faster solidification of the slurry. An intermediate layer with less porosity was also formed as a diffused boundary layer, where the evaporation of the molten camphene and solidification of the slurry had synchronized.

Figures 4(A)–(C) show the degree of densification and porosity developed in these three layers, namely, dense, intermediate, and porous layers. A low solid content of 20 vol% was used to prepare the ceramic/camphene slurry. Therefore, under normal conditions, the sintered sample is expected to have a high degree of porosity. However, the top surface was exposed to the air in order to evaporate the molten camphene, where the solid content increased, thereby producing a dense layer. This layer showed almost full densification with some small pores, as shown in Fig. 4(A). Although the green density of this region was not measured, it was expected that this layer had a solid content \(\gtrsim 50\ \text{vol}\%\), considering the minimum green density of the ceramic compact needed to achieve the full densification. Immediately beneath this dense layer, an intermediate layer showed two types of pores, namely, small (\(<1\ \mu\text{m}\)) and large pores, as shown in Fig. 4(B). It is believed that the small and large pores were formed as a result of molten and solid camphene sublimation, respectively. This suggests that the evaporation of the molten camphene and the solidification of the slurry were synchronized at this region. A highly porous layer was observed beneath this intermediate layer, as shown in Fig. 4(C). Three-dimensionally interconnected pore channels were formed, which were representative of the entangled dendritic growth of the frozen camphene. The average porosity and pore size of this region measured from SEM images were \(\approx 56\%\) and \(\approx 17\ \mu\text{m}\), respectively.

Figures 5(A) and (B) show the densification and growth of the YSZ in the dense and porous layers, respectively. The free
surface of the sample on the top surface showed almost full densification without any noticeable defects (Fig. 5(A)). The average grain size measured was \( \sim 1-2 \) \( \mu m \). In addition, the porous layer showed fully densified YSZ walls with 3-D pore channels, as shown in Fig. 5(B). During the solidification of the molten camphene, most of the ceramic particles in the slurry were rejected by the growing dendrites and became concentrated between the dendrite arms or the neighboring dendrites, thereby generating a dense ceramic wall. These results show that freeze casting is a very useful method for fabricating dense/porous bi-layered YSZ composites for possible applications in SOFCs. In addition, this simple approach will find very useful applications in diverse fields, for example, laminated composites.

IV. Conclusions

We fabricated a dense/porous bi-layered composite in situ using a freeze casting of ceramic/camphene slurry with a low solid loading of 20 vol%. The warm slurry prepared at 55 °C was cast into a mold at 25 °C and its top surface was exposed to air in order to allow controlled evaporation of the molten camphene. This method produced a highly packed layer in the top layer with negligible camphene while maintaining a low solid loading with 3-D-solidified camphene in the inner region. After sintering at 1400 °C for 3 h, the sample had a dense 125-μm-thick ceramic outer layer and a highly porous inner layer with a thickness of \( \sim 1.7 \) mm.

References


