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Materials Science and Engineering A 419 (2006) 269–275

MATERIALS SCIENCE & ENGINEERING A

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Microstructure control of continuously porous t-ZrO_2 bodies fabricated by multi-pass extrusion process

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Received 8 September 2005; received in revised form 28 December 2005; accepted 28 December 2005

Abstract

Continuously porous t-ZrO_2 bodies having different pore sizes were fabricated using the multi-pass extrusion process. The pore size depended on the number of extrusion passes, the extrusion ratio, and rod diameter and tube thickness. The pore size dramatically decreased as the number of extrusion passes and tube thickness increased. The pore sizes of the 2nd passed samples, which were made by a feed roll using different rod diameters and tube thickness, were about 260, 180, 150 and 90 μm in diameter while the 3rd passed samples which were made with different extrusion ratios (40:1 and 61:1) were about 80 and 35 μm in diameter, respectively. In the 2nd passed t-ZrO_2 bodies sintered at 1550 °C, the relative density and bending strength decreased as the pore size increased. In the 3rd passed sample having a pore size of 35 μm, the bending strength increased as the sintering temperature increased up to 1550 °C. The maximum bending strength of the 3rd passed t-ZrO_2 body was about 297 MPa.

Keywords: Extrusion process; Porous t-ZrO_2 ceramic; Microstructure control

1. Introduction

Recently, yttria stabilized zirconia (t-ZrO_2) and Al_2O_3 have been considered for use as ceramics for implants such as prostheses, dental materials and femoral heads due to their compability, as well as desirable material properties such as strength, chemical stability and wear resistance [1–4]. However, the pore size, shape and porosity are also important factors to consider improving the compability of ceramics for implants because they are closely related to cell attachment, growth behavior and bond strength between the tissue and the artificial implant in the human body [5]. Suitable pore sizes for implants were reported to be approximately 100–150 μm [6], 140–160 μm [7] and 200–1000 μm [8] in diameter.

In general, the processing of porous Al_2O_3 ceramic has been well developed using several methods such as the carbon method [9], hot isostatic pressing [10], extrusion process [11], etc. However, the reports on the processing and mechanical properties of porous t-ZrO_2 ceramic are very limited [12]. In fact, the inherent mechanical properties of t-ZrO_2 are superior to those of Al_2O_3 ceramic, due to a transformation-toughening mechanism [13]. Moreover, the mechanical properties of these ceramics are determined by their structural parameters, such as porosity, pore size and pore structure [14]. It is well-known that the mechanical properties of porous bodies decrease as the porosity increases. Therefore, an innovative fabrication process is needed to make a continuously porous ceramic with well-controlled pore size and porosity as well as superior mechanical properties. Fracture-toughened ceramic composites and strong, continuously porous ceramics could be fabricated using the extrusion process [15,16].

In this work, as a new approach to fabricate the continuously porous t-ZrO_2 bodies, the multi-pass extrusion process was used. Different sizes of pores were prepared by increasing the number of extrusion passes as well as changing the tube thickness and rod diameters. This paper also focuses on the relationship between the microstructure and material properties of the continuously porous t-ZrO_2 bodies and compares it with that of continuously porous Al_2O_3 bodies from our previous work.

2. Experimental procedure

To fabricate the continuously porous t-ZrO_2 bodies, the starting t-ZrO_2 powder about 70 nm in diameter (Tosoh Corporation, Nanyo Manufacturing Complex, Japan) and pore forming agent, carbon, about 20 μm in diameter (Aldrich Chemical Company,

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doi:10.1016/j.msea.2005.12.033

USA) were used. The EVA, a type of polymer with a granular shape (Elvax 250, Dupont, USA) was composed of ethylene vinyl acetate and stearic acid ($CH_3(CH_2)_{16}COOH$, Daejung Chemicals & Metals Co., Korea). It was also added in a heated blender as a binder and lubricant, respectively. Using t-ZrO_2/EVA/stearic acid with a 50/40/10 (v/v/v), homogeneous mixtures were prepared using a shear mixer (C.W. Brabender Instruments, Shina Platech Co., Hwaseong Gyeong-Gi-Do, Korea). This mixture was used to produce tubes having different thicknesses (4.5, 7, 9 and 11 mm) by warm press. On the other hand, to make the rods having different diameters (21, 16, 12 and 8 mm), a pore-forming agent (carbon, Aldrich Chemical Company, USA), polymer and stearic acid (v/v/v, 50/40/10) were also mixed using a shear mixer at 120 °C for 1 h. The tubes and rods were assembled together, respectively, to prepare a feed roll 30 mm in diameter and extruded at 120 °C to make the 1st passed filaments with a diameter of 3.4 mm. The 1st passed filaments were cut 80 mm in length and reloaded into the extrusion die and re-extruded to make the 2nd passed filaments [5]. To remove the polymer binder, the 1st burn-out was performed in a tube furnace with a slow heating rate (45 °C/h) up to 700 °C in flowing nitrogen gas and the pore forming agent was removed by the 2nd burning-out process at 1000 °C in an air atmosphere. Finally, the pressureless sintering process was carried out at 1450–1600 °C for 1 h in flowing air.

Microstructures and fracture surfaces were observed using a scanning electron microscope (SEM, JSM-635F, Jeol, Japan). To identify the crystal structure and phases, an X-ray diffractometer (XRD, D/MAX-250, Rigaku, Japan) was used. The relative density was measured by the Archimedes method. The average bending strength was measured by a four-point bending test method with a universal testing machine (Unitech^{TM}, R&B, Korea) using five specimens (2.75 mm in diameter × 30 mm in length) with a crosshead speed of 0.1 mm/min.

3. Results and discussion

Fig. 1 shows TEM and HRTEM micrographs of raw t-ZrO_2 powder. It shows a spherical shape with an average particle size of about 70 nm in diameter, but some agglomeration appears. In the HRTEM micrograph of Fig. 1(b), some lattice distortion can be seen in the inner region. It seems to be caused by the solid solution of doped 3 mol% Y_2O_3. However, internal defects such as twins, or dislocations were not observed in t-ZrO_2 particles.

Fig. 2 shows low magnification SEM micrographs of the 2nd passed extruded bodies of pore-forming agents with diameters of (a) 150 μm and (b) 260 μm. In case of Fig. 2(a), the 2nd passed extruded bodies with a diameter of 150 μm were prepared using a feed roll 30 mm in diameter with an extrusion ratio of 61:1 and made by the assembly of a rod 12 mm in diameter and a tube 9 mm thick in diameter. On the other hand, the extruded bodies having a pore size of 260 μm in diameter, were made using a rod 21 mm in diameter and a tube 4.5 mm thick in diameter with the same extrusion ratio. From the SEM observation, it was clear that the diameter of the pore-forming agent increased as the rod diameter increased and as the tube thickness diameter decreased. From the EDS profiles taken of the P and Q regions of the SEM image Fig. 2(a), it was confirmed that the marked 'Q' and 'P' regions corresponded to the pore-forming agent and t-ZrO_2, respectively.

Fig. 3 is the SEM micrographs showing porous bodies (a) 260 μm, (b) 180 μm, (c) 150 μm and (d) 90 μm in diameter, which were the 2nd passed porous bodies sintered at 1550 °C. After the burning-out and sintering processes, the pore-forming agent was successfully removed and formed continuously porous t-ZrO_2 bodies with different pore sizes, as shown in Fig. 3. From the SEM images, it is clear that the pore size decreased remarkably as the rod diameter decreased.

Fig. 4 shows low magnification SEM micrographs of the 3rd passed t-ZrO_2 sintered bodies having pore sizes of (a) 80 μm and (c) 35 μm in diameter, respectively, and (b and d), enlarged images of (a and c), respectively. Both 3rd passed filaments were prepared using the 2nd passed filaments, which consisted of a pore-forming agent 260 μm in diameter. However, the extrusion ratios of both samples were different, with about 40:1 for Fig. 4(a) and 61:1 for Fig. 4(c), respectively. The microstructure and pore size was refined as both the number of extrusion passes and the extrusion ratio increased.

Fig. 5 shows low magnification SEM micrographs of a t-ZrO_2 porous body showing (a) a longitudinal direction and (b and c) enlarged pore frame and pore surface regions which

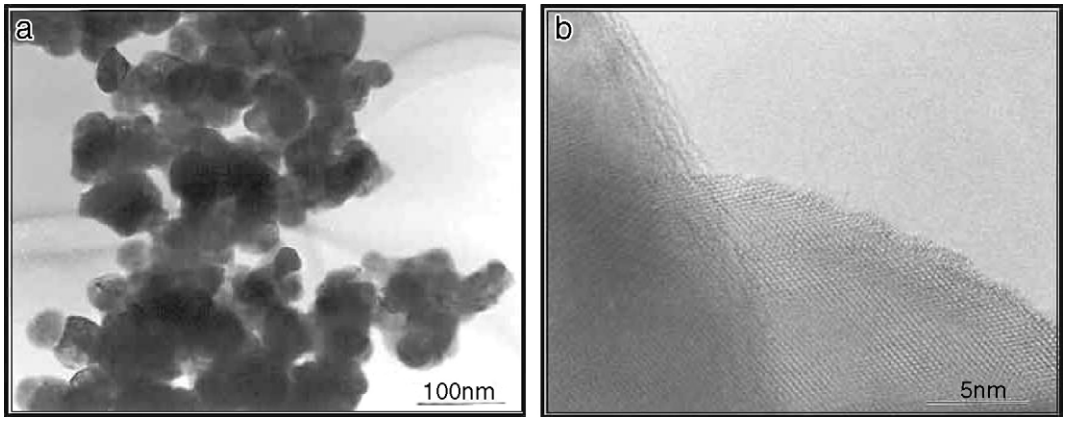

Fig. 1. (a) TEM and (b) HRTEM micrographs of raw t-ZrO_2 powder.