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Fabrication of Nanocrystalline ZrO_2-Spinel Composite

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High-energy ball-milling (HEBM) and spark-plasma-sintering (SPS) techniques were employed to synthesize nanocrystalline (nc) zirconia-base composite. As HEBM process proceeds, ZrO_2-spinel powders, which have initial particle sizes of 300-400 nm, can be reduced to less than 10 nm. After 400 h milling, an amorphous-like phase co-exists among the nc ZrO_2 and spinel particles, suggesting that HEBM process is a effective way for synthesizing nc ceramic powder. From the nc powder, nc ZrO_2-spinel composite with average grain sizes less than 100 nm can successfully be synthesized using SPS technique. The dense nc composite exhibits a slight increase in the hardness and Young modulus as compared with submicron-sized material.

Keywords: ZrO_2, nano-composite, high-energy ball-milling, spark-plasma-sintering (SPS)

1. INTRODUCTION

Ceramic materials are known to exhibit excellent mechanical properties when grain size is reduced to less than 100 nm[1-5]. For ceramic materials, since the lower mechanical properties have prevented from use in engineering applications, nano-crystallization seems to be one of the promising ways for improving the mechanical properties such as fracture toughness, fracture strength and deformability.

The present study was therefore performed to synthesize nano-crystalline (nc) ceramics. In this study, we have employed high-energy ball-milling (HEBM)[3-5] and spark-plasma-sintering (SPS)[3-6] techniques for the synthesis of nc ZrO_2-30vol% spinel composite. The reason for choosing this composite is that nano-crystallization of the ZrO_2-spinel composite can enhance the high-strain-rate superplasticity[7,8], leading to near-net-shaping applications at lower-temperatures. In addition, nano-crystallization has a potential for improving fracture toughness and fracture strength as well as superplasticity. In this report, we lay an emphasis on the fabrication and microstructural characterization of HEBM processed nc-powders and SPS processed nc-composite.

2. EXPERIMENTAL PROCEDURES

2.1 Material Preparation

The starting powders used were a high-purity 3mol%-Y_2O_3-stabilized tetragonal ZrO_2 powder (>99.97%, TZ-3Y, Tosoh Co., Ltd.,) and a high-purity $MgAl_2O_4$ spinel powder (Iwatani Co. Ltd., 300Fe_2O_3, 380SiO_2, 24Na_2O in wt ppm). The starting average particle sizes were ≈270 nm for ZrO_2 and ≈360 nm for spinel. Tetragonal ZrO_2 powder mixed with 30vol% spinel powder was milled with a planetary ball-milling machine (Fritsch Co., Ltd., Germany) for 0-400 h in ethanol using ZrO_2 ball media and pot.

The HEBM processed powders were consolidated with a SPS machine (Sumitomo Coal Mining Co., Japan). The powder mixtures were placed into a graphite die with 30 mm in inner diameter and pressed at 70 MPa. By applying the loading, the powders were rapidly heated up to 1573 K at a heating rate of about 100 °C/min under vacuum and then held at the temperature for 5 min. In this procedure, we have prepared dense sintered bodies of 30 mm in diameter and 2 mm in height.

2.2 Micrstructural Characterization

The phases of the HEBM processed powders and the SPSed specimens were determined by X-ray diffraction (XRD). The microstructural observations were conducted by TEM and SEM. For TEM observation, a small amount of powders dispersed in ethanol was dropped on micro-grid equipped with carbon substrate. For bulk specimens, thin sheets with a thickness of about 500 μm were cut from the SPSed materials with a low-speed diamond cutter, mechanically polished to about 100 μm in thickness and further thinned with an Ar ion-milling machine. For SEM observation, the surface of the specimens were mechanically polished and thermally etched at 1473 K for 10 min. The average grain size, d, was determined as 1.56 times of the average intercept lengths of grains[9].

2.3 Mechanical Properties

Mechanical properties such as hardness H and Young modulus E were measured by indentation

techniques. Prior to the indentation tests, the surface of the specimens was mechanically diamond polished to produce an optical surface.

The H value was determined using a Vickers indenter by applying loads of 10-500 N for a dwell time of 15 s. The E value was evaluated from elastic recovery of the diagonal dimension of Knoop indentation using the following relation developed by Marshall et al.[10];

$$E = 0.45H \Big/ \left(b/a - b'/a'\right) \quad (1)$$

where b/a is the diagonal dimension of Knoop indent, b/a = 0.143, and b'/a' is the dimension of Knoop indentation measured after unloading a load of 100 N for a dwell time of 15 s.

3. RESULTS AND DISCUSSION

3.1 HEBM Processed Nanocrystalline Powder

Figure 1 shows XRD profiles of ZrO_2-30vol% spinel powders before and after HEBM process. For the as-mixed powder, the detected diffraction peaks can be indexed from tetragonal (t) ZrO_2, monoclinic (m) ZrO_2 and spinel phases as shown in fig. 1(a). For HEBM processed powders, the peaks become broad with increasing milling time. After 400 h HEBM process, only the limited weak peaks can appear.

A change of the microstructure was characterized by TEM. For the as-mixed powder, the powder show sharp shape and corresponding selected area diffraction (SAD) pattern shows ring pattern as shown in Fig. 2(a). After HEBM process, although the appearance of powder morphology becomes indistinct, the powders appear to maintain almost similar size (Fig. 2(b)). The SAD pattern, however, becomes diffuse with an increase in milling time.

The details of the microstructure were characterized by high-resolution TEM. Before

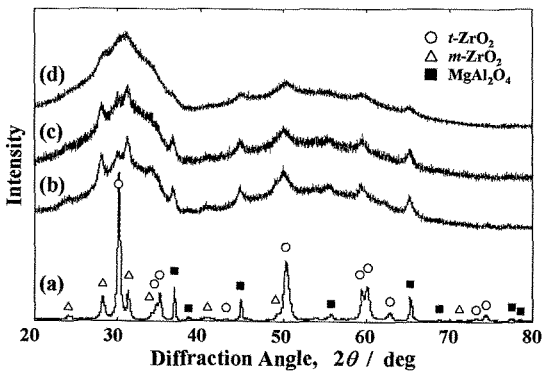

Fig. 1 XRD profiles of ZrO_2-30vol% spinel powders (a) before and (b)-(d) after HEBM process; (b) 50, (c) 250 and (d) 400 h.

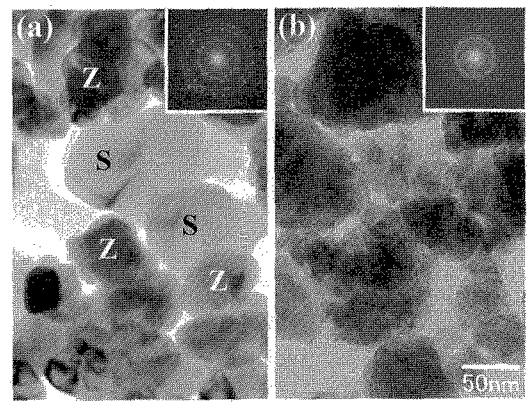

Fig. 2 Bright-field TEM images and corresponding SAD patterns of ZrO_2-30vol% spinel powders; (a) as-mixed and (b) HEBM processed for 400 h.

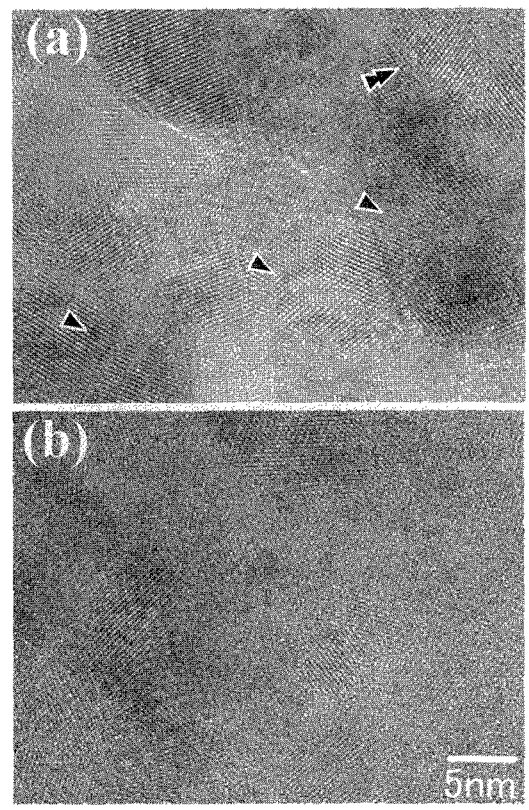

Fig. 3 High-resolution TEM images of powder after HEBM process for (a) 250 and (b) 400 h.

ball-milling, the each powder consisted of single or single-like crystals, whereas after 200 h ball-milling, the powder is composed of nc particles of about 10 nm or less as shown in Fig. 3(a). In should be noted that, after 400 h milling, an amorphous-like phase is found among the nc particles as shown in Fig. 3(b). The change in the microstructure consists well with the result of XRD shown in Fig. 1. For 250 h HEBM processed powder, since many lattice distortion (triangles) and twin (double

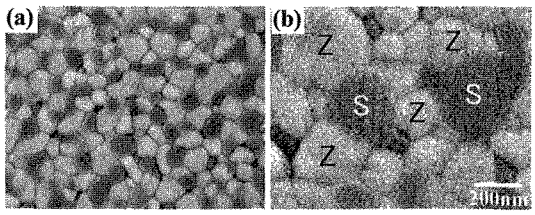

Fig. 4 SEM images of ZrO_2-spinel composite; (a) SPSed at 1573 K for 5 min and (b) pressureless-sintered at 1673 K for 2 h.

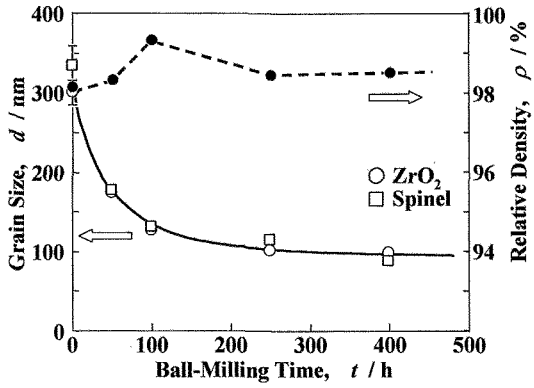

Fig. 5 Milling time dependence of grain size and relative density after SPS process.

triangle) were observed, the nano-crystallization and residual stress induced by impact energy of the ZrO_2 ball is likely responsible for the broadening of XRD profile. For 400 h HEBM processed powder, the occurrence of amorphization would result in the limited weak peak in the XRD patters in fig. 1(d).

EDS analysis confirmed that the amorphous-like phase consists mainly of the mixture of zirconium, aluminum and magnesium, suggesting that solid-state reaction can be induced by HEBM technique. This suggests that HEBM process is an effective way for synthesizing nc ceramic powder of particle sizes less than 10 nm and amorphous ceramic powder.

3.2 SPS Processed Nanocrystalline ZrO_2-spinel Composite

Figure 4 shows typical SEM images of ZrO_2-30vol% spinel composite. For comparison, the microstructure of the composite pressureless-sintered in air at 1673 K for 2 h, which is conventionally used for the sintering of ZrO_2 ceramics, is also shown in fig. 4(b). Under the conventional condition, although we can obtain dense sintered bodies with $\rho > 98$ %, the average grain size d has generally exceeded 300 nm. On the other hand, the composite consolidated using SPS at 1537 K for 5 min shows finer and homogenous microstructure.

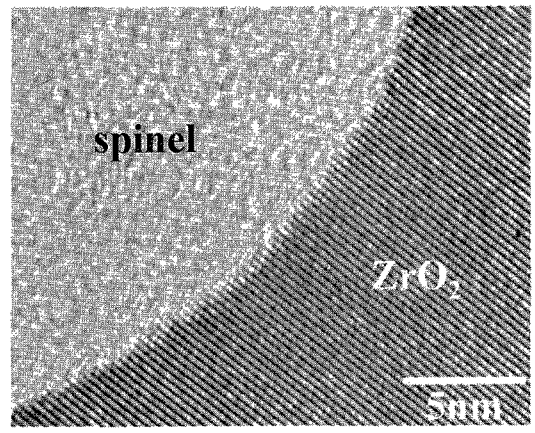

Fig. 6 Typical high-resolution TEM image of ZrO_2/spinel boundary SPSed at 1573 K for 5 min.

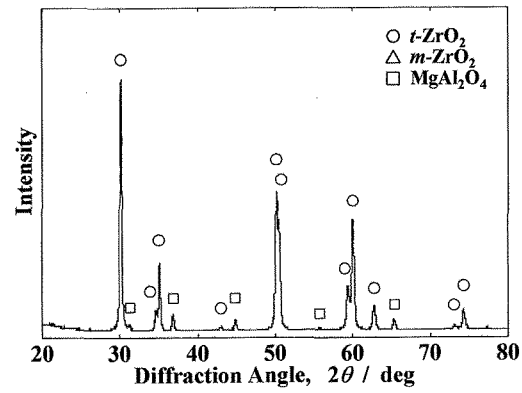

Fig. 7 XRD profile of nc ZrO_2-spinel composite SPSed at 1573 K for 5 min.

The combination of HEBM and SPS processes can effectively reduce grain size as shown in fig. 5. With maintaining density higher than 98 %, the grain size steeply decreases less than 150 nm at 100 h milling. After 400 h milling, fully dense nc ZrO_2-spinel composite of $d \approx 90$ nm can successfully be synthesized. The powders tend to agglomerate with a decrease in the size, resulting in the formation of pore. It is noted that the spinel particles disperse homogenously among ZrO_2 matrix and no agglomeration was found as shown in fig. 4(a).

The grain boundary microstructure was characterized using high-resolution TEM. Figure 6 is a typical microstructure of ZrO_2/spinel boundary. As shown in the image, the lattice fringes of each grain directly intersect at the boundaries without any second phases. In the present study, no amorphous phase was found along boundaries and at multiple-grain junctions.

After SPS process, the XRD profile of the dense nc ZrO_2-spinel composite shows sharp peaks as shown in Fig. 7. All the detected peaks can be indexed from

t-ZrO_2 and spinel phases and no peaks of m-ZrO_2 and cubic ZrO_2 phase was detected.

3.3 Mechanical Properties of Nanocrystalline Composite

The relationship between mechanical properties (H and E) and ball-milling time t was examined by indentation techniques. The values were slightly higher in the SPS processed composites than those of the pressureless- sintered one; $H \approx 15$ GPa and $E \approx 260$ GPa, and $H \approx 13$ GPa and $E \approx 210$ GPa for SPS processed and pressureless-sintered composites, respectively. The increment of the values, however, is independent of the milling-time (grain size).

IV. SUMMARY

In order to synthesize nc zirconia-spinel composite, HEBM and SPS techniques were employed. The results obtained are as follows.

1) Using HEBM process, the ZrO_2-spinel powders consisting nc-particles less than 10 nm can successfully be synthesized from the sub-micron grain sized powders of ≈300 nm.
2) After 400 h ball-milling, the powders consist of the mixture of an amorphous-like phase alloyed in atomic level and nc-ZrO_2 and nc-spinel particles of the sizes less than 10 nm. TEM observation shows that solid-state reaction is induced by HEBM process.
3) Using SPS technique, the nc-ZrO_2-spinel powders can be consolidated into dense nc composite with average grain sizes less than 100 nm.
4) The SPSed nc ZrO_2-spinel composite exhibits Young modulus of $E \approx 260$ GPa and Vickers hardness of $H \approx 15$ GPa, which are slightly higher than those of sub-micron grain sized composite.

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