FABRICATION AND MICROSTRUCTURAL CHARACTERIZATION OF NANO-CRYSTALLINE ZrO$_2$-BASED COMPOSITE

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Abstract. Nanocrystalline ZrO$_2$-spinel powders consisting of nano-particles of $\leq$10 nm can successfully be synthesized using high-energy ball-milling process. Using spark-plasma-sintering technique, the nanocrystalline powders can be consolidated into dense nanocrystalline composite with an average grain size of $<100$ nm. The mechanical properties of ZrO$_2$-spinel composite can significantly be improved by the nano-crystalization. Flexural strength $\sigma_f$ was heightened by a factor of 2.0-2.5: the maximum $\sigma_f$ of the nanocrystalline composite reached $\approx 2.4$ GPa. Flow stress of the nanocrystalline composite can be lowered by about 50% than that of submicrometer-sized composite.

1. INTRODUCTION

Tetragonal zirconia (t-ZrO$_2$) ceramics have excellent mechanical properties [1]. Use for engineering applications of ZrO$_2$, however, has been limited because of its lower formability. Although superplasticity attained in several ZrO$_2$-based ceramics [2], the available strain rates are too lower for near-net-shaping applications. Recently, we can improve the superplasticity of ZrO$_2$ ceramics by the dispersion of fine MgAl$_2$O$_4$ spinel particles: high-strain-rate superplasticity (HSRS) that is defined as an ability of a material to show a tensile elongation of $>200\%$ at strain rates of $\geq 10^{-2}$ s$^{-1}$ was attained in the ZrO$_2$-spinel composite at $\geq 1673$K [3,4]. For the use for near-net-shaping applications, further improvement of superplastic properties is required: low forming temperature and high available strain rate. In addition, mechanical properties are also important for engineering applications.

To attain these requirements in ceramic materials, nano-crystallization seems to be one of the promising ways. For superplasticity, grain size is a critical factor to improve forming temperature and available strain rate [2]. Furthermore, recent studies [5-10] have shown that, as compared with submicrometer-sized ceramics, the nanocrystalline ceramic materials can exhibit excellent mechanical properties as grain size is reduced to less than 100 nm.

The present study was therefore performed to synthesize the nanocrystalline ZrO$_2$-30vol.\% MgAl$_2$O$_4$ spinel composite. In order to synthesize the nanocrystalline composite, we employed high-energy ball-milling (HEBM) and spark-plasma-sintering (SPS) techniques.
2. EXPERIMENTAL PROCEDURES

2.1. Material preparation
The powders used were a high-purity 3mol.%-Y₂O₃-stabilized tetragonal ZrO₂ powder (>99.97%, Tosoh Co., Ltd.) and a high-purity MgAl₂O₄ spinel powder (>99.97, Taimei Chemical Co. Ltd.). The average particle sizes were ≈270 nm for ZrO₂ and ≈360 nm for spinel. Tetragonal ZrO₂ powder mixed with 30 vol.% spinel powder was milled with a planetary ball-milling machine for 0-400 h in ethanol using ZrO₂ ball and pot.

The ball-milled powders were consolidated with a SPS machine (Sumitomo Coal Mining Co., Japan). The powders were placed into a graphite die and rapidly heated up to 1573K at a heating rate of about 100 °C/min under vacuum, and then held at the temperature for 5 min. The temperature was controlled by monitoring the surface temperature of the graphite die with an optical pyrometer. In this procedure, we have prepared circular disks of 30 mm in diameter and 2 mm in thickness. The relative density of the SPSed specimens was measured by the Archimedes method, where the theoretical density was defined as 5.322·10³ kg/m³ according to the rule of mixture.

2.2. Microstructural characterization
The phases of the ball-milled powders and the SPSed specimens were determined by X-ray diffraction (XRD) using CuKα radiation operating at 40 kV and 300 mA. The microstructural observations were conducted by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). For TEM observation of HEBM processed powders, a small amount of powders dispersed in ethanol was dropped on Cu micro-grid equipped with carbon substrate. For bulk specimens, thin sheets with a thickness of about 500 µm were 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 bulk specimens were mechanically polished and thermally etched at 1473K for 10 min. The average grain size, d, was determined as 1.56 times of the average intercept lengths of grains [11].

2.3. Mechanical properties
Flexural strength σₐ was measured by three-point-bending test at room temperature. The SPSed circular disks were cut into rectangular bars of 2.4 mm width and 1.5 mm thickness. The measurements were performed at a 16 mm span and a cross-head displacement rate of 0.5 mm/min. For tensile tests, dog-bone-shaped flat tensile specimens were machined with gauge portions of 2·4·10 mm. Constant displacement-rate tensile tests were conducted at 1573-1723K and at initial strain rates of $\dot{\varepsilon}_0 = 3.3·10^{-4}$ – 0.7 s⁻¹ under vacuum.

3. RESULTS AND DISCUSSION

3.1. Ball mill processed powder
Fig. 1a shows XRD profiles of HEBM processed ZrO₂-30 vol.% spinel powders. For the as-mixed powder, all the sharp peaks can be indexed from tetragonal (t-) ZrO₂, monoclinic (m-) ZrO₂ and spinel phases but no cubic (c-) ZrO₂ phase was detected. For the HEBM processed powders, the peaks become broad as milling process proceeds. It can be seen from the inspection of the XRD profile that a gradual phase transformation from t-ZrO₂ to m-ZrO₂ occurs through HEBM process. The stability of the two phases has been interpreted mainly from surface energy and secondary from internal strains and impurities [12]. Since the surface energy of the t-phase is lower than that of the m-phase, the t-phase becomes stable rather than m-phase with a decrease in particle size. The present result appears to be inconsistent with this stability. From the broad XRD profile, it is clear that the large strain was induced into the crystals by high impact energy of the ZrO₂ ball. Although the difference in the transformation behavior is unclear at the present time, the large strain is likely to be responsible for the m-ZrO₂ transformation.

A change in microstructure was characterized by high-resolution TEM (HRTEM) and EDS. For the as-mixed powder, the particles had sharp shapes and the corresponding selected area diffraction (SAD) pattern showed a sharp ring pattern. HRTEM observation showed that the starting powders consisted of single or single-like crystals. After the HEBM process, the contrasts of the powders and the corresponding SAD pattern become diffuse as milling process proceeds. (Figs. 1b and 1c). HRTEM observation revealed that, after 250 h ball-milling, the powder is composed of nanocrystalline particles of about 10 nm or less. After 400 h ball-milling, an amorphous-like phase is formed among the nanocrystalline particles.

The change in microstructure corresponds to the result of XRD in Fig. 1a. For the HEBM processed powders, since much lattice distortion and
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3.1. Ball-milling process

many twins were observed in the nanocrystalline particles, the nano-crystallization and residual strain induced by impact energy of the ZrO$_2$ ball is likely to be responsible for the broadening of XRD profile. For 400 h HEBM processed powder, amorphization would result in the limited weak peak in the broad XRD patterns.

EDS analysis confirmed that the amorphous-like phase consists mainly of the mixture of zirconium, aluminum and magnesium, and no impurity was detected. Since such an amorphous-like phase was observed to form in the nanocrystalline powders as HEBM process proceeds, the contamination during HEBM process is unlikely responsible for the amorphization. According to the study by Hankey et al. [13], although large residual strain and reduced crystalline size are one of the important factors affecting solid state reactivity, the reactivity was enhanced mainly by high pressure shock. Therefore, the amorphization must occur through the solid state reaction induced by high impact energy induced during HEBM process.

3.2. Microstructure of SPSed materials

Fig. 2 shows SEM images of ZrO$_2$-30 vol.% spinel composite SPSed at 1537K for 5 min. For comparison, the microstructure of ZrO$_2$-spinel composite pressureless-sintered in air at 1673K for 2 h is also shown in Fig. 2a. For the pressureless-sintering, although we obtained dense sintered bodies with $\rho > 98\%$, the average grain sizes $d$ exceeded 300 nm. For the HEBM and SPS processed composites, dense nanocrystalline composite of $\rho > 98\%$ can be obtained as shown in Figs. 2b-2d.

The properties of nanocrystalline ZrO$_2$-spinel composite are listed in Table 1. Using HEBM process, the grain size steeply decreases smaller than 150 nm at 100 h milling. After 400 h milling, dense nanocrystalline ZrO$_2$-spinel composite of $d \approx 96$ nm can successfully be synthesized. In general, fine powders tend to agglomerate, resulting in residual flaws. It is noted, however, that the spinel particles disperse homogeneously among the ZrO$_2$ matrix and no detectable agglomeration was found as shown in Fig. 2d. After the SPS process, all the detected peaks can be indexed from the t-ZrO$_2$ and spinel phases.

3.3. Flexural strength

The flexural strength, $\sigma_f$, of the ZrO$_2$-spinel composite was examined as a function of grain size. $\sigma_f$ of
Table 1. The present data of ball-milling time $t$, grain size $d$ and density $\rho$, for ZrO$_2$-30 vol.% spinel composites ball-milled for 0-400 h.

<table>
<thead>
<tr>
<th>specimen</th>
<th>ball-milling time, $t$ (h)</th>
<th>density, $\rho$ (%)</th>
<th>average grain size $d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$-30 vol.% spinel</td>
<td>0</td>
<td>98.0</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>98.3</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>99.3</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>98.4</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>98.5</td>
<td>96</td>
</tr>
</tbody>
</table>

the composite tends to increase with decreasing grain size as shown in Fig. 3a. For the submicrometer-sized composite with $d = 300$ nm, an average $\sigma_f$ is about 0.9 GPa, which is lower than the $\sigma_f$ value in monolithic t-ZrO$_2$ [14]. For the nanocrystalline composite with $d = 96$ nm, on the other hand, $\sigma_f$ reached high values as high as 1.9 GPa. The maximum strength of $\sigma_f = 2.2$ GPa reached almost the same level of $\sigma_f = 2.4$ GPa reported in ZrO$_2$-Al$_2$O$_3$ composite [15,16], which is classed to the highest $\sigma_f$ in oxide ceramic materials. The refinement of grain size smaller than 100 nm can improve $\sigma_f$ of the ZrO$_2$-spinel composite by a factor of 2.0-2.5.

According to earlier studies [1,17,18], the flexural strength $\sigma_f$ of ZrO$_2$ ceramics has often been related to two different factors using the following equation

$$\sigma_f \propto K_{IC} a^{-1/2},$$

(1)

where $K_{IC}$ is the fracture toughness and $a$ is the radius of critical flaw. For ZrO$_2$ ceramics, the $K_{IC}$ value has often been related to stress-induced $t \rightarrow m$ phase transformation toughening, where the martensitic transformation strains can dissipate a portion of the energy of fracture [1,19]. As expected from Eq. (1), $\sigma_f$ will increase with toughness $K_{IC}$ for a constant $a$-value. XRD analysis showed, however, that a small amount of $t \rightarrow m$ phase transformation was detected on the fracture surfaces in the submicrometer-sized composite, but not for the high strength nanocrystalline composite. For the present composite, therefore, the strengthening would not contribute mainly to $K_{IC}$ due to the $t \rightarrow m$ phase transformation.

According to the relation between $\sigma_f$ and $a$ in Eq. (1), a reduction of residual flaw size is effective
3.4. Tensile properties

Fig. 3b shows flow stress (\(\sigma\))-strain rate (\(\dot{\varepsilon}\)) relationship of nanocrystalline ZrO\(_2\)-spinel composite. For comparison, the data of submicrometer-sized composite with \(d = 350\) nm is also shown by closed symbols [4]. It is apparent from the inspection of Fig. 3b that a decrease in grain size can improve the deformability. The nano-crystalization enhances strain rate of one order of magnitude and decreases deformable temperature of the order of 100K.

The flow mechanism has often been characterized by the strain rate sensitivity \(m\) defined by the following creep equation:

\[
\dot{\varepsilon} = A\sigma^m d^n,
\]

where \(\dot{\varepsilon}\) is the steady-state strain rate, \(d\) is the grain size, \(p\) is the grain size exponent and \(A\) is a constant. In the both materials, the \(m\)-value estimated from the slope in the \(\sigma\)-\(\dot{\varepsilon}\) relationship takes almost the same value of 0.5. For fine-grained ceramics with \(m = 0.5\), grain boundary sliding (GBS) process has generally been regarded as the most important high-temperature flow mechanism [2]. It is therefore reasonable to explain that the deformation of the nanocrystalline ZrO\(_2\)-spinel composite occurs primarily through GBS. The improvement of deformability would not result from the change in flow mechanism but from the decreases in grain size as expected from Eq. (2).

In general, tensile elongation tends to increase with decreasing flow stress. In the present composite, however, the elongation of nanocrystalline composite is lower than that of submicrometer-sized one though flow stress was lowered due to nanocrystallization. Although the limited elongation in nanocrystalline composite is unclear at the present time, the preexisted nano-sized flaw is likely to be responsible for the lower tensile elongation.

4. SUMMARY

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

(1) Using the HEBM process, nanocrystalline ZrO\(_2\)-spinel powders with particle sizes of \(\leq 10\) nm can successfully be synthesized. After 400 h ball-milling, the powders consist of the mixture of nanocrystalline particles of the sizes smaller than 10 nm and an amorphous-like phase alloyed in an atomic level.

(2) Using SPS technique, the nanocrystalline ZrO\(_2\)-spinel powders can be consolidated into dense nanocrystalline composite with \(\rho > 98\%\) and \(d < 100\) nm.

(3) Nano-crystalization can strengthen the ZrO\(_2\)-spinel composite by a factor of 2.0-2.5. The maximum \(\sigma_f\) of the nanocrystalline composite reached \(\approx 2.2\) GPa. The high \(\sigma_f\) can be associated mainly with a decrease in flaw size due to nano-crystalization.

(4) Flow stress of the nanocrystalline composite can be lowered by 50% than that of submicrometer-sized composite.

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REFERENCES


