Previous studies demonstrated that the strength of zirconia (ZrO₂) could be enhanced or reduced by respectively adding micrometer-sized alumina (Al₂O₃) or nickel (Ni) particles. In the present study, 5 vol% micrometer-sized Al₂O₃ particles and 1 vol% nanometer-sized Ni particles are incorporated into the ZrO₂ matrix, which is subsequently densified by pressureless sintering. The biaxial strength of the ZrO₂/(Ni+Al₂O₃) nanocomposite is nearly double that of the monolithic ZrO₂. The increase in strength correlated with a reduction in the critical flaw size and not with any change in toughness, which may be a result of grain boundary strengthening.

II. Experimental Procedures

Yttrium-doped ZrO₂ powder (TZ-3Y, ZrO₂+3 mol% Y₂O₃, d₅₀ = 230 nm, Tosoh Co., Tokyo, Japan) was mixed with 5 vol% Al₂O₃ (TM-DAR, d₅₀ = 210 nm, Taimei Chem. Co. Ltd., Tokyo, Japan) powder by ball milling in de-ionized water for 24 h. Ammonia drops were added to the mixed powder slurry to achieve a pH value of 9.2. A separate solution of Ni nitrate (Ni(NO₃)₂, 6H₂O, Showa Chem. Co., Tokyo, Japan) with the same pH value was also prepared. The mixed powder slurry was poured into the Ni nitrate solution; the whole mixture was stirred for 30 min. The amount of Ni in the slurry was 5 vol% of the ZrO₂-based powder mixtures, provided that all Ni ions were adsorbed onto the surface of the ceramic particles. The Ni-coated powder mixture was filtered, washed, and dried. The mixture was then reduced in pure hydrogen at 550°C for 1 h, followed by ball milling in ethyl alcohol for 24 h with ZrO₂ grinding media. Reference ZrO₂, ZrO₂/Al₂O₃, and ZrO₂/Ni specimens were also prepared with the same technique for comparison purpose.

The amount of Ni in the powder mixture was determined by inductive coupled plasma-atomic emission spectroscopy (ICP-AES, 3000DV, Perkin-Elmer, Optima, Boston, MA). Green compacts with a diameter of 25.4 mm and a thickness of 5 mm were formed by uniaxial pressing at 30 MPa. The compacts were then sintered within a covered graphite mold at 1600°C in an argon atmosphere, carbon monoxide mainly, was generated during sintering. The heating and cooling rates were 5°C/min.

Phase identification was performed by X-ray diffractionometry (XRD) with CuKα radiation. Two scanning rates were used: 0.05°/s for phase identification and 0.002°/s for quantitative analyses. The final densities of the specimens were determined by the Archimedes method. Assuming that the solubility between the materials used in the present study was low; the relative densities of the composites were estimated from the theoretical densities of ZrO₂, Al₂O₃, and Ni, which are 6.05, 3.98, and 8.90 g/cm³, respectively. The microstructure of the specimens was observed by scanning electron microscopy (SEM). Polished surfaces of the specimens were prepared by grinding and polishing with a 3 μm diamond paste and a 0.05 μm silica suspension. A thermochemical technique was used in the
present study to determine the grain boundaries of the composites. The polished specimens were subjected to chemical etching with a solution of 0.8 N orthophosphoric acid and 0.5 N nitric acid (3:1) for 4–5 min, followed by thermal etching at 1250°C for 30 min. The line intercept technique was used to determine the size of the matrix ZrO$_2$ grains; more than 200 grains were counted. The size of Ni inclusions in the fired composites was estimated from the XRD patterns by the Scherrer formula.$^{10}$ The amount of $m$-phase ZrO$_2$ was estimated using the formula proposed by Evans et al.$^{11}$

In preparation for mechanical testing, the sintered specimen disks were first ground with a 325 grit resin-bonded diamond wheel at depths of 5 μm/pass. The elastic modulus of the specimens was determined with an ultrasonic technique at 5 MHz (pulse receiver 505S PR and oscilloscope 9345CM, LeCroy Co., New York, NY). The strength of the disks was determined by a biaxial flexure technique$^9$ in a universal testing machine (MTS 810, MTS Co., Eden Prairie, MN). A one-ball-on-three-balls jig was used; the loading rate was 0.5 mm/min. Four disks of each composition were used for the strength measurement. The fracture toughness was determined by an indentation technique at a load of 196 N. The relationship proposed by Lawn et al.$^{12}$ was used to calculate the toughness from the indentation data. The magnetization curves were obtained by a SQUID magnetometer (MPMS7, Quantum Design Co., San Diego, CA). The dielectric constant was measured by an LCR meter (2330A, NF Electronic Instrument Co., Yokohama, Japan) at an excitation voltage of $\pm 1V$ at 1 kHz.

### III. Results

The ICP analysis showed that the amount of Ni in the ZrO$_2$/Ni and ZrO$_2$(Ni$_1$Al$_2$O$_3$) powder mixtures was much less than the amount originally added to the slurry (see Table I). This indicates that only part of the added Ni ions is adsorbed onto the surface of the ceramic particles. Most Ni ions are filtered and removed during the solution-coating stage. Figure 1 shows the XRD patterns of the specimens after sintering and surface grinding. A small amount of $m$-phase ZrO$_2$ was found on the ground surface. At faster scanning rates, XRD analysis showed neither Al$_2$O$_3$ nor Ni peaks. However, the (111) peak of Ni was detected at a slower scanning rate. The size of Ni inclusions can thus be estimated by measuring the full-peak width at half-maximum intensity (FWHM).$^{10}$ The size of Ni particles in the starting powder mixture was 20 nm. The Ni inclusions remained small after sintering: less than 40 nm (see Table I).

The densities of the ZrO$_2$/Ni and ZrO$_2$(Ni$_1$Al$_2$O$_3$) specimens were higher than 98%, indicating that dense Ni-containing nanocomposites can be prepared by pressureless sintering. Figure 2 shows the typical micrographs of the specimens. The

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ni (vol%)</th>
<th>Al$_2$O$_3$ (vol%)</th>
<th>Relative density (%)</th>
<th>ZrO$_2$ grains (μm)</th>
<th>Ni inclusion (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>—</td>
<td>—</td>
<td>97.5</td>
<td>0.79</td>
<td>—</td>
</tr>
<tr>
<td>ZrO$_2$/Al$_2$O$_3$</td>
<td>—</td>
<td>5.0</td>
<td>97.9</td>
<td>0.89</td>
<td>—</td>
</tr>
<tr>
<td>ZrO$_2$/Ni</td>
<td>0.9</td>
<td>—</td>
<td>100</td>
<td>1.4</td>
<td>37</td>
</tr>
<tr>
<td>ZrO$_2$/(Ni$_1$Al$_2$O$_3$)</td>
<td>0.7</td>
<td>5.2</td>
<td>98.3</td>
<td>1.2</td>
<td>35</td>
</tr>
</tbody>
</table>

**Fig. 1.** X-ray diffractometry patterns of specimens after pressureless sintering and surface grinding.

**Table I.** Composition of Specimens Investigated in the Present Study and Their Microstructural Features

**Fig. 2.** Typical micrographs of (a) ZrO$_2$/Al$_2$O$_3$, (b) ZrO$_2$/Ni, and (c) ZrO$_2$/(Ni$_1$Al$_2$O$_3$) composites after sintering at 1600°C for 1 h.
size of ZrO₂ grains in the composites was slightly larger than that of monolithic ZrO₂ (see Table I). The fracture surfaces of the specimens are shown in Fig. 3. The fracture mode of monolithic ZrO₂ is predominantly intergranular. A higher extent of transgranular fracture can be found in the ZrO₂/Al₂O₃, ZrO₂/Ni, and ZrO₂/(Ni + Al₂O₃) composites.

The elastic modulus of the ZrO₂/Al₂O₃, ZrO₂/Ni, and ZrO₂/(Ni + Al₂O₃) composites was slightly higher than that of monolithic ZrO₂ (see Table II). The strength of the composites, especially the Ni-containing ones, was higher than that of the monolithic ZrO₂ specimen. The addition of a small amount of Al₂O₃, Ni, or Ni + Al₂O₃, however, had little influence on the toughness of ZrO₂.

Figure 4 shows the magnetization curves of monolithic ZrO₂, ZrO₂/Ni, and ZrO₂/(Ni + Al₂O₃) nanocomposites. Although the Ni-containing nanocomposites exhibit ferromagnetic characteristics, both the saturated magnetization and coercivity were small. The dielectric constant $k$ at room temperature of the ZrO₂/(Ni + Al₂O₃) nanocomposite was 33, which is slightly higher than that of monolithic ZrO₂ ($k = 25$).

### Table II. Mechanical Properties of Monolithic ZrO₂, ZrO₂/Al₂O₃ Composite, and ZrO₂/Ni and ZrO₂/(Ni + Al₂O₃) Nanocomposites

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Toughness (MPam⁰⁵)</th>
<th>Griffith flaw size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>193</td>
<td>666 ± 23</td>
<td>3.4</td>
<td>20</td>
</tr>
<tr>
<td>ZrO₂/Al₂O₃</td>
<td>206</td>
<td>978 ± 37</td>
<td>3.6</td>
<td>11</td>
</tr>
<tr>
<td>ZrO₂/Ni</td>
<td>217</td>
<td>1351 ± 37</td>
<td>3.4</td>
<td>5</td>
</tr>
<tr>
<td>ZrO₂/(Ni + Al₂O₃)</td>
<td>211</td>
<td>1187 ± 78</td>
<td>3.6</td>
<td>7</td>
</tr>
</tbody>
</table>

### IV. Discussion

One previous study demonstrated that the addition of 20–40 vol% micrometer-sized Al₂O₃ particles prevented the coarsening of a ZrO₂ matrix. The amount of Al₂O₃ used in the present study was much lower than 20 vol%. The addition of a small amount of Al₂O₃ particles increases both the final density and
the grain size. From previous studies on Al2O3/SiC nanocomposites, the SiC particles may act as a grinding medium to Al2O3 agglomerates during the milling stage. The hardness of Al2O3 is higher than that of ZrO2, and therefore, the Al2O3 particles may also act as a grinding medium in ZrO2 agglomerates during turbo mixing. This is demonstrated by the fact that the fired density of the Al2O3/ZrO2 composites is higher than that of Al2O3 (see Table I). A faster densification rate and less large pores in the green compact then lead to a larger grain size after sintering.

The strength of ZrO2 is enhanced with Al2O3 inclusions. The Griffith flaw size \( c \) for the specimen can be estimated from the strength \( \sigma \) and toughness values \( K_{IC} \) with the following equation:

\[
c = \left( \frac{K_{IC}}{\sqrt{Y \sigma}} \right)^2 \quad (1)
\]

where \( Y \) is the stress intensity function of the crack. Assuming that the crack is half-penny shaped, \( Y = 2/\sqrt{\pi} \). The critical flaw size is reduced with the addition of Al2O3 particles to the ZrO2 matrix (see Table II), hence, the mechanical strength of ZrO2 is improved.

The solution coating technique is a powerful method of introducing nanometer-sized particles into micrometer-sized particles, as demonstrated by many previous studies. However, the amount of nanoparticles added may be limited by the availability of surface charge on the micrometer particles. The amount of surface charge on the ZrO2 particles is low under the current experimental conditions, and, therefore, the amount of nanometer-sized Ni introduced onto the surface of the ZrO2 particles is low: approximately 1 vol\%. The dispersion of the ZrO2 particles is aided by the presence of surface charges. The density of the Ni-containing composites is thus higher than that of the ZrO2 specimen.

In the present study, many fine Ni particles were found within the ZrO2 grains (see Fig. 2(b)), indicating that the fine Ni inclusions had a relatively small influence on the movement of ZrO2 grain boundaries. A faster densification can lead to a larger grain size, and therefore, the size of ZrO2 grains in the Ni-containing nanocomposites is larger than that in the monolithic ZrO2. The critical flaw size is smaller in the Ni-containing nanocomposites (see Table II); hence, the mechanical strength is higher.

Apart from the increase in strength, the amount of transgranular fracture in the ZrO2/Al2O3 composite is higher than that in the monolithic ZrO2. This indicates that the strength of the grain boundary is increased. The addition of excess Al2O3 (above the solubility limit) can exert a scavenging effect on the ZrO2 matrix, namely, the Al2O3 inclusions can attract silica onto their surfaces, resulting in cleaner grain boundaries, which may subsequently lead to larger ZrO2 grains in the ZrO2/Al2O3 composite. Furthermore, cleaner grain boundaries can give rise to a higher grain boundary strength.

A change in fracture mode from intergranular to transgranular can be noticed for the Ni-containing nanocomposites. This phenomenon has also been reported for Al2O3/SiC nanocomposites. The increase in grain boundary strength may have originated from: (1) crack deflection from grain boundary to grain by Ni particles and (2) change in local stresses because of the thermal expansion mismatch. For the Al2O3/SiC nanocomposites, the mismatch in thermal expansion between the matrix and inclusion leads to the formation of radial compressive stress within the inclusions and tensile stress in the matrix. The presence of tensile stress in the matrix grains favors the deflection of crack from grain boundaries into the adjacent grains.

The change in fracture mode has not yet been documented for the Si3N4/SiC and Al2O3/Ni nanocomposites. For these two systems, the thermal expansion of the inclusion is higher than that of the matrix, and therefore, the presence of residual stress may not underline the change in fracture mode. In the case of the ZrO2/Ni system, the thermal expansion of ZrO2 (12 × 10⁻⁶ K⁻¹) is slightly lower than that of Ni (13.3 × 10⁻⁶ K⁻¹). In a recent study on the ZrO2–Ni composites, a hard amorphous layer was observed around the Ni nanoparticles. Although the formation mechanism of this layer has not yet been investigated, the presence of such a hard layer may induce a crack path deflection.

One previous study demonstrated that adding NiO to the ZrO2 matrix promoted a transformation from a tetragonal to an m-phase. The addition of NiO to ZrO2 thus enhances the toughness of ZrO2. Careful quantitative XRD analyses have been conducted on the fracture and ground surfaces. The ground surface was prepared by grinding the surface with a resin-bonded diamond wheel at a depth of 5 or 20 μm. No significant difference was noticed between the amount of m-phase in the monolithic ZrO2 and that in the Ni-containing nanocomposites. Therefore, the toughness of the composites prepared in the present study is similar to that of monolithic ZrO2 specimen (see Table II).

Metallic Ni is a ferromagnetic material. The addition of Ni particles conferred a ferromagnetic characteristic to the matrix ZrO2. However, the saturated magnetization and coercivity of the ZrO2/Ni and ZrO2/(Ni-Al2O3) nanocomposites were low (see Fig. 4). These values are lower than those reported previously by Kondo et al. The Ni content in Kondo et al.’s nanocomposite is 1–2 vol\%, and the size was 100–200 nm, which is larger than the Ni inclusions in the present study. It is well-known that ferromagnetic properties depend strongly on the particle size. A particle with a size close to the size of a single domain exhibits excellent ferromagnetic behavior. This implies that the Ni inclusions prepared in the present study do not reach the critical size.

The introduction of metallic particles into an insulator reduces the size of effective electric field. However, the amount of Ni particles was much lower than the percolation threshold, and therefore, the dielectric constant remained low. This is also reflected by a high electrical resistivity (\( > 10^{12} \text{Ω cm} \)).

V. Conclusions

The addition of both Ni and Al2O3 inclusions significantly enhances the strength of ZrO2. The strength increase was due to a decrease in flaw size and not an increase in toughness, which may be a result of grain boundary strengthening. The addition of nanometer-Ni inclusions can transform ZrO2 from a non-ferromagnetic to a ferromagnetic and ferroelectric material. Although the saturated magnetization, coercivity, and relative permittivity of the nanocomposite are relatively low, these properties can be improved by increasing the Ni content or the Ni particle size. The present study demonstrates the versatility and potential of the ZrO2/(Ni-Al2O3) nanocomposite.

Acknowledgments

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References