Influence of Ni Addition on Mechanical and Magnetic Properties of Yttria-Stabilized Tetragonal Zirconia

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Abstract

Effect of NiO addition on microstructure, stability of tetragonal phase and mechanical properties was investigated. (Y, Ni)-TZP solid solution was obtained by pressureless sintering. The fracture toughness was increased by solid solution of NiO. Neither reaction phase nor glassy phase was observed at the grain boundaries. From these results, it was determined that solid solution of NiO was destabilized tetragonal phase of Y-TZP. Y-TZP/Ni nanocomposite that contained nano-sized Ni particles was also fabricated by internal reduction method. Some evaluations and discussions were carried out for both (Y, Ni)-TZP solid solution and Y-TZP/Ni nanocomposite.

Keyword: Y-TZP, NiO, Ni, internal reduction, solid solution, nanocomposite

1. Introduction

Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) has excellent mechanical properties, such as bending strength and fracture toughness. It is now generally accepted that the enhanced fracture strength and toughness of Y-TZP can be attributed mainly to martensitic transformation, which is tetragonal to monoclinic (t-m) phase transformation.

It has been reported that addition of small amount of oxide to Y-TZP improved some properties, such as sinterability, Low-Temperature-Degradation resistance, ionic conductivity and so on. Tsubakino *et al.* [1] reported that low temperature degradation resistance to t-m phase transformation was improved by adding only 1.2 wt% of Al_2O_3. Solid solution of HfO_2, Ta_2O_5 and Nb_2O_5 to Y-TZP was also reported [2, 3], and the addition of these oxides increases the tetragonal distortion of the cubic fluorite lattice resulting in enhancing t-m transformability and fracture toughness. On the other hand, solubility of NiO, Al_2O_3 and TiO_2 to yttria-fully-stabilized zirconia (Y-FSZ) were reported by Chen *et al.* [4], and it was found that the solubility of NiO into Y-FSZ were approximately 5 to 10 mol%. However, solid solution of NiO to Y-TZP has not been

investigated yet.

Nanocomposites are well known by their higher strength and unique functional properties. Recently, softer or weaker materials than ceramic matrix were used as a second phase dispersion and it was revealed that even these materials could improve mechanical properties of ceramic matrix. Sekino et al. [5] reported that metal which is softer and weaker than ceramics were effective as second phase dispersoid, and in Al_2O_3/Ni system, some good results were obtained.

In this work, influence of NiO addition on some properties of Y-TZP was investigated. In addition, Y-TZP/Ni nanocomposite was fabricated by internal reduction method and microstructure, mechanical properties and magnetic properties will be discussed.

2. Experimental procedure

All experimental work was performed with high-purity zirconia which contains 3 mol% Y_2O_3 (Sumitomo Osaka Cement Co., Ltd., Osaka, Japan) and NiO (Nakalai Tesque Inc., Kyoto, Japan). Table I shows some information about the characteristics of the powders. Zirconia and NiO powders were mixed by ball-milling. NiO contents in the mixed powders were 0, 0.3, 0.6, 1.5 mol%, that correspond to 0, 0.1, 0.2, 0.5 vol% of metallic Ni for Y-TZP/Ni nanocomposite after reduction. The mixed powders were uniaxially pressed and followed by cold isostatic pressing at 200 MPa. The green bodies with the shape of rectangular bar were sintered at 1500ºC for 24 h in air to obtain solid solution of Y-TZP and NiO that was referred to in this paper as (Y, Ni)-TZP solid solution. Then (Y, Ni)-TZP solid solution was heated again in a reducing atmosphere at 1300ºC for 2.5 h to get Y-TZP/Ni nanocomposite. The obtained rectangular bars of (Y, Ni)-TZP solid solution and Y-TZP/Ni nanocomposite were grinded and polished to the size of 3 x 4 x 40 mm. The following evaluations were carried out for both (Y, Ni)-TZP solid solution and Y-TZP/Ni nanocomposite.

The densities of sintered bodies were determined by Archimedes' method using toluene. The phase identification was performed by X-ray powder diffractometry (XRD) with CuKα radiation. The amount of monoclinic phase was estimated from XRD analysis using Toraya's equation [6]. Fracture strength was measured by three-point-bending test, and fracture toughness was obtained by indentation fracture (IF) method. Scanning electron microscopy (SEM) was used to observe the microstructures and to determine the grain size of Y-TZP matrix. Transmission electron microscopy (TEM) was employed to observe the particle size of precipitated Ni and interfaces between zirconia grain and Ni. Magnetic properties such as coercivities and saturation magnetizations ware obtained from magnetization curves measured by

SQUID magnetometer.

3. Result and discussion

(Y, Ni)-TZP solid solution

Solid solution of NiO to ZrO_2 has been reported in reference 4. On the other hand, Ramesh et al. [7] have reported coated 2.5Y-TZP and small amount of CuO system, and in the system, CuO and Y_2O_3 formed a liquid phase at the sintering temperature. However, detailed TEM observation for grain boundaries of Y-TZP-0.3 mol% NiO revealed that glassy phase was not existed in present system, as represented by Fig. 1. Therefore, it was considered that NiO was solid-soluted in ZrO_2.

Dens specimens were successfully obtained with only 0 and 0.3 mol% of NiO addition. More NiO doping makes microcracks in the sintered body. XRD analysis revealed that monoclinic phase of sintered bodies was increased with increasing NiO content, and the solid solution that contained 0 and 0.3 mol% of NiO had almost only tetragonal phase. Therefore, Y-TZP-0.3 mol% NiO solid solution was mentioned as (Y, Ni)-TZP solid solution in the rest of this paper, and following evaluations were carried out for Y-TZP monolith and (Y, Ni)-TZP solid solution.

Although the fracture strength of (Y, Ni)-TZP solid solution (590 MPa) was decreased compared with Y-TZP monolith (710 MPa) because of larger grain size of matrix (1 μm) than Y-TZP monolith (0.8 μm), the fracture toughness measured by IF method was remarkably increased. To explain the improvement of fracture toughness, change of the stability of tetragonal zirconia matrix must be considered. With respect to zirconia, the idea that the kind and amount of stabilizer strongly affects the stability of tetragonal phase of zirconia is generally acceptable. Ionic radii of Ni^{2+} and Zr^{4+} for the oxygen coordination number of 6 were 0.69 and 0.72 respectively. In a case of coordination number of 8, the ionic radius of Ni^{2+} is considered to be still larger than that of Zr^{4+}. From this point, it is concluded that solid solution of NiO increases the tetragonal distortion of the cubic fluorite lattice, in other words, solid solution of NiO destabilized tetragonal phase of zirconia. In addition, the grain size of matrix became larger than Y-TZP monolith. It can be concluded that these facts cause such remarkable improvement of the fracture toughness.

Y-TZP/Ni nanocomposite

(Y, Ni)-TZP solid solution was heated in a reducing atmosphere (H_2) to precipitate metallic Ni in the sintered body. Too long reduction time made cracking of the sintered bodies mainly due to the growth of grain size. Reduction temperature below 1300ºC also broke the sintered bodies because the temperature around 1200ºC was near the

stable region of monoclinic phase. After several conditions examined, it was found that the condition of 1300°C and 2.5 h is the most suitable to present system. Obtained Y-TZP/Ni nanocomposite had high density (>96.5%) with tetragonal phase kept. The TEM image of Y-TZP/0.1vol% Ni nanocomposite was shown in Fig. II, in which metal Ni particles with the size of several tens of nanometers were homogeneously dispersed. The fracture toughness of Y-TZP/Ni nanocomposite maintained the same value of (Y, Ni)-TZP solid solution. It is considered that all NiO in (Y, Ni)-TZP solid solution is not precipitated as metal Ni during reduction, but part of NiO is left solid-soluted into Y-TZP matrix.

Measurement of magnetic properties was carried out at room temperature by SQUID magnetometer. The shape of magnetization curve and the small hysteresis were typical for ferromagnetic behavior of metal Ni. The coercivity of the nanocomposite was improved (16 Oe) compared with pure Ni (1 Oe). It is well-known that coercivity of ferromagnetic materials is strongly depend on the particle size, and the smaller particle size is the larger coercivity is. Finally, the materials exhibited superparamagnetic behavior when the particle size becomes below its critical size. The critical size was reported about 20~30 nm [8, 9], although the critical size changes by fabrication process, residual stress, impurities, etc. In this study, the size of Ni was around the critical size as see in Fig. II. Therefore, a part of Ni is considered to became superparamagnetic state.

4. Conclusion

(Y, Ni)-TZP solid solution was successfully obtained by conventional pressureless-sintering. It was confirmed that NiO played the role of a destabilizer and as a result, improved fracture toughness was obtained. Y-TZP/Ni nanocomposite with fine Ni dispersion also was successfully obtained through internal reduction. The fracture toughness was the same level of (Y, Ni)-TZP solid solution, because part of NiO was left solid-soluted into Y-TZP matrix. Y-TZP/Ni nanocomposite exhibited ferromagnetic behavior with enhanced coercivity.

5. References

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Table I Some properties of starting powders.

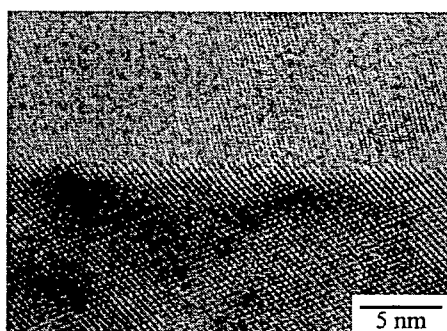|	Tetragonal ZrO_2	NiO
Purity	99.3 %	>97%
Grain size	33 nm	0.1-1 μm
Main impurities	SiO_2 0.0042wt%	Cu <0.05%
	Fe_2O_3 0.0004wt%	Zn <0.05%
	TiO_2 0.0015wt%	Fe <0.05%
	Cl 0.0075wt%	Co <0.05%

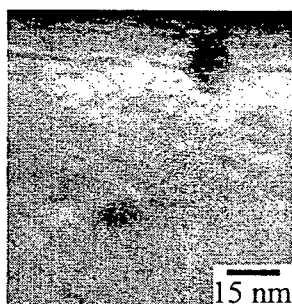Fig. I TEM image for interface between ZrO_2 grains of (Y, Ni)-TZP solid solution.

Fig. II TEM image of Ni particles in Y-TZP/Ni nanocomposite.