Mechanical and Magnetic Properties of Novel Yttria-Stabilized Tetragonal Zirconia/Ni Nanocomposite Prepared by the Modified **Internal Reduction Method**

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Dense ceramic/metal nanocomposite has been fabricated by internal reduction method, which includes a two-step process: sintering of ceramic-metal oxide solid solution and subsequent heat treatment in a reducing atmosphere to precipitate metal nanoparticles. This novel technique has been applied to yttriastabilized tetragonal zirconia (Y-TZP) and nickel oxide (NiO) system to fabricate Y-TZP/Ni nanocomposite. Dense Y-TZP and 0.3 mol% NiO solid solution ceramic was successively prepared by the pressureless sintering, and Y-TZP/Ni was fabricated by the internal reduction treatment. The obtained Y-TZP/ Ni nanocomposite possessed characteristic intragranular nanostructure with nano-sized metallic Ni particles of around 20 nm. Fracture toughness of both the solid solution and nanocomposite was remarkably improved because of the solid solution of NiO into Y-TZP and resultant destabilization of the tetragonal phase, and the Y-TZP/Ni nanocomposite was still destabilized by the remaining nickel solution after the reduction. The nanocomposite exhibited ferromagnetism, while the Y-TZP-NiO solid solution had diamagnetic nature. Comparison of saturation magnetization values revealed that 39.5 at.% of introduced nickel was reduced to metallic nanoparticle, proving the existence of residual NiO solute in zirconia that contributed to higher toughness value than the monolithic Y-TZP. It is concluded that the introduced internal reduction method is a suitable process to achieve multifunctional ZrO₂/Ni nanocomposite with high toughness and coexistent magnetic characteristic.

I. Introduction

REMARKABLE improvement of mechanical properties was A achieved in the ceramic-based nanocomposite system by dispersing nano-scaled second-phase particles into ceramic matrix.^{1,2} Such a dispersed second phase in a particular nanocomposite structure enables to drastically alter the behavior of material that exhibits new functions³⁻⁶ such as super-plasticity or high machinability like metal. The fabrication of the ceramic/ metal nanocomposite system is nowadays performed in such a way as to achieve a proper balance between enhanced mechanical properties and addition of new functions that are frequently based on electrical and magnetic behavior.⁷⁻⁹ The Al₂O₃/Ni ceramic/metal nanocomposite system that has been widely studied already is a good example of the system developed toward

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new functions combined with required mechanical properties.^{4,10,11} A fracture strength of 1090 MPa was reported for the Al₂O₃/Ni nanocomposite with 5 vol% Ni fabricated by reduction and hot-pressing method, which exceeds more than twice the fracture strength of monolithic Al₂O₃ prepared by the same procedure.⁴ Furthermore, the introduction of Ni nanoparticles into the sintered ceramic resulted in addition of ferromagnetic behavior⁴ and accompanied magnetic remote sensing capability of stress and/or fracture¹⁰ of the composite. Given the above-described success, the Ni nanoparticles were dispersed within yttria-stabilized tetragonal zirconia (Y-TZP), which led to remarkable improvement of fracture strength (1.9 GPa) achieved for Y-TZP/Ni nanocomposite system with 1–2 vol% of Ni. 12 Thus, the combination of enhanced strength and ferromagnetic properties demonstrated by the obtained new nanostructured material enabled to elaborate on its multifunctionality-the possibility of its application for stress sensor (see Kondo et al.¹²).

The ceramic/metal nanocomposites are often prepared using the reduction and hot-pressing method^{4,8-16} in which the powder mixtures of ceramic matrix and metal oxide are heated in hydrogen atmosphere to reduce metal oxide to metal, and subsequently hot pressed, as illustrated in Fig. 1(a). The advantage of this method is the possibility of obtaining relatively fine dispersion of metal particles, in contrast to other processes that use metal powder as the initial material.¹⁶

Furthermore, there were attempts to obtain ceramic/metal nanocomposite powders by solution chemical processing,4,17-20 which provided ceramic/metal nanocomposites with better nanostructure. Sekino et al.4 proposed a particular case of such a method, where $Ni(NO_3)_2$ nitride was chosen as a source material of metal dispersions. One should be aware, however, that in the conventional reduction and sintering process the metallic Ni tends to migrate and coalesce with other Ni particles during sintering, since in the majority of ceramic/metal systems the sintering temperature of ceramics (e.g., 1450° and 1500°C for Al₂O₃ and Y-TZP, respectively) is close to the melting point of nickel (1455°C).

In order to surpass the indicated difficulties, the present paper aims to introduce the internal reduction method that might allow producing bulk Y-TZP/Ni nanocomposite with the finest Ni particles (see Fig. 1(b)). The internal reduction method has already been applied to various mono- and mixed-oxide systems such as Fe_2O_3 ,²¹ (A,B)O,^{22–24} transition metal (Cr, Ni, Fe)-doped Al_2O_3 ,^{20,25–27} Fe-doped silicate,²⁸ and so on, in order to investigate reduction dynamics/kinetics and mechanisms, crystallographic characteristics of metal precipitates within oxide matrices, microstructures, and/or physical/mechanical properties. This method thus realizes ceramic/metal, or to be more precise, oxide/metal composite microstructures. In the case of Ni-Al₂O₃ composite,^{20,27} NiAl₂O₄ spinel compound was prepared first and then partially reduced to form the composite. However, size distribution of precipitated metal particles in the alumina matrix was large; some precipitates were in nanometer

V. Jayaram-contributing editor

Manuscript No. 10489. Received August 29, 2003; approved November 3, 2004. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan, under a Grant-in-Aid for JSPS Research Fellowships for Young Scientists (H. Kondo) No. 1907, and partly supported by the Ministry of Economy, Trade and Industry, Japan, as part of the Synergy Ceramics Project.

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Fig.1. Schematic drawing of materials preparation concept for the yttria-stabilized tetragonal zirconia/Ni nanocomposite by the conventional method (a) and the present internal reduction method (b).

scale and the others were large, micrometer sized.²⁰ The modified internal reduction method presented in this research consists of utilizing not only thermodynamic stability of doped element but also high oxygen ionic mobility of zirconia ceramic, which allows homogeneous reduction of selected element doped into dense sintered body by forming nanometer-sized metal precipitates, but maintaining the characteristics of matrices such as high strength and toughness.

Apart from the internal reduction method, the paper focuses on the properties of the obtained materials. Hence, the microstructure developments and mechanical and magnetic properties of Y-TZP/Ni nanocomposite fabricated by internal reduction method were investigated, which indicates usefulness of this fabrication technique. In addition, the present paper also discusses the effects of nickel oxide (NiO) addition on the phase stability and mechanical properties of obtained materials, Y-TZP–NiO solid solution, and internal-reduced Y-TZP/Ni nanocomposite.

II. Experimental Procedure

(1) Modified Internal Reduction Method

The general outline of the present fabrication method consists of two stages (see Fig. 1(b)). Firstly, the mixed powders of Y-TZP and NiO are sintered to obtain the dense Y-TZP-NiO solid solution. Secondly, the bulk Y-TZP-NiO solid solution is heated in reductive atmosphere (presumably pure hydrogen) to reduce the Ni²⁺ ions and form Ni particles within the dense ceramic matrix. The latter is realized mainly because of the oxygen iontransfer in zirconia polycrystal. The reductive atmosphere involves the decrease in chemical potential of oxygen in the solid, and results in the reduction of dissolved Ni²⁺ ions in the Y-TZP. Interestingly, the reduction of Ni²⁺ ions appears to be internal, in contrast to previously elaborated ZrO₂ in Y-TZP.^{12,29} Indeed, it is considerably easier to reduce Ni than ZrO₂ despite the fact that the ionic conductivity of the latter exceeds oxygen ionic conductivity of Y-TZP.¹² It is worth emphasizing that in the case of solid solution, one deals with nickel ions instead of particles, which provides an opportunity to produce Ni particles with a very small size.

The initial step in the present research was the investigation of the Y-TZP–NiO solid solution prepared by pressureless sintering (the detailed discussion of the results is given elsewhere³⁰), since it is believed that the properties of Y-TZP–NiO solid solution strongly, affect the final product of internally reduced Y-TZP/Ni nanocomposite.

Y-TZP-0.3 mol% NiO solid solution was successfully obtained by pressureless sintering. The addition of a larger amount of NiO resulted in microcracking of the sintered body because of over-destabilization. As a consequence, the monolithic Y-TZP and Y-TZP-0.3 mol% NiO solid solution that in certain aspects correspond to Y-TZP/0.1 vol% Ni after complete reduction were selected for the present investigation. It was of great concern whether the selected Ni content would be too low. However, from the previous experience with nano-sized second phase, we suspected that even a small amount of nanoparticles, less than 2%, may result in drastic improvement of properties.¹²

(2) Powders and Specimens Preparation

The initial mixture used for fabrication of the solid solution and consequent nanocomposite contained tetragonal zirconia powder stabilized with 3 mol% yttria (3Y-TZP, 0.2 µm, Sumitomo Osaka Cement Co. Ltd., Tokyo, Japan) and NiO powder (350 mesh, Nakalai Tesque Inc., Kyoto, Japan). These powders were wet-ball milled using ethanol and zirconia ball as a solvent and mixing media, respectively. Dried mixtures were then dry-ball milled again. The NiO content was chosen to be 0 and 0.3 mol% to Y-TZP, which corresponded to 0 and 0.1 vol% Ni in the final products, respectively. The mixed powder was uniaxially pressed under the pressure of 20 MPa into a pellet (size of \emptyset 15 mm \times 4 mm) and subsequently cold isostatic pressed at 200 MPa. The pellets were consolidated by pressureless sintering at 1500°C in air. In order to obtain a dense and perfect solid solution of the Y-TZP and NiO, the sintering was carried out for 24 h (for details refer to Kondo *et al.*³⁰). The specimen size of \emptyset 12 mm × 3 mm was then obtained after the sintering.

For the internal reduction treatment, the sintered solid solution was heated for 2.5 h in a pure hydrogen (99.99%) atmosphere at 1300°C. The temperature was chosen to secure fine Ni precipitation and to avoid monolithic to tetragonal-phase transformation of zirconia matrix (see the respective phase diagram³¹) as well as grain growth of ZrO_2 matrix.

(3) Material Characterization

The phase composition of the prepared nanocomposite was examined by X-ray diffraction (XRD, RAD-C system, Rigaku Co., Tokyo, Japan) technique with CuK α radiation. The lattice parameters were determined using high-purity silicon as the internal standard. The density of the composite was determined by Archimedes' immersion method using toluene. The characterization of mechanical properties focused on fracture toughness that was determined by the indentation fracture (IF) method using Vickers indentation under the maximum load of 196 N and a loading duration of 15 s, while making use of an empirical equation for Palmqvist cracks³² and also by the single-edgeprecracked-beam (SEPB) method.³³ For the toughness determination, at least six indentations and five bending tests were performed and averaged for the IF and SEPB methods, respectively.

The selected specimens were thermally etched for 10 min at 1300°C in vacuum to facilitate the microstructural observations performed by scanning electron microscopy (S-5000, Hitachi Ltd., Tokyo, Japan), which enabled to determine average grain size of Y-TZP matrix by image analysis software (Scion Image, Scion Corporation, Frederick, MD).

In order to resolve the local phase composition in detail, microprobe laser Raman spectroscopy (SPEX1482D, SPEX Industries Inc., Edison, NJ, argon ion laser, $\lambda = 514.5$ nm, the beam diameter of approximately 3 µm, power 100 mW) was performed, since this technique proved to be well suited for ZrO₂-based systems.³⁴ Interestingly, the combination of indentation, Raman, and XRD techniques allowed to evaluate the volume fraction of monoclinic phase around the indentationinduced crack. This was accomplished using relative intensities of the most distinctive Raman bands of zirconia: 148, 181, 192, and 264 cm⁻¹, according to the formula:³⁴

$$C_{\rm m} = \frac{I_{\rm m}^{181} + I_{\rm m}^{192}}{F(I_{\rm t}^{148} + I_{\rm t}^{264}) + I_{\rm m}^{181} + I_{\rm m}^{192}},\tag{1}$$

where $C_{\rm m}$ is the monolithic concentration, $I_{\rm m}$ and $I_{\rm t}$ refer to the integrated intensities of monoclinic and tetragonal bands, while *F* stands for a factor required to convert the Raman intensity to

the XRD intensity of the reference material; for the present investigation, F = 0.97 was used according to the previous report.³⁴

Further, structural investigation was performed by transition electron microscopy (TEM, H-8100, Hitachi Ltd.) with an energy-dispersive X-ray spectrometer (PV9800 with ultra-thin window detector, EDAX Inc., Mahwah, NJ) for the elemental analysis of nanocomposites. Finally, the magnetic properties of the Y-TZP/Ni nanocomposite were determined by the super-conducting quantum interference magnetometer (MPMS2, Quantum Design Inc., San Diego, CA) at room temperature, which provided the amount of precipitated Ni particles by comparing theoretical and measured saturation magnetization values of the composites.

III. Results and Discussion

(1) Phase Development

The Y-TZP with 0.3 mol% NiO solid solution was densified after pressureless sintering without any crack.³⁰ After the reduction treatment of the sintered body at 1300°C, the light brown color of the Y-TZP-0.3 mol% NiO solid solution turned black, while the monolithic Y-TZP changed from white to light gray. The color change of the Y-TZP-0.3 mol% NiO system implies reduction of Ni^{2+} and precipitation of metallic nickel in the sintered body. The color change of the monolithic Y-TZP to light gray may be because of the increase in oxygen defects and/ or solid solution of carbon or hydrogen induced during reduction. Unfortunately, the XRD measurement for confirming the existence of metallic Ni embedded in the matrix could not detect the tiny amount of Ni phase or change of the lattice parameter. In addition, no signal attributing to elemental Ni was detected by preliminary X-ray photoelectron spectroscopy (XPS) investigation of the solid solution as well as the reduced sample, because of lesser quantity of the doped NiO than the detection limit.

(2) Fracture Toughness

In contrast to the XRD and XPS results, however, the fracture toughness of Y-TZP measured by the indentation method (see Table I) was remarkably influenced by the solid solution of only 0.3 mol% NiO to Y-YZP. Furthermore, a high value was maintained after the internal reduction treatment as listed in Table I. The present authors were aware that the indentation method frequently gave overestimated values of fracture toughness in the case of zirconia ceramics,³⁵ because of unusual *R*-curve behavior associated with transformation toughening of tetragonal zirconia.³⁶ As a consequence, the alternative SEPB method was also employed for fracture toughness measurement in this re-

Table I. Fracture Toughness and Average Grain Size of Y-TZP Matrix for the Sintered Y-TZP Monolith, Y-TZP– NiO Solid Solution and Y-TZP/Ni Nanocomposite Fabricated by the Internal Reduction Method

	Fracture toughness (MPa \cdot m ^{1/2})		
Sample	IF method	SEPB method	Average grain size (nm)
Y-TZP monolith Reduced Y-TZP	6.34±0.13	5.05 ± 0.14	830
monolith Y-TZP-0.3 mol%	6.53 ± 0.14	4.90 ± 0.32	850
NiO solid solution Y-TZP/Ni	9.97 ± 0.20	6.60 ± 0.12	1010
nanocomposite	9.43 ± 0.41	6.73 ± 0.24	950

Y-TZP monolith was reduced to confirm the effect of hydrogen treatment for comparison. Errors denote standard deviation of the measurement. Y-TZP, yttria-stabilized tetragonal zirconia; IF, indentation fracture; SEPB, single-edgeprecracked-beam.



Fig. 2. Schematic diagram illustrating the cracks introduced by Vickers indentation and the positions of microprobe laser Raman spectroscopy analysis.

search. Moreover, the monolithic Y-TZP heat treated in the same reduction atmosphere was prepared and tested for the sake of comparison (refer to Table I that also contains the data for the Y-TZP–NiO described elsewhere³⁰).

It is worth noticing that Table I contains the data of the average grain size of the zirconia matrix, since it is well known that this parameter affects the toughness of tetragonal zirconia. One may easily recognize that fracture toughness of the Y-TZP–0.3 mol% NiO solid solution measured by the SEPB method is again higher than that of the Y-TZP monolith, which is attributed to the larger average grain size in solid solution and destabilization of ZrO₂ tetragonal phase by NiO doping.³⁰ High toughness of the Y-TZP/Ni nanocomposite, close to the values obtained by both indentation and SEPB tests for the Y-TZP–0.3 mol% NiO solid solution, was unchanged after reduction. This suggests that the complete reduction of NiO to metallic Ni did not occur for the entire volume of NiO.

(3) Phase Transformation Behavior

In order to determine the amount of transformed monoclinic phase, microprobe laser Raman spectroscopy analysis was carried out in a selected location around cracks induced by Vickers indentation, as it is illustrated in Fig. 2. The three analyzed points comprising the polished and, hence, stress-free surface, point A being 50 µm distant from the crack root and point B located 50 µm from the crack tip, were selected (Fig. 2), and the results are listed in Table II. A very limited amount of monoclinic phase was detected at the location A of the monolithic Y-TZP, since the tetragonal-to-monoclinic (t-m) transformation zone was relatively narrow³⁰ (note the analyzed area was located 50 μ m away from the crack). In contrast, the Y-TZP-0.3 mol% NiO solid solution exhibited higher amount of monoclinic phase both in A and B positions than the monolithic Y-TZP. This can be readily explained by the fact that solid solution of NiO destabilizes tetragonal phase of the Y-TZP, which in turn tends to transform to monoclinic phase, and as a result, the t-m zone extends.36

 Table II.
 Amount of Monoclinic Zirconia Phase on the Free

 Surface and Near Cracks Calculated from Raman Spectroscopy
 Data

	Amount of monoclinic phase (vol%)		
Sample	Free surface	Point A	Point B
Y-TZP monolith Y-TZP–0.3 mol% NiO solid solution Y-TZP/Ni nanocomposite	0.0 0.0 0.7	2.3 14.7 14.6	0.0 1.2 6.4

See Fig. 2 for the geometry of analyzed points. Y-TZP, yttria-stabilized tetragonal zirconia. June 2005

A similar amount of monoclinic phase was detected in the Y-TZP-0.3 mol% NiO solid solution and the Y-TZP/0.1 vol% Ni nanocomposite that was a reduced sample of the former solid solution (compare Tables I and II). The Raman result agrees well with the fracture toughness measurements. This prompts us to conclude that t-m transformation of NiO-doped tetragonal phase is sensitive to stress and it is why the t-m transformation zone was extended in the Y-TZP/Ni nanocomposite. Indeed, the Raman analysis proved that a certain amount of NiO was still present in the Y-TZP/0.1 vol% Ni nanocomposite even after the internal reduction occurred, which suggested that the exact amount of precipitated Ni would be lower than 0.1 vol%. Details of this phenomenon will be discussed in the latter part.

(4) Nanostructure of Internal Reduced Specimen

The TEM micrographs of the nanocomposite, which was an internally reduced material of the sintered solid solution, shown in Fig. 3, reveal a characteristic structure with very fine particles with sizes approximately 20 nm, mainly within the ZrO₂ grains and some at the grain boundary. As shown in Figs. 3(a) and (b), there are two types of nanodispersion: one is a black-contrasted particle (Fig. 3(a)) and the other is a black particle accompanying the bright-contrasted region (Fig. 3(b)). These particles contain nickel, as proved by EDX analysis. The elemental composition of the area with a bright contrast visible in Fig. 3(b) was exactly the same as that of ZrO2 grains. Hence, the EDX results prompted us to conclude that the contrast comes from a pore or a part of ZrO₂ that had many vacancies or defects. The highresolution image for the latter type of nanodispersion is shown in Fig. 3(c). Since the shape of the discussed region was surrounded by flat planes, it is believed that the contrast is related to the precipitation of metallic Ni particles. When one assumes that the absorbed contrast is caused by a pore, such a void may be readily formed during reduction, since it involves volume decrease. Unfortunately, at the present stage of research, both explanations of the origin of the contrast (pore and precipitation) seem equally plausible.

The clear lattice image of the Ni nanoparticle was not confirmed in the high-resolution image (Fig. 3(c)). Nevertheless, another interesting feature found from the high-resolution image was that the facets consisted of low Miller index planes of zirconia such as {101} and {110}. A similar feature has already been reported by many researchers. In the case of Cr, metal precipitation from Cr-doped Al2O3, facet planes consisting mainly of a low-energy plane and crystallographic orientation between intragranular Cr precipitates and parent Al₂O₃ crystal were reported.²⁵ The formation of this kind of facet and corresponding shape can be related to the Wullf shape often observed for an internal pore and/or a precipitate in solid and/or at wet interface.^{37,38} It is therefore reasonable to think that formation of flat hetero-interface between nano-sized intragranular Ni metal and zirconia crystal as well as between pore and zirconia might be governed mainly by the formation of the Wulff structure during internal reduction, which minimized interfacial energy between zirconia and Ni and the accompanying pore. In addition, Cr precipitation at the grain boundary of Al₂O₃ was reported not to have clear orientation.²⁵ It is considered that the lack of crystallographic orientation between internally reduced Ni precipitates might be energetically disadvantageous in the case of such a precipitation phenomenon.

(5) Magnetic Properties and the Amount of Reduced Ni

The magnetic properties of the materials prepared by the present study exhibited an expected sequence. Hence, as is presented in Fig. 4, the Y-TZP–0.3 mol% NiO solid solution possessed a typical diamagnetic property that was of the same nature as monolithic Y-TZP (not shown), despite the fact that the cubic form of NiO had antiferromagnetism as its intrinsic magnetic characteristic. Such a behavior exhibits neither precipitation of NiO nor anti-ferromagnetic coupling between solute Ni²⁺ ions



Fig. 3. Transition electron microscopy micrographs of nano-sized Ni particles precipitated within a yttria-stabilized tetragonal zirconia (Y-TZP) grain in Y-TZP/Ni nanocomposite (a, b) and high-resolution image of a Ni precipitate and surrounding zirconia crystal (c) prepared by the internal reduction technique. Black and white arrows indicate Ni particles and the bright-contrasted part, respectively.

in tetragonal ZrO_2 cell because of very low concentration of Ni in Y-TZP (note that 0.3 mol% NiO was solid solute in Y-TZP).

In contrast, the Y-TZP/Ni exhibits ferromagnetic nature, as is seen in Fig. 4. The fact that the ferromagnetic properties of the nanocomposite are not shadowed by diamagnetism of the Y-



Fig. 4. Magnetization curves of yttria-stabilized tetragonal zirconia (Y-TZP)–0.3 mol% NiO solid solution and Y-TZP/Ni nanocomposite after the internal reduction treatment measured by the super-conducting quantum interference magnetometer at room temperature.

TZP–NiO solid solution proves that metallic Ni is certainly in the form of precipitations in Y-TZP/Ni nanocomposite after the internal reduction. The magnetization curve obtained for the Y-TZP/Ni nanocomposite was replotted using data for the monolithic Y-TZP in such a way by subtracting the effect of diamagnetism of the NiO-doped Y-TZP matrix. Furthermore, saturation magnetization (M_s) of the Y-TZP/Ni nanocomposite was obtained by the Arrott plot.³⁹

Assuming that all the added NiO was in the form of metallic Ni particles after reduction, the obtained $M_{\rm s}$ -value for the Y-TZP/0.1 vol% Ni nanocomposite equaled 21.7 emu/g (magnetization of a unit mass of metallic Ni). This was considerably lower than the one reported previously for pure bulk nickel (55 emu/g),⁴⁰ while the observed difference is because of the small amount of metallic Ni particles precipitated in the nanocomposite.

It should be noted again that fracture toughness of the Y-TZP–0.3 mol% NiO solid solution and its reduced product (Y-TZP/Ni nanocomposite) is practically of the same value, which indicated that solid solute NiO was not completely transformed into metallic Ni particles in the Y-TZP/Ni nanocomposite after the internal reduction process. These results well agree with the magnetic measurements, which proved the low value of M_s for the Y-TZP/Ni nanocomposite.

In order to evaluate the Ni content in the reduced sample, the $M_{\rm s}$ -values for pure bulk Ni were compared with the measured ones. Hence, it was found that the amount of metallic Ni in the Y-TZP/Ni nanocomposite was equal to 39.5 at.%, while using $M_{\rm s}$ -values of 21.7 and 55 emu/g for the nanocomposite and nickel, respectively. It indicates that the amount of Ni precipitate in Y-TZP is approximately 0.04 vol%, and hence the nanocomposite prepared in this investigation may be described as (Y,Ni)-TZP/0.04 vol% Ni. In materials of this type dealt with ceramics with embedded nano-sized metallic particles, the size effect could not be ignored. Indeed, the low angle neutron scattering study of nanostructured iron by Wagner et al.⁴¹ already revealed that the interface of ferromagnetic particles has significantly lower average magnetic moment than the grain interior. Consequently, they claimed lower saturation magnetization of nanostructured Fe than that of bulk material. Moreover, a similar research for nickel by Host et al.⁴² agrees with Wagner et al.'s⁴¹ results.

In the case of the present study, Ni particle size (20 nm) was smaller than the previous report (Ni with approximately 100 nm within Y-TZP/Ni nanocomposites prepared by a reduction and followed by sintering of TZP/NiO mixture),¹² i.e., the surface area of Ni dispersion was large, which inferred lower saturation magnetization of the Y-TZP/Ni nanocomposite. One should also notice that metallic Ni particles embedded in Y-TZP matrix are next to oxygen ions of ZrO_2 (the surface of Ni particle is surrounded by an oxide layer), which contribute to the observed reduction of M_s -value as is similar to the case of nanocrystalline Fe.⁴¹ Unfortunately, in this particular case of the present Y-TZP/Ni nanocomposite, it is impossible to estimate by how much the theoretical M_s -value was reduced because of the size effect, since we are dealing with a combination of two phenomena.

(6) Magnetic Coercivity and Size of Ni Precipitate

The magnetic coercivity of the Y-TZP/Ni nanocomposite determined from the magnetization curve (Fig. 4) was 0.81 kA/m, which was apparently 10 times higher than the values for demagnetized bulk Ni, 0.08 kA/m.⁴³ Indeed, the coercive force of the ferromagnetic material increases with decrease in the particle size and accompanies magnetic structure transition from multidomain to single-domain state to minimize the total magnetic energy.⁴⁴ The coercivity drastically reduces when the particle size becomes smaller than critical single-domain size, and the ferromagnetic material exhibits super-paramagnetic behavior as already reported by numerous researchers.^{45–50}

Hence, Gong *et al.*⁴⁸ determined the size of a single domain in Ni particles (32 nm) from the coercivity measurements and compared the result with calculated size (42 nm) according to the magnetic domain theory.⁴⁵ Further, Estournès *et al.*⁴⁹ claimed that Ni particles with a critical diameter of 20 nm behave super-paramagnetically, based on theory by Kneller and Luborsky.⁵⁰

The Ni particles investigated in the present study were as small as 20 nm (see the discussion of TEM results), the value that is lower than the single-domain size while higher than the super-paramagnetic particle size. Thus, merely a part of Ni particles in the Y-TZP/Ni nanocomposite might account for superparamagnetic behavior, which indicates that magnetic coercivity of the Y-TZP/Ni nanocomposite is lower than that reported earlier for ceramic/Ni nanocomposites with larger Ni particle size.^{4,12}

IV. Conclusions

The Y-TZP/Ni nanocomposite can be fabricated by the modified internal reduction method, which includes solid solutionprecipitation process. Fracture toughness of the nanocomposites produced by the indicated process was remarkably improved. The effect was caused by a small amount of NiO ($\sim 0.3 \text{ mol}\%$) that was solid solute into the Y-TZP, while the Y-TZP/Ni nanocomposite was still destabilized by the remaining nickel solution after the reduction treatment. The presented results were confirmed by Raman spectroscopy as well as TEM observations. In particular, high-magnification TEM revealed the characteristic microstructure of the Y-TZP/Ni nanocomposite, in which metallic Ni particles size embedded within the Y-TZP grains equaled approximately 20 nm. Precipitated Ni was found to accompany small pores and flat planes surrounding the nanoparticles, and pores consisted of low-energy crystal planes of zirconia.

The Y-TZP/Ni nanocomposite fabricated by the internal reduction method exhibits ferromagnetic behavior coexistence with high fracture toughness. Using the measured data of saturation magnetization, it was found that 39.5 at.% of doped nickel was *in situ* transformed into nickel nanoparticles during the reduction process. These results indicate that the nanocomposite material obtained by the present internal reduction is, to be exact, NiO-doped Y-TZP dispersed with 0.04 vol% of Ni (i.e., (Y,Ni)-TZP/0.04 vol% Ni nanocomposite). Nevertheless, the fact obtained in the present investigation serves as a proof that the method was entirely successful in the fabrication of ceramic/metal nanocomposite with multifunctional properties.

Acknowledgment

The authors acknowledge Prof. R. Nowak for his useful discussion and comments.

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