

Available online at [www.sciencedirect.com](http://www.sciencedirect.com/science/journal/09552219)

SciVerse ScienceDirect

[Journal of the European Ceramic Society 32 \(2012\) 335–341](dx.doi.org/10.1016/j.jeurceramsoc.2011.08.030)

www.elsevier.com/locate/jeurceramsoc

Toughening and strengthening zirconia through the addition of a transient solid solution additive

Chang-Ju Ho, Wei-Hsing Tuan ∗

Dept. of Materials Science & Engineering, National Taiwan University, Taipei 106, Taiwan Received 30 April 2011; received in revised form 13 August 2011; accepted 14 August 2011 Available online 9 September 2011

Abstract

A very small amount of nickel oxide (NiO), 0.18 mol%, could dissolve into yttria-stabilized zirconia (YSZ) during sintering in air at elevated temperature. The presence of Ni solutes enhances both the densification and grain growth of YSZ specimens. By heat-treating the NiO-doped YSZ specimen in a reducing atmosphere, nano-sized Ni particles are produced at the grain boundaries. The NiO thus acts as a transient solid solution additive for the YSZ-Ni nanocomposite. The formation of Ni nano-particles introduces an extra ferromagnetic performance into the YSZ specimen. Furthermore, the toughness and strength of YSZ are enhanced respectively by 120% and 40%. The toughness enhancement shows strong dependence on the size of $ZrO₂$ grains. Nevertheless, the strengthening is contributed by many factors. © 2011 Elsevier Ltd. All rights reserved.

Keywords: B. Nanocomposites; C. Strength; C. Toughness and toughening; Zirconia

1. Introduction

The applications of ceramics are often limited by their poor mechanical properties. Though the yttria-stabilized zirconia (YSZ) exhibits relatively high strength and toughness comparing with other engineering ceramics, $\frac{1}{1}$ [fu](#page-6-0)rther improvement on its mechanical properties is beneficial to its usage as structural components. Recent studies demonstrated that the addition of a very small amount, 0.3 mol %, of nickel oxide (NiO) could increase the transformation ability of zirconia phase.^{[2,3](#page-6-0)} The toughness of YSZ was consequently improved by 60%. To the surprise of the present authors, the results on the NiO-doped YSZ system had attracted relatively little attention. Furthermore, the strength of the NiO-doped YSZ had not been reported yet.

The most challenging part involving in the preparation of the NiO-doped YSZ system is its extremely low NiO content. Though the preparation of a uniform mixture containing a very small amount of additive is possible by reducing the size of additive particles; the surface coating technique, to be demonstrated in the present study, is an effective one.

0955-2219/\$ – see front matter © 2011 Elsevier Ltd. All rights reserved. doi[:10.1016/j.jeurceramsoc.2011.08.030](dx.doi.org/10.1016/j.jeurceramsoc.2011.08.030)

The strength of ceramics can be significantly enhanced through the addition of nano-sized metallic particles. $4-8$ For examples, the strength of zirconia is enhanced by 100% after the addition of 0.9 vol% nano-sized (37 nm) Ni particles;^{[4](#page-6-0)} or by 30% after the addition of 1 vol% fine (380 nm) Ni particles.⁸ However, the toughness of the $ZrO₂$ -Ni nano-composites was virtually unchanged after the addition of Ni particles. Previous studies demonstrated that either the strength or toughness could be enhanced; however, it was not possible to improve both the strength and toughness by adding only NiO or only Ni.

In the present study, apart from the pre-existed solid solution additive, Y_2O_3 , an extra additive, NiO, is added into ZrO_2 . Previous studies demonstrated that the toughness of zirconia could be enhanced by adding two dopants, such as Y_2O_3/Nb_2O_5 ,^{[9,10](#page-6-0)} and Y_2O_3/CeO_2 .^{[11](#page-6-0)} These additives could dissolve into zirconia grains during sintering. However, the strength of these systems had not been determined. In the present study, the possibility of using a small amount of NiO to enhance both the strength and toughness of Y_2O_3 -doped ZrO_2 is explored. Through the control of the oxygen partial pressure in the sintering atmosphere, the Ni solutes can be removed from within the $ZrO₂$ grains to form Ni particles. For the YSZ-Ni composite, the NiO thus acts as a transient solid solution additive. The effect of addition and removal of nickel solutes on the microstructure

[∗] Corresponding author. Tel.: +886 2 33663899; fax: +886 2 23659800. *E-mail address:* tuan@ntu.edu.tw (W.-H. Tuan).

evolution of zirconia is investigated, and its effect on the mechanical properties is also determined.

2. Experimental

An yttria-stabilized zirconia (YSZ) powder (TZ-3Y, 3 mol% Y2O3, Tosoh Co., Japan) was used as the starting powder. Slurry was prepared by mixing the powder and de-ionized water. An ammonia solution was added dropwise into the slurry to adjust its pH value to 10. A nickel nitrate (Showa Chemicals Inc., Tokyo, Japan) solution with the same pH value was prepared separately. The slurry and the solution was then mixed and stirred. The zirconia particles would be negatively charged in the slurry, 4 the nickel ions could adhere onto the zirconia particles. The nanosized Ni particles were obtained by heat-treating the coated powder in air and subsequently reduced in pure hydrogen at 550° C for 8 h. The amount of resulting metallic Ni content was determined using an inductively coupled plasma-atomic emission spectrum (ICP-AES, Model 3000DV, Perkin Elmer, Optima, USA). The powder mixtures were ball milled with zirconia grinding media for 4 h. For comparison purpose, the YSZ powder without the addition of nickel was also prepared with the same procedures. The disc-shaped green compacts were prepared by uniaxial pressing the powder at 13 MPa. Dense NiOdoped YSZ discs were obtained by sintering at 1500 ◦C in air for 24 h. The heating rate and cooling rate were 5 ◦C/min. For comparison purpose, some YSZ specimens were prepared by sintering at 1500° C in air for only 1 h. The dimensional change during the heating up stage was also monitored with a dilatometer (SETSYS 1600, TMA, Setaram Co., Caluire, France).

The metallic Ni particle added YSZ (denoted as YSZ-Ni) specimens were prepared by a modified internal reduction process developed by Kondo et al.[2](#page-6-0) Dense NiO-doped YSZ specimens, as prepared by the procedures mentioned above, were reduced at $1300\degree$ C for 2.5 h in a carbon monoxide (CO) atmosphere. The CO was generated by heating the specimens within a graphite powder bed. In the atmosphere, the oxygen partial pressure was as low as only 10^{-17} – 10^{-16} atm.^{[12](#page-6-0)} To be demonstrated later, most Ni solutes were precipitated at the grain boundaries to form Ni inclusions. The internal reduction process could ensure a uniform microstructure, especially when the second phase content was extremely low.[2](#page-6-0) The metallic Ni is a ferromagnetic material. The extent of reduction from NiO to Ni in CO could be determined by measuring the magnetic properties of the sintered specimens.[2](#page-6-0) The magnetization curves were obtained using a SQUID magnetometer (MPMS7, Quantum Design Co., San Diego, USA). The specimens used for the magnetic measurement were not ground to avoid the effect from the machining induced strain. Pure metallic nickel specimens were prepared by sintering a Ni powder (T-123, Inco Co., Mississauga, Canada) at 1500 °C for 1 h in a 95% N₂/5%H₂ atmosphere.

The density was determined by using the Archimedes method. The relative density of the specimens was estimated by using a value of 6.05 g/cm³ as their theoretical density. The X-ray diffraction (XRD, model TTRAX, Rigaku Co., Tokyo, Japan) technique was used for phase identification with $CuK\alpha$ radiation. The voltage and current used for XRD analysis were

50 kV and 300 mA, respectively. The phase characterization was conducted in the 2 θ range from 27° to 32° with steps of 0.005° and 3 s/step. The monoclinic phase content was calculated using the Garvie and Nicholson's equation.^{[13](#page-6-0)} Prior to the microstructure observation, the cross-section of the specimens was exposed by cutting, grinding and polishing. The grain boundaries were revealed by thermal etching at $1400\degree$ C for 1 h. The scanning electron microscopy (SEM, XL30 & Leo 1530, Philip Co., Netherlands) was used to characterize the microstructure. The average grain size was calculated using the line intercept technique on SEM photographs. More than 300 grains were counted for each specimen.

Before the measurement of strength, the specimen discs were ground with a 325 grit resin-bonded diamond wheel at depths of $20 \mu m /p$ ass. The residual stress in the ground surface was determined using the sin² ψ method.^{[14](#page-6-0)} The final dimensions of the ground specimen were 18.3 mm in diameter and 2–2.5 mm in thickness. The elastic modulus and Poisson's ratio of fully dense YSZ specimens were determined with an ultrasonic technique at 5 MHz (pulse receiver 5055PR and oscilloscope 9354CM, LeCroy Co., New York, NY). The biaxial strength of the discs was determined with a universal testing machine (MTS810, MTS Co., USA) at ambient conditions. A one-ball on threeball fixture was used. The loading rate was 0.48 mm/min. Four specimens were used to obtain each average strength value. The fracture toughness was determined with the indentation technique at a load of 98 N. The relationship proposed by Lawn et al[.15](#page-6-0) was used to calculate the fracture toughness. The crack length induced by the indentation was measured using SEM.

3. Results

3.1. NiO-doped YSZ system

In the present study, a surface coating technique was used to coat nickel nitrate onto the YSZ particles. The coated powder was heat-treated in air to remove the NO*x* and to produce nickel oxide particles.[4](#page-6-0) The technique allowed us to prepare a uniform YSZ/NiO powder mixture even when the amount of NiO was very low. The powder mixture was then reduced in hydrogen. The amount of metallic nickel could then be determined using the ICP-AES technique. The resulting Ni content was only 0.088 wt%, corresponding to 0.18 mol% NiO as the metallic Ni particles were fully oxidized.

During sintering in air, the nano-sized nickel particles would oxidize first to produce nickel oxide particles; then the fine nickel oxide particles dissolve into zirconia grains. The dwell time was as long as 24 h to ensure the complete solution of NiO into $ZrO₂$. Since the vapor pressure of nickel oxide is low, 16 the amount of nickel ion in YSZ is estimated as 0.18 mol%. [Fig. 1](#page-2-0) shows the densification curves for the NiO-doped YSZ specimen. The curves for the YSZ specimen are also shown for comparison. Though the amount of NiO is small, the peak densification rate for the NiO-doped YSZ specimen is located at 1300 °C, which is around 40 ◦C earlier than that observed for YSZ specimen.

[Fig. 2](#page-2-0) shows the microstructure of the NiO-doped YSZ specimen, its microstructural characteristics are shown in [Table 1. I](#page-2-0)n Table 1

Microstructure characteristics of NiO-doped YSZ and YSZ-Ni specimens. The data for the YSZ specimen prepared by sintering at 1500 ℃C in air for 1 h are shown for comparison purpose.

^a The weight percent of Ni in the starting composition was 0.088%.

Fig. 1. Shrinkage and shrinkage rate for YSZ and NiO-doped YSZ specimens. The heating rate used was 5 ◦C/min.

the table, the microstructure characteristics for the YSZ specimens sintered at 1500 ◦C for 1 h and 24 h are also shown for comparison. The density of the specimens is very close to each other. The increase of sintering time from 1 h to 24 h enlarges the

Fig. 2. Typical micrograph for NiO-doped YSZ specimen.

size of zirconia grains from $0.50 \mu m$ to $0.95 \mu m$. The solution of nickel ions further increases the size of zirconia grains from $0.95 \mu m$ to 1.1 μ m.

The mechanical properties of the NiO-doped YSZ specimens are shown in [Table 2.](#page-3-0) The hardness of the NiO-doped YSZ is close to that of the YSZ specimens. The residual stress for the specimens after surface grinding is also shown in the table. The compressive stress was introduced into the surface region through the grinding process. The residual stress for the specimens is close to each other; furthermore, the residual stress is much smaller than the strength. It indicates that the strength enhancement due to the increase of dwell time at sintering and the addition of nickel oxide is genuine. The increase of dwell time from 1 h to 24 h enhances the strength of YSZ specimen by 20%. The presence of Ni solute further enhances the strength of YSZ by 10%.

The toughness of YSZ is enhanced by 40% after increasing the dwell time from 1 to 24 h, enhanced further by 30% after the solution of 0.18 mol% NiO. It demonstrates that the addition of NiO solutes is beneficial to both the strength and toughness of YSZ.

3.2. YSZ-Ni system

After heat-treating the dense NiO-doped YSZ specimens in the reducing atmosphere, nano-sized Ni particles were produced. [Fig. 3](#page-3-0) shows one typical micrograph for the YSZ-Ni composite. The fine Ni particles, around 100 nm, mainly locate at the grain boundaries and triple junctions of the $ZrO₂$ grains. Differ from the NiO-doped YSZ specimens, there are two phases in the YSZ-Ni specimens, t -ZrO₂ and Ni phases.

The magnetization curve for the YSZ-Ni composite is shown in [Fig. 4.](#page-3-0) The curves for the monolithic YSZ and Ni specimens are also shown in the figure. In order to compare the magnetic performance of YSZ-Ni and Ni specimens, the magnetization for the YSZ-Ni composite is normalized by the weight percentage of Ni added. The YSZ-Ni specimen exhibits a slightly lower magnetization than that of the monolithic Ni specimen. The mag-netization of Ni is affected by its amount and its size.^{[2](#page-6-0)} As the size of Ni is larger than tenths of nanometers, the size effect can be ignored. From the extent of magnetization, most NiO (around 80%) was reduced to Ni after the internal reduction treatment Table 2

Mechanical properties of NiO-doped YSZ and YSZ-Ni specimens. The data for the YSZ specimen prepared by sintering at 1500 °C in air for 1 h are shown for comparison purpose.

Note *, "−" denote "compressive" stress.
a The weight percent of Ni in the starting composition was 0.088%.

Fig. 3. Fracture surface of YSZ-Ni specimen. Several Ni particles are indicated with arrows.

at 1300 ◦C in CO for 2.5 h. Therefore, the YSZ-Ni specimen is in fact a mixture composing of YSZ (∼0.04 mol% NiO solute) and Ni (∼0.06 vol%). The magnetic coercivity of the YSZ-Ni nanocomposite is higher than that of monolithic Ni. It can be related to the size effect of the Ni grains.

Fig. 4. Magnetization curves for YSZ and YSZ-Ni specimens. The curve for monolithic Ni is shown for comparison.

The mechanical properties of YSZ-Ni specimens are shown in Table 2. The amount of Ni is low, the hardness of YSZ is not affected due to the presence of such small amount of Ni inclusions. The contribution of the residual stress induced by surface grinding on the flexural strength is small. For the YSZ + 0%Ni specimen, the specimen had gone through the sintering at $1500\degree C$ in air for 24 h and at $1300\degree C$ in CO for 2.5 h. The heat treatment at $1300\degree$ C in CO has minor influence on the microstructure ([Table 1\)](#page-2-0) and on the mechanical properties (Table 2) of the YSZ specimens. However, the presence of Ni and NiO enhances both the strength and toughness of YSZ.

4. Discussion

The present study demonstrates that both the strength and toughness of YSZ can be enhanced through the addition of a very small amount of NiO or Ni. Comparing the YSZ specimen prepared by sintering at $1500\degree C$ in air for 1 h, the addition of 0.18 mol% NiO enhances the strength and toughness of YSZ by respectively 35% and 90%; the formation of nano-sized Ni particles enhances the strength and toughness of YSZ by 40% and 120%, respectively. Since zirconia is a crack-resistant material, its toughness is sensitive to the crack length introduced during the toughness measurement.^{[17](#page-6-0)} In the present study, the cracks were produced through the indentation at a load of 98 N. The length of the indentation-induced crack varied from 70 to 110μ m. The toughness values reported in the present study is thus valid only when the crack length is around $100 \mu m$. It may imply that the toughness of NiO-doped YSZ may be even higher as the crack length is longer. In any case, it demonstrates that the toughness of YSZ is improved significantly by adding NiO. Apart from the toughness increase, the strength is also enhanced. For the first time, the possibility of using two solid solution additives, NiO and Y_2O_3 , to enhance both the strength and toughness of zirconia is demonstrated.

Our experimental data demonstrate that the densification of YSZ was enhanced due to the addition of NiO ([Fig. 1](#page-2-0) and [Table 1\).](#page-2-0) The relative density of some specimens was slightly higher than 100%. It may be due to that the theoretical density for the systems investigated in the present study is underestimated. Nevertheless, it demonstrates that the specimens are close to fully dense. The comparison can therefore be made between YSZ and NiO-doped YSZ, YSZ-Ni systems. The size of $ZrO₂$ grains was also increased slightly after the solution of NiO ([Table 1\).](#page-2-0) It indicates that the diffusion rate of the controlling species for zirconia is faster after the solution of NiO into zirconia. Previous study indicated that the addition of a small amount (0.5 mol%) of MgO enhances the densification of 8 mol% Y_2O_3 -stabilized ZrO_2 .^{[18](#page-6-0)} The increase in densification was related to the decrease of surface energy. The solubility of NiO in ZrO_2 , as reported in the previous studies, $19-21$ was around 2–5 mol% at 1600 ◦C. The amount of NiO used in the present study was only 0.18 mol%. All the nickel oxide is likely dissolved into zirconia after prolonged sintering at 1500 ◦C. The ionic radius of Ni²⁺ ion (0.069 nm) is close to that of Zr^{4+} ion (0.072 nm). The substitution of Zr^{4+} ion with Ni²⁺ ion is thus possible. One possible defect reaction equation for the solution of NiO into $ZrO₂$ is shown below²²:

$$
\text{NiO} \frac{\text{ZrO}_2}{\text{Ni}'} \text{Zr} + \text{V}_0^{\bullet\bullet} + \text{O}_0^{\text{X}} \tag{1}
$$

The above reaction suggests that the addition of Ni^{2+} solute may increase the concentration of oxygen vacancy. If the densification and grain growth of zirconia are controlled by the diffusion of oxygen vacancy, the addition of NiO could be beneficial.

Other possible reasons had also been proposed.[19,21,23–25](#page-6-0) $Chen²¹ suggested that the grain growth was enhanced due to$ $Chen²¹ suggested that the grain growth was enhanced due to$ $Chen²¹ suggested that the grain growth was enhanced due to$ the increase of lattice diffusivity. The grain growth rate of YSZ also showed dependence on the ionic radius of solute.^{[26,27](#page-6-0)} The addition of a solute with ionic radius smaller than that of yttrium ion (0.09 nm) could lower the activation energy of grain growth. Zhang thus proposed that the enhanced densification was due to the decrease of the apparent activation energy when NiO is dissolved into $YSZ²⁵$ $YSZ²⁵$ $YSZ²⁵$. No consistent account for the effect of $Ni²⁺$ solute on the sintering of YSZ is available yet. We would prefer the argument on the enhancement of diffusion through the increase of oxygen vacancy. It can be further confirmed by the subsequent heat-treatment in the reducing atmosphere.

During the heat-treatment of zirconia in a graphite powder bed, extra oxygen vacancy may be produced as demonstrated below[28](#page-6-0)

$$
zero \to V_o^{\bullet \bullet} + 2e'' \tag{2}
$$

Both reactions (1) and (2) produce oxygen vacancy, the reaction (2) may compete with the reaction (1). The solubility of Ni^{2+} solute in $ZrO₂$ may thus be reduced as the NiO-doped YSZ specimen is fired in an environment with low oxygen partial pressure. Some metallic Ni inclusions are thus produced at the boundaries of $ZrO₂$ grains. A very small amount of NiO remains within the $ZrO₂$ grains after the internal reduction treatment at 1300 °C. The Ni-doped YSZ specimen is therefore a composite composing of nano-sized Ni particles and $ZrO₂$ grains containing both Y^{3+} and Ni²⁺ solutes.

In order to estimate the transformation ability of zirconia phase, the amount of monoclinic (m) phase on the as-sintered specimens was determined. The amount of m phase was also estimated from the fracture surface, [Table 3. T](#page-5-0)he table demonstrates that the addition of Ni solutes enhances the transformation

Fig. 5. Correlation for the toughness and grain size for all the specimens investigated in the present study.

ability. The toughness increase can thus attribute to the transformation toughening. The ease of transformation from tetragonal phase to monoclinic phase is also affected by the size of zirconia grains.[29,30](#page-6-0) Such correlation is also observed in the present study, as demonstrated in Fig. 5. The figure suggests that as the size of zirconia grains is larger, the toughness is higher. The addition of NiO increases the size of the $ZrO₂$ grains; the toughness is consequently enhanced. Two possible reasons underline the toughness enhancement for the NiO-doped YSZ specimens. One reason is related to the increase of grain size due to the addition of NiO. Another one is the increase of oxygen vacancy concentration due to the solution of NiO, as demonstrated by the Eq. (1). The increase of oxygen vacancy may stabilize the t-phase, [Table 3.](#page-5-0) As more t-phase remains in the NiO-doped YSZ specimens after sintering, more phase transformation can take place during the fracturing process. The increase of grain size also encourages the phase transformation during the frac-turing process.^{[29,30](#page-6-0)} Both reasons contribute a higher toughness for the NiO-doped YSZ specimens. However, it is not possible to determine which reason dominates the toughening behaviour for the NiO-doped YSZ specimen. More direct experimental evidence is still needed to confirm the toughening mechanism for the system.

As NiO-doped YSZ specimen is firing in an atmosphere of low oxygen partial pressure, some nano-sized Ni particles are produced. The amount of Ni particles in YSZ matrix is very small, 0.06 vol%. The movement of grain boundary may be prohibited as second phase particles are located at the grain boundary. Tuan et al. had suggested that at least one secondphase particle per grain boundary is needed to prohibit the grain growth.[31](#page-6-0) Such critical amount of second phase particles can be estimated by using the following relationship

$$
F_{\min}^{1/2} = \left(\frac{\pi}{6}\right)^{1/2} \frac{d}{G}
$$
 (3)

.
. . . .

where F_{min} is the minimum volume fraction of second phase, d the size of second phase particles and G the grain size. Since the Ni particles in the YSZ-Ni specimens is 100 nm and the size of $ZrO₂$ grains is 1 μ m, the value of d/G is 0.1. The minimum Table 3

Phase analysis results for the NiO-doped YSZ and YSZ-Ni specimens. The data for the YSZ specimen prepared by sintering at 1500 ◦C in air for 1 h are shown for comparison purpose.

^a The weight percent of Ni in the starting composition was 0.088%.

amount needed is around 0.5 vol%. It indicates that an amount of 0.06 vol% of Ni particles is not enough to occupy every grain boundary. It can be confirmed by microstructure observation. As demonstrated in [Fig. 3,](#page-3-0) only several nano-sized Ni particles are found among many $ZrO₂$ grains. Since the amount of Ni particles is far too low, the size of zirconia grains increases slightly after the heat treatment at 1300 \degree C for 2.5 h. The toughness is thus further enhanced after the heat treatment. However, with such low Ni content, the contribution of the plasticity of metallic nickel to the toughness enhancement is expected to be very small. The toughness enhancement may thus be contributed mainly by the transformation toughening, which is resulted from the increase of grain size, as demonstrated in the [Fig. 5.](#page-4-0)

The flaw size within brittle solid can be estimated by using the Griffith relationship. The estimated size for the critical flaw is shown in [Table 2.](#page-3-0) The flaw size is not reduced by increasing the dwell time, and by the addition of NiO. The strength increase is thus not contributed by the flaw size reduction. A prolonged dwell at elevated temperature in air for YSZ specimen increases the amount of monoclinic phase and cubic phase, Table 3. Such increase had been related to the precipitation of Y^{3+} ions at the boundaries of ZrO_2 grains.^{[32–35](#page-6-0)} The addition of Ni2+ solute reduces the m-phase content in the as-sintered specimen, Table 3. It may imply that the grain boundaries are α occupied by Ni²⁺ ions, which inhibit further precipitation of Y^{3+} ions. As the Y^{3+} ions remain within the ZrO_2 grains, the t-phase remains stable. In any case, the grain boundary chemistry is modified due to the increase of dwell time (results in the precipitation of Y^{3+} ions) and the addition of NiO (results in the precipitation of Ni^{2+} ions), the strength of YSZ specimen is enhanced. Through careful microstructure characterization on the fracture surface of YSZ and NiO-doped YSZ specimens, the change on fracture mode was not significant. The strength increase can thus be related, only partly, to the change of grain boundary chemistry. However, the depletion of solutes from the center of the grains may reduce the low-temperature stability of YSZ specimens.^{[35](#page-6-0)} Further investigation on the lowtemperature degradation behaviour for the NiO-doped YSZ is needed.

All the strength and toughness values are collected and shown in Fig. 6. There is a positive correlation between the toughness and strength. The increase of dwell time at 1500 ◦C

Fig. 6. Correlation for the strength and toughness for all the specimens investigated in the present study.

from 1 h to 24 h increases the density of specimen slightly [\(Table 1\).](#page-2-0) The long dwell time at $1500\,^{\circ}$ C for 24 h and $1300\,^{\circ}$ C for 2.5 h is thus beneficial to the strength increase. Furthermore, the figure implies that the strength enhancement can be related, at least partly, to the toughening effect. 36 For the most materials, the toughness usually decreases with the increase of strength. However, many biological materials exhibit both high strength and high toughness. For example, the presence of ∼1 vol% soft protein enhances the strength and toughness of nacre considerably.³⁶ The unique mechanical properties are related to their hierarchical microstructure. For the present system, an amount of 0.06 vol% Ni can also enhance both the strength and toughness of zirconia. The correlation between the strength and toughness for the YSZ-Ni specimens needs in-depth investigations.

5. Conclusions

The present study demonstrates that both the strength and toughness of yttria-stabilized zirconia (YSZ) specimen can be enhanced through the addition of a transient solid solution additive. The NiO addition dissolves first to enhance the densification and coarsening of YSZ. Then, the solutes can be removed and precipitated at the grain boundaries to form nano-sized Ni

particles by firing in a reducing atmosphere. Since the transformation ability of zirconia increases with the increase of grain size, the toughness of YSZ is therefore enhanced through the increase of dwell time. The toughness is enhanced further by applying a post-sintering heat treatment. The strength of YSZ is enhanced after the addition of nano-sized Ni particles. The strength increase is contributed by many factors, such as density increase, change of grain boundary chemistry and toughness enhancement.

Acknowledgement

The present study was supported by the National Science Council of Taiwan through the contract NSC97-2221-E002-030.

References

- 1. Basu B. *Toughening of yttria-stabilized tetragonal zirconia ceramics*. *Int Mater Rev* 2005;**50**(4):239–56.
- 2. Kondo H, Sekino T, Tanaka N, Nakayama T, Kusunose T, Niihara K. *Mechanical and magnetic properties of novel yttria-stabilized tetragonal zirconia/Ni nanocomposite prepared by the modified internal reduction method*. *J Am Ceram Soc* 2005;**88**(6):1468–73.
- 3. Kondo H, Sekino T, Kusunose T, Nakayama T, Yamamoto Y, Wada M, et al. *Solid-solution effects of a small amount of nickel oxide addition on phase stability and mechanical properties of yttria-stabilized tetragonal zirconia polycrystal*. *J Am Ceram Soc* 2003;**86**(3):523–5.
- 4. Tuan WH, Liu SM, Ho CJ, Yang TJ. *Biaxial strength of ZrO2/(Ni + Al2O3) nanocomposite*. *J Am Ceram Soc* 2006;**89**(2):754–8.
- 5. Chen RZ, Tuan WH. *Pressureless sintering of Al2O3/Ni nanocomposites*. *J Eur Ceram Soc* 1999;**19**:463–8.
- 6. Díaz LA, Valdés AF, Díaz C, Espino AM, Torrecillas R. *Alumina/molybdenium nanocomposites obtained in organic media*. *J Eur Ceram Soc* 2003;**23**:2829–34.
- 7. Yeomans JA. *Ductile particle ceramic matrix composites-scientific curiosities or engineering materials*. *J Eur Ceram Soc* 2008;**28**:1543–50.
- 8. Kondo H, Sekino T, Choa Y-H, Kusunose T, Nakayama T, Wada M, et al. *Mechanical and magnetic properties of nickel-dispersed tetragonal zirconia nanocomposites*. *J Nanosci Nanotechnol* 2002;**2**(5):485–90.
- 9. Kim DJ, Jung HJ, Jang JW, Lee HL. *Fracture toughness, ionic conductivity, and low-temperature phase stability of tetragonal zirconia codoped with yttria and niobium oxide*. *J Am Ceram Soc* 1998;**81**(9):2309–14.
- 10. Yuh SD, Lai YC, Chou CC, Lee HY. *YNbO4-addition on the fracture toughness of ZrO2(3Y) ceramics*. *J Mater Sci* 2001;**36**:2303–11.
- 11. Yeh TH, Chou CC. *Development of ceria-doped zirconia electrolytes with high toughness and ionic conductivity*. *Solid State Ionics* 2009;**180**:1529–33.
- 12. Gaskell DR. *Introduction to the thermodynamics of materials*. New York: Taylor & Francis 2008.
- 13. Garvie RC, Nicholson PS. *Phase analysis in zirconia systems*. *J Am Ceram Soc* 1972;**55**(6):303–5.
- 14. Cullity BD, Stock SR. *Elements of X-ray diffraction*. 3rd ed., New Jersey: Prentice Hall 2001.
- 15. Lawn BR, Evans AG, Marshall DB. *Elastic/plastic indentation damage in ceramics: the median/radial crack system*. *J Am Ceram Soc* 1980;**63**(9–10):574–81.
- 16. Johnston HL, Marshall AL. *Vapor pressures of nickel and of nickel oxide*. *J Am Chem Soc* 1940;**62**(6):1382–90.
- 17. Ruhle M, Evans AG. *High toughness ceramics and ceramic composite*. *Prog Mater Sci* 1989;**33**:85–167.
- 18. Majumdar R, Gilbart E, Brook RJ. *Kinetics and densification of alumina–zirconia ceramics*. *Br Ceram Trans J* 1986;**85**:156–60.
- 19. Kuzjukevics A, Linderoth S. *Interaction of NiO with yttria-stabilized zirconia*. *Solid State Ionics* 1997;**93**:255–61.
- 20. Kuzjukevics A, Linderoth S. *Influence of NiO on phase stabilization in 6 mol% yttria-stabilized zirconia*. *Mater Sci Eng A* 1997;**232**: 163–7.
- 21. Chen S, Shen P, Gan D. *Growth kinetics of sintered NiO/ZrO2 (5 mol.% Y2O3) composite*. *Mater Sci Eng A* 1992;**158**:251–8.
- 22. Delaforce PM, Yeomans JA, Filkin NC, Wright GJ, Thomson RC. *Effect of NiO on the phase stability and microstructure of yttria-stabilized zirconia*. *J Am Ceram Soc* 2007;**90**(3):918–24.
- 23. Chen S, Deng W, Shen P. *Stability of cubic ZrO2 (10 mol.% Y2O3) when* alloyed with NiO, Al_2O_3 or TiO₂: implications to solid electrolytes and *cermets*. *Mater Sci Eng B* 1994;**22**:247–55.
- 24. Zhang TS, Chan SH, Kong LB, Sheng PT, Ma J. *Synergetic effect of NiO and SiO2 in the sintering and properties of 8 mol% yttria-stabilized zirconia electrolytes*. *Electrochim Acta* 2009;**54**:927–34.
- 25. Zhang TS, Du ZH, Li S, Kong LB, Song XC, Lu J, et al. *Transitional metal-doped 8 mol% yttria-stabilized zirconia electrolytes*. *Solid State Ionics* 2009;**180**:1311–7.
- 26. Allemann JA, Michel B, Märki H-B, Gauckler LJ, Moser EM. *Grain growth of differently doped zirconia*. *J Eur Ceram Soc* 1995;**15**:951–8.
- 27. Yoshida H, Nagayama H, Sakuma T. *Small dopant effect on static grain growth and flow stress in superplastic TZP*. *Mater Trans* 2003;**44**(5): 935–9.
- 28. Carniglia SC, Brown SD, Schroeder TF. *Phase equilibria and physical properties of oxygen-deficient zirconia and thoria*. *J Am Ceram Soc* 1971;**54**(1):13–7.
- 29. Wang J, Rainforth M, Stevens R. *The grain size dependence of the mechanical properties in TZP ceramics*. *Br Ceram Trans J* 1989;**88**:1–6.
- 30. Garvie RC, Goss MF.*Intrinsic size dependence of the phase transformation temperature in zirconia microcrystals*. *J Mater Sci* 1986;**21**:1253–7.
- 31. Tuan WH, Chen JR, Ho CJ.*Critical zirconia amount to enhance the strength of alumina*. *Ceram Int* 2008;**34**:2129–35.
- 32. Matsui K, Horikoshi H, Ohmichi N, Ohgai M. *Cubic-formation and graingrowth mechanism in tetragonal zirconia polycrystal*. *J Am Ceram Soc* 2003;**86**:1401–8.
- 33. Ruiz L, Readey MJ. *Effect of heat treatment in grain size, phase assemblage, mechanical properties of 3 mol% Y-TZP*. *J Am Ceram Soc* 1996;**79**:2331–40.
- 34. Casellas D, Cumbrera FL, Sánchez-Bajo F, Forsling W, Llanes L, Anglada M. On the transformation toughening of Y-ZrO₂ ceramics with mixed Y-*TZP/PSZ microstructure*. *J Eur Ceram Soc* 2001;**21**:765–77.
- 35. Chevalier J, Deville S, Münch E, Jullian R, Lair F. *Critical effect of cubic phase on aging in 3 mol% yttria-stabilized zirconia ceramics for hip replacement prosthesis*. *Biomaterials* 2004;**25**:5539–45.
- 36. Launey ME, Ritchie RO. *On the fracture toughness of advanced materials*. *Adv Mater* 2009;**21**:2103–10.