

## Microstructure and Mechanical Properties of Nickel-Particle-Dispersed Zirconia Composites

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Nickel-particle-reinforced zirconia matrix composites have been prepared by pressureless sintering. Two different sizes of nickel particles with micrometer and nanometer scales were incorporated into partially stabilized zirconia matrix. The influence of nickel particle size on microstructure and mechanical properties of the nickel-particle-dispersed zirconia composites has been investigated. The results showed that the fracture toughness of the composites was improved as the nickel content increased, though the flexural strength was reduced. The composites with a micrometer size of nickel particles exhibited higher fracture toughness values, compared to those with nanosized Ni particles. Although a crack can be propagated along the interfaces between nickel particles and matrix in small sized nickel-dispersed composites, larger nickel particles are more effective in deflecting and bridging cracks, hence contributing to enhanced fracture toughness.

Key words: ceramic matrix composites, metal inclusion, fracture toughness, crack bridging, nanosized particles

### 1. INTRODUCTION

The practical applications of ceramics as structural components are often limited by their brittleness. In order to improve the fracture toughness of ceramics, various energy-dissipating components, such as whiskers, fibers, platelets, and particulates, have been attempted to incorporate into ceramic matrices to create ceramic matrix composites. During the last decades, the incorporation of ductile metallic phases has been proved to be one of the promising approaches to toughen ceramics. The reason for increased toughness in a ceramic-metal composite is the ability of ductile metal phase to bridge an advancing crack and to exert crack closure stresses on the crack wake [1,2]. Earlier work was primarily concerned with the addition of metal particles with micrometer scale. In recent years, however, much attention has been paid to nanometer sized metal particles, which were dispersed within ceramic grains and at grain boundaries [3,4]. Such ceramic-metal nanocomposites improved the mechanical properties significantly (in particular fracture strength), when compared to the monolithic ceramics.

It is evident that the toughening effect of metal reinforcements depends to a large extent on the properties of metal inclusions themselves (including particle size, shape, orientation as well as their mechanical and physical properties) and the interface characteristics between metal and ceramic matrix. So far, some attempts have been made to understand the effect of metal particle size on stress-strain response, bridging stress, crack resistance curve and toughness [5-8]. But somewhat controversial results have been obtained. In the present work, metallic nickel second-phase particles with micrometer and nanometer sizes were incorporated into partially stabilized zirconia matrix. The main objective of this investigation was to further understand the influence of metal particle size on mechanical properties of ceramic-metal composites, with emphasis

on the dependence of fracture toughness and responsible toughening mechanism on the sizes of metallic nickel particles embedded in zirconia matrix.

### 2. EXPERIMENTAL PROCEDURE

A commercially available partially stabilized zirconia (PSZ) powder doped with 3mol%  $Y_2O_3$  (average particle size of 0.7 $\mu$ m) was used as the starting material for matrix of the composites. As a metallic second-phase reinforcement, nickel from two different sources was chosen: high-purity metallic nickel powder with an average particle size of 5 $\mu$ m, and nickel nitrate (corresponding composites are denoted as Micro-Ni and Nano-Ni, respectively).

The Ni-PSZ composites with different Ni contents, 0, 5, 10, 15, and 20vol% were prepared via a powder metallurgy route. When the Ni powder was used as a starting material, the Ni and PSZ powders were ball-milled in ethanol for 24h. After drying, the mixed powders were crashed by pestle and mortar and passed through a 200 mesh sieve. In the case of the nickel nitrate, weighted nickel nitrate powder, corresponding to 5-20%Ni in the final composites, were dissolved in ethanol first. Subsequently, the PSZ powder was added to the above solutions and ball-milled for 24h. The slurry of the powder mixtures was dried and again dry ball-milled for 24h. The resulting powders were calcined in air at 450°C for 2h to decompose the nickel nitrate into nickel oxide, and then reduced in hydrogen at 700°C for 2h to obtain Ni-PSZ mixed powders. The mixed powder mixtures were consolidated by uniaxially pressing at 50MPa, followed by cold-isostatic pressing (CIP) at 300MPa. The pressureless sintering was performed in  $H_2/Ar$  atmosphere at 1400°C for 1h.

The bulk density of the sintered samples was measured by the Archimedes method. The crystalline phases present in dried, calcined and reduced powders as well as in sintered samples were identified by X-ray

diffraction (XRD) with  $\text{CuK}\alpha$  radiation. Microstructural characterization was performed by optical and scanning electron microscopy (SEM). The flexural strength was measured by four-point bending test. The hardness and fracture toughness ( $K_{IC}$ ) were determined by using a Vickers indenter with a load of 98N. The  $K_{IC}$  values were calculated according to the equation proposed by Niihara *et al* [9].

### 3. RESULTS AND DISCUSSION

#### 3.1 XRD analysis and microstructures

As a representative example, Fig.1 shows the XRD patterns for Nano-Ni samples with a nominal composition of 15%Ni but in different processing periods. For dried mixed powder, the XRD pattern (Fig.1(a)) exhibited peaks of zirconia and nickel nitrate, as expected. After calcination at 450°C, the nickel nitrate phase disappeared; instead, the NiO peaks were confirmed, as the result of the decomposition of nickel nitrate into NiO (Fig.1(b)). The resultant NiO was then transformed into metallic Ni completely after the reduction in hydrogen at 700°C (Fig.1(c)).

It was found from Fig.1 that, the PSZ matrix was subjected to phase transformation in different periods of calcination, reduction, and sintering. The PSZ consisted of tetragonal (*t*) and monoclinic (*m*) phases in the dried mixed powder. After the powder was calcined in air at 450°C, the relative intensities of peaks for monoclinic phase increased. This suggests that the *t* → *m* transition occurred during the calcination process, with the nickel nitrate being decomposed into NiO. With regard to the sintered sample, well-defined peaks of *t* phase and Ni were easily observed (Fig.1(d)) and no *m* or other phases were detected. These facts indicate that the *m* phase was completely transformed into *t* phase, and no chemical reactions between Ni and PSZ took place during the sintering.

Fig.2 illustrates the optical micrographs showing the microstructures of Micro-Ni composites. The light and gray phases in the micrographs are Ni inclusions and

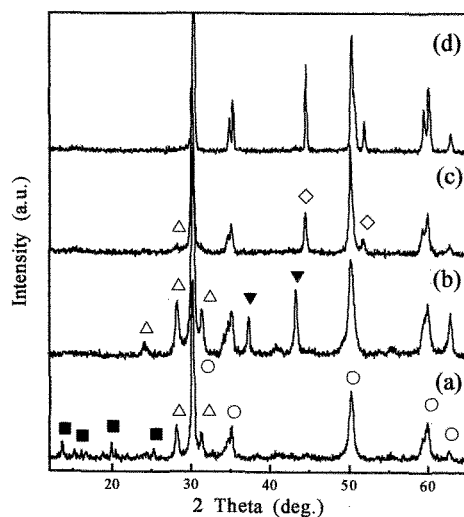


Fig.1 XRD patterns for Nano-Ni samples with 15%Ni in different processing periods. (a) mixed powder, (b) after calcination, (c) after reduction, and (d) after sintering. (Δ) *m*-ZrO<sub>2</sub>, (○) *t*-ZrO<sub>2</sub>, (▼) NiO, (◇) Ni, and (■) nickel nitrate.

PSZ matrix, respectively, and the dark spots are pores remaining after sintering. The Ni inclusions were uniformly dispersed in the PSZ matrix as discrete and isolated particles. The measurements of the particle sizes from the micrographs revealed that there was no significant increase in size of the Ni particles, although an increase trend in the size could be found as the Ni content was raised. The Ni particles possessed sizes ranging from 1 to 9μm, similar to the initial Ni powder with an average particle size of 5μm. This means that no evident coarsening of Ni particles occurs in the range of the Ni content investigated. The coarsening of Ni particles appears to be strongly impeded by the PSZ phase during the densification.

The microstructures of Nano-Ni composites using nickel nitrate as a Ni source are shown in Fig.3. The nanosized Ni particles were distributed in the PSZ matrix homogeneously. The Ni particles were much smaller (<250nm) in comparison with the microstructures shown in Fig.2. From the SEM micrographs, the average sizes of Ni particles were measured as 120, 150, 200, and 240nm for the composites with Ni contents of 5, 10, 15, and 20%, respectively. That is to say, with the increase in the amount of Ni second phase, the sizes of Ni particles gradually become large. This may be attributed to the agglomeration of nickel nitrate or NiO particles in the periods of drying and calcining, thus resulting in the formation of larger Ni particles in subsequent reduction and sintering stages.

#### 3.2 Mechanical properties

The variations of relative density and Young's modulus of the Ni-PSZ composites with nickel content

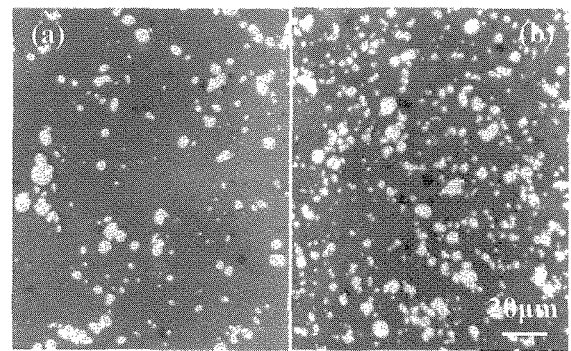


Fig.2 Optical micrographs showing the microstructures of Micro-Ni composites with (a) 10%Ni and (b) 20%Ni.

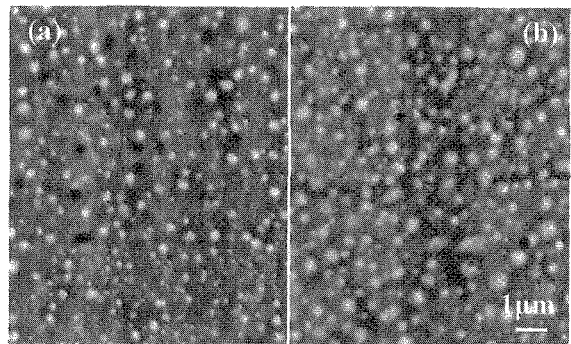


Fig.3 SEM microstructures of Nano-Ni composites with (a) 10%Ni and (b) 20%Ni.

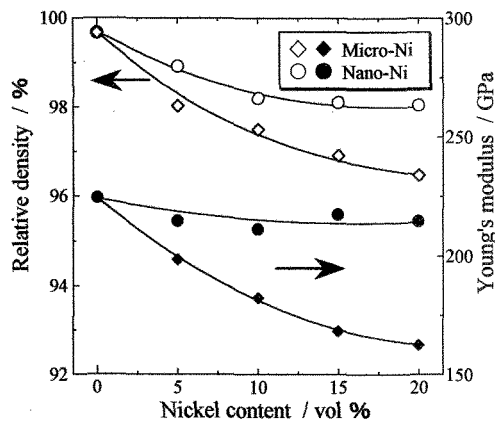


Fig.4 Variations of relative density and Young's modulus of Ni-PSZ composites with nickel content.

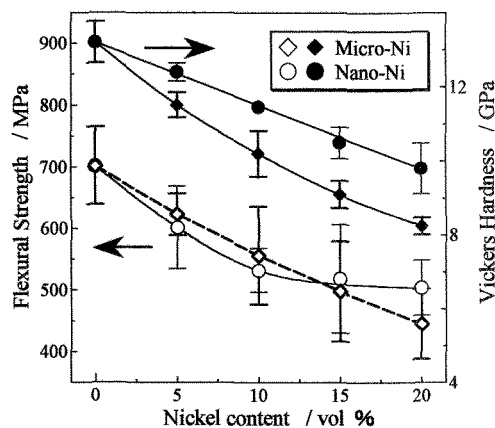


Fig.5 Flexural strength and Vickers hardness of Ni-PSZ composites as a function of nickel content.

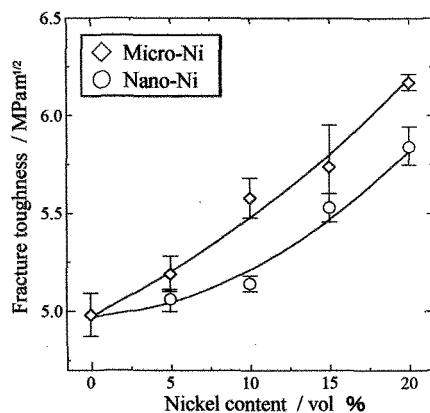


Fig.6 Dependence of fracture toughness on nickel content for Ni-PSZ composites.

are shown in Fig.4. As the nickel content increased, the relative density gradually decreased for two kinds of composites with different Ni sizes. This is the result of the inhibition of Ni particles on the densification of the PSZ matrix. Obviously, this inhibition effect depends on the Ni content; a larger Ni content leads to a lower density easily. It can be seen from Fig. 4 that the composites with a smaller Ni size (Nano-Ni) had higher density values than those with a larger Ni size (Micro-Ni), indicating that nanosized Ni particles has

small inhibition effect on densification of composites during sintering. This is in good agreement with the results reported in the work [4] concerning Ni reinforced alumina matrix composites.

As shown in Fig.4, the Young's modulus of Nano-Ni composites reduced slightly with increasing the Ni content. In the case of Micro-Ni composites, however, the Young's modulus decreased monotonously with nickel content. The values of Young's modulus for PSZ and Ni are 220GPa and 200GPa, respectively. Since these two values are very close, the Ni-PSZ composites with different compositions should have similar values according to the rule of mixtures. Lower values of Young's modulus for Micro-Ni composites are likely to be due to the following two reasons. One is their lower values of relative density in comparison with Nano-Ni composites. The other may be due to the damages existed around interfaces between the Ni particles and PSZ matrix, such as microcracking or debonding (see Fig.8).

The flexural strength and Vickers hardness of the composites are shown as a function of nickel content in Fig.5. As a whole, the strength of the composites decreased with the increase in nickel content, although there existed some data scatters. The Micro-Ni and Nano-Ni composites showed a similar strength level up to 10%Ni. When the Ni content was  $\geq 10\%$ , the strength of Nano-Ni kept almost the same, while the strength of Micro-Ni decreased with increasing the Ni content. In particular, Nano-Ni had a higher strength than Micro-Ni at 20%Ni. Moreover, Nano-Ni exhibited a higher hardness level than Micro-Ni in overall range of Ni content. These results are believed to be associated with smaller grain sizes of the PSZ matrix in Nano-Ni, because nanosized Ni particles strongly inhibit the grain growth of the matrix. Besides, larger density values of Nano-Ni also contribute to higher strength and hardness.

The dependence of fracture toughness on nickel content in the composites is given in Fig.6. The fracture toughness was improved by incorporating the Ni second-phase particles in PSZ matrix. The toughness value increased with increasing the Ni content. It is noted that the Micro-Ni composites with larger sized Ni particles revealed higher toughness values than the Nano-Ni composites with nanosized Ni particles. This trend coincides with the results of Mo reinforced alumina [7] and mullite [8] matrix composites.

### 3.3 Crack propagation and fracture surfaces

Fig.7 shows some examples of the propagation behavior of cracks, which were introduced by a Vickers indenter on polished surfaces. For Micro-Ni composite, the crack was deflected at some sites of Ni particles (marked with arrows A in Fig.7(a)). At the same time, crack bridging by Ni particle was confirmed. A Ni particle marked with B in Fig.7(a), served as a ligament to bridge the crack. It seemed that necking occurred and the particle was subjected to plastic deformation during the crack propagation. With regard to the Nano-Ni composite (Fig.7(b)), the crack path introduced by indentation was relatively straight with small deviations, and no significant deflection occurred, although the crack propagated along the interfaces between Ni particles and PSZ matrix.

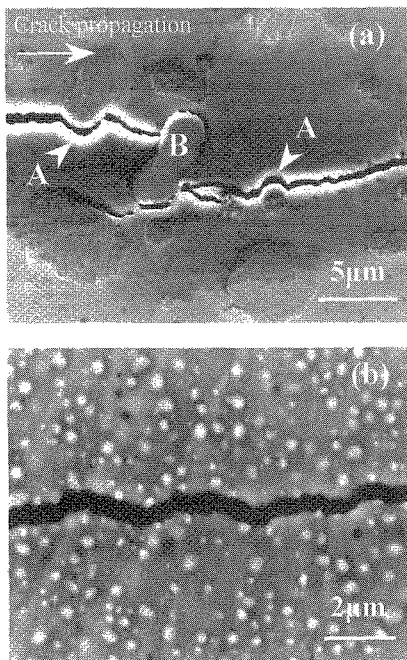


Fig.7 SEM micrographs showing crack propagation around Vickers indentation for 15%Ni-PSZ composites: (a) Micro-Ni (SEI mode) and (b) Nano-Ni (BEI mode).

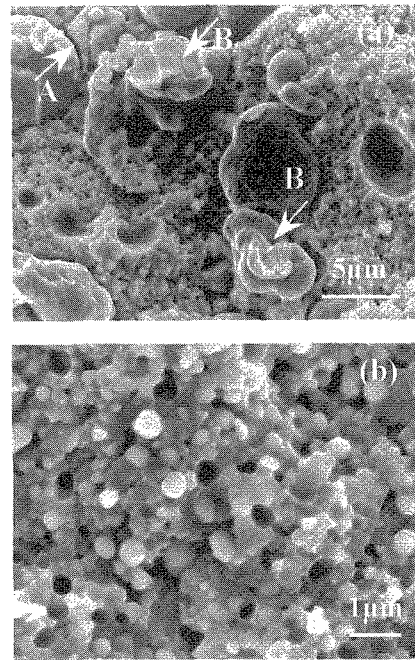


Fig.8 SEM micrographs of fracture surfaces of 15%Ni-PSZ composites after four-point bending tests. (a) Micro-Ni and (b) Nano-Ni composites.

The fracture surfaces after bending tests are shown in Fig.8. It appears that some Ni particles have been pulled out on the fracture surfaces in both Micro-Ni and Nano-Ni composites. In particular, a lot of voids, which are mainly ascribed to the pull-out of Ni particles, were observed on the surface of the Nano-Ni sample (Fig.8(b)). Furthermore, there existed partial interface debonding between Ni particles and PSZ matrix (as indicated with an arrow A in Fig.8(a)). The debonding is thought to be the result of stress concentration, which arises from the thermal expansion mismatch between Ni and PSZ, as well as applied stress. These results suggest that the bonding of Ni-PSZ interfaces is not very strong. As it can be seen in Fig.8(a), however, some Ni particles were plastically stretched (marked with arrows B) in Micro-Ni composite, showing strong interfacial bonding. The reason for the difference in interfacial bonding is not very clear; a likely probable explanation is that particle-matrix bonding depends to some extent on particle morphology, surface roughness and orientation with respect to crack plane. Meanwhile, it is difficult to find any deformation of Ni particles on the fracture surface of the nanocomposite from Fig.8(b).

From the above observations, in Nano-Ni composites, a crack seems to be easily bypassed by small equiaxed Ni particles when propagating. For Micro-Ni composites, however, in addition to crack deflection, crack bridging by plastic deformation of some large Ni particles is another responsible mechanism for enhanced fracture toughness. Accordingly, a higher fracture toughness level is achieved in Micro-Ni composites, compared to Nano-Ni composites.

#### 4. CONCLUSIONS

Nickel-particle-reinforced zirconia matrix composites were prepared by pressureless sintering. The fracture

toughness of the composites was enhanced as the nickel content increased, though the flexural strength was reduced. The size of nickel second-phase particles has a significant effect on the fracture toughness and responsible toughening mechanism. It has been demonstrated that the composites with a micrometer size of nickel particles exhibited higher fracture toughness values, compared to those with nanosized Ni particles. Larger nickel particles are more effective in deflecting and bridging cracks. For the composites with nanosized Ni particles, the crack is easily propagated along the interfaces between Ni particles and matrix. In the case of the composites with a micrometer sized Ni particles, in addition to crack deflection, crack bridging by ductile Ni particles is another mechanism for enhanced fracture toughness.

#### REFERENCES

- [1] M.F. Ashby, F.J. Blunt and M. Bannister, *Acta Metall.*, **37**, 1847-57 (1989).
- [2] O. Raddatz, G.A. Schneider and N. Claussen, *Acta Metall.*, **46**, 6381-95 (1998).
- [3] M. Nawa, T. Sekino and K. Niihara, *J. Mater. Sci.*, **29**, 3185-92 (1994).
- [4] T. Sekino, T. Nakajima, S. Ueda and K. Niihara, *J. Am. Ceram. Soc.*, **80**, 1139-48 (1997).
- [5] L.R. Thompson and R. Raj, *Acta Metall. Mater.*, **42**, 2477-85 (1994).
- [6] N. Nagendra and V. Jayaram, *J. Mater. Res.*, **15**, 1131-44 (2000).
- [7] O. Sbaizero and G. Pezzotti, *Acta Metall.*, **48**, 985-92 (2000).
- [8] J.F. Bartolome M. Diaz and J.S. Moya, *J. Am. Ceram. Soc.*, **85**, 2778-84 (2002).
- [9] K. Niihara, R. Morena and D.P.H. Hasselman, *J. Mater. Sci. Letts*, **1**, 13-16 (1982).