

Nickel and zirconia toughened alumina prepared by hydrothermal processing

Husheng Jia · Xin Liu · Tianbao Li · Hong Yan ·
Xuguang Liu · Bingshe Xu

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Ceramics are attractive candidates for structural systems due to their strength at high temperatures. However, the major limitation to their application is their low fracture toughness. A major research objective for ceramic communities has, therefore, been to improve the fracture toughness of ceramics. The past two decades have seen the emergence of a number of studies concerned with toughening [1–3]. There are two types of mechanisms to improve the resistance to crack propagation, that is, by increasing the inherent toughness (energy dissipation) of the material and reducing the local crack-tip driving force [4], such as residual stress effects, phase transition toughening, crack deflection, nano-composites toughening, and bridging by ductile particles, fibers, and whiskers [5]. The addition of a dispersed second-phase inclusion, which limits the propagation of cracks is one of the most commonly used approaches. With the addition of either zirconia particles [6] or silicon carbide whiskers [7], the fracture toughness and strength were increased [8, 9]. Alternatively, continuous metal and ceramic phases can improve fracture toughness and creep resistance, respectively. A tri-phase structure is of benefit for the suppression of grain growth [10]. In this paper, two toughening agents, nickel and zirconia particles,

were added to an alumina matrix to enhance its toughness. Although the simultaneous use of nickel and zirconia particles is not new, few studies have been reported on tri-phase composite powders obtained by combining hydrothermal processing with co-precipitation. In the present communication, two-phase and tri-phase composites were investigated.

Aluminum hydroxide was prepared by precipitation by slowly adding ammonia liquor into a 1 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution while vigorously stirring to attain the desired pH value of the solution in contact with the precipitated solid. In general, the pH value was controlled to be in the range of 10–10.5 [11]. The as-obtained aluminum hydroxide was washed by centrifugal filtration with deionized water and methanol for several times and then washed in methanol accompanied by ultrasonic mixing.

The addition of Y_2O_3 to ZrO_2 is known to increase the stability of the t- ZrO_2 phase in composite powders [3]. Zirconium oxychloride octahydrate was dissolved in deionized water and yttria was dissolved in a hydrochloric acid solution. The yttrium ionic solution was added into the zirconium oxychloride solution. ZrO_2 was doped with yttrium to stabilize its final structure. Colloidal zirconium hydroxide was precipitated by drop-wise addition of 2 M ammonia solution into the mixture under vigorous stirring until precipitation reaction was completed. Colloid was washed by centrifugal filtration with deionized water and methanol for several times and then washed in methanol accompanied by ultrasonic mixing.

Nickel chloride hexahydrate was dissolved in absolute ethyl alcohol, as also described by Gibson and Kathy [12]. The nickel was reduced by the drop-wise addition of 2 M NaOH containing hydrazine hydrate. The activation of Ni ions by coordinating and surface absorption may overcome

H. Jia · X. Liu · T. Li · H. Yan · X. Liu · B. Xu (✉)
Key Laboratory of Interface Science and Engineering
in Advanced Materials, Ministry of Education,
Taiyuan University of Technology, Taiyuan 030024, China
e-mail: xubs@public.ty.sx.cn

H. Jia · X. Liu · T. Li · H. Yan · X. Liu · B. Xu
College of Materials Science and Engineering, Taiyuan
University of Technology, Taiyuan 030024, China

kinetic barriers and realize the reduction of nickel ions. Ni precursor was washed by centrifugal filtration with deionized water and methanol for several times and then washed in methanol accompanied by ultrasonic mixing.

Alumina and zirconia precursors were mixed under vigorous stirring. The two components were mixed by stirring for 20 min in a conical flask with nickel precursor mentioned above. The mixture was heated for 12 h at 300 °C under autogenous pressure of 1,4-butanediol solution under continuous stirring at 400 rpm in an autoclave (internal volume of 100 mL). The $\text{Al}_2\text{O}_3(\text{ZrO}_2 + \text{Ni})$ composite was obtained.

About 12 vol.% zirconia and 12 vol.% nickel particles were chosen as the amount of secondary phases for the alumina matrix, based on the conclusions of Chen et al. [8]. The grain size of powders was critical to the property of the composite. For example, it was reported that the critical size (D_c') for stress-induced transformation of ZrO_2 particles to m- ZrO_2 was approximately 0.1 μm [3, 13–15]. The mean size of the metal particles should be smaller than 0.5–1 μm in diameter [16]. Thus it was important to limit the grain sizes during the processing stages.

Preliminary trials were carried out to compare the particle sizes, morphologies and mechanical properties of the tri-phase composite obtained by hydrothermal processing.

1. Ni/ $\text{ZrO}_2/\text{Al}_2\text{O}_3$ composite was prepared from the mixture of alumina precursor, zirconia precursor and nano-nickel;
2. Ni/ Al_2O_3 composite was prepared from the mixture of alumina precursor and nano-nickel;
3. $\text{ZrO}_2/\text{Al}_2\text{O}_3$ composite was prepared from the mixture of alumina and zirconia precursor;
4. Pure Al_2O_3 was prepared.

Boehmite was calcined to obtain $\alpha\text{-Al}_2\text{O}_3$ in a vacuum oven. Then powder compacts with dimensions of $d13 \times 1$ mm were formed uniaxially at 55 MPa. The green compacts (Al_2O_3 , Ni/ $\text{ZrO}_2/\text{Al}_2\text{O}_3$, and Ni/ Al_2O_3) were sintered in a graphite crucible at 1,600 °C for 1 h in vacuum of 3×10^{-3} Pa. The heating and cooling rates were both 10 °C/min. For comparison, $\text{ZrO}_2/\text{Al}_2\text{O}_3$ and Al_2O_3 green compacts were also sintered under the same conditions. The fracture toughness (K_{IC}) was determined by indentation following Evans and Charles [17]:

$$K_{IC} \Phi = 0.48 \left(\frac{c}{a} \right)^{-1.5} \text{HV}a^{0.5}$$

where $2c$ is indentation and crack size, $2a$ is the indentation diagonal line length, HV Vickers-hardness and the restraining factor was $\Phi \approx 3$.

Figure 1 presents the X-ray diffraction (XRD, Rigaku; D/max 3C) patterns of boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and the

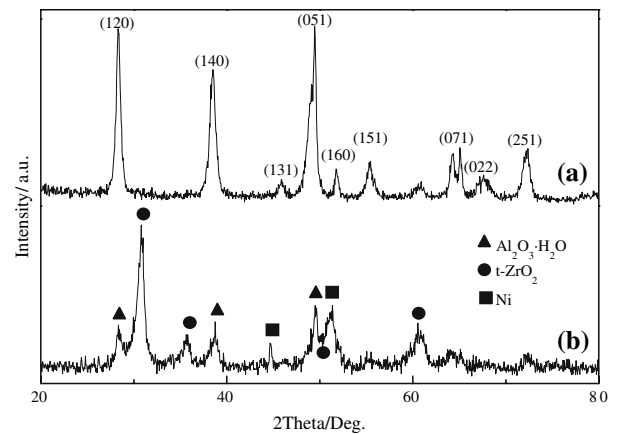


Fig. 1 XRD patterns of (a) boehmite and (b) tri-phase composite

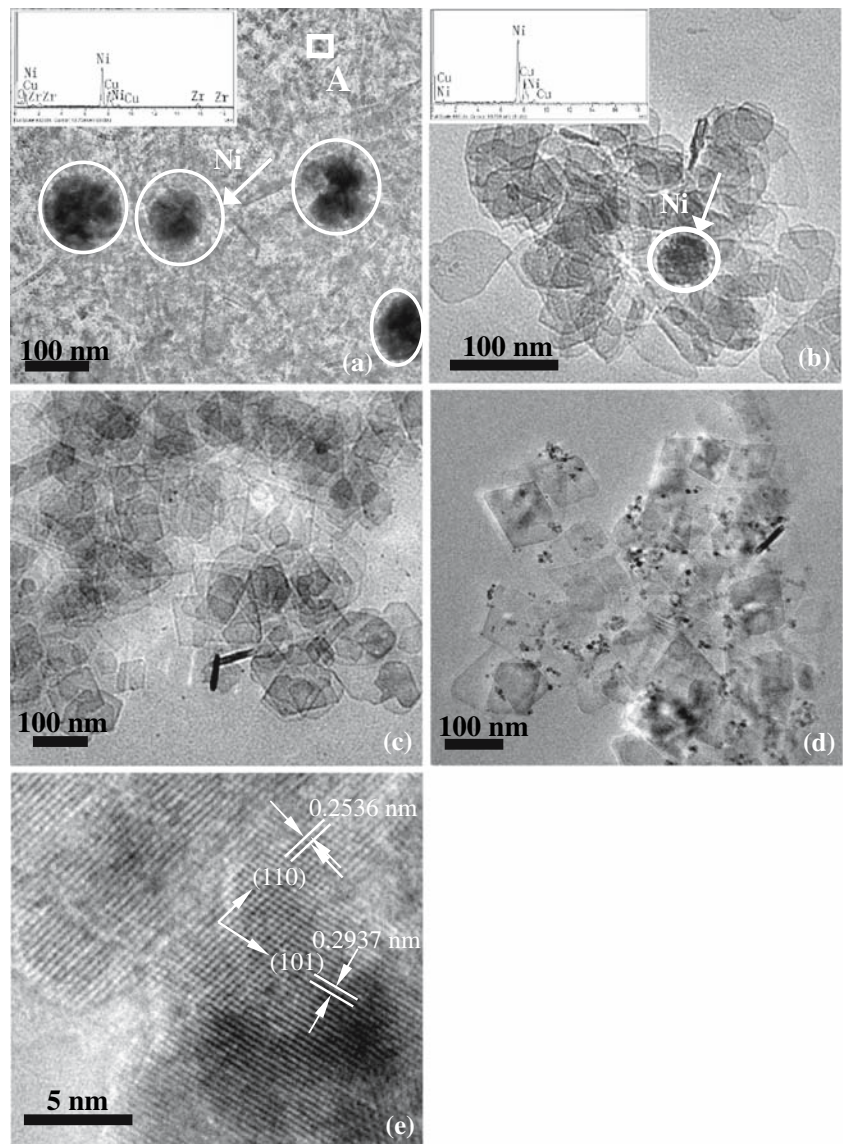
$\text{Al}_2\text{O}_3(\text{ZrO}_2 + \text{Ni})$ composite hydrothermally synthesized in 1,4-butanediol solvents at 300 °C for 12 h. $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, t- ZrO_2 and Ni were detected in the tri-phase composite, and no new phase was found by XRD analysis. Calcining was required to form $\alpha\text{-Al}_2\text{O}_3$.

Transmission electron micrographs (TEM, JEOL 2010) of the powder mixtures containing $\text{Al}_2\text{O}_3(12 \text{ vol.}\% \text{ZrO}_2 + 12 \text{ vol.}\% \text{Ni})$, $\text{Al}_2\text{O}_3(12 \text{ vol.}\% \text{Ni})$, Al_2O_3 and $\text{Al}_2\text{O}_3(12 \text{ vol.}\% \text{ZrO}_2)$ are shown in Fig. 2. X-ray energy dispersive spectroscopy was used to identify the local constituents. A phase contrast TEM micrograph of the t- ZrO_2 is shown in Fig. 2e. The ZrO_2 particles and Ni inclusions were distributed in the composite powder, and the size of ZrO_2 particles was much smaller than that of Ni inclusions.

After sintering $\alpha\text{-Al}_2\text{O}_3$, t- ZrO_2 and Ni were detected by XRD (Fig. 3). Typical scanning electron micrographs (SEM, JEOL; JSM-6700F) of the composite containing 12 vol.% ZrO_2 , 12 vol.% Ni or 12 vol.% $\text{ZrO}_2 + 12 \text{ vol.}\% \text{Ni}$ are shown in Fig. 4. The ZrO_2 particulates and Ni inclusions were distributed uniformly in the Al_2O_3 matrix. The sizes of the Ni inclusions or ZrO_2 particulates were much smaller than those of Al_2O_3 matrix grains, which made it possible to distinguish the Ni or ZrO_2 particulates from the Al_2O_3 matrix by EDS analysis. The size of Ni particles in Fig. 4a are larger than those in Fig. 4b, indicating the ZrO_2 particulates promoted grain growth of the nickel. This phenomenon requires further investigation. Moreover, the existence of nickel and zirconia particles can result in segregation to the alumina grain boundaries and limit grain growth by solution-drag, in addition to particle-drag. The results of characterization indicate that the size of ZrO_2 and Ni particles in the matrix are smaller than the critical ones mentioned above.

The final density of the sintered specimens was determined by the Archimedes method in water. The relative density of the sintered Ni/ $\text{ZrO}_2/\text{Al}_2\text{O}_3$ composite was

Fig. 2 (a) TEM micrograph of Al_2O_3 (12 vol.% ZrO_2 + 12 vol.% Ni) composite and EDS pattern of a nickel particle, (b) TEM micrograph of a nickel inclusion in Al_2O_3 (12 vol.% Ni) composite and EDS pattern of a nickel particle, (c) TEM micrograph of the flake $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, (d) TEM micrograph of t- ZrO_2 dispersed in Al_2O_3 (12 vol.% ZrO_2) composite, and (e) HRTEM micrograph of area A in (a)



estimated by using the theoretical density of 3.98 g/cm^3 for Al_2O_3 , 6.05 g/cm^3 for ZrO_2 and 8.90 g/cm^3 for Ni. The density of the composite is 4.671 g/cm^3 . The relative density of the sintered Ni/ ZrO_2 / Al_2O_3 composite is 97%.

The fracture toughness of the composites was measured by Vickers indentation at a load of 100 N (Akashi hardness tester, model M-400-H1). The K_{IC} value is $9.56 \text{ MPa m}^{0.5}$ for the Ni/ ZrO_2 / Al_2O_3 composite, and $2.97 \text{ MPa m}^{0.5}$ for pure alumina. In ceramic-metal composites, there are different mechanisms of energy dispersion, which can occur the same time. An example of indentation and crack propagation in the composite is presented in Fig. 5a, in which a crack passing through a Ni particle and plastic deformation of metal particles can be observed. As shown in Fig. 5b, the nickel inclusion was pulled-out, and a hole was observed on the fracture surface. Furthermore, the

crack surfaces were bridged by the nickel inclusions. This indicates that the nickel inclusions can enhance the toughness of Al_2O_3 by pull-out and plastic deforming.

The toughening mechanisms in ceramic matrix composites using t- ZrO_2 include phase transition toughening, micro-cracking, and deflection. If a high proportion of the tetragonal phase with the ability to transform under applied stress can be obtained, phase transition toughening will work. The constraint applied on the ZrO_2 particles is reduced due to the presence of Ni inclusions in the Al_2O_3 matrix such that more tetragonal ZrO_2 particles transform to the monoclinic phase during fracture [8]. Therefore, the zirconia particles must have a homogeneous size distribution. On the other hand, continuous or discontinuous ductile inclusions are also expected to be obtained. Nickel is a prime candidate for a ductile reinforcer of alumina.

Fig. 3 (a) XRD patterns of the Al_2O_3 sintered sample, (b) XRD patterns of the 12 vol.% Ni/ Al_2O_3 sintered sample, (c) XRD patterns of the 12 vol.% ZrO_2 / Al_2O_3 sintered sample, and (d) XRD patterns of the 12 vol.% Ni/12 vol.% ZrO_2 / Al_2O_3 sintered sample

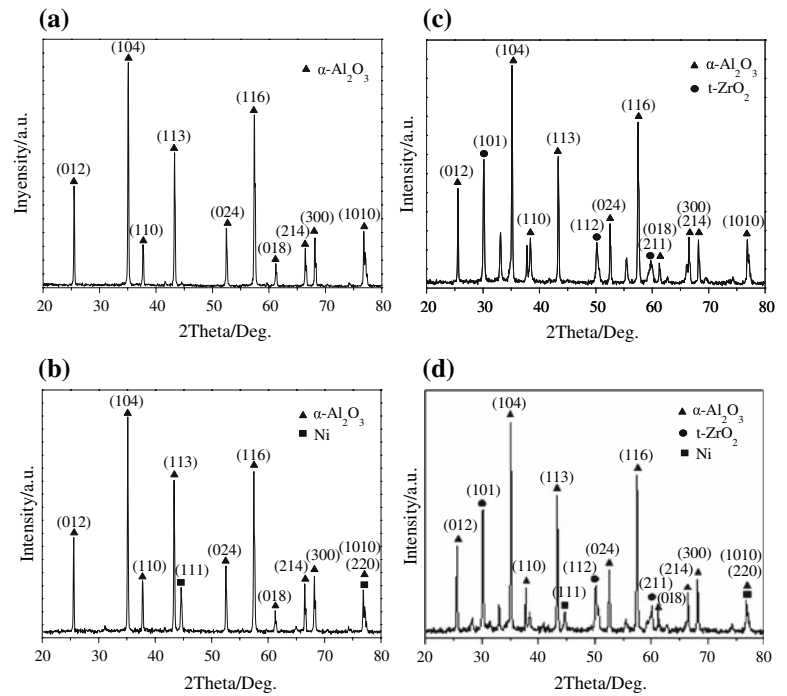
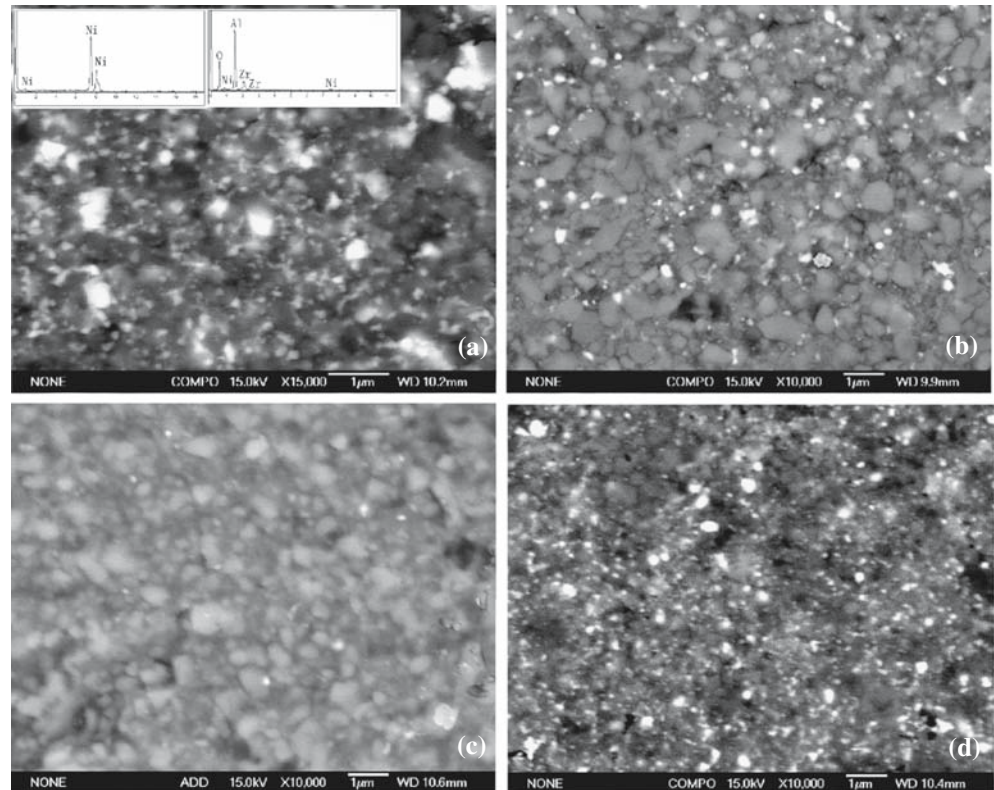


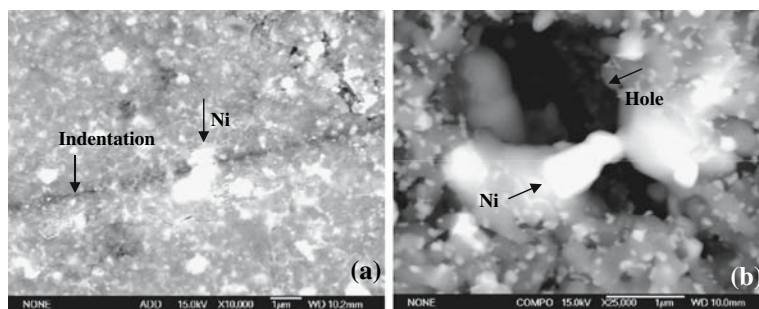
Fig. 4 Scanning electron micrograph of the sintered microstructure: (a) Al_2O_3 (12 vol.% ZrO_2 + 12 vol.% Ni), (b) Al_2O_3 (12 vol.% Ni), (c) Al_2O_3 , and (d) Al_2O_3 (12 vol.% ZrO_2) gray: Al_2O_3 ; white: ZrO_2 and Ni



Although the wetting angle and the thermal expansion of nickel and alumina are mismatched, previous studies have demonstrated that nickel can serve to reinforce alumina [18]. Since Ni has a face-centered cubic structure, it will plastically deform when cracks meet the Ni particles. At

the same time, the crest truncation of cracks will reduce the crack growth rate, and plastic deformation will absorb the energy to improve the toughness. Pull-out and plastic deforming plays an important role in the toughening mechanisms. The contribution to the increase in toughness

Fig. 5 SEM images of (a) indentation and crack propagation in the composite Al_2O_3 (12 vol.% ZrO_2 + 12 vol.% Ni) (a), (b) the fracture surface of the composite containing 12 vol.% ZrO_2 + 12 vol.% Ni



from the ZrO_2 and Ni particles can thus be added together, as long as the secondary phases are homogeneously distributed throughout the matrix. However, traditional processing methods, such as mixing and milling, do not always result in homogenous distributions of the reinforcing phases. There are a number of methods available to obtain these fine particles, including solution chemistry, vapor-phase synthesis and mechanical milling of solid phase. The results presented in this study show that zirconia and nickel particles with a narrow size distribution can be homogeneously dispersed in an alumina matrix by hydrothermal synthesis at relatively low temperatures [19].

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References

- Garvie RC, Hannink RHJ, Pascoe RT (1975) *Nature* (London) 258:703
- Claussen N (1976) *J Am Ceram Soc* 59(1–2):49
- De Aza Antonio H (2003) *J Am Ceram Soc* 86(1):115
- Ritchie RO (1988) *Mater Sci Eng* 103A:15
- Ashby MF, Blunt FJ, Bannister M (1989) *Acta Metallurg* 37:1847
- Claussen N (1984) In: Claussen N, Rühle M, Heuer AM (eds) *Advances in ceramics*. American Ceramic Society, Columbus, OH, pp 325
- Wang J, Stevens R (1988) *J Mater Sci* 23:804
- Chen RZ, Chiu YT, Tuan WH (2000) *J Eur Ceram Soc* 20:1901
- Vekinis G, Sofianopoulos E, Tomlinson WJ (1997) *Acta Mater* 45(11):4651
- Kim BN, Hiraga K, Sakka Y (2001) *Nature* 413:288
- James HA, Sridhar V, Seung-Beom C et al (1998) United States Patent, US005759213A
- Gibson CP, Kathy JP (1995) *Science* 267:1338
- Messing GL, Kumagai M (1989) *J Am Ceram Soc* 72(1):40
- Srdic VV, Radonjic L (1997) *J Am Ceram Soc* 80(8):2056
- Thevenot F, Homerin P (1992) In: Thevenot F (ed) *Ceramiques composites a Particules. Cas du Frittage-Reaction (FORCE-RAM)*. Septima, Paris, France, p 39
- Davidge RW, Green TJ (1968) *J Mater Sci* 3:629
- Evans AG, Charles EA (1976) *J Am Ceram Soc* 59:371
- Lieberthal M, Kaplan WD (2001) *Mater Sci Eng A* 302(1):83
- Mills H, Blackburn S (2000) *J Eur Ceram Soc* 20:1085