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Minimum amount of nano-sized nickel particles to enhance the strength of alumina

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Abstract

Previous studies demonstrated that the strength of alumina could be enhanced by incorporating >5 vol.% nano-sized nickel particles. In the present study, the possibility of using a much smaller amount, <0.5 vol.%, of nano-sized Ni particles to improve the mechanical properties of Al_2O_3 is explored. As the Ni content is low, the densification of Al_2O_3 is affected little and the Ni inclusions remain small after pressureless sintering at 1600 °C. The presence of Ni inclusions can refine the matrix grains; the strength of Al_2O_3 matrix is consequently enhanced.

Keywords: B. Nanocomposites; Grain size; C. Strength; D. Al_2O_3

1. Introduction

The strength of ceramics can be enhanced through the refinement of the microstructure.[1,2] One of the most effective methods to reduce the grain size is through the addition of second phase particles. Most previous studies added more than 5 vol.% inclusions to prohibit the growth of matrix grains.[3–5] Two penalties accompany the addition of a large amount of second phase. The first penalty is the drop of sintering activity.[5] Expensive processing techniques, such as hot-pressing, are usually needed to achieve densification.[3] The second one is the coarsening of the inclusions during sintering. The possibility of preparing the nanocomposite is often ruined due to such a coalescence process.[4] In order to avoid these penalties, the alternative of using a smaller amount of second phase is explored in the present study. The success of this alternative is evaluated by the measurement of strength.

In the present study, the Al_2O_3–Ni system is used as the model system to evaluate the feasibility of using a very small amount of second phase to tailor the microstructure. The solubility between Al_2O_3 and Ni is very low.[3–5] Furthermore, the strength of Al_2O_3 is enhanced significantly by adding nano-sized Ni particles. For example, the strength of an alumina has been enhanced by 54% after the addition of 5 vol.% of 100 nm Ni particles.[4] However, the coarsening of nano-sized Ni particles, especially above the melting point of Ni (1453 °C), is very fast during the densification process.[5] Therefore, it imposes serious challenges for the preparation of Al_2O_3/Ni nanocomposites. In the present study, a very small amount, 0.03–0.21 vol.%, of nano-sized Ni particles is added into Al_2O_3. The nanocomposites are prepared by pressureless sintering at a temperature of 1600 °C. The microstructure-strength relationship of the nanocomposites is determined.

2. Experimental

An alumina (TM-DAR, Taimei Chem. Co. Ltd., Tokyo, Japan) powder was milled by ball milling in de-ionized water for 24 h. The milling media used was yttria-stabilized zirconia balls. Ammonia was added drop by drop into the slurry to reach a pH value of 9.2. After soaking for 10 min, the slurry was filtered, the powder washed and dried. Various amounts (0–210 g) of nickel nitrate, $Ni(NO_3)_2{\cdot}6H_2O$ (Showa Chem. Co., Japan), was added into distilled water. The pH value of the nickel nitrate solution was also adjusted to 9.2. The alumina powder with the amount of 300 g was poured into the nickel nitrate solutions (1500 cm^3) and then stirred for 30 min. The Ni^{2+} ion could then be adsorbed onto the surface of the Al_2O_3 particles. The resulting powder

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mixtures after coating were filtered and washed with water for several times. The powder mixtures were reduced in pure hydrogen at 550 °C for 1 h, followed by ball milling in ethyl alcohol for 24 h. A pure Al_2O_3 powder was also prepared with the same technique. The amount of Ni in the powder mixtures was determined by using the inductive coupled plasma-atomic emission spectroscopy (ICP-AES, 3000DV, Perkin-Elmer, Optima, USA).

Green compacts with the dimensions of 7 mm × 6 mm × 50 mm were formed by uniaxially pressing at 44 MPa. The compacts were then sintered within a covered graphite mold at 1600 °C for 1 h. The heating and cooling rates were 5 °C/min. A graphite powder was also used to cover the green compacts. A reducing atmosphere, carbon monoxide mainly, was generated during sintering. The final density of the specimens was determined by the Archimedes method. Thermal etching was conducted at 1450 °C for 1 h to reveal the grain boundaries. The microstructure was observed by using scanning electron microscopy (SEM). Polished surfaces were prepared by grinding and polishing with diamond paste to 3 μm and with silica suspension to 0.05 μm. The line intercept technique was used to determine the size of matrix Al_2O_3 grains. More than 200 grains were counted.

The sintered rectangular bars were machined longitudinally with a 325 grit resin-bonded diamond wheel at a depth of 5 μm/pass. The final dimensions of the specimens were 3 mm × 4 mm × 36 mm. The strength of the specimens was determined by four-point bending with the upper and lower spans of 10 and 30 mm, respectively. The rate of loading was 0.5 mm/min. The fracture toughness was determined by the single-edge-notched-beam (SENB) technique. The notch was generated by cutting with a diamond saw. The width of the notch was approximately 0.3 mm. The elastic modulus of the specimens was determined with an ultrasonic technique at 5 MHz.

3. Results

The ICP analysis detects only 0.03–0.21 vol.% Ni in the Al_2O_3-Ni powder mixtures (see Table 1). Fig. 1 shows the green density and fired density of the Al_2O_3/Ni composites as a function of Ni content. Due to the fact that the Ni content is very low, the green density and final density of the composites are very similar to each other. The elastic modulus of alumina decreases slightly as a small amount of Ni is added. The decrease of the elastic modulus can be related to the presence of Ni inclusions.

Table 1
Nickel content, final density and elastic modulus of the Al_2O_3/Ni composites

Ni content (vol.%)	Relative density (%)	Elastic modulus (GPa)
0	99.9	423
0.03	99.5	417
0.12	99.5	416
0.13	99.3	416
0.15	99.2	411
0.21	99.0	407

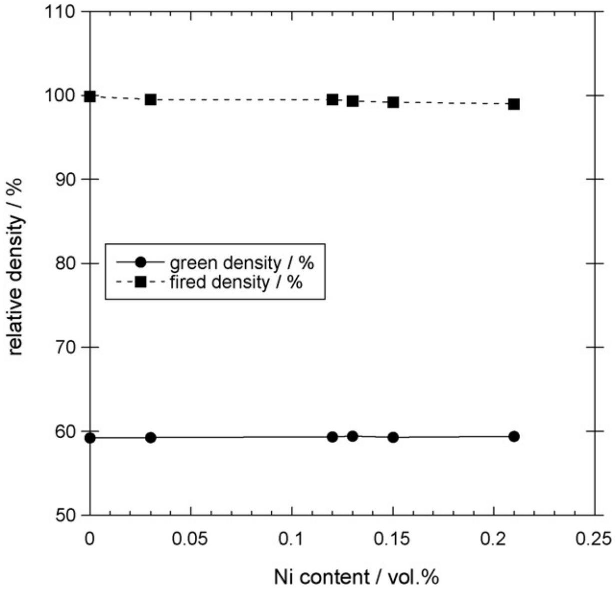

Fig. 1. Green density and sintered density of Al_2O_3/Ni composites as function of Ni content.

Fig. 2 shows the SEM micrographs of the fracture surface of composites. Though the amount of Ni added is very small, the size of Al_2O_3 grains decreases significantly with the increase of Ni content. Furthermore, the amount of transgranular fracture increases with the increase of Ni content. Fine Ni particles with the size around 100 nm can be found at the grain boundaries of Al_2O_3. As the Ni content is as small as 0.03 vol.%, only several fine Ni particles can be found for many Al_2O_3 grains (see Fig. 2b). The number of Ni particles increases significantly with increasing Ni content. Almost every Al_2O_3 grain in the Al_2O_3/0.13% Ni composite displays at least one Ni particle at its own grain boundary. As the Ni content increases from 0.03 to 0.21 vol.%, the size of the Ni particles remains around 100 nm. Fig. 3 shows the size of Al_2O_3 grains as a function of Ni content. By adding 0.13 vol.% Ni, the size of Al_2O_3 grains reduces by 50%. Fig. 4 shows the flexural strength of the composites as a function of Ni content. The strength of alumina is enhanced by 35% and 48% as only 0.13 and 0.21 vol.% nano-sized Ni particles are, respectively, added. All the specimens, including the pure alumina specimens, were prepared by pressureless sintering at 1600 °C for 1 h. The size of the Al_2O_3 grains in the pure alumina specimen is large; the strength of the specimen is thus low. The benefit of using fine Ni inclusions to tailor the microstructure is demonstrated. Fig. 5 shows the fracture toughness of the composites as a function of Ni content. The toughness of alumina is enhanced only by 6% and 17% as 0.13 and 0.21 vol.% Ni are added, respectively.

4. Discussion

The amount of Ni inclusions used in the present study to strengthen Al_2O_3 is lower than 0.5 vol.%. Though the Ni content is low, the coarsening of the Ni inclusions during sintering

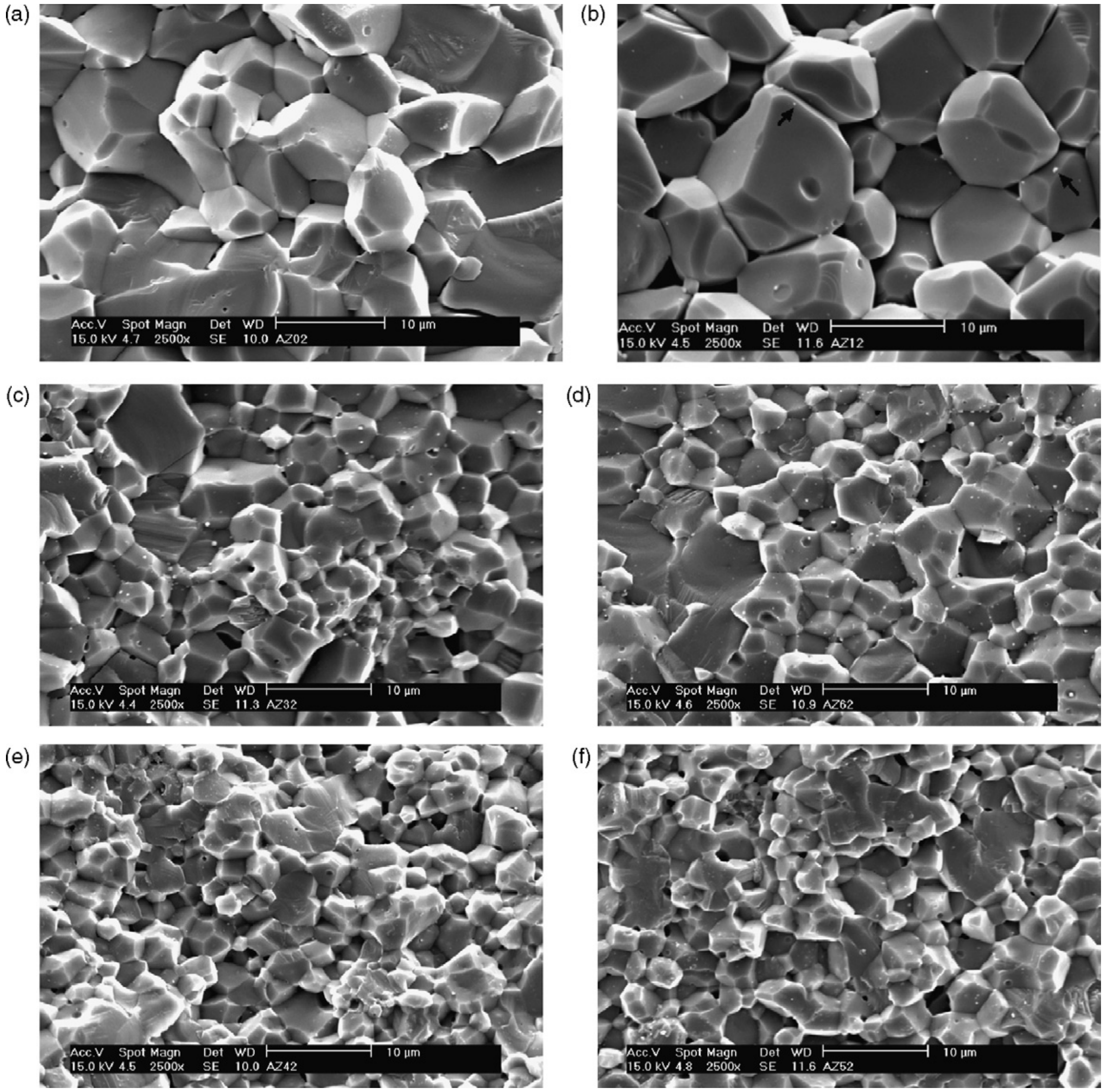

Fig. 2. Typical micrographs of the composites containing: (a) 0, (b) 0.03, (c) 0.12, (d) 0.13, (e) 0.15 and (f) 0.21 vol.% Ni. The white fine particles at the grain boundaries of Al_2O_3 are Ni inclusions. Several Ni inclusions in (b) are arrowed.

is limited. The size of the Ni inclusions is around 100 nm in all the Al_2O_3/Ni composites. Due to the fact that the Ni inclusions are much smaller than that of Al_2O_3 grains, the number of fine Ni inclusions is much higher than that of Al_2O_3 grains. However, the Ni inclusions can be found on the fracture surface of Al_2O_3/0.03% Ni composite are sparse (see Fig. 2b), implying that many Ni inclusions are present within the Al_2O_3 matrix grains. Furthermore, the size of Al_2O_3 grains is little changed due to the presence of 0.03 vol.% Ni particles. The strength of the composite is thus very close to that of the pure Al_2O_3 specimen (see Fig. 4). It suggests that an amount of 0.03 vol.% is too low to prohibit the growth of grains.

There are many nano-sized Ni inclusions found in the Al_2O_3/0.13% Ni composites (see Fig. 2d). Many Ni inclusions are found locating at the boundaries of Al_2O_3 grains. Furthermore, at least one Ni inclusion is found for most Al_2O_3 grain boundaries. The size of Al_2O_3 grains in the Al_2O_3/0.13% Ni composites reduces significantly from 10.1 (for pure Al_2O_3) to 5.3 μm. It indicates that an amount as low as 0.13 vol.% of Ni is sufficient to inhibit the movement of most grain boundaries. As the Ni content becomes higher than 0.13 vol.%, the strength of Al_2O_3/Ni composites is further enhanced with the increase of Ni content. Fig. 6 shows the strength of the nanocomposite as a function of the size of Al_2O_3 grains. It demonstrates that the Ni addition is effective to refine the microstructure of Al_2O_3. The slope of the straight line shown in the figure is $-1/2$, indicating that the strength of the nanocomposites follows the Griffith-Orowan relationship.[6] The strengthening effect can thus be related to the microstructure refinement. Though the size of Al_2O_3 grains decreases with increasing Ni content, the amount of transgranular fracture increases with Ni content. It indicates that the grain boundary strengthening mechanism[7,8] also contributes partly to the strength enhancement for the nanocomposites.

It is of interest to estimate the minimum amount of nano-sized Ni particles needed to prohibit the grain growth of Al_2O_3 grains. Assuming that there are n inclusions at one grain boundary as the case shown in Fig. 7, the volume fraction of the inclusions

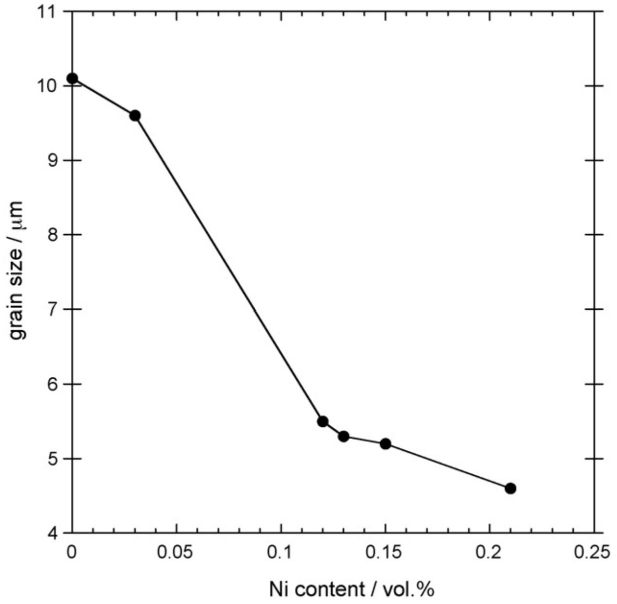

Fig. 3. Size of Al_2O_3 grains in the composites as function of Ni content.

can be estimated as

$$F = n\left(\frac{d}{G}\right)^3\left(\frac{14}{2}\right) \quad (1)$$

where F is the volume fraction, d the inclusion size and G is the grain size. There are 14 faces for each polyhedron; therefore, a constant 14/2 is used in the above equation. The minimum volume fraction corresponds to the case that the number of inclusion at each grain boundary is one ($n = 1$). For the case that $G = 1$ μm and $d = 100$ nm, the minimum volume fraction is only 0.7 vol.%. Furthermore, the minimum volume fraction drops quickly with the increase of grain size.

The equation above demonstrates that the minimum amount needed to prohibit the growth of matrix grains depends strongly

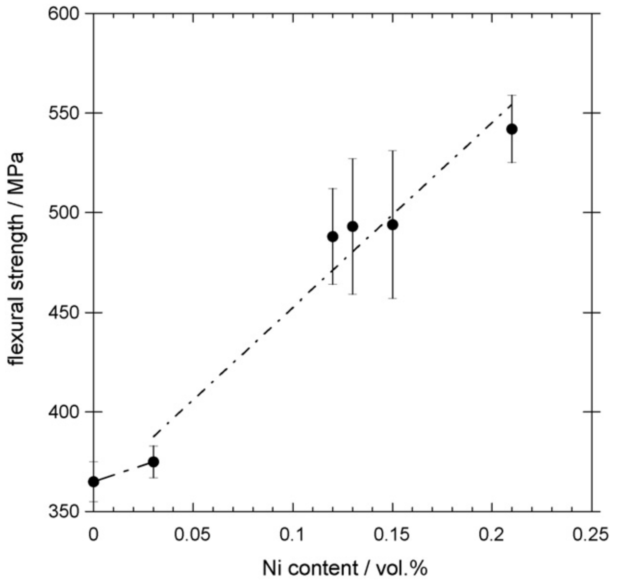

Fig. 4. Strength of the Al_2O_3/Ni composites as function of Ni content.

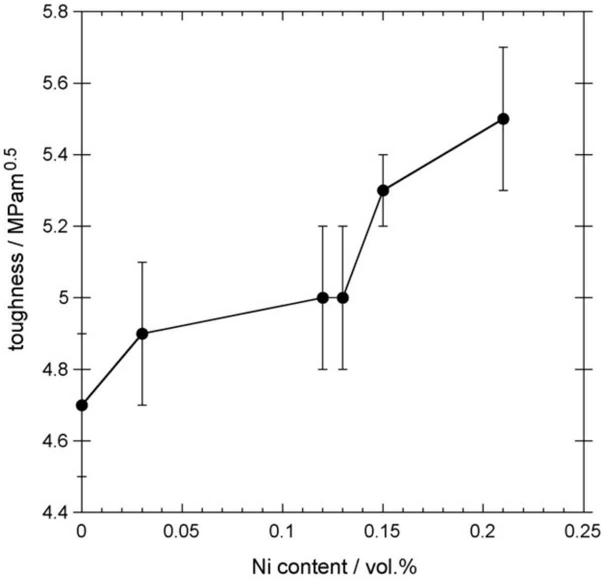

Fig. 5. Toughness of the Al_2O_3/Ni composites as function of Ni content.

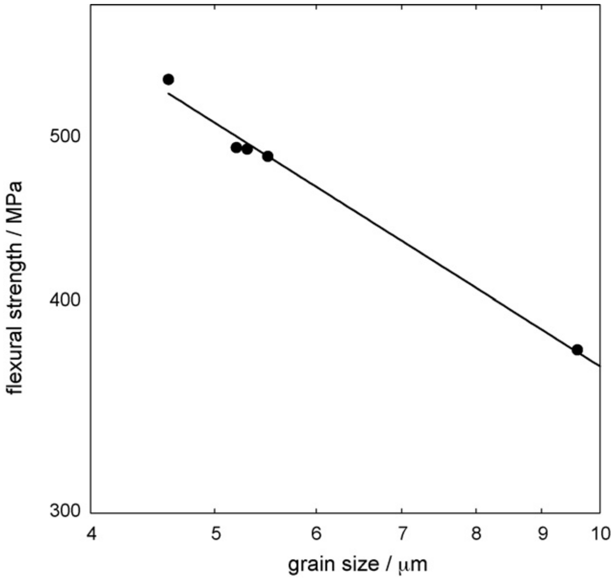

Fig. 6. Strength of Al_2O_3/Ni composites as function of Al_2O_3 grain size.

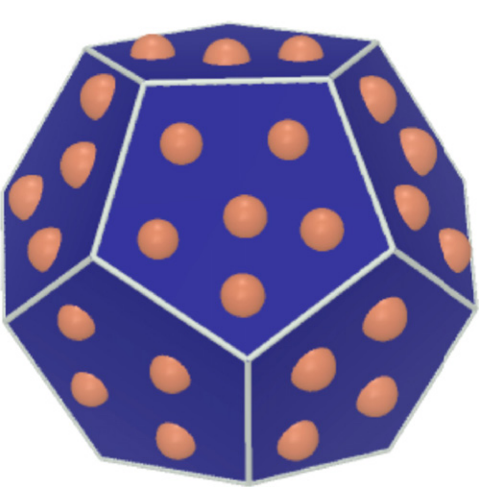

Fig. 7. Schematic of a grain with inclusions at its boundaries.

on the ratio of inclusion size over grain size. For the Al_2O_3/Ni nanocomposites prepared in the present study, the size of Ni inclusions is around 100 nm, the ratio of inclusion size over grain size varies from 0.02 to 0.1. The equation suggests an amount below 0.7 vol.% is enough to deliver a refined microstructure. The experimental result matches well with the analysis. As the number of inclusions at each grain boundary is higher than unity, $n > 1$, the capability of the inclusion to prohibit the growth of matrix is further enhanced. Therefore, $n = 1$ can be treated as the minimum value needed to improve the strength of composite.

However, there are two limits on the minimum amount of inclusion. Firstly, the inclusion content has to be higher than the solubility of inclusion in matrix. Secondly, the inclusion should not breakaway from the grain boundary. However, both the boundary of matrix grain and inclusion can move during sintering. As the velocity of grain boundary, v_b, is much higher than that of inclusion, v_i, as shown in the following equation.

$$v_b > v_i^{\max} \tag{2}$$

the breakaway can take place. By adopting the relationships for the separation between pore and grain boundary,[9] the criteria for the breakaway can be estimated. For the grain boundary, its mobility is controlled by the diffusion across the grain boundary, D^*, the Boltzmann's constant, k, and the absolute temperature, T. The force on the grain boundary is controlled by the grain boundary energy, γ_{gb}, and grain size, G. The velocity of boundary, v_b, can then be expressed as,[9]

$$v_b = M_b F_b = \frac{D^*}{kT}\frac{\gamma_{gb}}{G} \tag{3}$$

The movement of the inclusion is a diffusional process, an effective diffusion coefficient, D_{eff}, to illustrate the mobility of the inclusion is used as,[10]

$$M_i = \frac{D_{eff}\Omega}{kTd^m} \tag{4}$$

where Ω is the volume of controlling ions, m a constant depending on the mechanism. The force on the inclusion is also provided by the grain boundary energy. The force on an inclusion is expressed as.[9]

$$F_i = 2\pi d\gamma_{gb} \tag{5}$$

The velocity of particle, v_i, is

$$v_i = M_i F_i = \frac{D_{eff}\Omega}{kTd^m} 2\pi d\gamma_{gb} \tag{6}$$

By comparing Eqs. (3) and (6), the following equation is obtained,

$$\frac{D^*}{2\pi D_{eff}\Omega} > \frac{G}{d^{m-1}} \tag{7}$$

The analysis above demonstrates that there is a critical value for the ratio of grain size over inclusion size. Since the coarsening of inclusions is limited as the second phase amount is low, the breakaway of the grain boundary and inclusion is virtually controlled by the growth of matrix grains. From the microstructure observation, the critical size for the Al_2O_3 grain boundary to breakaway from the Ni inclusion is around 10 μm. The analysis above demonstrates that there is a critical amount for the second phase to prohibit the coarsening of matrix grains. The critical amount of the second phase is a function of the ratio of grain size over particle size. For the present system under the processing conditions used, the critical amount of inclusions is only 0.1 vol.%.

The toughness of Al_2O_3/Ni also increases with the increase of Ni content (see Fig. 5); though the increase is relatively marginal comparing to strength increase. The Al_2O_3–Ni interface is relatively weak,[4] the presence of such weak interface encourages the deflection of crack path.

5. Conclusions

In the present study, the Al_2O_3/Ni nanocomposites with Ni content smaller than 0.21 vol.% are prepared by pressureless sintering. The strength of the Al_2O_3/0.21% Ni composite is 50% higher than that of monolithic Al_2O_3. Both the microstructure refinement and grain boundary strengthening contribute to the strength increase. The implications can be drawn from the present study are:

(1) The amount of second phase needed to increase the strength of composite depends strongly on the sizes of matrix grains and of second phase.
(2) As far as the preparation of nanocomposite is concerned, the amount of nano-sized particles can be very low. As the amount of the nano-sized particles is low, the densification of the nanocomposite is no longer difficult.

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