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Preparation of Al_2O_3/Ni Composites by Pressureless Sintering in H_2

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Abstract: Brittle solids can be toughened by introducing ductile inclusions. In the present study, Al_2O_3/Ni composites are prepared by reducing Al_2O_3 and NiO powder mixtures or by reducing Al_2O_3/$NiAl_2O_4$ compacts in hydrogen. The flexural strength and fracture toughness of the Al_2O_3/Ni composites are determined. Due to the thermal expansion mismatch between alumina and nickel, a circumferential crack is formed at the interface as the nickel inclusion is larger than 2 μm. The toughness of the composites is enhanced by a crack bridging mechanism or by microcrack toughening. However, the strength of the Al_2O_3/Ni composites is decreased significantly as the microcracks are formed.

1 INTRODUCTION

Brittle ceramics can be toughened by the incorporation of ductile metallic inclusions. This approach has been successfully employed in several systems.[1–4] Previous studies[4–6] have indicated that crack bridging is usually the dominant mechanism. In order to activate the bridging mechanism, the metallic inclusions need to be firmly bonded to the brittle matrix. If the ductile inclusion is weakly bonded to the matrix, the crack will propagate along the interface and the contribution of the ductile phase to the toughening effect will be negligible.

If the thermal expansion coefficient of the ductile inclusions is larger than that of the brittle matrix, the ceramic/metal interface is subjected to a radial tensile stress. If the size of the inclusion is bigger than a critical value, the microcrack at the interface is generated spontaneously as the composite cools from the firing temperature.[7] The ductile inclusions can no longer be plastically deformed due to the presence of microcracks at the interface. However, the presence of microcracks at the interface can deviate the propagation of a major crack.[8] The toughness may also be enhanced due to the presence of a microcrack.

The nickel-toughened-alumina system has been investigated by Tuan and Brook.[4,9] In their studies, the Al_2O_3/Ni composites were prepared by pressureless sintering in carbon monoxide. Depending on the processing conditions employed, amorphous carbon or graphite inclusions were found at the interface or within the nickel inclusions, respectively.[10] The toughness of the composites shows a strong dependence on the resulting microstructure. The strength of the composites was not measured in their studies. In the present study, the sintering behaviour of Al_2O_3/Ni composites in hydrogen is investigated. The resulting strength and toughness are determined. The correlations between the microstructure and the mechanical properties are established.

2 EXPERIMENTAL

Three processing routes were used to prepare Al_2O_3/Ni composites, Fig. 1. For process 1, alumina (TM-DR, Taimei Chem. Co. Ltd., Tokyo, Japan) and 0–30 vol% nickel oxide (Johnson Matthey Co., UK) were tumble milled together first. The grinding media used was zirconia balls. The slurry of the powder mixtures was dried with a rotary evaporator. The dried lumps were crushed and passed through a plastic sieve. Powder compacts were formed by uniaxially pressing at 18 MPa then by cold-isostatic pressing (CIP) at 250 MPa. The sintering was performed in hydrogen.

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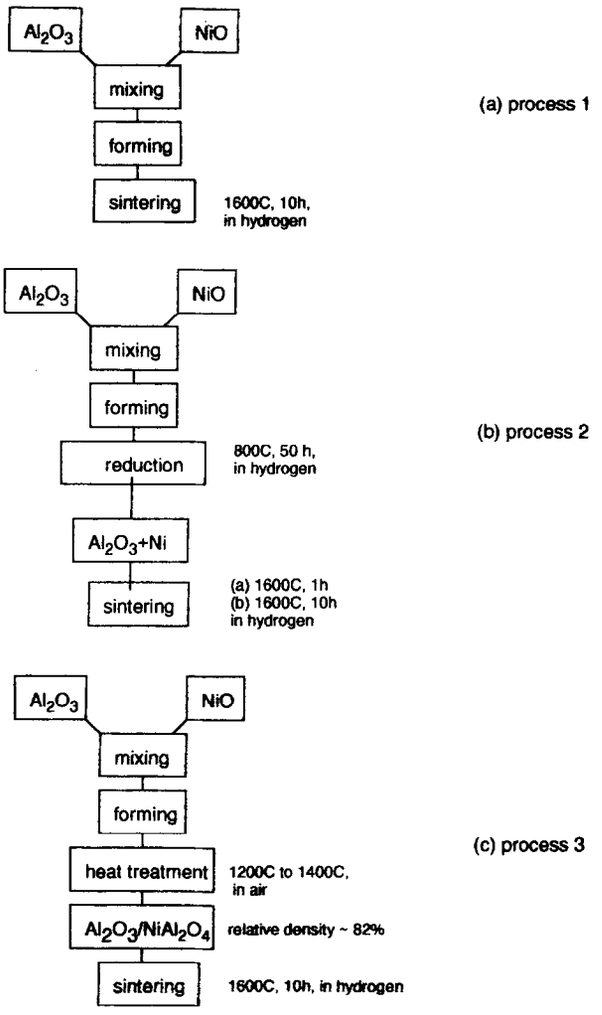

Fig. 1. The processing routes used for the preparation of Al_2O_3/Ni composites.

The heating and cooling rates were 5°C/min. For process 2, the procedures were similar to those of process 1, except the powder compacts were first reduced in hydrogen at 800°C for 50 h. The compacts were then sintered at 1600°C for 1 h (process 2a), or at 1600°C for 10 h (process 2b). For process 3, alumina and nickel oxide powder mixtures were first heat treated at 1200–1400°C in air for 1 h. Compacts composed of Al_2O_3 and $NiAl_2O_4$ were formed after the heat treatment step. A suitable temperature was chosen to prepare the Al_2O_3/$NiAl_2O_4$ compacts with a relative density of 82%. If the relative densities of the compacts were higher than 82%, the compacts were not able to be reduced fully to Al_2O_3/Ni composites within 10 h. If the relative densities of the compacts were lower than 82%, the compacts were broken into pieces after the reduction step.

The sintered specimens were machined longitudinally with a 325 grit resin-bonded diamond wheel at cutting depths of 5 μm/pass. The final dimensions of the specimens were (2 × 5 × 37) mm^3. The flexural strength of the specimens was determined

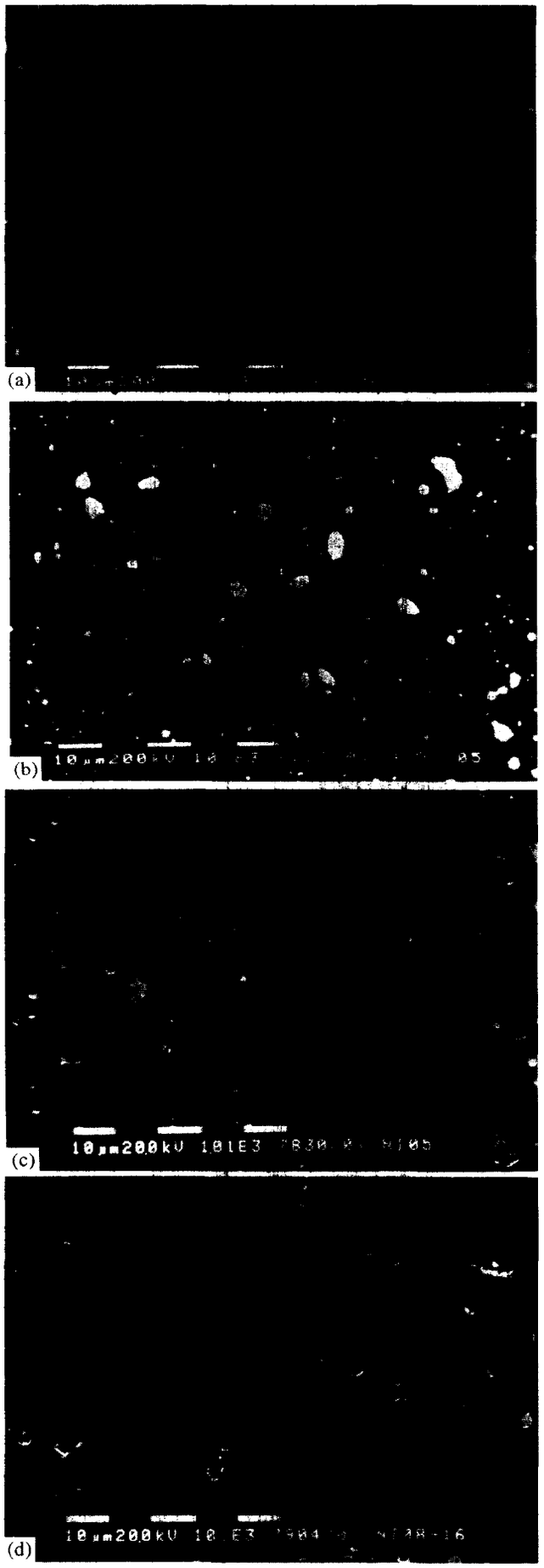

Fig. 2. The microstructures of the composites containing 5 vol% Ni. The composites are prepared by (a) process 1, (b) process 2a, (c) process 2b and (d) process 3.

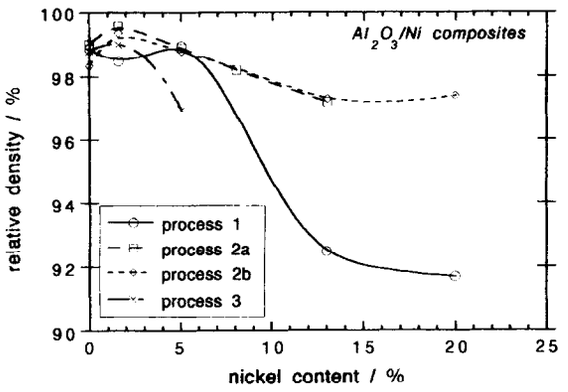

Fig. 3. The density of the composites as a function of nickel content.

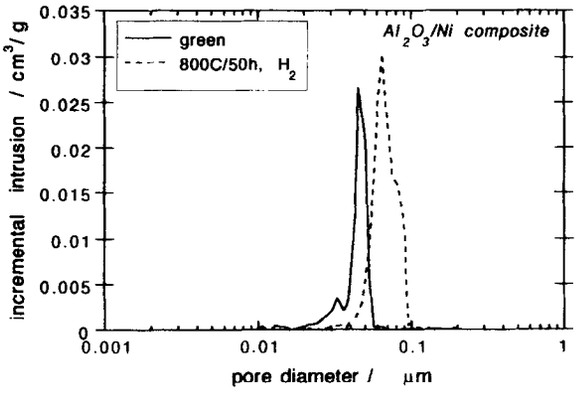

Fig. 4. The pore size distribution for the green and heat treated Al_2O_3/Ni powder compact.

by the 4-point bending technique at ambient conditions. The upper and lower spans were 10 mm 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 final density was determined by the water displacement method. Before submerging the specimen in water, a wax was applied to the surface to prevent water penetration. The polished surfaces were prepared by grinding and polishing with diamond paste to 6 μm and with silica slurry to 0·05 μm. Microstructural observation was conducted by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The size of the nickel inclusions was determined by using the linear intercept technique. Phase identification was performed by X-ray diffractometry (XRD) with CuK_α radiation.

3 RESULTS AND DISCUSSION

For the composites prepared by process 1, the XRD results show that nickel aluminate spinel ($NiAl_2O_4$) is first formed as the powder mixtures are heated in hydrogen. The spinel can then be fully reduced in hydrogen to alumina and nickel at 1600°C for 10 h. Al_2O_3/Ni composites are thus prepared by sintering at 1600°C for 10 h in hydrogen. For the composites prepared by process 3, only the composites containing less than 5 vol% Ni can be fully reduced in hydrogen at 1600°C for 10 h. The microstructures of the composites containing 5 vol% nickel are shown in Fig. 2.

The relative density of the composites is shown as a function of nickel content in Fig. 3. Since the sintering temperature is higher than the melting temperature of nickel, 1453°C, nickel inclusions are melted during sintering. However, the wetting of alumina by the nickel melt is poor.[11] Furthermore, the solubility of alumina in nickel is negligible.[10] The nickel melt is thus not an effective liquid phase sintering aid. The presence of nickel inclusions prohibits the densification of the ceramic matrix. The density of the composites is therefore decreased with the increase of the nickel content. The density of the composites prepared by process 2 is the highest. The composites have been heat treated at 800°C for 50 h first. Nickel oxide particles are reduced completely to nickel particles after this treatment. As indicated by Chu *et al.*,[12] by employing a heat treatment at 800°C for 50 h first, alumina can be sintered to a higher density. They suggested that a more uniform pore size distribution can result from the heat treatment. The pore size distribution of the powder compacts before and after heat treatment is shown in Fig. 4. The small pores of the Al_2O_3/Ni composite have disappeared after the heat treatment. However, contrary to the finding of Chu *et al.*[12] the pore size distribution of the composites is broadened after the heat treatment. This may result from the decomposition of nickel oxide. Nevertheless, the heat treatment step is beneficial to the preparation of the composites. For the composites prepared by processes 1 and 3, nickel aluminate spinel is formed first before the densification is started. As the reaction,

$$Al_2O_3 + NiO = NiAl_2O_4 \quad (1)$$

takes place, a 4 vol% expansion occurs with the reaction. The densification of the spinel-containing composites is retarded due to the formation of the spinel. Therefore, high density is difficult to achieve by employing processing routes 1 and 3. The size of nickel inclusions is shown as a function of nickel content in Fig. 5. The inclusion in the composites prepared by process 2 is the smallest.

The strength and the toughness of Al_2O_3/Ni composites are shown as a function of the nickel content in Figs 6 and 7, respectively. Each point in the figures represents the average values of 3–4 specimens. The strength and toughness of the

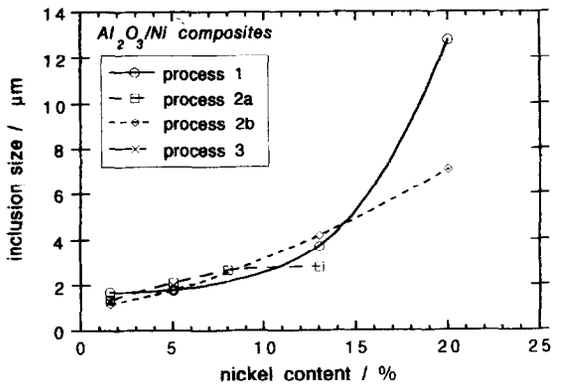

Fig. 5. The size of nickel inclusions found in the composites shown in Fig. 3.

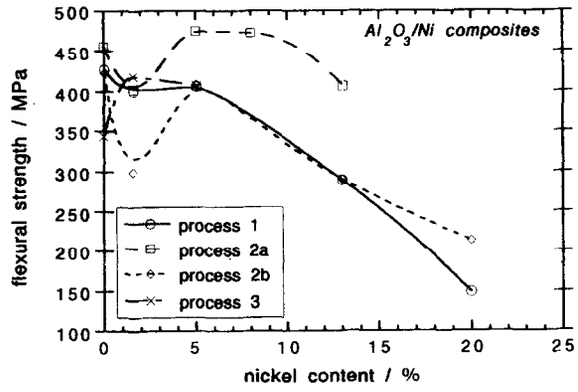

Fig. 6. The flexural strength of the composites in Fig. 3 as a function of nickel content.

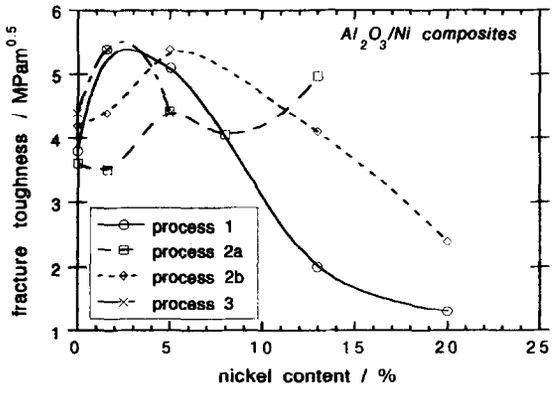

Fig. 7. The fracture toughness of the composites in Fig. 3 as a function of nickel content.

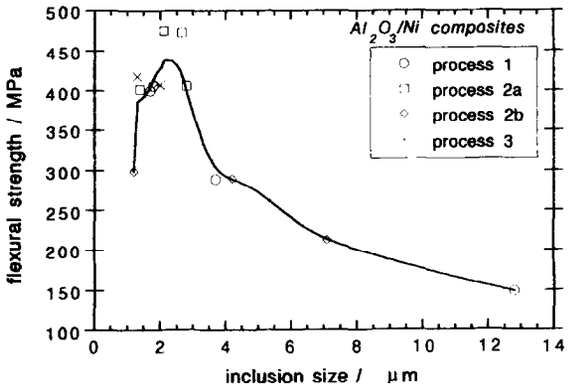

Fig. 8. The flexural strength of the composites as a function of inclusion size.

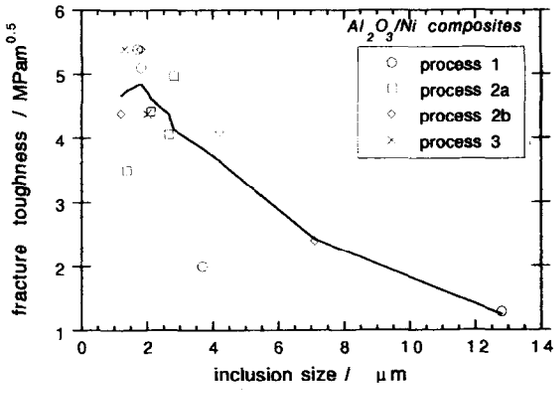

Fig. 9. The fracture toughness of the composites as a function of inclusion size.

Fig. 10. Typical microstructure observed for the Al_2O_3/Ni composites. The microcrack is arrowed. A stands for alumina.

composites are shown as a function of the inclusion size in Figs 8 and 9. If the inclusion size of the composites is larger than 2 μm, the strength and toughness are decreased significantly. From microstructural observations (Fig. 10), circumferential microcracks are observed around the inclusions which are larger than 2 μm. It indicates that the critical size for the nickel inclusions is 2 μm. Furthermore, no reaction phase can be observed at the interface.

Typical interactions between crack and nickel inclusions are shown in Fig. 11. The crack is bridged by the small inclusion and deflected by the large inclusion. As the coarse inclusion is larger than 2 μm, the crack propagates along the interface due to the presence of microcracks. If the inclusion is smaller than the critical value, the interface is strong enough to sustain the thermal stress. The fine inclusion can thus be plastically deformed. Therefore, for the composites containing

Fig. 11. The interactions between a crack and nickel inclusions.

inclusions smaller than 2 μm, the toughness is enhanced by a crack bridging mechanism. For the composites containing inclusions larger than 2 μm, microcracks exist within the microstructure (Fig. 10). By assuming one microcrack per inclusion,[13] the microcrack density, d_{mc}, can be expressed as[13]

$$d_{mc} = \frac{3F}{4\pi r^3} \tag{2}$$

where F is the volume fraction and r the radius of the inclusion. The toughness of the composites containing inclusions larger than 2 μm is shown as a function of microcrack density in Fig. 12. The figure suggests that the composites are toughened due to the presence of microcracks. As far as the strength of the composites is concerned, the presence of microcracks degrades the strength. Therefore, to optimize the mechanical properties of Al_2O_3/Ni composites, the inclusion size should remain close to 2 μm.

4 CONCLUSIONS

The present study demonstrates that Al_2O_3/Ni composites can be prepared by reducing powder mixtures of Al_2O_3 and NiO or by reducing Al_2O_3/$NiAl_2O_4$ compacts in hydrogen. The presence of nickel inclusions retards the densification of the alumina matrix, the density of the composite is thus decreased with an increase of the nickel content. If the powder mixtures of Al_2O_3 and NiO are reduced to Al_2O_3 and Ni at 800°C first, nearly fully dense composites can then be prepared by sintering at 1600°C for 10 h in hydrogen. The strength and toughness of the Al_2O_3/Ni composites show a strong dependence on the inclusion size. Due to the thermal expansion mismatch, the critical size for nickel inclusions is 2 μm. The toughness of Al_2O_3/Ni composites is the highest if the inclusion size is roughly 2 μm. The presence of microcracks is beneficial to the toughness, although it is detrimental to the strength of the composites.

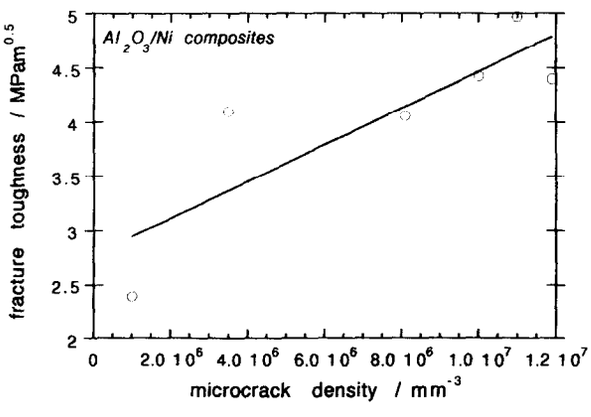

Fig. 12. The toughness of the composites containing inclusions larger than 2 μm as a function of microcrack density.

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