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Self-healing and mechanical properties of reinforced nickel-dispersed alumina hybrid nanocomposites

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Dense specimens of 5 vol%Ni/Al_2O_3 nanocomposites with fine grain size of Al_2O_3 and nano-Ni particles were fabricated by the pulsed current sintering technique. Vickers hardness, fracture toughness and bending strength of the nanocomposites were investigated at room temperature. Self-healing performance was evaluated at temperatures ranging 1100 ~ 1300 °C for 1 ~ 24 h. Bending tests were conducted on samples before and after heat-treatment in order to clarify the self-healing performance. As a result, fabricated sample achieved 995 MPa in bending strength and 6.1 MPam$^{1/2}$ in fracture toughness. Introduced cracks on sample surface completely disappeared after heat-treatment at 1100 °C for 24 h. However, only 80% of cracks disappeared after heat-treatment at 1200 °C for 1 h in air. Bending strength of samples that were introduced cracks recovered up to the level as high as that of sintered samples after heat-treatment at 1200 °C for 6 h in air.

Key words: Self-healing, Nanocomposites, Al_2O_3, $NiAl_2O_4$.

Introduction

Development of high-temperature materials has been one of key factors responsible for improvement in performance of gas turbine engines. The materials being used today are nickel and cobalt base superalloys. These superalloys can be operated at temperatures up to 1100 °C in which the superalloys almost reach to their melting temperature. Consequently, there is a strong need to develop materials which are able to withstand at temperature higher 1100 °C.

Ceramics are refractory materials, thus, suitable for high-temperature applications. Monolithic ceramics such as alumina (Al_2O_3), mullite (Al_2O_3-SiO_2), silicon nitride (Si_3N_4) have been known as potential candidates with advantages of high hardness, high mechanical strength and excellence heat resistance. However, these ceramics are brittle materials. They do not have adequate damage tolerance and fail catastrophically. Reinforcement of these ceramics by non-oxide phases such as nickel (Ni), cobalt (Co) and silicon carbide (SiC) could be a solution for the disadvantages [1-3]. Among of them, Ni-dispersed Al_2O_3 composites have been proposed due to possessing several outstanding properties such as self-healing, magnetic properties as well as excellent mechanical properties [4].

Our group has been studying the mechanism of self-healing function on nano-Ni/Al_2O_3 over the past few years [5-8]. Recovery of bending strength on Ni/Al_2O_3 was caused by self-healing of cracks on sample surface at high temperatures. The cracks were filled up by the oxidation product, $NiAl_2O_4$, via diffusion of Ni^{2+} and Al^{3+} along grain boundaries. This fact implies that self-healing function of Ni/Al_2O_3 could be accelerated by using finer Al_2O_3 grain size. In order to accelerate this phenomenon as well as improve mechanical properties of 5 vol% Ni/Al_2O_3, sample preparation of this material with very fine Al_2O_3 grain size was proposed.

In this study, 5 vol% Ni/Al_2O_3 hybrid nanocomposite was fabricated by pulsed electric current sintering (PECS) technique with finer α-Al_2O_3 powder and proper powder processing. Self-healing function was investigated at temperatures ranging from 1100 to 1300 °C for 1 ~ 24 h annealing in air. Bending tests were conducted with as-sintered, as-cracked and as-healed samples in order to estimate the recovery of mechanical strength.

Experimental Procedure

Specimen preparation of 5%vol Ni/Al_2O_3 nanocomposite was conducted in the following procedure. A slurry mixture containing $Ni(NO_3)_2 \cdot 6H_2O$ (Kojundo Chemical Laboratory Co. Ltd), α-Al_2O_3 (Taimei Chemicals Co. Ltd, TM-DAR, $d = 0.14$ μm) and distilled water was prepared by using ball-milling for 24 h. This slurry mixture was dropped into a glass tube which was pre-heated at 400 °C. The dried powder mixture then was dried ball-milled in a plastic bottle with Al_2O_3 balls for 3 h. A reduction process was conducted at 600 °C for 12 h in a stream of Ar-1%H_2 gas mixture. After reduction, the powder mixture was ball-milled again with Al_2O_3 balls

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and ethanol for 24 h in order to lessen agglomeration of the powder. After drying at 80 °C for 12 h in a drying oven, the powder mixture was sintered in a graphite die by PECS at 1200 °C for 5 min holding time under 50 MPa uni-axial pressure in vacuum.

Relative density of all the fabricated specimens attained at least 99% of the theoretical density. Fig. 1 shows fractured surface of the as-sintered sample. Ni particles, which could be observed as bright contrast dots, were homogeneously dispersed in Al_2O_3 matrix. Average particle size of Ni was approximately 100 nm, while that of Al_2O_3 was 500 nm.

Mechanical properties of the material such as relative density (R.D), Vickers hardness (H_v), fracture toughness (K_{IC}) and bending strength (σ_b) were evaluated through Archimedean method with toluene, Vickers hardness, Indentation fracture method [9] and three-point bending test, respectively.

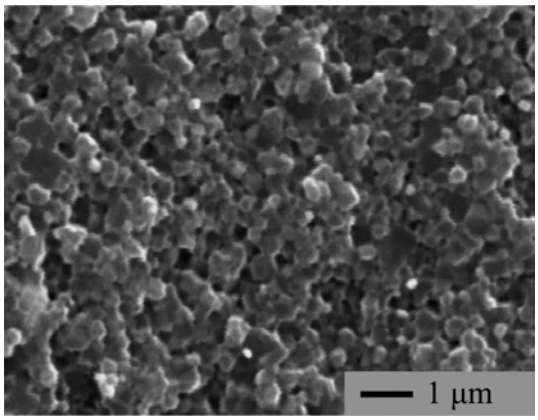

Fig. 1. SEM image shows fractured surface of as-sintered sample.

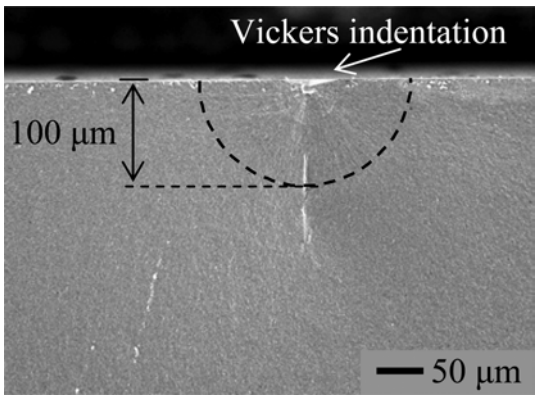

Fig. 2. SEM image of crack induced by the Vickers indentation observing from fractured surface.

In order to investigate self-healing performance and recovery of bending strength, three cracks were induced on polished surface for each sample by Vickers indentation at a loading of 49 N for 10 s. Average length and depth of cracks induced on sample surface were 200 μm and 100 μm, respectively (Fig. 2). Effectiveness of surface crack-disappearance after heat treatment at temperatures ranging from 1100 to 1300 °C for 1 ~ 24 h was estimated by scanning electron microscope (SEM) and X-ray diffraction (XRD) for phase identification.

Results and Discussion

Mechanical properties of Ni/Al_2O_3 composites in comparison with the other reported results [1, 8, 10-13] were summarized in Table 1. Depending on the starting materials and fabricating method, some materials achieved very fine Ni and Al_2O_3 grain size but had not completely densified yet [1, 10]. On the other hand, some materials had improvement in density, however grain growth occurred rapidly [11, 12]. By applying a proper fabrication and using very fine Al_2O_3 powder, the 5 vol% Ni/Al_2O_3 of this study was almost fully densified and resulting to very fine grain size after sintering. The nanocomposites achieved outstanding fracture toughness of 6.1 ± 0.5 $MPam^{1/2}$ and maintained very high level of bending strength, 995 ± 90 MPa.

Fig. 3 shows XRD patterns of sintered samples before and after heat-treatment in air in order to identify compounds formed on sample surface. Before heat-treatment, there were only two dominant substances that were α-Al_2O_3 and Ni detected on sample surface (Fig. 3d). After heat-treatment at 1100 °C for 24 h in air, appearance of $NiAl_2O_4$ significantly rose and replaced for the existence of Ni-metallic particle, as shown in Fig. 3c. Fig. 3b shows the intensity of $NiAl_2O_4$, which formed after heat-treatment at 1200 °C for 1 h, was almost similar to the term of sample after heat-treated at 1100 °C for 24 h. At 1200 °C for 6 h (Fig. 3b), there were some weak intensity peaks of Ni metallic particles

Table 1. Mechanical properties of Ni/Al_2O_3 fabricated by various methods.

Sample	Fabrication method	R.D. [%]	$d_{Al_2O_3}$ μm	d_{Ni} μm	K_{IC}/ $MPam^{1/2}$	σ_b/ MPa	H_v/ GPa
5%Ni/Al_2O_3 [This study]	PECS	> 99	0.5	0.1	6.1	995	20
5%Ni/Al_2O_3[8]	PECS	> 99	1.1	0.3	5.8	490	20
5%Ni/Al_2O_3 [10]	Pressureless	> 96	0.5	0.15	4.2	526	–
5%Ni/Al_2O_3 [1]	Hot press	> 98	0.64	0.1	3.5	1090	–
5.5%Ni/Al_2O_3 [11]	Hot press	> 98	1.2	0.6	4.1	500	–
5%Ni/Al_2O_3 [12]	PECS	> 98	1.4	0.3	3.2	650	16
α-Al_2O_3 [13]	Pressureless	> 98	5	–	3.5	380	15

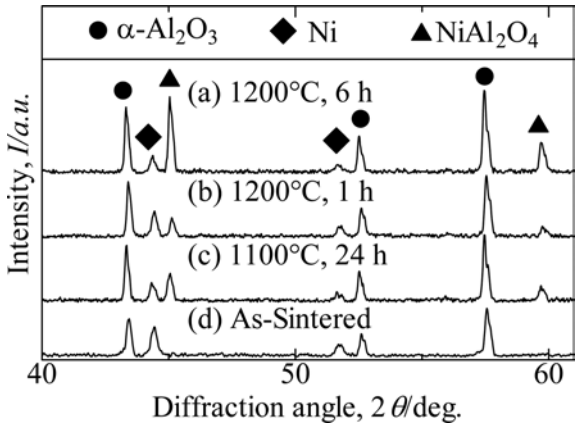

Fig. 3. XRD patterns of the sintered Ni/Al_2O_3 samples with and without heat-treatments.

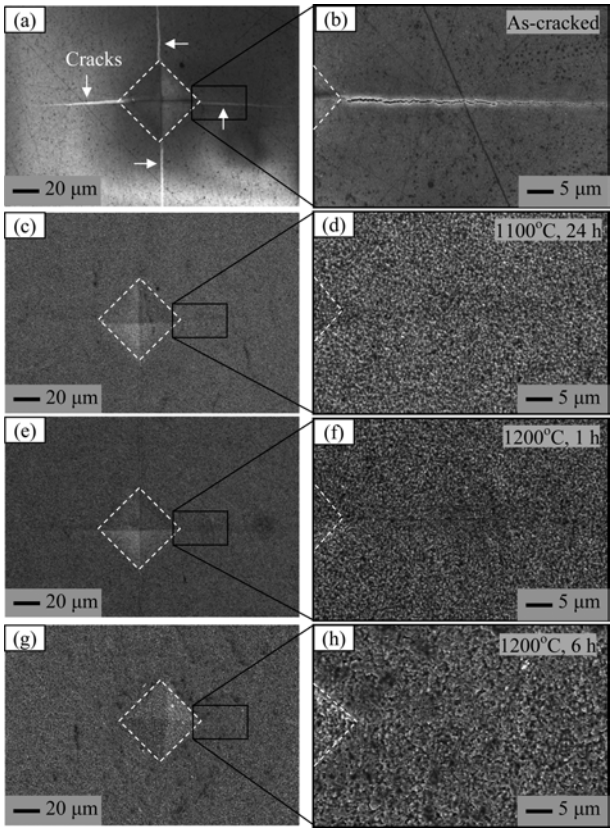

Fig. 4. SEM images of surfaces of as-cracked sample (a) and (b), sample heat-treated at 1100 °C for 24 h in air (c) and (d), sample heat-treated at 1200 °C for 1 h in air (e) and (f), sample heat-treated at 1200 °C for 6 h in air (g) and (h).

detected. Instead of that, $NiAl_2O_4$ that was attributed to be a key factor responsible for crack-healing rapidly formed and covered sample surface.

Fig. 4 shows SEM images of sample surfaces with introduced cracks before and after heat-treatment at various conditions. Dashed lines present the outline of Vickers indentation. Without heat-treatment, cracks that are indicated by white arrows could be observed clearly as shown in Fig. 4a. Length and width of these cracks were approximately 60 and 0.5 μm, respectively

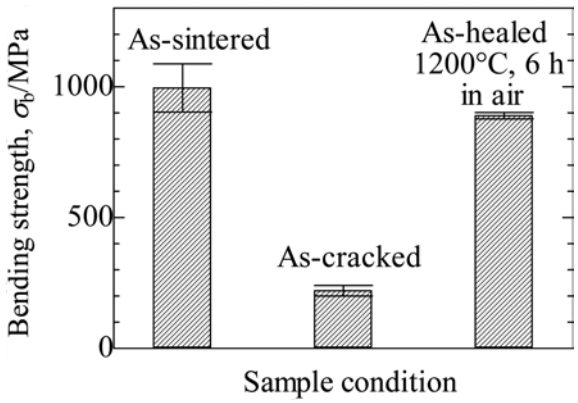

Fig. 5. Bending strength of as-sintered, as-cracked and as-healed samples.

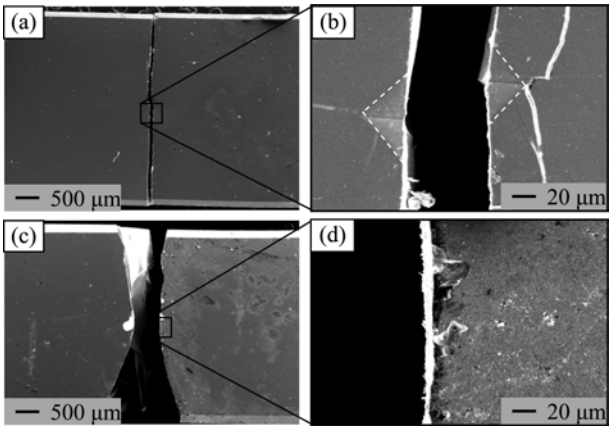

Fig. 6. SEM images of bending tested samples; as-cracked (a) and (b), as-healed at 1200 °C for 6 h (c) and (d).

(Fig. 4b). At 1100 °C, surface cracks completely disappeared after heat-treatment for 24 h (Fig. 4c and d). With shorter annealing time, cracks only partly disappeared at this condition. Heat-treatment at 1200 °C for 1 h, $80 \pm 14\%$ of cracks disappeared on sample surface, as shown in Fig. 4e and Fig. 4f. Increasing annealing time, cracks on sample surface completely disappeared as shown in Fig. 4g and Fig. 4h. According to Maruoka *et al*. [8], effectiveness of self-healing was depended on formation of $NiAl_2O_4$ which is referred to diffusion of Ni^{2+} along grain boundaries. Therefore, finer grain size of Al_2O_3 leads to accelerate self-healing performance. Besides, finer microstructure involves in formation of oxidation product more homogeneously on sample surface.

Bending tests were conducted on as-sintered, as-cracked and as-healed samples in order to estimate influence of surface crack-disappearance to recovery of flexure strength. Fig. 5 shows results of these bending tests. Bending strength of sintered samples was 995 ± 90 MPa in average. With three Vickers indentations introduced on sample surface, bending strength of as-cracked samples dropped to about 220 ± 15 MPa. By heat-treatment at 1200 °C for 6 h in air, bending strength of samples with the Vickers indentations recovered up

to 890 ± 12 MPa.

Fig. 6 shows SEM images observed on sample surface of bending tested samples. Figs. 6a and b show the fracture mechanism occurred on as-cracked samples. The Vickers indentation outlined by dashed lines indicates that the failure of as-cracked samples during bending test was originated along these indentations. After heat-treatment at 1200 ºC for 6 h in air, cracks induced by Vickers indentations were completely filled up by $NiAl_2O_4$. Figs. 6c and d show the fracture mechanism of as-healed samples was different from that of as-cracked sample. The failure of as-healed samples was originated in the region which was containing the Vickers indentations. This region was also the center of sample and under highest stress concentration. This fact implies that the mechanical strength of the cracked region was recovered up to the same level as that of region without cracks.

Conclusions

Consolidated samples of 5 vol% Ni/Al_2O_3 with high density and fine Al_2O_3 grain size were fabricated by PECS. Sintered samples achieved 995 MPa in bending strength and 6.1 $MPam^{1/2}$ in fracture toughness. Introduced cracks on sample surface completely disappeared after heat-treatment at 1100 ºC for 24 h. Finer microstructure of the material involved in improvement of self-healing performance. After heat-treatment at 1200 ºC for 6 h in air, bending strength of as-cracked samples recovered up to the level as high as that of sintered samples.

Acknowledgments

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