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*Research Article*

# Mechanochemical Synthesis and Rapid Consolidation of Nanocrystalline 3NiAl-$Al_2O_3$ Composites

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Nanopowders of 3NiAl and $Al_2O_3$ were synthesized from 3NiO and 5Al powders by high-energy ball milling. Nanocrystalline $Al_2O_3$ reinforced composite was consolidated by high-frequency induction-heated sintering within 3 minutes from mechanochemically synthesized powders of $Al_2O_3$ and 3NiAl. The advantage of this process is that it allows very quick densification to near theoretical density and inhibition grain growth. Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties. The relative density of the composite was 97%. The average Vickers hardness and fracture toughness values obtained were 804 kg/mm$^2$ and 7.5 MPa $\cdot$ m$^{1/2}$, respectively.

## 1. Introduction

NiAl has a high melting temperature (1711 K), good thermal conductivity (75 W/mK), low raw material cost, good oxidation resistance, and low density (5.91 g/cm$^3$). These properties make NiAl a promising candidate for use in the aircraft and automotive industries [1]. However, like many intermetallics, use of NiAl in industry has been limited due to low fracture toughness, around 5.4 MPa m$^{-1/2}$ and a low hardness of about 430 HV [1–3]. The mechanical properties can be improved significantly by reinforcing NiAl with hard ceramic particles such as $Al_2O_3$ [3] and by fabrication of nanostructured composite [4]. $Al_2O_3$ has a density of 3.98 g/cm$^3$, a Youngs' modulus of 380 GPa, excellent oxidation resistance and good high-temperature mechanical properties [5]. Hence, a microstructure consisting of NiAl and $Al_2O_3$ may have sufficient oxidation resistance and high-temperature mechanical properties to be a successful high-temperature structural material. NiAl composites have been prepared by several methods, including high-energy ball milling, pressureless sintering, and pulse plasma sintering [3, 6].

Nanocrystalline powders were recently developed by such thermochemical and thermomechanical processes as the spray conversion process (SCP), coprecipitation, and high-energy milling [7–9]. However, the grain sizes in sintered materials become much larger than in presintered powders due to fast grain growth during conventional sintering. Therefore, even though the initial particle size is less than 100 nm, grain size increases rapidly up to 2 $\mu$m or larger during conventional sintering [10]. Controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. High-frequency induction-heated sintering, which can yield dense materials within 2 min, is effective for controlling grain growth [11, 12].

The purpose of this work is to produce dense nanocrystalline 3NiAl-$Al_2O_3$ composite within 3 minutes from mechanically synthesized powders using high-frequency induction-heated sintering and to evaluate its mechanical properties (hardness and fracture toughness).

## 2. Experimental Procedures

Powders of 99.9% NiO (−325 mesh, Alfa) and 99% pure Al (−325 mesh, Cerac, Inc.) were used as starting materials. 3NiO and 5Al powder mixtures were first milled in a high-energy ball mill, a Pulverisette-5 planetary mill, at 250 rpm for 10 h. Tungsten carbide balls (8 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of ball to powder was 30 : 1. Milling resulted in a significant reduction in grain size.

The grain sizes of NiAl and $Al_2O_3$ were calculated by Suryanarayana and Grant Norton's formula [13]:

$$B_{\mathrm{r}}\left(B_{\text{crystalline}} + B_{\text{strain}}\right)\cos\theta = \frac{k\lambda}{L} + \eta\sin\theta, \qquad (1)$$

where $B_r$ is the full width at half-maximum (FWHM) of the diffraction peak after instrument correction, $B_{\text{crystalline}}$ and $B_{\text{strain}}$ are FWHM caused by small grain size and internal stress, respectively, $k$ is constant (with a value of 0.9), $\lambda$ is the wavelength of the X-ray radiation, $L$ and $\eta$ are grain size and internal strain, respectively, and $\theta$ is the Bragg angle. The parameters $B$ and $B_r$ follow Cauchy's form with the relationship: $B = B_{\mathrm{r}} + B_s$, where $B$ and $B_s$ are the FWHM of the broadened Bragg peaks and the standard sample's Bragg peaks, respectively.

After milling, the mixed powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the high-frequency induction-heated sintering system made by Eltek in South Korea, shown schematically in reference [11, 12]. The four major stages in the synthesis are as follows. Stage 1: evacuation of the system; stage 2: application of uniaxial pressure; stage 3: heating of sample by induced current; stage 4: cooling of sample. Temperatures were measured by a pyrometer focused on the surface of the graphite die. The process was carried out under a vacuum of 40 mTorr.

The relative densities of the synthesized sample were measured by the Archimedes method. Microstructural information was obtained from product samples that were polished at room temperature. Compositional and microstructural analyses of the products were completed through X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). Vickers hardness was measured by performing indentations at a load of 50 kg and a dwell time of 15 s on the sintered samples.

## 3. Results and Discussion

The interaction between 3NiO and 5Al, that is,

$$3\mathrm{NiO} + 5\mathrm{Al} \longrightarrow 3\mathrm{NiAl} + \mathrm{Al_2O_3}, \qquad (2)$$

is thermodynamically favorable.

X-ray diffraction results of high-energy ball-milled powders and sintered specimens are shown in Figures 1(a) and 1(b). The reactant powders of NiO and Al were not detected in Figure 1(a) but products, NiAl and $Al_2O_3$, were detected. From the above result, the mechanochemical synthesis occurs completely during the high-energy ball milling.

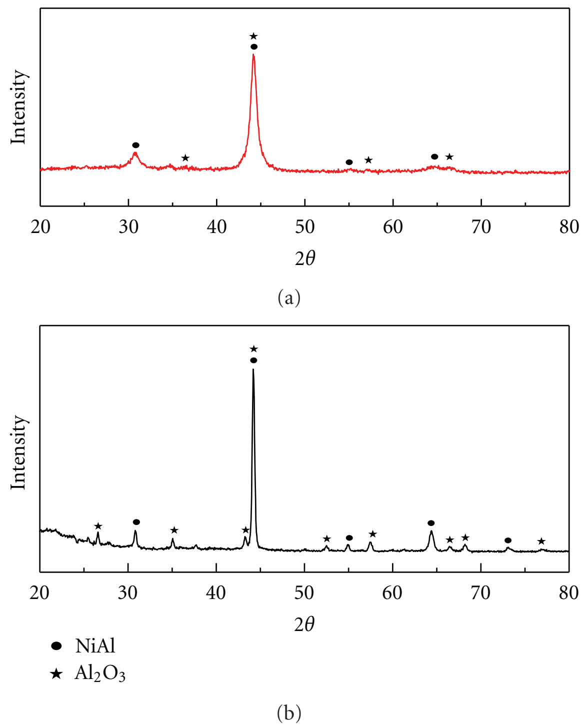
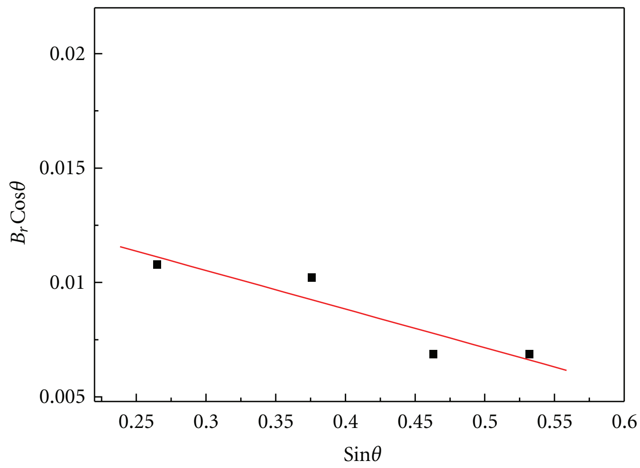


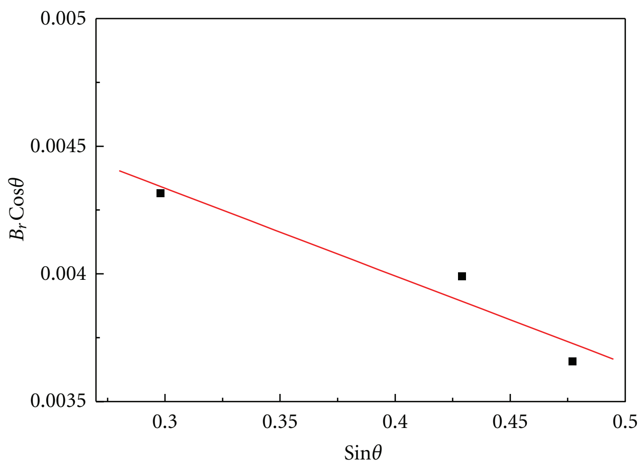

Figure 1: XRD patterns of mechanically synthesized powder (a) and sintered specimen.

Figure 2 shows a plot of $B_{\mathrm{r}}(B_{\text{crystalline}} + B_{\text{strain}})\cos\theta$ versus $\sin\theta$ of NiAl and $Al_2O_3$ in milled powders. The average grain sizes of NiAl and $Al_2O_3$ measured by Suryanarayana and Grant Norton's formula are about 9 nm and 26 nm, respectively. The variations in shrinkage displacement and temperature of the surface of the graphite die with heating time during processing of NiAl and $Al_2O_3$ systems are shown in Figure 3. As the induced current was applied, thermal expansion occurred and then the shrinkage displacement abruptly increased at about 900°C.

Figure 4 shows the FE-SEM image and EDS analysis of NiAl-$Al_2O_3$ composites sintered at 1100°C. The relative density of NiAl-$Al_2O_3$ composites is about 97%. The NiAl-$Al_2O_3$ composites consist of nanocrystallites. In EDS, Al, Ni, and O peaks are detected and heavier contaminants, such as W and Fe from a ball or milling container, were not detected. Figure 5 shows a plot of $B_{\mathrm{r}}(B_{\text{crystalline}} + B_{\text{strain}})\cos\theta$ versus $\sin\theta$ of NiAl and $Al_2O_3$ in sintered composite. The structure parameters, that is, the average grain sizes of NiAl and $Al_2O_3$ obtained from the X-ray data by Suryanarayana and Grant Norton's formula, were 43 nm and 69 nm, respectively. The average grain sizes of the sintered NiAl and $Al_2O_3$ were not significantly larger than the grain sizes of the initial powders, indicating the absence of significant grain growth during sintering. This retention of the grain size is attributed to the high heating rate and the relatively short exposure of the powders to the high temperature. The role of current in sintering has been the focus of several attempts to explain the observed enhancement of sintering and the improved characteristics of the products. The role played by




(a)




(b)

FIGURE 2: Plot of $\sin\theta$ versus $B_r\cos\theta$ for NiAl (a) and $Al_2O_3$(b) in mechanically milled powders.

the current has been hypothesized to involve a fast heating rate due to Joules heating, the presence of plasma in pores separating powder particles, and the intrinsic contribution of the current to mass transport [14–17].

Vickers hardness measurements were made on polished sections of the 3NiAl-$Al_2O_3$ composite using a 50 $kg_f$ load and 15 s dwell time. The calculated hardness value of 3NiAl-$Al_2O_3$ composite was 804 kg/mm$^2$. This value represents an average of five measurements. Indentations with large enough loads produced median cracks around the indent. From the lengths of these cracks, fracture toughness values can be determined using an expression proposed by Anstis et al. [18]:

$$K_{IC} = 0.016\left(\frac{E}{H}\right)^{1/2} \cdot \frac{P}{C^{3/2}}, \tag{3}$$

where $E$ is Young's modulus, $H$ is the indentation hardness, $P$ is the indentation load, and $C$ is the trace length of the crack measured from the center of the indentation. The modulus was estimated by the rule of mixtures for a 0.37 volume fraction of $Al_2O_3$ and 0.63 volume fraction of NiAl using $E(Al_2O_3)$ = 380 GPa [5] and $E$(NiAl) = 193 GPa [19].

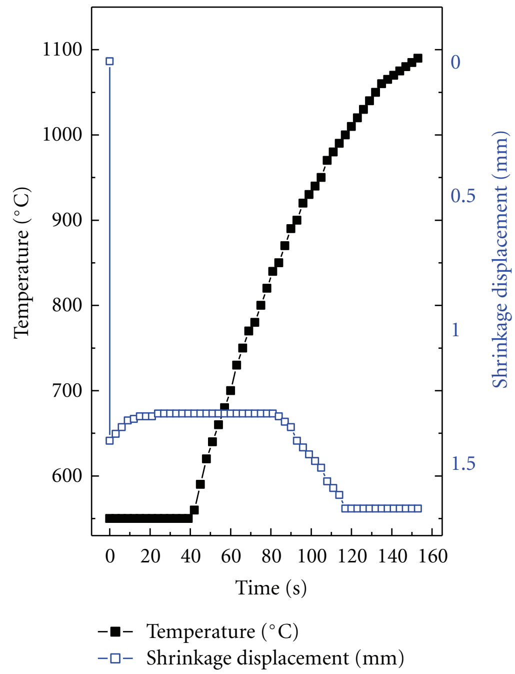
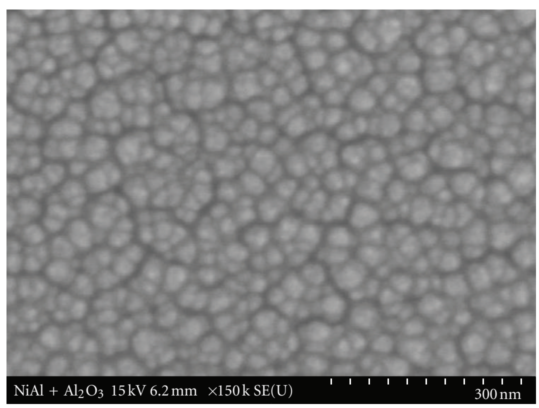
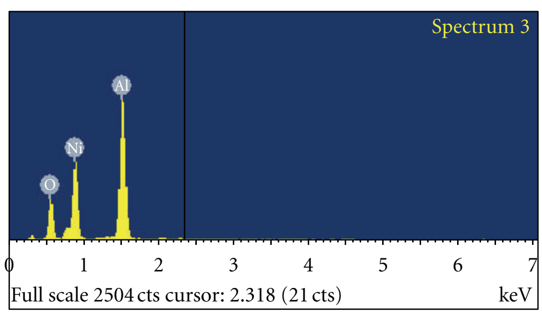



FIGURE 3: Variation in temperature and shrinkage displacement with heating time during high-frequency induction-heated sintering of 3NiAl + $Al_2O_3$.




(a)




(b)

FIGURE 4: FE-SEM image and EDS of 3NiAl-$Al_2O_3$ composites heated to 1100°C.

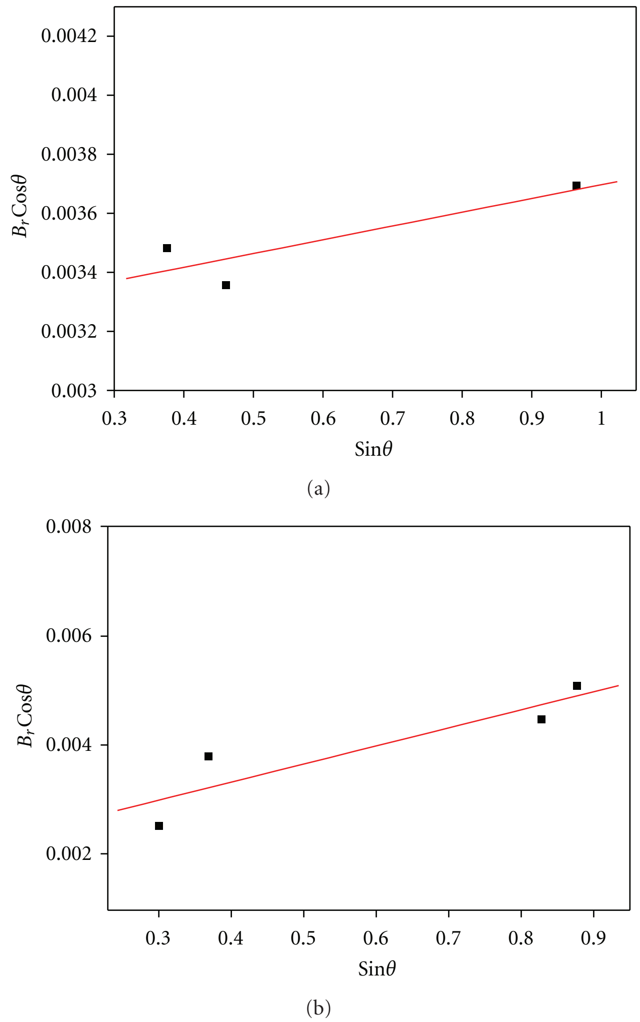



Figure 5: Plot of $\sin\theta$ versus $B_r \cos\theta$ for NiAl (a) and $Al_2O_3$ (b) in sintered composite.

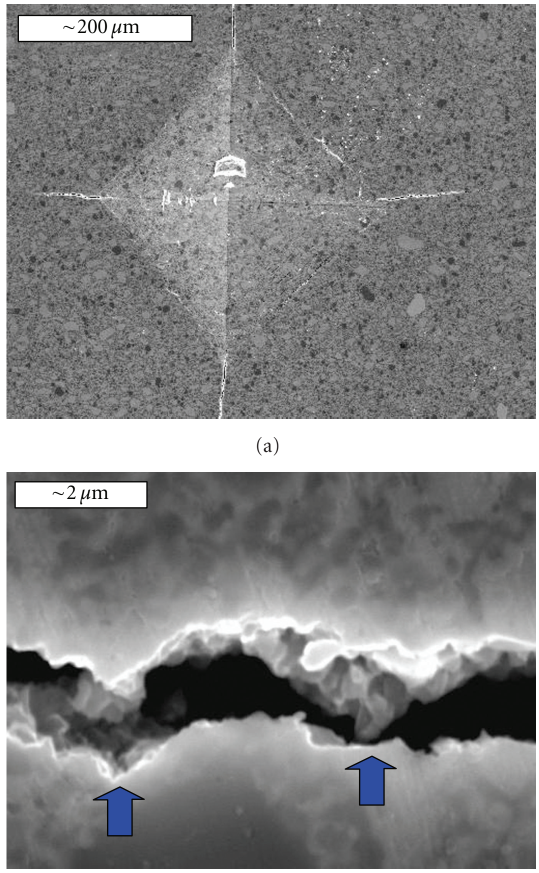



Figure 6: (a) Vickers hardness indentation and (b) median crack propagation in the NiAl-$Al_2O_3$ composite.

As in the case of hardness values, the toughness values were derived from the average of five measurements. The toughness value obtained by the method of calculation is 7.5 MPa·$m^{1/2}$. A typical indentation pattern for the NiAl-$Al_2O_3$ composite is shown in Figure 6(a). Typically, one to three additional cracks were observed to propagate from the indentation corner. A higher magnification view of the indentation median crack in the composite is shown in Figure 6(b). This shows that the crack propagates deflectively (↑). The hardness and fracture toughness of NiAl are reported as 430 kg/$mm^2$ and 5.4 MPa·$m^{1/2}$, respectively [3]. Not only the hardness but also the fracture toughness of 3Ni-$Al_2O_3$ composites is higher than that of monolithic NiAl due to addition of hard phase of $Al_2O_3$ and crack deflection by $Al_2O_3$.

## 4. Conclusions

Nanopowders of NiAl and $Al_2O_3$ are synthesized from 3NiO and 5Al powders by high-energy ball milling. Using the high-frequency induction-heated sintering method, the densification of nanocrystalline $Al_2O_3$-reinforced NiAl composites were accomplished from mechanochemically synthesized powders. Complete densification can be achieved within 3 minutes. The relative density of the composite was 97% for an applied pressure of 80 MPa and an induced current. The average grain sizes of NiAl and $Al_2O_3$ prepared by HFIHS were about 43 nm and 69 nm, respectively. The average hardness and fracture toughness values obtained were 804 kg/$mm^2$ and 7.5 MPa·$m^{1/2}$, respectively. Not only the hardness but also the fracture toughness of 3NiAl-$Al_2O_3$ composites is higher than that of monolithic NiAl due to addition of hard phase of $Al_2O_3$ and crack deflection by $Al_2O_3$.

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