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Mechanical and magnetic properties of Ni-Co dispersed Al_2O_3 nanocomposites

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Effects of the fabrication processing on the microstructure and properties of composites were investigated. High-density Ni-Co dispersed-Al_2O_3 (Al_2O_3/Ni-Co) composites were obtained by hydrogen reduction and consolidated using hot pressing and pulse electric current sintering (PECS) of Al_2O_3, $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ powder mixtures. Microstructural investigations of the hot-pressed composite fabricated using again wet/dry ball-milled powder mixture after calcination revealed that fine Ni-Co particles, about 145 nm in diameter, dispersed homogeneously at the matrix grain boundaries. In particular, fine microstructure of dispersion with the average size of 90 nm was realized for the specimen consolidated by PECS method. High strength of over 1 GPa and hardness of 19 GPa were measured for the nanocomposites prepared from the again ball-milled powder mixture. The ferromagnetism of nano-sized Ni-Co contributes to the magnetic properties of the composites. A change in the coercive force with dispersion size was observed. Also, the extent of magnetic response by an applied stress was strongly influenced by the size of Ni-Co particles. The relations between microstructure and mechanical as well as magnetic properties are discussed. © *2001 Kluwer Academic Publishers*

1. Introduction

There has been strong interest during recent years in the concept of nanocomposites involving the incorporation of the nano-phase (of order 100 nm in size) into a ceramic matrix phase [1]. Advantageous effects reported include enhancement of mechanical properties, e.g. strength, toughness and improvement in high temperature properties. In fact, the strengths were reported to increase from 350 MPa for Al_2O_3 to over 1 GPa for the 5 vol% SiC composite. Moreover, ceramic nanocomposites that have nano-sized functional materials as the dispersion, such as Ni-dispersed Al_2O_3 [2] or $BaTiO_3$-dispersed MgO [3], have also been found to exhibit attractive magnetic and electronic functions without loosing their excellent mechanical properties due to the peculiar role of incorporated nano-sized phases in physical properties.

Motivated by an interest in a synergetic combination of improved mechanical properties and excellent functionality in metal-dispersed-Al_2O_3 systems, we investigated the feasibility of the fabrication of Ni-Co dispersed Al_2O_3 (Al_2O_3/Ni-Co) composite with the inverse magnetostriction [4, 5]. This earlier study indicated that the nanocomposite with desired microstructure and high strength above 1 GPa could be fabricated by the hydrogen reduction and the hot pressing of Al_2O_3, $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ powder mixtures. Also, the fabricated nanocomposites showed the inverse magnetostrictive response to applied stress, because of the Ni-Co dispersions. This result implies a big possibility to introduce new functions such as stress sensing into structural ceramics.

Considering the sensitive dependence of magnetic properties on magnetic domain state [6], it is expected that microstructural characteristics such as dispersion size can give a significant influence on the inverse magnetostrictive behavior of the prepared composites. A closer study of how the microstructure affects the magnetic properties including mechanical properties is, therefore, considered to be of importance for fabricating the composite having desired properties. In the present study, the effect of dispersion size on the mechanical

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and magnetic properties is investigated for Al_2O_3/Ni-Co composites. To give the variation of microstructural characteristics in composites, we have applied the different powder preparation processing and the consolidation method.

2. Experimental procedure

High-purity $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (High Purity Chemetals Lab., Japan) powders were used as a source material for Ni-Co. The composition of Ni-Co was 95.5 wt% Ni-4.5 wt% Co. Weighted nitrate powders, corresponding to 10 wt% of Ni-Co in the final composite, were initially dissolved in 200 ml alcohol. Subsequently, α-Al_2O_3 powder (AKP-53, Sumitomo Chem. Co., Japan) was mixed with the above-mentioned solution and ball milled for 24 h with high purity Al_2O_3 balls. After calcination in air at 450°C, soft agglomerates of the calcined powders were crushed by dry ball-milling for 24 h (process A) or again wet/dry ball milled for 24 h using Al_2O_3 balls (process B). The powder mixtures were kept in graphite die and reduced by H_2 gas at 700°C and 1100°C for 1 h. Then, sintering was performed at 1450°C for 1 h in Ar atmosphere with an applied pressure of 30 MPa. Pure Al_2O_3 was sintered under the same conditions as the composite. The processing details have been described in our previous paper [5].

For the variation of microstructural characteristic, the powder mixture of process B was consolidated by a pulse electric current sintering (PECS) method at 1350°C for 10 min in a vacuum under an applied pressure of 30 MPa, using a spark plasma sintering system (SPS-2080, Sumitomo Coals Mining Co. Ltd., Japan). After applying the given pressure, the sample was heated to the sintering temperature with the heating rate of 100°C/min. The composite prepared by PECS method is designated as process C.

The microstructure was characterized by scanning electron microscopy (SEM) and more detailed by transmission electron microscopy (TEM). The dispersion sizes were estimated from the measurements of more than 150 dispersions which were selected from TEM micrographs. The hot-pressed bodies were cut, grounded and polished into rectangular bars with $3 \times 4 \times 37$ mm in size. Then, more than five specimens were subjected to three-point bending tests (span: 30 mm) with a cross-head speed of 0.5 mm/min to determine the fracture strength. Vickers indentation, using 98 N-load applied for 15 s, was used to determine the hardness of the materials.

The magnetization change of the composites under an applied stress was estimated by measuring the AC susceptibility under uniaxial compression with Hartshorn bridge method, and the applied stress was varied from 0 to 150 MPa. The detailed instrument setup is described elsewhere [7].

3. Results and discussion

3.1. Microstructure

XRD analysis revealed that Ni- and Co-nitrate were completely converted to metallic Ni-Co, and all composites were composed entirely of Al_2O_3 and Ni-Co. Neither residual metal oxides nor reaction phase was observed. Almost full density of above 98.5% was achieved all composites.

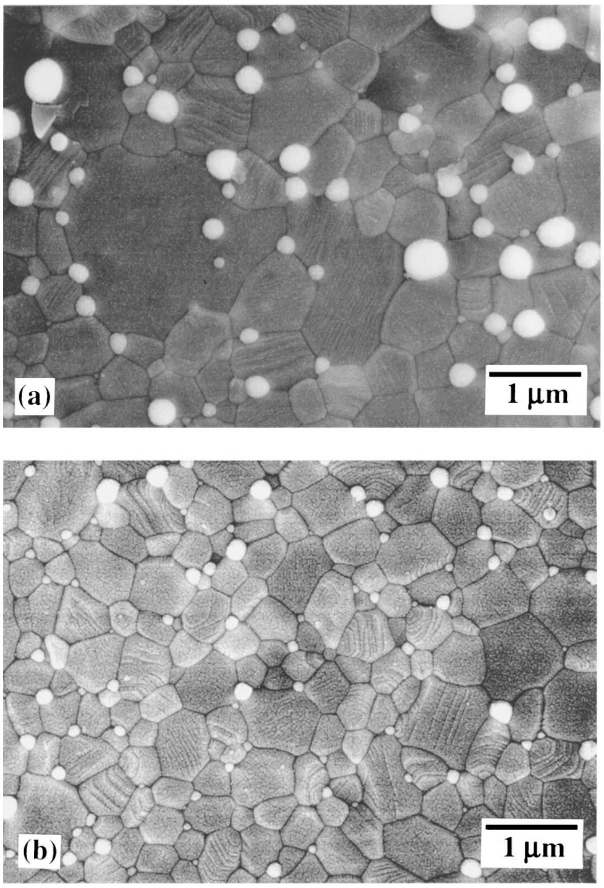

Figure 1 SEM micrographs of microstructures for the Al_2O_3/10 wt% Ni-Co composites hot-pressed at 1450°C for 1 h; The powder mixtures used were prepared by (a) process A and (b) process B. The composites were thermally etched at 1350°C for 15 min.

Typical SEM micrographs of the etched surfaces for the composites with different powder processing are shown in Fig. 1, in which the bright and spherical phases are the Ni-Co particles. The micrographs clearly show a strong effect of the milling condition on the microstructural evolution of the hot-pressed composites. As shown in Fig. 1a, the composite, fabricated by process A, exhibited abnormally grown matrix grains and large dispersion size. Conversely, the microstructure of the composite (Fig. 1b), fabricated from the powder mixture that was again ball-milled after calcination (process B), was characterized by a homogeneous dispersion of fine Ni-Co particles and uniform matrix grain size. As reported in earlier studies [5, 8], this discrepancy was attributed to the different mixing homogeneity of initial powder mixtures and resulting role of dispersion as grain growth inhibitor in microstructural evolution. Thus, the fact that a homogeneous dispersion of second-phase particles can be obtained by ball-milling after calcination explains the homogeneous microstructure obtained by process B.

The microstructures for the Al_2O_3/10 wt% Ni-Co composites that have been sintered by hot-pressing and PECS method using the same powder mixture of process B are shown in Fig. 2a and b, respectively.

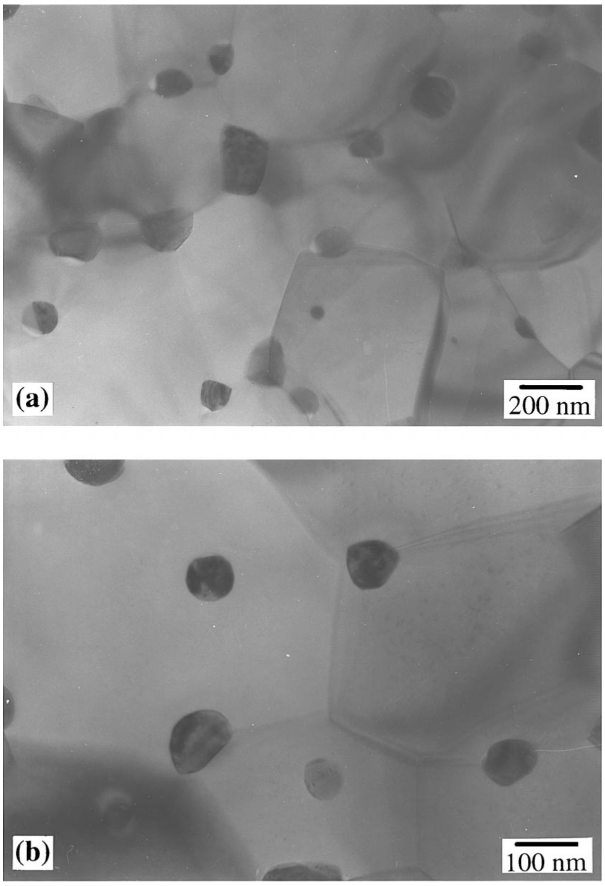

Figure 2 Typical TEM microstructure of the Al_2O_3/10 wt% Ni-Co composites; (a) process B, hot-pressed at 1450°C and 30 MPa for 1 h and (b) process C, sintered by PECS at 1350°C and 30 MPa for 10 min.

In the composite sintered by hot pressing (Fig. 2a), the Ni-Co particles (the dark and spherical phases) are homogeneously dispersed at the Al_2O_3-Al_2O_3 grain boundaries. From the TEM observations, the average size of dispersions was estimated to be 145 nm. Hence, in this investigation the composite is classified as an intergranular-type nanocomposite [1]. The microstructure of the composite sintered by PECS (Fig. 2b) showed the same features as the hot-pressed composite. However, the average dispersion size significantly decreased as 90 nm, and fine Ni-Co particles were dispersed within the Al_2O_3 matrix grains and at the grain boundaries. Considering the high heating rate and short sintering time in PECS method, it is suggested that the decrease in dispersion size for sintered composite was attributed to the minimized coalescence of dispersion particles [9].

3.2. Mechanical properties

The mechanical properties of the composites are summarized in Table I and compared to those of monolithic Al_2O_3. The hardness of the composites varied depending on the processing steps. In case of the composite prepared by process A, the hardness reached a value of 17.7 GPa. However, the composites prepared by process B and process C exhibited obvious hardening and obtained a maximum value of around 19 GPa. This hardening is supposed to be accounted for by the contributions of the fine-grained microstructure of Al_2O_3 matrix [10] as shown in Figs 1 and 2 and by the hardening itself of Ni-Co particles [11].

TABLE I Mechanical properties for Al_2O_3/10 wt% Ni-Co composites and Al_2O_3 fabricated by different processing

Sample	Vickers Hardness (GPa)	Fracture strength (MPa)
Composite (process A)	17.7 ± 0.44	722 ± 62
Composite (process B)	19.0 ± 0.48	1070 ± 72
Composite (process C)	19.1 ± 0.31	Not measured
Monolithic Al_2O_3	17.8 ± 0.26	524 ± 114

As summarized in Table I, by incorporating a fine dispersion, the composites prepared by process A and process B showed enhanced fracture strength. SEM investigations revealed that the average grain size of the monolithic Al_2O_3 was 1.3 μm, whereas that of the Al_2O_3 matrix in the composites prepared by process A and process B was reduced to 0.73 μm and 0.67 μm, respectively. Considering the measured grain sizes, it is reasonable to expect the fracture strength to increase as the grain size decreases, as suggested by the Griffith criterion for brittle fracture [12]. On the other hand, the fracture strength of the composite prepared by process B showed higher values than that of the composite prepared by process A. Generally, it is well known that an inhomogeneous distribution of a second phase and abnormally grown grains are harmful to mechanical properties, often acting as the fracture origin [13]. Therefore, the high strength of the composite prepared by process B may be caused by the refinement of the matrix grains and homogeneous microstructures.

Fracture strength for the composite sintered by PECS method (process C) was not measured, because of the small size of the sintered specimen (20 mm in diameter) for the three-point bending test with a span of 30 mm. However, it is generally known that the materials sintered by PECS method had improved mechanical properties than those obtained by hot pressing [14]. Also, considering the microstructure and hardness shown in Fig. 2b and Table I, the composite prepared by process C is believed to have enhanced fracture strength. Further investigation on the characterization of fracture strength is currently in progress.

3.3. Magnetic properties

The dependence of the mechanical properties on powder processing was discussed in the previous section. In this section, we discuss the modification of the magnetic properties of the composites that are caused by the dispersion of Ni-Co particles and different fabrication processing. The dependence of magnetization on the applied magnetic field for composites was estimated using a vibrating sample magnetometer with an applied magnetic field up to ±400 kA/m at room temperature. The parameters that are related to the magnetic properties are summarized in Table II.

The spontaneous magnetization for composites is almost the same at about 0.66 T (Tesla). The coercive

TABLE II Magnetic properties and dispersion size of Al_2O_3/10 wt% Ni-Co composites

Sample	Saturation magnetization (T)	Coercive force (kA/m)	Dispersion size (nm)
Composite (process A)	0.65	5.37	370
Composite (process B)	0.66	6.45	145
Composite (process C)	0.66	6.65	90

force of the composites showed different values depending on the processing, from 5.37 kA/m to 6.65 kA/m. The coercive force is well-known to be strongly dependent on the grain size, residual stress and dislocation density [15, 16]. When the particle size of a magnetic material decreases, its magnetic structure varies from a multidomain state to a single-domain state, to reduce the total energy of the system; hence a high coercive force is expected. In the present experiment, it is not clear whether the dispersed Ni-Co particles have single domain structure or not. However, considering that there are a number of smaller particles that exist in the composites prepared by process B and process C (Fig. 2), it seems that some of the dispersions might have a single-domain structure. Thus, it is suggested that the decreased dispersion size was mainly responsible for the increase in coercive force.

In our previous paper [4], the inverse magnetostrictive behavior in Al_2O_3/Ni-Co composites was confirmed by measuring the magnetization change subjected to applied stress. In this paper, we investigate the effect of microstructural characteristic on the inverse magnetostrictive behavior. Fig. 3 shows the magnetization change, abbreviated as $(\Delta M/M_0)$, against applied uniaxial stress for three composites with different processing route, where ΔM is the difference between the magnetization subjected to stress and the initial magnetization without applied stress (ΔM_0). It is evident that the magnetization change in all the composites increased linearly as the applied stress increased. Also, the composite prepared by process C is considered to be effective in amplifying the sensitivity. This result is suggested that the extent of magnetic response by an applied stress is strongly influenced by the microstructural characteristics which resulted from different processing route.

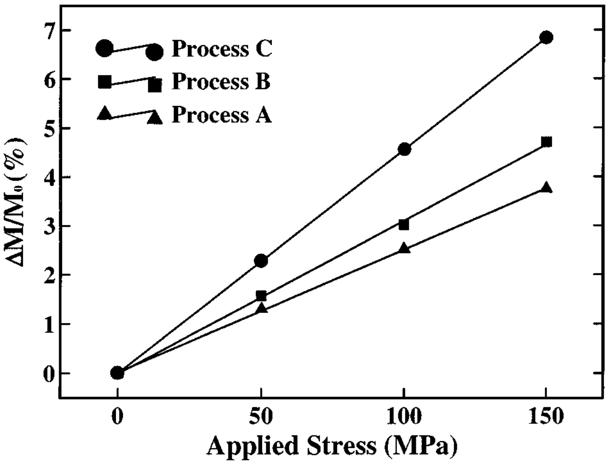

Figure 3 Magnetization change $(\Delta M/M_0)$ with applied uniaxial stress for the composites with different fabrication processing.

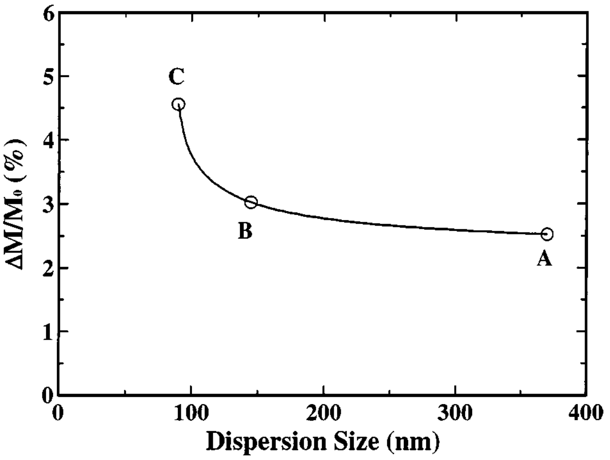

Figure 4 Effect of the dispersion size on the magnetization change $(\Delta M/M_0)$ at the same applied stress of 150 MPa. The symbol represents the process designations.

As summarized in Table II, the main difference among the composites was the size of magnets dispersion. Based on this consideration, the relationship between dispersion size and magnetization change was analyzed. Fig. 4 shows the magnetization change of composites at an applied pressure of 150 MPa, as a function of dispersion size. The tendency of increasing magnetization change with decreasing dispersion size is clearly shown in this figure. Considering that the inverse magnetostrictive response is mainly dependent on the magnet domain rotation and magnetostriction value of materials [6, 17, 18], the main influence of dispersion size on inverse magnetostriction is believed to arise through its effects on domain structure. However, the detailed effect of domain structure on the inverse magnetostriction is difficult to clarify here, because it still reveals an unclear feature. Although the effects of microstructure on extrinsic magnetic properties are difficult to describe theoretically, it however suggests that the sensitivity of the magnetization change under an applied pressure can be controlled by the dispersion size.

4. Conclusions

This work demonstrated the effects of processing on the microstructure and properties of composites. Al_2O_3/10 wt% Ni-Co nanocomposites prepared from the again wet/dry ball-milled powder mixtures after calcination (process B) showed marked refinement of Al_2O_3 grain size and homogeneous distribution of nano-sized Ni-Co. In particular, fine microstructure of dispersion was realized for the specimen consolidated by PECS method.

The composites fabricated by hot pressing and PECS, using the powder mixture of process B, exhibited obvious hardening and obtained a maximum value of around 19 GPa. Fracture strengths of over 1 GPa were measured for the nanocomposite prepared from the powder mixture of process B. The strengthening was caused by the refinement of the matrix grains and homogeneous microstructures.

The ferromagnetism of nano-sized Ni-Co contributes to the magnetic properties of the composites. A change in the coercive force with dispersion size was observed. Also, the extent of magnetic response by an applied stress was strongly influenced by the size of Ni-Co particles. The effect of dispersion size on the coercive force and the inverse magnetostriction was attributed to a possible change of domain structure.

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