

Microstructure and Properties of Nano-Sized Ni-Co Particulate Dispersed Al₂O₃ Matrix Nanocomposites

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Abstract In purpose of introducing the inverse magnetostrictive properties into the structural ceramics, Al₂O₃ based nanocomposites dispersed with nano-sized Ni-Co particles were studied. The composites were fabricated by the hydrogen reduction and hot-pressing of Al₂O₃ and NiO-CoO mixed powders. The mixtures were prepared by using Ni- and Co-nitrate (Ni(NO₃)₂ · 6H₂O and Co(NO₃)₂ · 6H₂O) as source materials for the Ni-Co particles. Microstructural observations revealed that nano-sized Ni-Co particles were dispersed homogeneously at Al₂O₃ grain boundaries. High strength above 1 GPa was obtained for the Al₂O₃/10 wt% Ni-Co nanocomposite fabricated by a controlled powder preparation process. The inverse magnetostrictive response to applied stress was obtained due to the presence of dispersed Ni-Co particles, which indicates a possibility to incorporate new functions into the structural ceramics without losing the mechanical properties.

1. Introduction

Following the novel concept of the ceramic-based nanocomposite systems for structural applications,^{1,2)} the recent investigations have led to the development of ceramic-metal nanocomposites such as Al₂O₃/W,³⁾ Al₂O₃/Cu⁴⁾ and Al₂O₃/Ni.⁵⁾ The mechanical properties of the composites were notably improved by the addition of the nano-sized metal particles dispersed in ceramic matrix. In case of the Al₂O₃/Ni system, ferromagnetic properties have been introduced to the nanocomposite in addition to the improvement of strength. Also, the magnetic property enables the sensing of the mechanical stress that is acting on the nanocomposite through the inverse magnetostriction effect.^{6,7)}

The success of the functional metal dispersed ceramic matrix nanocomposites implies the possibility to introduce new functions into structural ceramics without degradation of the mechanical properties. In this study, Al₂O₃/Ni-Co composites have been fabricated in an attempt to introduce an inverse mag-

netostrictive property into structural ceramics. The Ni-Co alloy (95.5 wt% Ni-4.5 wt% Co) was selected as a dispersion, because it is known to have a high magnetomechanical coupling factor,⁸⁾ which is defined as the response of a material to externally applied magnetic fields and stresses.

Starting with powder mixtures of Al₂O₃, Ni- and Co-nitrates produced by milling, a reduction and sintering process by hot-pressing was used to obtain Al₂O₃/Ni-Co composites. In this paper, differences in the preparation process and in the resulting microstructural and mechanical characteristics will be described for the Al₂O₃/Ni-Co system. Moreover, the effects of dispersed Ni-Co particles on inverse magnetostrictive properties of Al₂O₃/Ni-Co composites were discussed.

2. Experimental Procedures

High-purity Ni- and Co-nitrates supplied from High Purity Chemetals Lab., Japan were used as source materials for the Ni-Co. The composition of Ni-Co was 95.5 wt% Ni-4.5 wt% Co. Weighted powders,

corresponding to 5, 10 and 15 wt% of alloy in the final composite, were initially dissolved in alcohol. Subsequently, α -Al₂O₃ powders with mean particle size of 0.2 μ m supplied from Sumitomo Chem. Co., Japan were mixed with the above-mentioned solution and ball-milled for 24 h with high purity Al₂O₃ balls. Dried mixtures were calcined at 450°C for 2 h in air to obtain Al₂O₃/NiO-CoO mixed powders. Then, soft agglomerates of the calcined powders were crushed by dry ball-milling for 24 h (process A) or wet and dry ball-milled for 24 h using Al₂O₃ balls (process B). The powder mixtures were kept in a graphite die and reduced by H₂ gas at 700°C and 1100°C for 1 h. Consecutively, sintering was carried out at 1450°C for 1 h in Ar atmosphere with an applied pressure of 30 MPa. Pure Al₂O₃ was sintered under the same condition as the composite. The hot-pressed bodies were cut, ground and polished into rectangular bars with 3×4×37 mm in size.

Density measurements were made using the Archimedes method. All the samples had a relative density above 98.5%. The phase composition of the powders and composites was examined by X-ray diffractometry (XRD). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to observe the microstructure of the composites. The fracture strengths were measured by a three-point bending test with a span of 30 mm and a crosshead speed of 0.5 mm/min.

The magnetization change of the composites under an applied stress was estimated by measuring the AC susceptibility under uniaxial compression with Hartshorn bridge method in a weak applied magnetic field of 15 Oe. The dimensions of all samples were 3×4×2.5 mm, and the applied stress was varied from 0 to 150 MPa. The measurements of magnetization change were carried out at room temperature. The detailed instrument setup is described elsewhere.^{7,9)}

3. Results and Discussion

3.1. Phase composition and microstructure

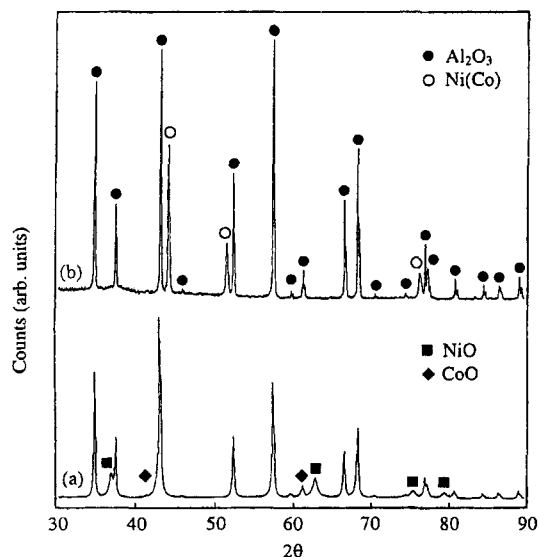


Fig. 1. XRD profiles of the powder mixtures at different stages of processing; (a) after calcination in air at 450°C for 2 h and (b) after reduction/hot-pressing at 1450°C and 30 MPa for 1 h.

The XRD profiles of the powder mixtures at different stages of processing are shown in Fig. 1. The XRD pattern after calcination (Fig. 1a) contains the characteristic peaks for α -Al₂O₃, NiO and CoO. After reduction in H₂ atmosphere and hot-pressing at 1450°C in Ar atmosphere, the specimens were composed of α -Al₂O₃ and Ni-Co alloy (Fig. 1b). Neither residual metal oxide nor reaction phase were observed.

Typical microstructures in SEM of the etched surfaces for the Al₂O₃/10 wt% Ni-Co composites with different powder processing are shown in Fig. 2. It clearly shows a strong effect of the milling condition on the microstructure of hot-pressed composites. In the composite fabricated by process A (Fig. 2a), an inhomogeneous distribution of alloy inclusions and large difference in both the size of dispersions and matrix grains were observed. Conversely, the specimen, fabricated from the powder mixture that was ball-milled again after calcination (process B), exhibited a homogeneous dispersion of fine alloy particles and more uniform matrix grain size (Fig. 2b).

It is generally expected that the homogeneous dispersion of second-phase particles can be obtained

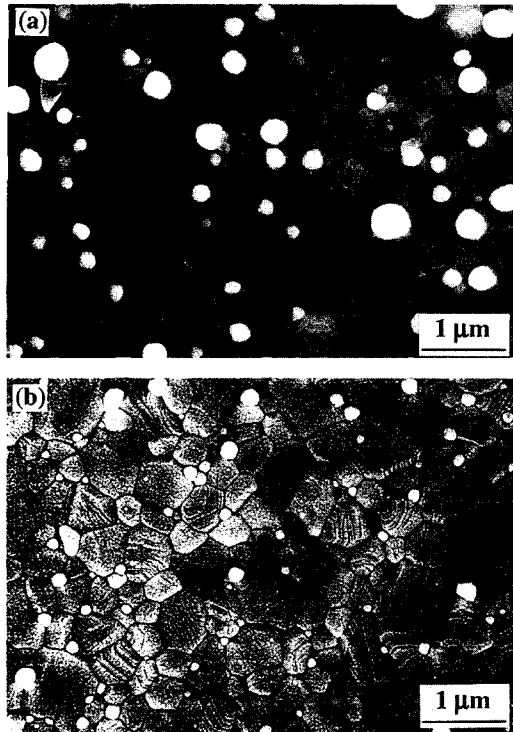


Fig. 2. SEM micrographs of microstructures for the hot-pressed $\text{Al}_2\text{O}_3/10$ wt% Ni-Co composites; The powder mixtures used were prepared by (a) process A and (b) process B. The composites were thermally etched in Ar at 1350°C for 15 min.

by optimized milling process such as prolonged ball-milling time and adequate ball content, and is directly related to the final microstructures of composites.^{10,11} If the second-phase particles are inhomogeneously dispersed in the initial powder mixture, it leads to local variations of densities and also to local abnormal grain growth, because of the ineffective role of inclusions as grain growth inhibitors for the matrix grains. Thus, the homogeneous microstructure obtained by process B (Fig. 2b) may have been explained by sufficient homogeneity of the powder mixture caused by prolonged ball-milling time.

Fig. 3 shows typical TEM image of the $\text{Al}_2\text{O}_3/10$ wt% Ni-Co composite prepared by process B. The Ni-Co particles (the dark and spherical phases) were located mainly on the Al_2O_3 grain boundaries and triple points rather than within the Al_2O_3 grains. The



Fig. 3. Typical TEM microstructure of the $\text{Al}_2\text{O}_3/10$ wt% Ni-Co composite prepared by process B. Sintering condition was 1450°C and 30 MPa for 1 h.

average particle size of Ni-Co was 145 nm. Hence, in this investigation the $\text{Al}_2\text{O}_3/10$ wt% Ni-Co composite is defined as an intergranular-type nanocomposite.¹⁾

3.2. Effect of microstructure on fracture strength

The relationship between fracture strength and the Ni-Co weight fraction is shown in Fig. 4. In general, fracture strength was increased by the addition of Ni-Co particles. For the composite prepared by process B, the strength was enhanced up to 1070 MPa by dispersing 10 wt% of Ni-Co. This value is about 2 times higher than that of the monolithic Al_2O_3 pre-

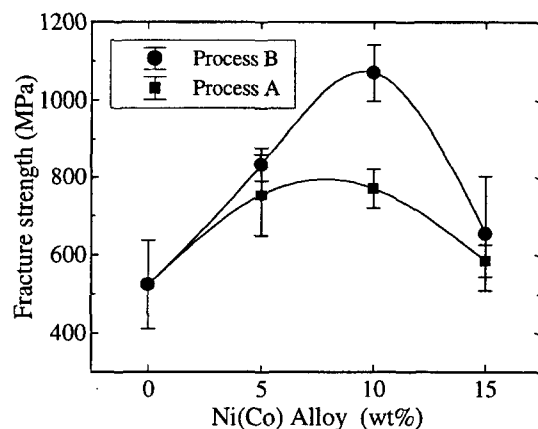


Fig. 4. Effect of the weight fraction of Ni-Co dispersion on the fracture strength for $\text{Al}_2\text{O}_3/\text{Ni-Co}$ composites fabricated using different powder processing. Error bars cover the extremes in the obtained values.

pared under the same conditions.

Fracture strength, σ_f , of brittle materials such as ceramics is known to be defined by the following equation:

$$\sigma_f = \left(\frac{1}{Y} \right) \frac{K_{Ic}}{c^{1/2}} \quad (1)$$

where K_{Ic} , c , and Y are the fracture toughness, one-half of the width of the initial flaw, and the geometrical parameter of flaw, respectively.¹²⁾ In general, c is proportional to the grain size, d , in dense polycrystalline materials. Thus, the strength increases when the grain size is small (Eq. (1)). Considering the measured Al₂O₃ matrix grain sizes of 0.67 μm for the composite and 1.1 μm for monolithic Al₂O₃, it is reasonable to expect the fracture strength increase with decreasing grain size. Also, the fracture mode of the nanocomposite, which has a fine matrix grain size, was both intergranular and transgranular as shown in Fig. 5b, while that of the monolithic Al₂O₃ with large grains exhibited mostly intergranular fracture (Fig. 5a). This significant change in fracture mode may be associated with the internal stresses supposed to be developed during cooling from the sintering temperature because of the thermal expansion mismatch between Al₂O₃ and Ni-Co. This leads to an increase in crack resistance in the material because once the crack front has progressed beyond this local residual stress field, the average transgranular fracture energy is greater than that of the grain boundary.¹⁾ The strengthening of Al₂O₃/Ni-Co composites is, therefore, explained mainly due to the refinement of the Al₂O₃ matrix and the change of fracture mode.

The fracture strengths of the composites prepared by process A showed lower values than that of the composites prepared by process B, as shown in Fig. 4. Generally, it is well known that an inhomogeneous distribution of second phase and abnormally grown grains are harmful to mechanical properties, often acting as the fracture origin.¹³⁾ Thus, the variation of fracture strength with the milling

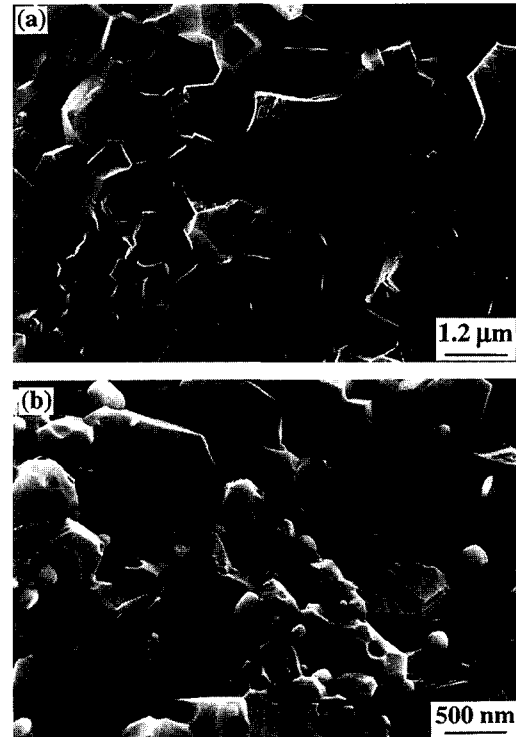


Fig. 5. Fracture surface of the hot-pressed materials; (a) monolithic Al₂O₃ and (b) Al₂O₃/10 wt% Ni-Co nanocomposite prepared by process B.

process qualitatively agrees with the microstructural change shown in Fig. 2. In this regard, the decrease in strength at 15 wt% of Ni-Co content also can be explained by the agglomeration of higher content Ni-Co dispersion during sintering.

3.3. Magnetic properties

In our previous paper,¹⁴⁾ the ferromagnetic behavior of Al₂O₃/Ni-Co composites was confirmed by measuring the magnetization with varying the magnetic field. Another noteworthy property of the present composite system is the inverse magnetostrictive response involving Ni-Co dispersions. Fig. 6 shows a marked effect of applied stress on the magnetization change behavior ($\Delta M/M_0$) of the composites, where ΔM (emu/g of Ni-Co) is the difference between magnetization subjected to stress and initial magnetization without applied stress (M_0). The mag-

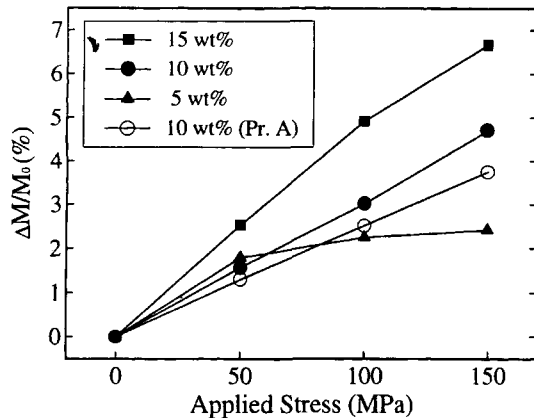


Fig. 6. Variation of the magnetization change ($\Delta M/M_0$) for $\text{Al}_2\text{O}_3/\text{Ni-Co}$ composites as a function of applied compressive stress.

netization change increased with increase in the applied stress and in the Ni-Co content at the same stress. In addition, an interesting factor is that the composite prepared by process B showed amplified sensitivity to the applied stress, compared with the composite prepared by process A.

It is suggested that the magnetization change by an applied stress was strongly influenced by the microstructure. The microstructural difference between the composites was mainly the average sizes of the dispersions measured as 145 nm and 370 nm for the composites prepared by process B and process A, respectively. Considering that the inverse magnetostrictive response is dependent on the magnetic domain rotation and magnetostriction value of materials,^{8,15} the main influence of dispersion size on inverse magnetostriction is believed to arise through its effects on domain structure. Further study on the effect of dispersion size on inverse magnetostrictive response is currently in progress.

4. Conclusions

This work has demonstrated that inverse magnetostrictive properties can be introduced into the structural ceramic without degradation of the fracture strength by processing of $\text{Al}_2\text{O}_3/\text{Ni-Co}$ nanocomposite.

Microstructural observations revealed that the Ni-Co dispersions in composites were located mainly at the matrix grain boundaries. In particular, the fine microstructure of both dispersion and matrix were obtained for the specimen prepared from the wet and dry ball-milled powder mixture after calcination (process B). The fracture strength of over 1 GPa was measured for the $\text{Al}_2\text{O}_3/10$ wt% Ni-Co nanocomposite prepared by process B. The strengthening was caused by the refinement of the microstructure. The Ni-Co having a high magnetomechanical coupling factor contributes to the inverse magnetostrictive response of Al_2O_3 -based composites. The magnetization change under applied stress has widened the possibilities for the utilization of these materials for stress and fracture sensing components.

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References

1. K. Niihara: *J. Ceram. Soc. Jpn.*, **99** (1991) 974.
2. A. Nakahira and K. Niihara, in *Fracture Mechanics of Ceramics*, Vol. 9 (eds., M. Sasaki, R. C. Bradt, D. P. H. Hasselman and D. Munz), p. 165, Plenum Press, New York (1992).
3. T. Sekino and K. Niihara: *J. Mater. Sci.*, **32**, (1997) 3943.
4. S.-T. Oh, T. Sekino and K. Niihara: *J. Europ. Ceram. Soc.*, **18**, (1998) 31.
5. T. Sekino, T. Nakajima, S. Ueda and K. Niihara: *J. Am. Ceram. Soc.*, **80**, (1997) 1139.
6. B. D. Cullity: *J. Metals.*, **23**, (1971) 35.
7. M. Awano, M. Sando and K. Niihara, in *Proceedings of the 14th International Japan-Korea Seminar on Ceramics*, p. 172, Kanazawa, Japan (1997).
8. J. R. Cullen, A. E. Clark and K. B. Hathaway, in *Materials Science and Technology*, Vol. 3B, (ed., K.H.J.

- Buschow), p. 554, VCH, Weinheim (1994).
9. M. Awano, *Ceramics (in Japanese)*, **32**, (1997) 997.
 10. Y.-K. Jeong, A. Nakahira, P. E. D. Morgan and K. Niihara: *J. Am. Ceram. Soc.*, **80**, (1997) 1307.
 11. S.-T. Oh, T. Sekino and K. Niihara: *Nanostruct. Mater.*, **10**, (1998) 327.
 12. W. D. Kingery, H. K. Bowen and D. R. Uhlmann, in *Introduction to Ceramics* (2nd ed), p. 785, John Wiley and Sons, New York (1976).
 13. M. P. Harmer, S. J. Bennison and C. Narayan: *Mater. Sci. Res.*, **15**, (1983) 309.
 14. S.-T. Oh, M. Sando and K. Niihara: *Scripta Mater.*, **39**, (1998) 1413.
 15. B. D. Cullity, in *Introduction to Magnetic Materials*, p. 266, Addison Wesley, Massachusetts (1972).