Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 259–264

www.elsevier.com/locate/jeurceramsoc

Fabrication of MgO based nanocomposites with multifunctionality

T. Nakayama[a,*], Bum-Sung Kim[a], Hiroki Kondo[a], Yong-Ho Choa[b], Tohru Sekino[a], Masaaki Nagashima[a], Takafumi Kusunose[a], Yamato Hayashi[a], Koichi Niihara[a]

[a]*The Institute of Scientific and Industrial Research, Osaka University, Osaka 567-0047, Japan*
[b]*The Graduate School of Industry and Management, Hanyang University, Ansan 425-791, South Korea*

Abstract

The nanocrysialline FeCo alloy dispersed MgO nanocomposites were fabricated by the reduction and sintering of mixtures. The powder mixtures of nano-sized FeCo alloy and MgO were obtained by the solution chemical processes and hydrogen reduction of MgO, Fe- and Co-nitrates powders. Fully densitified MgO/FeCo alloy nanocomposites were fabricated by a pulse electric current sintering (PECS) method. The fracture toughness increased with increasing volume fraction of FeCo alloy. Moreover, an inverse magnetostrictive response to applied stress was obserserved, because of the FeCo alloy dispersions, which indicates promise for incorporating multifunctions such as stress sensing into the structural ceramics with high fracture toughness.

Keywords: Magnetic properties; Mechanical properties; MgO; Multifunctionality; Nanocomposites

1. Introduction

Recent investigations have led to the development of ceramic–metal nanocomposites such as $A1_2O_3$/Ni[1] ZrO_2/Ni[2] and MgO/Fe.[3] In this field, reinforcement models underline the interest of a homogeneous dispersion of nano-sized metal particles in a ceramic matrix. Mechanical properties such as fracture strength and toughness are expected to be simultaneously improved by the nanocomposites technology for MgO/metal and/or alloy systems.

In addition, the studies of the ceramic/metal interface and the mechanical, magnetic and electrical properties represent other interesting subjects for future researches. With the recent progress in chemical processing, it is now possible to obtain desirable microstructures with homogeneous dispersions of nano-sized metal phases and which show unique physical propeities.[1–3] However, in order to develop such a material, optimization of the powder preparation and sintering process and an understanding of the roles of the nano-sized dispersions are still required to solve. In the present study, we have selected the FeCo alloy as the dispersant, because of this system show not only good mechanical properties but also high magnetic and magnetomechanical properties. In this paper, the relationship between the microstructure and the mechanical and magnetical properties will be described for the MgO/FeCo systems. In addition, the inverse magnetostrictive response to applied stress of nanocomposites will be discussed.

2. Experimental procedures

2.1. Preparation of materials

The solution chemistry route was selected to obtain the powder mixtures used for the composites. High-purity iron nitrate

$$\left(Fe(NO_3)_3{\cdot}9H_2O,\ 99.9\%\right)$$

and cobalt nitrate $\left(Co(NO_3)_2{\cdot}6H_2O, 99.9\%\right)$ were used as source materials for FeCo alloy dispersions. Weighted nitrate corresponding from 0 to 40 vol.% of FeCo alloy (Fe-50 at.% and Co-50 at.%) in final specimens was dissolved in alcohol. Subsequently, MgO powder ($d_{av.} = 100$ nm) was mixed with the earlier-mentioned solution and ball-milled for 24 h. When dried, the mixtures were dry ball-milled for 12 h and calcined at 673 K for 3 h in air to obtain oxide (MgO, γ-Fe_2O_3 and CoO) powder mixtures. The obtained powder mixtures were reduced to MgO/FeCo under hydrogen gas flow at 1373 K for 1 h. These reduced powders were sistered at 1473 K for 5 min by

* Corresponding author.
E-mail address: nky15@sanken.osaka-u.ac.jp (T. Nakayama).

0955-2219/03/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0955-2219(03)00237-1

the pulse electric current sintering (PECS) with an applied uni-axial pressure of 100 MPa. The heating rate was fixed at 200 K/min.

2.2. Evaluation

The phase composition of the powders was examined by X-ray diffraction (XRD). The microstnicture of the powders was observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The fracture toughness (K_{IC}) at room temperature was determined simultaneously by the indentation fracture (IF) method. The magnetization curve of the composites was measured using a SQUID magnetometer with an applied magnetic field up to ± 10 kÖe (= 1 Tesla) at 300 K.

The magnetization change of the nanocomposites under an applied stress was estimated by measuring the AC susceptibility under unaxial compression with Hartshorn bridge method in a weak applied magnetic field (5 Öe). The measurements were performed at 300 K. The detailed instrument setup is described elsewhere.

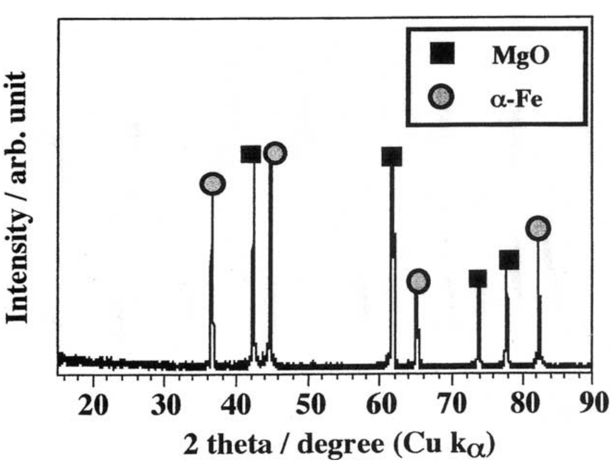

Fig. 1. XRD patterns for MgO/20 vol.% Fe composites.

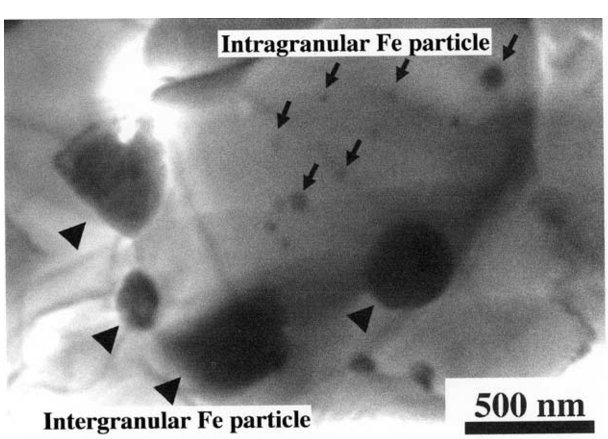

Fig. 2. The transmission electron microscopy micrograph of the MgO/2O vol% Fe composite.

The deformation produced in the system by an externally applied stress makes certain magnetization directions energetically favored, so that the system will tend to align its magnetization to those directions. This magnetization change under applied stress has opened up a range of possibilities for the utilization of ferromagnetic materials in practical applications such as the remote sensing of the mechanical stress.

3. Results and discussion

3.1. Phase composition and microstructure of the composites

Relative densities of above 98% were obtained with PECS at 1473 K at an applied pressure of 100 MPa. This temperature is 100–150 K lower than that by hot-pressing for obtaining dense MgO specimen.[4,5] The XRD patterns for the MgO/Fe nanocomposite prepared by sintering processes are shown in Fig. 1. Even after smntering, the XRD pattern contains the only MgO and metallic iron. This tendency was observed all other specimens, MgO/FeNi and FeCo alloy systems.

Fig. 2 shows the TEM micrograph of the MgO/20 vol.% Fe composite. Densely sintered MgO/Fe nanocomposites show the bimodal distribution of the particle size of metallic Fe dispersions, that is, 10–50 nm for intragranular dispersions and 300–500 am for intergranular dispersions at grain boundaries and triple junctions. The size of intergranular particle increased with increasing iron volume content. From these results, it is clearly understood that intergranular Fe particles were grown with increasing temperature during the sintering and volume fraction of Fe. This feature was due to migration and coalescence of metallic Fe particles, which the mobility of metallic Fe particles as a second phase in MgO/Fe system larger than that of MgO grain boundaries during the sintering (see Fig. 3). As a result, metallic Fe particles, which located at MgO grain boundary or triple junction were migrated with the movement of MgO grain boundaries, and the coalescence of metallic Fe particles was occurred. After metallic Fe particles were coalesced, the drag force of Fe particles was enhanced for the movement of MgO grain boundary, as a result, the growth of MgO grain was inhibited. MgO matrix grain size for MgO/20 vol % Fe composite sintered at 1473 K was approximately 1.3 μm and increased to be around 2.5 μm when the specimen was sistered at 1673 K. For MgO monolith, the grain size was about 4.2 μm when the specimen was sintered at 1673 K. It is, therefore, thought that the iron particulate dispersion can inhibit the matrix grain growth as likely to the SiC[6] dispersion in MgO.

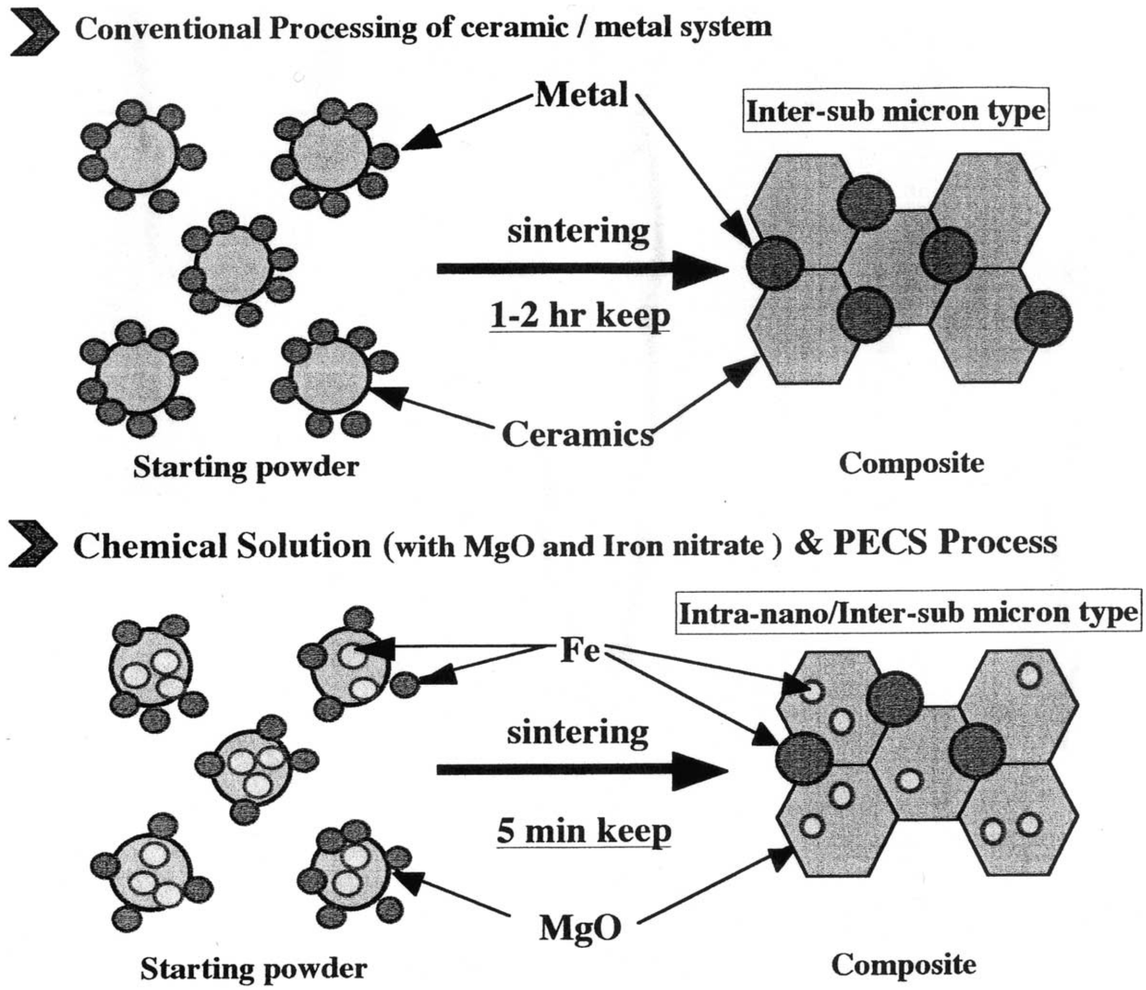

Fig. 3. Schematic drawings of the sintering mechanisms during the pulse electrical current sintering.

3.2. Mechanical properties

Fig. 4 shows the effect of iron content on the fracture toughness (K_{IC}) for MgO/Fe composites sintered at 1473 K. The Vickers hardness decreased with increasing volume fraction of iron. On the other hand, the fracture toughness of 1.85 MPa $m^{1/2}$ was achieved for the MgO containing only 10 vol.% of Fe, whereas highest toughness of 2.35 MPa $m^{1/2}$ was obtained for MgO/40 vol.% Fe composites. From SEM observation, it was found that the crack was partly deflected and partly bridging by intergranularly dispersed submicron sized iron particles. This result is in good agreement with HREM result that MgO and metal interface is strong.

In the metal/ceramic system, the main factors promoting PECS sintenng are the Joule heat generated by the metal power and the plastic flow of metals due to the application of pressure, and then the excess metallic iron was preferentially agglomerated.

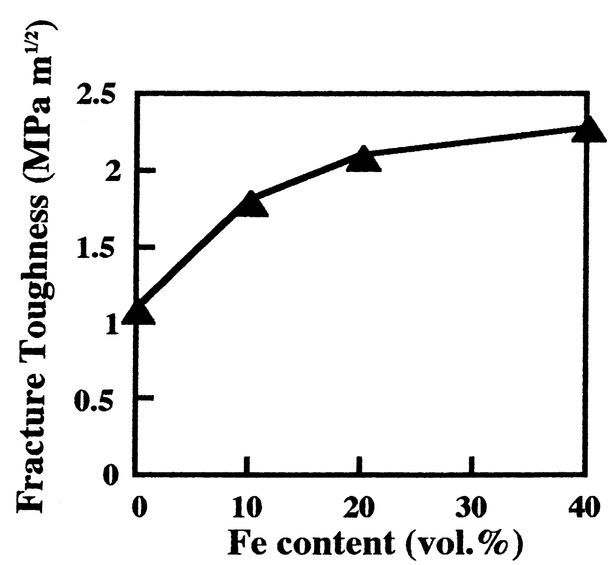

Fig. 4. Fracture toughness (K_{IC}) for MgO/Fe composites sintered at 1473 K.

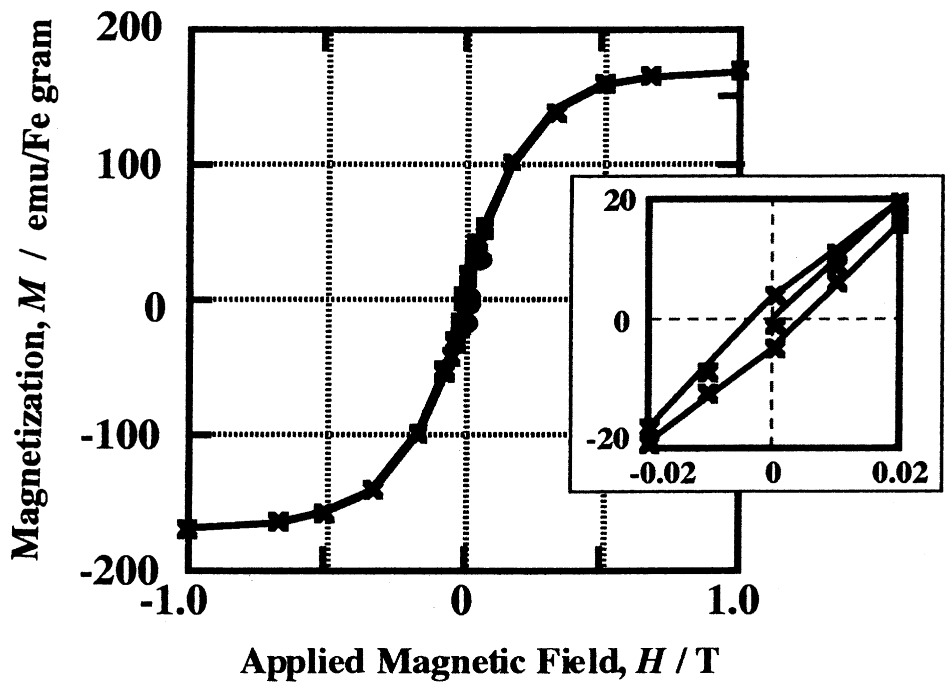

Fig. 5. Room temperature magnetization versus applied field curve for the MgO/20 vol.% Fe composite. Inset shows enlargement of the plot near the origin.

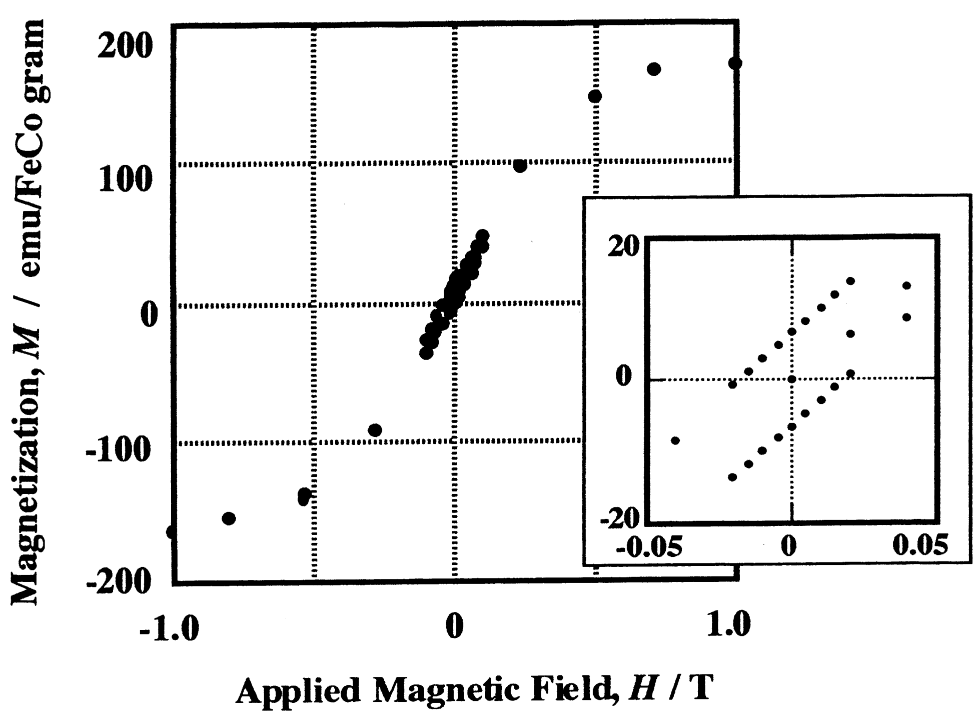

Fig. 6. Room temperature magnetization versus applied field curve for the MgO/5 vol.% FeCo alloy composite. Inset shows enlargement of the plot near the origin.

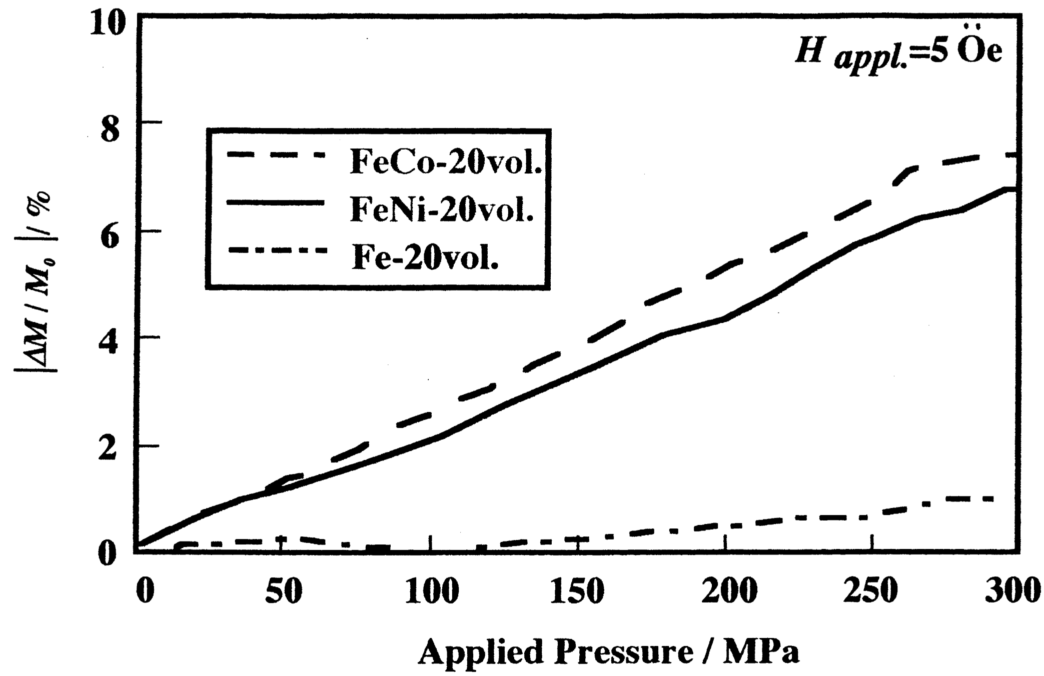

Fig. 7. The relationship between magnetization change ($\Delta M/M_0$) in the applied stress of 0–300 MPa.

Table 1
Magnetic properties and average grain sizes of MgO/Fe, Fe-Ni and FeCo composites

Materials	Saturation magnetization M_s^{Metal} (emu/metal gram)	Coercive force H_C(Öe)	Average grain size $d_{av.}$ (nm)
MgO/20 vol.% Fe composite	188	55	400
MgO/20 vol.% FeNi composite	137	27	420
MgO/5 vol.% FeCo composite	167	195	220
MgO/10 vol.% FeCo composite	183	98	390
MgO/20 vol.% FeCo composite	205	90	430

Table 2
The value of the magnetization change at the applied stress of 200 MPa and the saturated magnetostriction (λ_S) of standard samples

	$\lvert\Delta M/M_0\rvert$(%)	$\lambda_S(10^{-6})$
MgO/20 vol.% Fe composite	0.1.5	−9
MgO/20 vol.% FeNi composite	4.1	28
MgO/20 vol.% FeCo composite	4.8	65

3.3. Magnetic property

For the MgO/20 vol.% Fe and 5 vol.% FeCo composite systems a hysteresis loop of the *I–H* curve (Figs. 5 and 6) was obtained by SQUID magnetometer measured at 300 K, clearly showing the ferromagnetism of iron dispersed in the MgO matrix. The coercive force (H_c) is 55 *Ö*e (Fe) and 195 *Ö*e (FeCo), which is approximately two orders of magnitude larger than that of pure iron metal [0.14–1.4 Öe(≈11–111 A/m)].[7] H_c is well known to be strongly dependent on the grain size and dislocation density.[7,8] When the particle size of a magnetic material decreased, its magnetic structure varies from a multi domain state to a single domain state, to reduce the total energy of the system; hence H_c is presented.[8] The extremely high value of H_c was reported for particle size in the range of several 10 nm, with corresponds to the magnetic single domain structure. In this composite, the size of intragranular iron particle is almost same of this range. It seems that this type of iron dispersions might have a single domain structure.

The saturation magnetization (Ms) of the MgO/20 vol.% Fe, FeNi and FeCo composite are estimated by Arrott plot (Table 1). These values are close value of reference data[9,10] at room temperature. This result also support the XRD and HREM results that no reaction phases are observed. A relationship between applied stress and deviation of magnetization (permeability) in

MgO/metal or alloy nanocomposites were measured by the DC susceptibility measurement under uni-axial compressional stress applied through alumina rod. DC susceptibility was measured in applied weak magnetic field (5 Öe) under applied stress varied from 0 to 300 MPa uni-axially. Fig. 6 shows the relationship between magnetization change ($\Delta M/M_0$) in the applied stress of 0–300 MPa of the various phases.

It is evident that the magnetization change in all the composites increased as the applied stress increased in Fig. 7. Also, FeNi and FeCo alloys are considered to be effective in amplifying the magnetization sensitivity. Table 2 shows the value of the magnetization change at the applied stress of 200 MPa and the saturated magnetostriction of standard bulk materials.[9] These results suggest that the high volume magnetostriction factor contribute to the inverse magnetostrictive response of the MgO-based composites.

4. Conclusions

MgO-based composites with a homogeneous dispersion of nano-sized ferromagnetic dispersoids have been successfully fabricated by reducing and PECS of MgO/metal oxide composite powders prepared using a solution chemical route. These mixtures were easily obtained from the MgO and corresponding nitrate by calcination in air at a low temperature. The intergranularly dispersed ferromagnetic nano-particles inhibited grain growth of the MgO matrices. The fracture toughness increased with increasing volume fraction of Fe. The increased toughness due to the plastic deformation of metal was confirmed for the composites containing large amount of metal dispersion. The ferromagnetism of nanometer-sized ferromagnetic particles to exhibit the high coercive force was contributed to the nano-sized ferromagnetic dispersions in MgO-based composites. Magnetization response to applied uni-axial stress in the nanocomposites was observed by the amplified magnetostriction effect of nanodispersoids. This magnetization change observed with the applied stress implies that the MgO/ferromagnetic metal nanocomposites have a strong possibility to use the stress/fracture sensing. Remote sensing of the applied stress on the structural ceramics combining with the fracture mechanics enhances reliability of ceramics by controlling the operating condition.

These results suggested that the method used in this study is found to be of great advantage to fabricate ceramic/metal nanocomposites possessing desirable microstructure for the multi functional composites.

References

1. Sekino, T., Nakajima, T. and Niihara, K., Mechanical and magnetic properties of nickel dispersed alumina-based nanocomposite. *Mat. Lett.*, 1996, **29**, 165–168.
2. Sekino, T., Nakajima, T., Ueda, S. and Niihara, K., Reduction and sintering of a nickel-dispersed-alumina composite and its properties. *J. Am. Ceram. Soc.*, 1997, **80**, 1139–1148.
3. Nakayama, T., Choa, Y.-H., Sekino, T. and Niihara, K., Powder preparation and microstructure for nano-sized metallic iron dispersed MgO based nanocomposites with ferromagnetic response. *J. of Ceram. Soc. Japan*, 2000, **108**(9), 781–784.
4. Evans, A. G. and David, R. W., *Phill. Mag.*, 1969, **20**, 373.
5. Yasuda, K., Kim, S. D., Kanemichi, Y., Matsuo, Y. and Kimura, Y., *J. Ceram. Soc. Jpn.*, 1990, **98**, 1103.
6. Choa, Y.-H., Kawaoka, H., Sekino, T. and Niihara, X., Microstructure and mechanical properties of oxide based nanocomposites fabricated by spark plasma sintering K. *Key Eng. Mat.*, 1997, **132–136**, 13–20.
7. Luborsky, F. E., Mendelsohn, L. I. and Paine, T. O., *J. Appl. Phys.*, 1957, **28**, 344.
8. Luborsky, F. E. and Paine, T. O., *J. Appl. Phys.*, 1960, **31**, 68S.
9. Chikazumi, S., *Physics of Ferromagnetism-Magnetic Characteristics and Engineering Applications*, 2nd ed. Syokabo, Tokyo, 1984.
10. Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics*. John Wiley and Sons, New York, 1976.