Powder Preparation and Microstructure for Nano-Sized Metallic Iron Dispersed MgO Based Nanocomposites with Ferromagnetic Response

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強磁性を有するナノサイズ鉄を分散したマグネシア基ナノコンポジットの粉末合成法と微細構造

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MgO based nanocomposites including ferromagnetic iron particle dispersions, with a volume content < 40 vol%, were fabricated by a reduction/sintering of MgO and iron oxide powder mixtures. The oxide powder mixtures were prepared by solution chemical processes to obtain a suitable microstructure of ceramic/metal nanocomposites. Iron-nitrate as a source of metal dispersion was dissolved into alcohol and mixed with MgO powder. After calcination in air, the iron oxide in the powder mixture was reduced by hydrogen. Dense nanocomposites were obtained by pulse electric current sintering (PECS) process. Phase analysis of the synthesized powders as a function of calcination temperature and reduction process was carried out using a system for thermogravimetry and differential thermal analysis (TG-DTA), concurrently with X-ray diffraction (XRD) analysis. According to this preparation process, an MgO/Fe nanocomposite material with enhanced fracture toughness and ferromagnetic responses was successfully fabricated.

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1. Introduction

Recent investigations have led to the development of ceramic/metal nanocomposites such as $\text{Al}_2\text{O}_3/\text{W}$,^{1,2)} $\text{Al}_2\text{O}_3/\text{Ni}$,^{3,4)} ZrO_2/Ni ⁵⁾ and MgO/Ni .⁶⁾ The mechanical properties were improved due to the microstructural control associated with the nano-sized metal dispersion. Furthermore, Ni-dispersed Al_2O_3 nanocomposite exhibited both high strength and ferromagnetic properties.^{3,4)} This implies that another combination of matrix and metal dispersion will also allow us to obtain nanocomposite materials with superior multiple properties.

Therefore, we have focused on the development of Fe-dispersed magnesia composites. Iron is superior to nickel in both mechanical and magnetic properties, and MgO ceramics show the desirable refractory with respect to molten metal and lower reactive materials than Al_2O_3 ceramics. In this composite, enhanced mechanical and magnetic properties, which have already been shown for the $\text{Al}_2\text{O}_3/\text{Ni}$ ^{3,4)} and MgO/Ni ⁶⁾ systems, are expected.

However, in order to develop such a material, optimization of the powder preparation and sintering process and an understanding of the role of the nano-sized dispersions are required. Recently, pulse electrical current sintering process (PECS) has gained much interest as a new process similar to hot-pressing (HP), because the pressure is applied during heating. PECS enables to sinter at considerably higher heating rates, thereby giving the refinement of the second phase metal particle by skipping the coarsening region at low temperatures.^{7)–9)}

To fabricate the fine Fe-particle dispersed MgO composites, both reduction and PECS process was applied to MgO and iron oxide mixtures prepared by a solution chemically route. The purpose of the present work is to investigate the powder preparation process and the relationship between the microstructure and mechanical properties of MgO/Fe nanocomposites and to evaluate the magnetic properties which are closely relate to the microstructure.

2. Experimental procedure

The solution chemistry route was selected to obtain the powder mixtures used for the composites. High-purity iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.9%; Wako Pure Chemical Industries, Ltd.) was used as a source material for metal dispersion. Weighted nitrate corresponding to 0 to 40 vol% of metal in the final specimens was dissolved in alcohol. Subsequently, MgO powder with an average particle size ≈ 100 nm (Ube Material Industries, Ltd.) was mixed with the nitrate solution and ball-milled for 24 h. After drying, the mixtures were ball-milled for 12 h and calcined at 673 K for 2 h in air to obtain MgO/iron oxide mixed powders. The obtained oxide powder mixtures were reduced to MgO/Fe under hydrogen gas flow at 1373 K for 1 h. The pulse electric current sintering (SPS 3.20 MK-IV; Sumitomo Coal Mining Co., Ltd.) with an applied uni-axial pressure of 100 MPa was accomplished at 1473 K for 5 min under an Ar-gas atmosphere and a fixed heating rate of 200 K/min.

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) of the MgO/iron nitrate mixtures were performed using a Shimadzu DTG-50 in air at a heating rate of 10 K/min up to 673 K. All sintered samples were cut and polished by diamond pastes to get the mirror surfaces. The resultant phases were characterized by X-ray diffraction (XRD). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study the composite powder morphology and the microstructure of sintered materials. Density was measured by the Archimedes method using toluene. Hardness (H_V) was evaluated by Vickers indentation using a load of 98 N for 15 s in air. Fracture toughness (K_{IC}) at room temperature was determined by the indentation fracture (IF) method.¹⁰⁾ K_{IC} values were calculated using the empirical equation proposed by Niihara et al.¹⁰⁾ for a median crack. Magnetization curve of each composite was measured using a SQUID magnetometer with an applied magnetic field up to ± 15000 gauss.

3. Results and discussion

3.1 Phase composition of powders and sintered composites

TG-DTA curves of the MgO/Fe-nitrate mixture (MgO/20 vol% Fe) shown in Fig. 1 demonstrate that almost all of the weight loss occurs below 673 K due to loss of water of hydration and nitrate decomposition. After heating at 673 K for 1 h, the weight loss was complete. From these results, we fixed calcination temperatures to be 673 K for MgO/Fe-nitrate mixtures.

Fig. 1. Thermogravimetry and differential thermal analysis (TG-DTA) curves for the MgO/Fe-nitrate mixture (heating at 10 K/min up to 673 K).

Fig. 2. XRD patterns for the starting mixture prepared by solution chemistry route for the mixture of MgO and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (a) after drying, (b) after calcination, (c) after reduction and (d) after sintering.

The XRD patterns for the MgO/20 vol% Fe composite prepared by calcining, reducing, and sintering processes are shown in Fig. 2. The XRD pattern after drying (Fig. 2(a)) contains the characteristic peaks for MgO, $\text{Mg}(\text{OH})_2$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. After calcination at 673 K, the Fe-nitrate forms $\gamma\text{-Fe}_2\text{O}_3$ (Fig. 2(b)). No reaction phase such as Fe-spinel was observed in this experiment. After reduction at 1373 K, $\gamma\text{-Fe}_2\text{O}_3$ turned to metallic iron, however no other reaction phases are observed (Fig. 2(c)). In addition, no reduction of the MgO matrix was observed in this experiment. Even after sintering, the XRD pattern reveals metallic iron and MgO as the only crystalline constituents (Fig. 2(d)).

TEM observation of the calcined powder mixtures revealed that the primary particle size of $\gamma\text{-Fe}_2\text{O}_3$ was approximately 20–30 nm for the MgO/20 vol% Fe mixture. The produced $\gamma\text{-Fe}_2\text{O}_3$ particles mainly existed around MgO particles. The size distribution of iron metal has been initial stage not shown hydrogen reduction at 1373 K for 1 h as shown in Fig. 3(b).

A surprising results is that the particle size of MgO with of 100 nm (see also Fig. 3(a)) decreases down to several ten nm for the composite powders after hydrogen reduction at 1373 K for 1 h, while, after wet ball-milling and drying of only MgO powder with BuOH, the particle size of MgO powder was not changed under the same milling conditions. The reason for these observations may be found in the hydration (the formation of $\text{Mg}(\text{OH})_2$) of the MgO powder

Fig. 3. TEM micrographs of the (a) as-received MgO powder and (b) MgO/20 vol% Fe nanocomposite powder reduced at 1373 K.

via the water from nitrate. In the presence of MgO, the hydration of MgO is (relatively easy) formed,¹¹⁾ specially the hydration will be enhanced during the wet-milling process according to Eq. (2).

Thus, a fracture of the MgO powder reacted with water to nitrate, and sequentially the particle size of MgO is decreased when Mg(OH)₂ again decomposes to MgO by calcination at 673 K (Eq. (3)).

This reaction mechanism would explain, the presence of Mg(OH)₂ peaks in the XRD analysis of the dried powder mixture before calcination, as shown Fig. 2.

Sintering was performed under an Ar-gas atmosphere at 1473 K using PECS method. XRD analysis revealed that the specimens sintered by the fabrication sequence were only composed of MgO and Fe without any additional reaction phases. Figure 4 shows the TEM micrograph of the MgO/20 vol% Fe composite. The densely sintered MgO/Fe nanocomposite shows a bimodal distribution of the particle size of metallic Fe dispersions, that is, 10 to 30 nm for intragranular dispersions and 300–600 nm for intergranular dispersions at grain boundaries and triple junctions. The size of intergranular particles increased with increasing iron content (from 50–150 nm for MgO/5 vol% Fe to 300–600 nm for MgO/20 vol% Fe). From these results it is clearly understood that intergranular Fe particles were grown with increasing sintering temperature and increasing volume fraction of Fe. It is assumed that this feature was due to migration and coalescence of metallic Fe particles, owing to their higher mobility as a second phase in the MgO/Fe system, as compared to the MgO grain boundaries. As a result, metallic Fe particles, which are located at MgO grain boundaries or triple junction, dragged along during the movement of MgO grain boundaries, and the coalescence of metallic Fe particles was occurred. It is, therefore, reported above that iron particulate dispersion can inhibit the matrix grain growth similar to SiC¹²⁾ and Ni⁶⁾ dispersions in MgO.

MgO matrix grain size of the 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 sintered at 1673 K. In comparison, the corresponding grain size of the pure MgO monolith was about 4.2 μm after sintering at 1673 K. Coalescence of metallic Fe particles consequently increases the drag force required for the movement of MgO

grain boundary, which, as a result, inhibits the MgO grain growth.

3.2 Mechanical properties

Figure 5 shows the effect of iron content on Vickers hardness (H_V) and 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 1.1 MPa·m^{1/2} for the MgO monolith increased to 2.35 MPa·m^{1/2} for the MgO/40 vol% Fe composite. The toughening mechanism was considered to be crack deflection and particle bridging by ductile Fe particles. In Fig. 6, the SEM image of the crack propagation in the MgO/20 vol% Fe composite is shown. It was clearly found that the crack was deflected by Fe particles and partly bridging by ductile metallic Fe particles.

3.3 Magnetic properties

For the MgO/20 vol% Fe composite system, a hysteresis loop of the I - H curve was obtained by SQUID magnetometer measured at 300 K (Fig. 7). This figure clearly showing the ferromagnetism of metallic Fe particles dispersed in the MgO matrix. The saturation magnetization (I_s) of the composite is estimated by an Arrott plot. I_s is found to be 187 emu/iron gram, which is close to the value of pure iron at room temperature, 217.2 emu/gram. The coercive force (H_c) is 55 gauss, which is approximately two orders of magnitude larger than that of pure iron metal (less than 1.0 gauss¹³⁾). H_c is well known to be strongly dependent on the particle size and dislocation density.^{4),14)} When the particle size of a magnetic material decreases, its magnetic structure varies from a multi domain state to a single domain state, in

Fig. 5. Variation of the Vickers hardness, H_V and fracture toughness, K_{IC} with the Fe content for the MgO/Fe composites.

Fig. 4. TEM micrograph of MgO/20 vol% Fe composite PECSed at 1473 K for 5 min.

Fig. 6. SEM micrograph of typical crack propagation in MgO/20 vol% Fe composite.

Fig. 7. Magnetization curve for MgO/20 vol% Fe composite measured at 300 K.

order to reduce the total energy of the system; hence a high H_c is recorded.¹⁴ The extremely high value of H_c was reported for particle size in the range of several ten nm, which corresponds to the magnetic single domain structure. In this composite, the size of the intragranular iron particles lies in the few ten nm range (see Fig. 4), therefore, it is cogitabled that the present Fe particle dispersion has a single domain structure.

4. Conclusions

MgO based nanocomposites with ferromagnetic iron particle dispersions were successfully fabricated by reduction and PECS process of MgO/ γ -Fe₂O₃ composite powders prepared by a solution chemical route. The typical microstructure of the MgO/Fe composites showed that the dispersed Fe particles were composed of intragranular Fe nano-sized particles of a few ten nm and intergranular Fe particles of several hundred nm in size. This distinguished microstructure was due to migration and coalescence of metallic Fe particles during the sintering process. After metallic Fe par-

ticles were coalesced, the drag force of Fe particles acting on the MgO grain boundaries was enhanced and the growth of MgO grain was inhibited. The observed fracture toughness increased with increasing volume fraction of iron particles. The toughness increase was due to the crack deflection and plastic deformation of the ductile Fe particles, as revealed by SEM imaging. Furthermore, MgO/Fe composites showed an enhanced coercive force as compared to pure Fe materials, due to the presence of intragranular nano-sized iron particles.

References

- 1) T. Sekino and K. Niihara, *Nanostruct. Mater.*, **6**, 663–66 (1995).
- 2) T. Sekino and K. Niihara, *J. Mater. Sci.*, **32**, 1943–49 (1997).
- 3) T. Sekino, T. Nakajima and K. Niihara, *Mater. Lett.*, **29**, 165–69 (1996).
- 4) T. Sekino, T. Nakajima, S. Ueda and K. Niihara, *J. Am. Ceram. Soc.*, **80**, 1139–48 (1997).
- 5) H. Kondo, T. Sekino, Y.-H. Choa and K. Niihara, *Key Eng. Mater.*, **161–163**, 419–22 (1999).
- 6) Y.-H. Choa, H. Hayashi, T. Sekino and K. Niihara, *Key Eng. Mater.*, **161–163**, 493–96 (1999).
- 7) A. Kamiya, *J. Mater. Sci. Lett.*, **7**, 49–51 (1998).
- 8) I. Kondoh, T. Tanaka and N. Tamari, *J. Ceram. Soc. Japan*, **102**, 505–07 (1994) [in Japanese].
- 9) M. Omori and T. Hirai, *New Ceramics*, **7**, 4–8 (1994) [in Japanese].
- 10) K. Niihara, R. Morena and D. P. H. Hasselman, *J. Mater. Sci. Lett.*, **1**, 13–16 (1982).
- 11) T. Seta, Proceedings of an International Symposium held at the Massachusetts Institute of Technology in Cambridge, Massachusetts on June 13–16, 1983, Ed. by W. D. Kingery, Am. Ceram. Soc., Westerville (1984) pp. 541–46.
- 12) Y.-H. Choa, H. Kawaoka, T. Sekino and K. Niihara, *Key Eng. Mater.*, **132–133**, 2009–12 (1997).
- 13) H. Kaneko and M. Honma, “Zisei Zairyo,” Japan Inst. Metals (1977) p. 143.
- 14) R. Kamel and A. Reffat, *Solid State Commun.*, **8**, 821–23 (1970).