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Fabrication of Nano-sized Metal Dispersed Magnesia Based Composites and Related Mechanical and Magnetic Properties

Yong-Ho Choa, Tadachika Nakayama, Tohru Sekino and Koichi Niihara

The Institute of Scientific and Industrial Research, Osaka University
8-1 Mihogahoka, Ibaraki-shi, Osaka 567-0047, Japan
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MgO/metal nanocomposite powder mixtures were prepared by solution chemical processes to obtain suitable structure for ceramic/metal nanocomposites. Nickel or cobalt nitrate, as a source of metal dispersion, was dissolved into alcohol and mixed with magnesia powder. After calcined in air, these powders were reduced by hydrogen. Densified nanocomposites were successively obtained by Pulse Electric Current Sintering (PECS) process. The dispersed metal particle size depended on temperature and time in calcination and reduction processes. The phase analyses in the synthesized powders as a function of temperature were tracked using a dynamic high temperature X-ray diffraction (HTXRD) system. Phase and crystallite size analyses were done using X-ray diffraction and TEM. The MgO/metal nanocomposites were successfully fabricated, and ferromagnetic responses with enhanced coercive force were also investigated for these composites.

Key words: Metal dispersion, Nanocomposites, Mechanical property, Magnetic property, Microstructure

I. Introduction

Ceramic matrix composites containing well-bonded metal inclusions exhibit several advantages compared to single phase ceramics, e. g., high fracture toughness and strength, enhanced thermal shock resistance, high wear resistance, etc. Recently, there is a growing interest in a class of materials known as "nanocomposites," in which ceramic matrices are reinforced with submicrometer metal particles.[1-3] The improvement of mechanical properties was achieved by hot-pressing technique in the ceramic/metal systems. In the nanoparticle-dispersion-strengthening approach, it has been reported that the incorporation of a dispersion of ultrafine (several 10 to 100 nm) metal-phase particles into matrix gives rise to toughening and strengthening due to its high ductility and the possibility of exploiting its inherent toughness that are essential to improve the mechanical properties of ceramic materials.[4,5]

Furthermore, considering the magnetic properties of the composites, it is expected that the ferromagnetism of metal will be demonstrated by incorporating nanometer-sized metal into a ceramics. Fine particulate magnetic materials are already known to exhibit a high magnetic coercive force, because of their magnetic single-domain structure when the crystalline size becomes very fine.[6-8]

Therefore, to fabricate the fine metal particle dispersed MgO composites, we have applied reduction and PECS process which enables to get the fine microstructure by rapid sintering[9-11] to MgO/nickel and MgO/cobalt mixtures prepared by solution chemistry route.

The goals of the present work are to investigate the preparation process and in the resulting microstructural and magnetic properties of MgO/metal composite systems by rapid sintering.

II. Experimental Procedure

1. Preparation of materials

The solution chemistry route was selected to obtain the powder mixtures used for the composites. MgO powder (average particle size: 100 nm, Ube Industries Co., Japan,) was selected as a matrix phase, and high-purity nickel nitrate ($Ni(NO_3)_26H_2O$) or cobalt nitrate ($Co(NO_3)_26H_2O$) (Wako Pure Chemical Industries, Ltd., Japan) as a source material for Ni or Co, respectively. Weighted nitrate powders, corresponding to 5 and 20 vol% of each metal in the final composites, were initially dissolved in alcohol. Subsequently, MgO powder was mixed with above-mentioned solution and ball-milled for 24 h. After dried in microwave oven(in 60 Hz and 500 W) for 2 h, the mixtures were calcined at 500°C for 1h in air to obtain MgO/metal oxide mixed powders. The obtained oxide powder mixtures were reduced to MgO/Ni or MgO/Co under hydrogen gas flow at 800°C and 900°C, respectively, according to the nature of the metallic phase. Recently, pulse electrical current sintering process (PECS) is much interested as a new processing for sintering various kinds of powder materials.[9-11] The process is a type of solid compression sintering process that is similar to hot-pressing (HP) because some pressure is applied during heating. Main effects for enhancement of sintering in hot-pressing process are the

thermal diffusion and plastic flow due to high pressure, whereas it is indicated in the PECS process that self-exothermic effect due to electric discharge between particles at early stage of ON-OFF d.c. pulse application enhances the sintering, as well as effects of high pressure and rapid sintering. Recent reports[10,11] support these advantages of the PECS process by obtaining ceramic composites with high density and fine microstructure. Thus, the pulse electric current sintering (SPS 3.20 MK-IV; Sumitomo Coal Mining Co., Ltd.) with an applied uniaxial pressure of 30 MPa was accomplished at 1200°C to 1500°C for 5 min. under an argon gas atmosphere, and the heating rate was fixed as 150°C/min for all sintering (applied current; 2000 A, and applied voltage; 3 V). Sintered specimens, 2 mm x 2 mm x 15 mm in size, were cut by a diamond-blade wheel and polished with 9, 3, and 0.5 μm diamond pastes until the specimens possessed mirror surfaces.

2. Characterization

The phase composition of the powders and the composites was examined by X-ray diffractometry (XRD) using Cu*Kα* radiation (Model DMS-2000 system, Scintag Co., U.S.A.) even at high temperatures. The density was measured by the Archimedes method using toluene. The microstructure of the powder and composites was observed by scanning electron microscopy (SEM) (Model S-5000, Hitachi Ltd., Japan) and transmission electron microscopy (TEM) (Model H-8100, Hitachi). The magnetization curve of the composite was measured using a vibration sample magnetometer (Model BHV-55, Riken Denshi Co., Ltd., Japan). The mechanical properties, such as hardness and fracture toughness were measured by indentation fracture method at 19.6 N.

III. Results and Discussions

1. Phase composition of powders and sintered specimens

The XRD profiles for the MgO/Ni composite prepared by calcining, reducing, and sintering processes are shown in Fig. 1. The XRD pattern after drying (line "a" in Fig. 1) contains the characteristic peaks for MgO, $Mg(OH)_2$ and $Ni_3(NO_3)_2(OH)_4$ upto 400°C (line "b`" in Fig. 1). After calcination at 500°C, the other peaks are not observed any more, except for MgO peaks (line "c" in Fig. 1). This means that the Ni-nitrate directly form the solid solution with MgO without forming the NiO. However, Co-nitrate shows the different features because of a different solid solution limits with MgO, compared with the Ni-nitrate.

The key phenomenon in the fabrication process was the reduction of additives to metallic second phases. The thermodynamic conditions of reduction process for Al_2O_3/Ni nanocomposites have been well accomplished by Sekino et. al.[3] To reduce the nickel- and cobalt-oxide in present experimental condition, the calculated reduction temperatures were 340°C and 400°C, respectively.

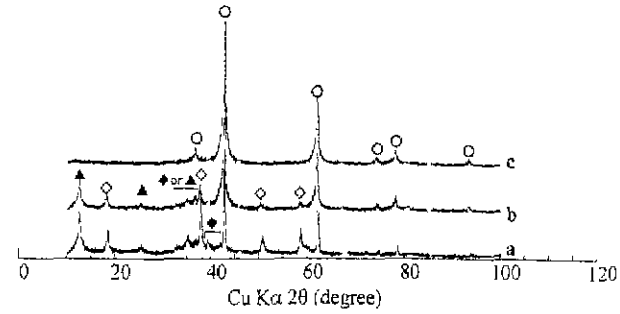

Fig. 1. XRD profiles for the starting mixtures prepared by solution chemistry route for the mixture of MgO and $Ni(NO_3)_2$ $6H_2O$ after dried (line "a"), calcined in air at 400°C (line "b"), and calcined at 500°C (line "c") (○: MgO, ◇: $Mg(OH)_2$, s: $Ni_3(NO_3)_2(OH)_4$ and u: $Ni(NO_3)_2$ nH_2O)

Because the actual experimental condition (reduction temperature and time) depends on the amounts of powder (20 to 50 grams for 1 batch for reduction) and the components of mixture powders (corresponding to 5 and 20 vol% of each metal in the final composites), however, the two kinds of oxide mixtures were reduced to MgO/Ni and MgO/Co under hydrogen gas flow at 800°C and 900 °C for 2 h, respectively. Below these reduction temperatures for each mixture, the remainder of oxide phase was observed.

The morphological characteristics of the mixtures were investigated by TEM for (a) as received MgO powder, and (b) MgO/Ni and (c) MgO/Co nanocomposite powders, as shown in Fig. 2. The shapeless matter coated the MgO particles before calcination, on the other hand, the nitrate was calcined and then turned into fine and spherical particles around 20 nm in size that homogeneously surrounded MgO. After hydrogen treatment at each optimized reduction temperature, the source materials for Ni or Co to be reduced to elemental metallic particles were identified by XRD analysis(see Fig. 3). The size and morphology of the precipitants did not vary (diameter of 10 to 40 nm; see Figs. 2 (b) and (c)).

A surprising result is that the particle size of MgO with 100 nm(see Fig. 2(a)) decreases into several 10 nm for all composite powders The reason for these observations may be found in the hydration (the formation of $Mg(OH)_2$) of the MgO powder: composite powders containing a large amount of water (from nitrate) are hydrated because chemical stability of MgO toward the hydration is relatively easy,[12] specially the hydration will be enhanced during the wet-milling process according to eq. (2).

Thus, a part of MgO powder reacted with water in nitrate (this process depends on the amount of water from the nitrate), and sequentially the particle size of MgO is decreased when $Mg(OH)_2$ decomposed to MgO by calcination at 500°C (eq. (3)).

$$Me(NO_3)_2\ nH_2O(s) + \text{alcohol} \longrightarrow Me(NO_3)_2\text{-}+nH_2O+\text{alcohol} \quad (1)\ \text{(in alcohol)}$$

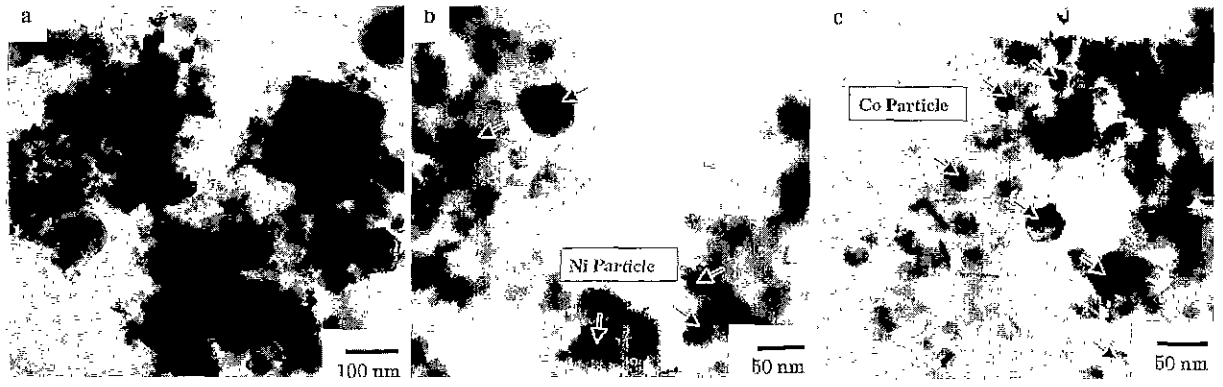

Fig. 2. *TEM micrographs of the (a) as received MgO powder and (b) MgO/Ni and (c) MgO/Co nanocomposite powders reduced at 800°C and 900°C, respectively.*

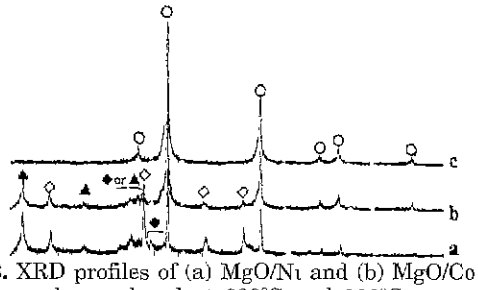

Fig. 3. XRD profiles of (a) MgO/Ni and (b) MgO/Co nanocomposite powders reduced at 800°C and 900°C, respectively.(○: MgO, ▲ : Ni and ◇:Co)

$$MgO(s) + H_2O(l) \text{ ---> } Mg(OH)_2(s) \quad (2) \text{ (during the wet-milling)}$$

$$Mg(OH)_2 \text{ ---> } MgO + H_2O(g) \quad (3) \text{ (during the calcination at 500°C)}$$

This feature is easily understood by the fact whose the XRD analysis revealed strong peaks of $Mg(OH)_2$ peaks at below 500°C is observed, and disappeared at 500 °C, as shown Fig. 1. Sintering was performed under an argon gas atmosphere at 1200°C to 1500°C using PECS method. XRD analysis revealed that the specimens that were sintered by the fabrication sequence were only composed of MgO and Ni or Co without any reaction phases.

2. Sinterability and Mechanical Properties

The densities of composites prepared by PECS processing were strongly dependent on the volume fraction of particulate dispersions and PECSed temperature. For the MgO-Ni composite, the densities of over 95 % were observed at 1400 to 1500°C depending on the volume fraction of Ni particles. The addition of Ni particle into the MgO matrix inhibits the densification and grain growth, as shown in Table 1. It is attributed that the grain boundary was dragged by the second phase Ni particles, as a result, the grain growth was inhibited. In addition, the Ni particle size was increased with increasing Ni content as shown in Fig. 4. The particle size of the nickel in the com-

Table 1. Some Properties of Monolithic MgO and MgO/Ni Composite Prepared at 1400°C

Ni content (vol%)	Relative density (%)	Matrix grian size (μm)	Particle size of Ni (nm)	K_{IC} ($MPam^{1/2}$)	Hv (GPa)
0	97.5	5.3	---	1.1	9.8
5	97	2.3	150	2.3	6.6
10	96	1.6	330	2.7	5.7
20	94	0.95	550	3.4	4.9
5#	91	0.3	50	---	4.4

Measured by Indentation Fracture Method at 19.6 N.
#Sintered at 1200°C

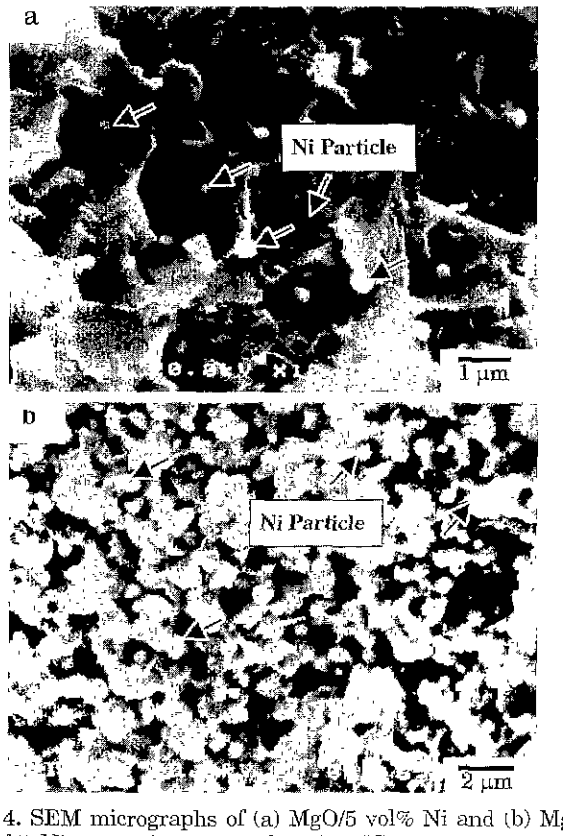

Fig. 4. SEM micrographs of (a) MgO/5 vol% Ni and (b) MgO/20 vol% Ni composite prepared at 1400°C.

Table 2. Magnetic Properties of MgO/5 vol% Ni and MgO/5 vol% Co Composites Prepared by PECS Method at 1200°C

Materials	Saturation magnetization (emu/g)	Coercive force (Oe)
MgO/5 vol% Ni	57.8	100.2
MgO/5 vol% Co	158.2	113.5

posites has been calculated from the several micrographs such as Fig. 4 by using an image analysis technique. The increasing of nickel particle size with its content is due to the coalescence of Ni particle with the grain growth of MgO matrix during the sintering process. Table 1 also shows the mechanical properties for the monolithic MgO and MgO/Ni composites with some compo- sition of Ni prepared at 1400°C. The Vickers hardness was linearly decreased by increasing of Ni content because Ni should be softened. The fracture toughness, K_{IC}, increases from 1.1 to 3.4 $MPam^{1/2}$ with 20 vol% Ni addition. Several previous reports on nickel dispersed ceramic matrix composites system admitted that the plasticity of nickel contributed to the toughening of ceramics.[13-15] A similar me- chanism may be expected in the present case.

3. Magnetic Properties

In the former section, we have already shown how the mechanical property of MgO is improved by dispersing fine metal particles. In this part, we will discuss the modification of the magnetic properties of the composite that are caused by the nano-sized metal particles. The dependence of magnetization (I) on the applied magnetic field (H) was investigated for the MgO/5 vol% nickel and MgO/5 vol% cobalt composites. Moreover, the parameters that are related to the magnetic properties are summarized in Table 2.

Saturation magnetization (Is) of MgO/5 vol% Ni nanocomposites was found to be 57.8 emu/g, which is almost same value with that of pure nickel at room temperature, 50 emu/g. The coercive force (Hc) is 0.1 KOe, which is approximately two orders of magnitude larger than that of pure nickel metal (0.75 Oe). Hc is well known to be strongly dependent on the grain size and dislocation density.[7,16] When the particle size of a magnetic material decreases, its magnetic structure varies from a multi-domain state to a single-domain state, to reduce the total energy of the system; hence, high Hc is presented.[16] Magnetic measurement of the aerosol nickel particles revealed that Hc increased when the particle size was < 300 nm. The extremely high value of Hc was reported for particle size in the range of several 10 nm, which corresponds to the magnetic single-domain structure.[6]

In the present experiments, the average size of dispersed nickel was 50 nm in the MgO/5 vol% Ni composite. It seems that the nickel dispersions might have a single-domain structure. Similar relationship between magnetic properties and microstructure was also observed for MgO/Co nanocomposite.

IV. Summary

The solution chemistry route based on the selective reduction of metal oxides as sources of metal dispersions allows the formation of essentially MgO/metal composite powders with a size in the nanometer level. The microstructure observations revealed that the nanocomposite powders with nanometer-sized MgO and metallic particles were obtained by means of appropriate calcination and reduction, and then it was possible to control the size of not only metal particles but also MgO matrix grains in the composites. The mechanical property of MgO was improved by metal dispersions, and simultaneously, fine metal dispersions into the MgO matrix give to the enhanced ferromagnetic property.

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