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Influence of annealing on the microwave-absorption properties of Ni/TiO_2 nanocomposites

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ABSTRACT

Annealing enlarges the grain size and releases the large microstrain in the Ni/TiO_2 nanocomposite prepared by mechanochemical synthesis. This greatly enhances the dielectric resonance and a clear Cole–Cole semicircle is observed for the annealed sample, for which a maximum of reflection loss (RL) as large as –45.2 dB at 12.6 GHz with RL values exceeding –10 dB in the whole Ku-band is obtained for a layer of 2.3 mm thickness. In particular, a 20 dB bandwidth over the frequency range from 16.4 to 18 GHz with a RL value of 41 dB is found at 17.1 GHz for 2.1 mm thickness. The great improvement of microwave-absorption properties after annealing can be ascribed to an enhanced dielectric resonance and an excellent match of magnetic and dielectric loss.

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1. Introduction

In recent years, much research has been focused on nanocomposites consisting of soft-magnetic metals and insulating oxidation/graphite as electromagnetic-wave-absorbing materials, such as Fe/C [1], Al_2O_3/FeCo [2] and Ni/C [3,4]. The nanocomposites possess a synergistic effect of high microwave permeability in the gigahertz range due to the high Snoek limit for ferromagnetic metals and the high resistivity of the dielectric components, which suppresses the eddy-current effect. Among the nanocompostites, it has been found that the content of the metallic component and the microstructure have large effect on the microwave-absorption properties. Ni/C nanocapsules with a graphite-shell thickness of 9 nm show the best microwave absorption due to an optimal electromagnetic match and an enhanced dipole polarization [4]. In Co/TiO_2 nanocomposites, the natural resonance shifts to lower frequency with decreasing Co content, which is ascribed to a decrease of the dipolar coupling interaction between Co grains [5]. Both the dielectric resonance and multiple magnetic resonances are closely related to the size of the Fe grains in Fe/TiO_2 nanocomposites produced by milling and annealing [6].

Thus far, very few investigations have been focused on the influence of annealing on the microwave-absorption properties of nanocompsites. The symmetry breaking of the lattice in the nanocomposites leads inevitably to surface spin disorder and frustration [7]. Meanwhile, a non-equilibrium solid solution may create a high level of defects/dislocations at the grain boundaries of the nanocomposites, leading to an increase of the effective anisotropy field. Therefore, it is meaningful to explore the influence of annealing on the magnetism, the microstructure and especially on the microwave-absorption properties of the nanocomposites. In the present paper, Ni/TiO_2 nanocomposites have been prepared by mechanochemical synthesis. Annealing leads to a greatly enhanced dielectric resonance at 13.1 GHz and an optimal reflection loss (RL) of −45.2 dB at 12.6 GHz with RL values exceeding −10 dB in the whole Ku-band which is obtained for a layer of 2.3 mm thickness.

2. Experimental procedures

Ni/TiO_2 nanocomposites were prepared by mechanochemical synthesis according to the reaction formula $2NiO + Ti \rightarrow 2Ni + TiO_2$. Mixtures of 7 g of NiO and Ti powder with purity of 99.9% were sealed in hardened-steel vials with steel balls of 12 mm diameter in a glove box filled with high-purity argon. The ball to powder weight ratio is 20:1. Mechanical alloying of the mixtures was carried out for 15 h using a high-energy ball-mill machine with a rotational speed of 800 rpm. During the milling process, not any stop was made. After the milling, 0.6 g of plate-like metal Ni had precipitated from the nanocomposite on the top edge of the steel vial. The as-milled powder was denoted as sample A. Then, part of the powder was annealed for half an hour at 500 °C under vacuum, which was named sample B. For comparison, we also prepared the Ni/TiO_2 nanocomposites with milling time of 5 h and 10 h, which are named as sample C and sample D, respectively.

X-ray diffraction (XRD) measurements of the Ni/TiO_2 nanocomposites were performed on a Rigaku DMAX/2000 diffractometer with small angular steps of $2\theta = 0.02°$ and a fixed counting time of 10 s. A rotating Cu target was used with a voltage of 50 kV and a current of 150 mA [8]. The magnetic properties were measured in a vibrating-sample magnetometer (Lakeshore 7407) at applied magnetic

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fields up to 6 kOe. The toroidal specimens for the measurement of the electromagnetic-wave-absorption properties between 2 and 18 GHz by means of a network analyzer Aligent 8722ES were prepared by uniformly mixing 40 wt% Ni/TiO_2 nanocomposites with a paraffin matrix. The morphology and size distribution of the samples were examined by means of a Hitachi-3400 N scanning electron microscope (SEM). The oxidation behavior was investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) in air atmosphere at a heating rate of 10 °C/min from 20 to 800 °C.

3. Results and discussion

Fig. 1a shows the XRD profiles of selected reflections of the samples A and B. The samples are composed of face-centered-cubic Ni and tetragonal TiO_2 (rutile). The Bragg reflections of Ni of the annealed sample are clearly narrowed, suggesting that after annealing the grain size of Ni increases and the microstrain of Ni decreases. In contrast, as shown in Fig. 1d, the samples C and D show a clear reflection of NiO, indicating an incomplete replacement reaction. The microstrain and grain size of the samples A and B have been determined by quantitative XRD analysis according to the Scherrer and Wilson equation:

$$\frac{\beta_{hkl}^2}{tg^2\theta_{hkl}} = \frac{\lambda_{K_{\alpha 1}}\beta_{hkl}}{D_{hkl}tg\theta_{hkl}\sin\theta_{hkl}} + 16\langle\varepsilon_{hkl}^2\rangle^{1/2}, \quad (1)$$

where λ represents the wavelength of Cu Kα1 radiation, θ_{hkl} and β_{hkl} are the centroid peak position and integral width of the physical broadening profile, respectively [8,9]. D_{hkl} and $\langle\varepsilon^2\rangle^{1/2}$ represent the thickness and mean lattice strain of the grains in the $\langle h\,k\,l\rangle$ direction, respectively. The calculated results show that the microstrain of TiO_2 is negligible for the two samples and in sharp contrast, that Ni has a large microstrain of 0.59% in the as-milled sample which, after annealing, has largely decreased to 0.04%. The large microstrain indicates that the non-equilibrium processing during mechanical alloying creates a high level of defects/dislocations at grain boundaries and after annealing the microstrain is released [9]. The calculated grain sizes of Ni and TiO_2 for sample A are 13.2 nm and 6.3 nm, respectively, while these values are 18 nm and 8.2 nm for sample B.

Fig. 1b and c show the SEM images of the samples A and B. It can be clearly seen that there is a quite large size distribution of the particles for the as-milled samples, varying roughly from 200 nm to 1 μm, whereas the particle size of the annealed sample has clearly increased with a size distribution from 200 nm to 1.5 μm. Analysis by means of energy-dispersive spectroscopy (EDS) shows the presence of the elements of Ti, Ni and O in the two samples. However, the presence of a small amount of Fe originating from the steel vials and steel balls during the milling process cannot excluded because the amount of Fe may be below the detection limit of 1% in the XRD or EDS analysis.

In order to explore the influence of annealing on the thermal stability and the anti-oxidation behavior of the Ni/TiO_2 nanocomposites, DSC and TGA were performed on the samples A and B. As shown in Fig. 2a, the TGA and DSC curves for the as-milled Ni/TiO_2 nanocomposites show a gradual weight gain in the temperature range from 270 to 360 °C, which is associated with an exothermic peak at 280 °C, indicating that Ni nanoparticles slowly oxidize. From 360 to 550 °C, the TGA curve exhibits an abrupt weight gain associated with a broad exothermic peak at about 430 °C, implying serious oxidation and/or self ignition of Ni particles. In comparison, the oxidation of the annealed sample takes place at higher temperatures and the two exothermic peaks shift about 40 °C to higher temperatures (shown in Fig. 2b). Furthermore, the peak corresponding to serious oxidation becomes more prominent. Wang et al. have reported that an increase of the thickness of graphite shell can remarkably enhance the thermal stability of Ni/C nanocapsules [4]. The oxidation temperatures of the graphite shell of Cu/C [10] and FeNi/C [11] nanoparticles are remarkably lower than those of carbon tubes and bulk-graphite. This can be ascribed to a greater defect density of the graphite layers. The enhancement of thermal stability of the annealed Ni/TiO_2 nanocomposites can be ascribed to the decrease of lattice defects and the increase of the Ni grain size.

The magnetic hysteresis loops of the samples A and B at room temperature (shown in Fig. 3a) show that, upon annealing, the saturation magnetization (M_s) increases from 28 to 30 emu/g, accompanied by a decrease of the coercivity from 219 to 157 Oe. According to the nucleation-field theory, the values of the coercivity are influenced by the effective anisotropy field, which is a function of microstrain [12]. A large density of defects like dislocations can react with domain walls and increase the coercivity [7]. As stated above, the annealing process reduces the microstrain from 0.59% to 0.04%. Therefore, the decrease of the coercivity should originate from the release of the residual stress and the reduction of defects/dislocations at grain boundaries, which are introduced during mechanical milling. For comparison, the magnetic-hysteresis loops of the samples C and D are shown in Fig. 3b. The M_s values of the two samples are 27 and 28 emu/g, respectively. As shown by the XRD analysis, upon increasing the milling time, the replacement reaction completes more fully and, accordingly, M_s increases.

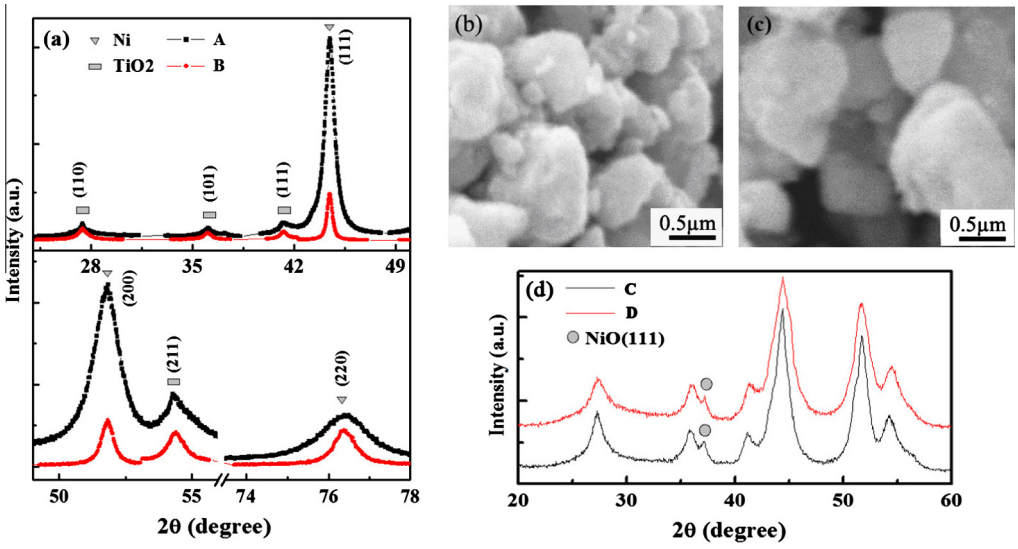

Fig. 1. (a) XRD profiles of samples A and B (b) SEM image of sample A, (c) SEM image of sample B and (d) XRD profiles of samples C and D.

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