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Analysis of exchange bias effect of NiO+$NiFe_2O_4$ composites

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ABSTRACT

Exchange bias (EB) and magnetic properties of ferrimagnetic (FI) $NiFe_2O_4$ and antiferromagnetic (AFM) NiO bulk composites, prepared by a chemical co-precipitation and post-thermal decomposition method from Fe-doped NiO matrix, have been investigated. Enhanced coercivities and shifted hysteresis loops are still observed for these samples after field cooling. But the vertical magnetization shifts are not observed. In comparison with the bulk samples, a NiO/10% $NiFe_2O_4$ nanocomposite was also prepared via direct mixture, in which both the horizontal and vertical shift in the hysteresis loops are observed at 10 K. The observed phenomena are explained in terms of interfacial exchange interaction between the two phases and the finite-size effect, respectively.

1. Introduction

To date, many experimental [1–4] and theoretical studies [5–8] have been performed in attempts to understand the exchange bias since the discovery of this phenomenon in 1956 [9]. There are two general manifestations [10] of exchange interactions that have been observed at the interface between a ferromagnet (FM) and an antiferromagnet (AFM). The first is an exchange bias of the magnetic hysteresis loop that is a consequence of pinned, uncompensated spins at the interface; the second is an enhancement of the coercive field of the ferromagnet as a consequence of enhanced spin viscosity. Even so, the precise origin of exchange bias effect in FM/AFM system is still missing. Recently, Tian et al. [11] reported that, in a granular system of $NiFe_2O_4$ nanoparticles embedded in an antiferromagnetic NiO matrix, both the magnetic hysteresis loop shift and vertical magnetization shift can be observed below 250 K after field cooling, which can be explained in terms of the exchange interaction between the ferrimagnetic phase and the spin-glass-like (SGL) phase at the interface. However, the observation of the shift of the magnetic hysteresis loops in $NiFe_2O_4$ nanoparticles prepared by ball-milled method at low temperature was reported by Kodama [12], and the exchange bias was ascribed to the exchange coupling of ferrimagnetically aligned core spins and a spin-glass-like surface layer. Simultaneously, Kodama [13] also found the antiferromagnetic NiO nanoparticles exhibit a large loop shift and a vertical magnetization shift at low temperature, where the exchange coupling between the frozen moments associated with uncompensated surface spins and the AFM core plays an important role. As one knows, the exchange bias depends upon many parameters, such as the magnetization, the anisotropy or the thicknesses of both layers. Besides, more subtle effects such as roughness or atomic intermixing at the interface also play an essential role. For these reasons, a deeper understanding of the mechanisms of the exchange bias in $NiFe_2O_4$/NiO composites is still challenging.

In this paper, in order to overcome the finite-size effect, we explore further an experimental investigation of a series of $Ni_{(1-x)}Fe_xO$ (x=0.15, 0.2, 0.3 and 0.5) bulk composites with average size ranging from 1 to 10 μm. Enhanced coercivities and shifted hysteresis loops are still observed for these samples after field cooling, while the vertical magnetization shifts vanish. Compared with these samples, a NiO/10% $NiFe_2O_4$ nanocomposite, in which both the horizontal and vertical shift in the hysteresis loops are observed at 10 K, was also prepared via directly mixing the sample NiO and $NiFe_2O_4$. However, the exchange bias disappears at 50 K in this nanocomposite, not in agreement with the phenomena in $NiFe_2O_4$/NiO nanocomposites [11]. These results suggest that the significant coupling interface between the FM phase and the AFM phase is important for exchange bias systems.

2. Experimental

The NiO+$NiFe_2O_4$ bulk composites were prepared by a chemical co-precipitation and post-thermal decomposition meth-

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od from Fe-doped NiO matrix, similar to the description in the literature [14]. Nominal amounts of $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were weighed and dissolved into distilled water. Appropriate amounts of aqueous NH_4HCO_3 solution were then slowly poured into the mixed solution under constant stirring. The resulting precipitation was dried at 80 °C to obtain precursor powders. After that, the precursor was ground and then calcined at 350 °C in air for 4 h. Finally, dry crystalline powders were pressed into spherical shaped pellets and fired at 650 °C for 12 h in air atmosphere to obtain the resultant $Ni_{(1-x)}Fe_xO$ (x=0.15, 0.2, 0.3 and 0.5) bulk samples with large particle size. In comparison with the above samples, 10% $NiFe_2O_4$ nanoparticles were directly mixed into NiO matrix to form a mixture, where the $NiFe_2O_4$ nanoparticles synthesized by a chemical co-precipitation were calcined at 500 °C in air for 2 h, and the NiO matrix synthesized by the same method were calcined at 650 °C in air for 4 h.

The phase compositions of the samples were investigated by X-ray diffraction (XRD) and the morphological characterization was performed by a field emission scanning electron microscopy (FE-SEM) equipped with energy dispersive X-ray spectrometer (EDX). Magnetic measurements were performed using a commercial physical properties measurements system (PPMS, Quantum Design).

3. Results and discussion

Fig. 1 shows the XRD pattern of all the bulk samples. Two sets of different XRD patterns corresponding to $NiFe_2O_4$ and NiO phase can be indexed, which suggests that the composites are composed of Ferri $NiFe_2O_4$ and AFM NiO phases. Furthermore, the peak intensity of $NiFe_2O_4$ in $Ni_{(1-x)}Fe_xO$ bulk samples increased gradually as x was increased up to 0.5.

The SEM photographs for the $Ni_{0.85}Fe_{0.15}O$ bulk sample and the NiO/10% $NiFe_2O_4$ mixture are shown in Fig. 2. One can see from Fig. 2(a) that the size of particles of the $Ni_{0.85}Fe_{0.15}O$ bulk sample becomes obviously big ones and the particle size ranges from 10 to 30 µm, which is approximately consistent with the average crystalline size of 24 µm, calculated using the Scherrer's equation according to the XRD. It is easy to distinguish $NiFe_2O_4$ from the NiO matrix in the NiO/10% $NiFe_2O_4$ mixture from the Fig. 2(b) according to the different particle size resulting from the difference of the sintering temperature. Furthermore, spot energy dispersive X-ray spectroscopy analysis (Fig. 2(c)) was used to confirm that the main composition at point is $NiFe_2O_4$. The average particle sizes of NiO and $NiFe_2O_4$ are estimated as about 100 and 20 nm, respectively.

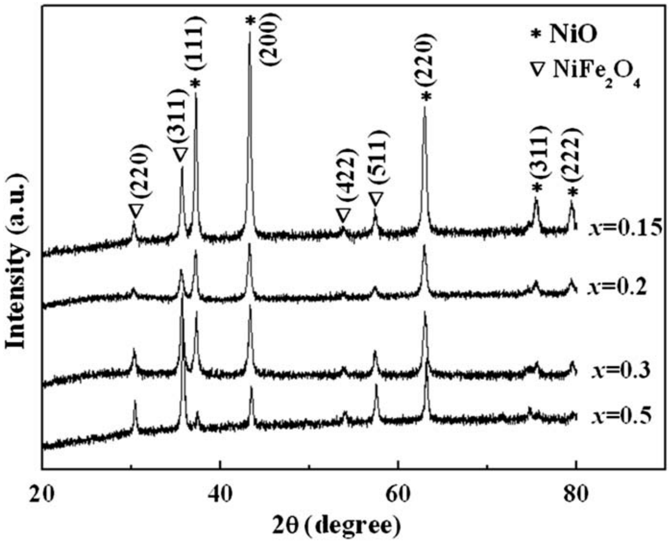

Fig. 1. XRD patterns of $Ni_{(1-x)}Fe_xO$ (x=0.15, 0.2, 0.3 and 0.5) bulk samples obtained after annealing treatment at 650 °C for 12 h.

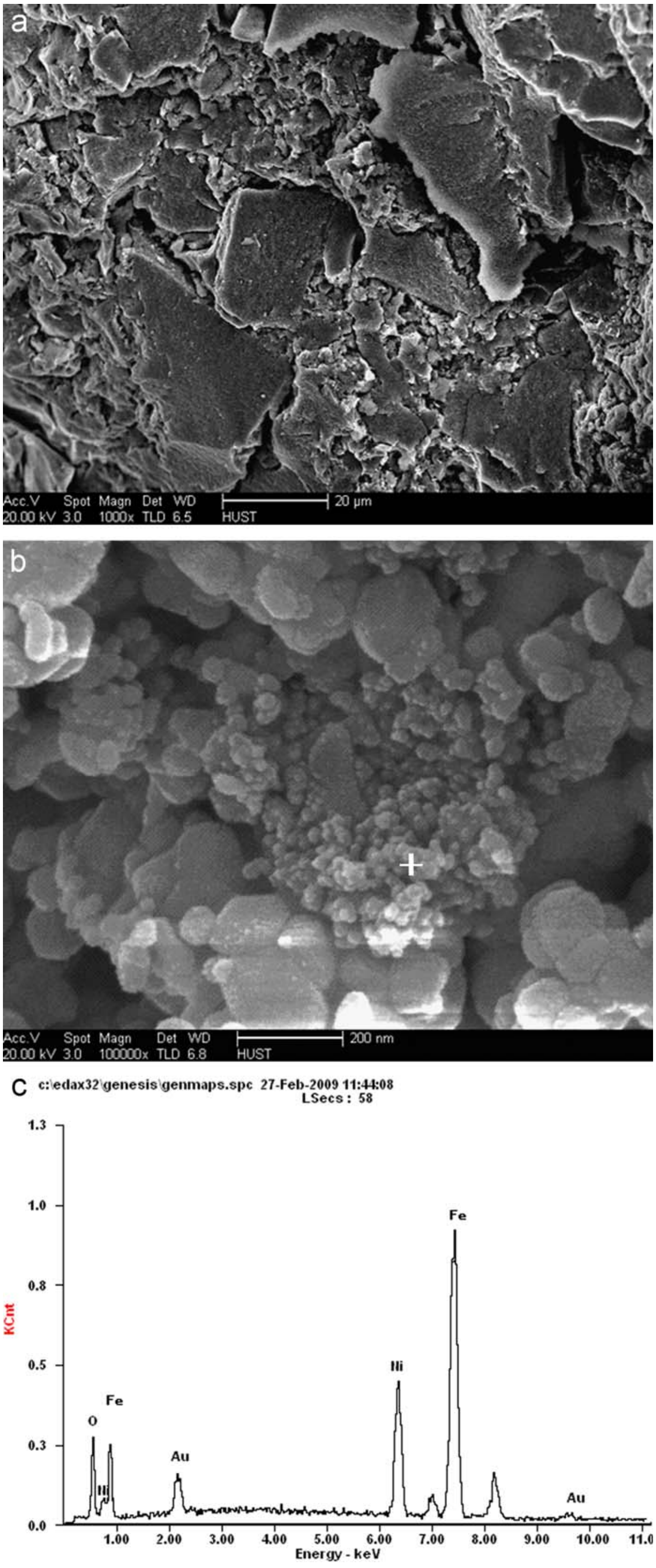

Fig. 2. (a) The SEM image of the $Ni_{0.85}Fe_{0.15}O$ bulk sample, (b) the SEM image of the NiO/10% $NiFe_2O_4$ mixture, and(c) EDX spectrum of labeled point for the NiO/10% $NiFe_2O_4$ mixture.