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Exchange bias and its training effect in Ni/NiO nanocomposites

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ABSTRACT

Exchange bias (EB) and EB training effect have been studied in Ni/NiO nanocomposites, in which a negative EB field of about 2.2 kOe at 5 K is achieved in as-milled Ni/NiO powders upon cooling in a field of 10 kOe. The coercivity of the Ni nanoparticles is significantly enhanced by coupling with NiO. The EB training effect is activated by consecutive application of magnetic hysteresis loops. Besides the FM/AFM interfacial interaction and bulk AFM domain-state model, the model presented by Hoffmann may play an important role to induce such a beneficial initial spin configuration for a typical EB training effect system. Furthermore, a phenomenological relaxation model proposed by Binek is used to describe the next spin configurational relaxation process of AFM interface magnetization towards equilibrium.

1. Introduction

The exchange-bias (EB) effect has been discovered by Meikjohn and Bean [1] in oxide-coated cobalt particles. The exchange interaction between an antiferromagnetic (AFM) and a ferromagnetic (FM) phase results in a unidirectional anisotropy and/or a coercivity enhancement [2–5]. The unidirectional anisotropy may create a shift of hysteresis loop, which is called the EB field (H_E). EB has drawn intense interest because of its intriguing mechanism. One of the interesting characteristics of EB is the training effect, which describes an aging phenomenon expressed by H_E vs n, where n is the number of loops cycled after first setting the EB via field cooling.

Since Néel's original explanation of the training effect [6], several models have been put forward to describe it. Zheng et al. have reported that the EB training effect in γ-Fe_2O_3 coated Fe nanoparticles can be well explained in terms of the modified Stoner–Wohlfarth model [7]. The decrease of the number of frozen spins along the cooling field direction reduces the EB field upon subsequent field cycling. Hoffmann [8] has pointed out that the special anistropy of the AFM layer plays a crucial role in the understanding of the training effect. However, the model can not be used to explain the whole process of EB training effect. A power law is perfectly describes the measured data for $n>1$, but there is a clear breakdown at $n = 1$. Binek et al. [9] have proposed to consider the EB training effect within a phenomenological framework of spin configurational relaxation. A phenomenological energy landscape is introduced to describe this spin configurational relaxation process, which depends exclusively on the deviation of the AFM interface magnetization from its equilibrium. Here, the expansion of free energy F is based on the assumption of time inversion symmetry, which is expected to be fulfilled experimentally. Therefore, as a result, a recursive sequence has been suggested for all loops including $n = 1$.

In the present work, we study the EB and the EB training effect of Ni/NiO nanocomposites prepared by mechanical alloying. The samples consist of Ni nanoparticles dispersed in a nanocrystalline NiO matrix, controlling the Ni amount and applying different annealing temperatures. A typical EB training effect has been observed, which can be described within a theoretical model.

2. Experimental

Ni/NiO nanocomposites were prepared by mechanical alloying of Ni and NiO with purity better than 99.5% mixed in a series of molar ratios. The mixtures of about 4 g were put in argon atmosphere in a hardened-steel vial with steel balls of 12 mm diameter. Mechanical alloying was carried out using a high-energy ball mill which was rotated in two dimensions perpendicular to the horizontal plane [10–12]. The rotation speed of the mill was chosen to be 600 rpm. The weight ratio of ball-to-powder was 30:1 and a milling time of 3 h, was selected. The mechanically alloyed samples were then annealed at 573 or 673 K for 30 min in a vacuum furnace that was directly connected to a closed glove box. The vacuum is better than 8×10^{-3} Pa. X-ray diffraction (XRD) of the powders was conducted using Cu-K_α radiation and the average grain size was determined by means of the Scherrer formula. The magnetic properties were measured in a superconducting quantum interface device (SQUID). The hysteresis loops were measured at different temperatures after field cooling (FC) in a field of 10 kOe. The EB field (H_E) was defined as $H_E = (H_1 + H_2)/2$, where H_1 and H_2 are fields at which the magnetization is zero in the hysteresis loop. We define the coercivity as $H_C = (H_1 - H_2)/2$.

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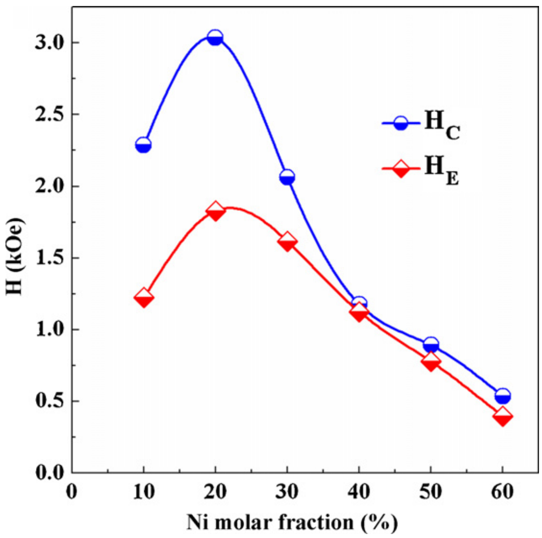

Fig. 1. Dependence of the loop shift (H_E) and the coercivity (H_C) on the FM (Ni) molar fraction for as-milled Ni/NiO powders, measured at 10 K.

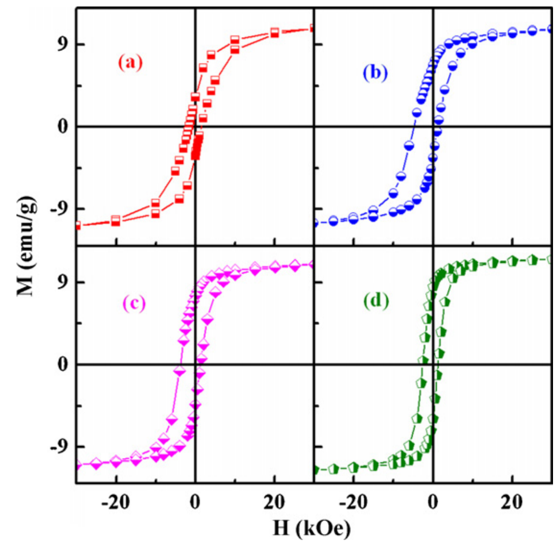

Fig. 3. Hysteresis loops measured at 10 K after field cooling at 10 kOe of a sample (b) milled for 3 h, and then annealed at (c) 573 K, and (d) 673 K; (a) hysteresis loop at 10 K measured after zero-field cooling of the sample milled for 3 h.

3. Results and discussion

The dependence of H_E and H_C on the FM (Ni) molar fraction for Ni/NiO powders milled for 3 h is shown in Fig. 1. Both H_E and H_C have been measured after FC in 10 kOe from 295 K to 10 K. The density of FM moments is very important in the EB mechanism. Therefore, both H_E and H_C progressively increase with the FM (Ni) molar fraction up to 20%. If the FM (Ni) molar fraction is larger than 20%, many Ni nanoparticles tend to give to rise to a percolation-network structure [5]. The physical origin of EB is generally accepted to be an interfacial-coupling effect. When the interface surface between the FM and AFM phase is reduced due to the appearance of agglomerates and percolated structures, the EB effect is sharp weakened, resulting in a clear decrease of H_E and H_C.

Fig. 2 shows the XRD patterns of (a) Ni/NiO powders, in which the FM (Ni) molar fraction is 20%, milled for 3 h, and annealed at (b) 573 K and (c) 673 K for 30 min. Broadened XRD reflections of NiO are observed after milling for 3 h, and also reflection corresponding to Ni is detected. The average grain size of the Ni/NiO powder increases with increasing annealing temperature. In the as-milled powders, the average grain size of NiO in is estimated to be about 7 nm whereas it is about 12 nm, in the powders annealed at 573 K.

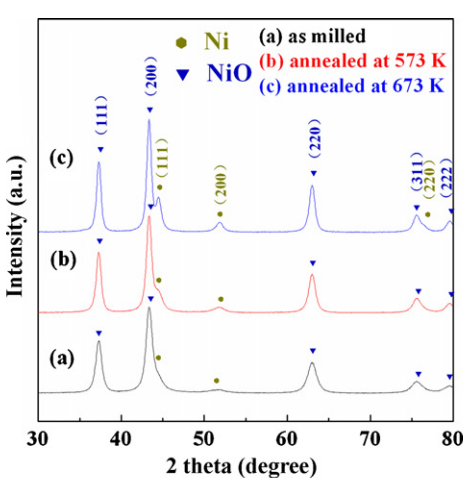

Fig. 2. X-ray diffraction patterns of samples (a) milled for 3 h, and then annealed at (b) 573 K, (c) 673 K for 30 min in a vacuum furnace.

Fig. 3 shows magnetic hysteresis loops at 10 K of the Ni/NiO nanocomposites milled for 3 h (b), and annealed at (c) 573 K and (d) 673 K measured after FC in a field of 10 kOe, and (a) as milled for 3 h and measured from 295 K to 10 K after zero-field cooling (ZFC). For as-milled Ni/NiO powders, the hysteresis loop after the FC process exhibits a clear shift in the negative magnetic field direction, and a large H_E of about 1.8 kOe and H_C of about 3.0 kOe can be seen in Fig. 4(b), in comparison with the ZFC counterpart in Fig. 4(a). After annealing at 573 K and 673 K, the average grain size of the Ni/NiO powders has increased (as revealed by XRD in Fig. 3). According to the domain-state model [13,14], EB acts as a result of a domain state in the AFM phase carrying an irreversible domain-state magnetization. In this model, the formation of AFM domain states is crucial, which can be enhanced by defects introduced during mechanical milling [12]. After annealing at 573 K and 673 K, the number of these defects reduces, leading to a weakening of the EB effect. Therefore, the pronounced maximum values of H_E and H_C can be observed in as-milled Ni/NiO powders.

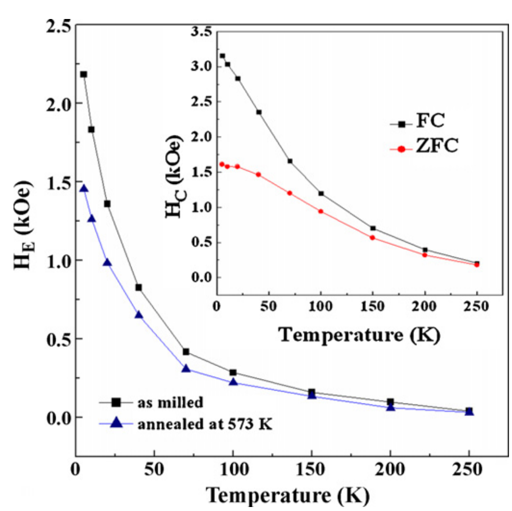

Fig. 4. Temperature dependence of H_E of powders, milled for 3 h and then annealed at 573 K for 30 min, after field cooling in 10 kOe from 295 K. Inset: coercivity of as-milled Ni/NiO powders vs temperature (T) measured after ZFC and FC.