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Journal of Magnetism and Magnetic Materials 258–259 (2003) 358–360
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Granular Fe–Al_2O_3 films prepared by self-propagating high temperature synthesis

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Abstract

Taking for example the initiation of the classical solid-state reaction between Fe_2O_3 and Al layers in films, it was shown that as a result, the granular Fe–Al_2O_3 films consisting of Fe nanoclusters embedded in an insulating Al_2O_3 matrix were made. It follows from the reaction equation that the Fe volume fraction in granular films is less than the percolation limit. This fact defines the magnetic properties of iron clusters, which are superparamagnetic. It is supposed that a nanocrystalline microstructure must be present in thin films after solid-state reaction, which occurs in self-propagating high temperature synthesis conditions.

Keywords: Self-propagating high temperature synthesis; Granular films; Magnetic nanoparticles

1. Introduction

Magnetic granular films consisting of ferromagnetic nanoclusters embedded in an insulating matrix were extensively investigated in the recent years because of their giant magnetoresistance [1], giant extraordinary Hall effect [2], magneto-optical features [3], quantum size effect [4] and potential magnetic recording applications [5,6].

Granular magnetic films containing nanoclusters of Fe, Ni, Co and their alloys in SiO_2 or Al_2O_3 matrix are a main part of these examinations. The most widespread granular film preparation method is the co-deposition of metal and insulator. In this case, the nanoclusters are distributed in matrix randomly and their size depends on annealing and depositing conditions. However, on successive deposition of metal and insulator, self-organization in metal nanocluster formation can be realized [7]. The creation of new methods of granular film preparation is important because it allows to enlarge the structure characters, which define the physical properties of nanocomposites.

2. Experimental procedures

In this paper, we present the deposition method and properties of Fe–Al_2O_3 nanogranular films. The preparation method was based on the use of classical solid-state reaction:

$$Fe_2O_3+2Al = Al_2O_3+2Fe. \quad (1)$$

It was shown [8,9] that solid-state reactions in bilayer thin films at major heating rates are the result of self-propagating high temperature synthesis (SHS). In thin films, the SHS represents a wave of surface burn and is characterized by initiating temperature T_0. The layers of Fe_2O_3 and Al_2O_3 were the reagents of reaction (1). The samples for solid-state reaction consist of two or more layers.

The multilayer Al/Fe_2O_3 structures were prepared by successive DC-sputtering of Al and Fe_2O_3 targets without vacuum destruction. The targets were bulk aluminum and conductive ferric oxide coat. This coat of 1 mm thickness was prepared by plasma deposition of

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PII: S0304-8853(02)01081-8

ferric oxide powders on massive copper plate in reduction atmosphere [10]. Sputtering was carried out in Ar atmosphere at a pressure 5×10^{-2} Pa on glass substrates at temperature $\sim$320 K. The deposition rate was 0.3 nm/s for Al and 0.2 nm/s for Fe_2O_3. The total film thickness was 15–50 and 45–140 nm for Al and Fe_2O_3, respectively. The post-deposited samples were heated at a rate not less than 20 K/s for initiating the SHS wave.

3. Results and discussion

The solid-state reactions of bilayer films took place in SHS mode at the above initiating temperature $T_0 \sim 800$ K.

The propagating front picture was observed visually and was typical for SHS of thin films [8,9]. The visualization of the multilayer film SHS front was difficult. Therefore, these samples were subjected to annealing which included heating above the initiating temperature to 10–20 K and an exposure at this temperature during 5–10 min (necessary time for reaction and post-annealing).

Fig. 1a shows the typical X-ray diffraction pattern of a (20 nm Al/40 nm Fe_2O_3) $\times$ 4 multilayer film before reaction, which contains reflections from α-Fe_2O_3. The formation of a small amount of Fe_3O_4 is also possible in initial samples. The absence of Al reflections means that Al films are amorphous or fine crystalline. After reaction (Fig. 1b) the reflections from α-Fe_2O_3 and Fe_3O_4 disappeared and reflections from amorphous α-Al_2O_3 appeared. The presence of diffractograms of reflections in (1 1 0)Fe and the feeble or complete absence of other reflections suppose that iron nanocrystals have preferential (1 1 0) orientation. In granular materials, the important factors defining their magnetic properties are the distribution of nanoclusters affecting the sizes and relative metal fraction X. From reaction (1) it follows, that $X_r = 0.365$. This value is less than the percolation limit, which for many granular systems of metal nanoclusters, embedded in dielectric matrix, is 0.5–0.6 [11]. It is supposed that metal nanoclusters are isolated from each other. This fact is confirmed by high electrical resistivity of the obtained samples $\rho = 10^{-6}$–$10^{-4}\,\Omega$ m, that is typical for metal clusters in a non-conductive matrix below percolation limit. The determination of iron grain size in a direction perpendicular to the plane from broadening of diffraction peak Fe(1 1 0), using the well-known Scherrer formula, yields an average value of 28 nm. This value coincides with the size at the lower end at which the particles are in single domain [12]. Assuming that in other directions the iron cluster size has the right value, it should be a single domain. The sample in this case is an ensemble of single-domain particles and its behavior is described by Stoner–Wohlfartht theory. For example, the magnetization curve of single-domain particles ensemble has a hysteresis loop with parameters $M_r = 0.5M_S$, $H_C = 0.58$ K/M_S [13]. Fig. 2 shows the typical magnetization curve of Fe–Al_2O_3 films received after the reaction (Eq. (1)). From the absence of hysteresis loop, it can be supposed that a considerable part of iron clusters is superparamagnetic.

This magnetization curve can be regarded as the superposition of superparamagnetic and ferromagnetic curves [14]. Coexistence of both superparamagnetic and ferromagnetic states is possible in magnetic iron nanoclusters embedded in a non-conductor matrix [15]. The critical cluster size, below which the iron nanoclus-

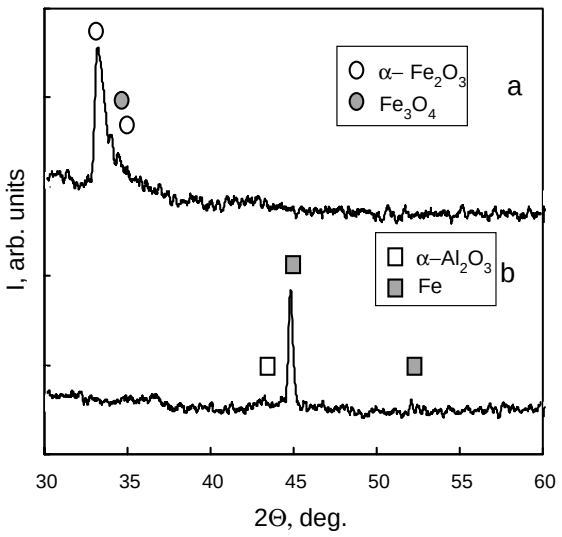

Fig. 1. X-ray diffraction pattern of (20 nm Al/40 nm Fe_2O_3) $\times$ 4 multilayer film: (a) initial sample, (b) after 10 min annealing at a temperature of 800 K.

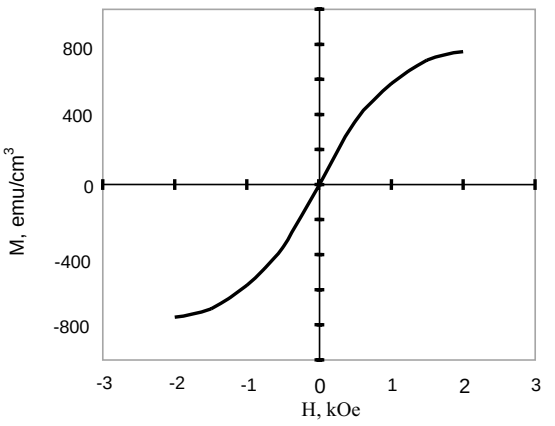

Fig. 2. Magnetization curve of (20 nm Al/40 nm Fe_2O_3) $\times$ 4 multilayer film after 10 min annealing at temperature 800 K. Magnetization is present per unit iron volume.

ters in matrix Al_2O_3 are superparamagnetic, is ~ 10 nm [12]. It is proposed that in the explored samples, the Fe nanocluster size distribution is in the size range of a few tens of nanometers. In this case, it is assumed that both superparamagnetic and ferromagnetic nanoclusters coexist in the obtained films. It is necessary to note that the hysteresis loop does not occur at temperature 77 K. It should be noticed that the blockage temperature T_B of iron nanoparticles, which are superparamagnetic, lies below this temperature (liquid nitrogen). The formation of reaction products occurs solely at the SHS front. The characteristic time of reaction will be defined as $t = \tau/V_f^2$, where τ is the thermal diffusivity of the bilayer sample. Supposing that τ is defined by the thermal diffusivity of metal oxide $\tau = (1–5) \times 10^{-7}$ m^2/s and the front rate of SHS initiation temperature $V_f \sim 1 \times 10^{-2}$ m^2/s, we shall obtain an estimate of the reaction characteristic time $t = 1 \times 10^{-3}c$. Supposing that reaction goes in solid phase at a temperature close to the metal's melting point and considering diffusion $D = 10^{-12}-10^{-14}$ m^2/s, we shall obtain an estimate of metal cluster size as $r = (Dt)^{1/2} = 3-70$ nm, which coincides well with the obtained Fe nanocluster size formed after the reaction (Eq. (1)). It is necessary to note that the cluster size observed directly under a transmission electron microscope coincides with the size determined by X-ray diffraction and calculation on the basis of the SHS front kinetic.

The rate of the SHS front depends on substrate temperature T_S ($T_S > T_0$) according to a law close to Arrheninus and hence it should determine the function of size distribution and average size of iron nanoparticles. Therefore, varying substrate temperature T_S at SHS initiation in bilayer Al/Fe_2O_3 films and also selecting the subsequent annealing conditions, it is possible to change the microstructure, which defines magnetic properties of Fe–Al_2O_3 granular films. It is necessary to note that nanostructure should be dominant after passage of the SHS wave in all samples, which contain more than two phases as the result of reaction. In particular, similar nanostructure and magnetic properties are observed in Fe–TiO_2 films after solid-phase reaction between Ti and Fe_2O_3 layers.

4. Conclusion

In the present report it was shown that solid-phase reaction, which takes place in SHS mode, could be utilized for deriving granular mediums. So granular Fe–Al_2O_3 films were obtained after solid-phase reaction between Al and Fe_2O_3 layers. The iron nanoclusters have (1 1 0) texture. The equation of reaction defines that the volume part of iron is lower than the percolation threshold. It is proposed that the iron nanoclusters in the obtained samples are in the form of superparamagnetic and ferromagnetic states.

Acknowledgements

The authors would like to thank Dr. I.A. Turpanov and Dr. S.M. Zharkov for technical assistance. Kranoyarsk Foundation of Science has supported this work under grant No. 11F001C.

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