Soft magnetic FeCo films produced by green chemistry technique

E A Denisova[1,2]**, L A Chekanova**[1]**, I V Nemtsev**[3]**, S V Komogortsev**[1,2] **and N A Shepeta**[2,4]

[1] Kirensky Institute of Physics, SB Russian Academy of Sciences, 50/38, Akademgorodok str., Krasnoyarsk, 660036, Russia
[2] Siberian Federal University, 79, Svobodny ave., Krasnoyarsk, 660041, Russia
[3] Scientific Center, Federal Research Center KSC SB RAS, 50, Akademgorodok str., Krasnoyarsk, 660036, Russia
[4] Reshetnev Siberian State University of Science and Technology, 31, Krasnoyarsky Rabochy ave., 660037, Krasnoyarsk, Russia

E-mail: len-den@iph.krasn.ru

Abstract. The saturation magnetizations, local magnetic anisotropy field and coercivity values of FeCo film plated under various processing conditions have been investigated to optimize soft magnetic properties. Herein, we introduce a very promising processing technique based on the electrodeless deposition of FeCo film with carbohydrates as reducing agents. The produced FeCo film demonstrated significantly better saturation magnetization values and less contaminations, compared to those for the sample preparing with conventional reducing agent (sodium hypophosphite). The surface morphology and coercivities of FeCo films are dependent on the iron content and type of reducing agent. The coercive force values range from 12 up to 30 Oe and the saturation magnetization from 150 to 240 emu/g depending on the bath composition and deposition parameters. Maximum of saturation magnetization magnitude is reached for FeCo film with 30% cobalt. The local anisotropy field value of FeCo alloys increases with a decrease in Fe content for all reducing agent types.

1. Introduction

In recent decades, future green chemistry methods have been extensively investigated to replace energy-consuming methods of producing functional materials, which uses toxic substances in the synthesis process. In 1998, Paul Anastas and John C. Warner published a set of principles to guide the practice of green chemistry [1].Recall some of them. The use of renewable material feedstocks and energy sources;the design of energy efficient processes. Chemical products should be designed to achieve their desired function while being as non-toxic as possible. Soft magnetic films have been widely used in the fields of magnetic recordings, magnetic sensors [2–3].

As a kind of typical soft magnetic materials, CoFe alloy films exhibit superior magnetic properties such as high Curie temperature, low coercivity, low magneto-crystalline anisotropy, high permeability and high saturation magnetization (can reach up to 245 emu/g). Although there are many methods available for the preparation of CoFe films, such as sputtering, molecular beam epitaxy, ion beam deposition, electrodeposition and so on [4–5]. Electrodeless plating shows low cost and no size or shape limit for the preparation of nano-scale films [6]. However, traditional reducing agents (sodium hypophosphite or borohydride, hydrazine) are often toxic. Green reducing agents, on the other hand, are generally derived from renewable resources and biodegrade to innocuous, often a naturally occurring product. So, researchers found that polysaccharides (e.g. chitosan, cellulose) could be an efficient, low-cost, and environmental alternative to conventional reducing agents [7].

Herein, we propose a nonconventional, very effective method for fabricating nanostructured FeCo films. We investigated the possibility of producing soft magnetic FeCo films by electrodeless plating using starch, arabinogalactan and sucrose as reducing agents. The FeCo alloy was directly synthesized on copper supports via electrodeless deposition with different carbohydrates as reducing agents. Magnetic studies of these films which exhibit high saturation magnetization are also reported in this work.

2. Materials and methods

The FeCo films were prepared by electrodeless reduction of metals from aqueous solutions of the corresponding salts at 80 ^{0}C. Each plating bath was comprised of source metal ion ($CoSO_4$ and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$), metal chelator (sodium citrate $Na_3C_6H_5O_7$), and reducing agent. The pH value was adjusted by adding NH_4OH solution. We used several types of carbohydrates as reducing agents: arabinogalactan - natural polysaccharide (series A), corn starch - $(C_6H_{10}O_5)_n$ (series B) and sucrose – $C_{12}H_{22}O_{11}$ (series C). For comparing the FeCo(P) films were produced by electrodeless deposition with a sodium hypophosphite as a reducing agent. The morphology of the deposited films was analyzed with scanning electron microscopy (SEM: Hitachi S-5500). Compositional analyses were performed via energy dispersive X-ray spectroscopy (EDS) associated with SEM. Structural analysis of the studied systems was carried out using X-ray diffraction (Cu-Kα). The magnetic properties were investigated using a vibrating sample magnetometer. Information on local anisotropy field H_a is obtained from investigation of approach magnetization to saturation law.

3. Results and discussion

Electrodeless deposition of FeCo alloys with different reducing agent was studied to determine how chemical and physical parameters affect the morphology of the deposited metal. The surface morphologies of the obtained samples are shown in Figure 1. The morphology of the samples can be varied by changing the Fe/Co molar ratio. With increase of Fe content in the film for all types of reducing agents, the surface morphology of the samples changed greatly, as shown in Figure 1. The metallized surfaces consist of agglomerates of spheroidal particles for FeCo films with Fe/Co < 0.5. The grains sizes were in range 20-50 nm. As it is seen from Figures 1 c and d, as a result of increasing Fe content up to 80%, a different morphology of grains is formed. There is a 5 time increase of the grain size when Fe/Co > 4. Replacing carbohydrates with conventional reducing agent (sodium hypophosphite) leads to the formation of surfaces consisting of larger, more faceted metal grains.

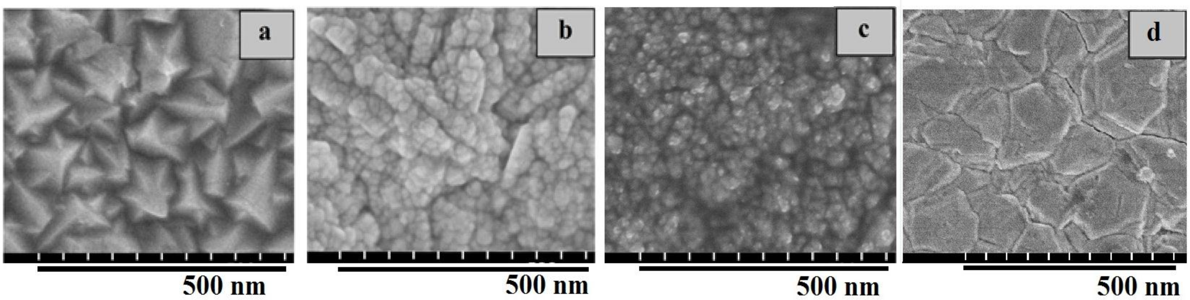

Figure 1. SEM images of the FeCo films surface prepared with different reducing agent: a – Fe/Co = 1.22 (sodium hypophosphite); b – Fe/Co = 0.5 series A; c – Fe/Co = 0.2 series C, d – $Fe_{94}Co_6$ series C.

As seen in Figure 2, there was no obvious difference among the XRD patterns of A, B and C film series. The XRD patterns of FeCo films revealed peaks that perfectly matched with those of the bcc phase of CoFe or fcc-Cu substrate and no oxides phases were observed within the detection limits of the X-ray diffractometer. These peak positions and relative peak intensities corresponded to the characteristic peaks of FeCo (JCPDS 49-1567); therefore, it was determined that magnetic FeCo films were successfully fabricated with all types of carbohydrates. The average crystallite size calculated using the Scherrer formula for the all types of reducing agents was in rage 10-27 nm. The bcc structure is found to be stable even for films with very high concentration of Co (~0.85) beyond the thermodynamically stable bcc regime for bulk $Fe_{1-x}Co_x$ alloys (0<x<0.25 [8]).

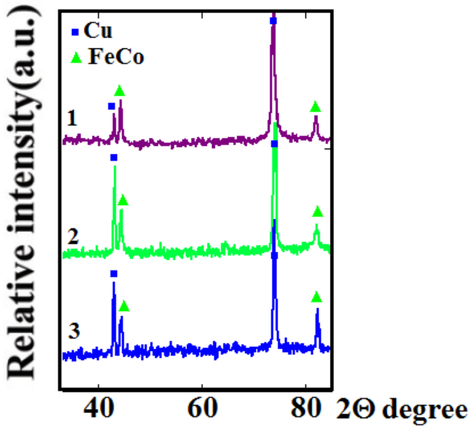

Figure 2. XRD patterns of the $Fe_{82}Co_{18}$ films produced with different reducing agent: starch (1), arabinogalactan (2), sucrose (3).

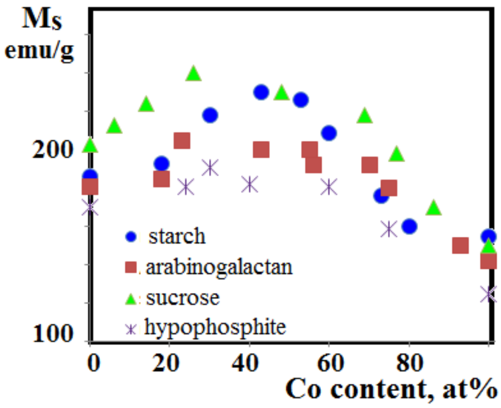

Figure 3. The saturation magnetization of FeCo films produced with different types of reducing agent as a function of cobalt content.

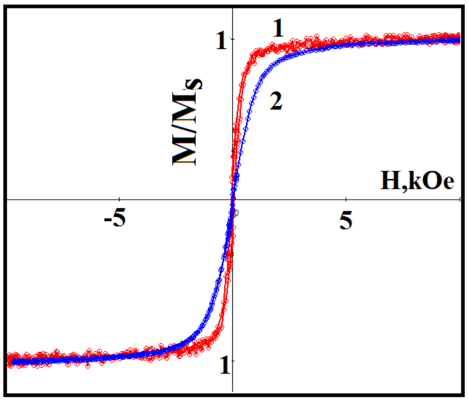

Figure 4. Hysteresis loops for $Fe_{77}Co_{23}$ films produced with different reducing agent: arabinogalactan (1) , starch (2)

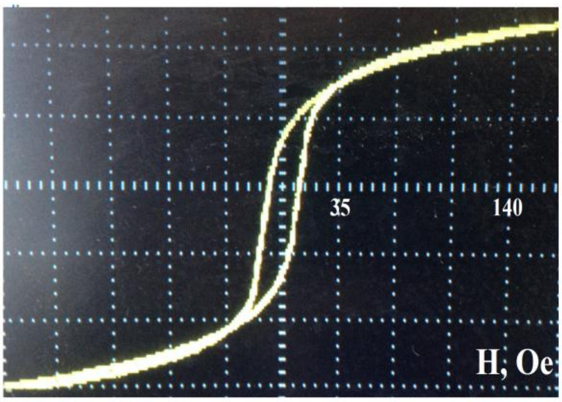

Figure 5. Hysteresis loop for $Fe_{95}Co_5$ film deposited with sucrose as reducing agent

The data show a strong dependence of the magnetic parameters on the iron content. Nonlinearity in the saturation magnetization M_s dependencies on Co content are expected for any type of the FeCo films series (Figure 3) [4]. Maximum of saturation magnetization magnitude is reached for FeCo film with 30% cobalt. The produced FeCo film demonstrated significantly better saturation magnetization values and less contaminations, compared to those for the sample preparing with conventional reducing agent (sodium hypophosphite). The M_s value for film reducing with hypophosphite does not exceed 190 emu/g due to phosphorus contaminations.

In cases FeCo film reduced with carbohydratesthe M_s values are 205, 235 and 240 emu/g for arabinogalactan, starch and sucrose respectively. The magnetization values of the samples are relatively higher than those of the usual FeCo-C alloy. It is mainly due to carbon not being included in the FeCo lattice during deposition process. Figure 4 shows typical hysteresis loops for FeCo film produced with different reducing agent. It has been found, that films of series A are characterized by the smallest value of local anisotropy field. Approach magnetization to saturation in the log-log plot follows $M(H) \sim (H)^{-2}$ dependence for H from 3 to 12 kOe for all film series. Magnetization approaches to saturation as $M \sim H^{a}$ with $0.75 < a < 1.1$ in the field range from 1 to 3÷6 kOe. Such behavior indicates that the FeCo alloy is nanocrystalline [9].

It was found that the local anisotropy field for all series of FeCo alloys depends on Fe content. The H_a value increases with a decrease in Fe content and was in range 360-2000 Oe. Hysteresis loop for FeCo film deposited with sucrose as reducing agent was shown at Figure 5. The coercivity values range from 12 up to 25Oe for films produced with carbohydrates. The best soft magnetic properties corresponded to the deposits with bcc structure and grain sizes less than 20 nm. When we use hypophosphite as reducing agent, the lowest value of the coercive force for CoFe filmis 35 Oe.

In general, soft magnetic properties of films with a smooth surface are better than those for films with a rough surface, since a smooth surface does not prevent domain wall movement during magnetization. As shown in the SEM images (Figure 1), the surface of the FeCo films A,B and C series is much smoother than those for the FeCo film produced with hypophosphite. Zhang et al.[10] and Yanai et al. [5] have plated Fe-Co thick-films by electroplating and reported the $Fe_{66}Co_{34}$ thick-film with coercivity of 16 Oe and 25Oe for $Fe_{76}Co_{24}$ film respectively. The improvement in the soft magnetic properties is one of our future works.

4. Conclusion

In summary, the FeCo films were synthesized by electrodeless plating with arabinogalactan, starch and sucrose as nontoxic reducing agents. It was found that Fe concentration and type of reducing agent affect the surface morphology. The local anisotropy field value increases with a decrease in Fe content for all series of FeCo alloys.

The highest value of the saturation magnetization of 240 emu/g was observed in the $Fe_{70}Co_{30}$ film, and the change in the saturation magnetization shows good agreement with the data for bulk FeCo alloys. The FeCo films prepared with sucrose as reducing agent exhibited the lowest coercive force value of 12 Oe.

5. Acknowledgments

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