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FABRICATION AND CHARACTERIZATION OF COBALT/IRON COMPOSITE COATINGS

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ABSTRACT

Cobalt/iron composite coatings are used in micro-equipments due to their high magnetic saturation values and Curie temperatures, as magnetic nanoparticles capable of killing cancer cells, for magnetic data storage and magnetic resonance imaging (MRI) and in coatings, plastics, nanowire, nanofiber and textiles as well as in certain alloys and in catalyst applications. Cobalt/iron composite coatings were prepared by using two types of solution consisting of oleic acid in diphenyl ether and cobalt formate strongly stirred then centrifuged and drayed. Obtained coatings were subjected to chemical and structural analysis by using EDAX and XRD techniques. Some magnetic characteristics have been estimated by drawing the hysteresis loop for various thicknesses of coatings.

KEYWORDS: cobalt/iron, coating, structure, magnetic properties

1. Introduction

For the last ten years, research in nanofield has been focused on preparing and studying the influence of dimension and shape of nanomaterials or nanostructures obtained by different techniques or methods on some magnetic, mechanic, electric or optic properties [1-3]. Applications of cobalt/iron nanocrystals include ones in electromagnetic machines and micro-equipments due to their high magnetic saturation values and high Curie temperatures, as magnetic nanoparticles capable of killing cancer cells, for magnetic data storage and magnetic resonance imaging (MRI) and in coatings, plastics, nanowire, nanofiber and textiles as well as in certain alloys and catalyst applications. For example, the papers of J. Park, T. Hyeon or S. Sun and their collaborators showed that certain magnetic properties are greatly reduced with decreasing size of spherical nanoparticles [4-6]. Other scientists such as N. Cordente or M. Aslam have been made attempts in order to improve the magnetic properties of nanocrystals by preparing anisotropic 1D nanostructured materials [7, 8] having the shape of rods or wires. In 2D nanostructures superior magnetic properties are expected, such as made by Y. Leng and co-workers who prepared nickel nanosheets having enhanced magnetic properties [9] or by V. F. Puntes together his collaborators who synthesized 2D disk-shaped cobalt packed crystal structure [9, 10].

In this paper it is reported the possibility to prepare 2D structure, namely cobalt/iron coatings, having interesting magnetic properties. The presence of iron in structure leads to increasing of coercive force of prepared 2D structures and it can be explained taking into account the enhanced anisotropic energy of cobalt in the presence of iron atoms, when thermodynamically unfavourable shapes appear. The anisotropic growth is induced by twin planes and is proposed to explain the formation of cobalt/iron coatings [11].

2. Experimental research

In order to prepare cobalt/iron coatings, two types of solution were initially introduced into separate flasks. The first flask contains 20ml diphenyl ether [$C_{12}H_6Br_4O_2$] solution of oleic acid [$C_{18}H_{34}O_2$] (6.0mmol) and cobalt formate [$Co(CHO_2)_2$] (3.0mmol). The mixture was strongly stirred and maintained at a constant temperature of 200^{o}C and in a nitrogen atmosphere.

The second flask contains a solution of iron pentacarbonyl [$Fe(CO)_5$] (2.0 mmol) and oleyl amine [$CH_3(CH_2)_7CH{=}CH(CH_2)_8NH_2$] (16 mmol). This solution was taken and quickly introduced in the first flask. The resulted mixture was maintained for half an hour at the same temperature of 200^{o}C, then it was cooled to room temperature, precipitated with ethanol and, finally, it was separated by centrifugation. Then, the precipitate was dried and subjected to structural characterization.

In figure 1 the technological schema of cobalt/iron coatings preparation process is presented. The composition of sample was estimated by EDAX technique (Quanta 200 EM); the structural analysis was made by XRD method using monochromatic Cu Kα radiation (DRON-3), and the morphology and size distribution were examined by SEM (Quanta 200 EM) and TEM (Phillips CM200) techniques. Relating to magnetic properties, they were investigated with an original device that allows carrying out the hysteresis loops by applying a magnetic field up to 12.10^{4} A/m.

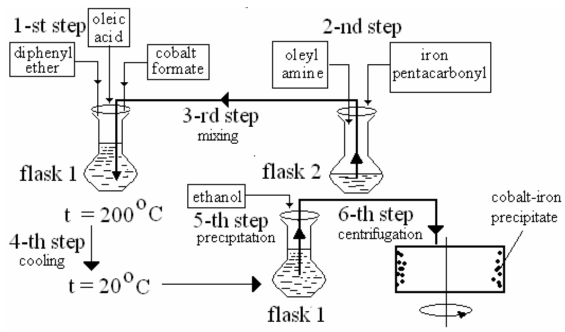

***Fig. 1**. Technological scheme of cobalt/iron composite coatings preparation*

3. Results

The chemical composition of the cobalt/iron coating was determined by EDAX and consists of two or three percent iron that probably has diffused into the crystalline lattice of cobalt. The XRD pattern presented in Figure 2 reveals that the prepared coatings are represented only of cobalt which has a hexagonal close-packed structure with lattice constants of a = b= 2.508 Å and c = 4.069 Å. These results show that indeed it is obtained pure cobalt. No signals from cobalt format are observed and there are not present iron oxides or the formation of amorphous iron in the sample even if the initial molar ratio of components is 1:2. It is important to control the mixture temperature and the ratio of iron pentacarbonyl to oleic acid. If the temperature is lower than 200^{o}C cobalt formate is difficult to decompose.

The SEM and TEM study shows that the cobalt/iron coatings present structural units having a hexagonal shape, with edge lengths varying from several tens to several hundreds of nanometers. The maximum thickness of prepared coatings was estimated to be about 120 nm. The thickness can be controlled by the quantity of iron pentacarbonyl introduced into the first solution that contains cobalt format and oleic acid. Due to the strong magnetic interaction between different structural units, these tend to overlap resulting in an anisotropic growth of coatings [15].

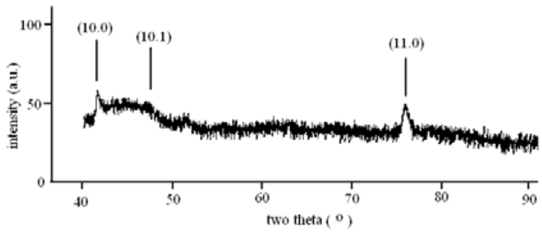

***Fig. 2**. XRD pattern of cobalt/iron composite coatings*

There are several mechanisms trying to explain this behaviour. The most representative one considers that the organic molecules influence the growing process or promote the addition of adsorptive atoms to the specific crystal faces. In figure 3, typical SEM (a) and HRTEM (b) images are presented when the edges of the different coatings are clearly distinguished although there is an overlap.

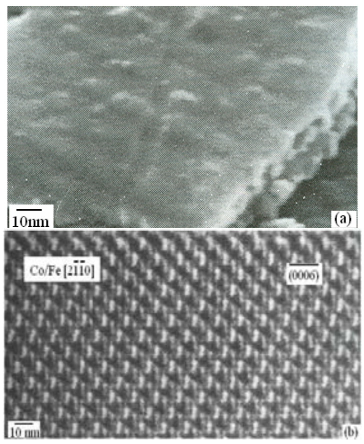

***Fig. 3**. SEM (a) and HRTEM (b) images of cobalt/iron composite coatings*

This provides good evidence that the coatings appear to be transparent under the electron beam. The transparent nature under the electron beam implies the ultra-thin cobalt/iron coatings. Comparable results were observed for other metals. For example, Y. Leng, N. Malikova, R. J. Cao and C. Salzemann obtained similar morphologies in case of nickel [9], gold [12], silver [13], and copper [14], respectively. The organic molecules, such as oleic acid and oleyl amine, have no special effect on cobalt anisotropic growth in our process. In complete contrast, by using iron pentacarbonyl to the reaction system, a large quantity of cobalt/iron coatings is produced after 15-20min. This implies that the iron species play an important role in the formation of cobalt/iron coatings. Iron atoms are produced immediately after using iron pentacarbonyl into the diphenyl solution, and then they are etched by oleic acid in the diphenyl ether during their growth. Iron atoms will be locked into twinned morphology because the twinned nanoparticles have a lower overall surface energy [16]. Finally, the adsorption of cobalt atoms along the plane having smaller atom density leads to the formation of coatings.

The magnetic properties the prepared cobalt/iron coatings were performed by recording at the room temperature of the normalized hysteresis loop. Figure 4 shows the normalized hysteresis loops for different thicknesses that range from 20 to 120 nm. It can see that the squareness and coercivity decreasing with increasing thickness and this behaviour can be connected to the grain size. Supposing a rotational magnetization process of slightly interacting fine particles, in fact, film coercivity is inversely proportional to particle size [17].

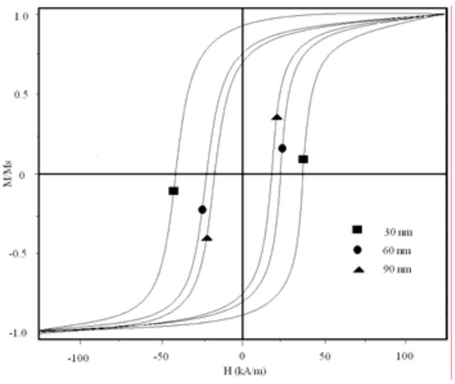

***Fig. 4**. Hysteresis loops of cobalt/iron composite coatings having various thicknesses*

The hysteresis loops of cobalt/iron coatings show that they have a typical ferromagnetic behaviour. The values of the coercitive force of obtained coatings depend on their thickness and it is superior both to the cobalt bulk and cobalt nanospheres ones. This aspect is probably due to their 2D structure.

4. Conclusions

The present paper shows the possibility to prepare by a synthesis process cobalt/iron coatings having a crystalline structure. Iron atoms and oleic acid have a determinant role in the synthesis process, they lead to the growth of a special structure having interesting magnetic properties. The magnetic properties of cobalt/iron coatings were studied taking into account hysteresis loops that are strongly influenced by the thickness of coatings. The coercitive force of cobalt/iron composite coatings is superior to the growth of a bulk or cobalt nanospheres.

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