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Nanostructure, surface and magnetic properties of Co-Cr alloy thin films

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Abstract

Co-Cr films were produced with electrodeposition with different pH at room temperature. The effect of electrolyte pH on the structural, surface morphology and magnetic properties of the films was studied. X-ray diffraction measurement showed that the films have hexagonal close packed structure. For the films deposited at different pH values, the surface morphologies with different-sized globular granules were observed whereas the morphology covered by uniformly distributed nanoscale grains was detected for the surfaces of all films produced from electrolytes with different Cr concentrations. Magnetic properties such as coercivity and saturation magnetization showed strong dependence on he electrolyte solution pH and consequently the crystallite size. The Co-Cr films with low Hc were achieved using relatively low electrolyte pH. The differences observed in the magnetic properties were attributed to the structural changes caused by the electrolyte pH. The Co-Cr films may have the potential applications in magnetic recording and sensors technologies.

Keywords: Co–Cr thin film, Electrodeposition, Nano-structure, Magnetic properties.

1. Introduction

Currently, device systems are becoming smaller while their performance is enhancing. This trend corresponds with a decrease in the material used for their thin-film elements, highlighting the crucial influence of the film's surface pattern on their functionality. It is widely recognized that materials and structures at the nanoscale behave differently than their larger counterparts. Hence, achieving improved control over the nanoscale topography during the film deposition process is highly advisable. Among these coatings, hard chromium electrodeposits are wellknown for their high hardness, perfect wear resistance, and good corrosion properties [1]. The alloy coatings obtained from these baths usually have a smaller grain size and better mechanical and tribological behavior than the pure chromium films [2]. Surviliene et al. [3] showed that the Co-Cr alloy coating had a better surface quality than the Cr electrodeposit. Co-Cr alloys are used for medical prosthetic implant devices, components in the power generation, marine, aerospace, and oil and gas industries due to their good wear, corrosion and fatigue resistance along with biocompatibility [4]. Optimum mechanical properties and corrosion resistance of these alloys are usually obtained in the presence of 10-30% chromium [5].

The Co–Cr electrodeposits can be an economic alternative for these expensive alloys [6]. These coatings are also a suitable substitute for hard chromium films [7]. Electrodeposition of chromium is widely used in aerospace, automotive, and other engineering industries to produce wear and corrosion resistant coatings with high hardness and good appearance [8].

In electrodeposition, the growth mechanism, morphology, and microstructural properties of the film depend on electrodeposition conditions such as electrolyte composition, electrolyte pH, additives and current density or deposition potential. The variations of these parameters have been shown to affect the growth mode mechanism, morphology, microstructure, and magnetic properties of the deposited Co–Cr film [9]. Generally, the aim of the work is to clarify the effect of deposition conditions on electrodeposited nickel films. It was observed that the solution pH changes the complexing condition of metal ions, which usually plays a key role to control the film properties [10]. A modification of bath pH can also affect the crystallite size and consequently the magnetic properties such as magnetoresistance of some materials obtained by electrodeposition [10]. Consequently, the bath pH has a crucial role on several properties of deposits.

In the present study, we present experimental results of the influence of electrolyte pH on the electrodeposition, morphology, structure, and magnetic properties of the, Co–Cr thin films films electrodeposited from chloride baths.

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2. Experimental

2.1. Material And Preparation

Aluminum plates of size 1.5×1.5 cm are used for substrates (cathode). A platinum wire was used as the counter electrode. All the applied potential was measured with respect to a saturated calomel electrode. These three electrodes were assembled and were connected to a potentiostat (AUTOLAB PGSTAT 30, Eco Chemie BV, Utrecht, the Netherlands) combined with a frequency response analyzer, controlled by a personal computer. The chemical composition and operating conditions of the electroplating bath are as shown in Table 1.

Table 1. Bath electrolyte composition and parameters for Co-Cr thin film electrodeposition

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Bath composition	$Cr_2(SO_4)_3.6H_2O$: 0.3 M, $CoSO_4.7H_2O$:0.1 M, H_3BO_3 0.9 M, Na_2SO_4: 0.6 M
pH	2–5
Bath temperature	25 °C
Stirring speed	250 rpm
Thichness	400 nm

2.2. Characterization

The film content was detected by the energy dispersive X-ray spectroscopy (EDX). The crystalline structure analysis was made with the X-ray diffraction (XRD) technique with the Cu-K_α radiation (λ= 0.15406 nm). The 2θ was scanned between 40◦ and 100◦ for the XRD measurements. The surfaces of the films were observed by the scanning electron microscope (SEM) at the same time with the EDX measurements. The surface roughness was investigated by the atomic force microscopy (AFM) to get detailed information about the surface of the films. The magnetic properties were studied with the vibrating sample magnetometer (VSM). The applied magnetic field was in the film plane and the measurements were performed at room temperature.

3. Results and discusion

3.1. Elemental analysis

According to elemental analysis of the Co– Cr films deposited using the electrolytes have different pH values, the film deposited at high pH value (5) consists of 78 at.% Co and 22 at.% Cr, as shown in Fig. 1. When the electrolyte pH was gradually decreased from 5 to 3.5 and then to 2, Co and Cr contents remained at the same values. It was revealed that the decrease in electrolyte pH did not provoke a change in film content.

Fig. 1. EDX spectrum of Co-Cr thin film produced at electrolytic pH of 5.

3.2. XRD analyis

The XRD patterns of the Co– Cr films deposited at different electrolyte pH values are presented in Fig. 2. These patterns reveal that the as deposition Co-Cr coatings have a crystalline structure. The pattern of the deposited alloy shows the presence of a hexagonal-close-packed (hcp) phase (JCPDS 01–1278). The lack of chromium peaks indicates that the alloy coatings are a substantial solid solution of Cr in Co, as also reported by other researchers [5,11-15]. However, Co with face-centered cubic (fcc) lattice have been observed by Kim et al. for Co- Cr films [16]. Moreover, results of Koutsoukis et al. showed the presence of both the fcc phase of Co and the hcp phase of Co for Co- Cr alloy [17].

Fig. 2. XRD patterns of the Co–Cr films deposited at electrolyte pH values of (a) 5, (b) 3.5 and (c) 2.

It is obvious in the figure that all films have the hexagonal close packed (hcp) of Co atoms. The hcp peaks appeared at 2 values of ~ 41◦ , 45◦ , 47◦ , 76◦ , 93◦ , 95◦ and labeled as (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 1 2) and (2 0 1), respectively. Besides, some changes occurred in the intensities of the XRD peaks when the electrolyte pH value was changed. As the pH value decreased, the intensity of the peaks (1 0 0), (0 0 2) and especially the intensity of the peak (1 0 1) decreased whereas that of the peak (1 1 0) clearly and gradually increased. While the highest peak was (1 0 1) for the film deposited at high pH value, the (1 1 0) peak was detected as the highest peak for the film deposited at the low pH value. Also, the peak of (2 0 1) disappeared from the XRD pattern as the electrolyte pH decreased.

3.3. SEM Study

Fig. 3 shows the SEM images of the Co– Cr films deposited at different electrolyte pH values. Electrodeposited film surfaces are sensitive to the electrolyte pH value [18]. The surface of the film grown at the high pH has a structure with numerous grains and their diameter is ~1 m. When the electrolyte pH gradually. Fig. 3. SEM images of the Co–Cr films deposited at different electrolyte pH values. decreased, the diameter of the surface grains decreased in accordance with the decreasing pH value and nano-scaled surface grains were obtained for the film deposited at the low pH value (2). The observed grains uniformly dispersed on the surfaces ofthe all films.

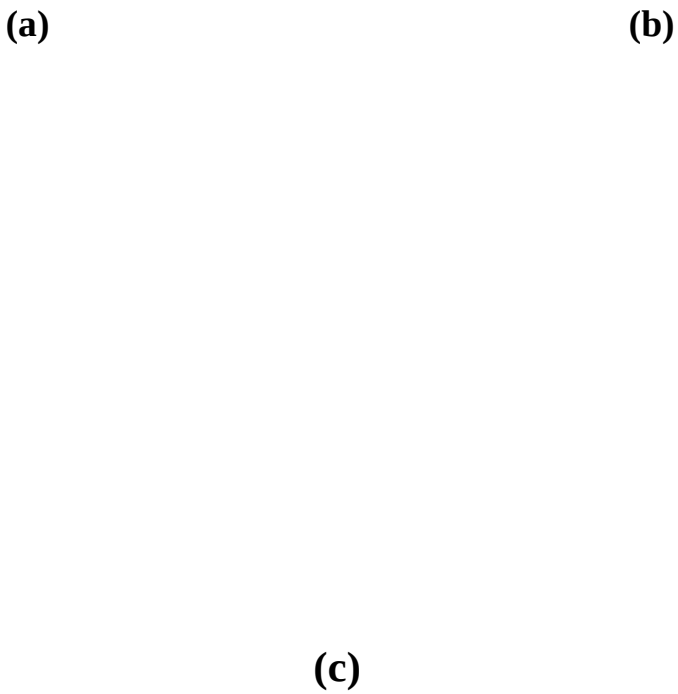

Fig. 3. SEM images of the Co–Cr films deposited at electrolyte pH values of (a) 5, (b) 3.5 and (c) 2.

3.4. AFM images

Fig. 4 shows the AFM images of the films deposited with different electrolyte pH values. The images prove the SEM images given in Fig. 3 in point of surface grain size and roughness. The surface roughness decreased with the decreasing size of the surface grains. Also, Fig. 4 indicates that the relatively lower stressed surfaces were obtained for the film deposited at the low pH value. It can be emphasized that the electrolyte pH has an important effect on the surfaces of investigated films.

Fig. 4. AFM images of the Co–Cr films deposited at electrolyte pH values of (a) 5, (b) 3.5 and (c)

3.5. VSM Study

The hysteresis loops of the Co– Cr films were illustrated in Fig. 5. As seen in figure 5, the Hc values were found as 157 Oe, 92 Oe and 43 Oe for the electrolyte pH values of 5, 3.5 and 2, respectively. The decrease of pH value resulted in a considerable reduction of Hc value. This points out to the magnetically smoother films as the electrolyte pH decreases. The decrease in Hc can depend on the changes in the structural properties especially the change in the

intensities of the XRD peaks, Since the detected peak intensities in the XRD patterns determine the preferential texture of the films [19, 20], and also the Hc are considerably affected by film texture as indicated in studies by Choi et al. [21] and Rahman et al. [22]. In these studies, it was shown that the Hc of the electrodeposited films is mainly affected by the crystallographic texture. In addition, it can be said that the decrease in the size of surface grains seen in figure 3 can provoke this decrease of Hc arising from the change of the peak intensities. It can be stated that since the homogeneity and the regularity of the surface appearance increased with the decrease in the size of surface grains (see figures 3 and 4), the low stressed surfaces, and hence coatings, were obtained for the films with nano-scaled surface grains. Therefore, the Hc, which is a quite sensitive property to the changes in internal factors of the magnetic materials [23], can be affected by the microstructure such as the size of surface grains. It was seen that the change in the electrolyte pH caused the magnetic properties to change. According to electrolyte pH investigation, the desired film properties, i.e. relatively smoother and lower stressed surfaces in addition to lower Hc values, can be obtained when an strong acidic electrolyte pH is preferred for the production of the Co–Cr films, as done in the present study.

Fig. 5. hysteresis loops of the Co–Cr films deposited at electrolyte pH values of (a) 5, (b) 3.5 and (c) 2.

4. Conclusions

The Co–Cr films were produced at various electrolytic pH using the electrodeposition and their structural, surface morphology and magnetic properties were studied to investigate their applications in magnetic recording and sensor technologies. The hcp structure was detected for the all films whereas the surface morphology varied depending on the electrolytic pH. The decrease in the electrolyte pH reduced the size of surface grains from micro-scale to nano-scale. By SEM measurements, we have shown that the bath pH has a great influence on the morphology, the shape, and the size of the crystallites. Finally, the magnetic properties showed a sensitive dependence with the pH and the observed structural changes. In addition, the high and unexpected coercivities reaching a maximum of 157 Oe at pH 5 can be attributed to the presence of residual stress in the film–substrate interface, which increased as the bath pH became more acidic and the crystallite size smaller.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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