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Electro-deposition of Co–La alloy films in urea melt and their performances

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Abstract

The Co–La alloy film was electro-deposited in urea melt. The co-deposition behavior, the effect of the cathodic current density on the composition and the surface morphology of the coating were examined, respectively. As a result, lanthanum is co-deposited with cobalt to form Co–La alloy under the inducement effect of cobalt. With the increase of the cathodic current density, La content of the deposit rises at first, then decreases, and reaches a maximal value at the current density of 30 mA cm⁻². Meanwhile, the size of the coating particles becomes small. The more content of Co in the deposit is, the more the saturation magnetization is. The crystallization behavior of the coating was studied by using the differential scanning calorimetry and the X-ray diffraction. The as-plated deposit consists of main amorphous phase and a little amount of hexagon cobalt phase ($P6_3/mmc$). The amorphous phase was converted into Co–La (Fm3m) phase at 438.9 °C, and hexagon cobalt phase was crystallized into cubic cobalt at 687.1 °C. The electro-catalytic activity of the hydrogen evolution for the Co–La alloy was studied by using electrochemical experiments. The results showed that the electro-catalytic activity of the hydrogen evolution of the alloy is better than that of cobalt. © 2006 Elsevier B.V. All rights reserved.

Keywords: Co-La alloy film; Electro-deposition; Urea; Performance

1. Introduction

Co-La alloys exhibit interesting magnetic, electric and hydrogen storage properties and have been used to make functional materials. Iron group (IG)-rare earth (RE) alloys is a type of important functional material for possessing magnetic, optical, and electric properties [1,2]. They are commonly prepared as bulk materials by means of a powder metallurgical sintering, melt spinning, and mechanical alloying routes, but there is great demand of film materials for micro-machine technology, recording media and other applications. Although the sputtering and vacuum evaporation methods are available for preparing the IG–RE alloy films, it is difficult to control the film composition by these methods [3–5]. Furthermore, the equipments are costly and the technique is complicated. Electrochemical deposition has been proven to be a good way to prepare these alloy films. It has many advantages. For examples, the phase and the composition of the alloy films can be easily controlled by adjusting the

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0925-8388/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2006.10.091 plating parameters, the films can be formed on various surface shapes and the technique is simple and economical. Recently the electro-deposition of IG–RE alloy films from an organic bath or low-temperature melt salt was reported. Some rare earth alloys, such as Sm–Co, Tm–Co, Gd–Co, Nd–Co, etc. were successfully deposited from a urea melt salt [6–11]. The urea melt salt system has lower eutectic points below 134 °C, greater solubility of metallic salt, and a wide electrochemical window. In this work, the Co–La film by electro-deposition from urea melt salt was investigated. Moreover, the influence of the operating conditions on the structure and the properties of the deposit, and the crystallization behavior and the electro-catalytic activity of the hydrogen evolution of the coating were studied.

2. Experimental details

All chemical reagents are analytically pure. $CoSO_4$ and $LaCl_3$ were obtained by the dehydration of $CoSO_4 \cdot 7H_2O$ and $LaCl_3 \cdot 7H_2O$ under vacuum at 393 K, respectively. Urea was also dried under vacuum at 393 K. The mixture of urea (83.3 wt%) and NaBr (16.7 wt%) was melted at a temperature high than 403 K.

The Co–La alloys were electro-deposited by controlling cathodic current density from the plating bath containing cobalt sulphate of 0.31 g, lanthanum chloride of 0.98 g, urea of 60.00 g and sodium bromide of 10.00 g. The

2.5

2.0

1.5

1.0

0.0

-0.5

-1.0

-1.5

-2.0

and sodium bromide of 10.00 g.

i/mA 0.5

experiments were controlled at 403 K by oil bath thermostat. The cathodic current density (J_k) was 10–40 mA cm⁻². The anodic electrode was a graphite sheet $(3.5 \text{ cm} \times 3.0 \text{ cm} \times 0.5 \text{ cm})$.

The electrochemical experiments were carried out using a CHI-660B electrochemical analyzer (CH Instruments). Cyclic voltammetric experiments (CV) were done in a conventional three-electrode cell (75 ml) and also controlled at 403 K by oil bath thermostat. The brass disc working electrode (0.1256 cm²) was fitted into a Teflon exposing circular, and its surface was mechanically polished with 600-grit sand paper, then with 30–50 nm α -alumina powder and was rinsed with alkaline solution and chemically etched before the experiments. The auxiliary electrode was a platinum sheet $(0.9 \text{ cm} \times 1.2 \text{ cm} \times 0.03 \text{ cm})$ and the reference electrode was platinum wire immersed in urea-NaBr melt in a glass tube with a Luggin capillary. The scanning potential rate was $50 \,\mathrm{mV \, s^{-1}}$. Linear sweep voltammetry experiments (LSV) were done in a conventional three-electrode cell (100 ml) at 298 K. The auxiliary electrode was a platinum foil $(1.0 \text{ cm} \times 1.5 \text{ cm} \times 0.05 \text{ cm})$ and the reference electrode was Hg-HgO (NaOH, 0.1 mol 1⁻¹). LSV experiments employed a carbon steel disc as the working electrode of 0.5 cm² in surface area. The Co-La electrode was plated in above electroplating melt at the cathodic current density 10.0 mA cm⁻², and cobalt electrode was deposited in above electroplating melt but not containing lanthanum chloride. The electrolyte solution is 10 wt% potassium hydroxide. The solution was de-aerated with nitrogen gas for 5 min before and during the experiments. The scanning potential rate was 1 mV s^{-1} .

The heat treatment experiments of the sample in a vacuum (0.67 Pa) were carried out at various temperatures for 1.0 h. The structure of the deposit was characterized by using an X-ray diffractometer (Rigaku, D/max-RC) with Cu K α radiation and a scan rate of 6° min⁻¹. The samples for the above measurements were plated on the carbon steel substrates of 3.0 cm² surface area. The crystallization temperature and the thermogravity analysis of the coating were measured by a differential scanning calorimeter (DSC-2960, TA Instruments) in an atmosphere of pure argon gas. To prepare specimens for the DSC and TG measurements, the alloy was deposited on the stainless steel sheets, and then mechanically peeled off from the substrate. The magnetic measurements were made using a vibrating sample magnetometer (VSM). The sample of VSM was plated on the copper substrate whose surface area is about 0.25 cm². The morphology and composition of the Co-La deposit was characterized with SEM (scanning electron microscope; Hitachi S3500N) and EDS (energy dispersive X-ray spectroscopy; Oxford INCA) attached in the SEM, respectively.

3. Results and discussion

3.1. The co-deposition behavior of Co-La alloy

Fig. 1 presents the cyclic voltammetric (CV) curves obtained using a brass disc as working electrode in urea-NaBr-CoSO₄ (a) and urea-NaBr-CoSO₄-LaCl₃ (b). The voltammetric scan was swept negatively at first. When the potential swept negatively, the cathodic current of the melt (a) increased initially, appeared a peak at about -0.860 V (versus Pt, urea + NaBr, the same as below), and then decreased. It is the reason that the electro-deposition process of cobalt is controlled by diffusion. When the potential is controlled below -1.000 V, the cathodic current of the evolution hydrogen appeared. In this time urea was reduced on working electrode surface covered with cobalt film, the reaction is

$2H_2N-CO-NH_2 + 2e = H_2 + 2H_2N-CO-NH^-$

The initiative deposition potential of the melt (b) was more negative than that of the melt (a). As the potential swept more negatively than -0.910 V, the cathodic current of the melt (b) was more than that of the melt (a). The melt (b) also showed the hydrogen evolution when the potential swept more negatively than -1.000 V. The anodic current of the melt (b) was



more than that of the melt (a). The curves of the melt (a) and the melt (b) all appeared in the current cross-ring, revealing that cobalt and cobalt-lanthanum was deposited from the each melt salt, respectively. In a word, this indicated that Co(II) and La(III) occurred co-deposition, and the reduction of La(III) may be induced by cobalt. The molten only containing RE(III) salt could not be reduced into metallic RE was approved by Liu et al. and they putted forward the inducement co-deposition of cobalt–lanthanum [6].

3.2. Effect of the cathodic current density on the composition of the Co-La films

The EDX spectrum of the Co–La deposit is shown in Fig. 2. It is found that the chemical composition is almost the same in the different zones, and the coating contains Co, La and small amount of O elements. The content of O in the coating might be due to the oxidation in the air when the coating was taken out from the plating bath. Fig. 2 also demonstrates the high purity of the coating.

Fig. 3 is the effect of the cathodic current density on the composition of the Co-La deposit. It can be seen that with the



Fig. 2. The EDX spectrum of the Co-La deposit obtained from J_k $(10 \,\mathrm{mA}\,\mathrm{cm}^{-2}).$



Fig. 3. Effect of the cathodic current density on the composition of the Co–La deposit.

increase of the cathodic current density, the La content in the coating goes up from 2.96 to 38.97 at% at first, reaches the most 38.97 at% at 30 mA cm^{-2} , and finally decreases to 7.04 at%. While the change trend of cobalt content in the deposit is oppo-

SE 06-Apr-06 WD19.5mm 15.0kV x2.0k 12um

(c

(a)

site to that of lanthanum. The increase of the cathodic current density favors the reduction of La^{3+} because of the induced co-deposition mechanism. However, when the cathodic current density is too high, the evolution of hydrogen occurs, leading to the decrease of the La content in the coating.

3.3. Effect of the cathodic current density on the surface morphology of the Co–La coatings

The surface morphology of the Co–La deposits plated from different cathodic current density is shown in Fig. 4. The Co–La deposits are grey with metallic luster in appearance. To analyze the effect of the cathodic current density on the surface morphology of the deposit, three deposits were prepared with the current density of 10, 30 and 40 mA cm⁻², respectively. The results clearly show the changes of surface morphology with the current density. At the current density of 10 mA cm⁻², the deposit is uniform, homogenous, and has not cracks on the surface. The round particles of the coating were stacked compactly, but there was some space among particles. With the increase of the cathodic current density, the amount of space among particles rises, and the size of the particles decreases initially and then increases. The surface morphology of the Co–La deposit





Fig. 4. The SEM photos of the Co-La deposit plated from different current density (mA cm⁻²): (a) 10, (b) 30 and (c) 40.



Fig. 5. The hysteresis curves of the Co–La deposit plated from different current density.

is different from that of the cobalt deposit plated by electrodeposition. The space among particles of the deposit is relative to the hydrogen evolution. Thus, the more the current density, the more the extent of the hydrogen evolution reaction, the more the amount of space among particles of the deposit.

3.4. Effect of the cathodic current density on the magnetism of the Co–La films

The hysteresis curves of the Co–La deposits plated from different current density is presented in Fig. 5. The deposit has high saturation magnetization (Ms) and coercive force (Hc), and therefore is suitable to be used as memory magnetic material. The saturation magnetization and the coercive force were determined from the magnetic hysteresis curves, respectively. With the increase of the current density from 10 to 30 mA cm⁻², the saturation magnetization of the coating moves up from 128.3 to 29.8 emu g⁻¹, and their coercive force was 53.4, 51.0 and 53.3 mT, respectively.

According to the magnetic theory, the saturation magnetization mainly depends on the composition of the deposit. Co atom has three lone electrons in 3d atomic orbital, and La atom has one alone electron in 5d atomic orbital. Therefore, the atomic magnetic moment of Co is more than that of La. From above studies of the deposit composition, with the increase of the cathodic current, the cobalt content of the deposit reduces, and the lanthanum content rises, resulting in the decrease of the saturation magnetization. The change scope of the coercive force of the deposit is less, and the change trend of it is no regular. It is the reason that the coercive force is sensitive to the structure of the alloy, which depends on the structure, the disfigurement, the stress, the thickness of the film, and so on.

3.5. The crystallization behavior of the Co-La alloy

The differential scanning calorimetry (DSC) and the thermogravity analysis (TG) curves of the Co–La coating are illustrated in Fig. 6. One exo-thermal and two endo-thermal peaks appear in



Fig. 6. The DSC and TG curves of the Co–La coating obtained from J_k (10 mA cm⁻²).

DSC curve, exo-thermal peak at about 264.5 °C is broad, and the first endo-thermal peak at 428.1–465.9 °C is strong, the another endo-thermal peak at 678.2–699.7 °C is weak. There are three weight loss steps at the corresponding temperature in TG curve. Fig. 7 is the XRD patterns of the deposit after heat treatment for 1.0 h at various temperatures. In accordance with the XRD patterns, the peaks of the XRD pattern for the as-plated deposit at 2θ of 42.02° , 44.56° , 47.75° , 76.05° and 92.68° correspond to the (100), (002), (101), (110) and (112) of planes of hexahedron cobalt ($P6_3/mmc$) phase (α -Co), respectively. There is also a broad peak at about 2θ of 44.6° in the as-plated deposit XRD pattern, which indicates the deposit contains amorphous phase. These reveal that the structure of the as-plated deposit consists of main amorphous phase and a little amount of hexagon cobalt phase (α -Co). The deposit XRD pattern after heat treatment at 300 °C is basically the same as that of the as-plated deposit. Therefore, the first exothermic peak in DSC curve at about 264.5 °C is ascribed to the evolution of hydrogen gas. It can be calculated that the as-plated coating (after removed the coating containing little water) has 4.4 wt% hydrogen storage from TG



Fig. 7. The XRD patterns of the deposit obtained from J_k (10 mA cm⁻²) after heat treatment for 1.0 h at various temperatures.

curve. The crystallization peaks of the deposit heated at 500 °C at 44.45° , 51.38° , 76.15° and 92.45° is the $(1\ 1\ 1)$, $(2\ 0\ 0)$, $(2\ 2\ 0)$ and (311) plane diffraction of cubic Co–La (*Fm3m*) phase (β -CoLa), respectively. There are also peaks at 42.02° , 44.56° , 47.75° , 76.05° and 92.68° in XRD pattern of the deposit heated at 500 °C. This indicates that the deposit contains both hexahedron cobalt phase and cubic cobalt phase. This deposit also has a little amount of amorphous phase. Thus, the strong endothermal peak in DSC curve at 428.1–465.9 °C corresponds to the amorphous phase transformation into cubic Co phase. The phase structure of the coating after heat treatment at 600 °C is similar to that of the coating at 500 °C. The XRD pattern of the coating heated at 700 $^\circ C$ shows peaks at 44.45°, 51.38°, 76.15°, 92.45° and 97.73°, revealing that the coating only contains cubic cobalt phase. Hence, the endo-thermal peak at 678.2–699.7 °C in DSC curve is ascribed to the phase transformation from hexahedron cobalt to the cubic cobalt. It should be pointed out that the intermetallic compounds of cobalt and lanthanum, such as Co₁₃La, Co₅La, Co₇La₂ and Co₃La₂, and the phase of sole lanthanum were not found in all XRD patterns.

The atomic radius of La (0.188 nm) is far larger than that of Co (0.125 nm), and La is more active than that of Co. It is obvious that lanthanum may be dissolved in cobalt crystal lattice to form eutectic alloy, which lanthanum atom replaces cobalt atom in crystal lattice position. These destroyed the structure of cobalt phase, and so the amorphous phase was formed. Because the content of Co of the Co–La coating is far more than that of La, so the remain cobalt in the deposit itself formed the hexagon cobalt phase (α -Co). The structure of the IG–RE alloy prepared by electro-deposition in the melt is also amorphous phase [10,11].

3.6. The electro-catalytic activity of the hydrogen evolution of the Co–La alloy

Cobalt itself is a good electro-catalytic material of the hydrogen evolution. The cathodic polarization curves in 10 wt% KOH solution of the Co–La alloy and Co electrode were shown in Fig. 8. As the potential was scanned to about -0.968 V(versus Hg–HgO, $0.1 \text{ mol } L^{-1} \text{ OH}^-$, the same as below), the Co–La alloy electrode began to produce hydrogen, and the amount of the evolution hydrogen and the cathodic current all increased when the potential shifted more negatively. While the hydrogen evolution phenomenon for the Co electrode was not obvious in the scope of the swept potential, and its cathodic current is far less than that of the Co–La alloy. Thus, the performance of the hydrogen evolution for the Co–La electrode is better than that of Co.

When the cathodic polarization curves was negative than -1.100 V, the relationship between the over potential (η) and the natural logarithm of current density is Tafel formulary, which is shown as below:

 $\eta = a + b \ln i$

here, Tafel constants is

$$a = -\frac{RT}{\alpha nF} \ln i_0$$
 and $b = \frac{RT}{\alpha nF}$



Fig. 8. The cathodic polarization curves in 10 wt% KOH solution of the Co–La alloy obtained from J_k (10 mA cm⁻²) and Co electrode.

Table 1 The Tafel constants and the kinetics coefficient of hydrogen evolution for the Co–La and Co

	<i>a</i> (V)	<i>b</i> (V)	$i_0 ({ m mA}{ m cm}^{-2})$
Co	0.869	0.214	0.018
Co–La	0.696	0.192	0.466

where the over potential (η) is the potential subtract the open circuit potential, *i* the cathodic current density, *i*₀ the exchange current density, *R* the gas constant, *T* the Kelvin temperature, α the transfer coefficient, *n* the transfer electron number, and *F* is the Faraday constant.

The over potential (η) versus the natural logarithm of current density (ln *i*) was plotted in accordance with Fig. 8 as the electrochemical polarization was higher (the figure was omitted). The calculated results were shown in Table 1. It is evident that the exchange current density of the hydrogen evolution for the Co–La is far more than that of Co. Therefore, the electrocatalytic performance of the hydrogen evolution for the Co–La electrode is better than that of Co.

4. Summary

The Co–La alloy films were electro-deposited in urea–NaBr melt. Lanthanum was co-deposited by inducement effect of cobalt to form Co–La alloy. With the increase of the cathodic current density, the content of La of the deposit rises at first, then reduces, and reaches maximal value at current density 30 mA cm^{-2} ; at the same time the size of particles of the coating becomes less. The more the content of Co in the deposit is, the more the saturation magnetization is. The Co–La alloy film is suitable to be used as memory magnetic material. The structure of the as-plated coating consists of main amorphous and a little amount of hexagon cobalt ($P6_3/mmc$) phases. During heat treatment, the deposit was converted from amorphous phase into cubic Co (Fm3m) phase at 438.9 °C, and hexagon cobalt phase was transformed into cubic cobalt at 687.1 °C. The

electro-catalytic performance of the hydrogen evolution for the Co–La electrode is better than that of Co.

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