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Electrochemical preparation of Er-Co-Bi thin film in organic bath by cyclic electrodeposition method①

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Abstract: Cyclic electrodeposition was used to investigate the preparation of Er-Co-Bi alloy thin film in DMSO system. Experimental results indicate that Er-Co-Bi alloy thin film containing 14.83 %－32.65 % Er is prepared from 0.1 mol/L $ErCl_3$+ 0.1 mol/L $CoCl_2$+ 0.1 mol/L $Bi(NO_3)_3$+ 0.1 mol/L LiCl + DMSO system by cyclic electrodeposition on Cu substrate. The optimum cyclic potential of electrodeposition is that upper potential is within a potential range from －0.50 V to － 1.00 V and lower potential is within a potential range from － 2.00 V to － 2.60 V. The surface of alloy thin film observed by scanning electron microscope is black, adhesive and has metallic luster. The film is amorphous proved by the X-ray diffractometry.

Key words: Er-Co-Bi thin film; rare earth; cyclic electrodeposition; dimethylsulfoxide
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1 INTRODUCTION

Alloys based on rare earth(RE) and transition metal(TM) are known as useful magnetic materials for the production of magnetooptical memory materials with high remanent magnetic inductions and high coercive fields[1－7]. Bi has also attracted much attention because it is a semi-metal and possesses several unique physical properties. For example, the Fermi wavelength of the semi-metallic Bi is as large as 400 Å, as compared to a few scores of nanometers for most metals[2]. The Carrier's mean free path in Bi can be as much as a few millimeters at 4.2 K, several orders of magnitude larger than that in most metals. Bi-based alloy systems also have a very long relaxation time on the scale of more than 10 000 s at room temperature. Because of many potential and actual applications in photoelectronic, thermoelectric, photoelectrochemical devices, solar selective and decorative coatings, RE-TM-Bi alloys are of continuous interest for investigators from the preparative and characteristic point of view in order to test their suitability for a particular and desired application.

The electrodepositon technique has a major advantage over other production methods of alloy thin film, namely, the possibility of performing deposition at normal conditions of pressure and temperature, requiring relatively inexpensive equipment. But it is difficult to electrodeposit amorphous RE-TM-Bi alloy thin films in aqueous solutions due to the activity of rare earth(RE), and the temperature of electrodeposition in molten salts system would be high. If the RE-TM-Bi alloy thin films can be prepared in organic solvent at room temperature by electrodeposition, it will greatly improve their application in functional materials. Recently, the authors have studied the electrodeposition process of rare earths and their alloy thin films in organic bath at room temperature[8－11]. In this paper, the cyclic voltammetry and cyclic electrodepositon are used to investigate the preparation of Er-Co-Bi alloy thin films in LiCl-DMSO system

2 EXPERIMENTAL

The dehydrated $ErCl_3$ was obtained by the reaction of Er_2O_3(99.99%) with HCl(AR) and dehydrating in vacuum at 393 K. The supporting electrolyte LiCl(AR) was dehydrated in vacuum at 453 K[12－14]. Before use, DMSO(AR) was dehydrated with 4A molecular sieves and distilled under a reduced pressure to remove impurities.

A simple three-electrode glass cell was used in the electrochemical experiments. The working electrodes were platinum(99.9%) and copper(99.9%), with area of 0.07 cm^2. A platinum foil was used as a counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode which was connected to the cell with a double salt bridge system. All potential values determined in this study were the values versus SCE.

All the experiments were carried out at a temperature of (298 ±0.5) K, under argon atmosphere.

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Zahner Elektrik IM6e electrochemical workstation was used for electrochemical measurement and cyclic electrodeposition. X-ray energy dispersive analysis (EDS) was adopted to determine the content of erbium, cobalt and bismuth in deposit and X-ray diffractometry(XRD) to determine the structures of the electrolytic product. The morphology of surface of the electrolytic product was observed with scanning electron microscope (SEM).

3 RESULTS AND DISCUSSION

3.1 Cyclic voltammogram of Er(Ⅲ), Co(Ⅱ) and Bi(Ⅲ) in LiCl-DMSO system

Fig. 1 shows the cyclic voltammogram of 0.1 mol/L $ErCl_3$ + 0.1 mol/L $CoCl_2$ + 0.1 mol/L $Bi(NO_3)_3$+ 0.1 mol/L LiCl+ DMSO system at 298 K. There are two cathodic waves. The starting potential and peak potential of the first cathodic wave I_c are − 0.25 V and − 0.52 V respectively, which are in according with the cyclic voltammogram of Bi (Ⅲ) in DMSO[15], so the first cathodic wave is caused by the reduction of Bi(Ⅲ) to Bi. The starting potential and peak potential of the second cathodic wave II_c are − 0.88 V and − 2.06 V respectively, and the cathodic wave is caused by the codeposition of Co(Ⅱ) and Er(Ⅲ).

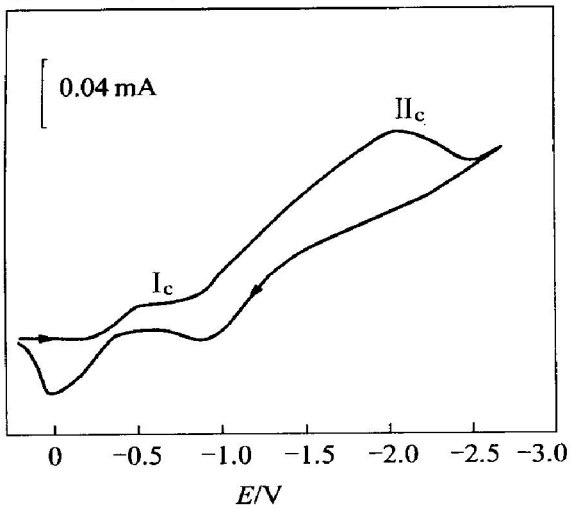

Fig. 1 Cyclic voltammogram of Pt electrode in 0.1 mol/L $ErCl_3$+ 0.1 mol/L $CoCl_2$+ 0.1 mol/L $Bi(NO_3)_3$+ 0.1 mol/L LiCl+ DMSO system (T = 298 K, v = 0.04 V/s)

3.2 Cyclic electrodeposition of Er-Co-Bi alloy thin film and effects of cyclic electrodeposition parameters

The deposition bath contained 0.1 mol/L $ErCl_3$ + 0.1 mol/L $CoCl_2$+ 0.1 mol/L $Bi(NO_3)_3$+ 0.1 mol/L LiCl+ DMSO. Electrodeposition was carried on the Cu foil by cyclic potential electrolysis in the system. The upper potential was chosen as − 0.51 V, the lower potential was chosen as − 2.06 V according to the cyclic voltammogram in the system at 298 K, and the time of cyclic electrodeposition was 30 min. The obtained thin film was about 1.18 μm thick and adheres firmly to the copper substrate.

When upper potential was chosen within a potential range from − 0.30 V to − 1.00 V, lower potential was chosen within a potential range from − 2.00 V to − 3.00 V, and the cycling rate was 0.02 V/s, the compositions of alloy thin films obtained by cyclic electrodeposition for 30 min were analyzed by X-ray energy dispersive analysis (EDS) and the results are shown in Fig. 2 and Fig. 3. Fig. 2 represents the content of Er in Er-Co-Bi alloy thin films when lower potential is kept constant at − 2.60 V and upper potential within a potential range from − 0.30 V to − 1.00 V. The content of Er in Er-Co-Bi alloy thin films decreases when the upper potential of electrodeposition shifts negatively. At the same time, it can be seen that the films are the thickest when the upper potential is − 1.00 V, and above this potential the film becomes thinner. Fig. 3 represents the content of Er in Er-Co-Bi alloy thin films when upper potential is kept constant at − 1.00 V and lower potential within a potential range from − 2.00 V to − 3.00 V. The content of Er in Er-Co-Bi thin films increases at first and then decreases when the lower potential of electrodeposition shifts negatively. The reason may be that the rate of electrodeposition of Er (Ⅲ) is increased when the lower potential of electrodeposition shifts negatively, but the concentration polarization is also increased and the rate of electrodeposition is controlled by it when the potential of electrodeposition is lowered to − 2.60 V. Furthermore, the surface of alloy thin films becomes coarse when the potential of electrodeposition is below − 2.60 V. On the basis of above results, the optimum cyclic potential of electrodeposition is that upper potential is within a potential range from − 0.50 V to − 1.00 V and lower potential is within a potential range from − 2.00 V to − 2.60 V.

The potential sweep rate is found to be important with respect to the adhesion of the thin films. Adhesion is improved at first and then deteriorates when the sweep rate is increased from 0.001 V/s to 0.100 V/s. When the sweep rate is 0.001 or 0.100 V/s, the thin film is very badly adhesive. So all the thin films are deposited with a sweep rate of 0.010 − 0.070 V/s. Also, the appearance of the thin film changes from gray to black when the sweep rate is increased. Nevertheless, adhesion still needs to be improved by adding tartaric acid as a complexing agent and polyethylene glycol-1 000 as a stabilizer.

Fig. 4 shows the content of Er in alloy thin film increases from 18.27% to 30.62% with decreasing sweep rate when the number of cycle was 20. How-

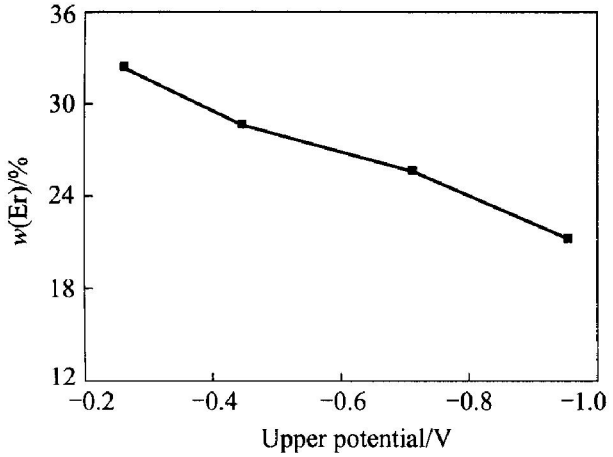

Fig. 2 Dependence of content of Er in Er-Co-Bi thin film versus upper potential

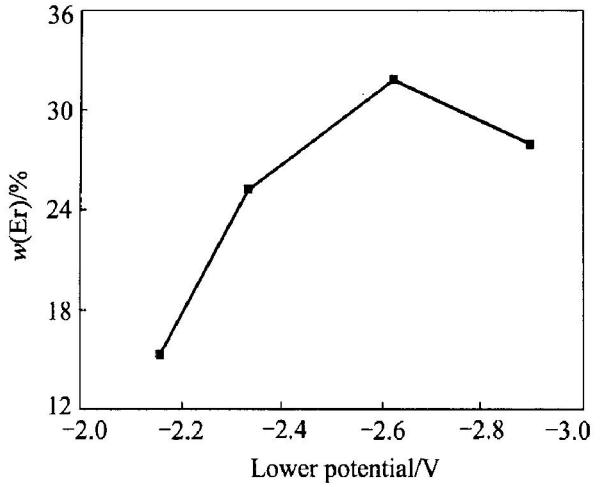

Fig. 3 Dependence of content of Er in Er-Co-Bi thin film versus lower potential

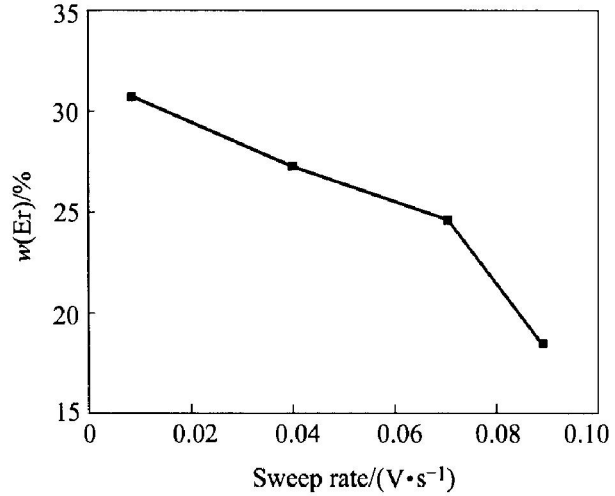

Fig. 4 Dependence of content of Er in Er-Co-Bi thin film versus sweep rate (number of cycle: 20; cyclic potential: − 2.50 V to − 0.50 V)

ever, when the sweep rate was 0.04 V/s, Er content also increases from 16.39% to 32.83% with increasing number of cycle from 10 to 25 (Fig. 5). Thus, the content of Er in the Er-Co-Bi thin film does not depend on sweep rate, and the key factor is the time of cyclic electrodeposition. Fig. 6 shows that the thin film thickness grows linearly with the deposition time, and this linearity gives an indication of the good stability of the electrodeposition process and system. The deposition rate was about 2.20 μm/h.

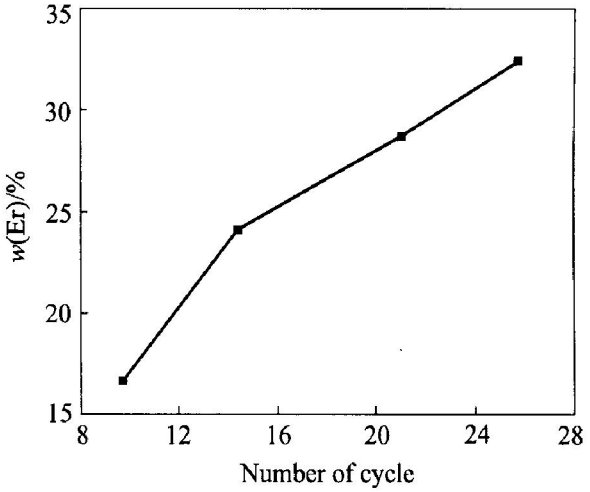

Fig. 5 Dependence of Er content of Er-Co-Bi thin film versus number of cycle (sweep rate: 0.04 V/s; cyclic potential: − 2.50 to − 0.50 V)

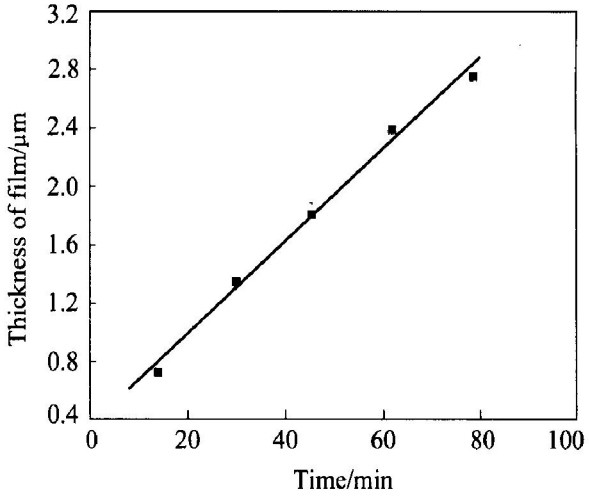

Fig. 6 Film thickness versus deposition time (cyclic potential: − 2.50 V to − 0.50 V)

3.3 Characterization of Er-Co-Bi alloy thin film

When the Er-Co-Bi alloy thin film was dissolved in 0.1 mol/L HCl, a large amount of gas released, which proved that the deposited layer was metal. The thin film was analyzed by EDS, as shown in Fig. 7. The K_α peaks of Er and Bi and K_β peaks of Co are strong, and these peaks belong to the L series of Er, Co and Bi. Other peaks of Co and Bi belong to their M series. The Cu peak is from the substrate.

The morphology of Er-Co-Bi thin film was observed by scanning electron microscope (SEM), as shown in Fig. 8. The image shows that the surface of the alloy thin film is compact, uniform and has the

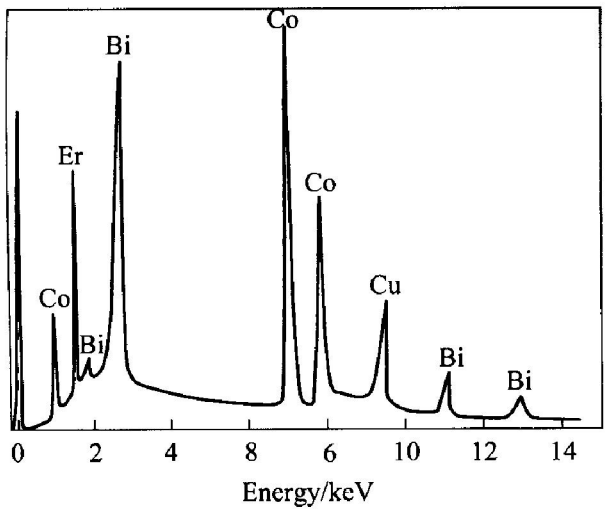

Fig. 7 EDS pattern of Er-Co-Bi thin film

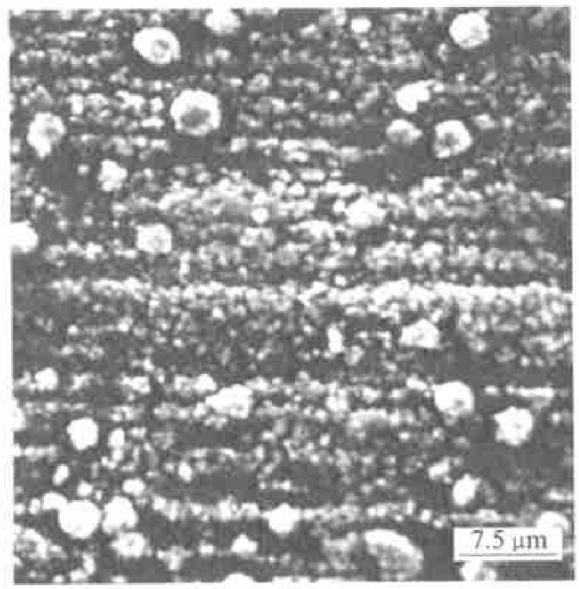

Fig. 8 SEM image of surface of Er-Co-Bi thin film

metallic luster.

The surface of the alloy thin film was analyzed by X-ray diffractometry(XRD). The XRD diffraction patterns of the deposition film were observed within the scanning angle range of 0°－80°. No diffraction peak was found in the XRD pattern besides the peaks of copper substrate, which suggested that the Er-Co-Bi thin film was amorphous.

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