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Electrochemical preparation of La-Co-Fe alloy films in dimethylsulfoxide (DMSO) ①

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[Abstract] Potentiostatic and pulse electrolysis techniques were used to prepare La-Co-Fe alloy films using ethylenediamine (EN) as complexant. Surfaces of alloy films obtained by these two techniques are smooth, adhesive, compact and metallic luster. The contents of La in alloy films obtained by potentiostatic electrolysis technique are in the range of 13.23%~ 47.67%. The contents of La in alloy films deposited by pulse electrolysis technique are in the range of 10.67%~ 16.29%.

[Key words] ethylenediamine; lanthanum; codeposition; dimethylsulfoxide; La-Co-Fe alloy films
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1 INTRODUCTION

Rare earths and their alloys have specific properties, such as magnetic, optical, electric and hydrogen storage. They have been widely applied to various function materials. The La-Co-Fe alloys have been put to use in magnetic materials. It was reported that the $LaCo_{13}Fe_{13}$ has good DC magnetic properties from 10 K to 1 273 K[1]. Since rare earth elements are very active, it is very difficult to deposit them in aqueous by electrochemical methods. We had prepared rare earths and their alloys by molten salt in 1980s and first-1990s[2, 3]. But high temperature was needed in the process of electrodeposition, facilities were corroded easily and energy was cost. In mid-1990s, we had studied electrodeposition of rare earths and their alloys at low temperature. But electrolysis temperature was up to 403 K[4]. Recently, we have studied electrodeposition of rare earths and their alloys in organic solutions at room temperature[5~ 7]. The paper studies the preparation of La-Co-Fe alloy films by electrochemical methods in DMSO at room temperature.

2 EXPERIMENTAL

The dehydrated $LaCl_3$ was obtained by the reaction of La_2O_3(99.99%), HCl(AR) and dehydration in vacuum at 393 K[8~ 10]. $CoCl_2$(AR) and $LiClO_4$ (AR) were dehydrated in vacuum at 453 K. $FeCl_2$ (AR) was washed by acetone and dehydrated in argon atmosphere at 453 K. Before experiment, the dimethylsulfoxide (DMSO) was dehydrated with 4A molecular sieves and distilled at reduced pressure to remove impurities[7].

A simple three electrodes cell was used in the study. Pt wire (99.9%, 0.05 cm^2) and Cu wire (99.9%, 0.02 cm^2) were used as working electrodes. Pt foil was used as the counter electrode. A saturated calomel electrode (SCE) connected to the cell with a double salt bridge system was used as the reference electrode, and all reported potentials were against the SCE. All experiments were carried out in argon atmosphere at room temperature.

A HDV-7C transistor potentiostatic instrument, a HD-1A low frequency-super low frequency functional generator and a 3086X-Y recorder were used for electrochemical measurement. A DM-1 pulse plating modulator was applied to pulse electrolysis. The electrodeposit obtained was analyzed by Oxford ISIS 300 EDAX to determine the contents of La, Co and Fe, and by D/MAX-3A X-ray diffraction (XRD) spectrum to determine the composition of electrolytic product. The morphologies of the surface of the alloy films was observed by Hitachi S-520 scanning electron microscopy (SEM).

3 RESULT AND DISCUSSIION

3.1 Cyclic voltammograms of La(Ⅲ), Co(Ⅱ) and Fe(Ⅱ) in DMSO

$LiClO_4$ as supporting electrolyte was added in DMSO. Ethylenediamine (EN) as complexant was added in system. Fig. 1(a) is cyclic voltammograms of Fe(Ⅱ), Co(Ⅱ) and La(Ⅲ) in their own study systems on Pt electrode at 304 K. There are the turn-

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ing potentials at − 0.550 V in curve(1), − 0.600 V in curve(2) and − 1.100 V in curve(3) due to the discharge of Fe(Ⅱ), Co(Ⅱ) and La(Ⅲ), respectively. Fig. 1(b) is cyclic voltammograms of Fe(Ⅱ), Co(Ⅱ) and La(Ⅲ) in their own study systems on Cu electrode at 304 K, and the turning potentials at − 1.550 V in curve(1), − 1.550 V in curve(2) and − 1.650 V in curve(3) are caused by the reduction of Fe(Ⅱ), Co(Ⅱ) and La(Ⅲ), respectively.

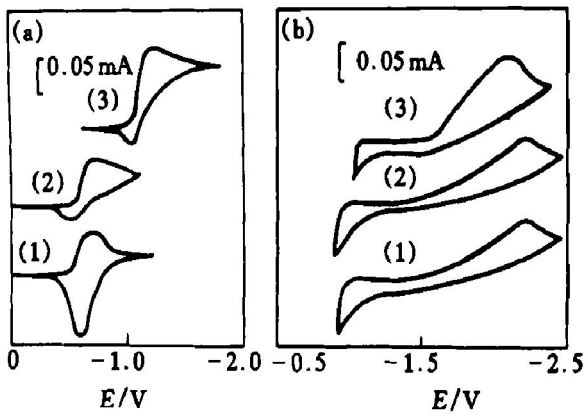

Fig. 1 Cyclic voltammograms of three kinds of studied systems
(a) —On Pt electrode (0.05 cm^2);
(b) —On Cu electrode (0.02 cm^2);
(1) —0.01 mol/L $FeCl_2$-0.1 mol/L $LiClO_4$-DMSO-EN;
(2) —0.01mol/L $CoCl_2$-0.1 mol/L $LiClO_4$-DMSO-EN;
(3) —0.01mol/L $LaCl_3$-0.1mol/L $LiClO_4$-DMSO-EN
at 50 mV/s 304 K

Fig. 2(a) and (b) are cyclic voltammograms of mixed system 0.01 mol/L $LaCl_3$-0.01 mol/L $CoCl_2$-0.01 mol/L $FeCl_2$-0.1 mol/L $LiClO_4$-DMSO-EN on Pt electrode and on Cu electrode at 300 K, respectively. There are two turning potentials at − 0.600 V and − 1.100 V in Fig. 2(a). Compared with Fig. 1(a), − 0.600 V is relative to reductions of Fe(Ⅱ) and Co(Ⅱ), and − 1.100 V is reduction of La(Ⅲ). There is only one turning potential at − 1.500 V in Fig. 2(b). When potential is more negative than − 1.500 V, three kinds of metals will

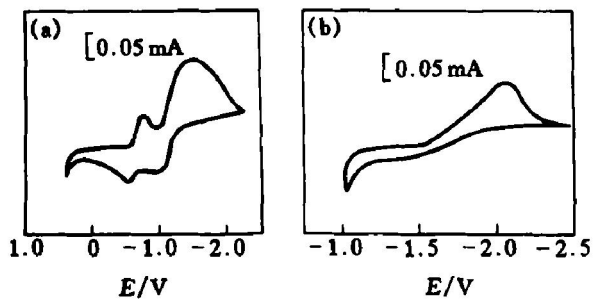

Fig. 2 Cyclic voltammograms of 0.01 mol/L $LaCl_3$-0.01 mol/L $CoCl_2$-0.01 mol/L $FeCl_2$-0.1 mol/L $LiClO_4$-DMSO-EN systems
(a) —On Pt electrode (0.05 cm^2) at 50 mV/s, 300 K;
(b) —On electrode (0.02 cm^2) at 50 mV/s, 300 K

codeposit. Standard potentials of iron and cobalt are far away from that of lanthanum, but, after adding EN as complexant, deposit potentials of three kinds of studied metals are very close on Cu electrode (shown in Fig. 1(b)). So it is advantageous to codeposit three kinds of metal on Cu electrode.

3.2 Preparation of La-Co-Fe alloy films by potentiostatic technique

La-Co-Fe alloy films were prepared by potentiostatic technique on the basis of cyclic voltammograms in Fig. 2(b). Four potentials were chosen to codeposit La-Co-Fe alloy films from − 1.500 V to − 2.250 V. A Pt foil was used as counter electrode. Pure copper was acted as cathode substrate. Three kinds of electrolyte systems were studied: 1) 0.0125 mol/L $LaCl_3$-0.1 mol/L $CoCl_2$-0.1 mol/L $FeCl_2$-0.1 mol/L $LiClO_4$-DMSO-EN (molar concentration ratio of La(Ⅲ), Co(Ⅱ) and Fe(Ⅱ) is 1∶8∶8); 2) 0.025 mol/L $LaCl_3$-0.1 mol/L $CoCl_2$-0.1 mol/L $FeCl_2$-0.1 mol/L $LiClO_4$-DMSO-EN (molar concentration ratio of La(Ⅲ), Co(Ⅱ) and Fe(Ⅱ) is 1∶4∶4); 3) 0.05 mol/L $LaCl_3$-0.1 mol/L $CoCl_2$-0.1 mol/L $FeCl_2$-0.1 mol/L $LiClO_4$-DMSO-EN (molar concentration ratio of La(Ⅲ), Co(Ⅱ) and Fe(Ⅱ) is 1∶2∶2). The contents of elements La, Co and Fe in alloy films were analyzed by EDXA. The contents of La in alloy films obtained by potentiostatic electrolysis technique are in the range of 13.23% to 47.67%.

Though ion molar concentration ratios are controlled in the studied systems severely, metal atom ratios in alloy films are not in accordance with ion molar concentration ratios in the systems. The content of La in deposit films rises with electrodeposition potentials to move more negative and La(Ⅲ) ion concentrations to increase in the systems, but the contents of Fe and Co in deposit films are ruleless. But in Fig. 3(a), when ion molar concentration ratio is 1∶4∶4 and deposit potential is − 2.230 V, La-Co-Fe alloy film(atom ratio 1∶5∶5) can be obtained. Morphology of La-Co-Fe alloy film prepared at − 2.150 V (vs SCE) is analyzed by scanning electron microscope (SEM) as shown in Fig. 4(a). Metal crystal size is about 2~3 μm. Morphology of La-Co-Fe alloy film prepared at − 2.150 V (vs SCE) after thermal treatment at 893 K shows metal crystal size to be enlarged.

3.3 Preparation of La-Co-Fe alloy films by pulse electrolysis technique

Pulse electrolysis technique is often applied to deposit alloys. Because grain matrix becomes smaller and improves quality of deposit through the technique. The pulse technique has three main electric parameters: the pulse electrolysis time(t_{on}), the pulse interval (t_{off}) and pulsing current. t_{on} and t_{off} are also represented by pulsing frequents and pulse working

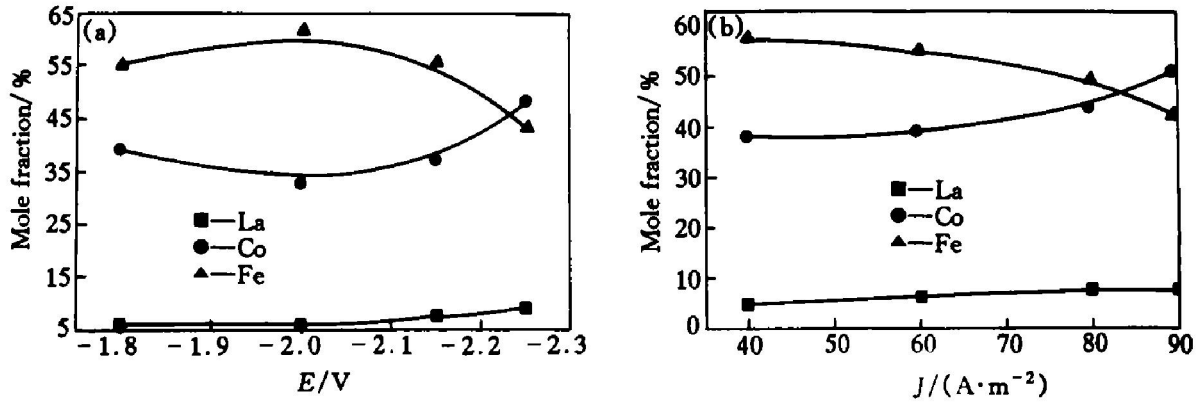

Fig. 3 Molar fraction of Fe, Co and La in alloy films vs deposit potentials in system B (a) and pulse current densities (b)

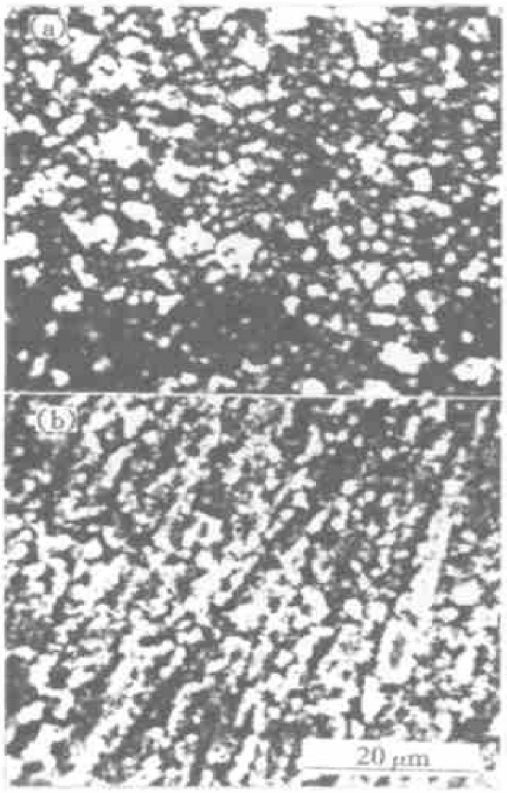

Fig. 4 Morphology of La-Co-Fe alloy film
(a) —Prepared at -2.150 V; (b) —Prepared at 60 A·m^{-2}

ratios ($t_{on}/(t_{on}+t_{off})$). t_{on} and t_{off} can be determined by the well-defined pulsing frequents and pulse working ratios. Therefore, it is important to choose the appropriate conditions of deposition for obtaining the fine deposit. Our study group has obtained the optimum condition of codeposition of rare earth-iron group alloys: pulsing frequent was 800 Hz and pulse working ratio was 10%[11]. Another advantage applying the pulse technique is that concentration polarization can be decreased to the lowest. Hence, larger current densities and higher current efficiency are obtained in the process of deposition.

Fig. 5 is dynamic polarization curve of 0.033 mol/L $LaCl_3$-0.1 mol/L $CoCl_2$-0.1 mol/L $FeCl_2$-0.1 mol/L $LiClO_4$-DMSO-EN system on Cu electrode at 300 K. Fig. 5 shows that serious concentration polarization exists in the process of codeposition of La-Co-Fe alloys. Hence, it is appropriate to choose the pulse electrolysis technique in the study. Pt foil was used as counter electrode. Pure copper was acted as cathode substrate. The La-Co-Fe alloy films were obtained in mentioned system by pulse technique. The surfaces of La-Co-Fe alloy films are silver-gray, compact, uniform, adhesive and metallic luster. The contents of elements in alloy films is analyzed by EDAX. The contents of La in alloy films are in the range of 10.67% to 16.29%. The correlation between the pulse current densities and the contents of the elements in alloy films is shown in Fig. 3(b). The contents of lanthanum and cobalt increase and content of iron decreases when pulse current densities rise. When ion molar concentration ratio is 1∶3∶3 and pulse current densities is 83 A·m^{-2}, the atom ratio 1∶6.6 of La, Co and Fe in alloy film can be obtained. Morphology of La-Co-Fe alloy film prepared at 60 A·m^{-2} by SEM shows in Fig. 4(b). Metal grain size of alloy film is about 1~2 μm. The formation of deposits is ordered. This state is still retained after

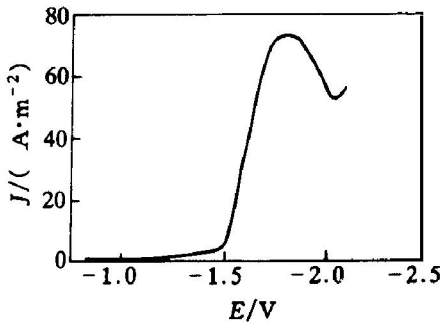

Fig. 5 Dynamic polarization curve of 0.33 mol/L LaCl-0.1 mol/L $CoCl_2$-0.1 mol/L $FeCl_2$-0.1 mol/L $LiClO_4$-DMSO-EN system on Cu electrode (0.55 cm^2) at 50 mV/s and 300 K

thermal treatment at 893 K. On the surface there are some white grains which may be oxide.

4 CONCLUSIONS

1) Using ethylenediamine(EN) as complexant in the studied system was studied. Their electrodeposition potentials become closer when different metal ions form complexes with EN. So codeposition of three metals is easier.

2) Fine electrodeposition films were obtained by applying potentiostatic technique and pulse technique. The surfaces of La-Co-Fe alloy films are compact, uniform, adhesive and metallic luster. The contents of La in alloy films obtained by potentiostatic electrolysis technique are in the range of 13.23% to 47.67%. The contents of La in alloy films deposited by pulse electrolysis technique are in the range of 10.67% to 16.29%.

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