Electrodeposition of La-Co Alloy Films in Dimethylsulfoxide (DMSO)*

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Abstract: This paper reported the electrodeposition of La-Co alloy films in dimethylsulfoxide (DMSO). Citric acid as the complexing agent and polyethylene glycol-1000 as the additive were discussed. Potentiostatic and pulse electrolysis techniques were used to prepare La-Co alloy films. 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 22.42% to 50.29%, while deposited by pulse electrolysis technique are in the range of 1.46% to 42.63%. The size of metal grains obtained by pulse technique is about 100 nm.

Keywords: rare earth; lanthanum; codeposition; dimethylsulfoxide (DMSO); La-Co alloy films
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Rare earths and their alloys have interesting properties, such as magnetic, optical, electric, and hydrogen storage. They have been widely applied to various functional materials. The La-Co alloys have been put into use in magnetic materials. It was firstly reported that the $LaCo_{13}$ has good a.c. magnetic properties in 1998[1]. Since rare earth elements are very active, it is very difficult to deposit them in aqueous solution by electrochemical methods. Our research group had prepared rare earths and their alloys by molten salt in 1980s and first-1990s[2~4], but the process of the electrodeposition needed high temperature, the facilities were corroded easily and the energy was highly cost. In the 1990s[5], we had studied the electrodeposition of rare earths and their alloys at low temperature, but the electrolysis temperature was still up to 403 K. Recently, we have studied the electrodeposition of rare earths and their alloys in organic solutions at room temperature[6,7]. This paper reports the preparation of La-Co alloy films by electrochemical methods in DMSO at room temperature.

1 Experimental

The dehydrated $LaCl_3$ was obtained by the reaction of La_2O_3 (w = 99.99%) and HCl (AR) and dehydration in vacuum at 393 K[8,9]. $CoCl_2$ (AR) and $LiClO_4$ (AR) were dehydrated in vacuum at 453 K. Before use, the dimethylsulfoxide (DMSO) was dehydrated with 4A molecular sieves and distilled at reduced pressure to remove impurities[10].

A simple three-electrode cell was used. A Pt wire (w = 99.9%, 0.05 cm^2) and a Cu wire (w = 99.9%, 0.03 cm^2) were used as working electrodes. A Pt foil was used as the counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode which was connected to the cell with a double salt bridge system and all potential determined values were converted to relative potential to 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 3086 X-Y recorder were used as electrochemical measurements. A DM-1 pulse platingmodulator was applied to pulse electrolysis. The electrodeposit products obtained were analyzed by an Oxford I-SIS 300 EDAX to determine the contents of La and Co and by a D/MAX-3A X-ray diffraction (XRD) to determine their compositions. The morphologies of the surfaces of the alloy films were observed by a Hitachi S-520 scanning electron microscopy (SEM).

2 Results and Discussion

2.1 Electrochemcial behavior of La (Ⅲ) and Co (Ⅱ) in DMSO

$LiClO_4$ as supporting electrolyte was added in DMSO. Citric acid as a complexing agent and polyethylene glycol-1000 as an additive were added into system. Fig.1 is cyclic voltammograms of 3×10^{-3} mol/L $LaCl_3$-0.01 mol/L $CoCl_2$-0.1 mol/L $LiClO_4$-DMSO-

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0.2 mol/L citric acid-polyethylene glycol-1000 on Cu electrode at 298 K. There is a turning potential at −1.050 V. When potential is more negative than −1.050 V, Co(Ⅱ) and La(Ⅲ) will codeposit. A anode peak potential is −0.350 V due to dissolution of La-Co alloy. Fig.2 is dynamic polarization curve of 0.037 5 mol/L $LaCl_3$-0.112 5 mol/L $CoCl_2$-0.1 mol/L $LiClO_4$-DMSO-0.2 mol/L citric acid-polyethylene glycol-1000 on Cu electrode at 298 K.

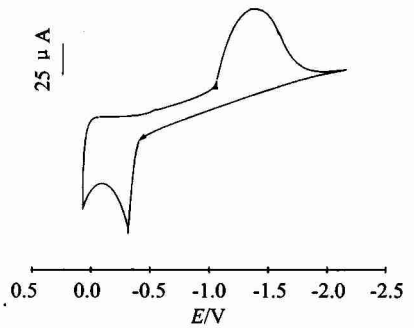

Fig.1　Cyclic voltammograms in 3×10^{-3} mol/L $LaCl_3$-0.01 mol/L $CoCl_2$-0.1 mol/L $LiClO_4$-DMSO-0.2 mol/L citric acid-polyethylene glycol-1000
s (Cu) = 0.03 cm^2; v = 50 mV/s; 298 K

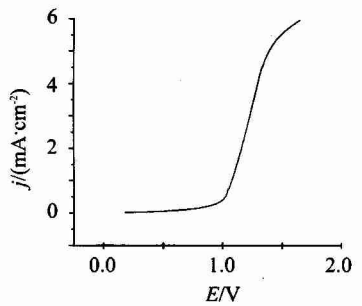

Fig.2　Dynamic polarization curve in 0.037 5 mol/L $LaCl_3$-0.112 5 mol/L $CoCl_2$-0.1 mol/L $LiClO_4$-DMSO-0.2 mol/L citric acid-polyethylene glycol-1000 system
s (Cu) = 0.55 cm^2; v = 50 mV/s; 298 K

2.2　Preparation of La-Co alloy films by pulse electrolysis technique

Pulse electrolysis technique is often applied to deposit alloys because the grain matrix becomes smaller and the quality of the deposit can be improved by this technique. In the process of pulse electrolysis, very larger overpotential is produced by instant peak current. Nucleus formation speed is far faster than grain growth speed under this condition. It was reported that the size of grains was 0.5 μm by pulse electrolysis technique[11]. The pulse technique has three main electric parameters: the pulse electrolysis time (t_{on}), the pulse waiting period (t_{off}) and the pulsing current. t_{on} and t_{off} are also represented by pulsing frequency and pulse working ratio ($t_{on}/(t_{on}+t_{off})$), respectively. The t_{on} and t_{off} can be determined by the well-defined pulsing frequency and pulse working ratio. Therefore, it is important to choose the appropriate conditions of deposition for obtaining the fine deposit. Another advantage of applying the pulse technique is that the concentration polarization can be decreased to the lowest. Hence, larger current density and higher current efficiency are obtained in the process of deposition. Three kinds of electrolyte systems were studied: A: 0.05 mol/L $LaCl_3$-0.1 mol/L $CoCl_2$-0.1 mol/L $LiClO_4$-DMSO-0.2 mol/L citric acid-polyethylene glycol-1000[c(La(Ⅲ)) : c(Co(Ⅱ)) = 1 : 2]; B: 0.037 5 mol/L $LaCl_3$-0.112 5 mol/L $CoCl_2$-0.1 mol/L $LiClO_4$-DMSO-0.2 mol/L citric acid-polyethylene glycol-1000 [c(La(Ⅲ)) : c(Co(Ⅱ)) = 1 : 3]; C: 0.03 mol/L $LaCl_3$-0.12 mol/L $CoCl_2$-0.1 mol/L $LiClO_4$-DMSO-0.2 mol/L citric acid-polyethylene glycol-1000 [c(La(Ⅲ)) : c(Co(Ⅱ)) = 1 : 4]. In the process of pulse electrolysis, pulsing frequency was 800 Hz and pulse working ratio was 20%. A Pt foil was used as the counter electrode. Pure copper acted as the cathode substrate. On the basis of Fig.2, pulse current densi-

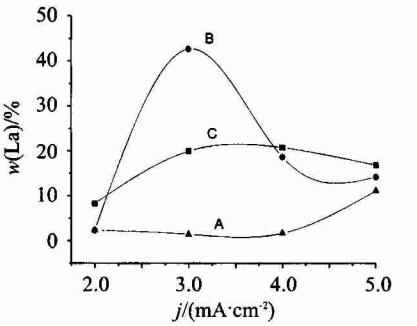

Fig.3　Contents of La in alloy films versus pulse current densities

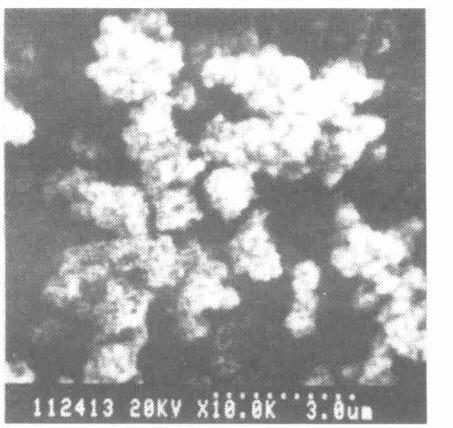

Fig.4　Morphology of La-Co alloy film obtained at 3 mA/cm^2 observed by SEM

ties were chosen from 1 mA/cm^2 to 5 mA/cm^2. The La-Co alloy films were obtained in above mentioned systems by pulse technique. The surfaces of La-Co alloy films are brown-red, compact, uniform, adhesive and metallic luster. The contents of La in alloy films are in the range of 1.46% to 42.63%. The correlation between the pulse current densities and the contents of the elements in alloy films is shown in Fig.3. The contents of lanthanum in alloy films are non-linear with pulse current densities and ion molar concentration ratios in systems. The morphology of La-Co alloy film prepared at 3 mA/cm^2 by SEM showed in Fig.4. The metal grain size in the alloy film is about 100 nm. It illustrates that the nanometer materials of rare earth alloys can be obtained by controlling electrodeposition conditions.

2.3 Preparation of La-Co alloy films by potentostatic technique

La-Co alloy films were prepared by potentostatic technique in 0.037 5 mol/L $LaCl_3$-0.112 5 mol/L $CoCl_2$-0.1 mol/L $LiClO_4$-DMSO-0.2 mol/L citric acid-polyethylene glycol-1000. On the basis of Fig.1, four potentials were chosen to codeposit La-Co alloy films from −1.500 V to −2.200 V. A Pt foil was used as counter electrode. Pure copper acted as the cathode substrate. Codeposition conditions, compositions and surface shapes of La-Co alloy films are listed in Table 1. The fine La-Co alloy films were obtained by potentostatic technique from −1.500 V to −2.000 V.

The contents of La in alloy films are in the range of 22.42% to 50.29%. The morphologies of La-Co alloy films observed by SEM found that size of metal grains was about 2 ~ 3 μm.

The surface of an alloy film analyzed by XRD is shown in Fig.5. The XRD experiment data of alloy films are 20.91 nm, 18.10 nm and 12.80 nm, in well agreement with the PDF card data[12] of copper (20.9, 18.15 and 12.82 nm). It illustrates that diffraction peaks belong to the substrate. It also proves that alloy films are amorphous.

Tab.1 Compositions and surface shapes of La-Co alloy films on Cu substrate

Potential of codeposition/ V	Time of codeposition/ min	Content/% of element in alloy film		Shape of deposit
		La	Co	
−1.500	30	38.09	61.91	Black uniform metallic luster alloy films
−1.800	30	46.38	53.62	Black smooth metallic luster alloy films
−2.000	30	50.29	49.71	Black smooth adhesive alloy films
−2.200	30	22.42	77.58	Deep black rough alloy films

3 Conclusions

Citric acid as the complexant and polyethylene glycol-1000 as the additive were used to improve quality of La-Co alloy films. Potentiostatic and pulse electrolysis techniques were used to prepare La-Co alloy films. 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 22.42% to 50.29% and deposited by pulse electrolysis technique are of 1.46% to 42.63%. The size of metal grains obtained by applying pulse technique is about 100 nm. It illustrates that the nanometer materials of rare earth alloys by controlling electrodeposition conditions can be obtained.

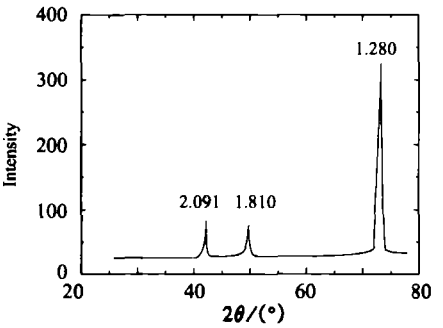

Fig.5 XRD spectrum of a La-Co alloy film at room temperature

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二甲亚砜中电沉积 La-Co 合金膜的研究

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摘　要：研究在非水溶剂二甲亚砜中电沉积 La-Co 合金膜．体系中加入柠檬酸为络合剂，聚乙醇-1000 为添加剂，用于改善沉积层的质量．在沉积过程中，应用了恒电位电解技术和脉冲电解技术．所得 La-Co 合金膜的表面是光滑，致密，粘附性好和有金属光泽．恒电位电解技术沉积得到的 La-Co 合金膜中 La 的质量分数是 22.42% ~ 50.29%．脉冲电解技术沉积得到的 La-Co 合金膜中 La 的质量分数是 1.46% ~ 42.63%．脉冲电解技术沉积得到的 La-Co 合金膜通过电镜观察发现金属粒子的大小约为 100 nm．

关键词：稀土；镧；共沉积；二甲亚砜；La-Co 合金膜

中图分类号：O614.33；TG153.1

（上接第 83 页）

Synthesis, Crystal Structure and Bioactivity of Heteropolyoxotungstate Substituted by Niobium

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Abstract: The new complex $K_4H_3[SiW_9Nb_3O_{40}]\cdot 4H_2O$ was synthesized and characterized by IR and UV spectroscopies. The crystal structure was determined by X-ray diffraction. It was showed that the compound remained Keggin structure and crystallized in the hexagonal system having space group is $P3_2$ with cell parameters a = 1.915 43(4) nm, c = 1.249 7 (3) nm, V = 3.970 6 (11) nm^3, D_c = 3.524 0 g/cm^3, Z = 3, μ = 21.018 mm^{-1}, F (000) = 368 0, R = 0.056 5, WR_2 = 0.097 2.

Keywords: heteropolyoxotungstates substituted; synthesis; crystal structure