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Preparation of Gd-Co alloy in dimethylsulfoxide by electrodeposition method①

Tong Yexiang(童叶翔), Liu Guankun(刘冠昆), He Shan(何 山), Wang Yu(王 宇)
School of Chemistry and Chemical Engineering,
Zhongshan University, Guangzhou 510275, P. R. China

Abstract: Electrodeposition of Gd-Co alloy film from dimethylsulfoxide (DMSO) electrolyte solutions has been investigated using cyclic voltammogram and potentiostatic technique. Potentiostatic depositions between - 1.20 V and - 2.70 V were applied to uncomplexed and complexed solution. The deposits obtained at potentials within - 2.30 ~ - 2.70 V from complexed solutions are silver gray smooth films.

Key words: Gd-Co; alloy; electrodeposition; dimethylsulfoxide **Document code: A**

1 INTRODUCTION

The films of rare earth iron group alloy are highly advanced materials and are now produced by sputtering or vacuum plating, but the cost is high, the productivity is low with high requirement to the equipments. To solve the problems electrodeposition may be a good way. Because the rare earth is very active, nonaqueous electrolytes are often used. For example, Yb-Ni and Dy-Ni alloys were obtained by electroreduction in molten chloride[1,2], yttrium-barium-copper trinary master alloy was prepared by electrodeposition from molten fluoride-oxide[3], yttrium was obtained from a nonaqueous bath by electrodeposition[4], Sm-Co thin films were prepared by electrodeposition[5], Nd-Fe was electrodeposited in organic electrolyte[6], Dy-Fe was obtained by pulsed electrodeposition[7], Nd-Ni and Y-Co films were prepared in organic electrolyte[8,9]. Therefore, the technological application for electrodeposition of rare earth metal and their alloys in nonaqueous electrolytes is promising. In this work we prepared Gd-Co alloy in the system of $Gd(ClO_4)_3$-$CoCl_2$-DMSO and $Gd(ClO_4)_3$-$CoCl_2$-EN-DMSO(here, DMSO stands for dimethylsulfoxide) by potentiostatic deposition, and EN (ethylene diamine) was studied as a complexing agent.

2 EXPERIMENTAL

The dehydrated $Gd(ClO_4)_3$ was obtained by the reaction of Gd_2O_3(99.99%) and $HClO_4$(AR grade) at 298 K and dehydration in vacuum at 433 K. $CoCl_2$(AR grade) was dehydrated in vacuum at 393 K. Before use, the DMSO was dehydrated with 0.4 nm molecular sieves and distilled at reduced pressure to remove impurities.

A simple three electrode cell was used in study. The working electrode was Cu wire (purity 99.9%, area 0.05 cm^2). A Pt foil was used as 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. All potentials were measured with respect to SCE. All experiments were carried out under argon atmosphere at room temperature.

HD-1A low-superlow frequence function generator, HDV-7C transistor potentiostat and 3086 X-Y recorder were used for electrochemical measurements. The product was analyzed by EDAX method to determine the content of Gd in deposits and by X-ray diffraction to determine

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the phase composition of electrolytic product. The morphology of the surface of the plated film was observed by scanning electron microscopy. The $Gd(ClO_4)_3$ and $CoCl_2$ concentrations in solution were measured by EDTA titration.

3 RESULTS AND DISCUSSION

Electrodeposition of alloy film depends upon the deposition potentials, temperature and composition of the electrolyte solution. The deposition potentials of Gd-Co alloy were estimated by studying the cyclic voltammogram curve.

Fig.1 is the cyclic voltammogram of Cu electrode in 0.02 mol·L^{-1} $Gd(ClO_4)_3$—0.02 mol·L^{-1} $CoCl_2$—DMSO at 298 K. Two cathodic waves appeared at -1.20 and -2.40 V. According to the previous study, the peak at -2.40 V correspond to the reduction of Gd^{3+}, namely $Gd^{3+} + 3e \rightarrow Gd$.

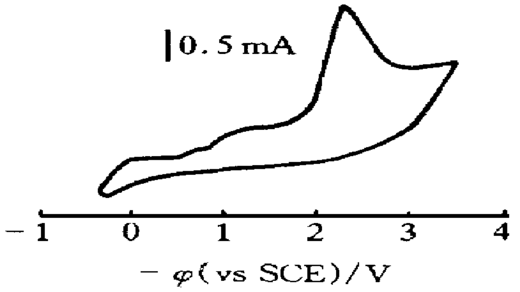

Fig.1 Cyclic voltammogram of $Gd(ClO_4)_3$—$CoCl_2$—DMSO (v= 50 mV·s^{-1}; T = 298 K)

The correlation between the deposition potential and the content of gadolinium in the electrodeposited film is shown in Fig.2. The content ratio of gadolinium and cobalt (1∶3; 1∶1; 3∶1) in solution is used as a parameter. The gadolinium content in the film increases with negative-going deposition potential and increasing gadolinium concentration in the solution. The effect of concentration ratio of gadolinium to cobalt in solution was weak as seen from Fig.2. However, the quality of the electrodeposition becomes poorer at higher polarizations.

Fig.2 Relation of deposition potential vs gadolinium content in film at 298 K

Next, the influence of adding a complexing agent (ethylene diamine) to 0.02 mol·L^{-1} $Gd(ClO_4)_3$—0.02 mol·L^{-1} $CoCl_2$—DMSO at 298 K was studied. The influence of the complexing agent on the deposit potential is shown in Fig.3. As can be seen clearly from Fig.3, the addition of the ethylene diamine leads the depositing potential of Co^{2+} shift to negative direction.

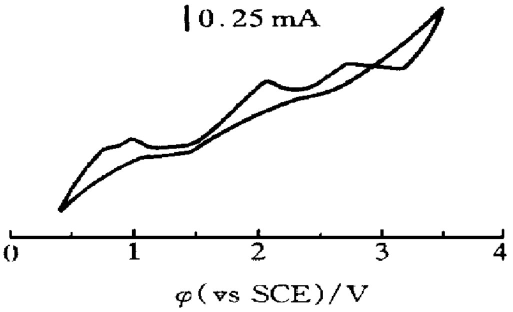

Fig.3 Cyclic voltammogram of $Gd(ClO_4)_3$—$CoCl_2$—EN—DMSO (v= 50 mV·s^{-1}; T = 298 K)

For the concentration ratios of gadolinium to cobalt in the solution mentioned above it caused increases in the quantity of gadolinium in the film (Fig.4). Compared with the system of $Gd(ClO_4)_3$—$CoCl_2$—DMSO, adding ethylene diamine can clearly improve the morphology of the deposited film and gadolinium content in the films. However, the films obtained at high concentrations were black powder and of poor quantity.

Fig.4 Relation of deposition potential vs gadolinium content in film
(In solution with ethylene diamine; $T = 298$ K)

Fig.5 is the SEM photograph for a film deposited for 1.5 h, which was 7 μm thick with a smooth surface. The film thickness for photomagnetic memory materials of Gd-Co alloy films is about 0.1 μm, which can be obtained within a short time, as shown in Fig.5.

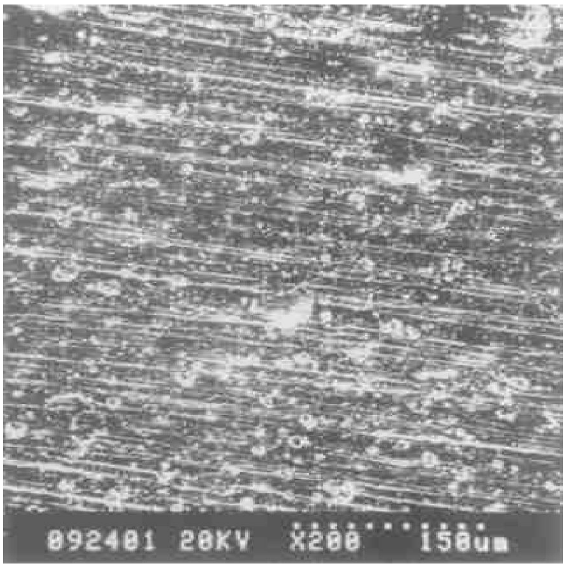

Fig.5 SEM morphology of Gd-Co film

The surface color and the shape of the deposited film depended on the deposition potentials and the Gd content in the film. If the deposition potential is high to - 2.70 V, the obtained film surface is smooth and sliver gray in color. The film obtained at potential low to - 2.70 V is crevassed on the surface. The best morphology of the deposition was found in the potential region of - 2.30 ~ - 2.70 V.

4 CONCLUSION

The Gd-Co alloy films can be deposited from uncomplexed and ethylene diamine complexed solution on copper substrate. It has found that the 0.1 mol·L^{-1} Gd(ClO_4)$_3$ —0.1 mol·L^{-1} $CoCl_2$ —0.2 mol·L^{-1} EN—DMSO system is suitable for Gd-Co alloy deposition at potentials within - 2.30 V to - 2.70 V.

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