Electrodeposition of basic compound of dysprosium from aqueous baths

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Electrodeposition of basic compound of dysprosium from aqueous acidic baths has been carried out onto stainless steel, copper, brass, titanium and Indium-Tin Oxide (ITO) coated glass substrates. Oxalic acid is found to be a suitable complexing agent and the deposition potentials are found to be dependent on the nature of the substrate and complexing agent. Yellowish-gray coloured films of the thickness up to 0.25 microns have been deposited. Some of the preparative parameters are optimized.

Electrodeposition of rare earth based compounds have been reported recently for the preparation of materials in thin film form of High Tc superconductors\(^1\). Slezak and Wieckowski have deposited YBaCu compound in stoichiometric form \(1:2:3\) from aqueous medium and reported the superconductivity of these materials\(^2\). Previously, amalgams of lanthanum, neodymium, cerium and samarium have been prepared from acidic solutions using electrolytic technique\(^3\). The major problem associated with aqueous deposition of rare earths is their high reactivity with water and, therefore, aqueous deposition of rare earths results into the electrodeposition of basic compounds of these metals.

In the present investigation, deposition of basic compound of dysprosium from aqueous baths has been reported. Some of the preparative parameters have also been optimized.

**Experimental procedure**—The baths prepared from reagent grade chemicals and double distilled water contained 50 mM dysprosium oxide and different complexing agents of 50 mM concentrations. The deposition was carried out in acidic medium \((pH = 2.74)\).

The electrodeposition was carried out under potentiostatic mode. The cathode substrates (1-2 cm\(^2\)) were stainless steel, copper, brass, titanium and Indium-Tin Oxide (ITO) coated glass (sheet resistance, 10-20 ohm/cm\(^2\)) and anode was a graphite plate. The substrates were smooth and mirror polished and the depositions were carried out under unstirred condition.

The polarization curves for electrodeposition of dysprosium-hydroxide were studied with Potentiostat Model-362 (EG and G). The potentials were measured with respect to SCE. Microscopic studies of the films were carried out with an optical microscope. The weight of film was determined by using weight difference methods. The crystallographic studies were carried out using Philips XRD Unit, PW-1710.

**Results and discussion**—In general, the reduction potentials of rare earths are between \(-2\) to \(-3.0\) V (NHE) and hydrogen evolution starts well before. This results into the formation of basic compound of rare earths. For example, for dysprosium, where reduction potential is \(-2.35\) V (NHE), following reaction takes place at cathode

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \ldots \ (1)
\]

Formation of \(OH^-\) ions will result into changing local pH value near substrate and Dy(OH)\(_3\) will be formed as,

\[
\text{Dy}^{3+} + 3\text{OH}^- \rightarrow \text{Dy(OH)}_3 \quad \ldots \ (2)
\]

This results into the deposition of basic compound of dysprosium alongwith dysprosium, which takes place below its standard reduction potential.

**Optimization of preparative parameters**

**Effect of substrates on electrodeposition potential**—In order to study the effect of substrates on electrodeposition potential, polarization studies were carried out. Fig. 1 shows the polarization curves for 50 mM Dy\(_2\)O\(_3\) solution onto different substrates. It is observed that initially the current remains constant and started rising abruptly in the potential range of \(-0.5\) to \(-1.5\) V (SCE) depending upon the nature of substrates. This abrupt rise in current was followed by hydrogen evolution on the substrate. Table 1 shows the electrodeposition potentials for different substrates. In all cases, hydrogen evolution was observed above the optimum potentials during deposition resulting into nonhomogeneous film formation.

**Effect of complexing agent on electrodeposition potential**—In order to study the effect of complexing agent, EDTA citric acid, oxalic acid, and tartaric acid were used. It was observed that the deposition potential shifted towards the positive
side with respect to the uncomplexed bath. Microscopics studies of deposits showed that homogeneous films are obtained with oxalic acid. Therefore, further studies were carried out by using oxalic acid as a complexing agent.

**Variation of thickness with time**—Using above bath, films were deposited onto stainless steel substrate for different time periods at 25°C. Fig. 2 shows the variation of film thickness with time. For the deposition period of 45 min, the rate of deposition is linear and films of the thickness of 0.25 microns could be deposited.

**Effect of bath temperature**—The effect of bath temperature in the range of 25-80°C on the deposition was studied. The bath consisted of 50 mM Dy$_2$O$_3$-50 mM oxalic acid and depositions were carried out onto stainless steel substrates. In the temperature range of 25-55°C, thin, adhesive, homogeneous and grayish films were deposited. Further rise in temperature results into less adher-
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Fig. 3 — Variation of current density with time for stainless steel substrate at different bath temperatures. Bath consisted of 50 mM Dy₂O₃-50 mM oxalic acid.

Summary shows the effect of bath temperature on the variation of current density with time. Upto the bath temperature of 55°C, the deposition current increased for first ten minutes and then decreased with time. This may be attributed to the formation of resistive film on the substrate.

The variation of film thickness with bath temperature from 50 mM Dy₂O₃ to 50 mM oxalic acid bath for the deposition period of 30 min is shown in Fig. 4. It is seen that the film thickness increased with increasing bath temperature up to 55°C and then decreased for further rise in bath temperature. The decrease in thickness after 55°C was due to matte nature of deposition, which was porous and easily removable from substrate. The films have been examined with XRD and the deposited compound is found to be Dy(OH)₃.

Conclusions — The basic compound of dysprosium, Dy(OH)₃ has been deposited onto different substrates from aqueous oxalate bath. The films deposited between temperature range of 25 to 55°C were yellowish-gray, uniform and adherent.

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References