

Electrodeposition of Rare Earth-Transition Metal Alloys from an Aqueous Electrolyte

Rohit Mishra and E. J. Podlaha
Department of Chemical Engineering
Louisiana State University
Baton Rouge, Louisiana 70803, USA

Rare earth-transition metal alloys offer a wide variety of applications in magnetic, magneto-optical and superconducting devices. For example, Gd-Co alloy exhibits perpendicular magnetic anisotropy for magneto-optical recording media [1]. Alloys of Tb-Fe and Tb-Fe-Dy are known to exhibit giant magnetostriction, such as Terfenol D ($Tb_xDy_{1-x}Fe_y$ ($0.27 < x < 0.30$, $1.9 < y < 2$)) used in transducers [2]. These materials can be fabricated by vacuum deposition techniques, although with inherent limitations such as high capital cost and difficulty to deposit conformal high aspect ratio structures such as nanowires and micro-features. Electrodeposition is an alternative method for rare-earth, high aspect ratio deposition, albeit with another set of challenges. Most limiting is the very negative reduction potentials of the rare-earth elements. Literature reports have focused on organic electrolytes [1,3] or a judicious choice of complexing agents for deposition from aqueous media [4, 5].

In this work, we have explored the influence of pH and applied potential of electrodepositing Tb-Co alloys from an aqueous electrolyte. The results suggest that the deposition mechanism of the cobalt and terbium are coupled. In addition, disparate compositions can be obtained from a single electrolyte of interest for designing compositionally modulated alloys.

Experimental

The cell contained a platinum mesh counter electrode, calomel reference and copper foil as the working electrode. Table 1 presents the composition of the electrolyte used for this experiment. Equimolar concentrations of cobalt and terbium were used with an excess amount of boric acid. The pH of the electrolyte was varied between 1.2 and 3. Sulfuric acid was treated as a variable and the pH was concomitantly altered.

Ingredients	Composition
CoSO ₄ ·7H ₂ O	0.1/0.2 M
TbCl ₂ ·6H ₂ O	0.1/0.2 M
Boric Acid	0.25/0.5 M
PH	1.2-3

Table 1. Composition of the electrolyte

Results and Discussion

Linear sweep voltammetry of the system on a copper electrode shows two distinct regions: one representative of only cobalt deposition and the other of the cobalt-terbium deposition (Fig 1). Cobalt deposition commences at $-0.6V$ vs. SCE and terbium deposition at about $-1.7V$ vs. SCE. Reducing the Co^{2+} content in the electrolyte shifted the deposition potential of terbium to a more positive value. When no cobalt was present in the bath, terbium deposition started at $-1V$ vs. SCE. In all cases terbium deposition is considerably more noble than expected from its reversible potential ($-2.31V$ vs. NHE). Potentiostatic deposition was also carried out. The measured steady state currents are also shown in Fig 1 and are in agreement with the voltammogram.

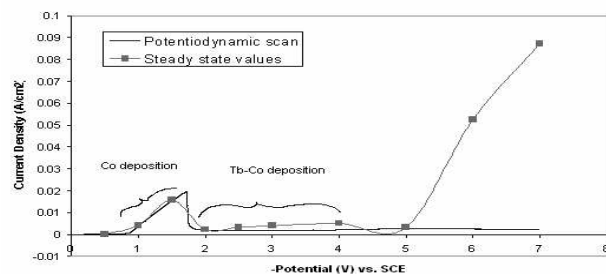


Fig 1. Polarization curve of the system at 2 mV/s

The sharp fall of total current density as shown in Fig 1 occurs at the point where Tb starts depositing, suggesting that Tb deposition inhibits the cobalt partial current density.

The composition of Tb in the alloy was found to depend on the pH of the bath and the applied potential, Fig 2. The natural pH of the electrolyte was 3.0. At higher pH the electrolyte was unstable. However, reducing the pH below 1.4 caused a sharp fall in the Tb content in the alloy and at pH 1.2, no Tb could be deposited. Tb rich alloys can be deposited at large negative potentials, and pure Co at more noble potentials, rendering it possible to deposit compositionally modulated multilayers from this electrolyte. Current efficiency depended upon the deposit composition: cobalt was over 80 % and the cobalt-terbium alloy was between 5-25 %.

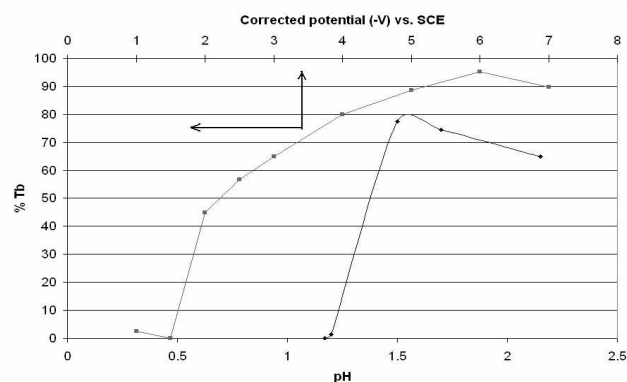


Fig 2. Effect of pH (bottom) at $-3V$ vs. SCE, and potential (top) at pH 2.15, on the terbium content in the alloy.

Conclusion

Tb-Co alloys were deposited from a boric acid electrolyte. Cobalt partial current inhibition has been observed by the deposition of terbium. Concurrently, there is also an apparent inhibition of terbium reduction by cobalt. The pH of the bath has been found to influence the composition and there exists a narrow window of pH range over which the terbium can be deposited as the alloy. The applied potential also affected the composition of the alloy. Tb rich alloys can be deposited at large negative potentials and pure Co at more noble potentials.

References

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