

## Electrochemical Formation of Tb-Fe Alloys in Molten Chlorides

Toshiyuki NOHIRA, Tetsuro KUBOTA  
and Yasuhiko ITO

Department of Fundamental Energy Science,  
Graduate School of Energy Science,  
Kyoto University  
Sakyo-ku, Kyoto 606-8501, Japan  
Email: nohira@energy.kyoto-u.ac.jp

### Introduction

Rare earth-transition metal alloys are attracting much attention for their functional properties, e.g., excellent magnetic properties (large coercive force, high maximum energy product and giant magnetostriction), magneto-optical properties, hydrogen absorbing or permeating properties, and catalytic properties. In this field, there has been a continuous request to prepare the alloy films having precisely controlled composition, thickness, metallographic structure, etc. In addition, the low production cost and the ease of scale-up are required for a practical application.

From this background, the authors have been studying the molten salt electrochemical process as a new formation method of the rare earth-transition metal alloy films [1-4].

Among the many functional alloys, the authors focused on Dy- and Tb-Fe alloys, especially DyFe<sub>2</sub>, TbFe<sub>2</sub> and (Tb-Dy)Fe<sub>2</sub>, due to their giant magnetostriction. The authors have already reported the electrochemical formation of Dy-Ni [3] and Dy-Fe [4] alloys in a molten LiCl-KCl-DyCl<sub>3</sub> system at 700-773 K. In the present work, the electrochemical formation of Tb-Fe alloys was investigated in a molten LiCl-KCl-TbCl<sub>3</sub> system at 723 K and in a molten NaCl-KCl-TbCl<sub>3</sub> system at 1073 K. The alloy formation was also conducted using a new type of substrate, i.e., an Fe film prepared on Cu substrate by electroplating in aqueous solution.

### Experimental

The LiCl-KCl or NaCl-KCl eutectic (LiCl:KCl = 58.5:41.5 mol% and NaCl:KCl = 50.6:49.4 mol%; reagent grade, Wako Pure Chemical Co., Ltd.) was contained in a high purity alumina crucible, and were kept under vacuum for more than 72 hours at elevated temperatures (473-573 K for LiCl-KCl and 773 K for NaCl-KCl. Anhydrous TbCl<sub>3</sub> (99.9 %, Kojundo Chemical Lab Co., Ltd.) was added directly to the melts.

The working electrodes were a Mo plate (20 x □ x 0.20 mm, 99.9 %, The Nilaco Corp.) and an Fe plate (20 x 5 x 0.2 mm, 99.95 %, The Nilaco Corp.). The reference electrode was an Ag wire immersed in LiCl-KCl or NaCl-KCl eutectic containing 1 mol% AgCl in a Pyrex tube with thin film bottom (LiCl-KCl) or in a mullite tube (NaCl-KCl). The potential of this reference electrode was calibrated with the dynamic Li<sup>+</sup>/Li (LiCl-KCl) or M<sup>+</sup>/M, where M = alkali metal, (NaCl-KCl) electrodes, which was prepared by electrodepositing alkali metals on a Ni or a Mo wire. The counter electrode was a glassy carbon rod (50 x φ 5 mm, Tokai Carbon Co., Ltd.)

The samples were analyzed by XRD, SEM, EDX and optical microscope.

### Results and discussion

Figure 1 shows linear sweep voltammograms measured for Mo and Fe electrodes in a molten NaCl-KCl-TbCl<sub>3</sub> (1.0 mol%) system at 1073 K. Before the sweeps, both electrodes were kept at 0.20 V (vs. M<sup>+</sup>/M), at which Tb-Fe alloys are expected to be formed, for 60 seconds. Two distinct anodic peaks were observed only for an Fe electrode. They are considered as the anodic dissolutions of Tb from the previously formed Tb-Fe alloy. Based on this result, potentiostatic electrolysis was conducted for an Fe electrode at 0.10 V for 1 h to prepare the alloy sample. The formation of TbFe<sub>2</sub> was confirmed by XRD analysis. Figure 2 shows a cross-sectional SEM image and the results of EDX line-analysis for the sample. It is found that

TbFe<sub>2</sub> layer is uniform and adherent having about 12 μm thickness.

Similar investigations were also conducted in a molten LiCl-KCl-TbCl<sub>3</sub> (0.5 mol%) system at 723 K. A cyclic voltammogram for an Fe electrode showed several cathodic peaks and the corresponding anodic peaks, indicating the formation of several different Tb-Fe alloy phases. However, the alloy formation has not been confirmed by XRD or EDX, so far. This is possibly due to the bad adhesiveness and low growth rate of the alloy layer.

### References

1. G.Xie, K.Ema and Y.Ito, *J. Appl. Electrochem.*, **23**, 753 (1993).
2. Y.Ito and T.Nohira, *Electrochim. Acta*, **45**, 2611 (2000).
3. H.Konishi, T.Nohira and Y.Ito, *J. Electrochem. Soc.*, **148**, C506 (2001).
4. H.Konishi, T.Nohira and Y.Ito, *Electrochim. Acta*, **48**, 563 (2003).

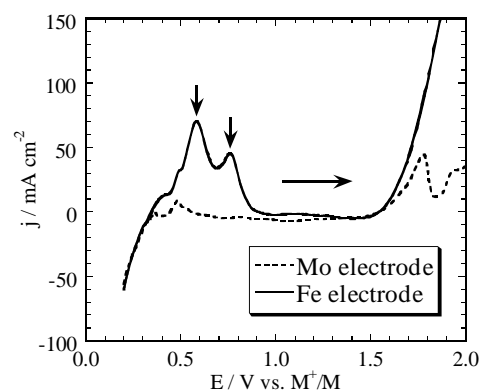


Fig. 1 Linear sweep voltammograms at Mo and Fe electrodes in a molten NaCl-KCl-TbCl<sub>3</sub> (1.0 mol%) system at 1073 K. Scan rate: 0.1 V s<sup>-1</sup>.

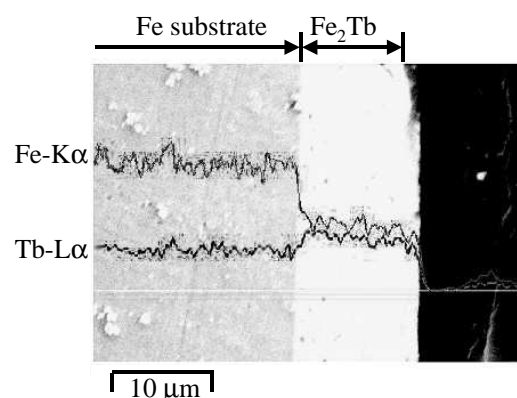


Fig. 2 Cross-sectional SEM image of the sample obtained by electrolysis at 0.10 V (vs. M<sup>+</sup>/M) for 1 h in a molten NaCl-KCl-TbCl<sub>3</sub> (1.0 mol%) system at 1073 K.