ABSTRACT

As a new formation method of giant magnetostrictive materials, electrochemical formation of Tb-Fe alloys were investigated in molten chlorides. In a molten LiCl-KCl-TbCl3 system at 723 K, electrode behaviors of Fe suggested the formation of Tb-Fe alloys. However, formation of the alloys could not be confirmed by XRD, SEM and EDX. In a molten NaCl-KCl-TbCl3 (1.0 mol%) system at 1073 K, formation of TbFe2 was confirmed by XRD, SEM and EDX. A uniform and adhesive TbFe2 layer having about 12 µm thickness was formed on a Fe substrate by potentiostatic electrolysis at 0.10 V (vs. M+/M) for 1 hour. Formation of TbFe2 layer on a non-ferromagnetic Cu substrate was also achieved by using a Fe-electroplated Cu electrode.

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 their practical applications.

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]. This method has several advantages as follows: (1) There is a possibility to control the composition, thickness and metallographic structure of alloys by electrolysis conditions, e.g., an electrode potential, a current density and a temperature, (2) There are little limitations on size and shape of the substrate. That is, small- to large-sized and/or complex-shaped alloy films can be prepared, and (3) The scale-up is easy owing to the simplicity of the apparatus and the operation under an atmospheric pressure.

Among the many functional alloys, the authors focused on Dy- and Tb-Fe alloys, especially DyFe2, TbFe2 and (Tb-Dy)Fe2, 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-DyCl3 system at 700-773 K. In the present work, the electrochemical formations of Tb-Fe alloys were investigated in a molten LiCl-KCl-TbCl3 system at 723
K and in a molten NaCl-KCl-TbCl₃ system at 1073 K. The alloy formation was also conducted using a new type of substrate, i.e., an Fe-electroplated Cu plate which was prepared in aqueous solution.

**EXPERIMENTAL**

LiCl (99.0 %, Wako Pure Chemical Co., Ltd.) and KCl (99.5 %, Wako Pure Chemical Co., Ltd.) were mixed to have an eutectic composition (LiCl:KCl = 58.5:41.5 mol%). This was contained in a high purity alumina crucible and kept under vacuum for more than 72 hours at 473 K for drying. NaCl (99.5 %, Wako Pure Chemical Co., Ltd.) and KCl (99.5 %, Wako Pure Chemical Co., Ltd.) were also mixed to have an eutectic composition (NaCl:KCl = 50.6:49.4 mol%), and introduced in a high purity alumina crucible. This was kept under vacuum for more than 72 hours at 773 for drying. Anhydrous TbCl₃ (99.9 %, Kojundo Chemical Lab Co., Ltd.) was added directly to the melts.

The working electrodes were a Mo plate (20 x 5 x 0.20 mm, 99.9 %, The Nilaco Corp.), an Fe plate (20 x 5 x 0.2 mm, 99.95 %, The Nilaco Corp.) and an Fe-electroplated Cu plate. The Fe-electroplated Cu plate was prepared by a galvanostatic electrolysis using a Cu plate (20 x 5 x 0.20 mm, 99.99 %, The Nilaco Corp.) cathode at 100 mA cm⁻² for 15 minutes in an aqueous electrolyte at 298 K. The electrolyte used for the Fe plating was 0.90 mol l⁻¹ FeSO₄·7H₂SO₄. The pH of the electrolyte was adjusted to 1.5 with H₂SO₄. 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). In the case of LiCl-KCl, potential of the reference electrode was calibrated with the dynamic Li⁺/Li electrode which was prepared by electrodepositing Li metal on a Mo wire. In the case of NaCl-KCl, potential of the reference electrode was calibrated with the dynamic M⁺/M, where M = alkali metal, electrode which was prepared by electrodepositing alkali metals on a Mo wire. The counter electrode was a glassy carbon rod (50 x φ 5 mm, Tokai Carbon Co., Ltd.).

An automatic electrochemical measurement system (HZ-3000, Hokuto Denko Corp.) was used for cyclic voltammetry, open-circuit potentiometry and potentiostatic electrolysis. The alloy samples were prepared by potentiostatic electrolysis, and rinsed in distilled water. They were then analyzed by XRD (Cu Ka, 40 kV, 40 mA, Multiflex, Rigaku Corp.) and SEM (S-2600H, Hitachi), EDX (E-MAX ENERGY EX-200, Horiba Corp.) and optical microscope (VHX-100, KEYENCE Corp.).

**RESULTS AND DISCUSSION**

**Phase diagram of Tb-Fe system**

As general information on the Tb-Fe system, the reported phase diagram [5] is shown in Fig. 1. The diagram shows the presence of four intermetallic compounds (TbFe₂, TbFe₃, Tb₆Fe₂₃, and Tb₂Fe₁₇). Therefore, there is the possibility of formations of these intermetallic compounds by the molten salt electrochemical process.
A LiCl-KCl-TbCl₃ System

Cyclic voltammetry Before investigating the Tb-Fe alloy formation, the electrochemical behavior of Tb (III) ion was investigated using a Mo electrode because Mo has been reported to form no alloy with Tb [5]. Figure 2 shows the obtained cyclic voltammograms before and after addition of 0.50 mol% TbCl₃ at 723 K. Before addition of TbCl₃, only the currents corresponding to deposition and dissolution of Li metal are observed. After addition of TbCl₃, new currents attributed to deposition and dissolution of Tb metal are observed around 0.5 V (vs. Li⁺/Li).

Figure 3 shows a typical cyclic voltammogram for a Fe electrode after addition of 0.50 mol% TbCl₃. For comparison, a voltammogram for a Mo electrode was shown in a dotted curve. For the Fe electrode, several cathodic current peaks are observed in the potential region of 0.5-0.7 V. Since this potential region is more positive than the Tb metal deposition, the cathodic currents are thought to be caused by the formation of Tb-Fe alloys. When the potential scanning direction is reversed at 0.40 V, the sharp anodic current peaks rise up from 0.50 V, 0.62 V, 0.71 V, and 0.90 V. These anodic current peaks except for 0.50 V are suggested to correspond to Tb dissolution from different Tb-Fe alloy phases.

Open-circuit potentiometry Open-circuit potentiometry was conducted to further investigate the formation of Tb-Fe alloys. Figure 4 shows the obtained potentiogram for a Fe electrode after depositing Tb at 0.40 V for 2 minutes. Four potential plateaus are observed at 0.49 V, 0.60 V, 0.70 V and 0.88 V, respectively. These potential plateaus are considered to correspond to different coexisting Tb-Fe alloy phases. Here, these potential values agree with the rising potentials of anodic current peaks in Fig. 3.

Sample analysis Based on the above results, a sample was prepared by potentiostatic electrolysis of a Fe electrode at 0.51 V for 4 hours. From the result of EDX, concentrations of elements at the surface were found to be 22 at% Tb, 48 at% Fe, 15 at% O and 15 at% Cl. However, the alloy formation was not confirmed by XRD. It is considered that a thin Tb-Fe alloy layer was formed but it was almost oxidized by washing in water.

A NaCl-KCl-TbCl₃ System

Since the growth rate of Tb-Fe alloy in a molten LiCl-KCl-TbCl₃ system at 723 K was thought to be very slow, a molten NaCl-KCl-TbCl₃ system was used at 1073 K to enhance the alloy formation rate and obtain thicker alloy films.

Linear sweep voltammetry Figure 5 shows linear anodic sweep voltammograms measured for Mo and Fe electrodes in a molten NaCl-KCl-TbCl₃ (1.0 mol%) system at 1073 K. Before the sweeps, both electrodes were kept at 0.20 V (vs. M'/M), at which Tb-Fe alloys are expected to be formed, for 60 seconds. Two distinct anodic peaks were observed only for a Fe electrode. They are considered as the anodic dissolutions of Tb from the previously formed Tb-Fe alloy.
Formation of Tb-Fe alloy on Fe substrate  Based on the above result, potentiostatic electrolysis was conducted for an Fe electrode at 0.10 V for 1 h to prepare an alloy sample. As shown in Fig. 6, the formation of TbFe$_2$ was confirmed by XRD analysis. Figure 7 shows a cross-sectional SEM image and the results of EDX line-analysis for the sample. It is found that the TbFe$_2$ layer is uniform and adhesive having about 12 μm thickness.

Formation of Tb-Fe alloy on Fe-electroplated Cu substrate  Considering practical applications, TbFe$_2$ films are required to be formed on a non-ferromagnetic substrate. Thus, we prepared a Fe-electroplated Cu substrate by electroplating Fe film of about 15 μm on a Cu substrate in an aqueous electrolyte. Potentiostatic electrolysis was conducted for the Fe-plated Cu electrode at 0.10 V for 1 h. As shown in Fig. 8, the formation of TbFe$_2$ was confirmed by XRD analysis. Figure 9 shows a cross-sectional optical microscope image. As the same for the Fe substrate, the TbFe$_2$ layer is uniform and adhesive having about 13 μm thickness. Although a Fe layer of about 5μm remained unchanged in this sample, it is presumed that whole Fe layer becomes TbFe$_2$ when the electrolysis time is prolonged.

CONCLUSION

In a molten LiCl-KCl-TbCl$_3$ (0.50 mol%) system at 723 K, electrode behaviors of Fe suggested the formation of Tb-Fe alloys. However, formation of the alloys could not be confirmed by XRD, SEM and EDX, which is explained by the slow formation rate and the oxidation during the washing treatment in water. In a molten NaCl-KCl-TbCl$_3$ (1.0 mol%) system at 1073 K, formation of TbFe$_2$ was confirmed by XRD, SEM and EDX. A uniform and adhesive TbFe$_2$ layer having about 12 μm thickness was formed on an Fe substrate by potentiostatic electrolysis at 0.10 V (vs. MFe/M) for 1 hour. Formation of TbFe$_2$ layer on a non-ferromagnetic Cu substrate was also achieved by using a Fe-electroplated Cu electrode.

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Figure 1. Phase diagram of Dy-Fe system [5].
Figure 2. Cyclic voltammograms at a Mo electrode in a LiCl-KCl eutectic melt and a molten LiCl-KCl-TbCl₃ (0.50 mol%) system at 723 K. Scan rate: 0.01 V s⁻¹.

Figure 3. Cyclic voltammograms at Mo and Fe electrodes in a molten LiCl-KCl-TbCl₃ (0.50 mol%) system at 723 K. Scan rate: 0.01 V s⁻¹.
Figure 4. Open-circuit potentiogram at an Fe electrode after Tb deposition at 0.40 V for 2 minutes in a molten LiCl-KCl-TbCl₃ (0.50 mol%) system at 723 K.

Figure 5. Linear sweep voltammograms at Mo and Fe electrodes in a molten NaCl-KCl-TbCl₃ (1.0 mol%) system at 1073 K. Scan rate: 0.10 V s⁻¹.
Figure 6. XRD pattern of the sample obtained by electrolysis at 0.10 V (vs. M/HM) for 1 h in a molten NaCl-KCl-TbCl$_3$ (1.0 mol%) system at 1073 K. Substrate: An Fe plate.

Figure 7. Cross-sectional SEM image of the sample obtained by electrolysis at 0.10 V (vs. M/HM) for 1 h in a molten NaCl-KCl-TbCl$_3$ (1.0 mol%) system at 1073 K.
$^{7}$/$^{8}$M) for 1 h in a molten NaCl-KCl-TbCl$_3$ (1.0 mol%) system at 1073 K. Substrate: An Fe-electroplated Cu plate.

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