Electrochemical formation of Dy alloy films in a molten LiCl-KCl-DyCl₃ system

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Abstract. As to the electrochemical formation of Dy-Ni alloy films in a molten LiCl-KCl-DyCl₃ system at 700 K, the growth of DyNi₂ film and behavior of anodic dissolution of Dy from the formed DyNi₂ film were investigated. The DyNi₂ films were formed by potentiostatic electrolysis at 0.55, 0.62 and 0.70 V with Ni electrodes. The growth rates of DyNi₂ films are higher at less noble potential, i.e., 0.47 µm min⁻¹ at 0.55 V, 0.32 µm min⁻¹ at 0.62 V and 0.14 µm min⁻¹ at 0.70 V. From RBS analysis, it was suggested that the Dy-Ni alloy film was formed for 10 or 30 s during electrodepositing Dy at 0.30 V with a Ni electrode. Moreover, the growth rate of Dy-Ni alloy film was faster than that of Dy-Fe alloy film. Anodic electrolysis of the formed DyNi₂ film with thickness of 15 µm was conducted at 0.90 V, 1.30 V and 1.90 V, respectively. The formed DyNi₂ were transformed to other phases, i.e., DyNi₃, DyNi₅ and Ni, by selective anodic dissolution of Dy. The transformed Ni film was about 10 µm in thickness and had a porous structure with a pore diameter of 1~2 µm.

1. Introduction
Rare earth (RE) - transition metal (TM) alloy films attract great interest of many researchers for functional properties, e.g., excellent magnetic, hydrogen absorbing / permeable and others. Generally, these RE-TM alloy films are manufactured by PVD, CVD, ion implantation and ion plating. However, in near future, novel methods to produce more functionalized RE-TM alloy films will be required. Among novel methods, the authors focused on the molten salt electrochemical process. The molten salt electrochemical process has been studied by the authors [1, 2, 3]. And the authors reported the noticeable phenomenon in the RE-TM alloy films [1]. In the case of DyNi₂ formation, the alloy film of 60 µm thickness was formed merely in 2 hours at 700 K. The growth rate of the DyNi₂ film, 60 µm in 2 hours at 700 K, was extremely high, when considering conventional solid phase diffusion at the temperature lower than the half of melting point T(DyNi₂) = 1446 K [4]. The growth rate was found to be extremely fast and strongly affected by electrochemical parameters such as potential and current density. The phenomenon was termed “electrochemical implantation”, since the phenomenon was difficult to be explained by ordinary concepts of electrodeposition followed by solid phase diffusion. Furthermore, they reported that the anodic polarization of the formed DyNi₂ resulted in the rapid
dissolution of Dy to form other Dy-Ni phases. The obtained phase and morphology were dependent on applied potential. The phenomenon is regarded as “electrochemical displantation”.

From these backgrounds, in this study, regarding the electrochemical formation of Dy-Ni alloy films in a molten LiCl-KCl-DyCl₃ system at 700 K, the growth of DyNi₂ film and behavior of anodic dissolution of Dy from the formed DyNi₂ film were investigated.

2. Experimental

All chemicals were anhydrous reagent grade. The LiCl-KCl eutectic (LiCl : KCl = 58.5 : 41.5 mol%; Wako Pure Chemical Co., Ltd.) was introduced in a high purity alumina crucible (99.5 wt% Al₂O₃; SSA-S grade, NIKKATO Co., Ltd.), and kept under vacuum for more than 72 hours at 473 K to remove water. All experiments were performed in LiCl-KCl eutectic melts under dry argon atmosphere at 700 K. DyCl₃ (99.9 %, Kojundo Chemical Laboratory Co., Ltd.) of 0.50 mol% was added directly to the melts. To remove residual water and metal impurities, pre-electrolysis was conducted at an electrolysis voltage of 2.80 V with an Al plate cathode and glassy carbon anode. A chromel-alumel thermocouple was used for temperature measurement. The working electrodes were Mo (5 mm × φ 1 mm, 99.95 %, Nilaco Co., Ltd.) and Ni (5 mm × φ 1 mm, 99.99 %, Nilaco Co., Ltd.) wires for the investigation of electrochemical behavior in this system. For the formation of Dy-Ni alloy samples, rectangular shaped plates of Ni (10 mm × 5 mm × 0.2 mm, 99.7 %, Nilaco Co., Ltd.) were used as the working electrodes. The reference electrode was a silver wire immersed in LiCl-KCl containing 1 mol% of AgCl, placed in a Pyrex glass tube with thin bottom to maintain electrical contact with the melt. The potential of this reference electrode was calibrated with reference to that of a Li⁺ / Li electrode, which was prepared by electrodepositing Li metal on a Mo wire. All the potentials given hereafter are referred to Li⁺ / Li electrode potential on a Mo wire. The counter electrode was a glassy carbon rod (50 mm × φ 5 mm, Tokai Carbon Co., Ltd.) or an Al rod (50 mm × φ 5 mm, 99.9 %, Nilaco Co., Ltd.). A potentiostat / galvanostat (Solartron: SI1287) was used for cyclic voltammetry and open-circuit potentiometry. The Dy-Ni alloy samples were prepared by potentiostatic electrolysis using the same apparatus. After the electrolysis, the samples were rinsed with distilled water, and analyzed by XRD (Rigaku Denki Co., Ltd.: ultraX 18HB) with CuKα line at 50 kV and 300 mA. Cross-sections of these samples were also observed by SEM (Hitachi Co., Ltd.: S-2300). Moreover, these samples were analyzed by RBS (Rutherford backscattering spectrometry).

3. The growth of DyNi₂ film

It has been found that the equilibrium potential values of 0.762, 0.913, 1.181 and 1.344 V obtained from several independent open-circuit potential measurements at 700 K correspond to coexisting phase states of (DyNi₂+DyNi₃), (DyNi₃+Dy₂Ni₅), (Dy₂Ni₇+DyNi₃) and (DyNi₅+Ni), respectively [3]. Combining this result with the Dy(III)/Dy potential value, 0.47 V (vs. Li⁺/Li) [1], the DyNi₂ was found to be stable at least in the potential region of 0.55-0.75 V. The following experiment was conducted in this potential region. In order to investigate the dependence of applied potential on the DyNi₂ film growth, potentiostatic electrolysis were conducted at 0.55, 0.62 and 0.70 V with Ni electrodes at 700 K. The electrolysis times were changed from 0.5 to 5.0 h at all potentials. Since all potential values are within the stable potential region of DyNi₂, Dy metal does not deposit at these potentials. Figure 1 shows the obtained transient curve of measured cathodic current density at 0.55 V as an example. Although large cathodic current of 15 mA cm⁻² flowed at the beginning, the currents decreased to the constant value of about 8 mA cm⁻² in 1.0 h. Similar transient curves were observed in the cases, at 0.62 and 0.70 V, except the constant current value became smaller as the potential value increased. All samples obtained after electrolysis were identified as DyNi₂ by XRD analysis. The relationship between thickness of the formed DyNi₂ films and the electrolysis time at 0.55, 0.62 and 0.70 V is shown in figure 2. Almost linear relation is seen for all potentials. Moreover, the slopes, which mean growth rates, are higher at less noble potential, i.e., 0.47 µm min⁻¹ at 0.55 V, 0.32 µm min⁻¹ at 0.62 V and 0.14 µm min⁻¹ at 0.70 V.
Concerning the observed linear growth of DyNi₂ film, the following explanation can be proposed. According to the obtained transient curve in figure 1, as the measured current directly shows the film growth rate, the film growth at the initial period (within 15 min) seems to follow the parabolic rate law, but afterwards the growth changes to follow the linear rate law.

4. RBS analysis of Dy alloy films

The Dy alloy films obtained by potentiostatic electrolysis were analyzed by RBS. RBS is the powerful method in analyzing the composition and thickness of thin films. RBS with beam energy of 2.0 MeV incident He²⁺ was performed on a tandem type accelerator. Figure 3(a) shows the spectra for the samples prepared by electrodepositing Dy at 0.30 V with Ni electrodes. The counts for Dy at about 1.8 MeV increases with the electrolysis time, which means that Dy is electrodeposited. The rising shoulder at about 1.5 MeV indicates the existence of Ni. The increasing of counts from 1.5-1.8 MeV corresponds to the growth of Dy-Ni alloy film. From this result, it was suggested that the Dy-Ni alloy film was formed for 10 or 30 s. On the other hand, the spectra for the samples obtained by electrodepositing Dy at 0.30 V with Fe electrodes as the comparative samples are shown in figure 3(b). The counts for Dy also increase with the electrolysis time. However, the counts from 1.5-1.8 MeV with Fe electrodes are lower than those with Ni electrodes. This result indicated that the growth rate of Dy-Ni alloy film was faster than that of Dy-Fe alloy film.

5. Selective anodic dissolution of Dy from the DyNi₂ alloy films

Selective anodic dissolution of Dy from the formed DyNi₂ film was performed at 0.90, 1.30 and 1.90 V, respectively. The DyNi₂ film was prepared by potentiostatic electrolysis at 0.55 V for 20 min at 700
K. Thickness of the DyNi₂ film was found to be about 15 \( \mu \)m by cross-sectional SEM measurement (figure 4(a)). These potential values, 0.90, 1.30 and 1.90 V, were chosen as intermediate values between the adjoining plateaus. The original DyNi₂ was transformed to the Dy-poor phase (DyNi₃) at 0.90 V for 1 h. In figure 4(b) the thickness of the DyNi₃ film was about 10 \( \mu \)m. The alloy film had some cracks and pores, that were thought to be caused by the volume change during the selective anodic dissolution of Dy. The identified phase of sample obtained at 1.30 V for 3 h was DyNi₅. The thickness of the obtained film was found to be about 10 \( \mu \)m in figure 4(c). The obtained film contained more micropores than the DyNi₃ film. It was found that the alloy phase of the sample obtained at 1.90 V for 3 h was transformed to Ni. In figure 4(d), the transformed film was about 10 \( \mu \)m and had a porous structure with a pore diameter of 1~2 \( \mu \)m.

When quite noble potential step is applied to the starting DyNi₂ film, dissolution of Dy into the melts rapidly occurs and large anodic currents are observed. Therefore, the author considered that such rapid transformation process should be related to the feature of morphological change during anodic dissolution. Since Dy is considered to mainly diffuse through microscopic cracks and/or grain boundaries in the DyNi₂, its diffusion behavior is assumed to be strongly affected by the number of microscopic cracks and/or grain boundaries.

![Cross-sectional SEM images of the samples prepared by potentiostatic electrolysis with a Ni electrode at (a) 0.55 V for 20 min and by anodic dissolution of Dy with the formed DyNi₂ electrode at (b) 0.90 V, (c) 1.30 V and (d) 1.90 V.](image)

**Figure 4.**

6. Conclusions
Concerning the electrochemical formation of Dy-Ni alloy films in a molten LiCl-KCl-DyCl₃ system at 700 K, the growth of DyNi₂ film and behavior of anodic dissolution of Dy from the formed DyNi₂ film were investigated. The DyNi₂ films were formed by potentiostatic electrolysis at Ni electrodes at 0.55, 0.62 and 0.70 V. The growth rates were higher at less noble potential, i.e., 0.47 \( \mu \)m min⁻¹ at 0.55 V, 0.32 \( \mu \)m min⁻¹ at 0.62 V and 0.14 \( \mu \)m min⁻¹ at 0.70 V. It was suggested that the Dy-Ni alloy film was formed for 10 or 30 s during electrodepositing Dy at 0.30 V with the Ni electrode from RBS analysis. The formed DyNi₂ were transformed to other phases, i.e., DyNi₃, DyNi₅ and Ni, by selective anodic dissolution of Dy. The transformed Ni film was about 10 \( \mu \)m and had a porous structure with a pore diameter of 1~2 \( \mu \)m.

Acknowledgements
This study was supported by Priority Assistance for the Formation of Worldwide Renowned Centers of Research - The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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