POTENTIAL RESPONSE
DURING THE ALLOYING PROCESS
AFTER MOLTEN SALTS ELECTROLYSIS

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ABSTRACT
Lanthanum or magnesium was electrodeposited on a Ni substrate in molten chlorides and hydrogen absorption alloy films such as LaNi₅ and Mg₂Ni were formed through the alloying reaction between the deposits and the Ni substrate. The change of open-circuit potential of the Ni substrate was also measured during the alloying process after the electrolysis in the molten salts. It was found that the potential increased with time, and several potential plateau regions were observed until reaching the rest potential of the Ni substrate. The specimens were picked up at the various plateau potentials, cooled rapidly and subjected to the X-ray diffraction analysis, EPMA line analysis and SEM observation to identify the alloy phase formed at each potential during the alloy process. The equilibrium potentials corresponding to the hydrogen absorption alloys such as LaNi₅ and Mg₂Ni, the other intermetallic compounds and the Ni substrate were considered from these results.

INTRODUCTION
In order to obtain hydrogen absorption alloy films, sputtering and ion-plating methods have been investigated widely [1-3]. As an alternative method, authors have proposed the electrolysis process in molten salts. This method has the advantage that the hydrogen absorption alloy is formed as a film on the substrate in a single direct process from chloride sources, without using costly and active metals such as lanthanum or magnesium. Though many other previous works have mainly dealt with the processing of hydrogen absorption alloy from metallic resources and its evaluation, the alloying behavior was not investigated in detail from electrochemical method.

In our previous works concerning the electrodeposition of La or Mg ions on a Ni substrate in molten salts, the alloying reaction between the electrodeposits and the Ni substrate led to the formation of LaNi₅ or Mg₂Ni alloy film, respectively [4-6].
paper, the investigation of alloying behavior was conducted by measuring the open-circuit potential during the alloying process after the electrodeposition in molten salts for the La-Ni system and the Mg-Ni system.

**EXPERIMENTAL**

In the La-Ni system, an equi-molar mixture of KCl-NaCl containing 10 mol% LaCl₃ was used [5]. In the Mg-Ni system, the content of molten salts was a NaCl-KCl-CaCl₂ (25 - 5 - 70 mol%) mixture as a supporting electrolyte and additionally 10 mol% MgCl₂ with respect to the supporting electrolyte as a Mg-ion source [6]. The molten salts were held for more than 86.4 ks in the drying box at 373 K before setting in the furnace. The working electrode was a Ni sheet with 1.5×1.5 cm² square, 0.1 mm thickness and 99.7 mass% purity. The Ni sheet was polished and degreased before the electrolysis. The reference electrode was a silver wire immersed in NaCl-KCl (50-50 mol%) or NaCl-KCl-CaCl₂ (25-5-70 mol%) containing 10 mol% AgCl in a mullite tube for La or Mg electrodeposition, respectively. A graphite rod with the diameter of 6 mm was used as a counter electrode. The electrodes and the mixed salts were put into the chamber and held in vacuum at 393 K for 86.4 ks. Pre-electrolysis was carried out potentiostatically at -1.5 V in order to remove some impurities and moisture from the molten salts using another Ni working electrode. Lanthanum and magnesium were electrodeposited galvanostatically onto the Ni substrate under argon atmosphere at the temperature range of 833-1073 K. The current density was 0.1 Acm⁻² and the electrolysis period was 0.2 ks. After the electrolysis, the specimen was kept in the molten salts and the open-circuit potential of working electrode in the molten salts was measured by potentiometer. When the open-circuit potential reached a constant value, the specimen was pulled out from the chamber and rapidly cooled by spraying He gas. After cooling, deposits on the specimen were subjected to XRD analysis and SEM observation to identify the alloy phase formed at the plateau potential. Furthermore, the composition and the thickness of the alloy phase were estimated by EPMA line analysis of the cross section of the specimen. Cyclic voltammograms were measured in the molten salt with 0.1 Vs⁻¹ at potential region between -0.1 V and -2.1 V for the La-Ni system and between 0 V and -1.8 V for the Mg-Ni system, respectively.

**RESULTS AND DISCUSSION**

**The La-Ni System**

The deposition and dissolution behavior of La were determined from the dynamic I-V profiles in La-Ni system. Figure 1 shows the cyclic voltammogram of a Ni electrode in NaCl-KCl-LaCl₃ molten salts at the time in stable state after several cycles, performed with a scan rate of 0.1 Vs⁻¹ at 1023 K. In the cathodic domain, lanthanum ions might be reduced and deposited onto the Ni electrode. The lanthanum deposits form alloys with the Ni substrate with time. The cathodic current increase at the potential of -1.6 V (R₁ in Fig. 1) seems to correspond to the La deposition. On the other hand, four anodic current peaks appear at the potentials of -1.82 V, -1.65 V, -1.42 V and -0.40 V, O₁ - O₄...
in Fig. 1, respectively. These anodic current peaks are considered to be the response of the dissolution of lanthanum and lanthanum in each La-Ni compound such as LaNi$_3$, La$_2$Ni$_7$ and LaNi$_5$ into the molten salts.

In order to clarify this alloying and/or dissolution behavior in the La-Ni system, the open-circuit potential change was measured after the electrolysis. Figure 2 shows the potential change with time after the electrolysis for 200 s with 0.1 A cm$^{-2}$ at 1023 K. It is clear that the potential shifts to positive values as the immersion time elapses. The potentials in a constant value, i.e. potential plateaus, are observed at -1.88 V, -1.76 V, -1.45 V, -0.50 V and -0.27 V until the potential reaches a value close to the rest potential, -0.25 V for the Ni substrate. These potential plateaus are defined as (a) ~ (e) in Fig. 2 and (f) shows a potential measured immediately after the electrolysis. In each potential points, the compounds on the surface of the electrode were identified by the XRD analysis, the EPMA line analysis, and SEM observation for the specimen cooled rapidly. The X-ray diffraction patterns and the results of the EPMA line analysis of the cross section and SEM observation of the surface of the specimen are shown in Fig. 3 and Fig. 4, respectively. In the XRD patterns, only Ni substrate is observed at the highest potential (a). At this potential, lanthanum element is not observed. At the potential (b), the peaks corresponding to LaNi$_5$ and Ni are detected in the XRD patterns. Lanthanum element is not detected on the surface of this specimen, however, La-Ni film is observed inside of the specimen with thickness of about 1 μm. Furthermore, several pinholes are observed on the surface of the specimen cooled rapidly at both potentials (a) and (b). Therefore, it is considered that these pinholes were formed as a result of lanthanum dissolution from the La-Ni compound film. Although detected peaks in the XRD analysis of the specimen cooled rapidly at the potential (c) is the same as (b), peaks corresponding to LaNi$_5$ increase and Ni peaks decrease. At the potential (d), (e) and (f), the co-existing two phases of LaNi$_5$/La$_2$Ni$_7$, La$_2$Ni$_7$/LaNi$_3$ and LaNi$_5$/LaOCl are mainly detected in the XRD analysis, respectively. Lanthanum-nickel compound films (about 10 μm thickness) were observed on the Ni substrate at these potentials (c) ~ (f), furthermore, lanthanum-rich phase was observed on the La-Ni compound film at only (f) in the EPMA line analysis. The peaks of LaOCl observed in XRD pattern at (f) means that metallic La is remaining just after the electrolysis, because LaOCl was formed when the La-deposited Ni was pulled out to the air to cool rapidly by spraying He gas. The surface morphology show the crystal-like structure at the potentials (c) ~ (f), and many pinholes in (a) and (b). Therefore, only electrodeposited La exists on the Ni substrate at the potential (f) at first, and then the alloying reaction between La and Ni progresses with immersion time. Each plateau potential of (c), (d) and (e) corresponds to the equilibrium potential of LaNi$_5$/Ni, La$_2$Ni$_7$/LaNi$_3$ and LaNi$_5$/La$_2$Ni$_7$, respectively. The drastic increase of the potential after about 6.0 ks corresponds to dissolution of La component from LaNi$_5$. And potential change from (b) to (a) is caused by the La dissolution from residual LaNi$_5$ gradually. The potentials at which anodic current peaks O$_1$, O$_2$, O$_3$ and O$_4$ were observed in Fig. 1 correspond to those potentials (e), (d), (c) and (b) mentioned above.
The composition of the surface analyzed by EDX is shown in Fig. 5. It is found that the nickel composition increases when the plateau potential is higher. From these results, we considered the relationship between the change of the potential, formation of alloy and dissolution of lanthanum from alloy as follows:

1. After the electrodeposition of lanthanum, two reactions, diffusion between La and the Ni substrate and dissolution of lanthanum take place simultaneously.
2. Until LaNi₅, the equilibrium intermetallic compound for Ni₅ is formed on the substrate diffusion reaction mainly occurs under the potential of -1.45 V.
3. Over -1.45 V, only the dissolution of lanthanum from alloy occurs and several pinholes are formed on the surface.

It is found that the potential, at which hydrogen absorption alloy LaNi₅ is stable, is between (c) -1.42 V and (d) -1.76 V in molten salts at 1023 K.

In order to examine the reason for La dissolution, we measured the potential change of LaNi₅ ingot in molten salts. Figure 6 (a) and (b) show the potential change of LaNi₅ ingot in NaCl-KCl with and without LaCl₃, respectively. The potential (a) is about 0.75 V higher than potential (b). After measuring the potential change for 4 ks, LaNi₅ ingots were subjected to XRD analysis. Nickel peaks are detected in XRD pattern of ingot in the potential (a). They were not detected before immersing in molten NaCl-KCl-LaCl₃. Potential (a) suggests the selective dissolution of La from LaNi₅. Potential (b), about -1.5 V, is the stable potential for LaNi₅ mentioned above and XRD peaks of this ingot did not change. It is considered that the dissolution of La is caused by a disproportionation through the contact of La in La-Ni alloy on the specimen and La ions in molten salts.

The Mg-Ni System

In the Mg-Ni system, plateau potentials were observed at -1.63 V, -1.40 V and -0.15 V. Comparing to the results in La-Ni system, these potentials were thought to correspond to Mg-Ni alloys. However, Mg-Ni alloy film was not observed clearly. It is considered that the reaction rate between Mg and Ni is slower and Mg dissolution into molten salts is faster than La-Ni system.

CONCLUSION

The potential after the electrolysis increased as the time elapsed in both the La-Ni system and the Mg-Ni system. The plateau potential was observed at -0.50 V, -0.27 V, -1.45 V, -1.76 V and -1.88 V in the La-Ni system and these potentials corresponded to each La-Ni alloys, which were detected by XRD and EPMA line analysis. It was found that the potential, at which hydrogen absorption alloy LaNi₅ is stable, is between -1.42 V and -1.76 V in molten salts at 1023 K. In the Mg-Ni system, plateau potentials were observed at -0.15 V, -1.40 V and -1.63 V. These potentials also thought to correspond to Mg-Ni alloys. However, the Mg-Ni compound was not observed clearly. It was considered that the reaction rate and dissolution rate of La and Mg was related to the difference of formed alloy phase in both systems.
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Fig. 1 Cyclic voltammogram of Ni in NaCl - KCl - LaCl₃ with a scan rate of 0.1 Vs⁻¹ at 1023 K.

Fig. 2 Potential change after the La electrolysis with 0.1 Acm⁻² for 0.2 ks at 1023 K.
Fig. 3 XRD patterns on the surface of the rapidly cooled specimen at (a) -0.27 V, (b) -0.50 V, (c) -1.45 V, (d) -1.76 V, (e) -1.88 V and (f) -2.30 V after electrolysis with 0.1 A cm\(^{-2}\) for 0.2 ks at 1023 K in the La-Ni system. ▲:LaOCl, ■:Ni, △:LaNi\(_3\), □:La\(_2\)Ni\(_7\), ○:LaNi\(_5\).
Fig. 4 EPMA line analysis of the cross section and SEM photographs of the surface after the rapidly cooled specimens at (a) -0.27 V, (b) -0.50 V, (c) -1.45 V, (d) -1.76 V, (e) -1.88 V and (f) -2.30 V at 1023 K in the La-Ni system.
Fig. 5 The result of EDX analysis of the specimens cooled rapidly.
 ○: La composition, □: Ni composition.

Fig. 6 Potential changes of LaNi$_5$ ingot in molten salts at 1023 K.
(a): in NaCl-KCl-LaCl$_3$, (b): in NaCl-KCl.