Electrochemical Formation of RE Alloys (RE = Dy, Nd) in a Molten LiCl-KCl System and Separation of Dy

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Abstract: Potentiostatic electrolysis were conducted at 0.55 V (vs. Li^+ / Li) for 0.5, 1, 2, 3, 4 and 6 h with Ni plate cathodes at 723 K to confirm the formation of Nd-Ni alloys in LiCl-KCl eutectic melts added $NdCl_3$ (0.50 mol%) at 723 K. All samples obtained after electrolysis at 0.55 V were identified as $NdNi_2$ by XRD analysis. The growth rate of $NdNi_2$ seems to be almost linear, 9.8 μm h^{-1}. In order to investigate the electrolysis potential for the separation of Dy and Nd, cyclic voltammetry was conducted on a Ni electrode in LiCl-KCl eutectic melts added $NdCl_3$ or $DyCl_3$ at 723 K. In the cathodic scanning for the Ni electrode, cathodic current was observed from 1.00 V due to the formation of Dy-Ni alloys in LiCl-KCl eutectic melts added $DyCl_3$. On the other hand, cathodic current due to the formation of Nd-Ni alloys was observed from 0.60 V in LiCl-KCl eutectic melts added $NdCl_3$. From these results, it was suggested that separation of Dy and Nd could be achieved in the potential region of 0.60-1.0 V. Based on the result of cyclic voltammetry, an alloy sample was prepared by potentiostatic electrolysis at 0.65 V for 1 h with a Ni plate cathode in LiCl-KCl eutectic melts added $NdCl_3$ and $DyCl_3$. From the result of ICP-AES analysis, the mass ratio of Dy/Nd in the alloy sample was found to be 72. This result indicated a possibility of selective separation of Dy in a molten LiCl-KCl-$DyCl_3$-$NdCl_3$ system.

Key words: Molten salt, Separation, Recycle, Rare earth, Electrochemical process

1. Introduction

The utilization of RE-TM in several industrial fields has increased drastically over the past few decades. In particular, the demand for Nd-Fe-B magnet added Dy is rapidly increasing because it is dispensable for high performance motors of electric vehicles (EVs) and hybrid electric vehicles (HEVs). These magnets are required to possess enough thermal stability when these magnets are used as the motors for EVs and HEVs under high temperature environment. Thus, the Dy addition is necessary to improve the thermal stability of Nd-Fe-B magnet. However, the world may soon face a shortage of RE metals, which is related with the uneven distribution of RE resources. In 2009, China produced over 97% of the world's RE supply [1], even though it has only 37% of the proven RE reserves. From these backgrounds, it is necessary to develop an inexpensive and environmentally friendly recovery/separation process for RE metals, especially the recovery of Dy and Nd from magnet scraps.

Therefore, we have proposed the new separation and recovery process for RE metals from scraps using molten salt and an alloy diaphragm [2, 3]. The new process is based on our previous finding phenomena, i.e., "electrochemical implantation" and "electrochemical displantation" [4-7]. Figure 1 shows the principle of the proposed molten salt electrochemical process using an alloy diaphragm. Scrap metal containing RE is used as an anode. RE-TM alloy is used

as the diaphragm, which functions as a bipolar electrode. During the electrolysis, all the RE metals in the anode are dissolved into the molten salt as RE ions. One or several specific RE ions are selectively reduced to form RE-TM alloys on the alloy diaphragm according to their formation potentials and/or alloying rates. Subsequently, the RE atoms chemically diffuse through the alloy diaphragm and are dissolved into the molten salt as RE ions at the cathode space. The permeated RE ions are then finally deposited on the Mo or Fe cathode as RE metals. The RE ions remaining in the anode room can be collected by the electrolysis using another cathode in the anode space. Almost all impurities are supposed to remain in the anode room as anode slime.

As a first step to apply the new separation and recovery process for RE metals from scraps using molten salt and an alloy diaphragm to chloride melts, the present study focused on the electrochemical formation of RE alloys (RE = Dy, Nd) in a molten LiCl-KCl-$NdCl_3$ system at 723 K. Furthermore, the separation of Dy and Nd was investigated with a Ni electrode in a molten LiCl-KCl-$DyCl_3$-$NdCl_3$ system.

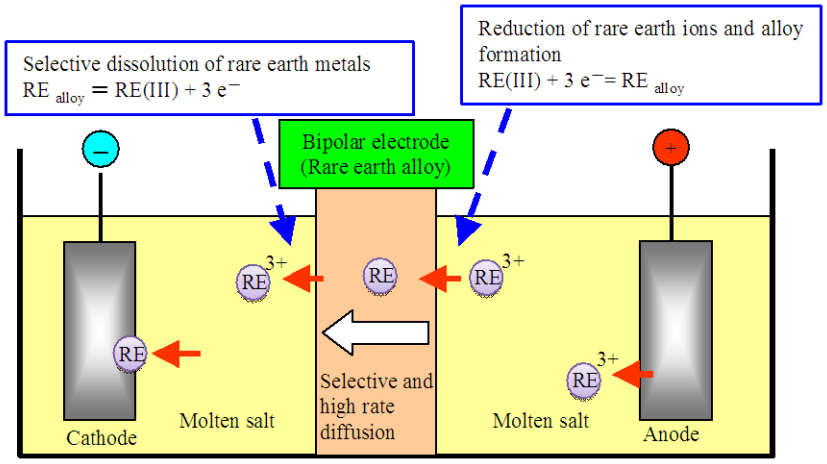

Fig. 1 A schematic drawing of the process for separation and recovery of rare earth metals

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, and kept under vacuum for more than 24 h at 473 K to remove water. A schematic representation of the experimental apparatus used is shown in Figure 2. All experiments were performed in LiCl-KCl eutectic melts under dry argon atmosphere at 723 K. Each $NdCl_3$ and $DyCl_3$(99.9 %, Kojundo Chemical Laboratory Co., Ltd.) of 0.50 mol% was added directly to these melts. 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 %, Nilaco Co., Ltd.) wires for the investigation of electrochemical behavior in this system. For the formation of alloy samples, rectangular shaped plates of Ni (10 mm × 5 mm × 0.2 mm, 99 %, 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.). A potentio / galvanostat was used for cyclic voltammetry and open-circuit potentiometry. The 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. Cross-sections of these samples were also observed by SEM. The compositions of the samples were analyzed by EPMA. The mass of Dy and Nd in the alloy samples were measured by the ICP-AES analysis.

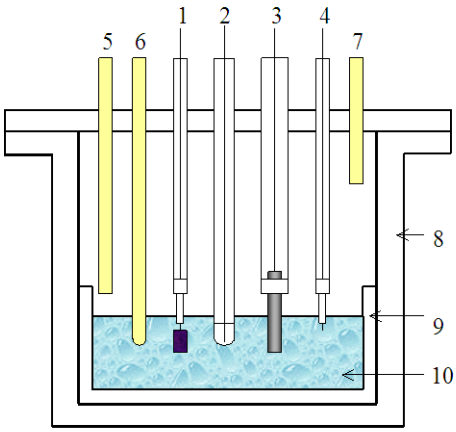

Fig. 2 Schematic drawing of experimental apparatus
1: Working electrode (Mo, Ni), 2: Reference electrode (Ag^+ / Ag),
3: Counter electrode (Glassy carbon), 4: Li^+ / Li electrode (Ni wire),
5: Ar gas inlet, 6: Thermocouple, 7: Ar gas outlet, 8: Pyrex glass holder,
9: High purity alumina crucible, 10: LiCl-KCl eutectic melts

3. Results and discussion

3.1 Electrochemical behavior of Nd(III) with Mo and Ni electrodes

As shown in Figure 3, the phase diagram of the Nd-Ni system shows the presence of seven intermetallic compounds (Nd_3Ni, Nd_7Ni_3, NdNi, $NdNi_2$, $NdNi_3$, Nd_2Ni_7 and $NdNi_5$) at the experimental temperature of 723 K [8].

Taking into account the possibilities of the formation of these various Nd-Ni intermetallic compounds, cyclic voltammetry was conducted on a Ni electrode in LiCl-KCl eutectic melts added $NdCl_3$ (0.50 mol%) at 723 K. Before investigating the Nd-Ni formation, the electrochemical behavior of Nd (III) was investigated using a Mo electrode as a working electrode, since Nd does not dissolve in a Mo metal. Figure 4 shows the obtained cyclic voltammograms for Mo and Ni electrodes after addition of 0.50 mol% $NdCl_3$ at 723 K. The scanning rate was set as 0.1 V s^{-1}. The broken curve represents the voltammogram with a Mo electrode. In the cathodic scanning for a Mo electrode, the small cathodic current shoulder is observed at 0.50 V. It suggested that this shoulder was caused for the reduction from Nd(III) to Nd(II). Furthermore, a significant increase of cathodic current is observed at 0.40 V (vs. Li^+ / Li). Since Nd-Mo alloys do not exist in the Nd-Mo phase diagram, the cathodic current is considered to correspond to Nd metal deposition. After reversing the scan direction at 0.30 V, an anodic current peak is observed, which should be due to the

anodic dissolution of the Nd metal. On the other hand, the solid curve represents the voltammogram with a Ni electrode. The large cathodic current is observed from 0.60 V. Since this potential value is more positive than that of Nd metal deposition (0.40 V) observed, this cathodic current suggested the formation of Nd-Ni alloys. When the potential scanning direction is reversed at 0.30 V, several anodic peaks are observed. These anodic peaks indicated the Nd dissolution from the different Nd-Ni alloy phases into the melt. However, the number of anodic peaks was less than the number of alloy phases shown in the Nd-Ni phase diagram.

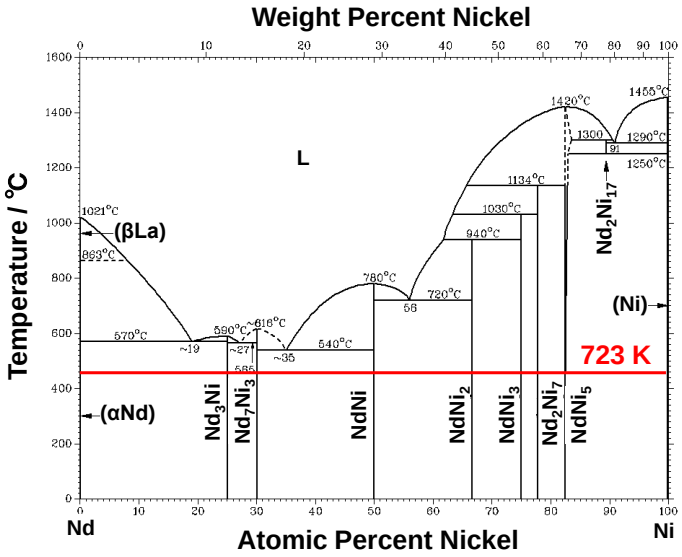

Fig. 3 Phase diagram of the Nd-Ni system [8]

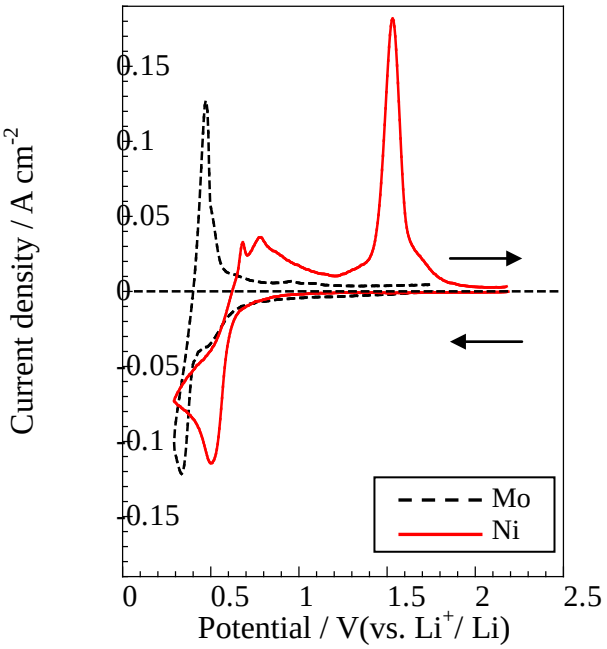

Fig. 4 Cyclic voltamograms for Mo and Ni electrodes in LiCl-KCl eutectic melts added $NdCl_3$ (0.50 mol%) at 723 K, Scan rate: 0.1 V s^{-1}

3.2 Electrochemical formation of Nd-Ni alloys

Potentiostatic electrolysis were conducted at 0.55 V for 0.5, 1, 2, 3, 4 and 6 h with Ni plate cathodes at 723 K to confirm the formation of Nd-Ni alloys in LiCl-KCl eutectic melts added $NdCl_3$ (0.50 mol%) at 723 K. This potential value is more positive than the Nd metal deposition potential (0.40 V) from cyclic voltamograms in Figure 4. The phases of the samples were analyzed by XRD, and their cross-sections were also observed by SEM. Figure 5(a) shows the XRD pattern of the sample obtained at 0.55 V for 1 h, where the alloy phase is identified as $NdNi_2$. The cross-sectional SEM image of the sample is shown in Figure 5(b). This $NdNi_2$ film was dense and coherent with thickness of 14.4 μm.

All samples obtained after electrolysis at 0.55 V for 0.5, 1, 2, 3, 4 and 6 h were identified as $NdNi_2$ by XRD analysis. The relationship between thickness of the formed $NdNi_2$ films and the electrolysis time at 0.55 V is shown in Figure 6.

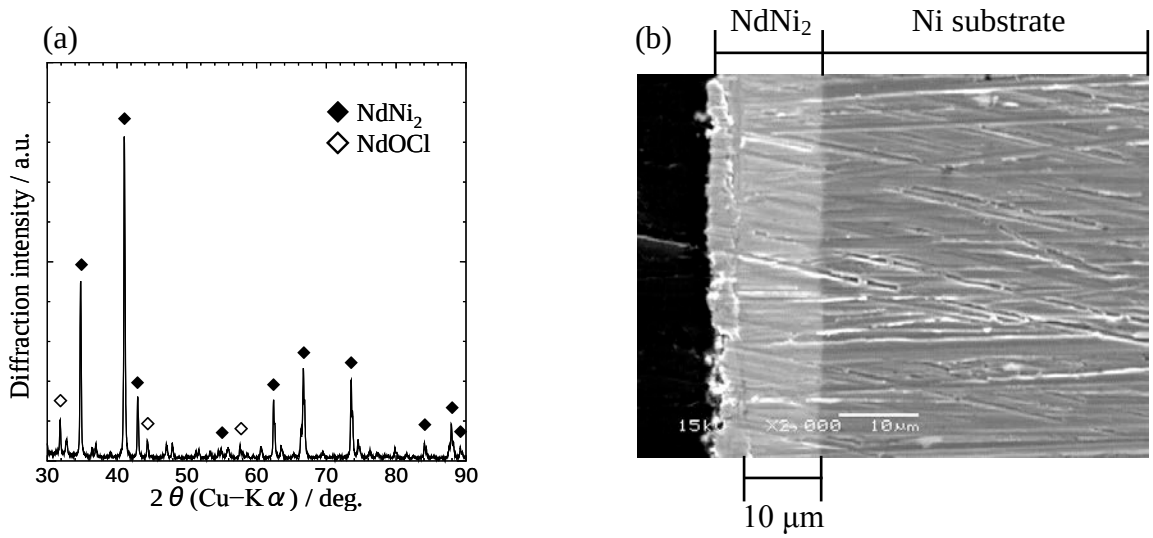

Fig. 5 (a) XRD pattern and (b) cross-sectional SEM image of the sample prepared by potentiostatic electrolysis with a Ni plate cathode at 0.55 V for 1 h in LiCl-KCl eutectic melts added $NdCl_3$ (0.50 mol%) at 723 K

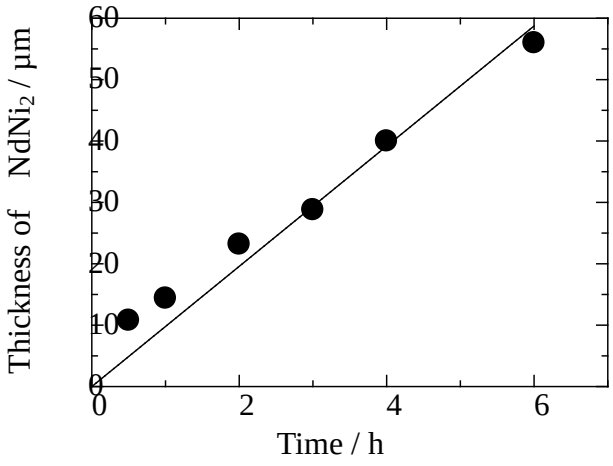

Fig. 6 Relationship between the thickness of $NdNi_2$ film and the electrolysis time in LiCl-KCl eutectic melts added $NdCl_3$ (0.50 mol%) at 723 K

The growth rate of $NdNi_2$ seems to be almost linear, 9.8 μm h^{-1}. However, comparing with the growth rate of $DyNi_2$, i.e., 28.2 μm h^{-1} [6], the growth rate of $NdNi_2$ was about one-third as slow as that of $DyNi_2$ at 723 K. From this result, in case of keeping at 0.55 V, the separation of Dy might be possible by utilizing the difference between the growth rates of $NdNi_2$ and $DyNi_2$ in a molten LiCl-KCl-$DyCl_3$-$NdCl_3$ system.

3.3 Separation of Dy and Nd by potentiostatic electrolysis with Ni electrodes

In order to investigate the electrolysis potential for the separation of Dy and Nd, cyclic voltammetry was conducted on a Ni electrode in LiCl-KCl eutectic melts added $NdCl_3$ or $DyCl_3$ (0.50 mol%) at 723 K. Figure 7 shows the obtained cyclic voltammograms for Ni electrodes after addition of 0.50 mol% $NdCl_3$ or $DyCl_3$. The solid and broken curves represent voltammograms of Dy-Ni and Nd-Ni system, respectively. In the cathodic scanning for the Ni electrode, cathodic current is observed from 1.00 V (vs. Li^+ / Li) due to the formation of Dy-Ni alloys in LiCl-KCl eutectic melts added $DyCl_3$. On the other hand, cathodic current due to the formation of Nd-Ni alloys is observed from 0.60 V in LiCl-KCl eutectic melts added $NdCl_3$. From these results, it was suggested that the separation of Dy and Nd could be achieved in the potential region of 0.60-1.0 V. Based on the result of cyclic voltammetry, in order to confirm the separation of Dy and Nd, alloy samples were prepared by potentiostatic electrolysis at 0.55-0.80 V for 1 h with Ni plate cathodes in LiCl-KCl eutectic melts added $NdCl_3$ (0.50 mol%) and $DyCl_3$ (0.50 mol%) at 723 K. Figure 8 shows the mass ratio of Dy/Nd in the alloy samples measured by the ICP-AES analysis. From the result of ICP-AES analysis, the mass ratio of Dy/Nd in the alloy sample at 0.65 V was found to be the highest, i.e., 72. This result indicated a possibility of the separation of Dy in a molten LiCl-KCl-$DyCl_3$-$NdCl_3$ system.

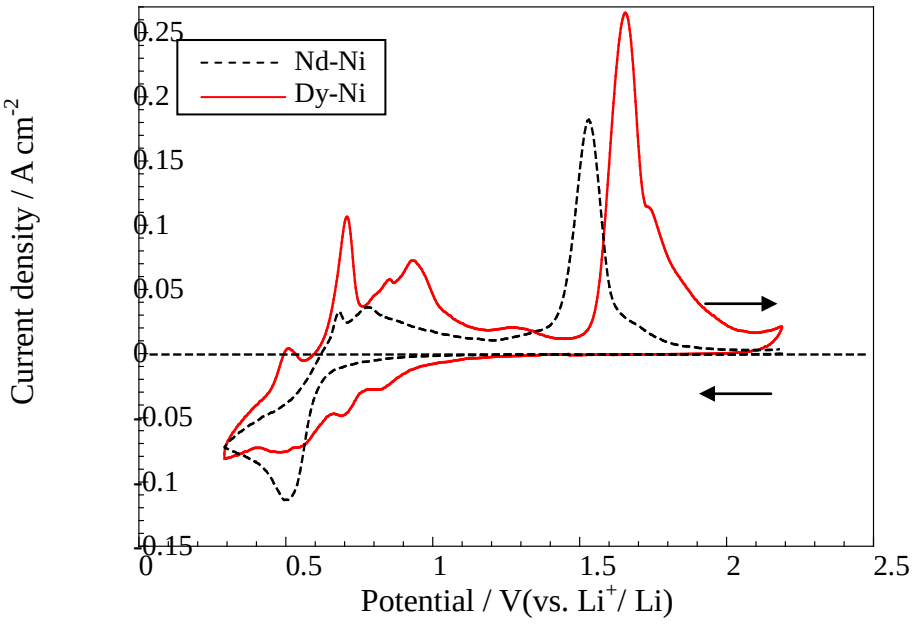

Fig. 7 Cyclic voltamograms for Ni electrodes in LiCl-KCl eutectic melts added $NdCl_3$ or $DyCl_3$ (0.50 mol%) at 723 K, Scan rate: 0.1 V s^{-1}

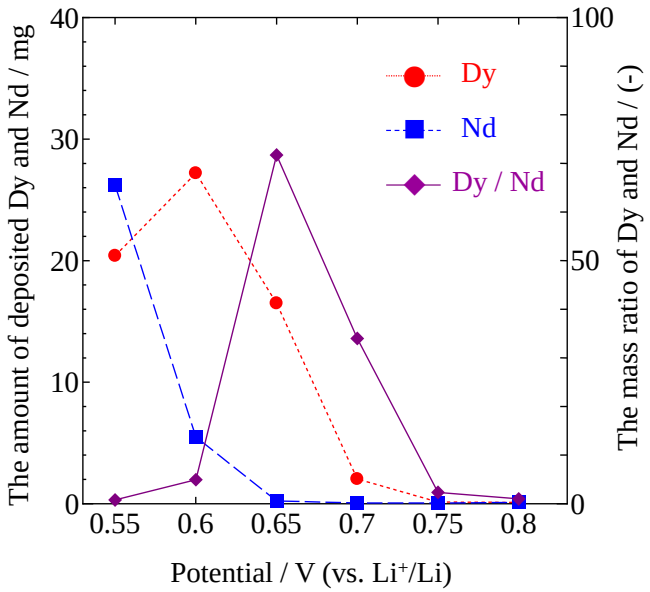

Fig. 8 Potential dependence of the amount of deposited Dy and Nd, the mass ratio of Dy/Nd in LiCl-KCl eutectic melts added $NdCl_3$ (0.50 mol%) and $DyCl_3$ (0.50 mol%) at 723 K

4. Conclusions

Electrochemical formation of RE alloys (RE = Dy, Nd) and separation of Dy was investigated with a Ni electrode in a molten LiCl-KCl-$DyCl_3$-$NdCl_3$ system at 723 K. Firstly, potentiostatic electrolysis at 0.55 V resulted in the formation of a dense and coherent $NdNi_2$ in LiCl-KCl eutectic melts added $NdCl_3$ (0.50 mol%) at 723 K. The growth rate of $NdNi_2$ was almost linear, 9.8 μm h^{-1}. Secondary, alloy samples were prepared by potentiostatic electrolysis at 0.55-0.80 V for 1 h with a Ni plate cathode in LiCl-KCl eutectic melts added $NdCl_3$ (0.50 mol%) and $DyCl_3$ (0.50 mol%) at 723 K. From the result of ICP-AES analysis, the mass ratio of Dy/Nd in the alloy sample obtained at 0.65 V was found to be the highest, i.e., 72.

Acknowledgement

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