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Selective Extraction of Rare Earth Elements from NdFeB Scrap by Molten Chlorides

Zhongsheng Hua,*[†] Jian Wang,[†] Lei Wang,[†] Zhuo Zhao,[†] Xinlei Li,[†] Yanping Xiao,[†] and Yongxiang Yang[†,‡]

[†]School of Metallurgical Engineering, Anhui University of Technology, 59 Hudong Road, Ma'anshan 243002, P. R. China

[‡]Department of Materials Science and Engineering, Delft University of Technology, 2628 CD Delft, The Netherlands

Supporting Information

ABSTRACT: With rapid growth in the use of NdFeB magnets and growing concerns for environmental protection as well as conservation of rare earths (REs), the recycling of NdFeB magnet scrap is becoming a hot issue for current society. In this study, it is demonstrated that the rare earths in a NdFeB magnet can be selectively extracted using molten $MgCl_2$−KCl salts at temperatures of 600−1200 °C. After crushing to granules, the scrap was subjected to molten chlorides in a dry argon atmosphere. The reaction process between NdFeB scrap and molten $MgCl_2$−KCl was directly observed using a high-temperature contact angle measuring instrument to clarify the phenomena that occur when rare earth chlorides are formed in situ. Furthermore, the effects of reaction temperature, holding time, and mass ratio of $MgCl_2$/NdFeB were investigated to transform REs in the scrap to $RECl_3$ as completely as possible. The reaction products were examined with the necessary analytical techniques including SEM, EDS, XRD, and ICP. The overall extraction efficiency for REs was found to be more than 90% under the optimum operating conditions. The obtained $RECl_3$ in the molten $MgCl_2$−KCl can be processed with molten salt electrolysis for the direct production of Mg−Nd alloy.

KEYWORDS: *NdFeB magnet scrap, Rare earths, Extraction, Molten chlorides, Recycling*

INTRODUCTION

The NdFeB magnet exhibits superior magnetic properties, such as magnetic intensity, coercive force, and energy density, to all other magnetic materials and possesses good mechanical properties. This permanent magnet has a wide range of applications such as in various motors, as a magnetic field generator for magnetic resonance imaging (MRI), in generators in hybrid and electric vehicles ((H)EVs), and in loudspeakers, mobile phones, computer hard disk drives (HDDs) and so on because it was developed in 1984.[1−3] It is already an important material due to its excellent performance in the permanent magnet at the present time.[4] These wide applications lead to high market demand and a rapid increase in production. The production of the NdFeB permanent magnet in China was 94,000 tonnes in 2013, which was about 91% of the total world production.[5] A large amount of new scrap that accounts for about 30% of the total production is inevitably generated during the production process of cutting and polishing to the demanded size. Moreover, the magnet scraps from end-of-life (EOL) products containing rare earth elements (REEs) increase year by year. If this type of scrap is released to the environment without any treatment, it is not only a contamination of environment but is also a waste of resources.

With increasing environmental legislation and demand for even higher degrees of energy efficiency and resource conservation, material recycling is of great importance for sustainable development all over the world. The in-plant scrap is recycled by the manufacturers, while the magnets placed in end-of-life products and the new scrap from commercially sold semiproducts are not properly recovered. In fact, recycling of NdFeB is limited not just by technology but even more by product design because the tiny amounts of NdFeB used in complex products such as HDDs make recovery very difficult.[2,6] Using life cycle assessment (LCA) methodology, it is reported that compared to the production of NdFeB magnets from virgin material the production process via recycling scores significantly better with respect to most environmental impact categories.[7] Moreover, REEs have been defined as critically scarce materials in the transition period toward a global low-carbon energy system.[8,9] From this sense, recovery of rare earths from NdFeB scrap becomes extremely important.

Currently, the traditional route for extraction of rare earths from permanent magnets is via hydrometallurgical technol-

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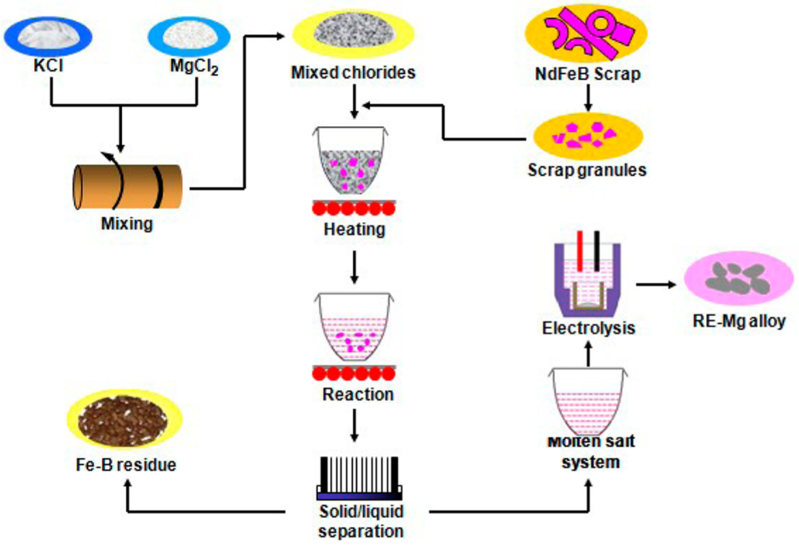

Figure 1. Illustration of flowsheet of RE recovery from NdFeB scrap using molten chlorides.

ogy.[10−15] First, the magnet scrap is preprocessed to remove organic residues and is then dissolved in strong mineral acids. Iron is precipitated as $Fe(OH)_3$ to be removed by charging a strong alkali solution. Then, REEs isolated by using solvent extraction are selectively precipitated as oxalates. Finally, the oxalates are oxidized into oxides by calcination to be the raw materials for molten salt electrolysis. In this recycling process, large amounts of chemicals and clean water are consumed, and a great deal of waste acid and effluent is discharged. Certain unwanted elements such as Fe, Ni, and Co also go into solution together with the REEs in the selective leaching process,[2] which requires further purification before the REEs separation step.

Pyrometallurgical methods also have been applied to extract REEs from NdFeB scrap using molten salt extraction,[16,17] gas-phase extraction,[18,19] and liquid metal extraction.[20] These recycling methods are based on the selective reaction between REEs and the extractant such as molten $FeCl_2$, NH_4Cl, vapor Cl_2, and $AlCl_3$ and liquid metal Mg and Ag. Generally, pyrometallurgical methods are applicable to all types of magnet composition with no generation of wastewater and have fewer processing steps than hydrometallurgical technology. But they have their own disadvantages[2] and have not been adopted in commercial production. For example, large energy input is required using molten salt extraction to recycle REEs as the corresponding oxides,[17] and liquid metal extraction cannot be applied to the oxidized magnet scrap. The major shortcoming in gas-phase extraction is the consumption of large amounts of chlorine gas.

In the present work, a new process for recycling rare earths in NdFeB scrap is proposed, as shown in Figure 1. On the basis of the reactions between REs and $MgCl_2$, REs in the scrap can be selectively extracted by using molten $MgCl_2$−KCl to form $RECl_3$. So far, reports on extracting REEs from NdFeB scrap using molten $MgCl_2$−KCl salts are very limited. This study focuses on the salt extraction process for REEs. As part of the total recycling route, the extracted $RECl_3$ in the molten chlorides can be processed with molten salt electrolysis for the direct production of Mg−Nd-based alloy, as codeposition of Mg−RE master alloys in molten chlorides has been widely investigated.[21−23] Furthermore, rare earth metals can be also obtained by evaporating Mg out of the Mg−RE alloy.[24]

■ EXPERIMENTAL SECTION

Raw Materials. An off-specification NdFeB magnet with a zinc coating film was used as the scrap sample for the experiment. The zinc coating film was mechanically removed by polishing on a grinder, and the scrap was crushed to granules with diameters of 5−7 mm for extraction of REEs. Anhydrous magnesium chloride ($MgCl_2$, 99% purity) and potassium chloride (KCl, 99.5% purity) were used for preparing molten chlorides. Corundum crucible (Al_2O_3, 99% purity) was used to hold the molten chlorides, and argon (Ar, 99.99% purity) was used as the shielding gas to protect anhydrous chlorides from deliquescing.

Experimental Procedures. First, anhydrous $MgCl_2$ and KCl powders were homogeneously mixed in a rotating drum for 30 min. A NdFeB scrap granule was put on a alumina mesh in a crucible and covered with a mixture of chlorides. Ti powder was placed in a stainless steel reactor, and subsequently, the atmosphere inside the reactor was purged and filled with high purity Ar gas. The corundum crucible was heated to a temperature of 600−1200 °C and kept constant. After reaction for 1 to 12 h, the heating power was cut off. Then, the residual scrap was taken out and separated from the molten chlorides. After the experiment, the trace amount of chlorides deposited on the residual scrap was removed by dissolving in distilled water. Finally, the residual scrap and obtained salts were ground into powder with a size less than 75 μm subjected to analysis.

Analysis of Samples. Differential scanning calorimetry (DSC) and thermal gravimetric (TG) analysis experiments were performed using a simultaneous TG-DSC instrument (Setsys Evolution 18/24 TGA-DTA/DSC-MS, Setaram) in Ar with a constant heating rate of 5 °C/min. The concentrations of Nd, Pr, and Dy in the mixed chlorides and residual scrap were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The reaction process between the NdFeB scrap and mixed $MgCl_2$−KCl was directly observed using a high-temperature contact angle measuring instrument (OCA15LHT-HTFC1700, Dataphysics). The reaction products were examined by scanning electron microscopy (SEM: SSX-550, Shinadzu Corporation) at an accelerating voltage of 15 kV. Chemical analysis was performed simultaneously with SEM using energy dispersive X-ray spectroscopy (EDS). The crystal structures of the scrap powder, residual scrap, and obtained salts were analyzed by X-ray diffraction spectroscopy (XRD) (D8 ADVANCE, BRUKER AXS) using the monochromatic target of Cu Kα.

Determination of Extraction Efficiency. The REs extraction efficiency R_i was calculated from the following formula

$$R_i = 1 - \frac{w_{i,\text{residue}}}{w^0_{i,\text{scrap}}} \times 100\% \tag{1}$$

where i is Nd, Dy, or Pr; $w_{i,\text{residue}}$ is the mass of rare earths element i in the residual scrap after the experiment, and $w^0_{i,\text{scrap}}$ is the initial mass of rare earths element i in the NdFeB scrap. Data for extraction efficiency were gathered on the basis of four experiments.

■ RESULTS AND DISCUSSION

Description of Process Concept. In our work, the recycling process is mainly composed of two steps: (1) extraction of REEs from NdFeB scrap to form molten $RECl_3$–$MgCl_2$–KCl and (2) electrolysis in molten chlorides to prepare a RE–Mg-based alloy. In the first step, REEs in the NdFeB scrap selectively react with $MgCl_2$ to form $RECl_3$, leaving solid Fe–B alloy and impurity elements behind. KCl is added in this process to gain the binary molten salt system of $MgCl_2$–KCl, which exhibits a lower melting point and viscosity, as well as volatility compared to pure $MgCl_2$ melt. This binary system has also higher conductivity and surface tension beneficial for the extraction of REEs and the subsequent electrolysis of REs metals. The obtained molten salts are electrolyzed using liquid Mg metal as the cathode. This recycling process is highly feasible from an industrial point of view for the following reasons: (1) The process is fairly simple. (2) The solid/liquid separation (molten chlorides/Fe–B residue) is easy to operate and suitable for massive treatment. (3) The energy consumption in subsequent processing is low after removing most of the FeB residue. (4) No waste solution and solid are generated, and the FeB residue can be sold to the cement industry or steel plants as an alternative raw material.

Thermodynamic Analysis. Selective extraction should be the prerequisite for the recycling of REEs in NdFeB scrap using molten chlorides. Figure 2 shows the Gibbs free energy variation of reactions between elements in NdFeB and $MgCl_2$ at 400–1300 K. It is obvious that REEs can selectively react with $MgCl_2$ thermodynamically above 400 K, while the effects of chemical reactions between $MgCl_2$ and the other components such as Fe, B, Al, and Ni will not appear. It indicates that it is possible to extract REEs from the magnet scrap via chemical reactions.

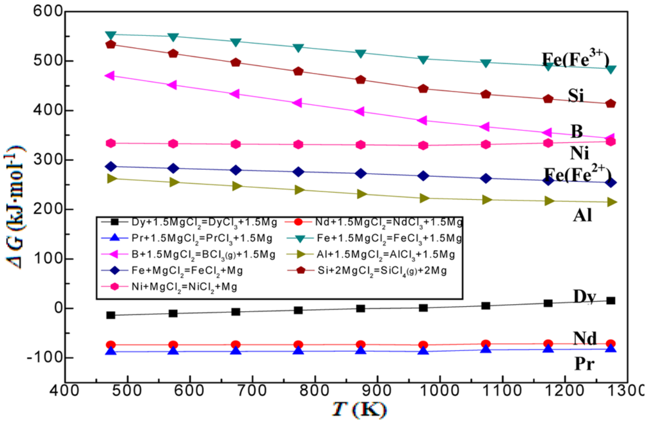

Figure 2. Gibbs free energies variation of reactions between elements in NdFeB and $MgCl_2$ at 400–1300 K.

The chemical reactions involved in the extraction of REEs with $MgCl_2$ are as follows

$$2Nd_{(s)} + 3MgCl_{2(l)} = 2NdCl_{3(l)} + 3Mg_{(l)} \tag{2}$$

$$2Pr_{(s)} + 3MgCl_{2(l)} = 2PrCl_{3(l)} + 3Mg_{(l)} \tag{3}$$

$$2Dy_{(s)} + 3MgCl_{2(l)} = 2DyCl_{3(l)} + 3Mg_{(l)} \tag{4}$$

TG-DSC Analysis. Before the differential scanning calorimeter and thermogravimetry experiments, the NdFeB scrap was ground into powders and then mixed with the chlorides to form a NdFeB/$MgCl_2$–KCl mixture. Figure 3 shows the TG-DSC curves of the NdFeB/$MgCl_2$–KCl mixture. Two distinct endothermic peaks appear from room temperature to 200 °C in the DSC curve, and a mass reduction of about 2% is shown in the TG curve. As is known, anhydrous $MgCl_2$ is prone to deliquescing and turns into $MgCl_2 \cdot nH_2O$ (n = 1–6) during preparation of the TG-DSC measurement sample, and $MgCl_2 \cdot nH_2O$ will dewater during the heating process. The dehydration reaction involves several stepwise stages at different temperatures.[25] The endothermic peaks at 150 and 190 °C and the mass reduction can be attributed to the dehydration reaction of $MgCl_2 \cdot nH_2O$ during the heating process.

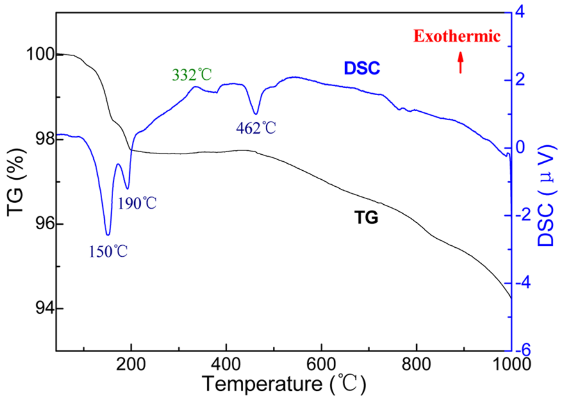

Figure 3. TG-DSC curves of the NdFeB/$MgCl_2$–KCl mixture.

As mentioned above, REEs can selectively react with $MgCl_2$ thermodynamically when the temperature is above 400 K. The melting point of the mixed chlorides $MgCl_2$–KCl used in this experiment is 470 °C when their mole ratio is 6:4.[26] Between 200 and 500 °C, there is an exothermic peak at 332 °C and an endothermic peak at 462 °C, which can be attributed to the exothermic reactions between REs and $MgCl_2$ and the melting change of solid $MgCl_2$–KCl to molten chlorides. During these two processes, the mass did not change, so the TG curve is comparatively flat. The DSC signals indicate that there is no chemical change between 500 and 1000 °C. When the temperature is higher than 470 °C, the molten chlorides start to volatilize. High temperature promotes the volatilization of the molten salt, so the mixed chlorides lose mass continuously with an increase in temperature, as shown in the TG curve.

Effect of Reaction Conditions on REs Extraction Rate. Representative results of the extraction experiments are shown in Figure 4. Figure 4(a) shows that the REEs extraction efficiency increases generally with increasing reaction temperature. Extraction efficiencies of Nd, Pr, and Dy after reaction at 1000 °C and holding for 3 h were 86.6%, 89.2%, and 79.7%, respectively. The extraction efficiencies for the three REEs reach 93.2% when the reaction temperature was raised to 1200 °C. In other words, most REEs in the NdFeB scrap can be extracted into molten chlorides at sufficiently high temper-

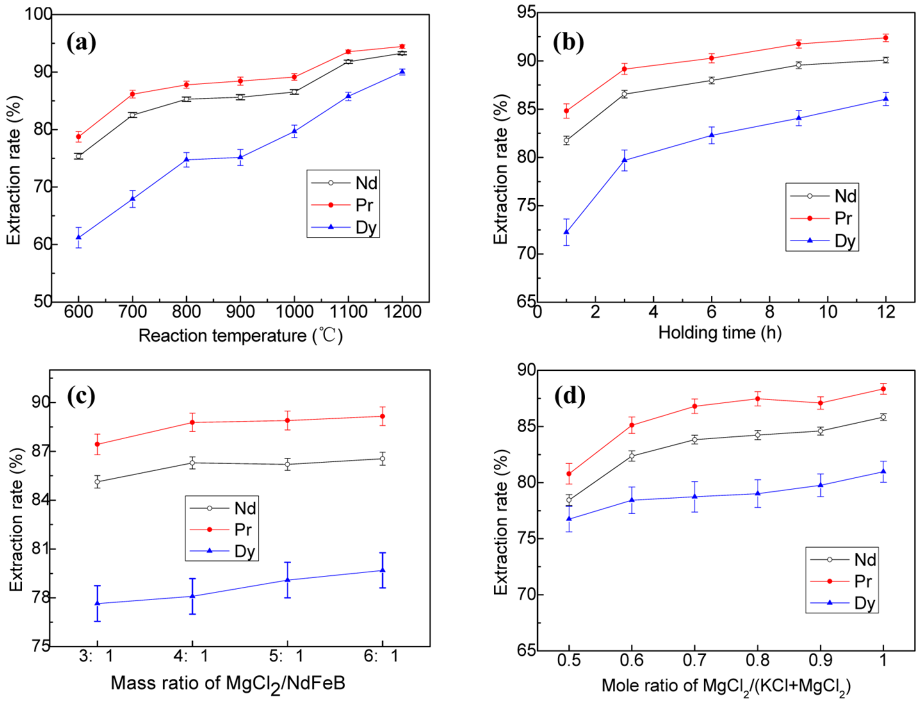

Figure 4. REs extraction rate as a function of (a) reaction temperature, (b) holding time, (c) mass ratio of $MgCl_2$/scrap, and (d) mole ration of $MgCl_2$/(KCl+$MgCl_2$).

atures. Generally, the viscosity of molten chlorides decreases while raising temperature, and the diffusion of reactant and product in the melt is accelerated. That is favorable to the extraction process. Nevertheless, the Gibbs free energy of reactions between REEs and $MgCl_2$ increases with an increasing reaction temperature, which implies that high temperature is not beneficial for the extraction thermodynamically. This phenomenon is related to the rate-controlling step of the reaction between REEs and $MgCl_2$.

The extraction rates of Nd, Pr, and Dy with different holding times at 1000 °C are shown in Figure 4(b). The extraction of Nd quickly reached 86.6% within 3 h and showed only a slight increase as holding time extended to 12 h. The extraction behaviors of Pr and Dy also show a similar tendency. As the reaction progressed, the concentration gradient between the reaction interface and the bulk melt declined because of a decrease in reactant concentration and an increase in product concentration in the melt, which resulted in a decrease in reaction rate. After reaction at 1000 °C for 9 h, the total extraction rates for the three REEs increased from 81.4% to 86.4% with the holding time increasing from 1 h to 3 h, and it extends to 90.1% when 12 h of holding time is reached.

In Figure 4(c), the extraction rate gradually increased with an increase in mass ratio of $MgCl_2$ to NdFeB scrap. A high $MgCl_2$/scrap mass ratio is beneficial for extraction. $MgCl_2$ content in the mixed chlorides used in the experiments is 60% (mole fraction). Nearly 84.8% of the REEs in the scrap could be extracted with a $MgCl_2$/scrap mass ratio of 3:1 at 1000 °C and holding for 3 h, while the extraction rate reaches 86.4% as the mass ratio turns to 6:1. The stoichiometric ratio of the reaction between $MgCl_2$ and the REEs is 1.5:1. According to the composition of the NdFeB scrap, the amount of $MgCl_2$ for complete extraction of REEs from 10 g of scrap is about 3.36 g, which implies that the mass ratio of $MgCl_2$ to scrap is 0.336:1. It is obvious that excessive $MgCl_2$ was added in the experiments with a $MgCl_2$/scrap mass ratio of 3:1 to 6:1, which is much higher than the stoichiometric ratio necessary for complete extraction of Nd, Pr, and Dy. So, the extraction rate shows only a slight increase when the $MgCl_2$/scrap mass ratio varies from 3:1 to 6:1.

In the mixed molten chlorides, only $MgCl_2$ was consumed as the reactant, while KCl was added to decrease the melting temperature and viscosity, as well as the volatility of the melts. The effect of the mole ratio of $MgCl_2$/(KCl+$MgCl_2$) on the extraction rate at 1000 °C and holding for 3 h is shown in Figure 4(d). The extraction rate shows a rapid increase with the mole ration of $MgCl_2$/(KCl+$MgCl_2$) increasing from 0.5 to 0.6 and shows a slight increase when the mole ratio further increases from 0.6 to 1. According to the phase diagram of $MgCl_2$−KCl, when the mole ratio of $MgCl_2$/(KCl+$MgCl_2$) varies in the range from 0.5 to 1, the binary system with a mole fraction of 0.6 has a relatively lower melting temperature. Therefore, while the temperature was raised to 1000 °C, the binary system with a mole fraction of 0.6 was first to convert into melt and react with the scrap. Meanwhile, a higher KCl content in the $MgCl_2$−KCl melt was favorable to reduce the viscosity, which thus accelerated the mass transfer process in the melts. Subsequently, there is a sharp improvement in extraction rate with a mole ratio of $MgCl_2$/(KCl+$MgCl_2$) rising from 0.5 to 0.6. On the other hand, the higher the mole ratio of $MgCl_2$ was the more chance for REEs to contact with $MgCl_2$ and react; thus, more REEs in the scrap could be extracted.

In addition, as shown in Figure 4(a)−(d), the extraction rate of the three REEs increased in the order of Dy < Nd < Pr, which could be attributed to their chemical activity. As illustrated in Figure 2, the reaction between Pr and $MgCl_2$ also possesses the lowest Gibbs free energy and thus has a higher reaction driving force.

Direct Observation of Reaction Process. To clarify the phenomena that occur when $RECl_3$ is formed in situ, the reaction process between the NdFeB scrap and mixed chlorides $MgCl_2$−KCl was directly observed. Figure 5 shows the images investigated by a high-temperature contact angle measuring instrument at different temperatures. At 50 °C, the mixed chlorides keep the original appearance, and the chlorides stood on NdFeB scrap by point contact. Also, there is no chemical reaction between the two, as shown in Figure 5(a). With the temperature rising to the melting temperature of mixed $MgCl_2$−KCl, the chlorides begin to melt and spread out on the NdFeB scrap, as shown in Figure 5(c) and (d). It is worthwhile to note that the molten chlorides show properly good wettability with NdFeB scrap. The perfect wettability is beneficial for accelerating the reaction between the NdFeB scrap and molten chlorides. As mentioned above, a fraction of anhydrous $MgCl_2$ inevitably deliquesces before the experiment and becomes $MgCl_2 \cdot nH_2O$. According to the following thermal decomposition mechanisms,[25] $MgCl_2 \cdot nH_2O$ will turn into MgO finally when the temperature is raised to 415 °C.

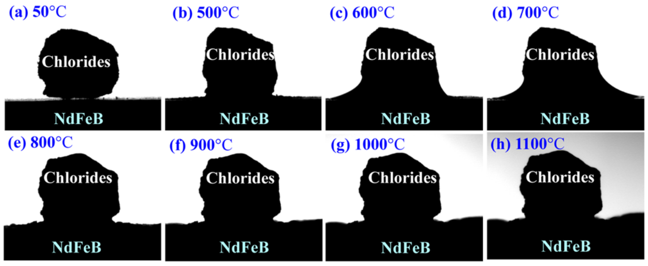

Figure 5. Images investigated by a high-temperature contact angle measuring instrument at different temperatures.

$$MgCl_2 \cdot nH_2O \rightarrow Mg(OH)Cl \cdot 0.3H_2O + HCl + (n - 1.3)H_2O \quad (1 \leq n \leq 2) \tag{5}$$

$$Mg(OH)Cl \cdot 0.3H_2O \rightarrow MgOHCl + 0.3HCl \tag{6}$$

$$MgOHCl \rightarrow MgO + HCl \tag{7}$$

MgO has a high melting point of 2852 °C and cannot melt under the experiment temperature. Thus, the mixture chloride still keeps its initial outline during the heating process, as shown in Figure 5(b)−(h). It is obvious in Figure 5(e)−(h) that reaction products have formed on the NdFeB scrap and have made the smooth surface out-of-flatness. High temperature favors REs extraction efficiency but aggravates the volatilization loss of mixed molten salts at the same time. The volatilized chlorides deposit on the camera lens of a high-temperature contact angle measuring instrument and darken the obtained images when the temperature is raised to 1000 °C, as shown in Figure 5(g) and (h). In this sense, an exorbitant reaction temperature is not proposed when using molten chlorides to extract REEs from NdFeB scrap.

Characterization of Reaction Product. After the experiment, the scrap granules still retained their original shape. The resultant residue after reaction at 1000 °C for 9 h was characterized by SEM/EDS, as shown in Figure 6. It is shown in Figure 6(a) that the resultant residue was not dense in microstructure. The result of EDS analysis indicates that the residue after reaction was mainly composed of Fe. This confirms that most Nd, Dy, and Pr in the NdFeB scrap have been extracted into the molten chlorides leaving unreacted Fe−B alloy in the residue. Owing to the light element and low content of B in the NdFeB magnet (about 1 wt %), B could not be detected by EDS.

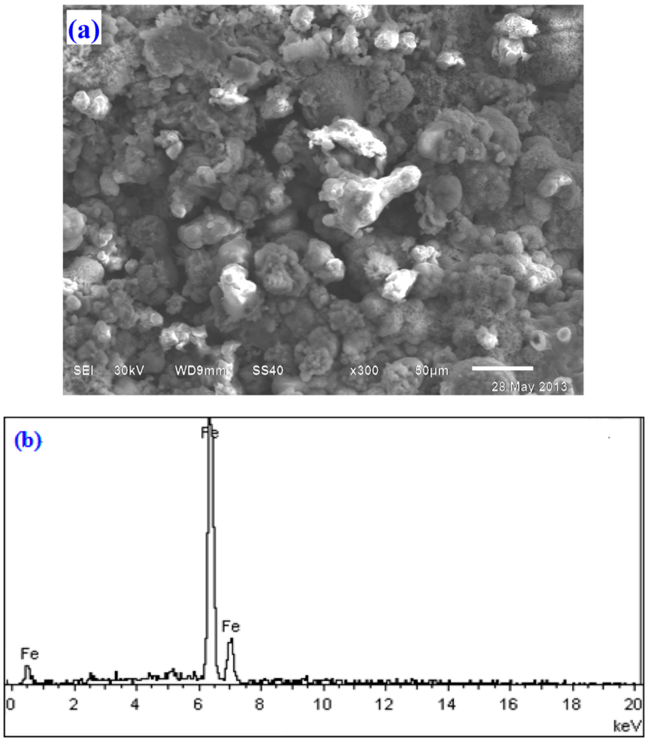

Figure 6. SEM image (a) and EDS analysis (b) of the resultant residue.

To clarify the chlorination reaction of NdFeB scrap in a molten $MgCl_2$−KCl mixture, XRD measurements were carried out on the initial reactants and the obtained products after the experiment. Figure 7 shows the XRD patterns of the powder scrap and the salts before and after the experiment at 1000 °C for 3 h. The XRD pattern of the unreacted magnet scrap was assigned as the tetragonal phase of $Nd_2Fe_{14}B$ (curve a), and only diffraction peaks of pure Fe were detected from the residual scrap after the experiment (curve b), which is in good agreement with the result of the EDS analysis. In this experiment, the mole ratio of $MgCl_2$ and KCl was 6:4, and the molten chlorides mixture was crystallized to form the orthorhombic phase of $KMgCl_3$ during cooling to room temperature. Meanwhile, diffraction peaks of $KMgCl_3 \cdot 6H_2O$ were also detected owing to the deliquescent property of magnesium chloride, as shown in curve c. Besides $KMgCl_3$ and $KMgCl_3 \cdot 6H_2O$, trivalent rare earth chlorides ($NdCl_3$, $PrCl_3$, and $DyCl_3$) were found in the obtained salts (curve d). In addition, formation of $NdCl_2$ was also found. Because Nd has a relatively higher content than that of Pr and Dy, the following reaction may occur between Nd remaining in the scrap and $NdCl_2$ generated during chlorination.[27]

$$Nd + 2NdCl_3(melt) \rightarrow 3NdCl_2(melt) \tag{8}$$

Mechanism Discussion. The extraction of REEs proceeds through the following steps occurring successively during the extraction process: (1) transport of $MgCl_2$ from bulk melt to the exterior surface of the ash layer through a melt boundary layer, (2) diffusion of molten reactant ($MgCl_2$) through the ash layer to the reaction surface, (3) chemical reaction of REEs with $MgCl_2$, (4) diffusion of molten product ($RECl_3$) outward through the ash layer, and (5) transport of the molten product

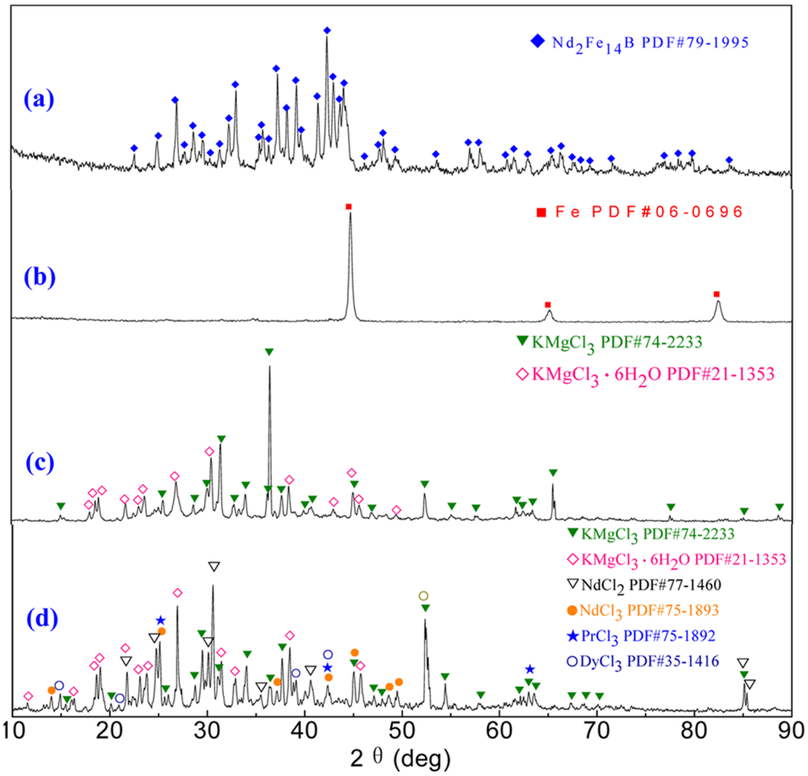

Figure 7. XRD patterns of reactants and products: (a) initial magnet scrap, (b) residual scrap after experiment, (c) initial molten chlorides, and (d) obtained salts.

($RECl_3$) from the exterior surface of ash layer to the bulk melt. Each step may contribute resistance to the completion of the extraction process. The slowest step among these five will provide the largest resistance to the overall reaction, and it is called the rate-controlling step. In this process, it is hypothesized that $MgCl_2$ in the molten chlorides diffuses into the inner ash layer until only the ash layer remains after complete extraction of the REEs, so the unreacted shrinking core model (shown in Figure 8) can be adopted to illustrate the extraction process. Many kinetic equations of the solid−liquid reaction are reported in the literature.[28,29] In this study, eq 9 based on the chemical reaction-controlled mechanism, eq 10 based on the diffusion-controlled mechanism, and eq 11 based on the mixed-controlled mechanism are applied to determine the rate-controlling step

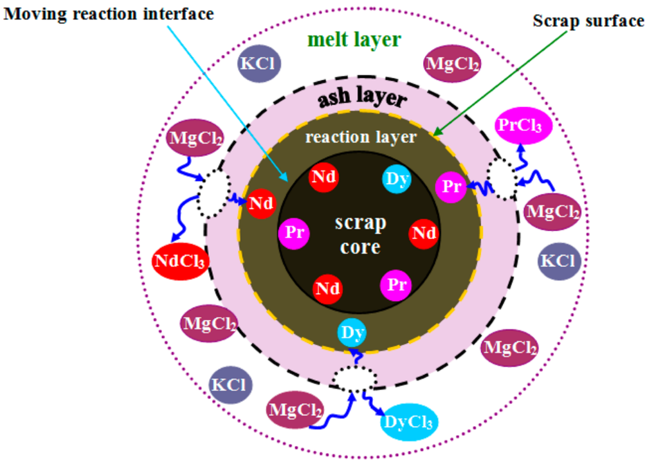

Figure 8. Schematic diagram of the unreacted shrinking core model for the extraction of REs from NdFeB scrap.

$$kt = 1 - (1 - R)^{1/3} \tag{9}$$

$$kt = 1 - 3(1 - R)^{2/3} + 2(1 - R) \tag{10}$$

$$\frac{t}{1 - (1 - R)^{1/3}} = \frac{\beta}{\alpha} + \frac{1}{6\alpha}[1 - (1 - R)^{1/3}][2(1 - R) + 1] \tag{11}$$

where R is the extraction rate of the three REEs; k is the apparent rate constant for the ash layer diffusion, t is the reaction time, and α and β are constants.

The extraction process can be represented as follows: REEs existing on the surface of the granule magnet scrap reacted with molten $MgCl_2$ leaving FeB residue behind to form an ash layer, and the reaction product penetrated toward the bulk molten chlorides. During the chlorination process, $MgCl_2$ in bulk melts diffused through the ash layer to the surface of unreacted scrap to facilitate the extraction of REEs, and the reaction interface was moving gradually toward the core of magnet scrap. Consequently, the ash layer grew thick, and the unreacted scrap core became small until the completion of reaction, as shown in Figure 8. The rate-controlling step of the reaction plays an essential role in optimizing and understanding the extraction process. For the unreacted shrinking core model, the mathematical formulations for the chemical reaction, diffusion, and mixed control are investigated in eqs 9, 10, and 11, separately. If the plot of $1 - (1- R)^{1/3}$ versus t gives a straight line, the rate-controlling step is the chemical reaction. If the plot of $1 - 2/3R - (1 - R)^{2/3}$ versus t gives a straight line, the rate-controlling step is diffusion. If it is mixed control, the plot of $t/(1-(1-R)^{1/3})$ versus $[1-(1-R)^{1/3}][2(1-R)^{1/3}+1]$ would give a straight line.

The analysis results for the extraction process are shown in Figure 9. They indicate that the kinetic plots of the diffusion control have a better linear relationship compared to the chemical reaction control and mixed control. Therefore, the rate-controlling step for the extraction of REEs from NdFeB magnet scrap using molten $MgCl_2$−KCl chlorides is diffusion control. It can be expected that during the extraction process the reaction between REEs on the surface of the magnet scrap and $MgCl_2$ finishes within a short time, and the ash layer would provide the resistance for $MgCl_2$ to penetrate toward the core of the unreacted magnet scrap. Therefore, ash layer diffusion could be considered as the rate-determining step.

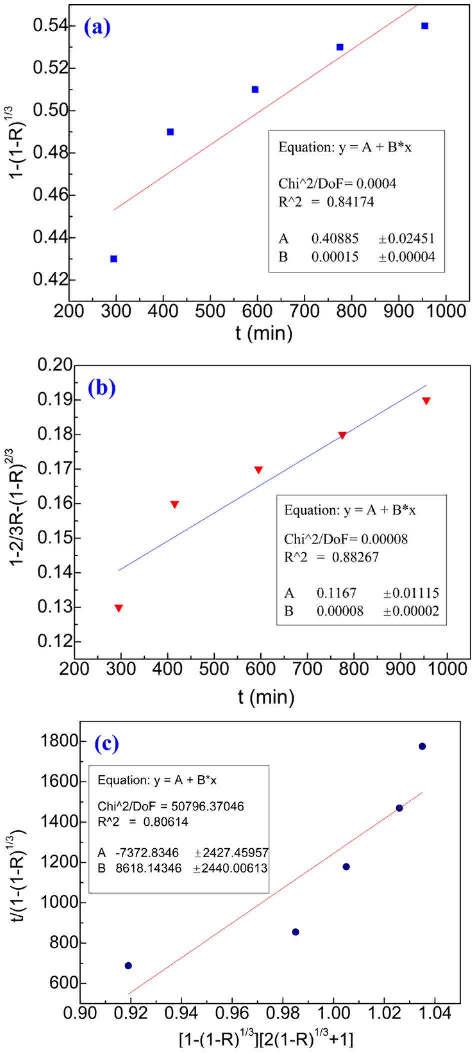

Figure 9. Kinetic plots of (a) chemical reaction control, (b) diffusion control, and (c) mixed control of REEs extraction at 1000 °C.

Potential of Different Recycling Methods for NdFeB Scrap. In the long term, recycling of NdFe magnet scrap is the main route for rare earth recovery. The optimal approach for recycling of a NdFeB magnet should be reusing it in its current shape, but this option is only suitable for the large and easily accessible magnets.[2] In the current industrial application, NdFeB scrap is recovered via hydrometallurgy including many wet steps, as well as two high-temperature steps (calcination and electrolysis) to generate new REs metals.[2,10−13] However, the obtained molten chlorides can be directly processed with electrolysis to prepare metals by the technology proposed in this study, which is obviously of low energy consumption. An overview of the comparison between the proposed route and hydrometallurgical route for NdFeB recycling is given in Table 1. Although several other novel processing routes[16−20] have also been investigated, they cannot meet the practical use in the current stage. So, the proposed technology in this study can be regarded as an environmentally friendly and promising process for recycling of NdFeB scrap because of its excellent environmental and economic benefits,

CONCLUSION

In the present study, a new recovery route was proposed and investigated using molten $MgCl_2$−KCl salt mixture as the extractant to achieve efficient selective recovery of REEs from NdFeB magnet scrap. Experimental results indicate that the REEs extraction rate increased with increasing the reaction temperature and reaction time, while the mass ratio of $MgCl_2$/scrap and the composition of the chlorides mixture also had a slight influence on the extraction rate. Good wettability is beneficial for promoting the reaction process between NdFeB and the molten chlorides. More than 90% of REEs in the scrap can be extracted into molten chlorides by keeping contact with $MgCl_2$−KCl at the optimum operating conditions. The results of EDS and XRD analyses confirmed that REEs in NdFeB magnet scrap can be selectively extracted using molten chlorides, and rare earth chlorides were generated in the obtained salts leaving Fe and B in the solid residue. Using model-fitting methods, the reaction mechanism was discussed,

Table 1. Overview of Comparison between Hydrometallurgical Route and Proposed Route for NdFeB Recycling

method	hydrometallurgical route	proposed route
processing steps	many wet processing steps calcination molten salts electrolysis	chlorination extraction molten salts electrolysis
types of magnet processed	generally possible to all types of magnet compositions	generally possible to all types of magnet compositions
REs recycling rate	>90%	>90%
energy consumption	high energy consumption	lower energy consumption required than hydrometallurgical route
chemical use	larger amount of mineral acid and oxalate organic solvent strong alkali	only magnesium chloride consumed potassium chloride used as flux but not consumed
emissions	large amount wastewater and acid	no emissions
resource utilization	portion of Fe lost in wastewater	nearly complete utilization of REs and Fe

and the rate-controlling step in the extraction process was proved to be diffusion. The experimental results in this study propose a new efficient REEs recycling process for NdFeB magnet scrap. In this process, only anhydrous $MgCl_2$ is consumed. The obtained rare earths chlorides can be directly used as the raw materials in electrolysis to prepare a REs alloy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

* E-mail: huazs83@163.com. Tel/Fax: +86 555 2311571.

Notes

The authors declare no competing financial interest.

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