The chlorination of La2O3 by MgCl2 in the LiCl-NaCl melts: Postprint

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Date: 2023-06-18T00:00:00+00:00

Abstract

The chlorination of rare earth oxides by MgCl2 was investigated in the molten chlorides. To reduce the solvent salt volatility, the LiCl-NaCl mixture was selected as a solvent by comparing the mass loss of the LiCl-NaCl with LiCl-KCl melts after the addition of MgCl2 in the temperature range of 873 K to 1073 K. The dissolution behavior of La2O3 was investigated in the LiCl-NaCl-MgCl2 melts by XRD measurements and ICP-AES analysis of the melts, which indicated that La2O3 was chlorinated by MgCl2 to produce LaCl3. The reduction peak of La(III) in the LiCl-NaCl-MgCl2-La2O3 melts was observed from cyclic voltammogram and square wave voltammogram. The Mg-La alloy obtained by galvanostatic electrolysis in the LiCl-NaCl-MgCl2-La2O3 melts was characterized by XRD and SEM-EDS, indicating that the Mg-La alloy consisted of Mg and La2Mg17 phases.

Full Text

Preamble

ChinaXiv Cooperative Journal NUCLEAR SCIENCE AND TECHNIQUES 26, S10310 (2015)

The chlorination of La_2O_3 by $MgCl_2$ in the LiCl-NaCl melts∗

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(Received May 9, 2014; accepted in revised form October 23, 2014; published online December 20, 2014)

The chlorination of rare earth oxides by $MgCl_2$ was investigated in molten chlorides. To reduce solvent salt volatility, the LiCl-NaCl mixture was selected as a solvent by comparing the mass loss of LiCl-NaCl with LiCl-KCl melts after the addition of $MgCl_2$ in the temperature range of 873 K to 1073 K. The dissolution behavior of La_2O_3 was investigated in LiCl-NaCl-$MgCl_2$ melts through XRD measurements and ICP-AES analysis of the melts, which indicated that La_2O_3 was chlorinated by $MgCl_2$ to produce $LaCl_3$. The reduction peak of La(III) in LiCl-NaCl-$MgCl_2$-La_2O_3 melts was observed in cyclic voltammograms and square wave voltammograms. The Mg-La alloy obtained by galvanostatic electrolysis in LiCl-NaCl-$MgCl_2$-La_2O_3 melts was characterized by XRD and SEM-EDS, indicating that the Mg-La alloy consisted of Mg and La_2Mg_{17} phases.

Keywords: LiCl-NaCl-$MgCl_2$ melts, Chlorination, La_2O_3, Mg-La alloy
DOI: 10.13538/j.1001-8042/nst.26.S10310

Introduction

Molten salts, particularly molten chlorides, are well known as excellent reaction media for selective solubilization or precipitation in chemical reactions and have been proposed as a promising route for raw material treatment [1]. More recently, pyrochemical separation processes in molten media have been suggested as a viable option for the future nuclear fuel cycle [2, 3]. Since rare earth chlorides are extremely sensitive to O_2 and H_2O, rare earth oxides are employed as raw materials for rare earth elements, which greatly simplifies the production process and reduces costs. However, rare earth oxides are usually insoluble in molten chlorides [4], prompting investigation into the direct chlorination of rare earth oxides in molten salts.

Sakamura et al. [5] reported that rare earth oxides could be chlorinated by $ZrCl_4$ in LiCl-KCl eutectic melts, while our previous work demonstrated that $AlCl_3$ could chlorinate Pr_6O_{11} [6] and Eu_2O_3 [7] in KCl-LiCl melts. However, $AlCl_3$ and $ZrCl_4$ have very low melting points and sublime easily [8]. To avoid sublimation of the chlorination reagent, $MgCl_2$ was selected to chlorinate rare earth oxides. Since the melting and boiling points of magnesium chloride are higher than those of $AlCl_3$ and $ZrCl_4$, an appropriate solvent was chosen by measuring the mass loss of LiCl-NaCl and LiCl-KCl melts after adding $MgCl_2$ at high temperature. The chlorination of La_2O_3 by $MgCl_2$ in the selected LiCl-NaCl melts was then explored using a series of techniques. To further confirm the chlorination of La_2O_3 by $MgCl_2$, galvanostatic electrolysis was performed to produce Mg-La alloy, which was characterized by XRD and SEM-EDS.

II. Experimental

A. Preparation and purification of melts

Mixtures of LiCl-NaCl (60:30 wt.%, analytical grade) and LiCl-KCl (40:50 wt.%, analytical grade) were first dried under vacuum for more than 24 h at 573 K

to remove excess water, then melted in an alumina crucible placed in a quartz cell inside an electric furnace. The melt temperature was measured with a nickel chromium-nickel aluminium thermocouple sheathed in an alumina tube. Magnesium and lanthanum ions were introduced into the bath in the form of dehydrated $MgCl_2$ (99.9%, analytical grade) and La_2O_3 powder (99.9%, analytical grade). The concentration of La_2O_3 in LiCl-NaCl-$MgCl_2$ melts was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo Elemental, IRIS Intrepid II XSP). All experiments were performed in an inert argon atmosphere (99.999%, high purity liquid argon) to prevent moisture contamination.

B. Electrochemical apparatus and electrodes

All electrochemical measurements were carried out using an Autolab electrochemical workstation (Metrohm Co., Ltd.) with the Nova 1.10 software package. A silver wire (d = 1 mm) dipped into a solution of AgCl (0.070 mol/kg) in LiCl-NaCl melts contained in a pyrex tube served as the reference electrode, and all potentials were referred to the Ag/AgCl couple. A spectrally pure graphite rod (d = 6 mm) served as the counter electrode. The working electrodes were tungsten (W) wires (d = 0.9 mm, 99.99% purity), which were polished thoroughly using SiC paper and cleaned ultrasonically with ethanol (99.8% purity) in an ultrasonic bath prior to use.

C. Preparation and characterization of samples

All samples were cleaned in ethanol in an ultrasonic bath to remove salts and stored in a glove box for analysis. These deposits were analyzed by X-ray diffraction (XRD, X'Pert Pro; Philips Co., Ltd.) using Cu Kα radiation at 40 kV and 40 mA. Microstructure and microzone chemical analyses were also carried out using scanning electron microscope with energy dispersive spectroscopy (SEM-EDS, JSM-6480A; JEOL Co., Ltd.).

III. Results and Discussion

A. The choice of new chloride system

There are numerous selection criteria for choosing a molten salt system, including salt stability, volatility, solubility of metallic species, and so on. It is important to select appropriate salt mixtures as solvent media to reduce salt loss and increase the solubility of RE_2O_3 in molten salts. Anhydrous LiCl-NaCl-$MgCl_2$ (6.0:3.0:1.5 wt.%) and LiCl-KCl-$MgCl_2$ (4.0:5.0:1.5 wt.%) powder mixtures were placed in a corundum crucible and heated to specified temperatures in an electric furnace under argon atmosphere. The mass loss of both LiCl-NaCl-$MgCl_2$ and LiCl-KCl-$MgCl_2$ systems was measured every 30 min using an electronic balance in the temperature range from 873 K to 1073 K. The comparison of mass loss in these two systems is shown in [Figure 1: see original paper]. The results demonstrated that mass loss in LiCl-KCl-$MgCl_2$ molten salts was much greater

than in LiCl-NaCl-$MgCl_2$, proving that LiCl-NaCl-$MgCl_2$ melts are more stable than LiCl-KCl-$MgCl_2$ melts in the experimental temperature range. Based on these results, a new salt system, LiCl-NaCl melts, was selected as the solvent.

B. Chlorination of La_2O_3 by $MgCl_2$ in the LiCl-NaCl melts

The concentration of La_2O_3, i.e., the concentration of La(III) ions in LiCl-NaCl melts, was determined by ICP. Anhydrous LiCl-NaCl-La_2O_3 (6.0:3.0:0.5 wt.%) and LiCl-NaCl-$MgCl_2$-La_2O_3 (6.0:3.0:1.5:0.5 wt.%) powders in a corundum crucible were heated to 873 K in an electric furnace under argon atmosphere and stirred to dissolve fully. Supernatant fluid from the molten salts was extracted and analyzed by ICP-AES and XRD. [Figure 2: see original paper] shows the ICP-AES analysis results of supernatant fluid from LiCl-NaCl-La_2O_3 and LiCl-NaCl-$MgCl_2$-La_2O_3 melts. The results indicate that La_2O_3 can hardly dissolve in LiCl-NaCl-La_2O_3 melts, but the concentration of La_2O_3 in LiCl-NaCl-$MgCl_2$-La_2O_3 melts can reach 3.68 wt.%. Evidently, the presence of $MgCl_2$ accelerates the solubilization of La_2O_3.

Figure 3: see original paper shows the XRD pattern of the dissolved supernatant salt from LiCl-NaCl-$MgCl_2$ melts, revealing that $LaCl_3$ exists in LiCl-NaCl-$MgCl_2$ melts. Since rare earth oxides and oxychlorides are insoluble in KCl-LiCl eutectic melts [9], MgO and La_2O_3 remain as solid particles and precipitates in LiCl-NaCl melts. The cooled melts were washed with water to remove soluble salts, then filtered to obtain insoluble substance. The insoluble substance was characterized by XRD, shown in Figure 3: see original paper, which indicated that it contained LaOCl and MgO. According to Bentouhami [10], LaOCl may form due to hydrolysis of $LaCl_3$ during washing of the melts with water. Based on these results, we propose that La_2O_3 is chlorinated by $MgCl_2$ to form $LaCl_3$ according to the reaction:
$3MgCl_2 + La_2O_3 \rightarrow 2LaCl_3 + 3MgO$.

Figure 4: see original paper shows typical cyclic voltammograms (CVs) in LiCl-NaCl melts before and after the addition of 1.0 wt.% $MgCl_2$ on W electrodes at 873 K. In curve 1, the cathodic signal A observed in the absence of $MgCl_2$ in LiCl-NaCl melts is ascribed to the deposition of Li(I) ions, since no alloy or intermetallic compounds exist in the W-Li binary system phase diagram [11] at 873 K. In the reverse scanning direction, an anodic peak A' corresponds to the dissolution of Li metal. After adding 1.0 wt.% $MgCl_2$, peaks C/C' appear in addition to peaks A/A', which are associated with the reduction and reoxidation of Mg metal. These results are consistent with our previous work [12]. Figure 4: see original paper shows CVs in LiCl-NaCl-La_2O_3 (2 wt.%) melts before and after the addition of 1.0 wt.% $MgCl_2$ on W electrodes at 873 K. The shape of curve 3 is identical to curve 1 in Figure 4: see original paper, indicating that the reduction peak of La(III) ions does not exist, i.e., La_2O_3 powder is nearly insoluble in LiCl-NaCl-La_2O_3 melts. In curve 4, the CVs show two new redox couples after adding 1.0 wt.% $MgCl_2$ to LiCl-NaCl-La_2O_3 melts. The C/C' peaks correspond to the deposition and subsequent oxidation of Mg metal,

while the cathodic peak B observed at approximately −2.07 V is ascribed to the reduction of La(III) ions. These results agree with those reported by Masset et al. and our previous work [13, 14]. The CVs indicate the existence of La(III) ions in LiCl-NaCl-La_2O_3 melts after the addition of $MgCl_2$.

[Figure 5: see original paper] shows square wave voltammograms from LiCl-NaCl-La_2O_3 melts before (a) and after (b) the addition of $MgCl_2$ at a step potential of 1 mV and frequency of 25 Hz. Only one peak C appears at −1.80 V, corresponding to the formation of pure Mg in LiCl-NaCl-La_2O_3 melts (Figure 5: see original paper). However, two distinct peaks B and C are observed at −1.80 V and −2.07 V, attributed to the formation of Mg and La metals in LiCl-NaCl-La_2O_3 melts after the addition of $MgCl_2$ (Figure 5: see original paper). This result indicates that the reduction of La(III)/La(0) occurs, confirming that La_2O_3 can be chlorinated by $MgCl_2$ to form La(III) ions.

C. Preparation and characterization of Mg-La alloy

The existence of La(III) ions in LiCl-NaCl-$MgCl_2$-La_2O_3 melts was explored using electrochemical techniques. To further demonstrate the chlorination effect of $MgCl_2$ on rare earth oxides, galvanostatic electrolysis was conducted in LiCl-NaCl-$MgCl_2$(10 wt.%)-La_2O_3(2 wt.%) melts. To obtain a large mass of Mg-La alloy in a relatively short time, electrolysis must be performed at a more negative current density. [Figure 6: see original paper] shows the XRD pattern of Mg-La alloy obtained by galvanostatic electrolysis at 1 A for 3 h. As seen from the XRD pattern, the Mg-La alloy is composed of Mg and La_2Mg_{17} phases.

To examine the distribution of Mg and La elements in the Mg-La alloy, elemental mapping analysis was employed. [Figure 7: see original paper] shows SEM and EDS mapping analysis of the Mg-La alloy obtained from LiCl-NaCl-$MgCl_2$ (10 wt.%)-La_2O_3 (2 wt.%) melts at 873 K. The La element is found to distribute mainly in the grey zone of the alloy's SEM photograph. To further investigate the elemental distribution, SEM equipped with EDS quantitative analysis was performed (Figure 7: see original paper and Figure 7: see original paper). The EDS results from points labeled A and B in the grey and dark grey zones indicate that the deposit is composed of Mg and La elements.

IV. Conclusion

Based on the determination of La(III) concentration in LiCl-NaCl-$MgCl_2$-La_2O_3 melts and XRD pattern measurements, La_2O_3 can be solubilized through chlorination by $MgCl_2$. A series of electrochemical techniques and the formation of Mg-La alloy obtained by galvanostatic electrolysis further confirm the existence of La(III) in LiCl-NaCl-$MgCl_2$-La_2O_3 melts. The results indicate that La_2O_3 can be chlorinated by $MgCl_2$ according to the reaction: $3MgCl_2 + La_2O_3 \rightarrow 2LaCl_3 + 3MgO$, which may be applicable for the treatment of waste nuclear fuel through pyrometallurgy.

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