



Investigation on the reaction progress of zirconium and cuprous chloride in the LiCl–KCl melt



Yanqing Cai^a, Hongxia Liu^a, Qian Xu^{b,*}, Qiushi Song^a, Liang Xu^a

^aSchool of Materials Science and Metallurgy, Northeastern University, Shenyang, 110004, PR China

^bSchool of Materials Science and Engineering, Shanghai University, Shanghai, 200072, PR China

ARTICLE INFO

Article history:

Received 11 October 2014

Received in revised form 8 February 2015

Accepted 9 February 2015

Available online 11 February 2015

Keywords:

zirconium

CuCl

molten chlorides

reaction progress

electrochemical test

ABSTRACT

The in-situ preparation of LiCl–KCl–ZrCl₄ melt was investigated by the replacement reaction between Zr and CuCl in LiCl–KCl melt at 500 °C, and the reaction progress was also investigated by a series of electrochemical techniques, such as cyclic voltammetry, square wave voltammetry and open circuit chronopotentiometry. The electrochemical signals show that the concentration of Zr(IV) ions increases gradually and then reaches to the maximum value with the reaction time increasing from 0 to 180 min, while the concentration of Cu(I) ions decreases rapidly and drops to below the detection limit of the electrochemical tests. Meanwhile, the concentrations of Cu and Zr ions in the melt were determined over time by chemical analysis in the course of reaction. The results are in good agreement with the electrochemical tests. Finally, LiCl–KCl melts with (0.837 wt.% ~ 1.709 wt.%) ZrCl₄ are obtained, and the final concentration of Cu(I) in the melt has dropped to below 0.025 wt.% when the reaction lasted for 180 min.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Zirconium is an important component for the nuclear-power industry. It can be used in nuclear reactors for cladding the nuclear fuels and for structural purposes because of its low neutron-capture cross-section and good resistance to corrosion under normal service conditions [1]. The nuclear power industry consumes around 90% of the zirconium prepared each year, which must be nearly free of hafnium because hafnium absorbs neutrons very strongly.

There are mainly four methods for refining of zirconium, such as iodide refining process, electrorefining process, zone melting process, and electron beam melting process [1]. Among them, the most commonly used method is the iodide refining process. Although the high-purity zirconium with a total content of impurities up to 10⁻⁶ can be obtained by this process, the iodide process is expensive and not very productive, and should be replaced by more promising methods. The electrorefining process based on molten salt containing zirconium chlorides or fluorides has been developed as a promising option for refining of zirconium from impure zirconium metal, alloy or spent metal fuels [2,3].

By the electro-chemical refining process, a low-melting Cu–Sn–Zr alloy is proposed to be a liquid anode [4] at the bottom of the

electrochemical cell in the study of refining the sponge zirconium (Zr ≥ 99.4%), which with a small amount of impurities, i.e. Hf, Ni, Cr, Mg, Al, etc., expecting to eventually obtain a higher purity nuclear grade zirconium at the cathode. The chosen of the liquid alloy anode can not only reduce the operating temperature, but also expect to provide a low cost and semi-continuous process for production nuclear grade zirconium. The electrorefining and electrochemical process of Zr has been studied in various molten salt systems, including all-chloride baths such as LiCl–KCl–ZrCl₄ [2,5–7], KCl–ZrCl₄ [8,9], all-fluoride baths such as LiF–NaF–KF–ZrF₄ and K₂ZrF₆ [10,11], LiF–KF–ZrF₄ [3], LiF–CaF₂–ZrF₄ [12] and chloride–fluoride–mixed baths such as KCl–NaCl–ZrF₄ [13], KCl–NaCl–K₂ZrF₆ [8,13,14], and LiCl–KCl–K₂ZrF₆ [15] at temperature ranges of 450 °C to 750 °C. However, the operating temperature of the all-fluoride baths is 100 °C ~ 200 °C higher, and the corrosion issue is more severe compared to those of all-chloride baths. In consideration of the melting point of liquid alloy anode and a moderate experimental condition, the Zr electrorefining process is proposed in LiCl–KCl–ZrCl₄ molten salt at 500 °C in the initial stage of research. However, the starting zirconium compound, ZrCl₄, usually sublimates at 331 °C [1,5], and some will be lost if it is directly introduced into the salt. Thus, the preparation of the molten salt with the content of ZrCl₄ has become one of the most challenges in the research of electrorefining zirconium in the molten salt.

A few papers have been published on the in-situ preparation of chlorides for electrorefining of alloy or reprocessing spent metal

* Corresponding author. Tel.: +86 24 83684943; fax: +86 24 83687731.
E-mail address: qianxu201@mail.neu.edu.cn (Q. Xu).

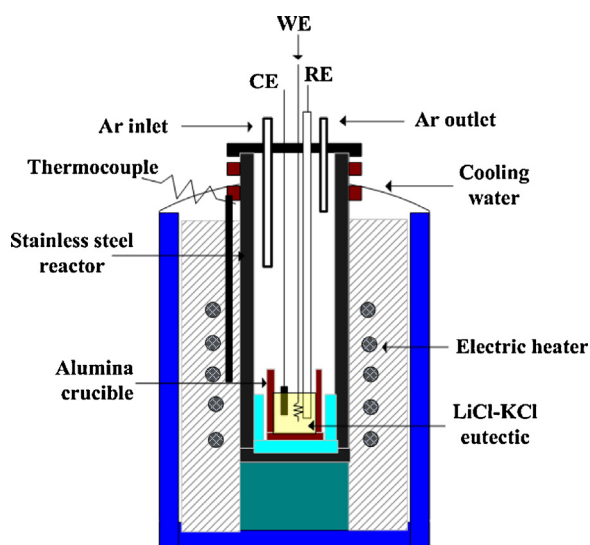


Fig. 1. Schematic diagram of experimental apparatus.

fuels. Murakami et al. [6] have reported the method about the preparation of LiCl–KCl–ZrCl₄ melt with CdCl₂ and zirconium metal according to the equation (1). And the electrochemical behavior of Zr at a liquid Cd electrode for recovering Zr on Cd electrode has also been investigated. The chemical equilibration of U–Pu–Zr fuel with stoichiometric amounts of CdCl₂ in LiCl–KCl molten salt, which leads to the formation of UCl₃ and PuCl₃, has also been reported by Kuznetsov et al. [16] and Ghosh et al. [17]. However, the chlorinating and oxidizing agent, CdCl₂ is toxic and expensive, and the final product Cd will be an impurity and cause heavy metal pollution. What's more, the details about the reaction progress between CdCl₂ and zirconium or uranium metals were not mentioned in their researches.



Since cuprous chloride is nontoxic and easily obtained, and the redzate Cu will return to the Cu–Sn–Zr anode, without introducing impurities, then it is chosen as the reactant in the replacement reaction with Zr. Hence the present work focused on the in-situ preparation of ZrCl₄ by the chemical equilibration of zirconium with cuprous chloride in the LiCl–KCl melt, which can be used as the electrolyte in the electrorefining of Zr with the low-melting liquid alloy anode. There are few reports on investigation about reaction between Zr and CuCl in the molten salt. We try to use the electrochemical behavior changes of Zr and Cu in the LiCl–KCl melt to monitor the reaction progress in-situ by several electrochemical methods, such as cyclic voltammetry, square wave voltammetry and open circuit chronopotentiometry. A special attention was paid to the occurrence of intermediate compounds. Furthermore, the final composition of the melt was examined by ICP–AES analysis.

2. Experimental

2.1. Electrochemical apparatus and chemicals

The experimental apparatus used in this work is shown in Fig. 1. A three-electrode electrochemical cell was assembled in an alumina crucible, which was positioned in a stainless steel vessel and heated in the electric furnace. A chromel–Alumel thermocouple was used for temperature measurement with an accuracy of ± 2 K. The

reference electrode (RE) was self-assembled by a silver wire ($\varnothing 1$ mm, 99.99% purity) immersed in the LiCl–KCl melt with 1.0 wt.% AgCl, which was contained in a close-ended mullite tube. Therefore, all potentials were referred to this electrode unless otherwise stated. A graphite rod ($\varnothing 10$ mm, spectroscopically pure) was used as the counter electrode (CE), which was provided by the Shanghai new graphite material Co., Ltd. of Sinosteel Corporation (Shanghai, China). A molybdenum wire ($\varnothing 1$ mm, 99.95% purity) was served as the working electrode (WE) for the investigation of electrochemical behaviors. The active electrode surface area was determined by measuring the immersion depth of the electrode in the molten salt after each experiment. All of the electrochemical experiments were conducted under a high-purity argon atmosphere.

All chemicals used in this study were analytical grade. The LiCl–KCl eutectic (59:41 mol%) was used as electrolyte, which was dried for more than 72 h at 300 °C to remove residual water and melted under argon atmosphere in the set up shown in Fig. 1. In order to eliminate the residual water and other possible redox-active impurities, pre-electrolysis of the LiCl–KCl melt was conducted under 2.8 V for 2 h between two graphite rods. Copper (I) was introduced into the bath in the form of dehydrated CuCl powders (Sinopharm, China). Anhydrous zirconium tetrachloride was obtained from Aladdin and used as such without further purification. Molybdenum wire, silver wire, and zirconium rods were supplied by Rare Metallic Co., Ltd of Shenyang, which were used after polishing by sandpaper and then washing with alcohol.

All the electrochemical measurements were carried out with AUTOLAB/PGSTAT320 potentiostat from M/s. EcoChemie, Netherlands and the data acquisition was controlled by NOVA 1.6 software for square wave voltammetry and by GPES 4.9 software for cyclic voltammetry and open circuit chronopotentiometry. An X-ray diffractometer was employed to characterize the recovered precipitates. A quantitative compositional measurement of the melt at various times was made by using an inductively coupled plasma–atomic emission spectrometer (ICP–AES).

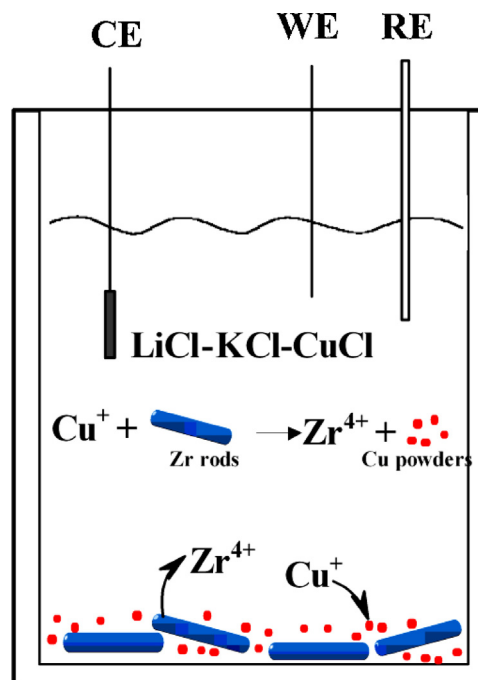


Fig. 2. Schematic diagram of the replacement reaction.

Download English Version:

<https://daneshyari.com/en/article/184172>

Download Persian Version:

<https://daneshyari.com/article/184172>

[Daneshyari.com](https://daneshyari.com)