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Controlling the leakage of liquid bismuth cathode elements in ceramic crucibles used for the electrowinning process in pyroprocessing

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ABSTRACT

Pyroprocessing has shown promise as an alternative to wet processing for the recycling of transuranics with a high proliferation resistance. However, a critical issue for pyroprocessing is the ceramic crucibles used in the electrowinning process. These ceramic crucibles are frequently damaged by thermal stress, which results in significant volumes of crucible waste that must be properly disposed. Transuranic waste (TRU) elements intrude throughout the pores of a damaged crucible. The volume of generated radioactive waste is a concern when dealing with nuclear power plants and decontamination issues. In this study, laser treatment and sintering were performed on the crucibles to minimize the TRU elements trapped within. Secondary ion mass spectroscopy was used to measure the intrusion depth of Li in the surface-treated ceramics.

1. Introduction

In pyroprocessing, the LiCl–KCl eutectic salts that contain the accumulated transuranic waste (TRU) elements and other rare-earth elements (RE) remaining after the electrorefining process are transferred to the electrowinning process. The electrowinning process recovers TRU, U, and other rare-earth elements from the molten salt by applying a voltage so that they deposit on liquid bismuth cathodes (LBCs) or liquid cadmium cathodes (LCCs) [1]. This is a key step to resolving nonproliferation concerns because TRU can be electrodeposited with only uranium and rare-earth fission products. A nonconductive crucible should be used to collect these elements. Various ceramics have already been used in crucibles, such as alumina, beryllia, and zirconia. However, none of those crucibles have been successfully applied to long-term use [2–5]. Vaden et al. [6] applied beryllia as a crucible material for an electrowinning process with an LCC. Compared to other ceramics, beryllia performed better with improved mechanical stability; this was mainly due to the chemical inertness of beryllia and its high thermal conductivity of 330 W/m·K.

In the electrowinning process, chemically reactive fission products react with the ceramic crucible to form oxides. Such chemical reactions increase the mechanical bonding stress between the crucible and LCC or LBC after solidification. Ku et al. [7] experimented with the intrusion of Li into beryllia. Li critically damaged the beryllia, which rendered the latter unusable. This phenomenon also leads to the migration of TRU and RE into the pores of ceramic crucibles. The loss of TRU and RE during the electrowinning process becomes a critical matter with regard to proliferation resistance measures for pyroprocessing. Minimizing the leakage of TRU and RE is also important to ensuring the mechanical and chemical stability of the ceramic crucibles.

In previous research, the intrusion of elements during electrowinning was attributed to inherent pores on the surface of the ceramic crucibles. The surface characteristics of the ceramic material can be controlled by regulating the surface morphology and porosity [8,9]. Laser surface treatments have been conducted to eliminate the pores on an alumina surface [10]. Hence, laser surface treatment was performed in the present study to eliminate the pores and cracks on the surfaces of ceramic crucibles and minimize the intrusion of TRU elements. Sintering was also performed with alternative ceramic materials to achieve denser surface conditions

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Table 1
The calcium aluminate sintering condition and the relative density after sintering. (X: the samples were disappeared after sintering).

Sample numbering	Component	Sintering temperature, °C	Relative density, %	Compression power, MPa
1	Al_2O_3*CaO	1500	80.4	250 MPa
2	Al_2O_3*$CaCO_3$		94.9	
3	Al_2O_3*$Ca(OH)_2$		92.9	
4	Al_2O_3*CaO	1600	91.9	
5	Al_2O_3*$CaCO_3$		X	
6	Al_2O_3*$Ca(OH)_2$		X	
7	Al_2O_3*CaO	1550	86.8	
8	Al_2O_3*$CaCO_3$		95.3	
9	Al_2O_3*$Ca(OH)_2$		94.3	

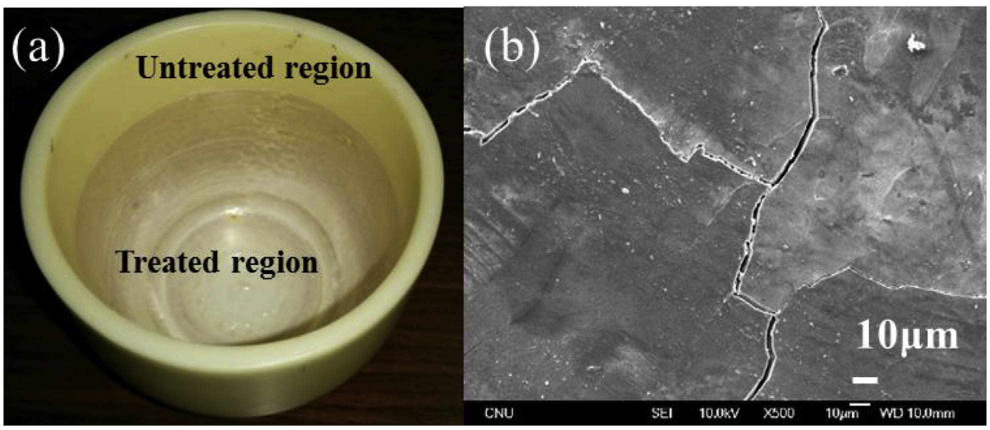

Fig. 1. The laser surface treated alumina crucible and SEM image.

than alumina crucibles. This paper describes the treatment of the porous ceramic surface to minimize the intrusion of LBC elements. The intrusion depths of Li and Bi in treated and untreated ceramics were analyzed with secondary ion mass spectroscopy (SIMS). Li and La were used as representative LBC materials because they are very reactive and TRU and fission products (FPs) could not be used owing to handling difficulties. The effect of Li on the ceramic crucible stability was evaluated under electrowinning process conditions.

2. Experimental

2.1. Laser surface treatment of ceramics

Laser surface treatment has been successfully performed on an Al_2O_3 plate to eliminate the surface pores [10]. Therefore, an Al_2O_3-based crucible was adopted as the near net shape. Mullite and calcium oxide can be used with laser surface treatment to eliminate pores within the ceramic surface layer. Thus, the ceramic samples were prepared by using mullite and CaO powder on an Al_2O_3 plate. CaO powder was doped on the Al_2O_3 plate by using a 3% solution of polyvinyl alcohol. The laser was applied to the ceramic surface by using a commercial CO_2 laser. The spot size of the laser was 1 mm, and the wavelength was 10.63 μm. The surface morphology after the laser surface treatment was analyzed by scanning electron microscopy set at 10 kV.

2.2. Surface morphology control with sintering

Smooth and pore-free surfaces were observed after the laser surface treatment of CaO in Al_2O_3; however, laser surface treatment with powder is difficult. The powder melted by the laser tends to make spherical shapes because of the surface tension, which makes it difficult to produce a flat surface. Using powder to make a flat surface is not impossible but complicates the fabrication of a crucible. Sintering is a promising method for developing a commercially viable process to make ceramic crucibles [11,12]. Here, CaO, $Ca(OH)_2$, and $CaCO_3$ were used to make calcium aluminate. $Al_2O_3 \cdot CaO$, $Al_2O_3 \cdot CaCO_3$, and $Al_2O_3 \cdot Ca(OH)_2$ compounds were ball-milled for 1 day to properly mix the compounds. The compounds were then compressed at a pressure of 250 MPa. Table 1 presents detailed information on the sintering conditions and relative

Table 2
Ceramic materials properties [10,13].

	Chemical stability	Melting	Thermal conductivity, W/mK	Porosity control
Al_2O_3	Middle	O	Middle, 35	LT (O), crack
MgO	Middle	X	Middle, 30	LT (X)
Y_2O_3	Good	–	Weak, 8–12	LT (X) Weak for thermal stress
BeO	Good	X	High, 330 → but, Toxic & Expensive	LT (X)
Mullite	Middle	O	Weak, 3.5	LT (X) Weak for thermal stress
$CaAl_2O_4$	Middle	O	Middle, 25	LT (O) → Sintering