

Research Article

Stability of Tungsten Crucible against Uranium, Rare Earth, Cadmium, and Chlorides for Cathode Process in Pyroprocessing

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The stability of W against U, rare-earth (RE) elements, Cd, and various chlorides was evaluated by melting and distillation testing. Three runs were performed with a W crucible to examine its reactivity: (i) RE melting by induction heating, (ii) salt distillation test of U-dendrite and various chlorides, and (iii) Cd distillation test from U–Cd alloy. The W crucible remained stable after the RE melting test using induction melting, exhibiting its applicability for induction heating systems. The salt distillation test with the W crucible at 1050°C exhibited the stability of W against U and various chlorides, showing no interaction. The Cd distillation test with the W crucible at 500°C showed that the crucible was very stable against Cd, maintaining a shiny surface. These results reveal that the W crucible is stable under operation conditions for both salt and Cd distillation, suggesting the high potential utility of W as a crucible material for application in cathode processes in pyroprocessing.

1. Introduction

Electrorefining is one of the most important pyroprocessing techniques for recovering uranium and transuranic (TRU) elements from spent fuel [1, 2]. In this process, the spent fuel is dissolved in a molten LiCl–KCl eutectic chloride salt via electrolysis and U is selectively deposited onto the surface of a cathode electrode [3–6]. Then, the U/TRU elements remaining in the eutectic salt are electrochemically recovered with rare-earth elements (REs) as contaminants by a liquid Cd cathode (LCC) [6–8]. Two types of product, i.e., U and U/TRU/RE, are therefore recovered by electrorefining.

The U and U/TRU/RE products contain many impurities, such as adhered salts (LiCl, KCl, and (U, RE)-chlorides) and/or Cd. Because these impurities have much higher vapor pressures than U and TRU, the products are purified by cathode process [9, 10]. Generally, the product is heated at a temperature above 900°C in a vacuum heating system. An induction heating furnace is used for the cathode process at the Idaho National Laboratory (INL) and the Korea Atomic Energy Research Institute (KAERI), because of its high heating efficiency and easy scalability. Graphite is used for the

crucible because it shows good thermal and electrical conductivity and a high melting temperature. However, graphite reacts with both U and TRU [11, 12]; therefore, ceramic crucibles or liners are adopted for the cathode process.

Operations at high temperatures inevitably generate significant ceramic waste which was produced by a crucible failure. Many researchers have thus investigated solutions to this problem [13]; one suggested method is the use of metallic crucibles instead of ceramics. W, Ta, and Mo are candidates possessing high melting temperatures. Among these metals, W is promising because it has good mechanical properties and a relatively low cost. Thus it is worth investigating the applicability of W as a crucible for the cathode process in pyroprocessing.

The objective of this study is to examine the stability of W against U, RE metals, Cd, and various chlorides, which can be contained in crucibles during cathode processes. In this study, we have used U instead of TRU as a surrogate. Three experiments were performed with a W crucible to examine its reactivity: (i) a RE melting test using induction heating, (ii) salt distillation of U-dendrite and various chlorides, and (iii) Cd distillation from a U–Cd alloy. The RE metal melting

TABLE 1: Experimental conditions for the tests of W stability.

	Feed Materials	Experimental Conditions	
		Temperature and Pressure	Holding Time [min]
RE melting	La, Ce, Nd	>1200°C, <10 ⁻⁴ Torr	60
Salt distillation	U, LiCl, KCl, NdCl ₃ , CeCl ₃	1050°C, <1 Torr	150
Cd distillation	U–Cd alloy	500°C, <1 Torr	200

test evaluated the reactivity of W crucible with RE metals and tested the applicability of a W crucible in induction heating systems. La, Ce, and Nd were used as representative RE metals. The salt distillation test examined the reactivity of the W crucible with U and various chlorides, simulating salt removal for the recovery of purified U. In the test, LiCl, KCl, UCl₃, NdCl₃, and CeCl₃ were used as representative chlorides, based on a previously reported flowsheet [14, 15]. The Cd distillation test evaluated the stability of W against Cd, simulating Cd distillation for U/TRU/RE recovery. Based on the obtained results, we discussed the applicability of W crucibles for the cathode process.

2. Materials and Methods

2.1. Sample Preparation. RE metal ingots (La, Ce, and Nd; >99.9% purity, Rare Metallic Co., LTD.) were used for the melting test. RE chloride powders (NdCl₃ and CeCl₃; >99.95% purity, Alfa Aesar) and Cd shot (>99.5% purity, Alfa Aesar) were used for the distillation test. U-dendrite was prepared by electrolytic deposition; details of its morphology can be found in the literature [16–19]. The U-dendrite contained approximately 30 wt% LiCl–KCl–UCl₃ adhered salt as impurities. A Cd–U alloy was also prepared for the simulated U/TRU recovery test. About 31.8 g Cd and 18.3 g U were loaded into the W crucible, which was heated to 500°C under atmospheric pressure and maintained at this temperature for 5 h to dissolve U into the Cd pool. The Cd–U alloy was then cooled to ambient temperature for use in the Cd distillation test. Table 1 shows the materials and experimental conditions for the test.

2.2. RE Melting Test. For the melting test, ~12 g of mixed RE metals (6.0 g La, 2.9 g Ce, and 2.9 g Nd) had been placed into a W crucible with an outer diameter (OD) of 30 mm and a height of 30 mm (3mm of thickness). The crucible was placed in an induction heating furnace (Y&I Tech., ATECF-10/380T (10kW, 20-40 kHz)) which was evacuated to a pressure of <10⁻⁴ Torr by a rotary pump and a diffusion pump. The evacuated furnace was heated to 1200°C for approximately 1 h and then cooled to atmospheric temperature.

2.3. Distillation Test. Distillation was performed using Cd/salt distillation equipment fabricated in the laboratory [20]. The apparatus was composed of a two-zone tube furnace, an internal vacuum tube, an evacuation system, and a control unit. The two-zone tube furnace was designed to heat the internal vacuum tube to >1200°C. Before distillation, the internal vacuum tube was evacuated with a rotary pump

to a pressure below 10⁻¹ Torr. For the removal of residual salt or Cd, the product was loaded into a furnace and heated to the target temperature (salt distillation test – 1050°C; Cd distillation – 500°C) at a rate of 6°C/min. The heating conditions are also listed in Table 1.

2.4. Characterization. The morphology of the products was observed with scanning electron microscopy (SEM; Hitachi, S-8010) in conjunction with energy-dispersive X-ray spectroscopy (EDS; Horiba, EX-250 X-max). The product after distillation was dissolved in concentrated HCl and HNO₃ on a hot plate at 200°C. Then, the composition was analyzed via an inductively coupled plasma–optical emission spectrometer (ICP-OES; ACTIVA M, Horiba Jobin Yvon SAS).

3. Results

3.1. RE Melting Test. The stability of W crucibles against RE (La, Ce, and Nd) metals was evaluated at a temperature above 1200°C (above the melting temperatures of 921, 799, and 1021°C for La, Ce, and Nd, respectively). In total, 12 g RE metals were loaded into the W crucible and heated using the induction heating system. Figure 1 shows the loaded RE metals before and after the melting test.

After the melting test, the ingot-shaped RE metals are successfully melted, as shown in Figure 1(c). The entire crucible and resolidified RE metals were cut and characterized by SEM. Figure 2 shows the macroscopic and microscopic morphology of the cross-section.

No interaction between the crucible and RE is observed visually (Figure 2(a)). The cross-sectional SEM image confirms the stability of the W crucible against molten RE metals (Figure 2(b)). The RE metal was then sampled and characterized by ICP-OES to evaluate the stability. Table 2 shows the composition of the solidified product.

The amount of W is below the detection limit of ICP-OES, which is consistent with the SEM results. The composition of RE metals differs slightly from that of the loaded feed metals. We attribute this small difference to detection errors in ICP-OES (<10% depending on the materials).

3.2. Salt Distillation for U Purification. The stability of the W crucible during salt distillation for U recovery was evaluated. About 10.5 g (6.0 g U + 2.6 g LiCl–KCl–UCl₃ + 1.0 g CeCl₃ + 0.9 g NdCl₃) of the feed materials had been loaded in a W crucible. Figure 3 shows the feed materials before and after the salt distillation test for U purification.

U dendrites containing LiCl–KCl–3 wt% UCl₃, as formed by U electrorefining, are used for the test (Figure 3(a)).

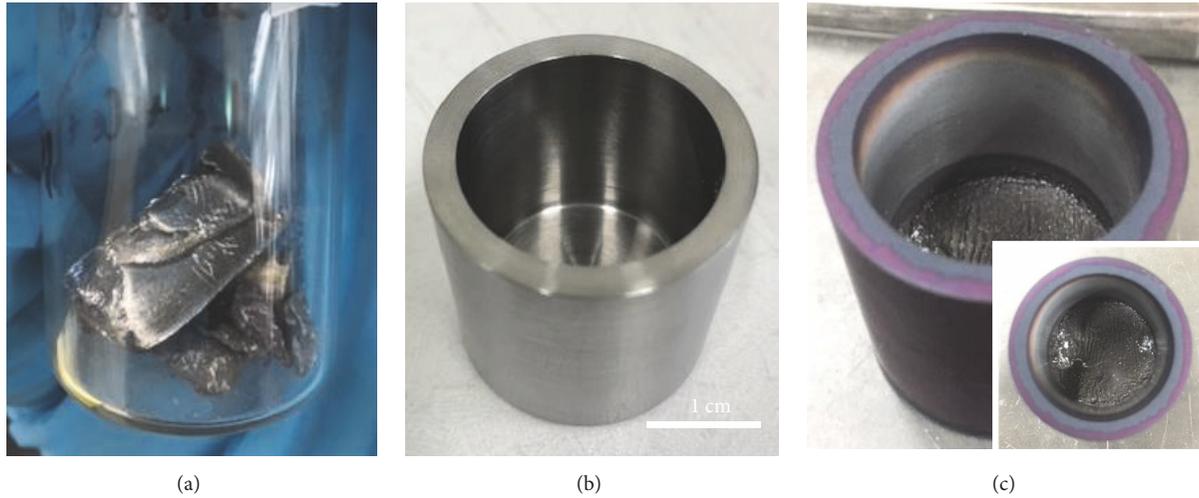


FIGURE 1: RE metals before (a, b) and after melting test (c); (a) RE metals, (b) W crucible, and (c) molten and resolidified RE metals in crucible.

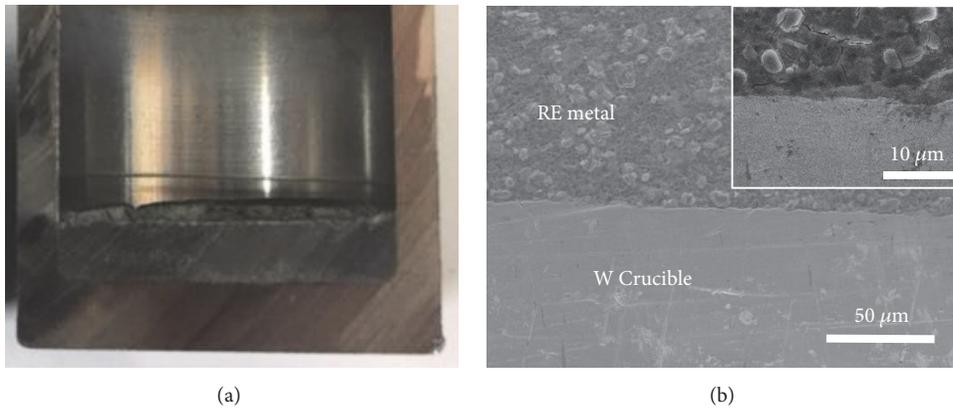


FIGURE 2: Images of molten RE metals in W crucible. (a) Macroscopic and (b) microscopic morphology of the resolidified product cross-section.

TABLE 2: Chemical composition of the resolidified RE metals in W crucible.

Elements	Composition [wt%]			
	La	Ce	Nd	W
RE product	53.0	22.1	24.8	<0.01

TABLE 3: Chemical composition of U-dendrite remains after salt distillation test.

Materials	Composition [wt%]			
	U	Ce	Nd	W
U remains	99.96	0.02	0.02	UD*

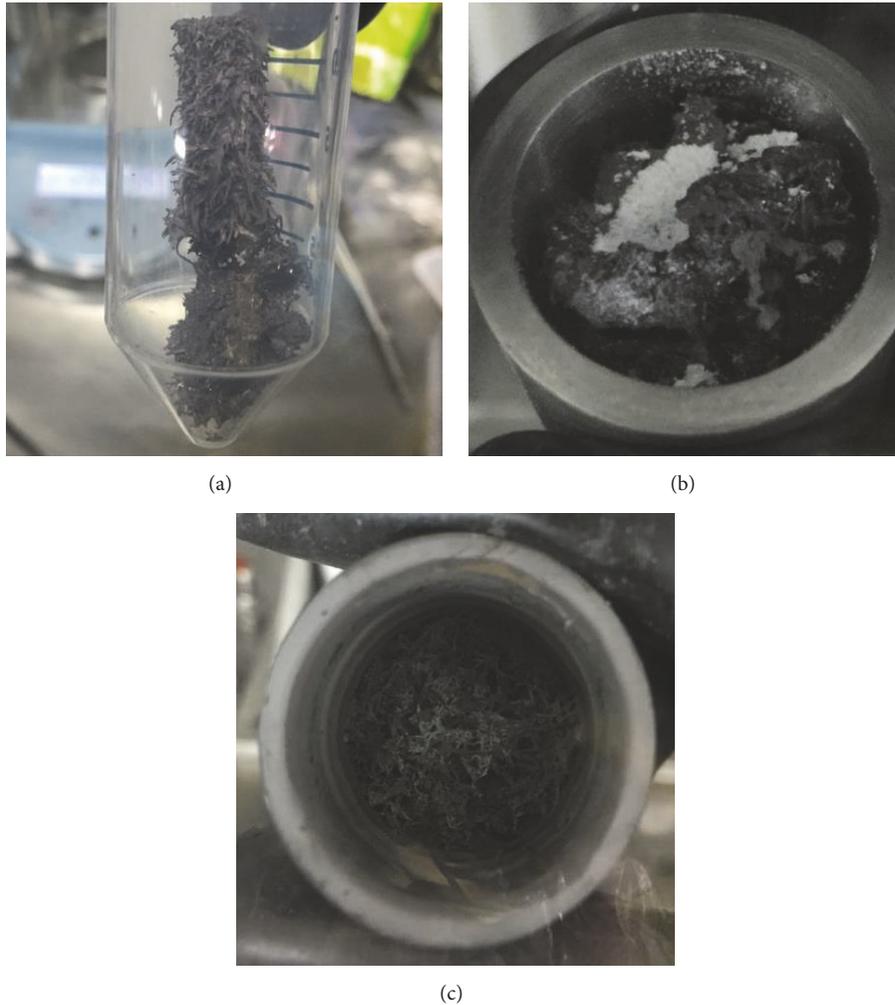
* Under detection limit of ICP-OES.

The dendrites are loaded and mixed with RE chlorides in a W crucible (Figure 3(b)) to simulate salt distillation via pyroprocessing [10]. The loaded crucible is heated to 1050°C in a vacuum for 150 min. The temperature is sufficient to evaporate LiCl, KCl, UCl₃, and the RE chlorides; the

evaporation temperatures of LiCl, KCl, UCl₃, and the RE chlorides are reportedly approximately 710, 760, 830, and 890°C, respectively [21]. Figure 4 shows the temperature and pressure changes as a function of the distillation time.

The pressure is slightly increased at the beginning of distillation. We attribute the pressure increase around 300–400°C to the evaporation of adhered moisture [22]. The pressure becomes high at approximately 700°C, indicating the evaporation of the LiCl–KCl salts. The pressure is slightly decreased with further increases in temperature and stabilizes at 1050°C. We attribute this to the termination of evaporation. Figure 3(c) shows the remains after distillation. Because the operation temperature is below the melting temperature of U (i.e., 1132°C), the shape of the dendrites is observed to remain after testing. Table 3 shows the composition of the remains, as characterized by ICP-OES.

It is clear that W is not dissolved into the U during salt distillation, as no W is detected in the remains. In the initial loading, ~4 g of salt (~43 wt% of the feed materials) was mixed with U-dendrite, but the salt is almost completely removed after heating. Very small amounts of RE metals are



(a)

(b)

(c)

FIGURE 3: Images of materials (a, b) before and (c) after salt distillation test; (a) U dendrites, (b) mixture of dendrites with salts, and (c) remains.

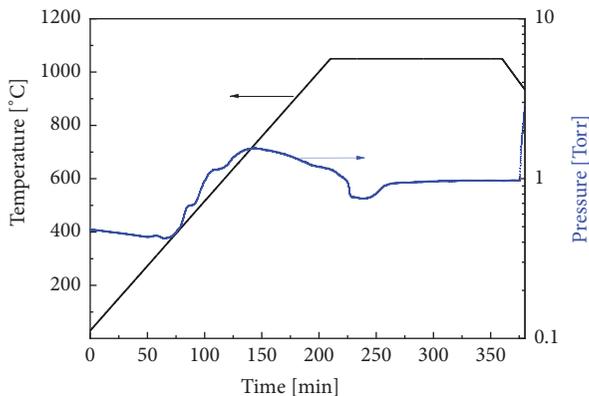


FIGURE 4: Temperature and pressure profiles as a function of time during salt distillation.

detected. We consider that RE oxide impurities in the RE chlorides remain in the crucible without evaporation. The

results suggest that the W crucible is applicable for the salt distillation process.

3.3. Cd Distillation for U/TRU Purification. The stability of the W crucible during Cd distillation for U/TRU/RE recovery was evaluated using a Cd/U alloy to simulate a U/TRU/RE/Cd alloy. Figure 5 shows the feed materials before and after the Cd distillation test.

To fabricate the Cd-U alloy, a U ingot and Cd shot are loaded into the W crucible (Figure 5(a)) and melted at 500°C (Figure 5(b)). They are then distilled at the temperature of 500°C in vacuum. Figure 6 shows the temperature and pressure changes as a function of distillation time.

The pressure is slightly increased with increasing temperature. We attribute the increase in pressure at ~300–400°C to the evaporation of moisture. The pressure is further increased at 500°C, indicating the evaporation of Cd [20]. The pressure is decreased after 220 min of distillation, indicating the termination of Cd evaporation. Figure 5(c) shows the morphology of the remains, exhibiting the removal of the

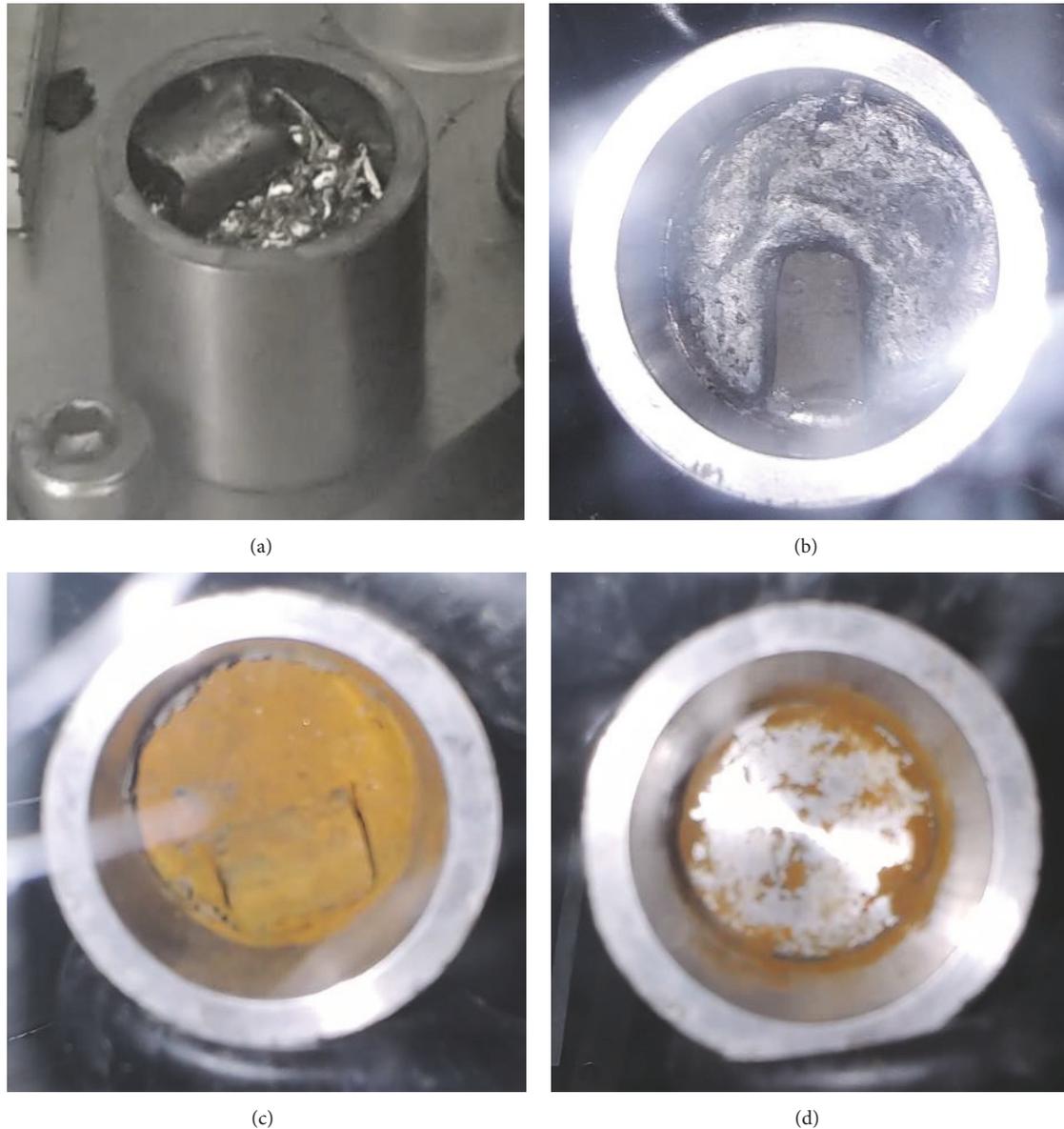


FIGURE 5: Images of the W crucible before and after the distillation test: (a) W crucible loaded with U and Cd was loaded, (b) after fabrication of U-Cd alloy, (c) after Cd distillation test, and (d) after dumping of the remains.

metallic Cd. Furthermore, the bottom of the W crucible retains a shiny metallic finish after dumping of the remains (Figure 5(d)). The result reveals that the W crucible is very stable at the low operation temperature used for the Cd distillation. The remains are easily dumped out without any scraping, supporting the stability of the W crucible for Cd distillation.

4. Discussion

We evaluated the stability of W crucibles against U, RE metals, Cd, and various chloride salts, which are possible crucible contents in cathode processes, according to the materials flowsheet for pyroprocessing [14, 15]. The cathode

process can treat two types of product. One is U-dendrite (salt distillation), and the second is U/TRU/RE dissolved in molten Cd (Cd distillation).

Regarding the U-dendrite recovery, the crucible contained about 30 wt% of adhered salt after the electrorefining process. The main purpose of the cathode process of U-dendrite is the removal of residual salt, which may contain PuCl_3 . The evaporation temperature of chloride salts is approximately 900°C [10]; therefore, we believe that the operation temperature of 1050°C used for U-dendrite purification (Figure 4) is sufficient to remove adhered salts in this study. The major component of the remains after high-temperature heating is U. Kurata previously reported the binary U-W phase diagram [23] and showed that W is very stable against

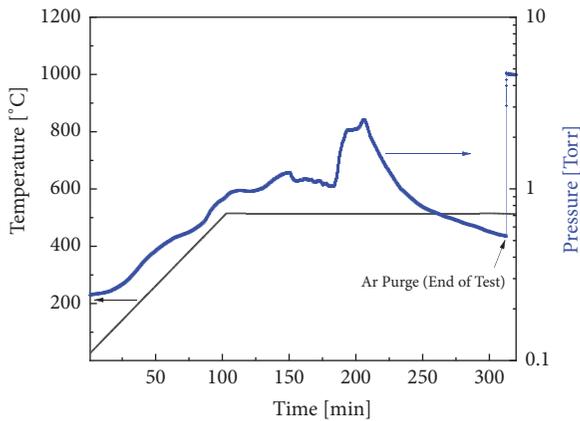


FIGURE 6: Temperature and pressure profiles as a function of time during Cd distillation test.

U below the U melting temperature. This estimation supports the experimental results very well. The experimental results demonstrate that the W crucible is stable against U and various chlorides in operation below 1050°C, indicating that the W crucible is feasible for the cathode process to purify U-dendrite.

For U/TRU/RE recovery, U/TRU/RE is dissolved in molten Cd during the electrorecovery process. The purpose of the cathode process of this product is the removal of Cd to yield a U/TRU/RE alloy [9]. The evaporation temperature of Cd is approximately 400°C [20], which is relatively low compared to that used for salt distillation in U purification. The experimental results thus confirm that the W crucible is very stable against Cd for the removal of Cd from the Cd-U alloy, maintaining a shiny surface. W is also very stable against U at this temperature, as shown in the salt distillation test. Simultaneously, the RE metal melting test demonstrates that W is stable against RE metals. Kurata reported that W is stable against Pu below the U-Pu eutectic temperature of 640°C [23]. These results suggest that W is stable against U, TRU, RE metals, and Cd at temperatures below 500°C, which is the operation temperature used in Cd distillation. Therefore, a W crucible is feasible for use in cathode processing to remove Cd from U/TRU/RE.

The successful melting of RE metals with the induction heating furnace indicates that the W metal crucible is applicable to induction melting systems. Moreover, the reactivity test of the W crucible against U, RE, Cd, and various chloride salts reveals that the W crucible is stable for operation conditions of both salt and Cd distillation. These results suggest the high potential of W crucibles for applicability to cathode processes in pyroprocessing.

5. Conclusions

We evaluated the stability of W as a crucible against U, RE metals, Cd, and various chloride salts, which are possible reagents in cathode processes. The following results were obtained:

- (i) The W crucible remained stable after the melting of RE metals using an induction melting furnace, exhibiting the applicability of the crucible for the induction heating system.
- (ii) U purification by salt distillation with a W crucible at 1050°C demonstrated the stability of W against U and various chlorides. No interactions were observed between the crucible and U or chlorides by SEM or ICP-OES observation.
- (iii) U recovery testing by Cd distillation from a U-Cd alloy in a W crucible at 500°C showed that the W was very stable against Cd, maintaining a shiny surface.
- (iv) These reactivity tests with U, Cd, RE metals, and various chlorides revealed that the W crucible was stable for the operation conditions of both salt and Cd distillation.

These results suggest the high potential of W as a crucible material for applications of cathode processes in pyroprocessing.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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