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Chemical reactivity of oxide materials with uranium and uranium trichloride

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Abstract−A graphite crucible is used for the manufacturing of uranium ingots in the uranium casting equipment of the electrorefining process. Uranium and uranium alloys are typically induction melted in graphite crucibles under a vacuum condition; however, due to the chemical reactivity of uranium and most alloying elements with carbon, a protective ceramic coating is generally applied to the graphite crucibles. To investigate the most suitable ceramic coating material for application to graphite melting crucibles used for the melting uranium in uranium casting equipment, firstly, a thermodynamic analysis using HSC software was performed to examine the chemical reactivity of ceramic oxide materials with uranium and uranium trichloride, and also, experiments concerning the reactivity of molten uranium in some ceramic coated crucibles were performed at 1,300 °C. From the results, yttria was finally selected as the most suitable ceramic coating material for application to graphite crucibles for melting the uranium.

Key words: Reactivity, Uranium, Yttria, Ceramic Materials, Graphite Crucible

INTRODUCTION

The electrorefining process is one of the most important processes of a pyroprocess for the recovery of useful elements from spent fuel. In the electrorefining process, pure uranium is electrodeposited onto a solid cathode from the spent fuel which is dissolved in a molten LiCl-KCl eutectic salt by electrolysis. Uranium deposits from an electrorefining process contain about 30 wt% salts including a little uranium trichloride. The salt is recovered by a salt distillation process. After the salt distillation process, in order to recover pure uranium and convert it into a uranium ingot, lab-scale uranium casting technology is being developed using a high frequency induction coil denerator. A graphite crucible is used for melting uranium deposits in the U ingot casting equipment. But, due to the strong reactivity of uranium with carbon, a protective ceramic coating is generally applied to the crucibles [1].

Ceramic oxides, by virtue of their high melting temperature and stability in an oxidizing environment, are widely used for coating applications. The choice of the specific ceramic material is decided by its thermal stability, chemical stability in the operating environment, etc [4]. In general, coating materials for high temperature applications should meet the following requirements:

- High melting point (>2,000 K)
- Low thermal conductivity (ideally about 1 $Wm^{-1}K^{-1}$ or less)
- Low thermal expansion coefficient
- Resistance to corrosion by the medium and chemical stability with the substrate material
- Improved thermal shock properties

Common crucible coatings include zirconia (ZrO_2), magnesia (MgO) and yttria (Y_2O_3). Table 1 lists some of the commonly used ceramic materials for high temperature thermal and chemical coating barrier applications.

Table 1. Prospective ceramic coating materials for high temperature applications

Materials	Characteristics	Density	Fire resistance	Porosity
Al_2O_3	Porous material, >99%	3.2	2,030 °C	17%
MgO	Porous material, >99%	2.8	2,600 °C	20%
CaO	Porous material, >98%	2.7	2,570 °C	17-20%
ZrO_2	Porous material, >93%	4.2	2,350 °C	22%
Y_2O_3	Porous material, >99.5%	3.8	2,410 °C	23%

Yttria is one of the most stable oxides and is ideally suited for high temperature application. It has superior resistance to aggressive chemical attack by molten metal, salts, slag and glass at high temperature, as well as thermal stability. It is also seen to be fairly stable with graphite up to 1,600 °C. Thus, it is used for coating crucibles and molds that handle highly reactive molten metals like uranium, titanium, chromium, beryllium and their alloys [6]. Aluminum oxide, due to its reasonably high melting point (2,300 K), chemically inert nature and availability is widely used for many thermal and chemical barrier applications. The commonly used prospective ceramic coating materials for high temperature applications include aluminum oxide, magnesium oxide, zirconium oxide, yttrium oxide, and yttria stabilized zirconia (containing about 7 wt% Y_2O_3) [1-3]. Standard coatings for graphite crucibles for melting uranium have generally been zirconia based and have been applied as a paint or by flame spraying. However, these coatings do not provide adequate protection at the temperatures normally required for melting uranium alloys. Yttria is stable in many reactive environments including carbon and molten metal and provides superior protection above 1,300 °C but becomes less satisfactory above 1,450 °C [1,3].

A protective ceramic coating should be applied to the graphite crucibles used for melting uranium deposits due to the strong reac-

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tivity of uranium with carbon. The aim of this study is to select the most suitable ceramic coating material to apply graphite crucibles for a melting crucible used in uranium casting equipment. For this, first, a thermodynamic analysis using HSC software was performed to examine the chemical reactivity of several ceramic oxide materials with uranium and uranium trichloride, and also, some experiments concerning the chemical reactivity of oxide materials with uranium were carried out at 1,300 °C in a high frequency induction coil furnace.

EXPERIMENTAL SECTION

1. Thermodynamic Analysis Using HSC Software

HSC software is the favorite thermochemical calculation software based on independent chemical reactions using thermodynamic databases. The name of the software is based on the fact that calculation modules automatically utilize the same extensive thermochemical database which contains enthalpy (H), entropy (S) and heat capacity (Cp) data for more than 25,000 chemical compounds.

To theoretically investigate the chemical reactivity between uranium and several prospective coating materials, first, the values of Gibbs free energy change (ΔG) for the reaction of uranium in ceramic coated crucibles were calculated using HSC as follows:

$$\Delta G = G_{products} - G_{reactants} < 0\text{: spontaneous reaction}$$

When the value of ΔG is negative, a chemical reaction of the ceramic materials with uranium may occur spontaneously.

Fig. 1. Experimental apparatus (with high frequency induction coil generator).

2. Experiment and Procedure

The experiments were carried out in a high frequency induction coil furnace under a dynamic vacuum better than 10^{-3} Pa obtained by a diffusion pump. The experimental apparatus is shown in Fig. 1. The material of the graphite crucible was the isotropic material, R4340, purchased from Dong-Bang carbon company in Korea; it's size was 25 mm OD×30 mm H×6 mmT. Graphite crucibles were coated with common porous ceramic materials by a Plasma spray coating method. Before plasma spraying coating, crucibles were ultrasonically cleaned in alcohol, and in order to favor mechanical adhesion the surface to be coated was sand blasted before the thermal spray process. Coatings were obtained by the plasma spray process using plasma spraying equipment (PRAXAIR 3710, USA) at Dandan Inc. in Korea shown in Fig. 2. The principal plasma spraying parameters for coating are shown in Table 2. The schematic diagram for plasma spraying coating is shown in Fig. 3.

The chemical reaction of the ceramic coating materials with ur-

Fig. 2. Plasma spraying equipment for plasma spraying coating.

Table 2. Plasma spraying parameters for coating

Plasmagen gas rate	400-700 m/sec
Plasmagen gas pressure	1.38×10^{5} Pa
Spraying distance	100 mm
Current intensity	900 A
Voltage	37 V
Plasma powder output rate	600 m/sec
Plasma central temperature	15,000 °K

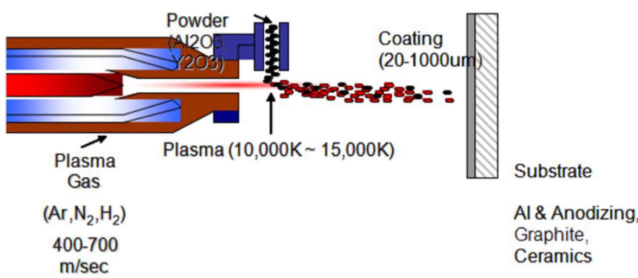


Fig. 3. Schematic diagram for plasma spraying coating.

Fig. 4. Molds of graphite crucible for the reaction between ceramic coating materials and uranium.

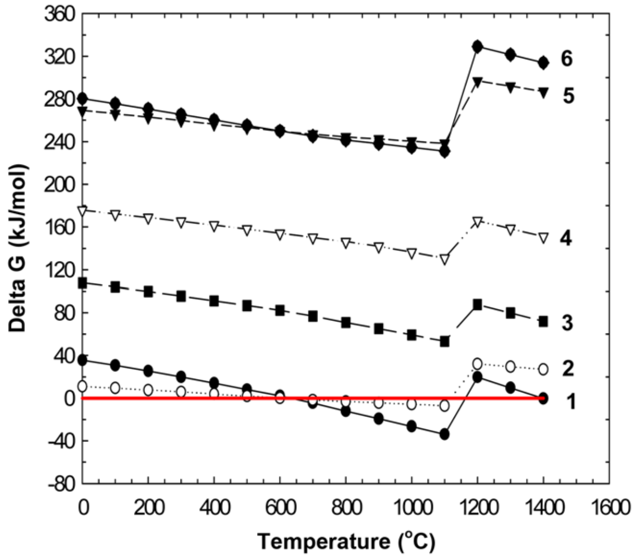


Fig. 5. Chemical stability of oxide materials with uranium according to the temperature.

anium was investigated by melting uranium metal in a ceramic coated crucible. The crucible was about 25 mm in diameter and 30 mm in height. About thirty grams of uranium were added to a ceramic coated crucible. The crucible was heated in a vacuum induction furnace using a high frequency induction coil generator. The temperature of the crucible was increased to the uranium melting temperature (1,300 °C) and held for about a hour. Fig. 4 shows molds of the graphite crucible used for the reaction experiments.

After the experiments, each reaction layer and ingredient of the samples was analyzed by SEM/EDX, Model JEOL 6300 to examine the reactivity, XRD was also used to evaluate the change in aspect of the powder for a coating material and a coating layer.

RESULTS AND DISCUSSION

1. Thermodynamic Analysis Using HSC Software

The reactivity of uranium in ceramic-coated crucibles can be thermodynamically evaluated by calculating the values of Gibbs free energy according to the temperature because a spontaneous reaction occurs at negative values of Gibbs free energy. The values of Gibbs free energy for the reactions of ceramic coated crucibles in liquid uranium and uranium trichloride were calculated using the HSC software.

The possible reactions between uranium and ceramic coating materials are as follows:

$$Al_2O_3+1.5U=1.5UO_2+2Al \quad (1)$$

$$ZrO_2+U=UO_2+Zr \quad (2)$$

$$2MgO+U=UO_2+2Mg \quad (3)$$

$$2CaO+U=UO_2+2Ca \quad (4)$$

$$Y_2O_3+1.5U=1.5\ UO_2+2Y \quad (5)$$

$$ZrO_2+Y_2O_3+2.5U=Zr+2Y+2.5UO_2 \quad (6)$$

Fig. 5 shows the chemical stability of oxide materials with uranium according to the temperature. As shown, the values of their Gibbs free energy according to the reaction temperature indicate a negative in the case of alumina and zirconia in the temperature range of 700 °C to 1,100 °C; therefore, these ceramic coating materials may react with the molten uranium. However, the coating materials other than the aluminum oxide and zirconium oxide show a positive value of Gibbs free energy in the total temperature range; thus, a reaction between uranium and ceramic oxides cannot be occurring spontaneously. From the results of the thermodynamic analysis, reactivity of the ceramic materials other than alumina and zirconia with uranium is not found in the temperature range of concern.

A study on the reactivity between uranium trichloride and ceramic coating materials was also carried out because uranium deposits from an electrorefining process may include a little uranium trichloride (UCl_3) after the salt distillation process. The possible reactions between uranium trichloride and ceramic materials are as follows:

$$3CaO+2UCl_3=3CaCl_2+UO_2+UO \quad (1)$$

$$3MgO+2UCl_3=3MgCl_2+UO_2+UO \quad (2)$$

$$Y_2O_3+2UCl_3=2YCl_3+UO_2+UO \quad (3)$$

$$ZrO_2+UCl_3=ZrCl_3+UO_2 \quad (4)$$

$$ZrO_2+Y_2O_3+3UCl_3=ZrCl_3+2YCl_3+2UO_2+UO \quad (5)$$

Fig. 6 shows the chemical stability of oxide materials with uranium trichloride according to the temperature. As shown, the value of Gibbs free energy for calcium oxide and magnesium oxide is negative through all the range of reaction temperatures. But the value of Gibbs free energy shows positive for the other ceramic materials. From the thermodynamic calculation results, calcium oxide and magnesium oxide may react with uranium trichloride; however, the other coating materials do not react with uranium trichloride.

Based on the thermodynamic calculation results using HSC software, yttria and yttria stabilized zirconia (YSZ) are shown to be the most suitable coating materials.

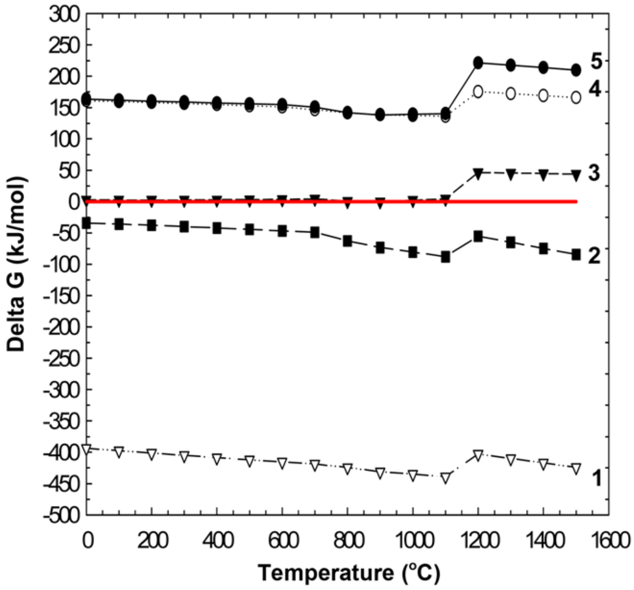


Fig. 6. Chemical stability of oxide materials with uranium trichloride according to the temperature.

2. Experimental Results

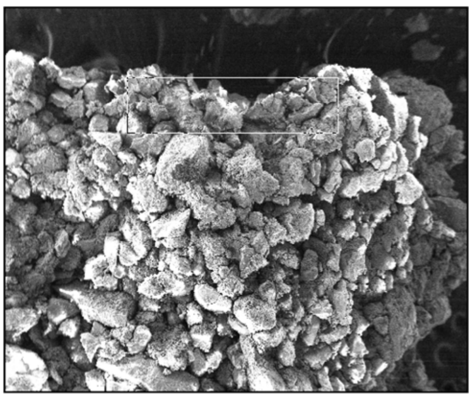
Some experiments were performed to investigate the reaction between uranium and ceramic coating materials, and then the results were compared with those of a thermodynamic analysis using HSC software. Fig. 7 shows the result of a SEM/EDX analysis of zirconia (ZrO_2) by reaction with U. From the result of the thermodynamic analysis shown in Fig 5, the ΔG indicates a little negative value in the case of zirconia in the temperature range of 700 °C to 1,100 °C, so it is possible that chemical reaction between uranium and zirconia may occur. However, based on the experimental result shown in Fig. 7, there was no chemical reaction between uranium and zirconia. When a graphite crucible is coated with zirconia, the application of excess ZrO_2 leads to the formation of dross and the subsequent loss of the uranium product due to the following reaction.

$$ZrO_2+U=UO_2+Zr$$

The crucible must be cleaned and coated after each run [5]. Therefore, zirconia is not appropriate.

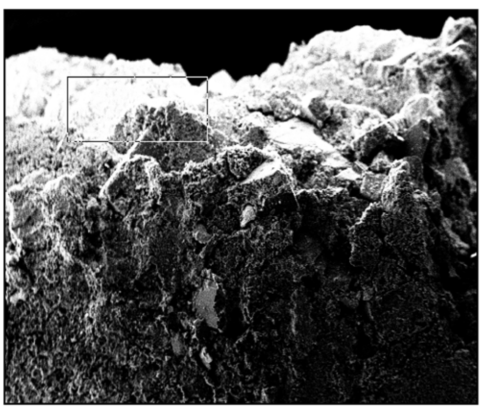
Fig. 8 shows the result of a SEM/EDX analysis of magnesia (MgO) by reaction with U. As shown, a reaction between uranium and magnesium oxide was not found and the coating layers were also maintained. This experimental result is the same as the result of thermodynamic analysis using HSC. But, from the thermodynamic calculation results shown in Fig. 4, magnesium oxide may react with uranium trichloride. Therefore, magnesia is not appropriate.

Fig. 9 shows the result of a SEM/EDX analysis of yttria (Y_2O_3) by reaction with U. As shown, it was observed that there was no chemical reaction between yttria and uranium, which is the same as the result of thermodynamic analysis using HSC software.



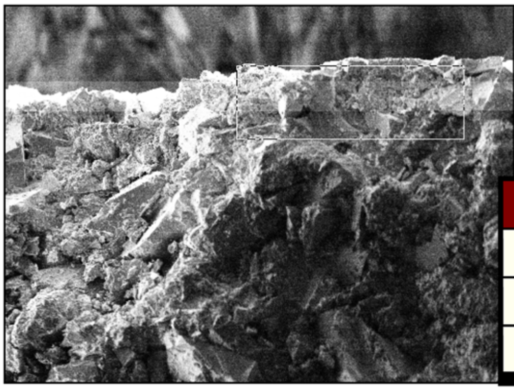
Matrix correction: ZAFElement	Wt%	At%
O K	44.18	81.86
ZrL	55.82	18.14
U L	00.00	00.00

Fig. 7. Result of SEM/EDX analysis of zirconia (ZrO_2) by reaction with U.



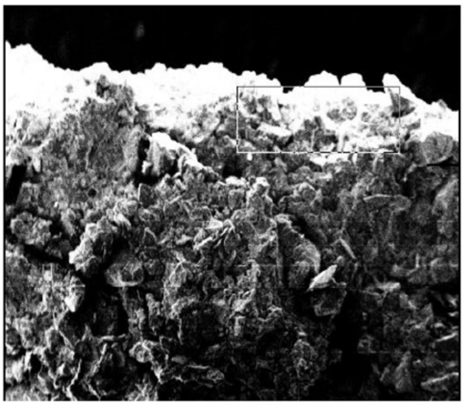
Matrix correction: ZAFElement	Wt%	At%
O K	34.19	44.69
MgK	64.12	55.16
U L	01.69	00.15

Fig. 8. Result of SEM/EDX analysis of magnesia (MgO) by reaction with U.



Matrix correction: ZAFElement	Wt%	At%
O K	44.64	58.16
Y K	54.02	41.73
U L	01.34	00.12

Fig. 9. Result of SEM/EDX analysis of yttria (Y_2O_3) by reaction with U.



Matrix correction: ZAFElement	Wt%	At%
O K	31.41	72.34
Y L	05.36	02.22
ZrL	62.79	25.37
U M	00.44	00.07

Fig. 10. Result of SEM/EDX analysis of yttria stabilized zirconia (YSZ) by reaction with U.

Fig. 10 shows the result of a SEM/EDX analysis of yttria-stabilized zirconia (YSZ) by reaction with U. According to the experimental result, a reaction between uranium and yttria-stabilized zirconia was not found, which is the same as the result of a thermodynamic analysis using HSC software. However, yttria-stabilized zirconia becomes less satisfactory above 1,200 ºC when directly applied on graphite, while yttria provides superior protection above 1,300 ºC and also has superior resistance to aggressive chemical attack by molten metal and salts at high temperature as well as thermal stability [1].

Based on the results from the thermodynamic analyses and experiments, yttria was finally selected as the most suitable ceramic coating material for application to graphite crucibles for melting the uranium in the casting equipment.

CONCLUSIONS

A graphite crucible is used for the manufacturing of uranium ingots in casting equipment. But, due to the chemical reactivity of uranium and most alloying elements with carbon, graphite crucibles used in uranium casting equipment should be coated with protective ceramic coating materials.

Thermodynamic analyses using HSC software and experiments concerning the reactivity of molten uranium in some ceramic coated crucibles at 1,300 ºC were performed to investigate the chemical reactivity of ceramic oxide materials with uranium and uranium trichloride.

From the these results in this study, yttria was finally selected as the most suitable ceramic coating material for application to graphite crucibles for melting uranium at 1,300 ºC in uranium casting equipment because yttria has superior resistance to aggressive chemical attack by molten metals and salts at high temperature, as well as thermal stability, while yttria-stabilized zirconia becomes less satisfactory above 1,200 ºC when directly applied on graphite.

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