The feasibility of using molten carbonate corrosion for separating a nuclear surrogate for plutonium oxide from silicon carbide inert matrix

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ABSTRACT

Silicon carbide is one of the prime candidates as a matrix material in inert matrix fuels (IMF) being designed to reduce the plutonium inventories. Since complete fission and transmutation is not practical in a single in-core run, it is necessary to separate the non-transmuted actinide materials from the silicon carbide matrix for recycling. In this work, SiC was corroded in sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3), to form water soluble sodium or potassium silicate. Separation of the transuranics was achieved by dissolving the SiC corrosion product in boiling water. Ceria (CeO_2), which was used as a surrogate for plutonium oxide (PuO_2), was not corroded in these molten salt environments. The molten salt depth, which is a distance between the salt/air interface to the upper surface of SiC pellets, significantly affected the rate of corrosion. The corrosion was faster in K_2CO_3 than in Na_2CO_3 molten salt at 1050 °C, when the initial molten salt depths were kept the same for both salts.

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1. Background

The search for a material to function as the matrix in IMFs to reduce inventories of plutonium and to carry out the transmutation of the long half-life actinides has been a goal for several years. Silicon carbide (SiC) has become one of the prime IMF candidate materials [1–4], since both silicon and carbon have a small thermal neutron absorption cross-section. Silicon carbide is also well known for its chemical inertness, good thermal conductivity and excellent mechanical properties.

Not all of the actinides will be consumed during an in-core cycle. Therefore, it is necessary to separate the non-transmuted or non-fissioned materials from the inert matrix for recycling. Reprocessing and separating transuranic species and unburned fuels from a silicon carbide matrix have been a challenge to date because of the excellent chemical inertness of bulk SiC. Recently, Bourg et al. [4] developed a separation method by using Cl_2 to oxidize micron-size SiC powder, in which 75% of SiC was volatilized in the form of $SiCl_4$ at 900 °C in 5 h. The remaining solid carbon was removed by oxidation under O_2 at 400 °C. This paper did not consider the toxicity of Cl_2, if the system were applied on a large scale. Hydrogen chloride (HCl) produced by Cl_2 and water vapor is highly corrosive to equipment. Moreover, grinding the SiC fuel rods into micron-size powder has the potential to cause considerable nuclear

contamination to the milling equipment. Disposal of contaminated equipment could be prohibitively expensive. Additionally, the fine particles of nuclear fuels are more hazardous than pellet fuels since they might disperse in air.

In this work, a potential process for separation was proposed. Ceria, a widely used surrogate of plutonium oxide (PuO_2) [5–7], can be filtered from a solution of water-soluble SiC corrosion products (e.g., potassium silicate) formed by SiC corrosion in the molten carbonates. Several parameters which may affect the SiC corrosion rate are also reported in this paper.

2. Experimental

2.1. Dissolution of SiC powder

An open-ended tube furnace (F79340-33 manufactured by Barnstead Thermolyne) was preheated to 900 °C in air. The temperature profile was measured to assure that the region where samples were located has a constant temperature. SiC powders (purchased from Alfa Aesar) with different diameters (30 nm and 1 μm) were tested. Alumina crucibles containing mixtures of SiC powder and anhydrous Na_2CO_3 salt, after ball milling for 1 h, were placed midway in the tube furnace. The samples were held at 900 °C for various times up to 0.5 h, after which they were rapidly quenched in air and then immersed in boiling de-ionized water to dissolve the products and residual Na_2CO_3. The unreacted SiC and solution were then transferred to centrifuge tubes, centrifuged, and dried. The non-reacted SiC was weighed. The average SiC weight

loss percent of three samples was determined. An X-ray Diffraction Philips APD 3720 was used to identify the product. Blank experiments, in which SiC powder without mixing with salt experienced the same heat treatment and washing procedures, were performed to determine the weight loss of SiC due to the handling error.

2.2. Dissolution of SiC pellets

Reaction-bonded SiC (diameter: 5 mm) rods (purchased from Goodfellow Corporation; theoretical density: 95%) were cut into pellets with a uniform thickness (2 mm). The pellets were then polished with fine grit grinding papers to remove any tool markings. The same tube furnace, with caps on each end, was preheated to 1050 °C in air. A constant air flow (170 standard cubic per centimeter) was applied in the furnace. Weight loss of the pellets corroded in molten K_2CO_3 salt was measured after isothermal corrosion, washing in boiling water and drying in a vacuum oven. Sufficient salt was used in order to completely cover the SiC pellets during corrosion and to form water soluble silicates.

2.3. Corrosion of ceria in the molten carbonates

Ceria was used as a surrogate material for plutonium oxide (PuO_2). CeO_2 powder and pellets were purchased from Alfa Aesar. Experiments on ceria fine powder (5–9 μm) and ceria pellets (theoretical density: 88%; purity: 99.9%; metal basis) corroded by alkali salts (Na_2CO_3 and K_2CO_3) at a 10:1 M ratio to CeO_2 were performed at 1050 °C for 40 h. Three parallel tests were performed for each reactant combination to determine the mean value. The initial weight of the ceria powder and the ceria pellet were approximately 0.5 g and 3 g for each experiment. The weight difference was measured between the original ceria and the residue ceria after washing away the alkali salts. The ceria pellets were dried in the vacuum oven at 6800 Pa for 12 h at 80 °C to remove the water absorbed in open pores. The average ceria weight change percent was calculated at the end. Blank experiments on CeO_2 powder were also performed. The CeO_2 weight change, due to transferring the powder from one container to another and washing, was measured to determine the operation error of the weight change measurement.

3. Results and discussion

SiC exposed to an oxidizing atmosphere is covered by a thin silica layer which retards SiC from further oxidation by preventing oxygen from reaching the underlying silicon carbide. When exposed to molten salts, silica forms crystalline silicates. Since the silicates have a much lower density compared to silica, both the diffusivity and the solubility of gaseous oxygen in the silicates will be high enough to allow further oxidation and corrosion of SiC [8,9]. At temperatures above the melting points of the silicates, the alkali silicate layer will be dissolved in the molten salts. This phenomenon allows the molten salts to contact with the SiC, producing new silicates and continuing the corrosion process.

3.1. Dissolution of SiC powder

The weight loss percentage of SiC powder (1 μm) vs. time is shown in Fig. 1, in which complete SiC powder (1 μm) dissolution in Na_2CO_3 molten salt was achieved in 30 min at 900 °C. After reaction for 30 min, a small amount (less than 1%) of unreacted SiC powder was found at the bottom of the crucible. The average weight loss due to handling error on 1 μm SiC powder was 1%. Under the same condition, this result is a negligible operation error. SiC powder (30 nm) dissolved totally in the Na_2CO_3 molten salt
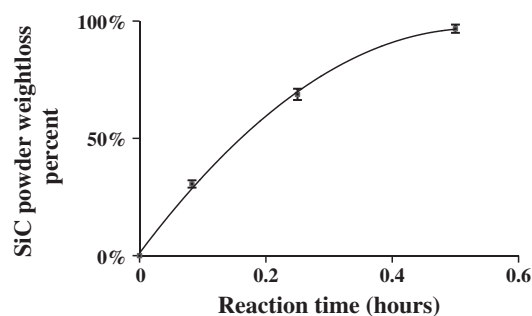

Fig. 1. Weight loss percent of powder SiC corroded in the molten Na_2CO_3 salt at 900 °C as a function of reaction time.

after 20 min. This illustrates, as expected, that the nanometer sized SiC has a higher activity than micron-size SiC, due to the higher specific surface area and thus the higher surface free energy. The corrosion product, sodium metasilicate Na_2SiO_3, in Na_2CO_3 salt was identified by an X-ray Diffraction study. The same product was also found by Jones et al. [10], who utilized nuclear magnetic resonance spectroscopy to determine the composition of products in SiO_2–Na_2CO_3 at 900–950 °C.

3.2. Dissolution of SiC pellets

Based on the promising results obtained in the powder work, further study was conducted to dissolve monolithic pellets of SiC. The weight loss of SiC pellets was found to be very low under the same experiment conditions as the powder dissolution, even at an elevated temperature e.g., 900–1050 °C up to 15 h. A number of reports postulated that the formed silicates retarded the ion transportation to explain this phenomenon [8–11]. Since the crystalline silicates were formed at the interface between SiO_2 and the molten salt, the continuation of the reaction requires mobile sodium ions to transport across the increasing layer of crystalline sodium silicates. The amount of molecules and ions diffusing through the interface would decrease as the silicate layer increases. Once the silicate layer grows to a critical thickness, molten salt ions may not pass through the thick silicate layer and result in SiC dissolution. Corrosion will be terminated as a consequence.

Two methods can be considered to prevent termination of the SiC recession:

(1) Grinding bulk SiC into micron-size powder which results in total consumption of SiC before formed silicates reach a critical layer thickness.
(2) Removing the silicate layer from SiC pellets by dissolving it in the molten salts above the melting temperature of silicates.

The first method is not practical in the nuclear industry due to the potential radiological contamination. The second method was selected, since this method can be applied on a large scale. Crystalline sodium silicate [12] in hot corrosion has a melting temperature at 1090 °C. In comparison, if potassium carbonate instead of sodium carbonate is used as the molten salt for SiC corrosion, the formed potassium silicate has a melting temperature of 977 °C [12,13]. Therefore, the K_2CO_3 salt was selected.

All of the SiC samples used in these experiments were confirmed to be totally immersed in molten salts during corrosion based upon density calculation of the molten salts [14] and observation after corrosion.

The corrosion temperature for the bulk SiC was increased to 1050 °C in order to assure the melting of the potassium silicate

layer formed on the SiC surface. A significant SiC weight loss of about 20% was found in an experiment in which an 8 mm RB-SiC rod was corroded in the K_2CO_3 molten salt at 1050 °C for 8 h. An amorphous product which contained potassium (K), silicon (Si) and oxygen (O) was identified through the X-ray Diffraction (XRD) and Energy Dispersive Spectroscopy (EDS). No crystalline potassium silicates were detected. This result indicated that the potassium silicates formed on the surface during corrosion were liquid at 1050 °C. An interesting phenomenon was observed that a flat surface facing towards the air was created on the SiC rod. The cross-section of the SiC rod before and after corrosion is shown in Fig. 2. The faster corrosion rate of the upper part of SiC rod than the bottom can be explained by a hypothesis that diffusion of oxygen in the K_2CO_3 molten salt controls SiC corrosion at 1050 °C. Solubility and diffusivity of the oxygen in the molten salt system affect the rate of SiC oxidation, as is predicted in the Fick's first law of diffusion:

$$J = -D(\Delta C/\Delta x) \tag{1}$$

where J is the oxygen flux approaching to SiC surface, ΔC is the oxygen concentration at the gas/molten salt interface, which depends on the solubility of oxygen in the molten salt, assuming that the oxygen concentration at the SiC/molten salt interface is equal to zero due to immediate SiC/oxygen reaction, Δx is the oxygen diffusion distance from the gas/molten salt interface to the SiC/molten salt interface and D is the oxygen diffusion coefficient. The oxygen flux increases with a decreasing oxygen diffusion distance, an increasing diffusion coefficient and an increasing solubility of the oxygen which largely depends upon the partial pressure of oxygen in the gas phase. Maru et al. [15,16] summarized that the solubility of oxygen within a temperature range of 600–800 °C in molten carbonates is controlled by the reactions with the melt to generate peroxide (O_2^{2-}), superoxide (O^{2-}) ions and carbonate dioxide (CO_2). The solubility of oxygen in the molten carbonates will be enhanced with a decreasing partial pressure of CO_2. Presence of the CO_2 in the gas atmosphere and the salt would be a negative factor to SiC corrosion since CO_2 is a product of oxygen dissolution and SiC corrosion in the molten salt. However, CO_2 has been reported as an oxidizer to SiC [17], which increases the complexity of the mechanism of SiC corrosion. The effect of those factors on the SiC corrosion rate will be discussed in a subsequent publication. Systematic data were collected in the following experiment to study if the oxygen diffusion distance affects the SiC corrosion rate.

3.3. Salt to SiC molar ratio

The reprocessing strategy reported in this work is based on formation of the water soluble silicates from which ceria can be filtered out. Water solubility of the alkali silicates which has the composition $Me_2O \cdot mSiO_2$ (Me = Na, K) highly depends on the salt to SiC molar ratio [11]. Silicates are easily dissolved in cold water if m is equal to or less than 1. A higher temperature of water is required for silicates, which have more SiO_2. Water superheated to 120 °C or 150 °C allows for complete dissolution of silicate, with SiO_2 content higher than 80% [11]. To achieve a high solubility of silicates in water, starting molar ratio salt to SiC would have to be no less than 1 to form silicate with m equal to or less than 1. Therefore, the salt to SiC molar ratio applied in this work were all higher than 1.

Since a change of the salt depth in the crucibles results in varying molar ratio, it is necessary to study if the molar ratio would affect the corrosion rate before examining the effect of the molten salt depth, given the sufficient amount of salt to produce water soluble silicates. Three crucibles A–C with various sizes contained the salts with the same depth (4 mm) but at different molar ratios to SiC, as illustrated in Fig. 3. After corrosion at 1050 °C for 1 h, the SiC pellets placed in three crucibles showed a similar weight loss in the molten K_2CO_3 salt or Na_2CO_3 salt as shown in Fig. 4. However, the SiC weight loss under the same corrosion condition in three crucibles was found to be unequal when the corrosion time was extended to 3 h. This result may be attributed to the molten salt depths in those crucibles reducing at different rates with extended reaction time. Calculated values of molten salt depth shown in this work represented the depth at the beginning of the corrosion process. Alkali carbonates volatized and decomposed at 1050 °C [18], which would result in reducing the salt depth. This result demonstrated that given an excess of salt, the salt to SiC molar ratio had little effect on the rate of corrosion when the salt
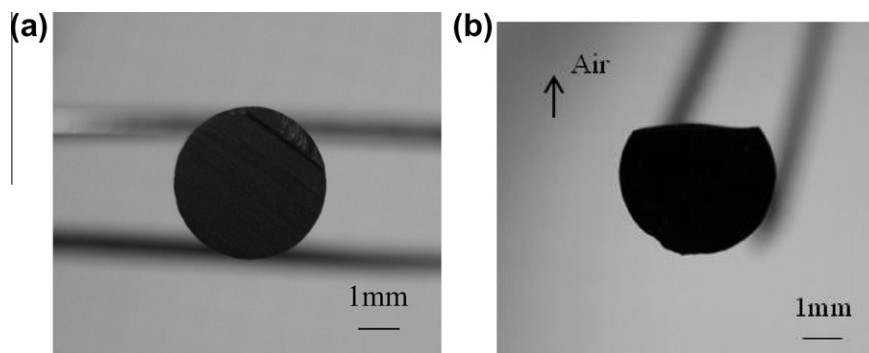

Fig. 2. The cross-section of the SiC rod (a) before corrosion and (b) after 8 h corrosion in K_2CO_3 molten salt at 1050 °C.
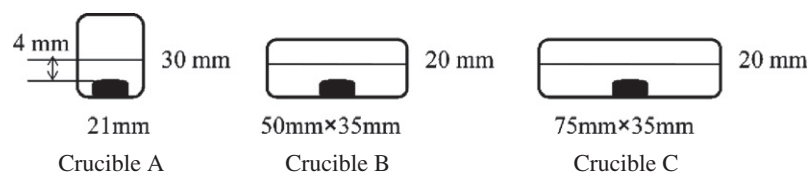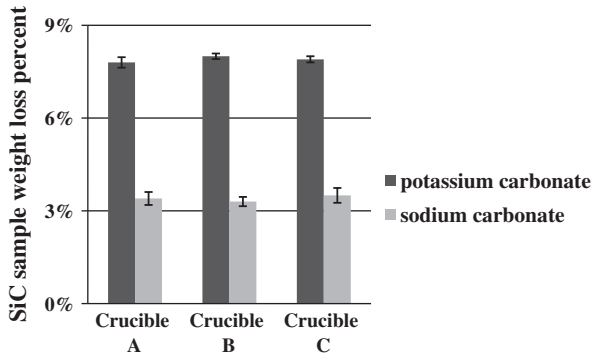

Fig. 3. Diagram of three crucibles with different dimension but the same salt depth (4 mm).
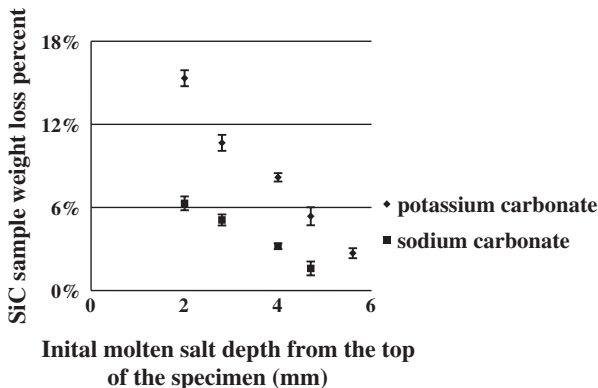
Fig. 4. Weight loss of SiC pellets corroded at 1050 °C for 1 h in molten K_2CO_3 and Na_2CO_3 salt, contained in three crucibles with different dimension. Note, the molten salt depths in crucibles were maintained at 4 mm at beginning of corrosion. Crucible A had a cylinder shape with 21 mm diameter and 30 mm height; crucible B had a rectangular shape with 50 mm length, 35 mm width and 20 mm height; crucible C had a rectangular shape with 75 mm length, 35 mm width and 20 mm height.

depth was unchanged. Therefore, the isothermal holding time was limited in 1 h in the experiment on the molten salt depth to minimize the salt loss due to vaporization. As observed in Fig. 4, SiC pellets dissolved faster in molten K_2CO_3 salt than in Na_2CO_3 at 1050 °C. The salt depth of Na_2CO_3 should decrease faster compared to K_2CO_3, because Na_2CO_3 has higher volatility rates than K_2CO_3 [18], which should accelerate the corrosion as a consequence. However, it was not observed experimentally. This result was consistent with the early hypothesis that potassium silicate melting enhanced SiC corrosion in K_2CO_3 salt at 1050 °C.

3.4. Molten salt depth

In order to investigate whether the rate of SiC corrosion in molten carbonate salts at 1050 °C was affected by the oxygen diffusion distance in the salt, various molten salt depths of K_2CO_3 and Na_2CO_3 salt were examined. The salt depth utilized in experiment was maintained at no less than 2 mm in order to render SiC pellets completely immersed in the molten salts during the corrosion. An increasing SiC dissolution rate was observed, as expected, with a decreasing depth of the molten salt K_2CO_3 and Na_2CO_3 salt at 1050 °C, as shown in Fig. 5. A higher corrosion rate in K_2CO_3, than in Na_2CO_3, was found of all molten salt depths. This result reinforced the hypothesis that oxygen diffusion may affect SiC corrosion in the molten alkali carbonates.

Fig. 5. Weight loss of reaction-bonded SiC pellets corroded in molten K_2CO_3 and Na_2CO_3 salt at 1050 °C for 1 h, as a function of the salt depth (a distance between the upper surface of SiC pellet and the molten salt surface in contact with air/oxygen).

3.5. Quantification of SiC corrosion in the molten K_2CO_3 salt

The residue of SiC pellets after corrosion was put back into the furnace with fresh salt until complete dissolution of SiC was achieved. A decelerating SiC weight loss was found when the salt depth was maintained at constant in each run, as shown in Fig. 6. Shrinkage of the SiC pellets during corrosion resulted in reducing the surface area while reacting with the molten salt. The rate of weight loss was decreased as a consequence. Additionally, extensive reaction time was required to completely dissolve SiC pellets in the salt with a longer salt depth. This result was predictable, according to the Fick's first law.

Surprisingly, the SiC weight loss followed a linear function shown in Fig. 7 as accumulative time of corrosion in the molten salt, when the salt to SiC molar ratio was kept constant in each run. This unexpected result may be attributed to a counterbalance of the effect of variables such as the SiC surface area and the salt depth controlled by the initial salt to SiC molar ratio and the salt vaporization rate. In conclusion, modeling SiC corrosion in the molten salts is very difficult since the changing of salt depth, CO_2 oxidation to SiC and its effect on oxygen solubility in salts should be considered.

3.6. Corrosion of ceria in the molten carbonates

The experimental results are summarized in Table 1 for the ceria powder (5–9 μm). The pellets did not have a significant weight change. The XRD spectra did not show new phases generated in molten salt corrosion tests, which confirms that ceria does not react with the molten salt at 1050 °C. The reason for using ceria powder is that fine powders are expected to have much higher reactivity than bulk material due to the higher specific surface area
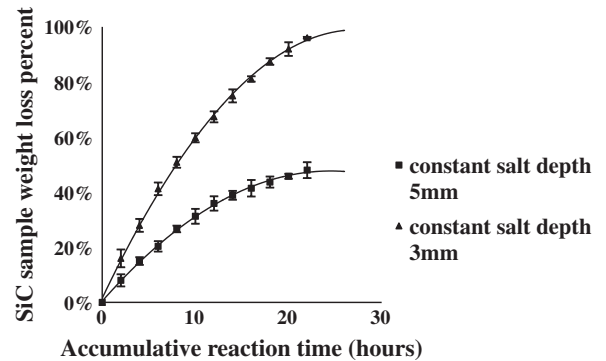
Fig. 6. Weight loss percent of SiC pellets as a function of accumulative reaction time in K_2CO_3 molten salt with two different salt depths, 5 mm and 3 mm at 1050 °C. (Weight loss of SiC samples measured periodically every 2 h with salt refilling to maintain a constant salt depth.)
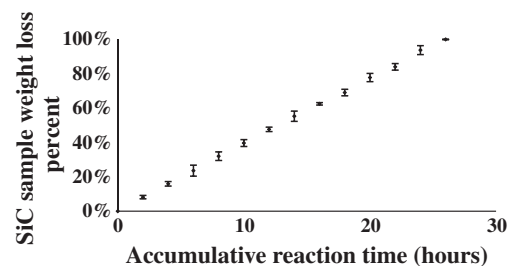
Fig. 7. Weight loss percent of SiC pellets as a function of accumulative reaction time in K_2CO_3 molten salt at 1050 °C (K_2CO_3 to SiC molar ratio = 10). (Weight loss of SiC samples measured periodically every 2 h with salt refilling at the same molar ratio to the residual SiC.)

Table 1
Weight change percent of bulk and powder ceria after corrosion in two molten carbonates ("−" represents weight loss and "+" represents weight increase).

Experiments	Blank experiment powder CeO_2 (%)	CeO_2 powder/Na_2CO_3 (%)	CeO_2 powder/K_2CO_3 (%)	CeO_2 pellet/Na_2CO_3 (%)	CeO_2 pellet/K_2CO_3 (%)
Ceria weight change percent	−0.60	−0.74	−0.56	0.01	0.02
Standard deviation	0.43	0.14	0.47	0.01	0.01

and thus the higher surface free energy. The weight loss of ceria powder after corrosion in the molten salt was negligible and approximately equaled to the ceria weight loss caused by handling error. The ceria pellets in the molten salts also showed negligible weight changes. The slight weight increase (0.0001–0.0006 g) of ceria pellets may be because water penetrating into the ceria open pores in the washing step would be difficult to be removed away completely from the ceria body, considering the low theoretical density (88%) of ceria pellets. This hypothesis was verified by experimental results that higher vacuum (3400 Pa) applied on ceria pellets resulted in complete weight recovery of ceria pellets. Due to plutonium oxide's similar chemical properties to ceria [5–7], it is expected that bulk plutonium oxide will not dissolve in this molten salt process. This result indicates the feasibility of the molten salt corrosion method in which SiC is corroded in K_2CO_3 molten salt to form the water soluble silicates but ceria is unchanged at 1050 °C.

4. Conclusions

A number of studies have focused on SiC as a suitable matrix for IMF. Efficient processes for separating the non-transmuted fuels from the SiC matrix have not been identified to date, which hinders the application of SiC as an inert matrix. This work described a possible method to separate ceria a surrogate for PuO_2 from bulk SiC. Studies on the SiC corrosion in different carbonates of various salt depths at 1050 °C provided a hypothesis to explain the faster SiC dissolution rate in molten K_2CO_3 with a short salt depth at 1050 °C.

Acknowledgement

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