

NUCLEAR ENERGY RESEARCH INITIATIVE

Separation of Nuclear Fuel Surrogates from Silicon Carbide Inert Matrix Final report

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Research Objectives

The objective of this project has been to identify a process for separating transuranic species from silicon carbide (SiC). Silicon carbide has become one of the prime candidates for the matrix in inert matrix fuels (IMF) being designed to reduce plutonium inventories and the long half-lives actinides through transmutation. Since complete reaction is not practical it becomes necessary to separate the non-transmuted materials from the silicon carbide matrix for ultimate reprocessing. This work reports a method for that required process.

An efficient process has been developed for separating transuranic species from a silicon carbide (SiC) matrix. At high temperature (above 850 °C) SiC can be oxidized in molten alkali salt such as sodium carbonate (Na₂CO₃) and potassium carbonate (K₂CO₃) and form water soluble products such as sodium or potassium silicate. SiC fine powder (1micron) was totally dissolved in Na₂CO₃ molten salt after 30 min heat treatment at 900 °C. SiC pellets were completely dissolved in K₂CO₃ molten salt after approximate 40 hours heat treatment at 1050 °C. Separation was achieved by dissolving the products obtained from SiC corrosion in water. Ceria (CeO₂) remained unchanged and was not corroded in these molten salt environments.

1. Background

The search for an inert matrix for inert matrix fuels (IMF) to function as a matrix to reduce inventories of plutonium and 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]. 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, all of which are requirements for a qualified IMF candidate [1-3].

Not all of the actinides will be consumed during a processing cycle. It is, therefore, necessary to separate the non-transmuted or non-fissioned materials from the inert matrix for reprocessing. Only limited techniques for processing and separating transuranic species and unburned fuel from a silicon carbide matrix have been previously identified. Recently, S. Bourg [4] developed a separation method by using Cl_2 to oxidize SiC powder (45 μm), in which 75 percent of SiC was volatilized in the form of SiCl_4 at 900 °C in 5 hours. The remaining solid carbon was removed by oxidation under oxygen at 400 °C. This paper fails to consider the toxicity of Cl_2 if the system is applied in a large scale. Hydrogen chloride (HCl) produced by Cl_2 and the water vapor is highly corrosive to equipments.

Molten salt hot corrosion is a process in which molten salts corrode the surface to which they come into contact. Separating nuclear fuel from SiC matrix can be achieved by filtering plutonium oxide (PuO_2) and fission products from a solution of water-soluble SiC corrosion products.

In previous research on gas turbine engine degradation and coal combustion process [5, 6, 7], it has been observed that carbonate salts of sodium and potassium dissolve SiC, because the passivating silica surface protecting the silicon carbide is removed by the fluxing action of the sodium or potassium ions as well as impurities that are present in the gaseous environment. This hot corrosion approach has been selected to address the reprocessing challenge due to its high corrosion rate of SiC.

2. Experimental Procedures

2.1 SiC powder dissolution

An open-ended tube furnace was preheated to 900 °C in air. SiC powder (from Alfa Aesar) with different size (30nm and 1 μm) was tested. Three crucibles containing the mixture of SiC powder

and Na_2CO_3 salt at approximately a one to one molar ratio were placed midway in an open ended tube furnace. The samples were held at selected temperature for a varying amount of time up to 1 hour after which, they were rapidly quenched by immersing them into boiling water to dissolve Na_2SiO_3 and residual Na_2CO_3 . The samples were then transferred to centrifuge tubes centrifuged, dried and the un-reacted SiC was weighed. The average percent of SiC remaining was determined.

Blank experiments for SiC powder in the absence of carbonate salts were also performed. The weight loss of the commercial SiC powder due to transporting and washing was measured in order to obtain the operation error.

2.2 SiC pellet dissolution

A 5mm diameter reaction bonded silicon carbide (RB-SiC from Goodfellow Corporation) was cut into pellets followed by grinding with fine grit grinding paper to remove any tool marks.

Experiments on SiC pellets were performed at 1050 °C for various time periods. A crucible containing a RB-SiC pellet (labeled A) and K_2CO_3 salt at approximately a one to one and half molar ratio were placed midway in the tube furnace. The residue of the SiC pellet after every 10 hours heat treatment was quenched in lab air followed by washing in boiling water. The SiC pellet weight loss was calculated and the pellet residue was put back into the furnace with fresh K_2CO_3 salt for the next run. The same procedure was followed until the SiC pellet was totally dissolved in the molten salt. A series of similar experiments were finished by applying another SiC pellet (labeled B) and K_2CO_3 at a one to ten molar ratio at the same temperature for 20 hours. The residue of the SiC pellet was taken out and weighed after each 4 hours.

Finally, experiments I, and II were performed at 1050 °C for 15 hours and the variables are summarized in Table 1.

2.3 Ceria powder/pellets corrosion

Ceria (CeO_2) was used as a surrogate material for plutonium oxide. Experiments on ceria fine powder (70nm-100nm) and ceria pellets corrosion by alkali salt (Na_2CO_3 and K_2CO_3) were performed at 1050 °C for 5 hours to verify that ceria is not corroded by this alkali salt at 1050 °C. The weight difference was measured between the original ceria and the residue ceria after washing away the alkali salt.

2.4 Cladding Zirconium alloy corrosion

A piece of Zirconium alloy metal was placed in an alumina crucible and corroded by K_2CO_3 in air for 4 hours at 1050 °C. After heat treatment the alkali salt was removed by immersing the crucible in boiling water. The weight difference of Zirconium alloy before and after heat treatment was calculated after drying.

3. Results and Discussion

SiC is covered by a thin silica layer which protects SiC from further oxidation by preventing oxygen from reaching the underlying silicon carbide. When exposed to molten salts, silica is easily attacked to form crystalline or molten silicates. Since the silicates have much lower density compared to silica, both diffusivity and solubility of gaseous oxygen in the silicates will be large enough to allow further oxidation and hot corrosion of the SiC.

3.1 SiC powder dissolution

The average weight loss percentage of SiC powder (1 μ m) vs. time is demonstrated in Figure 1. Complete SiC powder dissolution in Na_2CO_3 molten salt can be achieved in 30 min at 900 °C. The average weight loss of the blank experiments was 1.24%. So, the operation error has a negligible effect to the results.

A “Leveling off” effect occurred when SiC powder was not mixed homogeneously with Na_2CO_3 . In the first 2 hours, SiC (1 μ m) weight loss rate was significant, however, little weight loss occurred after 2 hours. The reaction appeared to level off and stopped at about 75% completion. Without mixing before heat treatment, the weight loss of finer SiC powder (30nm) after 2 hour reaction with Na_2CO_3 at 900 °C is 97.1% which is much higher compared with 75% weight loss of SiC powder (1 μ m). This experiment demonstrated that SiC powder in nano-range has higher reactivity than those with micron size due likely to the higher surface free energy of nanoparticles.

3.2 SiC pellet dissolution

Figure 2 shows the cumulative weight loss percentage of a SiC pellet A after each 10 hours heat treatment. The SiC pellet weight loss percentage at each period of time is shown in Figure 3. As the specific surface area increases due to SiC pellet dissolution in molten salt, the dissolution rate of SiC was enhanced. The actual time for the SiC pellet total dissolution was equal or less than

43 hours. The corrosion results of SiC pellet B illustrated in Figure 4 which shows the SiC weight loss percentage in several narrower time ranges.

Several authors [5, 8] concluded that once the silicate layer grows to a critical thickness and the temperature is sufficiently low, molten salt ions may no longer pass through the thick silicate layer and result in SiC dissolution. Corrosion will be terminated as a consequence. An alkali ion concentration gradient should exist from molten salt to the silica layer. If the temperature is considerably higher, for example, above the melting temperatures of silicates shown in phase diagrams [8], the alkali silicate layer will be dissolved in molten salt. Ions diffuse faster in melts than in solids, hence the molten salt species are able to contact silica and advance the corrosion process in a practical reaction period.

Two methods can be considered to prevent termination of SiC recession before the SiC pellet dissolves completely:

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

Choosing an optimum processing temperature is one important criteria to minimize the processing costs. The lowest temperature to melt sodium silicate (Na_2SiO_3) is 1090 °C [9]. Selecting an alkali salt of which the corresponding silicates have lower melting temperature could decrease the overall processing expense. Different molten salts were examined in experiment I and II to investigate which salt has a better corrosion effect on SiC pellets. Both pellets have approximately the same specific surface area and composition. The dissolution percentage for the pellets after 15 hours reaction in the furnace at 1050 °C in experiment I and II are 22.27% and 60.16% respectively. These results verified the assumption that potassium carbonate (K_2CO_3) has a favorable SiC corrosion efficiency compared to sodium carbonate (Na_2CO_3).

3.3 Ceria powder/pellets corrosion

No apparent weight change was found in ceria corrosion experiment which verified that Ceria does not react under the conditions of the proposed process.

3.4 Cladding Zirconium alloy corrosion

Since reprocessing would likely involve the Zircaloy cladding surrounding the fuel, the effect of a molten salt environment on Zircaloy-4 was also examined. After hot corrosion in K_2CO_3 salt, the weight of a Zircaloy-4 specimen was found to slightly increased and the metal surface was covered by a white thin layer of zirconium oxide which could not be washed away in boiling water. In the absence of molten potassium carbonate, a similar Zircaloy-4 specimen was completely oxidized. Separation cladding or of the produced zirconium oxide from actinide oxides was not part of this study and remains a topic for future research.

4. Project Summary

This feasibility project was completed at the end of this reporting period (9-12-08). The study has shown that:

- Silicon carbide nano particles can be completely oxidized in molten sodium carbonate to form water soluble silicates
- Micron size silicon carbide powders can also be completely oxidized if properly premixed with sodium carbonate
- Silicon carbide pellets are slowly corroded at 1050°C in molten sodium carbonate
- Silicon carbide pellets can be completely oxidized into water soluble silicates in molten potassium carbonate
- Ceria pellets and nanopowders are unaffected under these same conditions
- The project has provided supported for two Ph.D. candidates and one post doctoral student
- An article for publication has been drafted and will be submitted shortly.

References

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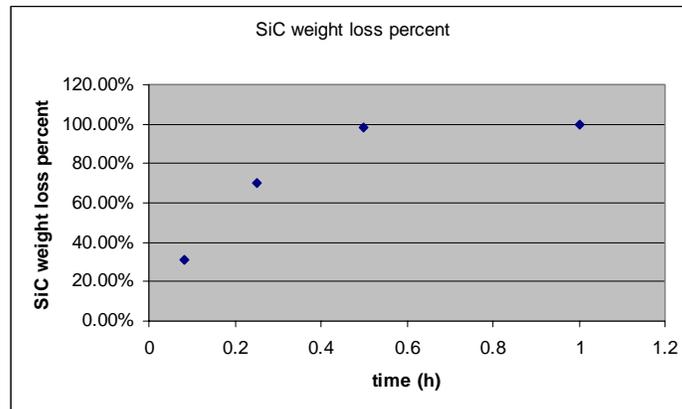


Fig. 1 SiC powder weight loss percent vs. reaction time

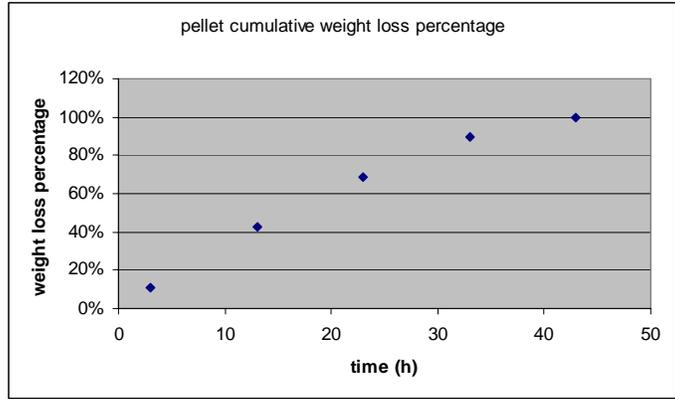


Fig. 2 SiC pellet (A) cumulative weight loss percent vs. reaction time

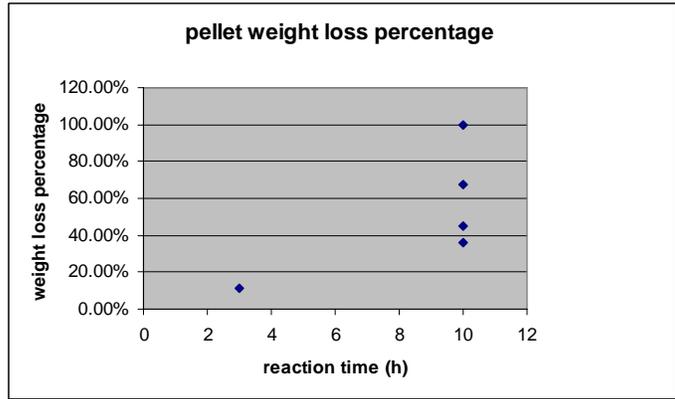


Fig. 3 SiC pellet (A) weight loss percent vs. reaction time

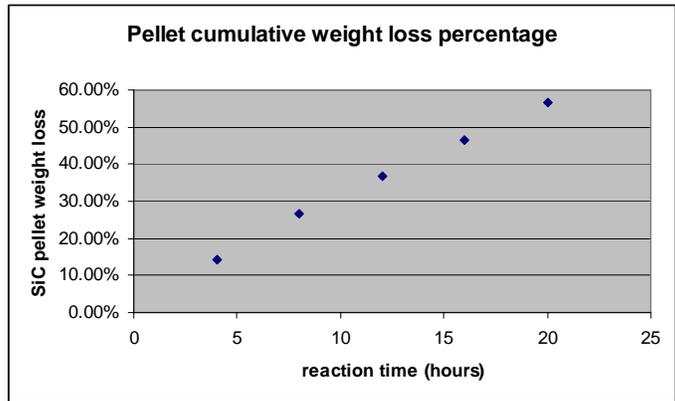


Fig.4 SiC pellet (B) cumulative weight loss percent vs. reaction time in first 20 hours

Table 1

| Experiment | SiC pellet composition | Pellet dimension (mm) | Pellet weight (g) | Molten salt |
|------------|------------------------|-----------------------|-------------------|---------------------------------|
| I | SiC | D=4.98 h=1.74 | 0.0970 | Na ₂ CO ₃ |
| II | SiC | D=5.01 h=1.91 | 0.1024 | K ₂ CO ₃ |