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The effects of oxygen, carbon dioxide and water vapor on reprocessing silicon carbide inert matrix fuels by corrosion in molten potassium carbonate

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ABSTRACT

The molten salt reaction/dissolution method for reprocessing silicon carbide based inert matrix fuels (IMF) is further developed in this paper through comparison of the corrosion rate in multiple gases and gas mixtures. Water vapor was firstly introduced in the SiC/K_2CO_3 corrosion system. The SiC corrosion rate in the H_2O atmosphere was dramatically enhanced 3–4-fold compared to the rate under an O_2 atmosphere. The corrosion rates in different atmospheres of O_2, CO_2, O_2/CO_2, H_2O, O_2/H_2O and CO_2/H_2O with various partial pressures were compared in order to determine the optimal reaction atmosphere and to better understand the reaction mechanism. The SiC pellets with 5 wt.% of CeO_2, a surrogate for PuO_2 were fabricated. CeO_2 was successfully separated from the SiC matrix by using the molten salt reaction/dissolution strategy.

1. Background

Silicon carbide is a promising candidate as the matrix material in inert matrix fuels (IMF) which has been designed to reduce plutonium inventories and the long half-life actinides through transmutation [1–5]. It is necessary to separate the non-transmuted actinides and non-fissioned Pu from the silicon carbide matrix, because complete transmutation or fission cannot be achieved in a single in-core run. A possible method to separate ceria, a surrogate for plutonium, was provided in a previous publication by filtering ceria from a solution of water-soluble SiC corrosion products (e.g. potassium silicate) formed by SiC corrosion in molten carbonates [5]. It was also found that the SiC reaction rate in the molten salts was increased with reducing the molten salt depth, which is a distance between the salt/air interface to the upper surface of SiC pellets. The K_2CO_3 salt is more effective at 1050 °C compared to Na_2CO_3, when the initial molten salt depths were kept the same for both salts. Reaction bonded SiC pellets were studied in the earlier report. However, the reaction bonded method may be impracticable to fabricate IMF pellets in the nuclear industry, since a large amount of Si metal phase will be remained after the reaction bonding process. Fissile atoms may arbitrarily diffuse in the liquid Si phase, which would make the microstructure of sintered IMF pellets difficult to control. Liquid phase sintering (LPS) has been widely proposed as a candidate method for sintering the SiC based IMFs. This method requires a considerable amount of sintering additives (7–30 wt.%) to form a liquid phase during sintering [2]. Since Am becomes dramatically volatile at high temperatures [6], it may be inappropriate to use hot pressing or a direct sintering method in which a high sintering temperature above 1900 °C is needed to produce dense SiC pellets. A method called pre-ceramic polymer process to sinter SiC at 1050 °C was used in this work, since this method does not require high temperature processing or a large amount of sintering additives [7]. The polymer precursor which contains carbon, silicon and hydrogen, undergoes a polymer to ceramic conversion under heat treatment. In an inert atmosphere, the polymer precursor becomes cross-linked at the curing temperature 180–400 °C and produces amorphous silicon carbide which has a 1:1 silicon to carbon atomic ratio at 850–1200 °C [8].

Air was used in the previous work to oxidize SiC [5]. Multiple oxidizers were evaluated in this work in order to accelerate the process. An unanswered question is whether CO_2 is a counter factor for SiC corrosion in the molten K_2CO_3 salt 1050 °C, since CO_2 is generated by carbonate decomposition and also the molten salt reaction with O_2 and SiC. Moreover, it has been reported that O_2 solubility in the molten carbonates can be affected by CO_2 partial pressure below 950 °C [9,10]. The effect of CO_2 on O_2 solubility at higher temperatures has not been reported. Both questions are studied in this paper in order to obtain a better understanding of the SiC corrosion mechanism in the molten K_2CO_3 salt at 1050 °C. Water vapor has been reported as a more efficient oxidizer for SiC than O_2 above 1000 °C [11,12]. However, no systematic investigation has been done on the role of water vapor in the SiC/molten carbonates corrosion process. Water vapor was introduced in the SiC/K_2CO_3 corrosion system in order to determine whether water vapor can accelerate the SiC reprocessing process. The SiC corro-

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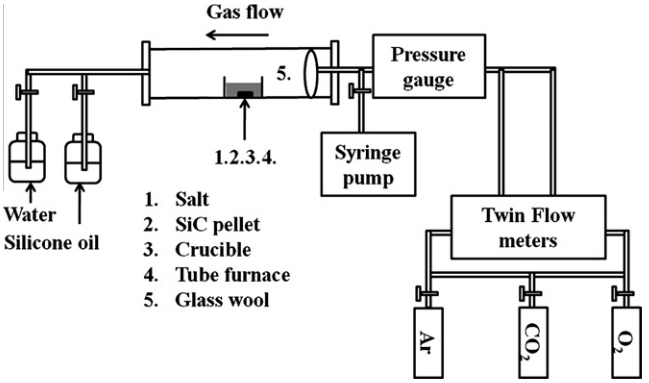

Fig. 1. Scheme of process design.

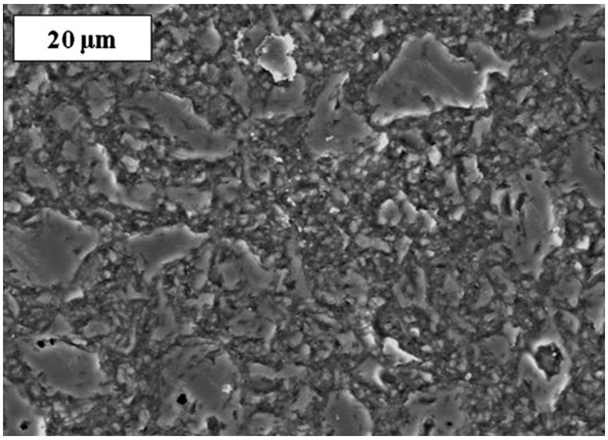

Fig. 2. SEM image of microstructure of the cross-section of a fabricated SiC pellet.

sion rates under different atmospheres such as Ar/O_2, Ar/CO_2, O_2/CO_2, Ar/H_2O, O_2/H_2O and CO_2/H_2O are compared in this work to determine the most efficient atmosphere for reprocessing SiC IMFs and to obtain a better understanding of the reaction mechanism. Finally, the SiC pellets with 5 wt.% of CeO_2 as a PuO_2 surrogate were fabricated. The molten salt corrosion/dissolution method was also applied to separate CeO_2 without the SiC matrix.

2. Experiment

2.1. Fabrication of SiC pellet with and without CeO_2

The fabrication processes of SiC pellets with and without CeO_2 have been described by Shih et al. [7]. β-SiC powders (from Superior Graphite) with 16.9 μm (coarse) and 0.6 μm (fine) nominal particle size were mixed at a 3:2 weight ratio with 10 wt.% of SMP-10 (from Starfire Systems Inc.) and with or without 5 wt.% CeO_2 in a ball mill for 1 h. The polymer precursor SMP-10 is an allylhydrido-poly-carbosilane which yields almost stoichiometric amorphous SiC. The mixed powder was uniaxially pressed into pellets of 3 mm in height and 13 mm in diameter at 600 MPa. The pellets were then heat treated in an alumina tube furnace up to 1050 °C with a constant ultra-high purity (UHP) argon flow. A standard heating profile recommended by Starfire Systems Inc. was followed in order to obtain the highest SiC yield.

After heat treatment, the pellet density was determined by the Archimedes' method. The pellet surface was mechanically polished to a mirror finish using diamond paste of different particle sizes from 15 to 1 μm. The crystal structure of both the raw materials and the pellets after heat treatment were determined by an X-ray diffractometer (XRD, Philips APD 3720). The microstructure of a SiC pellet was examined by using a scanning electron microscopy (SEM, JEOL 6335F).

2.2. Process design

A scheme of process design was illustrated in Fig. 1. Three different gases Ar, CO_2 and O_2 were supplied through the compressed gas cylinders. A twin flow meter was used to adjust the gas flows. The pressure change in the corrosion system was monitored by using a pressure gauge. A tube furnace (F79340-33 manufactured by Barnstead Thermolyne) with stain-less steel caps on both ends was used in the SiC corrosion experiments. The corrosion tests were conducted at 1050 °C. Nano-pure water contained in syringes was supplied through a syringe pump. At 1050 °C, the end-cap temperature was above 200 °C which allowed water to vaporize immediately once it was pumped into the furnace. A glass wool plug was placed near the inlet end to aid in equilibrating the water vapor flow. The partial pressure of water vapor in the gas mixture was varied by controlling the liquid water flow rate. Outflow gases were bubbling through two different liquids. Silicone oil was used in non-water vapor experiment in order to prevent any moisture backflow. Water was used to collect steam since the amount of moisture backflow would be trivial compared to steam supplied in experiment.

2.3. SiC pellet corrosion

Crucibles containing three synthesized SiC pellets and K_2CO_3 salt (from Alfa Aesar) were placed midway along the tube furnace. The initial molten salt depth, a distance between the molten salt/air interface to the upper surface of SiC pellets, was held constant. The tube furnace was heated to 1050 °C, followed by an isothermal hold up to 4 h.

Different atmospheres (Ar/O_2, Ar/CO_2, O_2/CO_2, Ar/H_2O, O_2/H_2O and CO_2/H_2O) with a constant total gas flow were applied in the furnace at the isothermal stage. The partial pressures of O_2, CO_2 and H_2O gases were varied by controlling their flow rates. After corrosion, the residues of SiC pellets were cooled to room temperature followed by immersing in nano-pure water to remove salt and silicate and drying in a vacuum oven. The average weight loss percent of SiC pellets was then obtained.

2.4. Ceria corrosion in the H_2O/Ar atmosphere

Ceria was employed as a surrogate material for plutonia (PuO_2) since they have the same crystal structure, oxidation state and the similar thermal dynamic properties [5,13]. In this work, ceria fine powder (5–9 μm, from Alfa Aesar) and ceria pellets (relative density: 88%; purity: 99.9%, metal basis, from Alfa Aesar) were corroded by the molten K_2CO_3 salt at 1050 °C for 15 h under water vapor. The weight difference was measured between the initial ceria and the residue ceria after washing away the salt. An X-ray Diffraction Philips APD 3720 was used to characterize the residual ceria.

2.5. Ceria separation from SiC matrix

Three SiC/CeO_2 pellets were corroded in the molten K_2CO_3 salt (from Alfa Aesar) at 1050 °C for 1 h in water vapor. After cooling to room temperature, the salt residues and products were dissolved in boiling water. The CeO_2 powder was separated from the washing solution by centrifuging, followed by drying in a vacuum oven. The average weight recovered was obtained.