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Gas-cooled fast reactor fuel fabrication

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Abstract

The gas-cooled fast reactor is a high temperature helium-cooled Generation IV reactor concept. Operating parameters for this type of reactor are well beyond those of current fuels so a novel fuel must be developed. One fuel concept calls for UC particles dispersed throughout an SiC matrix. This study examines a hybrid reaction bonding process as a possible fabrication route for this fuel. Processing parameters are also optimized. The process combines carbon and SiC powders and a carbon yielding polymer. In order to obtain dense reaction bonded SiC samples the porosity to carbon ratio in the preform must be large enough to accommodate SiC formation from the carbon present in the sample, however too much porosity reduces mechanical integrity which leads to poor infiltration properties. The porosity must also be of a suitable size to allow silicon transport throughout the sample but keep residual silicon to a minimum.

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1. Introduction

The gas-cooled fast reactor (GFR) is a Generation IV reactor design. The GFR is a high temperature, closed cycle fast spectrum helium-cooled reactor. In thermal gas-cooled reactor fuels, a relatively low density of fissile material is dispersed in large amounts of graphite. The GFR fuel will have a high fissile phase density and graphite cannot be used because of the excessive moderation it would cause as well as irradiation induced property changes. The graphite in thermal reactor systems provides a large thermal mass, which combined with good thermal conductivity, moderates temperatures in a loss of coolant accident. Because the GFR system cannot use large amounts of graphite, the thermal mass and overall thermal conductivity of the fuel is lower than thermal gas reactor fuels. Because of the lower thermal conductivity and thermal mass in a loss of flow accident core temperatures may reach as high as 1600 °C in minutes and remain there for hours. This extreme temperature necessitate a fuel that will withstand 1600 °C for extended periods of time and remain structurally intact and retain fission products. This requirement eliminates most commonly used fuel fabrication materials, and refractory metal use must be minimized in order to keep favorable neutronic conditions. Therefore, some of the most promising materials left for fuel fabrication are refractory carbide and nitride ceramics such as SiC, ZrC, TiC, TiN, and ZrN.

One fuel concept examined in the US contains 50 vol.% fuel dispersed in an inert matrix. Because of programmatic funding constraints fabrication studies could not be carried out on all possible candidate refractory materials. Therefore, because of

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the favorable high temperature properties, an existing irradiation behavior data base, and ease of fabrication work was focused on using SiC as the matrix material. The fuel design calls for a 410 μm (U,Pu)C kernel coated with a 17 μm thick porous buffer layer of SiC followed by an 18 μm thick dense SiC outer layer dispersed in an SiC matrix. SiC has been used in fuels before, however generally only as a coating as in the TRISO fuel particles not as a structural material except in a few cases [1]. The fuel form would be a hexagonal block with coolant holes throughout the block. These blocks would then be stacked together forming the core.

SiC is a covalently bonded ceramic which leads to its favorable mechanical and high temperature properties. But because it is covalently bonded, fully dense samples are difficult to obtain using traditional press and sinter technology without substantial amounts of sintering aids or temperature in excess of 2000 °C [2]. Addition of pressure, either uniaxial or isostatic, during heating helps lower the temperatures needed but these processes are not well suited for complex geometries or commercialization, respectively. Because of the difficulty of producing complex SiC shapes, reaction bonding was chosen as the fabrication method due to its near net shape fabrication abilities [3]. Reaction bonding is generally done by: (1) pressing a compact of SiC and carbon powders then infiltrating with molten silicon, or by (2) producing a porous carbon preform by pyrolyzing a high carbon yield material [4,5]. A hybrid process combining both SiC and carbon powders as well as a high carbon yield polymer was chosen for this research. A disadvantage to all SiC reaction bonding processes is excess silicon in the microstructure. The process labeled (1) above results in a continuous silicon matrix surrounding SiC. Using the polymer based process the microstructure obtained is a continuous matrix of reaction formed SiC surrounding isolated regions of free silicon. In both processes the free silicon amounts to approximately 10–15 vol.%. Because silicon melts substantially lower than the useful temperature of bulk SiC, the presence of free silicon in SiC lowers the high temperature mechanical properties. Because of this it is desirable to minimize the amount of residual free silicon in the final sample.

Preliminary experiments were carried out using only the polymer to produce preforms through pyrolysis. This was the preferred process because of the ability to cast complex shapes with the polymer, eventually followed by infiltration. However, upon pyrolyzation approximately 65 vol.% shrinkage occurred. Spherical surrogate fuel particles were added to the polymer, mixed, cured and pyrolyzed. These preforms would either disintegrate during pyrolyzation or would disintegrate upon handling after pyrolyzation. The disintegration, or lack of structural integrity, occurred because the high volume of spherical particles created a rigid skeleton. When the polymer pyrolyzed it pulled away from this skeleton leaving little or no support, thus no structural integrity. To reduce shrinkage the amount of polymer used was reduced by adding a filler powder consisting of SiC and/or carbon powders. The addition of filler powder reduced the shrinkage but also greatly affected the preform microstructure. The composition of the filler powder and pellet pressing pressure also affected the preforms.

Preliminary results show the fabrication concept to be a feasible fuel fabrication approach. However, it was seen that the fabrication process needed to be optimized in order to obtain a matrix free of cracking and with less than 5 vol.% residual silicon. It was decided that the best approach to fabrication refinement was to fabricate an optimized preform that would infiltrate to form an optimal matrix first. This would identify those features critical to producing the desire matrix microstructure and how the fabrication process and parameters influences these features. After successfully producing the matrix by itself, efforts would concentrate on reproducing these results with samples containing fuel particles. Accordingly, the work discussed here focused on the resulting effects of filler powder fraction and composition, and pellet pressing pressures on the microstructure of the preform and infiltrated sample without fuel particles, through a series of parametric studies.

2. Experimental

A furfuryl polymer was made by mixing furfuryl resin, furfuryl alcohol, a pore forming agent, and *para*-toluene sulfonic acid as a catalyst. The pore forming agent used was diethylene glycol. This mixture was mixed with the carbon and SiC powders in acetone for approximately 18 h. After mixing, the precursors are dried, sieved and pressed into pellets. These pellets are then cured at 60 °C for 2 h then 100 °C for approximately 12 h in order complete polymerization. After curing, the samples were raised to 1000 °C in argon at a rate of 20 °C per hour to pyrolyze the polymer. After the sample is pyrolyzed it can be infiltrated. Infiltration took place by laying the sample on silicon chips and heating to above the melting point of 1410 °C in an inert or vacuum environment. The process is shown in the flow chart, which can be seen in Fig. 1.

Samples were made with 0, 35, 50, and 80 wt% filler powders with the remainder being the pre-pyrolyzed polymer mixture. Preliminary experiments have shown that the samples made with only SiC powder as the filler contained more excess silicon than those which contained carbon fillers as well. However, samples made with only carbon fillers delaminated during infiltration. To determine the optimal filler composition the ratio of SiC to carbon powder was varied from 70 to 90 wt% SiC. The filler powder consisted of 100% compressed carbon black (acetylene derived), synthetic graphite (−325 mesh), and β-SiC (mean particle size of 0.592 μm). The carbon black and graphite were kept at a 25:75 weight ratio to each other. The large amounts of filler powder added led to the preform fabrication process being a powder pressing operation as opposed to a casting operation. In order to determine the optimal pellet pressing pressure, pressures were varied from 8.6 to 68.9 MPa (1250–10 000 psi). After pyrolyzation and infiltration samples were characterized using optical and scanning electron microscopy.

3. Results

The literature has shown that a ratio of 25:75 by weight furfuryl alcohol to furfuryl resin and 4 wt% (with regard to the furfuryl components) *para*-toluene sulfonic acid to be the optimum mixture [6]. If too much alcohol is added the reaction can progress too quickly and releases a large amount of heat and gas resulting in a hard foam like polymer seen in Fig. 2. If too much resin is added the reaction is too sluggish and takes excessively long for curing. The proper mix yields a liquid that can be cast and cured into shape or be mixed with other fillers and pressed into shape. Initially samples were made without carbon and SiC filler material, however this process was abandoned early on due to poor results as explained above. To reduce shrinkage filler materials were added. Table 1 shows the shrinkage results seen for four different filler amounts. All percentages are based on pre-pyrolyzed weights of the filler materials and the polymer precursor mixture.

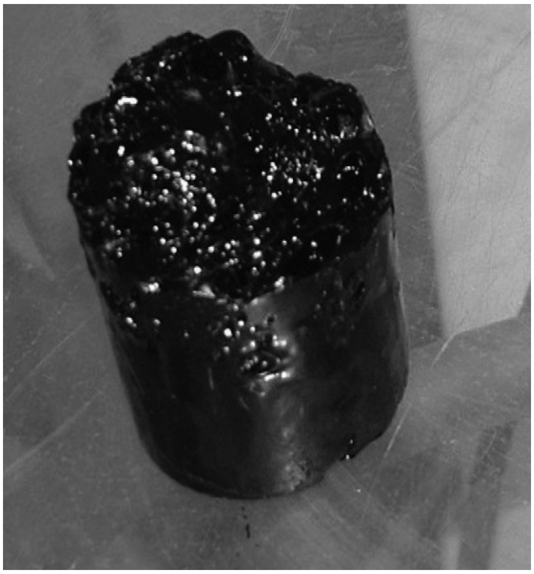

Fig. 2. Polymer made with no furfuryl resin.

Varying amounts of filler material also affect the microstructure of the preform as can be seen in Figs. 3–6. Figs. 3 and 4 show examples of samples made from the same polymer batch but one having 35% SiC filler material. The addition of filler material has a refining affect on the preform microstructure which leads to a more refined SiC microstructure

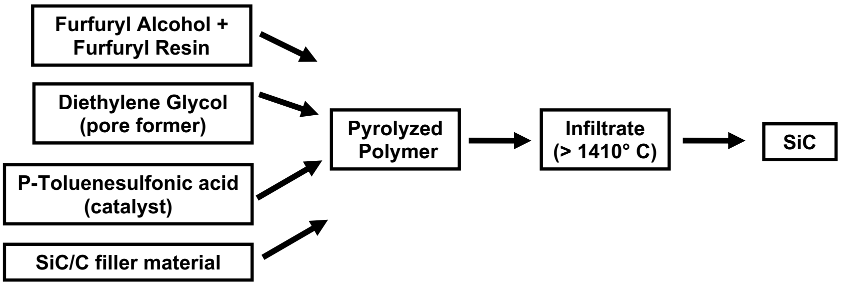

Fig. 1. Flowchart of process used to produce reaction bonded SiC samples.

Table 1
Effects of filler material amount on shrinkage

Filler material (wt%)	Shrinkage after pyrolyzation (vol.%)
0	65
35	55
50	22
80	5

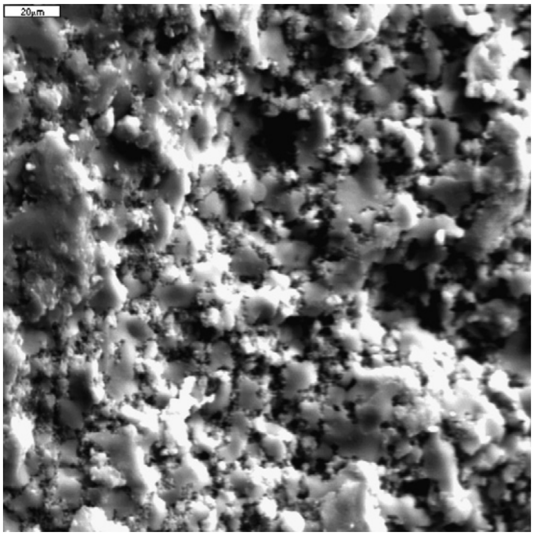

Fig. 3. Pyrolyzed preform microstructure without filler material.

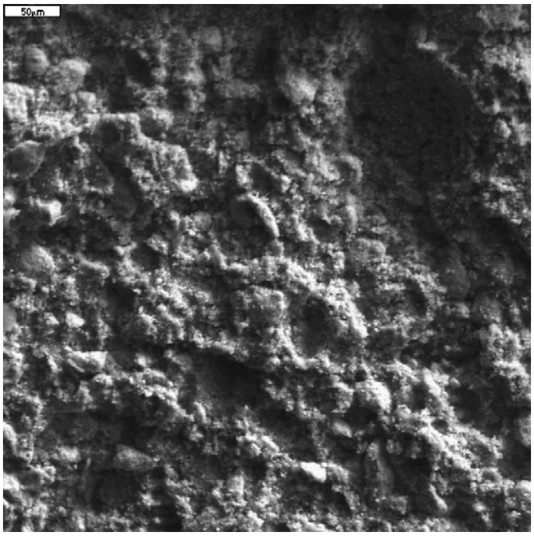

Fig. 4. Pyrolyzed preform microstructure with 35 wt% (based on pre-pyrolyzed masses) SiC filler.

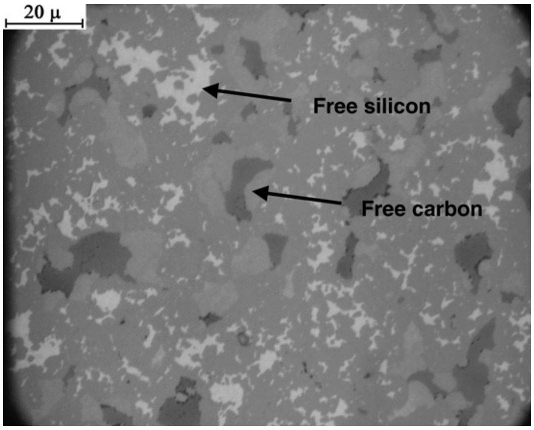

Fig. 5. Infiltrated microstructure resulting from a preform similar to one seen in Fig. 3.

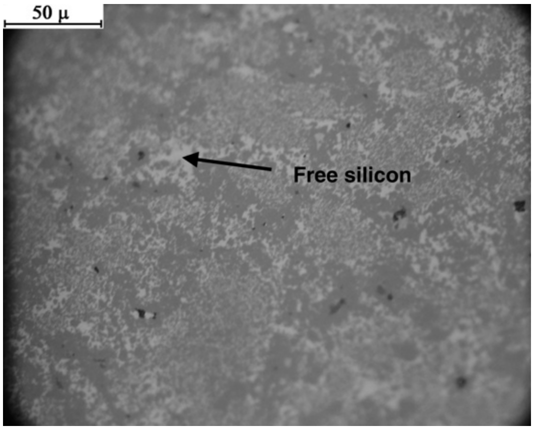

Fig. 6. Infiltrated microstructure resulting from a preform similar to one seen in Fig. 4.

after infiltration as seen in Figs. 5 and 6. Fig. 5 had no filler added and had a preform microstructure very similar to Fig. 3, while the sample in Fig. 6 had 35 wt% filler material and a preform microstructure similar to that seen in Fig. 4. Because the carbon preform microstructure in the sample from Fig. 6 was more refined all of the carbon was converted to SiC as opposed to the resulting matrix microstructure seen in Fig. 5, which contains unreacted graphite resulting from the coarser preform microstructure.

Because of the low amount of shrinkage seen in the 80% filler samples the remainder of the samples contained 80% filler material where the filler material consisted of 90% β-SiC, 80% β-SiC, and 70% β-SiC with the remaining portion being carbon in the form of carbon black and graphite as explained in the above section. After pyrolyzation the samples were weighed to determine mass loss and dimensionally characterized to characterize volumetric shrinkage. It was assumed that the initial amount of polymer added minus the mass loss gave the carbon formed on pyrolyzation. It was further assumed that the density of carbon was 2.0 and 3.2 g/cm^3 for β-SiC. Because the mass of SiC, initial carbon, and initial polymer is known the volume percent of each component can be calculated as seen in Table 2. When infiltrated the samples with 90% SiC filler remained intact but did not fully infiltrate, in many cases only the surface reacted to form a dense SiC outer layer. Samples with 80% SiC filler did fully infiltrate but there were many large cracks visible, which filled with excess silicon when adequate silicon was present. The 70% SiC filler samples also fully infiltrated, however, the resulting samples were very friable and had no structural integrity and often delaminated completely during infiltration. Fig. 7 shows typical pellets from each of the three groups after infiltration.

Because the samples with 90% SiC filler remained intact, and no cracks were seen on the sample that did partially infiltrate it was decided to focus on this composition. In the next batch of samples the pellet pressures were varied. Table 2 lists the specific parameters used and resulting pellet volume

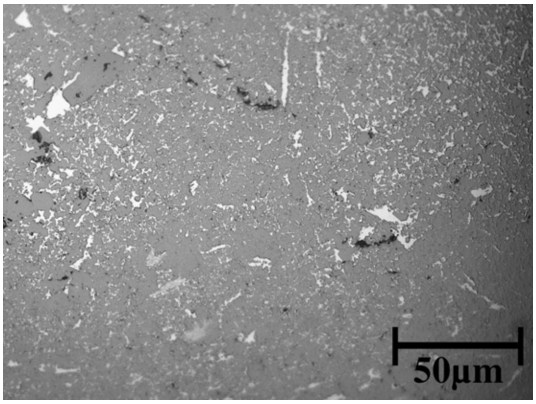

Fig. 8. Resulting SiC microstructure of a pellet with 90% SiC filler material and a porosity to carbon ration of 2.68.

Table 2
Results from pyrolyzation and infiltration of several pellets with different filler SiC loadings and pressing pressures

Sample	Pressing pressure (MPa)	Volume (cm^3)	SiC (vol.%)	Carbon (vol.%)	Porosity (vol.%)	Porosity/C	Infiltration results
90-1	17.2	0.45	45.0	15.7	39.3	2.50	Center portion not infiltrated
90-2	34.4	0.40	49.5	17.2	33.2	1.92	Surface only
90-3	51.7	0.41	51.2	17.8	31.0	1.74	Surface only
80-1	17.2	0.38	38.3	22.6	39.1	1.74	Delamination, friable
80-2	34.4	0.28	42.4	25.6	32.0	1.25	Large cracks
80-3	51.7	0.33	43.9	26.1	30.0	1.15	Large cracks
70-1	17.2	0.33	31.7	28.4	39.9	1.40	Delamination, friable
70-2	34.4	0.26	35.5	31.7	32.8	1.04	Delamination, friable
70-3	51.7	0.32	37.1	32.6	30.4	0.93	Cracks, slightly friable
90-4	8.6	0.42	36.3	12.0	51.7	4.31	Friable
90-5	17.2	0.35	44.6	15.1	40.4	2.68	Dense sample

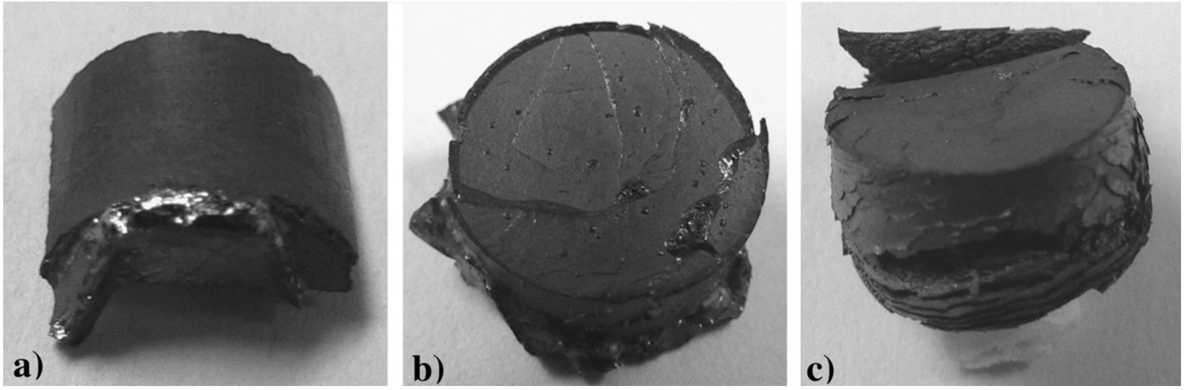

Fig. 7. Typical pellets after infiltration: (a) 90% SiC filler; (b) 80% SiC filler; (c) 70% SiC filler.

fractions. Infiltration results varied from a fully infiltrated dense pellet to a friable pellet with no structural integrity. Fig. 8 shows the microstructure of the fully infiltrated pellet. As can be seen the pellet is nearly 100% dense with very little residual silicon.

4. Discussion

When 80 wt% filler material is used the shrinkage is controlled to approximately 5%. The low amount of shrinkage is important because the preform will crack and often fall apart as the polymer pulls back away from the rigid particles if an appreciable amount of spherical particles are added. Pores are formed in the polymer by the pore forming agent which is rejected from the polymer precursor during polymerization. Once rejected the pore former acts as an inert component, which the polymerization will go around as the reaction continues [7]. The filler material has a refining affect on the microstructure for much the same reason. The polymerization occurs around the inert filler material, which is mixed throughout the polymer forcing the polymerization to occur around the inert filler particles. Because of the high loading of filler material the polymer acts as both a binder and carbon source. However, even after pyrolyzation the pellets are very robust because of the binding action of the carbon left from pyrolyzation. The preform microstructure influences the final microstructure because the silicon initially reacts with the carbon on the surface but is then stopped by the newly formed SiC from reacting with the remaining carbon, this can be seen in Fig. 5. Fig. 6 shows the resulting microstructure where the carbon is fine enough that full conversion to SiC takes place.

During reaction bonding the carbon present must be converted into SiC. Carbon has a molar volume of 5.3 cm^3/mol, SiC has a molar volume of 12.5 cm^3/mol. So in order to convert the carbon to SiC in the sample and remain intact there must be adequate room for the formation of the SiC. The carbon will increase 2.36 times its original volume during formation of SiC. Therefore, the porosity to carbon ratio must be greater than this value to ensure there is adequate space for the formation of SiC. As is seen from the figures and Table 2 the samples that remained intact while having an appreciable amount of infiltration had a porosity to carbon ratio of 2.5 and 2.6, respectively. If this ratio is low the samples will crack and delaminate in order to accommodate the SiC formation. However, if there is too much porosity the final sample will contain large amounts of porosity which will lead to a friable sample with little to no structural integrity or if adequate silicon is present the porosity will be filled with silicon increasing the amount of free silicon to unacceptably high levels. The size of the porosity is also important because the interconnected porosity is the transport mechanism of the molten silicon during infiltration. Regardless of if the correct relative amounts of carbon and porosity are present if the interconnected porosity is too small infiltration cannot take place. The silicon will start infiltrating on the surface, but the channels will quickly choke off with newly formed SiC leading to an SiC coated preform with no reaction formed SiC in the interior.

5. Conclusions

This work has used several parametric studies to optimize parameters in reaction bonding of SiC in support of GFR fuel fabrication development. Varying amounts of filler materials were mixed with the polymeric precursor to control shrinkage during pyrolyzation. It was seen that a loading of 80 wt% was needed to keep shrinkage down to a few percent. Filler material composition was also examined by varying the relative amount of SiC and C powders used. 90 wt% SiC/10 wt% C powder produced the best results, however, this may have been a function of the carbon to porosity ratio more than filler composition. However, previous work has shown that the best microstructure is achieved with a combination of both SiC and carbon fillers. Pellet pressing pressures were also varied in order to change the porosity volume within the samples. From this series of experiments it was seen that a porosity to carbon volume ratio of 2.5–2.6 produces samples with a dense SiC microstructure with minimal free silicon present. It was also seen that this ratio may be achieved at several different pressing parameters, because other factors affect the final density such as efficiency of drying. It is possible that the dense samples could be made at filler compositions other than 90% SiC 10% carbon, but another study would be needed to determine what other parameters would be needed to obtain the proper porosity and carbon ratios. In the actual fuel fabrication process fuel particles will also be added to the filler material. Past results have also shown this to have a profound effect on the preform microstructure and infiltration behavior. A few preliminary experiments have been run with low volume loading of surrogate fuel particles with promising results. However, the large fissile volume loading required will undoubtedly reduce the transport paths of the silicon carbide. Also a process must be developed to ensure evenly spaced particles completely surrounded by the SiC precursor materials. Further characterization of the resulting preform and matrix microstructures will also be necessary. In conclusion this process still seems to be a viable path to a dense SiC matrix dispersion fuel suitable for the GFR, but continued process development and product characterization will be needed.

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