Theoretical Considerations for Reaction-Formed Silicon Carbide (RFSC) Formation by Molten Silicon Infiltration into Slurry-Derived Preforms

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THEORETICAL CONSIDERATIONS FOR REACTION-FORMED SILICON CARBIDE

(RFSC) FORMATION BY MOLTEN SILICON INFILTRATION INTO SLURRY-DERIVED PREFORMS

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SUMMARY

For reaction-formed silicon carbide (RFSC) ceramics produced by silicon melt infiltration of porous carbon preforms, equations are developed to relate the amount of residual silicon to the initial carbon density. Also, for a slurry derived preform containing both carbon and silicon powder, equations are derived which relate the amount of residual silicon in the RFSC to the relative density of the carbon in the preform and to the amount of silicon powder added to the slurry. For a porous carbon preform that does not have enough porosity to prevent choking off of the silicon infiltration, these results show that complete silicon infiltration can occur by adding silicon powder to the slurry mixture used to produce these preforms.

INTRODUCTION

Advanced ceramics fabricated by tape casting techniques (refs. 1 and 2) have attracted a great deal of attention for a variety of structural, electronic, and optical applications. Tape casting processes typically consist of the preparation of a stable slurry of a ceramic powder in an aqueous or nonaqueous liquid and a dispersant to assure the stability of the suspension. This slurry is then cast on a surface through the action of a blade which levels the slurry. This tape is then dried and consolidated with other tapes to give desired shapes. Recently, there have been a number of activities in the processing of silicon carbide ceramics via slurry routes (refs. 3 and 4). Borom et al. (ref. 4) have fabricated preforms from tapes made using slurries containing chopped carbon fibers and silicon carbide particulates and infiltrated them with liquid silicon. The final reaction-formed silicon carbide (RFSC) material consisted primarily of silicon carbide with small amounts of unreacted carbon and residual silicon.

For RFSC ceramics in which the porous preforms are made by tape casting of a slurry, the initial relative carbon density (defined here as the weight of the carbon in the preform divided by the sum of the volumes occupied by the carbon and the pores in the preform) depends on the packing of the carbon powder and/or carbon fibers, the packing of fillers such as silicon carbide powder, the char yield of the organic binder, the ratio of added carbon to organic binder, and various other factors. The carbon source is not necessarily restricted to carbon powder. Other sources of carbon such as carbon fiber felt or chopped fibers alone or in combination with carbon powders can also be used. The inadequate control of relative carbon density throughout the preform can give rise to undesirable results i.e., choking off, excess silicon and/or unreacted carbon in the final material, as well as cracking of preforms during silicon infiltration (ref. 6).

The amount of residual silicon in the RFSC materials, made by the complete infiltration of silicon into carbon preforms, depends on the porosity of the preform and the composition of infiltrants (refs. 5 to 7). The volume occupied by the silicon carbide formed by reactive infiltration is larger than the volume occupied by the carbon in the preform. For complete infiltration and reaction of all the carbon to occur, there must be sufficient pore volume to allow for this volume change. If there is insufficient pore volume in the preform, choking off will occur during silicon infiltration. As the silicon starts to flow into the
pores they will become narrow and eventually will close, stopping the flow of silicon. Thus, we can define a critical relative carbon density, \( R^* \), for a preform as the relative carbon density which has just enough pore volume to accommodate the volume change during the reaction of silicon with carbon without choking off or excess silicon. That is, above \( R^* \), choking off will occur; while below \( R^* \), excess silicon will be included in the RFSC material.

There are a number of critical factors which influence the tape casting behavior of slurries. These are the properties of carbon powders, fillers and binders, and other ingredients used to control various aspects of the slurry such as powder agglomeration, slurry stability, and viscosity. If a slurry formulation produces a porous preform whose relative carbon density is higher than the critical value, the question is how to reformulate the slurry so that the resulting preform can be successfully infiltrated with silicon without appreciably changing other critical properties of the slurry.

In this paper, various possibilities are investigated to produce porous carbon preforms with and without silicon powder additions to the slurry mixtures. The necessary equations are derived to apply these ideas to actual slurry mixtures. The advantages of silicon powder additions to slurry formulations in which the packing of the carbon powder along with the other sources of carbon in the slurry produce relative carbon densities larger than \( R^* \), are discussed. Modeling results are used to show that slurry modifications with silicon powder can prevent choking off during silicon infiltration. This information will be very useful to researchers and industries involved in the fabrication of silicon carbide based ceramics and composites using tape casting and silicon infiltration.

THEORETICAL CONSIDERATIONS

In the following sections, we derive equations that show how the amount of residual silicon in the RFSC materials depends on the amount of porosity in (1) pure porous carbon preforms and in (2) silicon powder containing porous carbon preforms. These results are used to show the benefits of silicon powder addition to slurries in preventing choking off during liquid silicon infiltration.

**Pure Carbon Preforms**

We shall first consider the case of a RFSC material formed from a porous carbon preform which contains only carbon and pores. Experimental observations have shown that the external dimensions of the microporous carbon preforms with controlled amount of porosity, do not change during silicon infiltration (refs. 5 to 7). We will assume that this is also true for slurry derived preforms. The volume of a porous carbon preform will be the sum of volumes of \( U_C \), \( U_{CA} \), and \( U_P \), where \( U_C \) and \( U_{CA} \) are the volumes occupied by the carbon char from the binder and carbon powder added to the slurry mixture, respectively and \( U_P \) is the volume occupied by the pores. If the infiltration and reaction are completed without choking off, the total volume of the RFSC material after infiltration will consist of \( U_{SiC} \) and \( U_{Si} \) where \( U_{SiC} \) and \( U_{Si} \) are the volumes occupied by the silicon carbide and residual silicon, respectively. With the assumption of no total volume change and no residual porosity left based on experimental observations of a variety of RFSC materials (refs. 5 to 7), then

\[
U_C + U_{CA} + U_P = U_{SiC} + U_{Si} \tag{1}
\]
The relative carbon density, $R$, for the preform is

$$R = \frac{W_C + W_{CA}}{U_C + U_{CA} + U_P} \quad (2)$$

where $W_C$ and $W_{CA}$ are the weights of carbon derived from the carbon char and the carbon powder, respectively. Solving equation (2) for $U_C + U_{CA} + U_P$ and putting it into equation (1), we have

$$\frac{W_C + W_{CA}}{R} = \frac{W_{SiC}}{d_{SiC}} + \frac{W_{Si}}{d_{Si}} \quad (3)$$

We have replaced $U_{SiC}$ and $U_{Si}$ with $W_{SiC}/d_{SiC}$ and $W_{Si}/d_{Si}$, respectively, where $d_{SiC}$, $W_{SiC}$, and $d_{Si}$, $W_{Si}$ are the densities and weights of silicon carbide and silicon, respectively. For a preform that has sufficient pore volume so that choking off does not occur, all the carbon will be converted to silicon carbide. Thus, the number of moles of silicon carbide in the RFSC material will be equal to the number of moles of carbon in the preform, given as

$$W_{SiC} = \frac{W_C + W_{CA}}{M_C} \quad (4)$$

where $M_{SiC}$ and $M_C$ are the molecular weights of silicon carbide and carbon, respectively.

The weight of residual silicon in the RFSC material can be found by solving equation (4) for $W_{SiC}$ and substituting it into equation (3) and then solving equation (3) for $W_{Si}$ as

$$W_{Si} = (W_C + W_{CA}) \left( \frac{d_{Si}}{R} - \frac{M_{SiC}}{M_C} \frac{d_{Si}}{d_{SiC}} \right) \quad (5)$$

Obtaining $W_{SiC}$ and $W_{Si}$ from equations (4) and (5), the weight fraction, $X_{Si}$, of residual silicon in the RFSC is

$$X_{Si} = \frac{W_{Si}}{W_{SiC} + W_{Si}} = \frac{M_C}{M_{SiC}} d_{SiC} - \frac{R}{M_{SiC} \left( \frac{d_{SiC}}{d_{Si}} - 1 \right)} \quad (6)$$

It can be seen from the equation (6) that the weight fraction of residual silicon in the RFSC material depends, apart from the material constants, only on the relative carbon density of the porous carbon preform. Thus by measuring the relative carbon density, $R$, of a porous carbon preform, the amount of residual silicon in the silicon infiltrated preform could be calculated provided that choking off did not occur (that is if $R < R^*$). If, on the other hand, we wanted to make a RFSC material containing a given amount of residual silicon, we need to know the relative carbon density of the preform that would produce
the desired silicon content. This can be obtained by solving equation (6) for the relative carbon density, \( R \), as

\[
R = \frac{M_C}{M_{SiC}} \frac{d_{SiC}}{1 + \frac{X_{Si}}{1 - X_{Si}} d_{SiC}}
\]

The critical relative density, \( R^* \), can be obtained by setting \( X_{Si} \) equal to zero in equation (7), as

\[
R^* = \frac{M_C}{M_{SiC}} d_{SiC} = 0.963 \text{ g/cm}^3
\]

Preforms that have relative carbon densities greater than \( R^* \) cannot be completely infiltrated with silicon due to choking off during infiltration.

Effect of Silicon Powder Addition

Many slurry derived porous carbon preforms cannot be completely infiltrated with silicon as their relative carbon densities are greater than the critical density, \( R^* \). This is in part due to the dense packing of the carbon powder. In this section, we derive the relationship between the preform relative carbon density, the amount of silicon powder that is added to the slurry mixture, and the amount of residual silicon after silicon infiltration.

If silicon powder is added to the original slurry mixture, the resulting preform will have the added silicon powder along with carbon and pores. It is assumed as before that the total volume of the preform before silicon infiltration is equal to the total volume after infiltration, then

\[
U_C + U_{CA} + U_{SiA} + U_P = U_{SiC} + U_{Si}
\]

where \( U_{SiA} \) is the volume occupied by the added silicon powder. We shall obtain expressions for \( U_P, U_{SiC} \), and \( U_{Si} \) that express these quantities in terms of \( U_C + U_{CA} \). The relative carbon density, \( R \), of the preform is given by equation (2) which can be solved for \( U_C + U_{CA} + U_P \), as

\[
U_C + U_{CA} + U_P = \frac{W_C + W_{CA}}{R}
\]

As before, we let \( X_{Si} \) equal the weight fraction of residual silicon in the RFSC material, so that from equation (6),

\[
W_{Si} = \frac{X_{Si}}{1 - X_{Si}} W_{SiC}
\]
In equation (11), setting \( W_{Si} \) equal \( U_{Si}/d_{Si} \) and solving for \( U_{Si} \), we have

\[
U_{Si} = \frac{X_{Si}}{1 - X_{Si}} \frac{(W_{C} + W_{CA})M_{SiC}}{M_{C}d_{Si}}
\]

where we have replaced \( W_{SiC} \) from equation (4). We can now replace \( U_{C} + U_{CA} + U_{P}, U_{SiC}, \) and \( U_{Si} \) in equation (9) using equations (10), (4), and (12) respectively, which becomes

\[
\frac{W_{C} + W_{CA}}{R} + \frac{W_{SiA}}{d_{Si}} = (W_{C} + W_{CA}) \frac{M_{SiC}}{M_{C}d_{SiC}} + \frac{X_{Si}}{1 - X_{Si}} \frac{(W_{C} + W_{CA})M_{SiC}}{M_{C}d_{Si}}
\]

This equation can be solved for the weight fraction of silicon in the infiltrated preform, \( X_{SiA} = W_{SiA}/(W_{C} + W_{CA}) \), as

\[
X_{SiA} = \frac{W_{SiA}}{W_{C} + W_{CA}} = \frac{M_{SiC}}{M_{C}} \left( \frac{d_{Si}}{d_{SiC}} + \frac{X_{Si}}{1 - X_{Si}} \right) - \frac{d_{Si}}{R}
\]

This equation can also be used to find \( X_{Si} \) if \( R \) and \( X_{SiA} \) are known, or to find \( R \) if \( X_{Si} \) and \( X_{SiA} \) are known.

**Application to Slurry Formulations**

In this section, we consider porous carbon preforms that have relative carbon densities that are higher than the critical relative carbon density, \( R^* \), and thus would choke off during silicon infiltration. In practice, relative carbon densities greater than critical density, \( R^* \), are likely to result during slurry processing due to the packing of the carbon powder. We shall assume that these preforms are made from slurry mixtures and that they contain some carbon powder. We will use these equations to determine how much carbon powder must be replaced by silicon powder in these mixtures to produce a preform that after silicon infiltration will have a given amount of residual silicon. Because we do not want to change appreciably other properties of these slurry mixtures such as viscosity and/or tape casting ability, we will assume that keeping the volume of solids unchanged by removing a certain volume of carbon powder and replacing it by an equal volume of silicon powder will have little effect on slurry properties.

We shall consider two slurry mixtures, an initial mixture that produces a porous carbon preform with a relative carbon density, \( R^i \), larger than the critical relative density, \( R^* \), which would choke off during silicon infiltration. The second mixture is then a reformulation of the initial mixture. It differs from the initial mixture by replacing a certain volume of the carbon powder in the mixture by an equal volume of silicon powder. This reformulated mixture will be designated the final mixture. We then have

\[
U_{CA}^i = U_{CA}^f + U_{SiA}
\]

where \( U_{CA}^i \) is the volume of carbon powder in the initial mixture, \( U_{CA}^f \) is the volume of carbon powder in the final mixture, and \( U_{SiA} \) is the volume of silicon powder added in the final mixture. Using the
definition of relative carbon density given in equation (2), the relative carbon densities for the initial preform $R^i$ and for the final preform $R^f$ are,

$$R^i = \frac{W_C + W^i_{\text{CA}}}{U_C + U^i_{\text{CA}} + U_p}$$  \hspace{1cm} (16)$$

and

$$R^f = \frac{W_C + W^f_{\text{CA}}}{U_C + U^f_{\text{CA}} + U_p}$$ \hspace{1cm} (17)$$

Because the only change made in reformulating the initial mixture was to replace a volume of carbon powder with an equal volume of silicon powder, the weight of carbon char, $W_C$, derived from the slurry is the same for the initial porous carbon preform and final porous carbon preform containing the added silicon powder. This is also true for the pore volume, $U_p$, in each of these preforms. Equation (16) can be solved for $U_p$ and substituted into equation (17) which becomes

$$R^f = \frac{W_C + W^f_{\text{CA}}}{U^f_{\text{CA}} - U^i_{\text{CA}} + \frac{W_C + W^i_{\text{CA}}}{R_i}}$$ \hspace{1cm} (18)$$

By dividing equation (15) by the product of $d_{\text{CA}}$ and $d_{\text{Si}}$, replacing the volumes by their corresponding weights and solving for $W^f_{\text{CA}}$, we get

$$W^f_{\text{CA}} = W^i_{\text{CA}} - \frac{d_{\text{CA}}}{d_{\text{Si}}} W_{\text{SiA}}$$ \hspace{1cm} (19)$$

where $d_{\text{CA}}$ is the density of the carbon powder. Using equations (15) and (19), equation (18) becomes

$$R^f = R^i \frac{1 - \frac{W_{\text{SiA}}}{W_C + W^i_{\text{CA}}} \cdot \frac{d_{\text{CA}}}{d_{\text{Si}}}}{1 - \frac{W_{\text{SiA}}}{W_C + W^i_{\text{CA}}} \cdot \frac{R^i}{d_{\text{Si}}}}$$ \hspace{1cm} (20)$$

In the last section, we saw that equation (14) gave the weight ratio of silicon powder to the total weight of carbon for a preform of relative carbon density, $R$, which would on silicon infiltration have a residual silicon weight fraction of $X_{\text{Si}}$. This equation can be rewritten in terms of the present superscript notation, as
This equation can be solved for \( W_{SiA} \) after replacing \( R^f \) and \( W_{fA} \) using equations (19) and (20), as

\[
\frac{W_{SiA}}{W_c + W_{fA}} = \frac{M_{SiC}}{M_c} \left( \frac{d_{Si}}{d_{SiC}} + \frac{X_{Si}}{1 - X_{Si}} \right) - \frac{d_{Si}}{R^f}
\]

Equation (22) gives the weight of silicon powder that should be added to the reformulated slurry mixture to yield residual silicon fraction \( X_{Si} \). The weight of carbon powder, \( W_{fA} \), that is to be added to the reformulated slurry mixture can be obtained from equations (19) and (22).

RESULTS AND DISCUSSION

We shall first consider a porous carbon preform composed of carbon and pores. This preform may also contain additional inert materials such as silicon carbide powder, or any other material that does not react with the infiltrating silicon. The relative carbon density, \( R \), of this preform does not depend on the amount of inert material. After molten silicon infiltration of a preform whose relative carbon density is less than the critical relative carbon density, \( R^* \), has been completed, all the carbon will have reacted with the silicon to form silicon carbide, and in general the remaining pores will be filled with silicon. The amount of residual silicon that remains in a silicon infiltrated preform can be obtained using: equation (6).

Figure 1 is a plot (using eq. (6)) showing the dependence of the amount of residual silicon in a silicon infiltrated material on the relative carbon density of that preform. Porous carbon preforms that have relative carbon densities greater than the critical value (\( R^* = 0.963 \) g/cm\(^3\) for silicon infiltration) cannot be completely infiltrated.

We next consider a porous carbon preform that not only contains carbon and pores, but also silicon powder. As discussed earlier, this preform may also contain inert material that is not affected by the silicon infiltration. The amount of residual silicon in the silicon infiltrated preform not only depends on the relative carbon density of the preform, but also on the amount of silicon powder in the preform. Figure 2 is a plot made using equation (14) showing the effect of silicon powder addition on the amount of residual silicon in the final material for four carbon relative densities (0.963, 1.0, 1.2, and 1.5 g/cm\(^3\)). Here, we have plotted the weight fraction \( X_{SiA} \) versus the weight fraction of residual silicon, \( X_{Si} \), in the silicon infiltrated preform (eq. (22)). It can be seen from this plot that preforms that have relative carbon densities greater than the critical value (\( R^* = 0.963 \) g/cm\(^3\) for silicon infiltration) can be infiltrated without choking off problems as indicated by positive amounts of residual silicon.

As an example, we shall consider a slurry that contains 50 g of carbon powder. The binder in the slurry after burn out produces 5 g of carbon char. The relative carbon density of the preform after burn out is 1.2 g/cm\(^3\) which is well above the critical relative carbon density of 0.963 g/cm\(^3\). If we want to avoid choking off and produce a RFSC material which contain 3 wt % residual silicon, we can replace some of the carbon powder with silicon powder. The amount of silicon powder needed in the reformulated slurry can be obtained by using equation (22) where \( W_c = 5 \) g, \( W_{fA} = 50 \) g, \( d_{Si} = 2.4 \) g/cm\(^3\).
d_{CA} = 2.2 \text{ g/cm}^3, \quad R_i = 1.2 \text{ g/cm}^3, \quad M_{SiC} = 40 \text{ g/mol}, \quad M_C = 12 \text{ g/mol}, \quad d_{SiC} = 3.21 \text{ g/cm}^3, \quad \text{and } X_{Si} = 0.03. \quad \text{Thus, the weight of silicon powder in the reformulated slurry is } W_{SiA} = 13.76 \text{ g. The weight of carbon powder in the reformulated slurry can be obtained using equation (19), as } W_{CA} = 37.39 \text{ g.}

Figure 3 is a plot of the weight ratio, $X_{SiA} = W_{SiA}/(W_C + W_{CA})$, versus $X_{Si}$ (the weight fraction of residual silicon in the silicon infiltrated preform made by the reformulated slurry) for four different values (0.963, 1.0, 1.2, and 1.5 g/cm$^3$) of the relative carbon density of the original preform. This shows for example that for porous carbon preform having a relative density of 1.2 g/cm$^3$ to be successfully infiltrated with silicon, somewhat more than 20 percent by weight of the carbon in the initial preform would have to be replaced by silicon powder.

CONCLUSIONS

We have theoretically shown, that a slurry mixture that is used to produce a porous carbon preform whose relative carbon density is larger than the critical value for choking off, can be reformulated by replacing some of the carbon powder in the original mixture by an equal volume of silicon powder. This will produce a porous preform that can be silicon infiltrated without choking off. Although, silicon and carbon powders may have different surface characteristics, it is anticipated that there will be minimal changes in other desirable properties of the slurry such as its tape casting abilities. Part of our future work will be directed at experimental validation of these concepts for reaction-formed silicon carbide fabrication.

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REFERENCES

Figure 1.—Effect of relative carbon density of carbon preform on the residual silicon content of final material.

Figure 2.—Effect of silicon powder addition (weight ratio of silicon powder to total carbon from the slurry) on the residual silicon content of final material produced from original slurry mixture (R is the relative carbon density of the preform).

Figure 3.—Effect of silicon powder addition (weight ratio of silicon powder to total carbon from the slurry) on the residual silicon content of final material produced from a reformulated slurry mixture (R is the relative carbon density of the preform).
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Gathered information includes the development of equations to relate the amount of residual silicon to the initial carbon density. Additionally, for a slurry derived preform containing both carbon and silicon powder, equations are derived which relate the amount of residual silicon in the RFSC to the relative density of the carbon in the preform and to the amount of silicon powder added to the slurry. For a porous carbon preform that does not have enough porosity to prevent choking-off of the silicon infiltration, these results show that complete silicon infiltration can occur by adding silicon powder to the slurry mixture used to produce these preforms.