Growth Stress in SiO$_2$ Formed by Oxidation of SiC

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ABSTRACT

Growth stresses in amorphous SiO$_2$ scales formed during SiC fiber oxidation were calculated. A numerical method using Deal-Grove oxidation kinetics and shear-stress dependent SiO$_2$ viscosity was used. Initial compressive stresses in SiO$_2$ of ~25 GPa from the 2.2× oxidation volume expansion rapidly relaxes. At >1200°C, viscous flow of amorphous SiO$_2$ further relaxes stress to negligible levels. At 700° - 900°C, axial and hoop stress at the GPa level persist in SiO$_2$ near the SiC-SiO$_2$ interface. Radial expansion of the scale causes hoop stress to become tensile, and axial stresses are driven to tensile values by the Poisson effect. These tensile stresses can be >1 GPa for thick scales formed at lower temperatures on surfaces with high curvature. Approximate analytical expressions for growth stress are discussed. Effects of viscosity variation as well as other assumptions and limitations of the calculation method are discussed.

INTRODUCTION

Constraint of the 2.2× volume expansion during oxidation of SiC to SiO$_2$ generates very large growth stresses. Microstructural evidence for these stresses exists for crystalline scales. High dislocation densities in crystalline SiO$_2$ near the SiC-SiO$_2$ interface are diagnostic of high shear stresses during growth of new scale.[1-2] Axial cracks form in the outer scale from tensile hoop growth stress.[1, 3] Tensile growth stresses may decrease fiber strengths, which is significant for structural applications.

Growth stress has been extensively modeled for silicon oxidation, which has volume expansion similar to SiC oxidation.[4-5] Recent models recognize that flow at high stress is viscoelastic and use the Eyring model for shear-stress dependent viscosity.[6-8] Radial compressive and tensile hoop growth stresses are predicted for oxidation of silicon fibers.[9-10] Axial stresses are generally ignored.[6, 9, 11] For structural fibers this is an important omission, because axial residual stress affects fiber strength. Tensile stress increases silicon oxidation rates,[12-13] and recently this has also been demonstrated for SiC.[14]

A method to calculate all the growth stress components anywhere in a SiO$_2$ scale formed by oxidation of SiC fibers is presented. The method involves scale discretization and separate calculation for each increment. Calculations are done at temperatures from 700° to 1300°C for amorphous scales. Growth stresses for SiC fibers with different radii are examined. Assumptions and limitations of the method are discussed. Complementary results and a more thorough description of the background information and method are given elsewhere.[15]

METHOD

A schematic of SiC fiber oxidation with discretization of SiO$_2$ scale is in figure 1. There are two sources of stress. The first is the elastic constraint of the 2.2× volume expansion accompanying oxidation. The second is the circumferential expansion of old scale as it is radially displaced outward by formation of new scale (Fig. 1). This creates tensile hoop stress (σ$_θ$) in the outer scale,[16] and tensile axial stress (σ$_z$) by the Poisson effect.
The large volume expansion raises concerns for growth stress modeling. Elastic constraint of the $2.2\times$ volume expansion causes $\approx 25$ GPa compressive stress in SiO$_2$, much larger than stresses for which linear elasticity is valid.[4] However, high shear stresses relax very rapidly to values appropriate for linear elasticity if SiO$_2$ viscosity is shear-stress dependent,[6, 17-18] and discretization can confine incremental stress differences to values appropriate for linear theory.[7, 19-20] General models of oxidation growth stress are coupled diffusion-reaction and fluid-mechanical problems.[19] The oxygen diffusion rate drives the rate that stress in the oxide is generated. Stress, in turn, affects the oxygen diffusion rates. The experimentally measured oxidation rates for SiC inherently include the effect of growth stress. The effect of stress on oxidation rate will therefore not initially be considered when modeling growth stress.

The following assumptions are used in modeling the growth stress: 1. Oxidation volume expansion is dilational. 2. Stresses resulting from constraint of oxidation expansion are relaxed by flow of SiO$_2$ with shear stress-dependent viscosity. 3. Discretization of oxidation to small increments allows use of linear elasticity. 4. Growth stress effects on oxidation kinetics are not considered. 5. Stress relaxation in the SiC fiber is negligible.

**Fiber Oxidation Kinetics**

Fiber oxidation kinetics will not deviate significantly from flat-plate geometry kinetics until the oxidation product for 12 $\mu$m diameter fibers is several microns thick.[1, 9, 21] SiO$_2$ thickness ($w$) (Fig. 1) therefore obeys Deal-Grove kinetics for flat-plate geometry:[1-2, 22]

$$w = \frac{1}{2} A \sqrt{1 + \frac{4Bt}{A^2}} - 1$$

(1)

The parabolic and linear rate constants are $B$ and $B/A$, respectively. $B$ and $A$ obey the usual Arrhenius relationships. The SiC radius ($b$) after oxidation is (Fig. 1):

$$b = \sqrt{w^2 (\Omega^2 - \Omega)} + b_o^2 - \Omega w$$

(2)

where $b_o$ is the original fiber radius and $\Omega$ is the SiC/SiO$_2$ molar volume ratio.

**Elastic Growth Stress**

The elastic stresses and strains are determined by modification of a method used for sequentially deposited coatings.[23] For discretized fiber oxidation, the “deposition” sequence is
reversed; the last oxide increment forms at the SiC-SiO₂ interface, and the oldest is at the surface. The system is divided into the unoxidized SiC fiber, the SiO₂ added from time \( t(i-1) \) to \( t(i) \) at the SiC-SiO₂ interface, and the outer SiO₂ increment added from \( t(0) \) to \( t(i-1) \) (Fig. 1). The axial, radial, and hoop stresses in the SiC fiber at time \( t(i) \) are \( σ_{z,\text{SiC}}(i) \), \( σ_{r,\text{SiC}}(i) \), and \( σ_{θ,\text{SiC}}(i) \) respectively, and in the two SiO₂ increments are \( σ_{z,\text{SiO₂}}(i) \), \( σ_{r,\text{SiO₂}}(i) \), \( σ_{θ,\text{SiO₂}}(i) \), and \( σ_{z,\text{SiO₂}}(i-1) \), \( σ_{r,\text{SiO₂}}(i-1) \), \( σ_{θ,\text{SiO₂}}(i-1) \), respectively. The effect of the \( i \)th SiO₂ increment on elastic growth stresses is found using strain compatibility equations, which is outlined in detail in other publications.[15] Stresses in older increments are updated with the stress values calculated for the most recent increment.

**Relaxation of Elastic Stress**

The relaxation of the elastic stresses for all increments (\( j=1 \) to \( i \)) in time increment \( Δt = t(i) - t(i-1) \) are calculated next. Shear stress relaxation obeys a Maxwell viscoelastic model,[6, 24] and the Eyring model for shear-stress \( (τ) \) dependence of glass viscosity \( (η) \) is used for SiO₂.[6, 10, 24-26] The initial elastic shear stress at \( t(i-1) \) is \( τ_0 \). The relaxation of \( τ_0 \) to a new value \( (τ) \) in time increment \( Δt \) is:

\[
τ = \frac{4kT}{V_c} \text{Coth}^{-1} \left[ \frac{Gt}{e^{η_0}} \text{Tanh} \left[ \frac{V_cτ_0(j)}{4kT} \right]^2 \right] = 2τ_c \text{Coth}^{-1} \left[ \frac{Gt}{e^{η_0}} \text{Tanh} \left[ \frac{V_cτ_0(j)}{2τ_c} \right]^2 \right] \tag{3}
\]

where \( G \) is the SiO₂ shear modulus, \( V_c \) is the activation volume for plasticity in SiO₂, \( k \) is Boltzmann’s constant, \( τ_c \) is the critical shear stress above which plasticity is significant (typically \( \sim 100 \text{ MPa} \)), and \( η_0 \) is the stress-free SiO₂ viscosity that has an Arrhenius temperature dependence.[27] \( τ_0 \) is determined from the principal stresses for all the increments (\( j=1 \) to \( i \)) by the usual methods.[28]

Relaxation of \( σ_θ(j) \) and \( σ_z(j) \) is proportional to \( τ(j)/τ_0(j) \) and to their difference with \( σ_r(j) \), which is a boundary condition, being zero at the SiO₂ surface and near zero elsewhere. The relaxed values of \( σ_θ(j) \) and \( σ_z(j) \) \( (σ_θ(j)' \text{ and } σ_z(j)') \) are determined by solution of:

\[
\begin{bmatrix}
σ_θ(j)' \\
σ_z(j)'
\end{bmatrix} = \frac{τ(j)}{τ_0(j)} \begin{bmatrix}
σ_θ(j) - σ_r(j) \\
σ_z(j) - σ_r(j)
\end{bmatrix} + \begin{bmatrix}
σ_r(j) \\
0
\end{bmatrix} \tag{4}
\]

**Radial Displacement and Hoop Stress Generation**

Relaxation expands the SiO₂ scale radially. The individual radial displacement of the \( j \)th increment \( (u_r) \) is:

\[
u_r(j) = \frac{Ω_{\text{SiO₂}}}{Ω_{\text{SiC}} \left( 1 + ε_{z,\text{SiO₂}}(j) + ε_{θ,\text{SiO₂}}(j) + ε_{θ,\text{SiO₂}}(j)ε_{θ,\text{SiO₂}}(j) \right)} - 1 \tag{5}
\]

where strains in [5] are calculated from the stresses in [4]. The total radial displacement of the \( j \)th increment is the sum of the displacements of younger increments. This adds hoop strain \( (ε_{θ,\text{SiO₂}}) \) to outer layers as they are forced to a larger circumference (Fig. 1). The new hoop strain in each increment is:
Recalculation of Elastic Stress in the Scale and SiC Fiber after Radial Displacement

The stresses in each SiO₂ increment are recalculated for \( \varepsilon_{\theta}^{\text{SiO}_2}(j)' \) by solving the three strain compatibility equations for the three principal stresses. Revised axial stress \( \sigma_z^{\text{SiC}} \) is computed from the force exerted by the SiO₂ scale, which is the sum of the axial stress in each SiO₂ increment \( \times \) area of that increment:

\[
\sigma_z^{\text{SiC}}(i) = -\sum_{j=1}^{i-1} \sigma_z^{\text{SiO}_2}(j) \left[ 2c(i)(w(j) - w(j - 1) + w(j)^2 - w(j + 1)^2) \right] / b(i)^2
\]

where \( c \) is the scale + fiber radius. The revised radial and hoop stress in the SiC fiber are calculated by determining the net pressure \( p_n \) from the sum of the pressures in each annular increment:

\[
\sigma_r^{\text{SiC}}(i) = \sigma_\theta^{\text{SiC}}(i) = -p_n = -\sum_{j=1}^{i-1} \sigma_\theta^{\text{SiO}_2}(j) \left[ w(j) - w(j - 1) \right] / b(i)
\]

These revised stresses are added to the next increment \( i \) as the program loops back to equations [1-8]. For SiC oxidation when \( w(i) \ll b(i) \), the stress in SiC is much smaller than that in SiO₂.

RESULTS AND DISCUSSION

Growth stress calculations were done using [1-8] using scale discretization to 500 layers \((i=500)\). Calculations were done for oxidation of SiC fiber for amorphous scales of 500 nm thickness \((w)\) at 700, 800, 900, 1000, 1100, 1200, and 1300°C (Fig. 2). The sensitivity of these

\[\text{Figure 2. Calculations of hoop stress (}\sigma_\theta\text{- blue) and axial stress (}\sigma_z\text{- red) throughout a 500 nm thick SiO}_2\text{ scale on 1, 3, and 10 µm radii SiC fibers, and SiC flat plates.}\]
calculations to $10\times$ changes in scale viscosity ($\eta_o$) and oxidation kinetics parameters ($B_o$) are shown in figure 3. The Deal-Grove oxidation kinetics for SiC fiber have been reported for dry air between 700 and 1300°C, with $A_0 = 6.5 \times 10^{-4}$ m, $B_0 = 1.2 \times 10^{-8}$ m$^2$/s, $Q_{A} = 111$ kJ/mol, and $Q_{B} = 249$ kJ/mol.[1-2] A full list of all parameters used in the calculations is published.[15] The variation in growth stress with change in fiber radius was examined by calculations using $b_o = 1$ μm, 3 μm, 10 μm and “flat-plate” $b_o \to \infty$ (1 km). Calculations for other thicknesses and for crystallized scales are reported elsewhere.[15] The changes of $\sigma_\theta$ and $\sigma_z$ growth stresses with change in viscosity ($\eta_o$) or parabolic oxidation kinetics ($B_o$) parameters.

The changes of $\sigma_\theta$ and $\sigma_z$ throughout the scale with change in $b_o$ at 700°C to 1300°C are evident (Fig. 2). As fiber radius ($b_o$) increases, $\sigma_\theta$ and $\sigma_z$ become less tensile and more compressive. $\sigma_z$ is driven towards tensile values by the Poisson effect from tensile $\sigma_\theta$ caused by outward radial expansion. For a 1 μm radius fiber, tensile $\sigma_\theta$ develops at the scale surface at all temperatures, and is $>3$ GPa at 700°C; tensile $\sigma_z$ is $>1$ GPa. For a 10 μm radius fiber, tensile $\sigma_\theta$ does not develop until $T > 850°C$ and reaches a maximum of about 600 MPa at 1000°C; tensile $\sigma_z$ does not develop until $\sim 1100°C$ and reaches 100 MPa at that temperature. Compressive elastic stress of $\sim 25$ GPa for $\sigma_\theta$ and $\sigma_z$ is rapidly relaxed to $\sim 4$ GPa at 700°C and $\sim 1$ GPa at 1200°C just 1 nm away from the SiC-SiO$_2$ interface. At $T > 1200°C$ SiO$_2$ viscosities are so low that stress levels are insignificant at scale locations more than 20 nm from the SiC-SiO$_2$ interface. For flat plates $\sigma_\theta = \sigma_z$ and stress is always compressive. Note that a 500 nm scale takes $\sim 10^8$ s to form at 700°C and $\sim 10^5$ s to form at 1000°C, so the latter is of more practical interest. Calculations for crystalline SiO$_2$ scale and for several other scale thicknesses are reported elsewhere.[15] Crystalline scale viscosities are much higher than amorphous scale viscosities, so growth stresses are also larger. The carbon introduced in SiO$_2$ scales during SiC oxidation causes uncertainty in the actual SiO$_2$ viscosity ($\eta_o$).[15] Effects of a $10\times$ increase or decrease in $\eta_o$ and $B_o$ on growth stress at 1000°C for $b_o = 3$ μm are shown in figure 3. A $2\times$ difference in $\sigma_\theta$ is evident.

Differences between the effects of $\eta_o$ and $B_o$ on growth stress are only significant for very thin scales.

For the 500 nm thick scale a “continuous-state” develops for $\sigma_\theta$ tensile stress for $T > 900°C$ for $b_o = 3$ μm and $T > 1000°C$ for $b_o = 10$ μm. For thicker scales the continuous-state region develops at lower temperatures. For $\tau < \tau_c$ of 100 MPa [16] where a stress–free viscosity ($\eta_o$) [17] is applicable, an analytical expression for the continuous-state hoop stress [$\sigma_\theta(ss)$] can be derived:[15]

$$\sigma_\theta(ss) = \frac{2B \left( \frac{1}{\eta} - 1 \right) \eta_o}{\omega b}$$

(9)

For $\tau > 100$ MPa the stress dependence of viscosity is significant, and the shear stress-dependent viscosity $\eta$ must be substituted for $\eta_o$.[15]
SUMMARY AND CONCLUSIONS

A method to calculate the all growth stress components in SiO$_2$ scales generated by the $2.2\times$ volume expansion during SiC fiber oxidation was developed. The method can be applied to fibers of other materials. High compressive hoop and axial stresses of $\sim$25 GPa are very quickly relaxed at all temperatures. Radial expansion creates tensile hoop stress in the outer scale. Tensile hoop stress eventually drives axial stress to a tensile state by the Poisson effect. Tensile hoop and axial stress can reach values $>3$ and $1$ GPa, respectively for oxidation for long times at 700$^\circ$ - 900$^\circ$C on 1 $\mu$m radius SiC fibers. At temperatures greater than 1200$^\circ$C growth stresses are quickly relaxed to negligible levels by viscous flow of SiO$_2$. The accuracy of the growth stress calculation is likely to be limited by the accuracy of the amorphous silica viscosity. Tensile hoop stresses reach steady-state values that can be described by analytical expressions.

REFERENCES