Influence of Alumina Reaction Tube Impurities on the Oxidation of Chemically-Vapor-Deposited Silicon Carbide

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Pure coupons of chemically vapor deposited (CVD) SiC were oxidized for 100 h in dry flowing oxygen at 1300°C. The oxidation kinetics were monitored using thermogravimetry (TGA). The experiments were first performed using high-purity alumina reaction tubes. The experiments were then repeated using fused quartz reaction tubes. Differences in oxidation kinetics, scale composition, and scale morphology were observed. These differences were attributed to impurities in the alumina tubes. Investigators interested in high-temperature oxidation of silica formers should be aware that high-purity alumina can have significant effects on experimental results.

II. Experimental Procedure

CVD SiC coupons (99.999% purity, Morton International, Inc., Woburn, MA) of dimensions 3 cm × 1.5 cm × 0.3 cm were cleaned in detergent, deionized water, acetone, and alcohol. The alumina tubes (99.8% purity, Vesuvius/McDanel, Beaver Falls, PA) and fused quartz tubes (99.995% purity, Quartz Scientific, Fairport Harbor, OH) were cleaned in the same manner as the coupons. The samples were suspended from a microbalance (Cahn 1000, Cahn Instruments, Cerritos, CA) with sapphire rods (≤100 ppm impurities, Saphikon, Milford, NH) in 1 in.-diameter reaction tubes. Typical impurity levels for sample and TGA tube materials are shown in Table I. Oxygen gas flowed through the vertical reaction tube at a rate of 100 sccm after first being dried with Drierite (CaSO₄) and Mg(ClO₄)₂. Oxidation was initiated by raising the furnace, already at 1300°C, up around the sample. Oxidation times were typically 100 h. Sample weight change and temperature were recorded digitally as a function of time. After oxidation, the samples were examined by optical microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and secondary ion mass spectrometry (SIMS).

III. Results and Discussion

Macrogaphs of the CVD SiC coupons after 100-h oxidation in alumina and fused quartz tubes in dry flowing oxygen at 1300°C are shown in Fig. 1. The two coupons are quite different in appearance. The sample oxidized in an alumina reaction tube is light gray in color and has occasional spots on the scale. The

Fig. 1. Macrogaphs of CVD SiC coupons oxidized for 100 h at 1300°C in dry flowing oxygen. The sample on the left was oxidized in an alumina reaction tube and the sample on the right was oxidized in a fused quartz tube.
Table I. Manufacturers' Purity Specifications for the CVD Sample Material and the Reaction Tube Materials

<table>
<thead>
<tr>
<th>Material/Manufacturer</th>
<th>Purity (wt.%)</th>
<th>Manufacturers' Typical Values (ppm by weight)</th>
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<tbody>
<tr>
<td>CVD SiC (Morton International)</td>
<td>99.999</td>
<td>Mn (1.2), Fe (7.3), Co (1.0), Ni (0.6), Cu (5.5), Zn (1.5)</td>
</tr>
<tr>
<td>High-purity alumina (McDanel/Vesuvius)</td>
<td>99.8</td>
<td>SiO₂ (600), MgO (350), Na₂O (80), CaO (400), Fe₂O₃ (250), Cr₂O₃ (&lt;30), TiO₂ (&lt;40), B₂O₃ (&lt;10), K₂O (&lt;10)</td>
</tr>
<tr>
<td>Fused quartz (Quartz Scientific)</td>
<td>99.995</td>
<td>Al (16), Ca (0.6), Cr (0.05), Fe (0.3), K (0.7), Li (1), Mg (0.1), Mn (0.1), Na (1), P (1.5), Ti (1.1), Zr (1.5)</td>
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Fig. 2. Oxidation kinetics for CVD SiC coupons oxidized at 1300°C in dry flowing oxygen.

The oxidation kinetics for the two samples mentioned above are shown in Fig. 2. The rate constant for the sample oxidized in the alumina tube is about an order of magnitude higher than that for the sample oxidized in the fused quartz tube. The kinetic results for oxidation in either tube were very repeatable. The parabolic rate constants measured for three samples oxidized in alumina tubes averaged \( (1.68 \times 10^{-3}) \) mg/cm²·h. The rate constants measured for three samples oxidized in fused quartz tubes averaged \( (2.67 \times 10^{-4}) \) mg/cm²·h. The SEM cross sections of the oxide scale for the same two samples shown in Fig. 1 are shown in Fig. 3. The scale thickness is 4.7 ± 0.8 μm for the sample oxidized in alumina and 1.6 ± 0.4 μm for the sample oxidized in fused quartz. The rate constants can be calculated from the oxide thicknesses assuming a density of 2.32 g/cm³ for cristobalite as already described. They are \( (1.32 \pm 0.04) \times 10^{-7} \) and \( (1.63 \pm 0.01) \times 10^{-7} \) mg/(cm²·h) for the samples oxidized in alumina and fused quartz, respectively. The disparity between these values and those measured directly by TGA is explained as follows. SEM/EDS observations of oxidized SiC cross sections have shown that crystalline silica scales crack near the silica/SiC interface leaving a very thin silica layer on the SiC which is indistinguishable from the underlying SiC. Oxide thickness measurements made from the crack to the outer surface result in a slight underestimation of the oxide thickness, and thus \( k_p \).

The XRD results shown in Fig. 4 indicate that both tridymite and cristobalite are present in the scale of the sample oxidized in the alumina tube, whereas tridymite is barely detected in the sample oxidized in the quartz tube. It is known that the formation of tridymite is enhanced in the presence of impurities.

In previous work, sodium and aluminum impurities were detected by EDS on SiC samples oxidized in 10% water vapor with alumina tubes. Impurity concentrations in the scale on the sample oxidized in the alumina tube with dry oxygen, however, were below the detectibility limit of EDS. Oxidized coupons were therefore analyzed using SIMS (Perkin-Elmer PHI-6300 SIMS, work performed by AT&T Analytical Services, Alletown, PA). These results are shown in Fig. 5. The scale grown in the alumina tube has at least an order of magnitude higher sodium content than that grown in the quartz tube. Concentrations were not calculated because of the tendency of Na ions to be moved within the SiO₂ layer by the electron current used for charge neutralization. For the same reason the shape of the Na profile should be considered indeterminate. The Al concentration profiles, if shown relative to Si and for the same sputter time (depth) range, are nearly the same in both scales. The different ranges on the abscissa in Figs. 5(A) and (B) prevent this from being easily seen. Ca concentrations (not shown) were lower than Na and Al concentrations and were about the same at the surface of both samples. The Ca concentration in the bulk was about an order of magnitude greater in the scale grown in Fig. 3. SEM micrograph showing the oxide scale thickness for two CVD SiC coupons oxidized for 100 h at 1300°C in dry flowing oxygen. The sample on the left was oxidized in an alumina reaction tube and the sample on the right was oxidized in a fused quartz reaction tube.
Fig. 4. X-ray diffraction results for two CVD SiC coupons oxidized for 100 h at 1300°C in dry flowing oxygen. Diffraction pattern A was obtained from the coupon oxidized in an alumina reaction tube and pattern B was obtained from the coupon oxidized in a fused quartz tube.

Fig. 5. SIMS profiles for Na and Al impurities in the SiO$_2$ scale on SiC which had been oxidized in an alumina reaction tube (A) and a fused quartz reaction tube (B). Note that the range for the abscissa is different in (A) and (B).

IV. Conclusions

It has been demonstrated that the oxidation of pure CVD SiC is very sensitive to ≈100 ppm level of impurities. The oxidation kinetics, scale composition, and morphology were all affected by impurities (probably sodium) in "high-purity" alumina reaction tubes. It has been shown that fused quartz tubes provide a cleaner environment for high-temperature oxidation of silica formers in which growth rates are impurity sensitive.
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References
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10. E. J. Opila; unpublished work.