EVAPORATION RATE OF SILICON CARBIDE IN REDUCING GASES

R.A. Mendybaev1, 3, J.R. Beckett3, L. Grossman1, 2, E. Stolper3, R.F. Cooper4 and J.P. Bradley5. 1Dept. of the Geophysical Sciences, 2Enrico Fermi Institute, Univ. of Chicago, Chicago, IL 60637; 3Div. of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125; 4Dept. of Materials Science and Engineering, Univ. of Wisconsin, Madison, WI 53706; 5MVA, Inc., Norcross, GA 30093

**Summary:** Experiments were conducted to determine the rate of oxidative evaporation of CVD β-SiC in H2-CO2 and CO-CO2 at log fO2 = IW-2.8 and IW-6.0 and temperature from 1200 to 1500°C. The rate of weight loss, (4.7 ± 0.5)10^{-6} mg/min/mm² at 1200°C and (1.5 ± 0.1)10^{-5} at 1400°C, is independent of log fO2, P_{CO}, P_{H2O} and P_{CO2} over the ranges investigated, and the measured E_a = 563 ± 9 kJ/mole, indicating the self-buffering mechanism, SiC(s) + 2SiO2(g) = 3SiO(g) + CO(g). If the oxidation mechanism is the same under solar nebula conditions, then the lifetime of a 10 µm grain in the nebula is 174 days at 1200°C and 17 hr at 1400°C.

**Introduction:** Diamond, graphite and β-SiC of known interstellar origin are found in chondrites, bodies that accreted in the solar nebula. None of these phases are thermodynamically stable in a gas of solar composition at any temperature. Moreover, at low oxygen fugacities, SiC is known to undergo oxidative evaporation to form gaseous SiO and CO [1]. The fact that these minerals survived in the solar nebula has implications for the physical conditions and duration of their exposure. We have therefore begun an experimental study of the kinetics of evaporation of SiC in H-Si-C-O-gases with fO2's close to those of a solar gas.

**Experimental Procedure:** Starting materials were CVD β-SiC and single crystal α-SiC cut into wafers (typically ~ 6.1x2.6x0.3 mm, ~ 15-20 mg), polished to a 1-2 µm finish, thoroughly cleaned ultrasonically with acetone, isopropanol, ethanol and deionized water and stored in a desiccator before use. Initial geometric surface area of the wafers (~ 35-40 mm²) was measured with a precision better than ± 0.8 mm² or ± 2% of the total surface area. Experiments were conducted in a vertical Deltech furnace using gas mixtures of H2-CO2, sometimes diluted with He, Ne or Ar; a few experiments were done in H2-CO or (Ar)-CO-CO2. fO2's were measured with an yttria-stabilized zirconia sensors calibrated for non-Nernstian behavior at iron-wüstite (IW), C-Cr3O4-Cr2O3 and Ta-Ta2O5.

Evaporation rates were measured in the temperature interval 1200-1500°C at fO2's 2.8 and 6.0 log units below IW (e.g., log fO2 = -12.6 and -15.8 at 1400°C, the lower value corresponding to the fO2 of a solar gas at this T). With T and fO2 of the hot spot fixed, each wafer was placed in a Mo-wire cage, exposed to flowing gas (~ 1.0 cm/s; ~ 1 atm) for ~ 30 min to a few hr, depending on T, removed from the furnace, cooled, weighed with a microbalance to a precision of ± 0.5 µg (i.e., ± 1% of the weight change in each run), returned to the furnace and the process repeated several times. Total time in the furnace for each volatilization experiment varied from 2.5 to 70 hr, depending on T, and total weight loss was up to 1-1.5 mg, or 5-10% of the initial weight of the SiC wafers. After volatilization experiments, wafers were studied by optical microscopy, SEM and TEM.

**Results:** To obtain reaction rates, measured weight losses after each run were normalized to the initial geometric surface area of the wafers. In all experiments, the weight loss per mm² was a linear function of time (Fig.1), assuming that changes in surface area of the wafers were negligible. Average oxidation rates of β-SiC (with ± 1σ uncertainties) in H2-CO2 at log fO2 = IW-2.8 are (4.7 ± 0.5)10^{-6}, (1.3 ± 0.1)10^{-6}, (1.5 ± 0.1)10^{-5} and (1.6 ± 0.1)10^{-4} mg/min/mm² at 1200, 1300, 1400 and 1500°C, respectively (Fig. 1). Rates were reproducible to ± 10% for different wafers run under identical conditions. Plotting the logarithm of reaction rate, R, vs. 1/T (Fig. 2), we obtain an activation energy E_a = 563 ± 9 kJ/mole.

![Evaporation Rates of CVD β–SiC](image1)

![Temperature Dependence of SiC Evaporation Rate](image2)
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Based on thermodynamic calculations, the mole fractions of possible oxidizing agents at 1400°C in H₂-CO₂ with log $f_{O_2}$ = IW-2.8 are $x_{H_2O}$=5x10⁻², $x_{CO}$=5x10⁻², $x_{CO_2}$=10⁻⁵, $x_{O_2}$=5x10⁻¹ⁱ and $x_{O_3}$=3x10⁻¹³. To determine the most important gas species controlling β-SiC oxidation, we diluted H₂-CO₂ gas mixtures at 1390°C with 50 vol.% He, keeping $f_{O_2}$ constant but reducing the partial pressures of the major oxygen-bearing species (H₂O, CO and CO₂) by a factor of 2. The reaction rate in this experiment was identical (1.2 x 10⁻⁵ mg/min/mm²) to that in pure H₂-CO₂ at the same temperature. To test for an $f_{O_2}$ effect on the oxidation rate of β-SiC, we prepared an H₂-CO₂ gas mixture with essentially solar $f_{O_2}$ (log $f_{O_2}$ = IW-6.0). At 1200-1400°C, reaction rates (e.g., (2.0 ± 0.2)x10⁻⁵ at 1400°C) and $E_a$ (579 ± 19 kJ/mole) are within 2σ of those observed in this gas mixture with log $f_{O_2}$ = IW-2.8, despite the fact that partial pressures of all possible oxidizing species are lower by a factor of ~1000. Similarly, the reaction rate of β-SiC in CO-CO₂ (i.e., H₂O absent) at 1395°C is the same ((1.8 ± 0.2)x10⁻⁵ mg/min/mm²) as that in H₂-CO₂ at the same $f_{O_2}$ and T. Reaction rates of α-SiC are indistinguishable from those of β-SiC in H₂-CO₂ at log $f_{O_2}$ = IW-6.0 over the temperature interval 1230-1485°C.

At 1500°C, the reaction rate in H₂-CO₂ at log $f_{O_2}$ = IW-6.0 is ~2-2.5 times higher than that at log $f_{O_2}$ = IW-2.8. SEM study shows that these wafers (after only a couple of hours) have highly irregular surfaces. In contrast, little increase in surface irregularity is observed for wafers after heating at log $f_{O_2}$ = IW-2.8 (1200-1500°C) for ~100 hr or log $f_{O_2}$ = IW-6.0 (1400°C) for ~7 hr. Higher apparent reaction rates at 1500°C and log $f_{O_2}$ = IW-6.0 plausibly reflect an increase in surface area due to surface roughness. Experiments with wafers previously exposed to H₂-CO₂ at 1500°C and then exposed to the same gas mixture at lower T show that apparent reaction rates (weight losses normalized to initial surface area) remained ~2 times higher at all temperatures, supporting a surface area effect. The higher rate of development of surface irregularity on wafers exposed to log $f_{O_2}$ = IW-6.0 and 1500°C than at lower T or log $f_{O_2}$ = IW-2.8 may imply a different reaction mechanism under the former conditions.

**Discussion:** The lack of dependence of the β-SiC oxidation rate on externally imposed concentrations of O-containing gas species suggests that the system is self-buffering, most likely by formation on wafer surfaces of a layer which protects SiC from the surrounding gas. Indeed, TEM examination of the wafer exposed to H₂-CO₂ at log $f_{O_2}$ = IW-2.8 over the temperature range 1200-1500°C shows the presence of a uniform layer of crystalline SiO₂ ~1 μm thick on the surface of the SiC. The rate of weight loss of the SiC is therefore probably controlled by the reaction SiC(s) + 2SiO₂(s) = 3SiO(g) + CO(g). It is noteworthy that $E_a$ for this reaction at 1270-1380°C is 548 kJ/mole [2], very close to our measurement of 563 ± 9 kJ/mole. Because the rate of weight loss was the same even in the initial (5 min) stages of evaporation, the SiO₂ layer probably starts to form very quickly.

In addition to independence of the β-SiC evaporation rate on $f_{O_2}$ (e.g., at 1400°C, log $f_{O_2}$ varied from -12.6 to -15.7), our experiments also show that the reaction rate does not depend on partial pressures of CO in the range of ~10⁻³ atm, H₂O in the range of ≤ 1.3 x 10⁻⁶ - 5 x 10⁻⁶ atm, or CO₂ in the range of 10⁻³ - 3 x 10⁻⁷ atm. The investigated ranges of partial pressures bracket that of O₂ and approach that of H₂O but are substantially higher than those of CO and CO₂ expected in a gas of solar composition for which, at P^tot = 10⁻³ atm and 1400°C, for example, log $f_{O_2}$ = -15.8, P_H₂O = 7.5 x 10⁻⁷, P_CO = 6 x 10⁻⁷ and P_CO₂ = 1.7 x 10⁻¹⁰ atm. If it is assumed that the oxidation mechanism for β-SiC under solar nebular conditions is the same as in our experiments, then calculated lifetimes of 1, 5 and 10 μm SiC grains in the solar nebula are: 2, 9 and 17 hr at 1400°C; 22, 112 and 224 hr at 1300°C; 17, 87 and 174 days at 1200°C. These relatively short lifetimes would imply that interstellar SiC grains would not have survived the initial, hot stage of the solar nebula which is estimated to have existed for ~10⁴-10⁶ years [3,4], unless the SiC grains were coated with phases resistant to reaction and evaporation. It is noteworthy, however, that CO and SiO, abundant species in a solar gas, are both products of the oxidative evaporation reaction proposed above. It is important to point out that the partial pressures of these species could have a significant effect on the reaction rate and that we have not yet conducted experiments in which the partial pressure of either one of these has been controlled at the level expected in the solar nebula. Future experiments will address this issue.