EVAPORATION RATE OF SILICON CARBIDE IN REDUCING GASES

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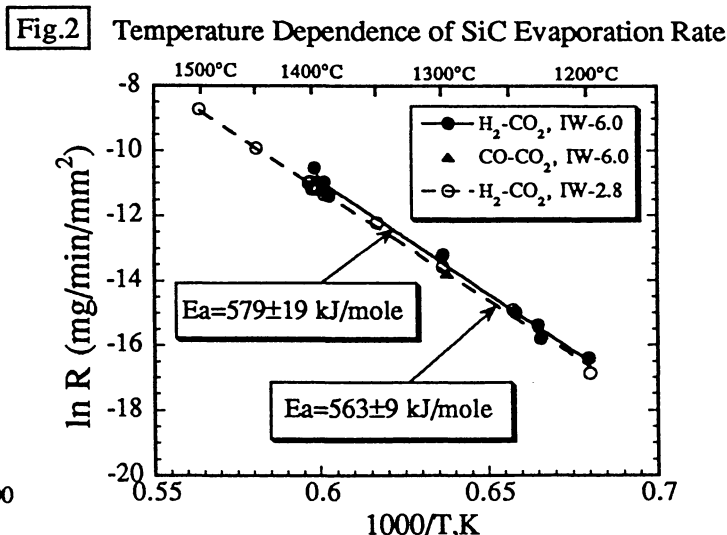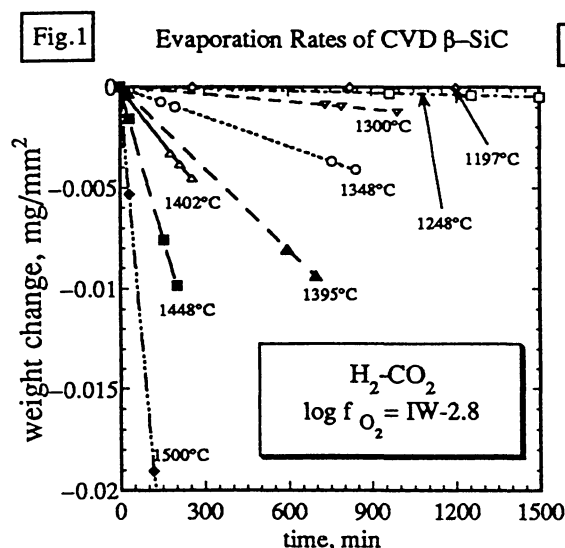
Summary: Experiments were conducted to determine the rate of oxidative evaporation of CVD β-SiC in H_2-CO_2 and CO-CO_2 at log f_{O_2} = IW-2.8 and IW-6.0 and temperature from 1200 to 1500°C. The rate of weight loss, $(4.7 \pm 0.5)10^{-8}$ mg/min/mm^2 at 1200°C and $(1.5 \pm 0.1)10^{-5}$ at 1400°C, is independent of log f_{O_2}, P_{CO}, P_{H_2O} and P_{CO_2} over the ranges investigated, and the measured E_a = 563 ± 9 kJ/mole, indicating the self-buffering mechanism, $SiC_{(s)} + 2SiO_{2(s)} = 3SiO_{(g)} + CO_{(g)}$. If the oxidation mechanism is the same under solar nebular 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-C-O-gases with f_{O_2}'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 mm^2) was measured with a precision better than ± 0.8 mm^2 or ± 2 % of the total surface area. Experiments were conducted in a vertical Deltech furnace using gas mixtures of H_2-CO_2, sometimes diluted with He, Ne or Ar; a few experiments were done in H_2-CO or (Ar)-CO-CO_2. f_{O_2}'s were measured with yttria-stabilized zirconia sensors calibrated for non-Nernstian behavior at iron-wüstite (IW), C-CO, Cr-Cr_2O_3 and Ta-Ta_2O_5.

Evaporation rates were measured in the temperature interval 1200-1500°C at f_{O_2}'s 2.8 and 6.0 log units below IW (e.g., log f_{O_2} = -12.6 and -15.8 at 1400°C, the lower value corresponding to the f_{O_2} of a solar gas at this T). With T and f_{O_2} of the hot spot fixed, each wafer was placed in a Mo-wire cage, exposed to flowing gas (~ 1.0 cm/s; P^{tot} ~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 mm^2 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 H_2-CO_2 at log f_{O_2}= IW-2.8 are $(4.7 \pm 0.5)10^{-8}$, $(1.3 \pm 0.1)10^{-6}$, $(1.5 \pm 0.1)10^{-5}$ and $(1.6 \pm 0.1)10^{-4}$ mg/min/mm^2 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.

Fig.1 Evaporation Rates of CVD β-SiC

Fig.2 Temperature Dependence of SiC Evaporation Rate

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Based on thermodynamic calculations, the mole fractions of possible oxidizing agents at 1400°C in H_2-CO_2 with log f_{O_2} = IW-2.8 are x_{H_2O}~5×10^{-2}, x_{CO}~5×10^{-2}, x_{CO_2}~10^{-3}, x_O~5×10^{-11} and x_{O_2}~3×10^{-13}. To determine the most important gas species controlling β-SiC oxidation, we diluted H_2-CO_2 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 (H_2O, CO and CO_2) by a factor of 2. The reaction rate in this experiment was identical (1.2×10^{-5} mg/min/mm^2) to that in pure H_2-CO_2 at the same temperature. To test for an f_{O_2} effect on the oxidation rate of β-SiC, we prepared an H_2-CO_2 gas mixture with essentially solar f_{O_2} (log f_{O_2} = IW-6.0). At 1200-1400°C, reaction rates (e.g., $(2.0 \pm 0.2)10^{-5}$ 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-CO_2 (i.e. H_2O absent) at 1395°C is the same (($1.8 \pm 0.2)10^{-5}$ mg/min/mm^2) as that in H_2-CO_2 at the same f_{O_2} and T. Reaction rates of α-SiC are indistinguishable from those of β-SiC in H_2-CO_2 at log f_{O_2} = IW-6.0 over the temperature interval 1230-1485°C.

At 1500°C, the reaction rate in H_2-CO_2 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 H_2-CO_2 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 H_2-CO_2 at log f_{O_2} = IW-2.8 over the temperature range 1200°-1500°C shows the presence of a uniform layer of crystalline SiO_2 ~ 1 μm thick on the surface of the SiC. The rate of weight loss of the SiC is therefore probably controlled by the reaction $SiC_{(s)} + 2SiO_{2(s)} = 3SiO_{(g)} + CO_{(g)}$. It is notewothy 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 SiO_2 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}-1 atm, H_2O in the range of ≤ 1.3×10^{-6} - 5×10^{-2} atm, or CO_2 in the range of 10^{-3}-3×10^{-7} atm. The investigated ranges of partial pressures bracket that of O_2 and approach that of H_2O but are substantially higher than those of CO and CO_2 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_{H_2O} = 7.5×10^{-7}, P_{CO} = 6×10^{-7} and P_{CO_2} = 1.7×10^{-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 ~ 10^4-10^6 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.

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