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Kinetics of conversion of silicon carbide to carbide derived carbon

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Abstract

Carbide derived carbon (CDC) was produced on SiC by reaction with flowing Ar–3.5% Cl₂ gas at 900 and 1000 °C. The thickness of the CDC layer increased with time during high temperature exposure according to a parabolic rate equation represented by $K_p = [2.48 \times 10^{-6} e^{-(165000/RT)}] \text{ m}^2 \text{ s}^{-1}$. Carbon loss due to the formation and spallation of graphitic powder was found to be negligible in these experiments. Residual chlorine contents in the CDC layer were measured, and a gradient in chlorine content increasing from the CDC/SiC interface to the CDC/gas interface was observed. This is consistent with diffusional transport of chlorine through the growing CDC layer as the rate controlling step in the CDC growth process. Because the value of the parabolic rate constant is high compared with solid state diffusion coefficients for carbon, transport by solid state diffusion is unlikely. Because the apparent activation energy of 165 000 J mol⁻¹ is high for a gas phase diffusion process, surface diffusion of adsorbed chlorine in the pores of the CDC is suggested as a transport mechanism for the growth of CDC under these conditions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbide derived carbon (CDC) is a new form of carbon produced by exposure of metal carbides to chlorine at temperatures in the range of 600–1200 °C [1, 2]. In this temperature range, chlorine will react with the metal component of the carbide to form a volatile product, leaving the carbon behind. Because CDC processing temperatures are low compared with graphitization temperatures, the residual carbon is not able to relax into the thermodynamically stable graphite phase, and instead remains in a metastable state containing amorphous carbon with both sp² and sp³ bonding as well as nanocrystalline diamond and nested fullerene structures (carbon ‘onions’) [3–5].

CDC can be conveniently grown on silicon carbide (SiC), a hard ceramic material widely used in tribological applications such as bearings and pump seal rings [6]. CDC conversion

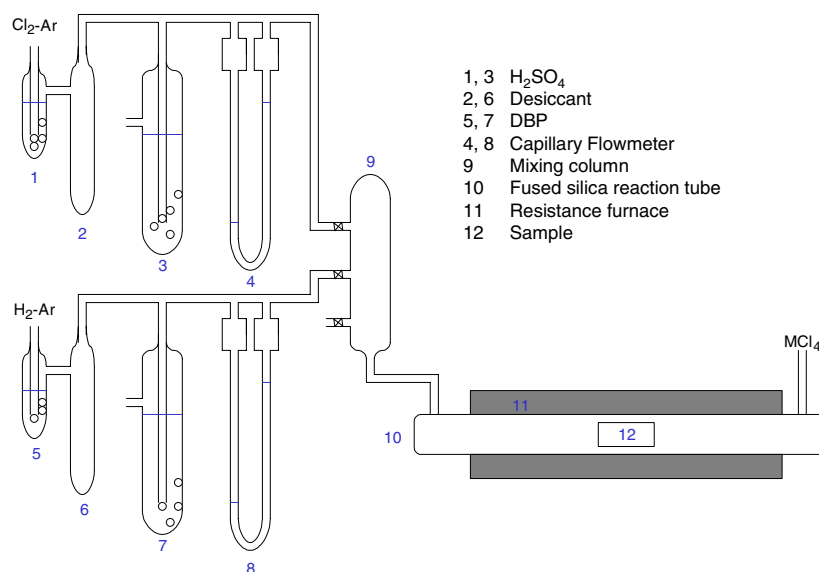


Figure 1. Schematic diagram of the horizontal tube furnace and gas flow control system used for CDC synthesis on SiC pump seal rings.

coatings on SiC reduce the friction coefficient in sliding wear and have better resistance to wear than graphite because of their higher hardness and better resistance to spallation than diamond coatings because of their graded mechanical properties, which match those of the carbide substrate across the interface [7–9]. Possible commercial applications of CDC coated SiC in these industries are currently being investigated.

A key requirement for commercial application of CDC coatings on carbide surfaces is accurate knowledge of the kinetics of the conversion reaction. In spite of considerable research, some inconsistencies remain regarding the thickness of the CDC layer produced by chlorine treatment as a function of time and temperature. Part of this ambiguity may result from different polytypes of SiC, which can be obtained in the form of single-crystal or polycrystalline materials and densified by different methods by the SiC material suppliers. In order to clarify the kinetics, a series of experiments were performed in which CDC was synthesized on the surfaces of commercial sintered SiC pump seal faces commonly used in the seal industry.

2. Experimental details

CDC was grown in a horizontal tube furnace, shown schematically in figure 1, under isothermal conditions using Ar–3.5 vol% Cl_2 at a superficial flow rate of 0.23 cm s^{-1} . CDC layers were grown at 900 and 1000 °C. Experiments were initiated by placing SiC coupons in a fused silica rack within the fused silica reaction tube and purging the tube with the chlorine containing gas. The furnace was then brought to the intended reaction temperature and held for a fixed period of time, after which the power was switched off and the specimen was cooled to room temperature.

Treated coupons were cleaned by ultrasonic cleaning in deionized water to remove any loose graphitic powder on the outside surface before the samples were mounted for microscopic examination. Subsequent to the chlorine exposures, the CDC layer thickness on each specimen was determined by optical microscopy on polished surfaces for thick layers of CDC, or by

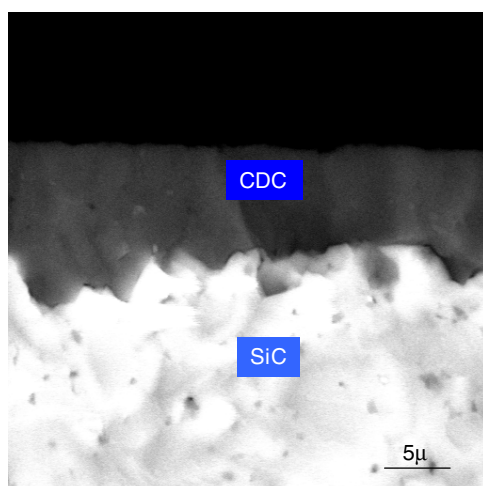


Figure 2. Backscattered scanning electron micrograph of a CDC layer produced on sintered alpha SiC after 1 h treatment in flowing Ar-3.5% Cl₂ at 1000 °C.

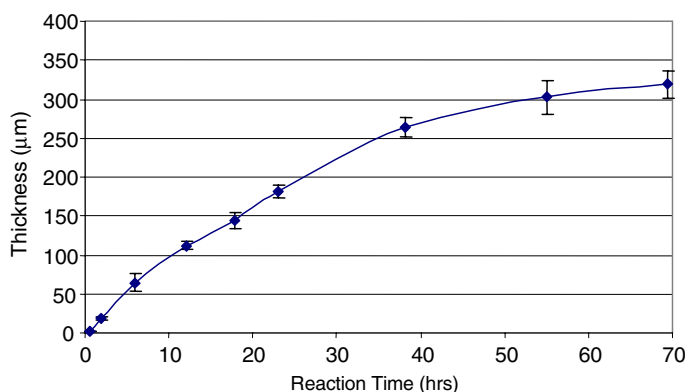


Figure 3. CDC layer thickness versus time for growth on alpha SiC in Ar-3.5% Cl₂ at 1000 °C.

scanning electron microscopy using backscattered electrons (as shown in figure 2) for thin layers of CDC. The micrographs show that CDC growth has little effect on the roughness of the external surface of the ceramic, but there is a rough interface between the CDC and the SiC on the scale of the SiC grain size. This is produced by differential CDC growth rates on SiC grains with different crystallographic orientations. This microscale roughness contributes to the adhesion between the CDC and underlying SiC, making these coatings resistant to spallation and delamination during tribological service.

Figure 3 shows the thickness of the CDC layer as a function of time for growth in Ar-3.5% Cl₂ at 1000 °C. The thickness of the layer increases with time in a manner that is consistent with parabolic kinetics. Similar results were observed for growth of CDC in the same environment at 900 °C, as shown in figure 4.

Figures 5 and 6 show the same data plotted as parabolic equations. The data are well fitted by parabolic kinetics and yield parabolic reaction rate constants at each temperature.

The parabolic kinetic rate constants obtained at 900 and 1000 °C can be fitted to an Arrhenius type equation to predict the temperature dependence of the CDC growth rate in

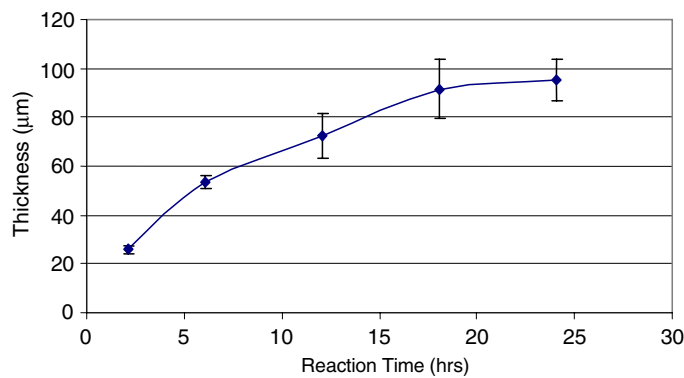


Figure 4. CDC layer thickness versus time for growth on alpha SiC in Ar-3.5% Cl₂ at 900 °C.

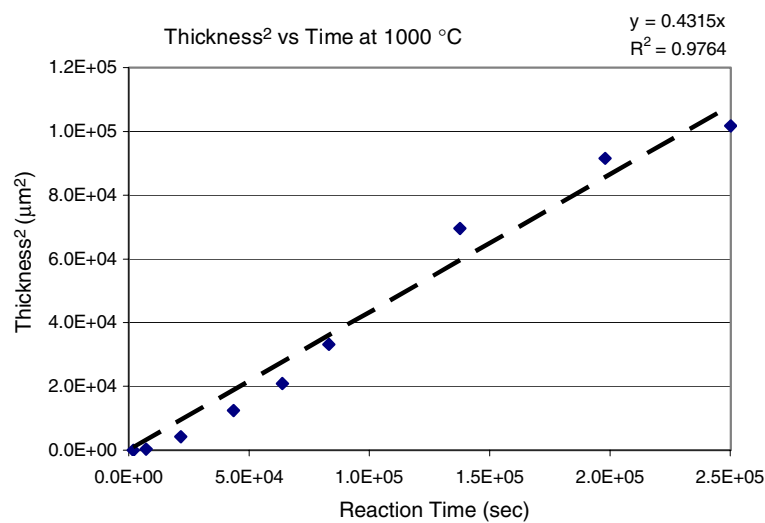


Figure 5. Thickness of the CDC layer on SiC at 1000 °C plotted as a parabolic equation; $K_p = 4.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$.

this temperature range. The result can be summarized in equation (1), which can be used to predict the average thickness of CDC layers formed in this environment as a function of time and temperature:

$$l = (2.48 \times 10^{-6} e^{-(165000/RT)} t)^{1/2} \quad (1)$$

where l is the layer thickness in metres, t is the time in seconds, R is the gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$) and T is the temperature in kelvins.

The parabolic growth kinetics for CDC contradicts the work by Ersoy who reported linear growth and slower kinetics in the same temperature range [2]. Reasons for this kinetic difference may lie in the different furnace designs and experimental procedures used in the two studies. More recent measurements in undiluted chlorine by Carroll gave thicknesses consistent with the present work ($\sim 60 \mu\text{m}$ after 6 h at 1000 °C, and $\sim 250 \mu\text{m}$ after 19.5 h at 1000 °C with some effects of specimen orientation) [10].

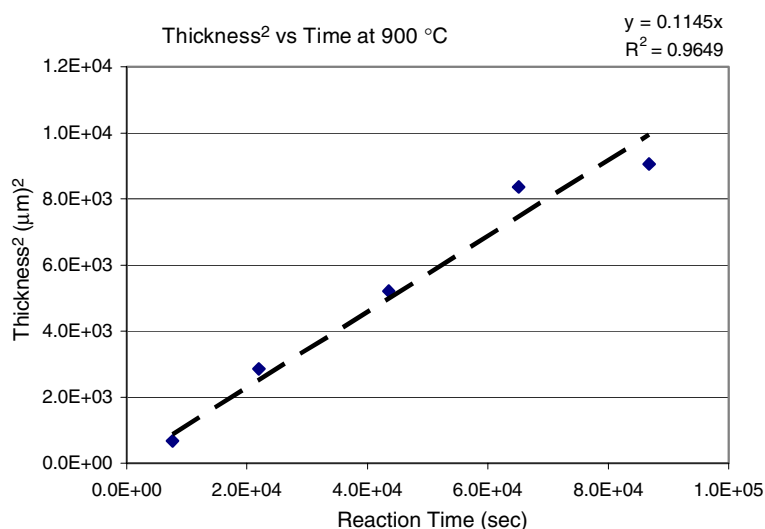


Figure 6. Thickness of the CDC layer on SiC at 900 °C plotted as a parabolic equation; $K_p = 1.14 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$.

3. Implications of parabolic kinetics

Whenever a reaction product scale is formed on a material as a result of an environmental reaction, a change from linear to parabolic kinetics is expected after long reaction times when the product scale becomes thick enough that transport through the scale limits the rate of the reaction. Parabolic kinetics, in which an initial linear reaction rate becomes parabolic after long reaction times, has been observed in many systems, such as the oxidation of silicon [13]. The time at which the kinetics changes from apparently linear to parabolic depends on the relative magnitudes of the linear and parabolic rate constants.

Parabolic kinetic rate laws for growth of reaction product layers in high temperature corrosion processes are usually associated with reaction rate control by diffusional transport of a reactant or a reaction product through the layer. In the case of CDC, which is known to contain nanoscale porosity, it is reasonable to expect the transport mechanism to be diffusional transport of gas species through the pores. However, the relatively high activation energy in equation (1) of $165\,000 \text{ J mol}^{-1}$ would be unusual for a gas phase diffusion process. Furthermore, the average diameter of pores in CDC is in the region of less than 1 nm [11], while SiCl_4 (the most thermodynamically stable silicon chloride) molecules would be expected to have diameters of approximately 0.45 nm, based on the Lennard-Jones parameters for the similar molecule SnCl_4 [12], and could not easily penetrate such fine pores. This suggests that the reactive species may be transported as adsorbed species on the pore surfaces rather than as gas molecules within the material.

In order to further clarify the mechanism of CDC growth and transport, a cross section of a CDC layer on SiC was produced after growth in Ar-3.5% Cl_2 for two hours at 1000 °C, as shown in figure 7. The CDC layer on this sample is approximately 10 µm thick. X-ray fluorescence microanalysis was performed at locations (a) to (g) in figure 7 using the scanning electron beam with a spatial accuracy of approximately 1 µm. The results were analysed using the INCAEnergy Energy Dispersive analysis system, and the variation of chlorine content with position through the CDC layer is shown in figure 8.

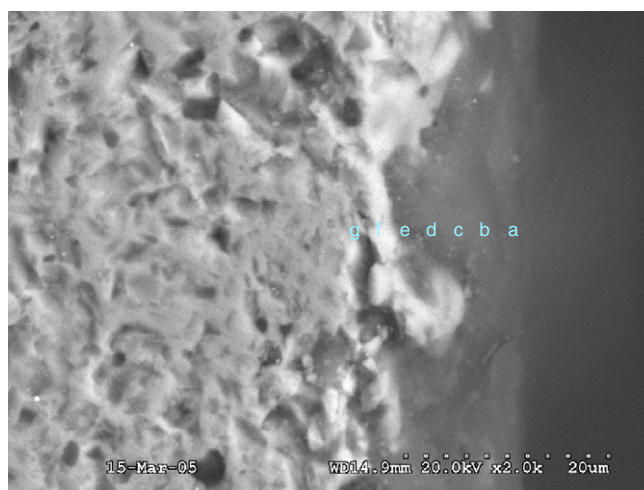


Figure 7. Cross section scanning electron micrograph of a CDC layer grown on SiC in Ar-3.5% Cl₂ for 2 h at 1000 °C. X-ray fluorescence analysis was performed for chlorine at positions (a)–(g).

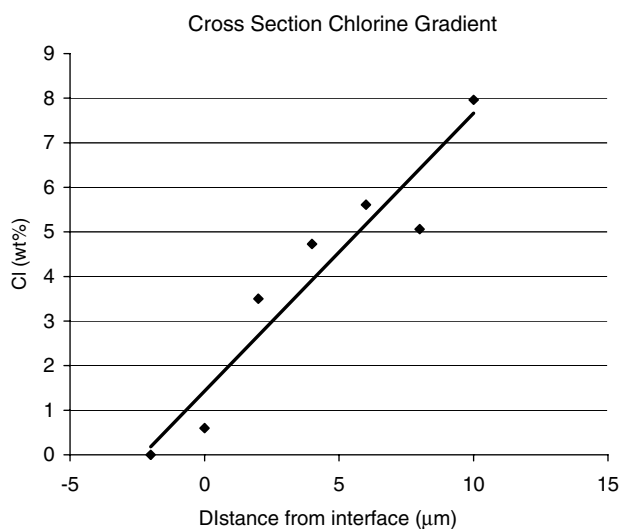


Figure 8. Chlorine concentration in CDC as a function of position within the CDC layer formed on SiC in Ar-3.5% Cl₂ for 2 h at 1000 °C.

As shown in figures 7 and 8, the chlorine concentration in the CDC decreases continuously from a high value of approximately 8% at the external surface to nearly zero at the interface with the SiC. Silicon analyses were performed at the same locations, but the gradient in Si concentration was in the opposite direction (highest at the SiC/CDC interface and lower at the CDC/gas interface), verifying that the Cl is not present at trapped SiCl₄ molecules. This profile is consistent with parabolic growth controlled by transport of chlorine from the reactive atmosphere to the reacting SiC interface. On the basis of the apparent activation energy for the rate equation, the chlorine is likely to be transported by surface diffusion along the pore network in the CDC.

Parabolic scale growth can result from either parabolic kinetics of CDC formation at the CDC/SiC interface, often associated with diffusional transport control, or formation of CDC according to a linear rate equation accompanied by degradation and removal of the CDC by a process that accelerates with time. It is known that some material is lost as a fine powder dislodged from the surface of the CDC during ultrasonic cleaning after each experiment. If this material accounts for a significant fraction of the total CDC formed, then the second mechanism is a possibility.

To test for this possibility, a very thick CDC layer, approximately 300 μm across, was formed on each side of a SiC specimen 0.32 cm thick by treatment for 55 h in a 3.5% Cl_2 -Ar mixture at 1000 °C. Although nearly 20% of the SiC coupon was converted to CDC, the overall specimen thickness is unchanged at $3190 \pm 10 \mu\text{m}$ at the end of the experiment. This demonstrates that material loss due to powder formation and dispersion in the ultrasonic bath is negligible in comparison to the overall CDC layer thickness and supports the diffusion mechanism for CDC growth kinetics. It is to be noted that the CDC layer thicknesses reported in earlier work by Ersoy *et al* [2] were consistently lower than those in this study, and may indicate that a larger fraction of the CDC was lost as powder in that work.

The low linear rate constants reported in the work of Ersoy *et al* [2] are not consistent with the parabolic kinetics observed in this work. Several of the experiments in that work were performed with platinum hardware in the reaction chamber. When platinum is present in the system, some platinum is transported as volatile species and deposits in the CDC, concentrating at the CDC/SiC interface [14]. Although this did not appear to affect the conversion kinetics at the time, this was based on a limited number of experiments, and it is possible that the presence of platinum affected the CDC growth kinetics, either by slowing the reaction or by increasing the rate of graphite exfoliation from the external surface.

4. Conclusions

The kinetics of conversion of SiC to CDC follow parabolic kinetics in the temperature range of 900–1000 °C. These kinetics and measured composition gradients through the scale are consistent with inward transport of chlorine through the scale as the rate controlling step in the conversion process. The value of the parabolic rate constant is too high in comparison to diffusion coefficients of graphitic carbon for solid state diffusion to be a likely transport mechanism, and the apparent activation energy for the process of 165 000 J mol^{-1} is too high to be consistent with gas phase diffusion in the pores. Surface diffusion of chlorine as an adsorbed species on the pore surfaces appears to be the most likely mechanism for transport of chlorine through the CDC.

Acknowledgments

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