Journal of Ceramic Processing Research. Vol. 3, No. 2, pp. 48~51 (2002)

J O U R N A L O F
Ceramic Processing Research

Simulation of a SiC conversion layer formed on graphite by a CVR method

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A two-dimensional Monte Carlo procedure was applied to the study of the formation of silicon carbide on a graphite substrate by a chemical vapor reaction (CVR) method. The CVR method is based on a carbothermal reduction of silica and silicon carbide is known to be one of the products of reaction between carbon and silica. The diffusion and reaction of SiO_2 and SiO is also important in the carbothermal reduction of silica. The Monte Carlo simulation is well suited for such study because Monte Carlo simulation has become widely used as a powerful tool for studying the statistical properties of atomic and molecular systems. The model employed maps the microstructure onto a discrete triangular lattice. A two-dimensional Monte Carlo simulation procedure has been used to investigate the effect of the sintering temperature and graphite substrate on the microstructural evolution of the silicon carbide conversion layer and the behavior of the initial-stage sintering.

Key words: SiC, graphite, simulation, Monte Carlo.

Introduction

Graphite has possible applications as a material for high-temperature structural applications because of its low density, relatively high strength, high fracture toughness, and good tribological properties. But, one serious drawback against actual use of graphite is its poor oxidation resistance in a high-temperature oxidizing atmosphere. On the other hand, Silicon carbide (SiC) is being used in industry because it has several favorable properties, such as high elastic modulus and hardness, good thermal and chemical stability, low thermal and electrical conductivities, and relatively low thermal expansion coefficient [1]. Therefore, SiC is one of the most promising candidate materials for a high-temperature oxidation-resistant coating for graphite [2, 3].

One method for fabricating silicon carbide coated graphite is a chemical vapor reaction (CVR) method [4]. The CVR method is based on carbothermal reduction of silica. In the CVR method, a silicon carbide conversion layer is formed by reaction between carbon in graphite and gaseous reactants such as SiO_2(g), SiO(g). The SiC-C composite of the functionally graded composite material has good adhesion between the graphite substrate and the silicon carbide conversion layer.

The silicon carbide conversion layer forming procedure in the CVR method is composed of thermally activated processes such as the diffusion process of gaseous reactants and the chemical reaction process between gaseous reactants and carbon. Hence the production of a silicon carbide conversion layer is mainly controlled by temperature, atmosphere, pressure, time, and the properties of the graphite substrate etc. and then the thickness and chemical composition gradient of the SiC conversion layer are determined by these factors.

Monte Carlo (MC) simulation has become widely used as a powerful tool for studying the statistical properties of atomic and molecular systems and so it is well suited for such this study [5, 6]. In order to incorporate the complexity of the graphite substrate topology into our model, the microstructure is mapped onto a discrete triangular lattice.

In this study, the two-dimensional Monte Carlo simulation procedure has been used to investigate the effect of the sintering temperature and the porosities of the graphite substrate on the microstructural evolution of SiC conversion layer.

Model and Simulation Method

A schematic figure of the SiC conversion layer is shown in Fig. 1. As shown in Fig. 1, gaseous reactants such as SiO_2 or SiO gas diffused though micropores in the graphite and then react with carbon at inner wall of graphite pores [4].

The functionally graded SiC coating by the CVR method is formed using the following process:

1. SiO is formed via the reaction between SiO_2 and carbon.
2. Functionally graded C/SiC coating is formed via the SiO reaction with the C-C substrate.
3. The top graphite layer is converted to a SiC layer via carbothermal reduction.

Carbon reacts with gaseous reactants that decrease

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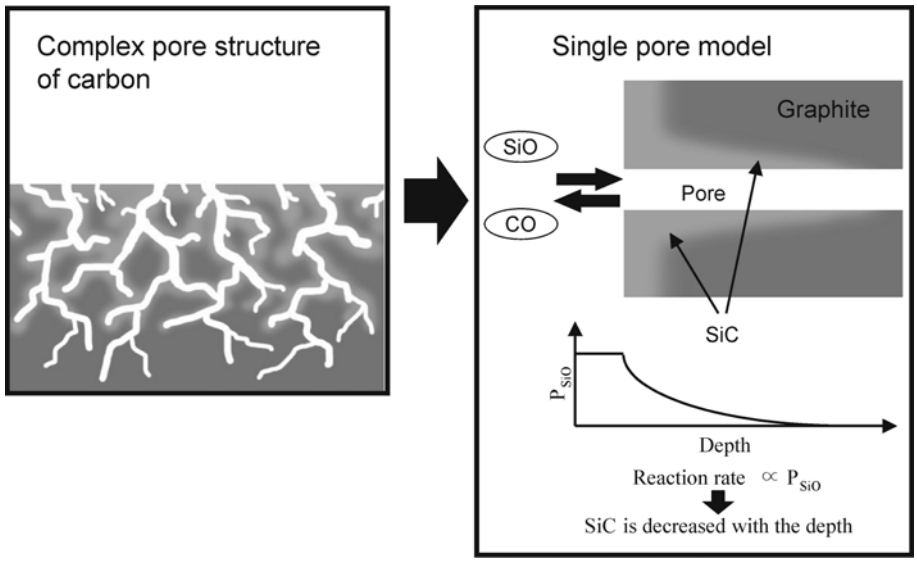

Fig. 1. Gaseous diffusion of SiO gas through carbon pores reacting at the inner wall of carbon pores.

from the surface due to the gaseous diffusion process. The SiC conversion layer is formed with a chemically graded composition, because SiC in the conversion layer is concentrated in diffused gaseous reactants. This can be made by a variety of methods, the most economical of which is the carbothermal reaction of silica with carbon, which may be written as follows [7, 8]:

$$SiO_2(g) + C(s) \rightarrow SiO(g) + CO(g) \quad (1)$$
$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g) \quad (2)$$
$$SiC(s) + 2SiO_2(g) \rightarrow 3SiO(g) + CO(g) \quad (3)$$

The first step consists of a reaction between carbon and silica leading to the formation of gaseous silicon monoxide and carbon monoxide. In the second step, SiO reacts further with carbon according to the gas-solid reaction. In addition, SiC reacts with silicon dioxide.

The exchange probability, *P*, was determined by the change in energy of the reaction during reduction of silica by carbon using Eq. (4). Then the exchange probability, *P*, is calculated using Boltzmann statistics as

$$P = \begin{cases} 1 & \Delta E \le 0 \\ \exp(-\Delta E/kT) & \Delta E > 0 \end{cases} \quad (4)$$

where ΔE is the change in energy caused by the diffusion or the reaction. Here k_B is the Boltzmann constant and T is the temperature [9].

The basic algorithm is simple: an initial configuration of the system is selected, and a random perturbation is attempted. The basic time unit in the present simulation is called one Monte Carlo step (MCS) and corresponds to a number of the change attempts equal to the numbers of sites in the lattice. Because the present simulations are performed on 100×100 lattices, 1 MCS corresponds to 10^4 attempts [10]. The experiment in this study was carried out for 1000MCS.

Results

The snapshots of the cross-sectional morphologies of (a) the initial graphite substrate and the silicon carbide conversion layer on the graphite substrate after simulat-

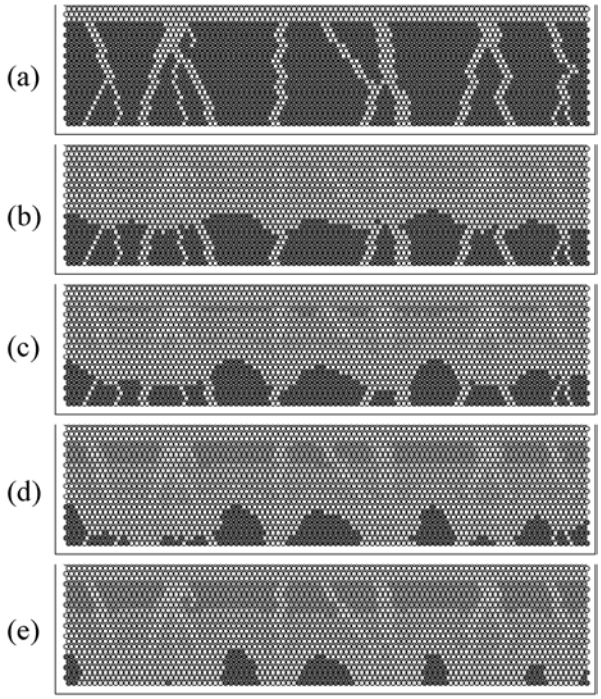

Fig. 2. The cross-sectional morphologies of (a) the initial graphite substrate and the SiC conversion layer on the graphite substrate after simulating at (b) 1900 K, (c) 2000 K, (d) 2100 K and (e) 2200 K.

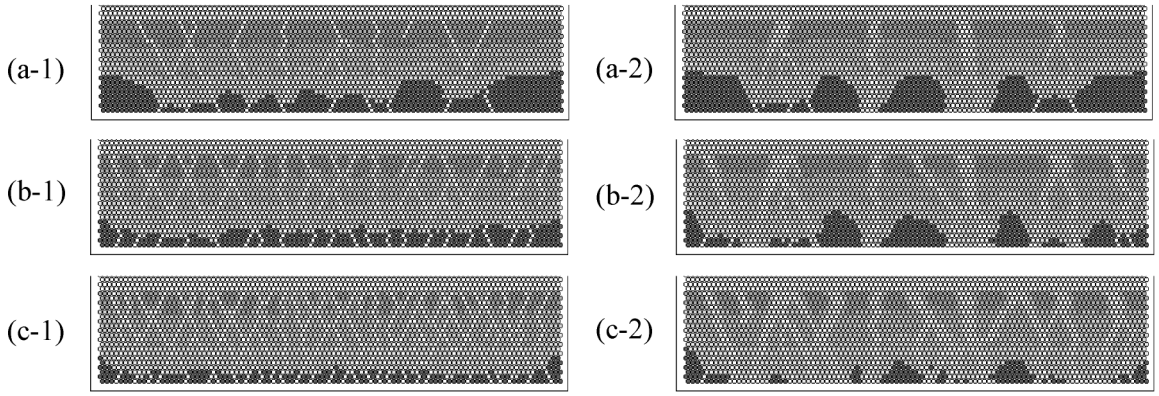

Fig. 3. The cross-sectional morphologies of the SiC conversion layer on different graphite substrates with porosities and pore sizes: (a-1) 10%, small pore size, (a-2) 10%, large pore size, (b-1) 20%, small pore size, (b-2) 20%, large pore size (c-1) 30%, small pore size, (c-2) 30%, large pore size

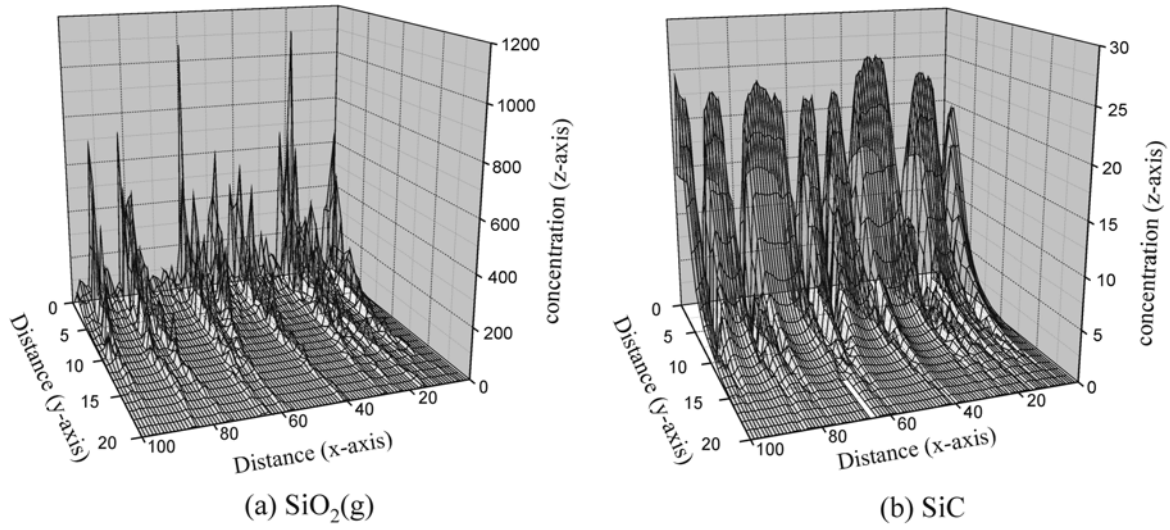

Fig. 4. The concentrations of (a) SiO_2(g) and (b) SiC in the graphite substrate with large pore size.

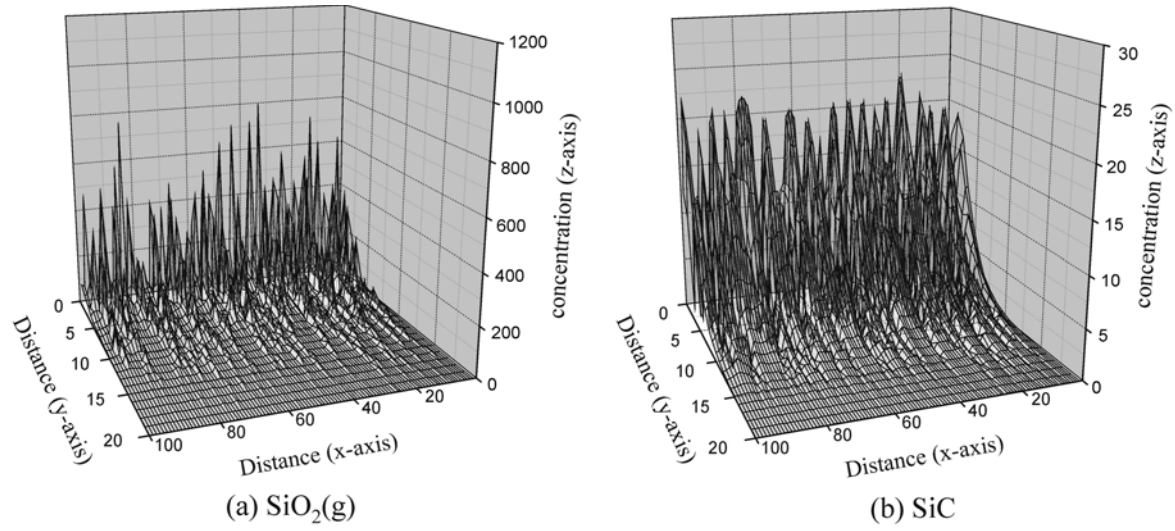

Fig. 5. The concentrations of (a) SiO_2(g) and (b) SiC in the graphite substrate with small pore size.

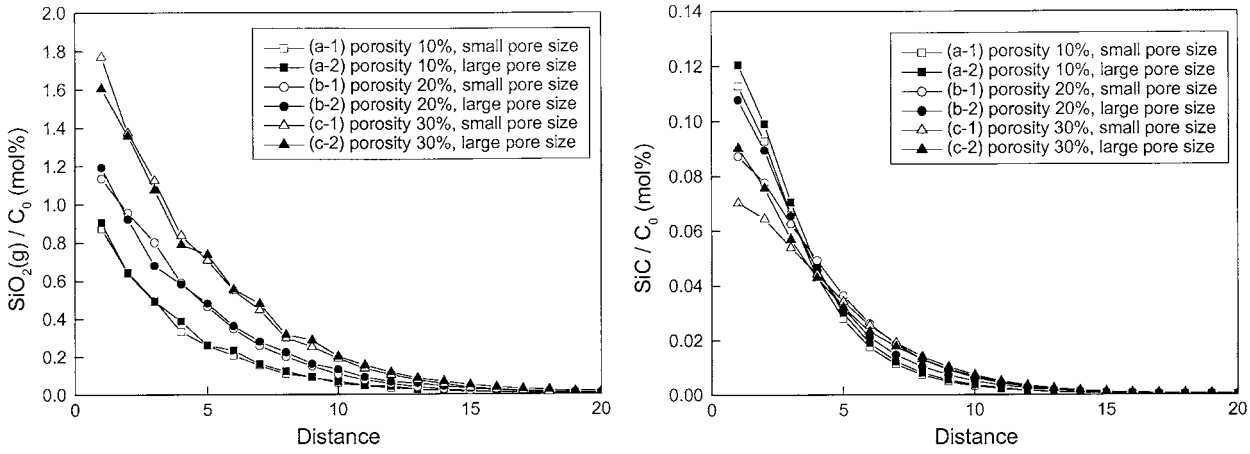

Fig. 6. The mole fractions of (a) $SiO_2(g)$ and (b) SiC to the initial carbon as a function of depth.

ing at (b) 1900 K, (c) 2000 K, (d) 2100 K and (e) 2200 K are shown in Fig. 2. Under the conditions of different porosities of the graphite substrate, the cross-sectional morphologies of the silicon carbide conversion layer on different graphite substrates with various porosities and pore sizes are shown in Fig. 3.

Fig. 4 shows the concentration of (a) $SiO_2(g)$ and (b) SiC(s) at each site in the graphite substrate with 20% porosity and large pore size after simulating at 2100 K for 1000MCS. Fig. 5 shows the concentration of (a) $SiO_2(g)$ and (b) SiC(s) at each site in the graphite substrate with 20% porosity and small pore size after simulating at 2100 K for 1000MCS.

Fig. 6 shows the mole fraction ratio of SiC to the initial carbon calculated from the simulation results of the SiC conversion layer on the different graphite substrates as shown in Fig. 3.

Summary

The formation of a silicon carbide conversion layer was successfully simulated by a two-dimensional Monte Carlo simulation method. The concentration of SiC formed was in proportion to the concentration of gaseous reactants and decreased from the surface to the graphite substrate. The formation of the SiC conversion layer was determined by the sintering temperature and the properties of graphite substrate. The shape and thickness of the SiC conversion layer formed by a CVR method could be expected to be estimated by these simulation results.

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