

Study of CVD SiC deposition for TRISO coated fuel material fabrication by computational simulation and actual experiment

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The silicon carbide (SiC) layer in tristructural isotropic (TRISO) coated fuel particles is a critical and essential layer for hydrogen production using high temperature gas cooled reactor (HTGR) since it is a protective layer against diffusion of metallic and gaseous fission products and provides mechanical strength for the fuel particle. In this study, SiC layers were deposited using a high temperature and high pressure horizontal hot wall chemical vapor deposition (CVD) system as an application of fluidized bed chemical vapor deposition (FB-CVD). Before the actual experiment, we performed computational simulations of the gas velocity, temperature profile and pressure in the reaction chamber with various process conditions. The simulation showed that the change of reactant states affects the growth rate at each position on the susceptor. As the deposition temperature increased, the microstructure, chemical composition and growth behavior changed and deposition rate increased. The simulation results were in good agreement with the experimental results.

Key words: TRISO, SiC, simulation, CVD.

Introduction

TRISO coated fuel particles are one of the most important elements for hydrogen production using HTGR. A TRISO particle is composed of three isotropic layers; inner pyrolytic carbon (IPyC), silicon carbide (SiC) and outer pyrolytic carbon (OPyC) layers. The functions of these coating layers are to retain fission products in the fuel particle [1-5]. Among the coating layers, the SiC layer is a critical and an essential layer for TRISO coated fuel particles since the SiC has prominent properties such as excellent strength, hardness, corrosion resistance, oxidation resistance and impurity protection at high temperature. In addition, the SiC coating layer provides mechanical strength for the particle and acts as a barrier against diffusion of metallic and gaseous fission products in the carbon layer [6, 7]. In order to deposit SiC layers for TRISO coated fuel particles, FB-CVD is usually used at a high temperature and high pressure in order to float particles. In this study, we used a CVD system which has several advantages such as good uniformity and high purity when depositing SiC at a high temperature and a high pressure. In addition, a CVD system not only produces highly pure and dense materials but also deposits films directly from vapors or gases. To apply the CVD system, we obtained the best deposition conditions of SiC through

a computational simulation process with different temperatures and input gas ratios. Using the simulation results, we deposited SiC films and characterized the properties of the films. In addition, we compared the experimental results with the simulation results.

Experiment Procedure

Before the actual experiment, computational simulations concerning input gas velocities, temperature profiles and pressures in the reaction chamber were performed using a thermodynamic simulation program (SOLGAS-MIX-PV) and a process simulation program (Fluent 6.0 computer. Fluent Inc.). A numerical process simulation was performed using the commercially available CFD code Fluent 6.0. The gas dynamics in the CVD chamber were simulated using the Navier-Stokes equations for low Mach flow number, heat and mass transport equations, taking into account homogeneous chemical reactions. The MTS (Methyltrichlorosilane, CH_3SiCl_3) source flow rate was fixed at 100 sccm and hydrogen dilution gas flow rate was varied from 3000 to 7000 sccm. The process temperature was varied from 1300 to 1500 °C.

With the simulation results, silicon carbide films were deposited in a horizontal hot wall tube furnace. The experimental principals and system were described in our previous report [8]. Silicon carbide was deposited on an isotropic graphite substrate which has a similar thermal expansion coefficient to that of SiC in order to improve the adhesion of SiC to the substrate. The graphite susceptor has three deposition positions (denoted as S1, S2, S3) in the same batch separated by

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2.5 cm. The three deposition positions were in the gas flow direction. Also the graphite susceptor was tilted by about 10° to reduce the depletion of the source gas.

MTS was used as a source since its equal ratio of Si to C make deposition of stoichiometric films easy. H_2 was used as a carrier gas and diluent gas to control the concentration of the mixture of MTS vapor and the carrier gas (H_2). The flow rate was controlled by a mass flow controller (MFC). The input gas ratio of diluent gas plus carrier gas to MTS ($\alpha = P_{(\text{diluent}+\text{carrier})}/P_{\text{MTS}}$) was varied from 30 to 70 and the total gas flow rate was fixed at 5000 sccm according to the simulation results while the total pressure was fixed at 684 Torr. (0.9 atm) in order to easily apply the process conditions of CVD to the FB-CVD process which needs a high total flow rate and atmospheric pressure.

In order to investigate the crystal phase and preferred orientation of the SiC layers deposited, X-ray diffraction (XRD) employing $\text{CuK}\alpha$ radiation was used. The microstructures and thicknesses of deposits were examined using scanning electron microscope (SEM).

Results and Discussion

Figure 1 shows calculated equilibrium compositions of SiC condensed phase, other condensed phases and gas phases in thermodynamically equilibrium conditions

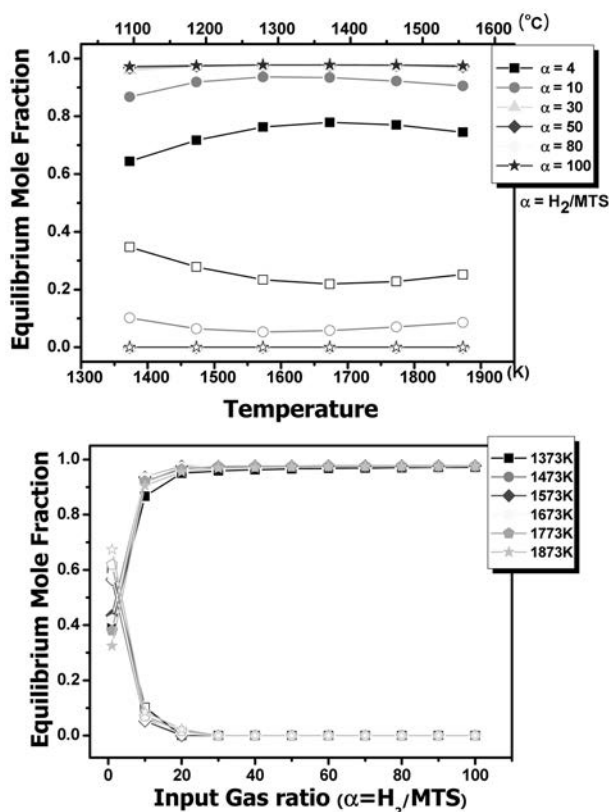


Fig. 1. Thermodynamic yield of SiC layer as a function of deposition parameters. (Closed and open symbols represent yields of SiC and graphite for the given α (input gas ratio) and deposition temperatures, respectively.)

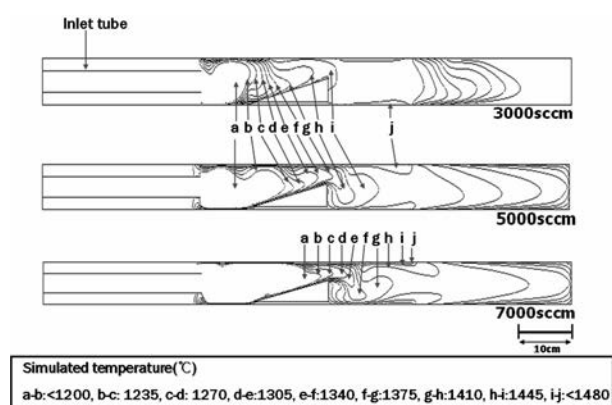


Fig. 2. Computer simulated temperature distribution in the hot wall horizontal CVD reactor.

as functions of temperature, pressure, and input gas ratio using the SOLGASMIX-PV program. The SiC layer deposited with MTS and H_2 showed a yield of over 90% when the input gas ratio was over 30 and the deposition temperature was between 1300–1550 $^\circ\text{C}$.

Figure 2 shows the computer simulated results of the temperature distribution in the CVD reactor at 1500 $^\circ\text{C}$. The system pressure was fixed at 684 Torr., the MTS source flow rate was fixed at 100 sccm and the hydrogen dilution gas flow rate was varied from 3000 to 7000 sccm. From the actual temperature profile of the CVD reactor which was measured using a thermocouple, the susceptor was located in the hot zone which applied to the boundary conditions of the analytical simulation. In our previous study, it was shown that as the diluent gas flow rate increased, the hot zone field moved toward the outlet direction [9]. The calculated distances of movement of the hottest isotherm were approximately 15 cm behind the typical concentric isotherm of the hot zone. These results are due to the narrow circular flows at the end of the susceptor which retains the heat of the chamber and prevents system cooling. The flow tendency of the gas stream is similar to laminar flow without turbulent flow which plays an important role in the whole system temperature.

Figure 3(a) and (b) show simulated temperature changes at S1, S2 and S3 where the substrate were placed on the susceptor at a temperature ranging from 1400 to 1500 $^\circ\text{C}$. In Fig. 3(a), the largest temperature gradient was observed at S1 while there was the least temperature gradient at S2 with a stable upward temperature curve. Although S3 did not show a large temperature gradient overall, we figured out that it would not be suitable for the deposition since it showed an unstable temperature gradient due to narrow outlet of the cliff edge caused by the 10° tilted structure of the susceptor. The entire temperature deviation of the susceptor was 106 $^\circ\text{C}$ at the process temperature of 1400 $^\circ\text{C}$ and the deviation decreased as the process temperature increased. The average temperature difference between S1 and S3 was the largest by 72 $^\circ\text{C}$ at 1400 $^\circ\text{C}$

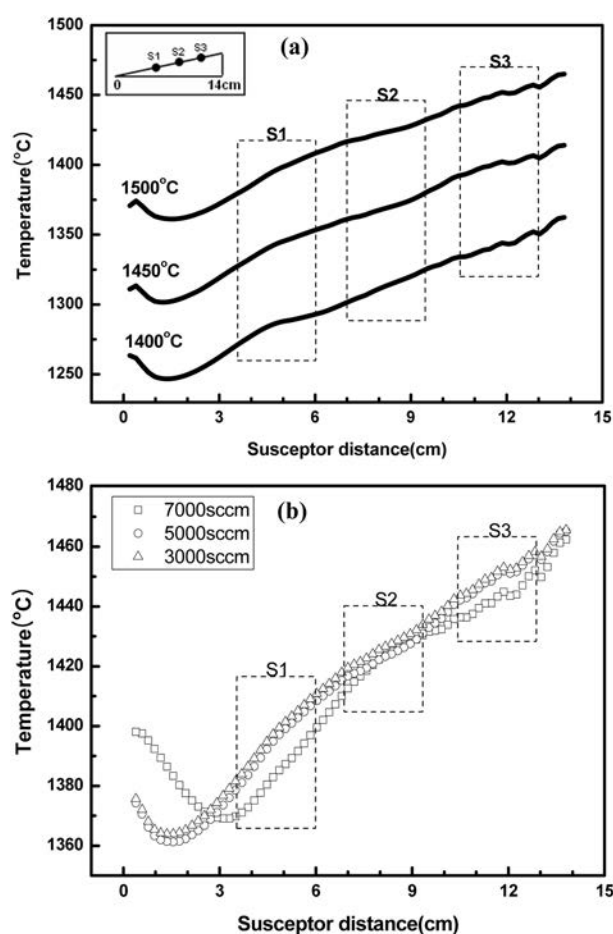


Fig. 3. (a), (b) Simulated temperature distribution which is based on susceptor distance (a) total flow rate: 5000 sccm (b) deposition temperature: 1500°C.

and the least by 56°C at 1500°C. Based on these results, we calculated the temperature difference of the susceptor at 1500°C with various H₂ flow rates 3000, 5000 and 7000 sccm. The temperature change behaviors of 3000 and 5000 sccm were similar while that of 7000 sccm showed a dissimilar upward curve. Regardless of flow rates, point S1 showed the biggest temperature deviation and point S2, where all three curves were closest to each other, had the least temperature deviation of approximately 14°C. In addition, the average temperature of the susceptor was the highest at 3000 sccm and the lowest at 7000 sccm since the temperature of the hot zone decreases as the amount of diluent gas increases. The average temperature difference between S1 and S3 was 67°C at 7000 sccm and about 53°C at 3000 sccm and 5000 sccm.

Summarizing the process simulation results with various deposition temperatures and gas flow rates at each position on the susceptor in the hot zone, point S2 with a temperature of 1500°C and H₂ gas flow rate of 5000 sccm would be the most stable position with the least temperature deviation. Based on this result, we mainly performed actual experiments at point S2 with process conditions of 1500°C and 5000 sccm

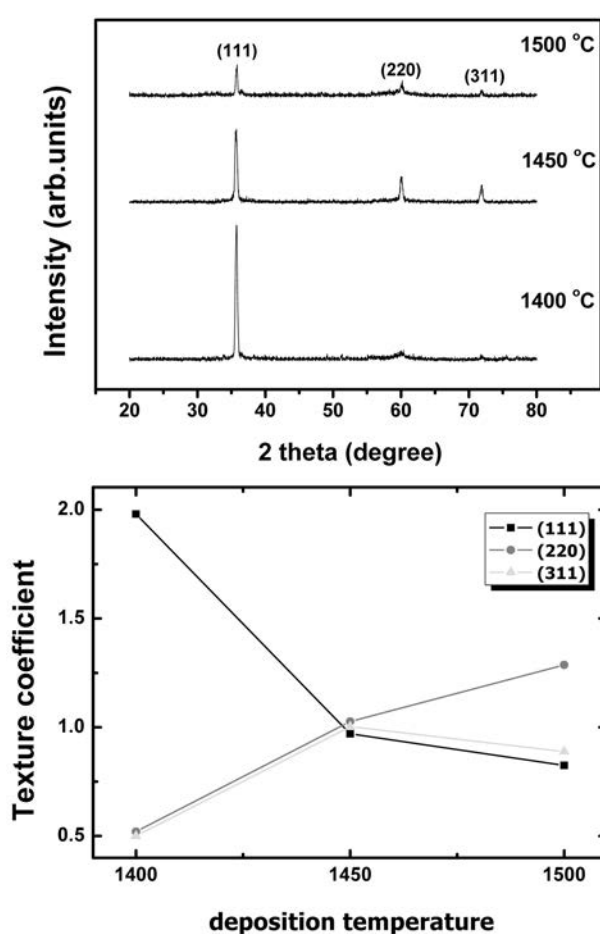


Fig. 4. XRD patterns and texture coefficient of SiC films as a function of deposition temperature ($\alpha=50$, 0.9 atm).

Figure 4(a) and (b) show XRD patterns of the SiC layer deposited at various temperatures with a gas flow rate of 5000 sccm and calculated texture coefficients, respectively. Peaks of XRD patterns were analyzed as (111), (220) and (311) planes of β -SiC. In particular, the XRD pattern of 1400°C specimen showed a (111) preferred orientation. As the temperature increased above 1450°C, the peak from the (111) plane became relatively weak and peaks of (220) and (311) planes appear at the same time. At a higher temperature and lower deposition rate, the preferred orientation takes place in the most densely populated atomic planes and at a higher temperature and higher deposition rate, the preferred orientation is caused in the less densely populated atomic planes [10, 11]. It is reported that as the deposition temperature increases, the preferred orientation of SiC changed from the (111) to (220) plane due to a faster deposition at higher temperatures [12].

Figure 5 shows SEM images of changes of the surface morphology of SiC films as a function of deposition temperatures from 1400°C to 1500°C. All the SiC films showed a faceted structure of SiC layers regardless of the deposition temperature. Usually, (111) preferred orientation β -SiC films have a granular pebble structure [13]. However, our β -SiC film which had a

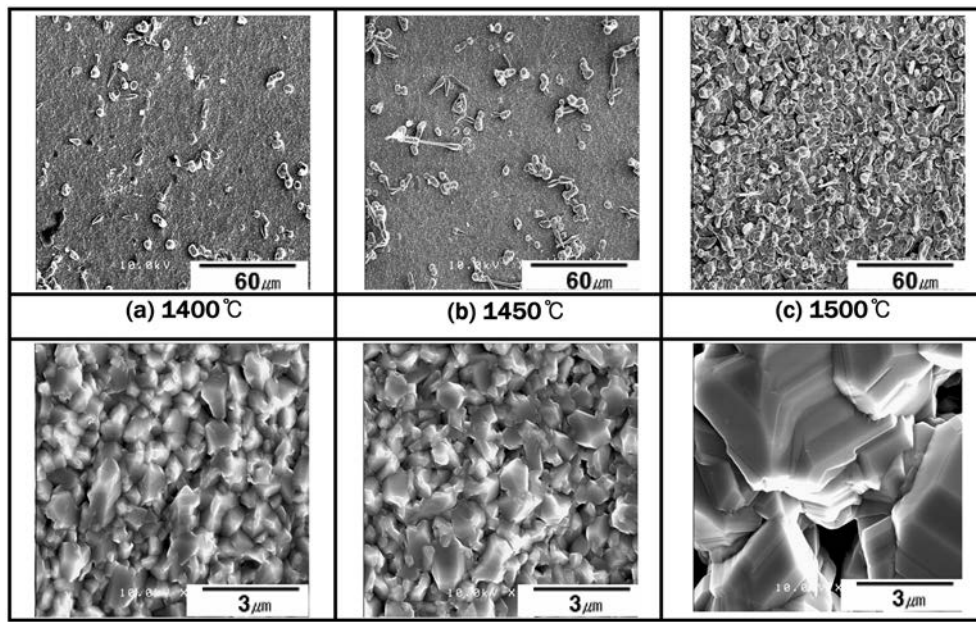


Fig. 5. SEM images of the surface morphology as a function of (a-c) deposition temperature (1400 °C, 1450 °C and 1500 °C, respectively) ($\alpha=50$, 0.9 atm).

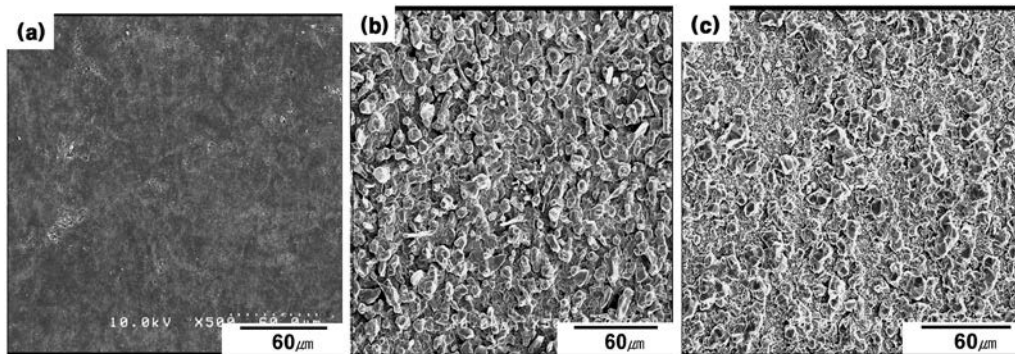


Fig. 6. SEM images of the surface morphology as a function of (a-c) input gas ratio (30, 50 and 70, respectively) (1500 °C, 0.9 atm).

(111) preferred orientation at a deposition temperature of 1400 °C showed a faceted structure. A Similar result was already reported in a previous study [14]. In addition, from grain size analysis, it revealed that the grain size increased as the deposition temperature increased. The reason is that surface reaction kinetics are dominant above 1400 °C. It has already been proven that this phenomenon is related with supersaturation and nucleation [15]. The occurrence of supersaturation at a lower temperature increases the nucleation rate and critical nucleation density, and therefore the average nucleation size decreases. Figure 6 shows SEM images of SiC surfaces as a function of input gas ratio at 1500 °C and 0.9 atm. Flatter surfaces were observed at lower input gas ratios. This result seems to be influenced by a comparatively higher density of the reaction gas.

Figure 7 shows the deposition rates of SiC films at various deposition temperatures at each susceptor position. As the deposition temperature increases from 1400 to 1500 °C, the deposition rate increases. In the simulation data of Fig. 3(a), the temperature of each deposi-

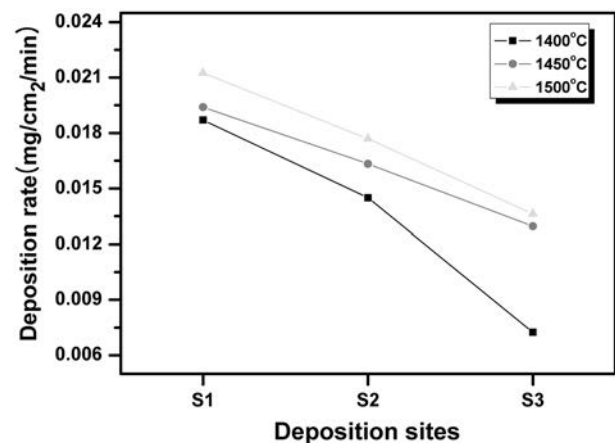


Fig. 7. Variation of deposition rate of SiC layers as a function of deposition temperature and susceptor position ($\alpha=50$, 0.9 atm).

tion position also increased from S1 to S3. Although this simulation data indicates that the deposition rate increases from S1 to S3, the deposition rate in the actual experimental results decreased from S1 to S3. It

seems that this result is caused by source depletion effect and flow velocity effect. In our previous report [16], it was confirmed that the source depletion effect affects the deposition rate and the deposition rate decreases as the deposition position moves far from the inlet. In addition it seems that the source residence time affects the deposition rate. In our study, it seems that as the deposition position moves from S1 to S3 the increase of flow velocity reduces the residence time of the source gas making the deposition rate decrease. It seems that the source depletion effect and flow velocity effect have a greater influence than the deposition temperature effect on the deposition behavior at different deposition positions.

Conclusions

We deposited silicon carbide on TRISO layers by a hot wall type CVD reactor using MTS and H₂ gas as source and carrier gas, respectively and the results were compared with simulation data. Deposited SiC layers were ascertained as β -SiC by an XRD technique. As the deposition temperature increased, the preferred orientation changed from (111) to (220) and (311) planes. The simulation results showed that temperature of the hot zone decreased due to the cooling effect caused by an increase of the diluent gas and the hot zone moved towards the outlet direction. Being different from the simulation data, the growth rate at each deposition position of the susceptor decreased. The deposition position moved from the inlet to the outlet direction due to the source depletion effect and the flow velocity effect caused by the 10° tilted susceptor shape. In addition, as the deposition temperature increased, the grain size and deposition rate increased.

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