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Deposition of compositionally graded SiC/C layers on C–C composites by low pressure chemical vapor deposition

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Abstract

To improve the oxidation and erosion resistance of the carbon-fiber reinforced carbon–carbon (C–C) composites, SiC/C compositionally graded layers were deposited between the C–C composite and SiC layer by the low pressure chemical vapor deposition method. The compositions of the graded layers were easily controlled in various steps by manipulating the input ratio of CH_3SiCl_3 to C_2H_2. The compositions of the SiC/C deposited layers were consistent with calculated compositions. All the SiC/C layers had dense microstructures and uniform distributions of C and SiC phases.

1. Introduction

Carbon–carbon (C–C) composites have received much attention as plasma facing materials of fusion reactor and high temperature structural applications [1,2]. These proposed applications, however, have been frustrated by the lack of resistance to hydrogen erosion in fusion environments and oxidation on exposure to ambient oxidizing conditions at high temperatures [3]. This limits the lifetime of the plasma facing components and dilutes the plasma with impurity ions. For improving these problems, carbide materials such as B_4C, TiC and SiC have been considered as possible coating materials for C–C composites [4,5]. Among the candidate materials, SiC shows excellent properties such as a high decomposition point, a low vapor pressure at modest temperature and a very low tritium permeability. However, many cracks are developed in the SiC coating due to a mismatch of the coefficient of thermal expansion (CTE) between SiC and C–C composites [6]. In recent years, in order to relieve the thermal stress, an introduction of functionally graded materials (FGM) on C–C composites has been widely studied using various processes such as pack cementation [7–9], melt infiltration [10] and the chemical vapor deposition (CVD) [12]. The CVD technique is an effective approach in fabricating FGM through a codeposition process using multi-component gas reactions [11]. The main advantage of the CVD technique is its ease of controlling the composition and microstructure of the deposited materials [12]. For effectual improvement of stress relief, it is necessary to know the properties of FGM layers and to control the layer properties.

In this study, we deposited SiC/C compositionally graded layers on C–C composites by the CVD method at 1300 °C using the CH_3SiCl_3–C_2H_2–H_2 system. The compositions of the SiC/C layers were controlled in several steps by manipulating the input gas ratio of CH_3SiCl_3 to C_2H_2. The deposition conditions and compositions of SiC/C compositionally graded layers were thermodynamically calculated and compared with the experimental observations. Properties of each SiC layer such as composition, microstructure and micro hardness were evaluated.

2. Experimental procedure

The composite material used in this work was a two-dimensional C–C composite (CX-31, Toyo Tanso,

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Japan) with a specific density of 1.61 g/cm^3. Samples with a size of 15 × 15 × 3 mm were cut from the composite panel and polished down to #2000 SiC paper. These were used as substrates for the SiC/C compositionally graded layer depositions.

CVD was carried out in an alumina tube in a horizontal furnace. Methyltrichlorosilane (MTS, 99%, Aldrich Chemical Co. Ltd.) and C_2H_2 gas were used as sources of SiC and C, respectively. Hydrogen (H_2) gas was used as a carrier gas and a diluent gas. The carrier gas was bubbled through the MTS precursor which was maintained in a 0 °C bath. The flow rate of MTS was controlled by controlling that of the carrier gas. The deposition of the SiC/C compositionally graded layers was conducted by varying the flow rates of MTS and C_2H_2 gas from 10 to 100 sccm and from 90 to 0 sccm, respectively. From the surface of C–C composites, the flow rate of C_2H_2 was decreased and that of MTS was increased step by step. A pure SiC layer was deposited after the deposition of the SiC/C layers. Deposition of SiC/C layers was performed at 1300 °C, 10 Torr for 6 h and the pure SiC layer was deposited at 1300 °C, 50 Torr for 3 h. The compositions of the SiC/C layers were thermodynamically calculated and compared with the experimental observations. The thermodynamic analysis was conducted with a modified form of the computer program SOLGASMIX-PV [13]. The calculations are based on free-energy minimization.

An energy dispersive X-ray spectroscope (EDS) attached to a scanning electron microscope (SEM) was used to determine the composition of the SiC/C layer and microstructures of the deposits were investigated using SEM. The phases present in the coating and the hardness of the SiC/C layer were analyzed using a X-ray diffractometer (XRD, D/MAX-3C, Rigaku Co., Japan) and a microhardness tester (HMV-2000, SHIMADZU, Japan), respectively.

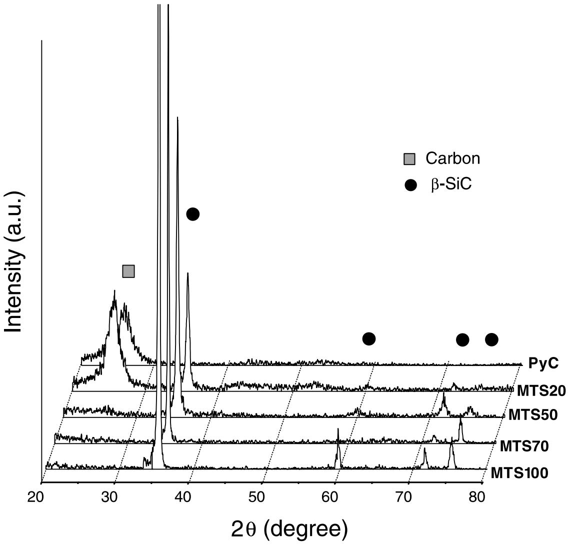

Fig. 1. XRD patterns of the SiC/C layers deposited by changing the input gas ratio of MTS to C_2H_2.

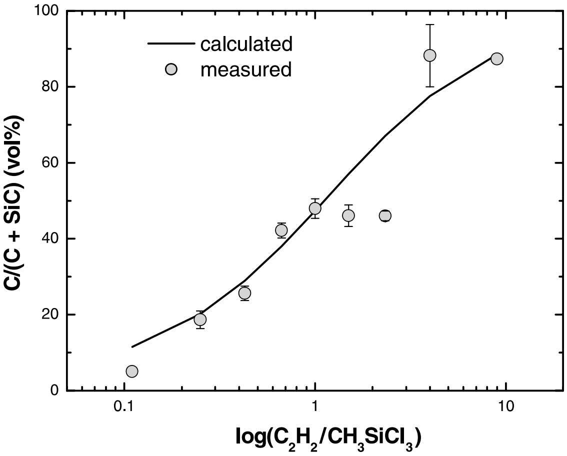

Fig. 2. Compositional variation of the SiC/C layers as a function of the input gas ratio.

3. Results and discussion

Fig. 1 shows the XRD patterns of the SiC/C layers with the increase of the MTS flow rate. For the XRD analysis, each SiC/C layer with different composition was deposited separately on graphite substrates, and the thickness of each layer was above 100 μm to preclude an intervention of the substrate. It can be seen in Fig. 1 that all the SiC/C layers consist of only two crystalline phases of C and β-SiC. As the flow rate of MTS increases, the intensity of the C peak decreases and that of the β-SiC increases. The theoretical compositions of the SiC/C layers by varying the input gas ratio of MTS to C_2H_2 were calculated using SOLGASMIX-PV. The result is shown in Fig. 2 and compared with the experimentally determined compositions by EDS analyses. The compositions of the deposited layers are consistent with the calculated compositions even though there are some scatters. It can be seen from these results that the SiC/C FGM layers can be controlled over the entire compositional range from pure C to SiC.

Fig. 3 shows the back scattered electron (BSE) images of the polished cross-sections of SiC-coated C–C composites interlayered with 2 and 9 step SiC/C compositionally graded layers. Fig. 3(a) and (b) show that the deposition rate of the SiC/C layer increases as the SiC content increases and the interfaces of each layer are well bonded without any delamination between the layers. Fig. 3(c) depicts the result of X-ray mapping for the Si element of the microstructure shown in Fig. 3(b). The concentration of Si increases sequentially from the

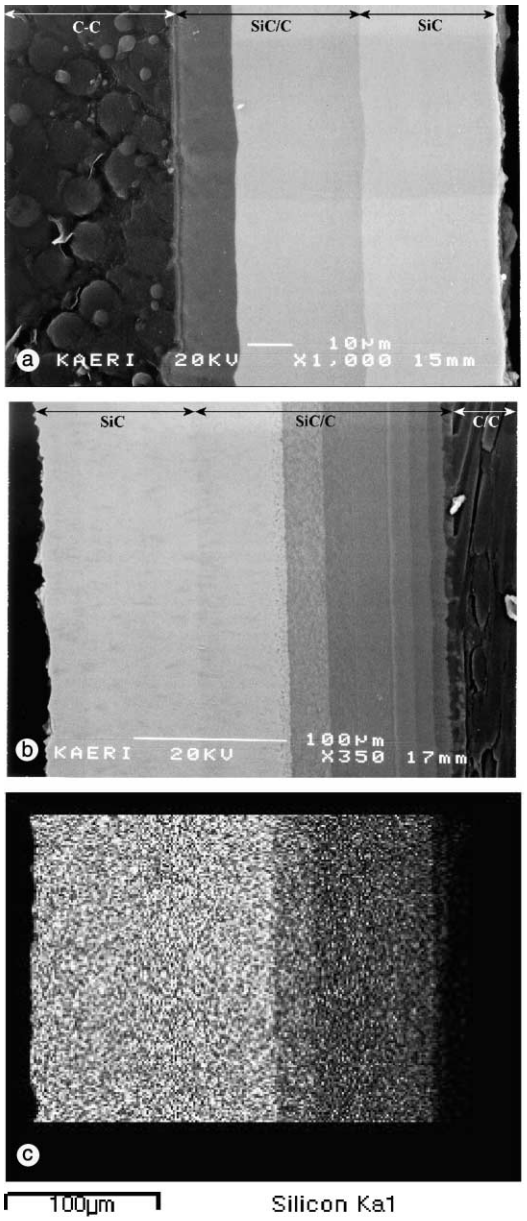

Fig. 3. BSE images of the polished cross-sections of the SiC-coated C–C composites with 2 (a) and 9 (b) step SiC/C interlayers, (c) is a X-ray mapping image for Si of (b).

C–C substrate to the SiC layer and the SiC and C phases are uniformly distributed without a phase segregation. Fig. 4 represents an enlarged BSE image of the polished surface of a typical SiC/C layer, in which the MTS to C_2H_2 ratio is 7/3. It shows a dense microstructure with no pores and no aggregation of the SiC or C phase can be found. As mentioned above in Fig. 2, we could easily prepare dense and uniform SiC/C FGM layers for the entire compositional range simply by varying the input gas ratio of MTS to C_2H_2 in the MTS–C_2H_2–H_2 system. Theoretical Vickers microhardness of the SiC/C layers is shown in Fig. 5 along with the experimentally determined values. The theoretical values were calculated by the rule of mixture assuming that the hardness of C and SiC were 1 and 30 GPa [14], respectively. The measured hardnesses of the deposited SiC/C layers are consistent with the calculated values. From this result, it can be confirmed that the SiC/C layers are constructed with a dense microstructure and uniform distribution of C and SiC phases.

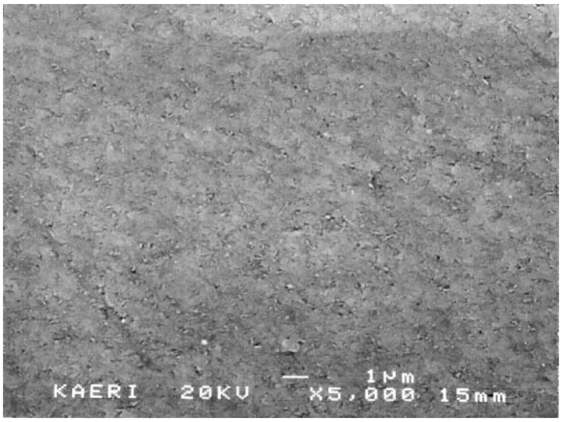

Fig. 4. BSE image of the polished surface of a typical SiC/C layer deposited using the MTS to C_2H_2 ratio of 7/3.

In most of the previous results concerning the codeposition of SiC/C by CVD, the composition of SiC/C has been limited to a narrow range [15–17] except for the extensive works performed by Wang et al. [18–20]. Although Wang et al. deposited SiC/C composites over all composition ranges using the $SiCl_4$–CH_4 system, the deposits contained many pores and had a large skeleton structure of SiC in some compositions. Moreover the

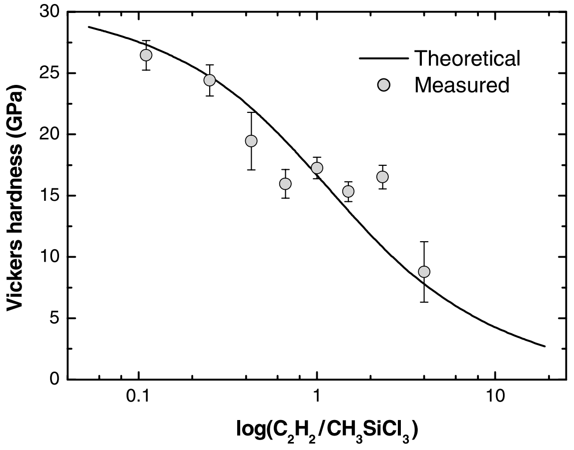

Fig. 5. Variation of microhardness of the SiC/C layers as a function of the input gas ratio.

thermomechanical properties such as CTE and thermal conductivity did not follow the rule of mixture. They attributed this to the porosity in the SiC/C mixture, the preferred orientation of C and the SiC skeleton structure [20,21]. Therefore, dense and uniform microstructures of the SiC/C layers obtained in this study are expected to facilitate the thermomechanical properties to be graded continuously. Investigations of the thermal properties and stress relief effect of the SiC/C layers are in progress and will be described elsewhere.

4. Conclusions

SiC/C layers were deposited on C–C composites over all composition ranges using the CVD method. The compositions of the SiC/C deposited layers were consistent with the calculated compositions and easily controlled in various steps simply by changing the input ratio of CH_3SiCl_3 to C_2H_2. All the SiC/C layers had dense microstructures and uniform distributions of C and SiC phases without a SiC skeleton structure and phase segregation. Microhardnesses of the SiC/C layers were varied by following the rule of mixture. Dense and uniform microstructures of the SiC/C deposits obtained in this study are expected to make the control of thermomechanical properties of each SiC/C layer easier and therefore to reduce effectively the thermal stress developed in the SiC coating on C–C composite.

Acknowledgements

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