Characterization of SiC/C Functionally Gradient Materials Growth Process by CVD Technique

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ABSTRACT

SiC/C functionally gradient materials (FGMs) were formed on graphite substrates by hot-wall chemical vapor deposition (CVD) technique using the $SiCl_4$-C_3H_8-H_2 chemistry. Thermochemical equilibrium calculations were carried out to investigate the deposition process. The effect of process variables on the deposition yield and the SiC/C ratio in deposited layers was studied in detail. Calculated results showed a reasonable agreement with the experiment in a qualitative sense. SiC/C FGMs with excellent mechanical and thermal properties could be successfully formed on graphite substrates by carefully controlling the compositions in the deposited layers.

INTRODUCTION

Since the concept of functionally gradient materials (FGM) was first proposed in 1984, the SiC/C FGMs have been extensively studied for the applications in the thermal shock resistant materials (1,2). The SiC/C FGM layers formed between the graphite substrate and the SiC cap layer are expected to relax the thermal stress caused by the difference of thermal expansion coefficients between SiC and graphite, thus overcoming the drawbacks of SiC monolithic coatings on graphite (3,4).

The SiC/C FGMs can be synthesized by chemical vapor deposition (CVD) technique. Recent studies of SiC/C FGMs utilizing the CVD technique revealed that the SiC/C ratio in the deposited layer could be controlled by varying either the C/Si ratio or the H/[C+Si] ratio in the source gas (4-8), but they did not show the systematic interpretation of the effect of process parameters related to the deposited layer composition. A full parametric study of the CVD process to achieve a superior thermal shock resistant property of SiC/C FGMs has not yet been reported.

This study reports both computational and experimental efforts to systematically understand the CVD process of depositing the SiC/C FGMs. A complex thermochemical equilibrium analysis was first carried out to investigate the effect of process variables (i.e., the deposition temperature, the reactor pressure, the gas phase molar ratios, etc.) on the deposition yield and SiC/C ratio in the deposited layers. The CVD phase diagrams were also constructed from the equilibrium calculations. The SiC/C FGMs were then actually formed on graphite substrates by hot-wall CVD technique using $SiCl_4$-C_3H_8-H_2 chemistry, and their mechanical and thermal properties were characterized.

THERMOCHEMICAL SIMULATION

A complex thermochemical equilibrium analysis was performed to simulate the CVD process in equilibrium conditions. The stoichiometric algorithm was employed in estimating the equilibrium properties of the system containing multi-phase, multi-component mixture involving chemical reactions. The Si-C-H-Cl system was investigated, and a full parametric study of the CVD process involving all the process variables was performed. The thermochemical species included in the numerical calculations and their themochemcial data were carefully selected and reviewed from the literature (9,10).

EXPERIMENTAL

A hot wall type horizontal CVD reactor with tilted susceptor was used for the deposition of SiC/C FGMs on the graphite substrate and is shown in Fig. 1. C_3H_8 and bubbled $SiCl_4$ were used as source gases, and H_2 was used for both the carrier and the atmosphere gas. Deposition temperature was fixed at 1573.15 K, and the source gas compositions could be varied by controlling the flow rates of the source and atmosphere gases in a stepwise fashion with mass flow controllers (MFCs). The reactor pressure was accurately controlled by the butterfly valve connected in the upstream of a rotary vacuum pump and was typically fixed at 10 Torr.

An X-ray diffractometer (XRD) was used for phase analysis. A scanning electron microscope (SEM), equipped with an energy dispersive spectrometer (EDS) and a wavelength dispersive spectrometer (WDS), were used for the microstructual observations for both the

deposit and fracture surfaces, and for compositional microanalysis of the deposited layers.

RESULTS AND DISCUSSION

Thermochemical calculations of the CVD process were carried out to predict the effects of process variables (i.e., the deposition temperature, the reactor pressure, the C/[C+Si] and H/[C+Si] ratio in the source gas) on the SiC/C ratio of deposited layers and the deposition yield. Fig. 2 shows an example of CVD phase diagram which was constructed from a series of calculations with varying process conditions. As clearly shown in the figure, there is quite a large process window to control the composition of deposited film, and this can be attained by varying the C/[C+Si] ratio in the source gas stream. Fig. 3 shows the corresponding dependence of film composition on the C/[C+Si] ratio in the gas phase. Calculations covering a wide range of process variables revealed that the suitable operating conditions are the deposition temperature between 1400 and 1600 K, the reactor pressure between 0.1 and 100 torr, and the H_2/[$SiCl_4+C_3H_8$] ratio between 1 and 100.

The SiC/C FGM structure was formed by varying the C/[C+Si] ratio in the inlet gas stream, and it is shown in Fig. 4. The deposition temperature of 1573.15 K, the reactor pressure of 10 torr, and the H_2/[$SiCl_4+C_3H_8$] ratio of 20 were used. The C/[C+Si] ratio was varied from 0.98 to 0.44 to form 4 intermediate FGM layers with the top covering SiC layer. The semi-continuous variation of the C/[C+Si] ratio in the gas phase, which included a step change in the gas phase composition between overlaying FGM layers but a continuous change across the interface, resulted in the films with smooth interfaces. The thermal shock resistance test was performed by using vertical furnace in which the samples were hanged by Pt wire. After heating up to 1573.15 K, the samples were suddenly dropped into the liquid N_2 by cutting the Pt wire. No cracks were formed in the SiC/C FGMs up to $\Delta T = 1600$ K, while the samples with monolithic SiC coating failed this test at $\Delta T = 1200$ K.

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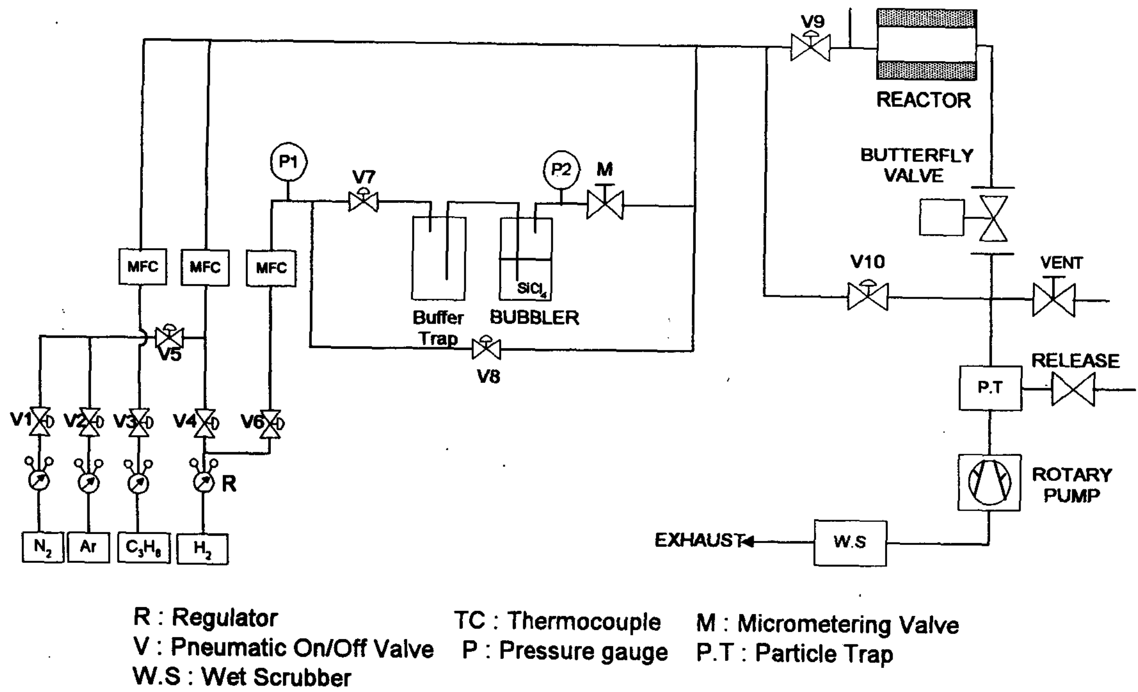

Fig. 1 The schematic description of horizontal hot-wall CVD system.

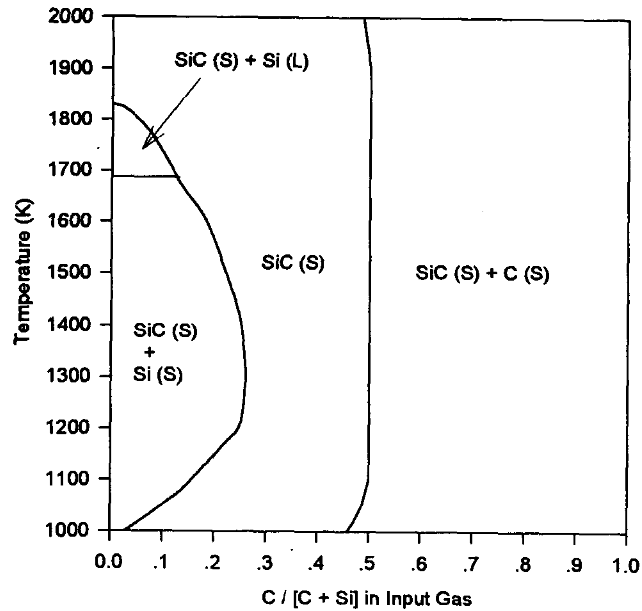

Fig. 2 The CVD phase diagram of the $SiCl_4$-C_3H_8-H_2 system (P = 10 Torr, H_2/[$SiCl_4$+C_3H_8] = 20).