Journal of Korean Institute of surface Engineering
Vol. 29, No. 5, Oct., 1996

THERMAL PROPERTIES OF SIC/C FUNCTIONALLY GRADIENT MATERIALS BY CVD

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ABSTRACT

The computer simulated CVD phase diagrams were completed by the stoichiometric algorithm. Three kinds of SiC/C FGMs: stepwise, semi-continuous, and continuous specimens were prepared according to the simulation. These three types of FGMs and SiC non-FGMs were compared through various thermal test and measurement. In overall judgment, the semi-continuously deposited FGM specimens out of three kinds showed excellent thermal properties as well as a good adhesion to each sub-layer.

INTRODUCTION

From late 1980's, the development of materials, which can be used under the severe temperature conditions, such as in aerospace and in nuclear fusion areas, has been undertaken[1,2]. One of the many approaches for that purpose is the so-called functionally gradient materials(FGMs) in which the material properties are continuously changed by gradually varying the compositions as well as morphologies[3-5]. Especially, the SiC/C FGMs by CVD were deposited for the development of thermal barrier materials to be used for space shuttle[6]. A design of SiC/C FGMs is being conducted taking advantage of the high oxidation resistance and high temperature strength of SiC as use in high temperature side of the materials, and for low temperature side use of carbon having a low Young's modulus and high thermal shock resistance is considered.

Chemical vapor deposition(CVD) is effective to fabricate FGMs through a co-deposition process using multi-component gas reactions[7]. The main reason to use CVD process is that composition and microstructure of the deposited materials could be easily controlled by changing the gas flow ratio.

There have been many publications on the SiC/C FGMs by CVD. Koizumi et al.[8] reported that a 300mm square shell sample of SiC/C FGM for the base of the fuselage of space planes and a 50mm diameter semispherical bowl for the nose-cone was successfully fabricated and tested in 1992. They turned out to be able to withstand both a maximum temperature of 2000K and a temperature difference of 1000K.

In the present work, the focus points were to measure the thermal property enhancement of FGMs compared to the monolithic SiC only and to improve the adhesion between the layers in the FGMs. A comparison between the SiC/C ratio data obtained from the simulated thermodynamic calculation and from experiment has also been made.

EXPERIMENTAL PROCEDURE

A revised computer simulation program which is stoichiometric algorithm type was used to expect the species and amount of the deposited materials at the actual deposition conditions. According to the simulated results, the experimental conditions were set and varied.

Propane, methane and bubbled silicon tetra-chloride($SiCl_4$) were used as source gases. The carrier gas was hydrogen and the atmosphere gases were hydrogen and argon. Argon and nitrogen gases were used for the purging purpose. A hot wall type CVD reactor was used for the deposition of SiC/C FGMs on the ATJ graphite substrate[9]. Deposition temperature was fixed at 1573K and the SiC/C ratio was changed by controlling the flows of the source and atmospheric gases in a stepwise fashion, in a continuous fashion, and in a semi-continuous fashion with mass flow controllers(MFCs). The total gas pressure(P_t) during the deposition was between 1.3 and 6.5 KPa.

An X-ray diffractometer(XRD) was used for phase analysis. Scanning electron microscope(SEM), equipped with energy dispersive spectrometer(EDS) and a wavelength dispersive spectrometer(WDS), were used for the microstructural observations for both the deposit and fracture surfaces, and for compositional microanalysis within the deposit layer.

RESULTS AND DISCUSSION

Simulation

In the present work, the CVD thermodynamic simulation program consists of three parts. The first, main program named TZVX. FOR calculate all the thermodynamic calculations and make outputs. The second, Source data file named MASTER35. DAT has a set of thermodynamic data of various species. The third, the program named CHDAVE. FOR select specific species from the set of whole thermodynamic data and make a input data file for the main program. The characteristics of the program is that optimum formation reaction equation set, calculation of reaction coefficient, and activity coefficient were determined by the stoichiometric algorithm[10].

Fig. 1 shows simulated CVD phase diagram in the $SiCl_4$-C_3H_8-H_2 system. Phases consists of four parts and the area of SiC +C was wide broad. This CVD phase diagram provide a guide line for the actual deposition.

Fig. 2 shows the relationship of SiC/[SiC+C] ratio versus eight different experimental conditions which are listed in Table 1. According to this simulation, it is expected that SiC rich and C rich phases could be obtained with the conditions in Table 1. However, it is difficult to get the ratio between 0.2 to 0.7.

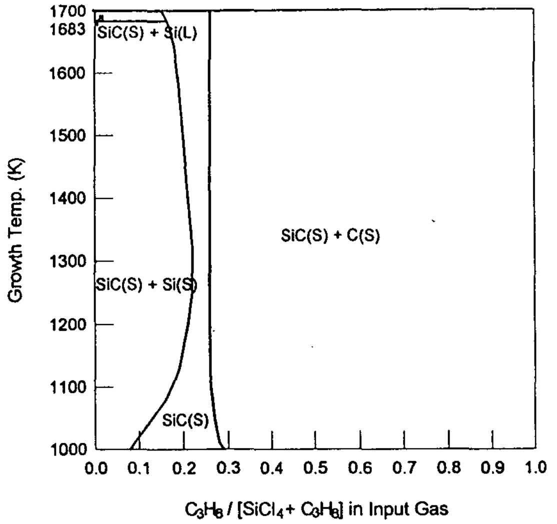

Fig. 1. The CVD diagram of the $SiCl_4$-C_3H_8-H_2 system.
(P_t=10 torr; H_2/[$SiCl_4$+C_3H_8]=100)

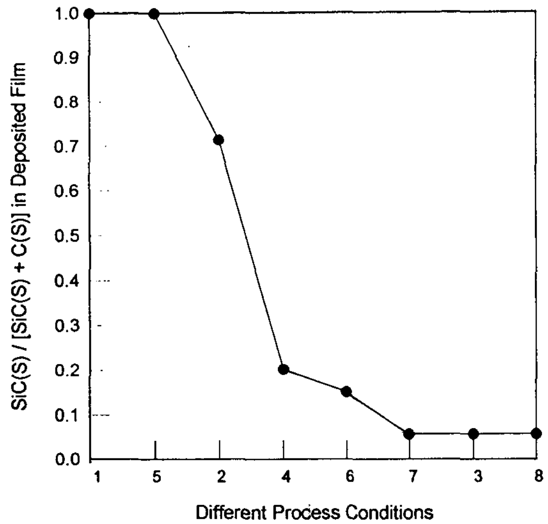

Fig. 2. SiC(s)/[SiC(s)+C(s)] radio of different process conditions. Each process conditions are listed in Table 1.(T=1573.15 K ; P_t=10 torr)

Deposition

SiC/C FGMs were deposited in three different fashions: stepwise, continuous, and semi-continuous. Stepwise, Semi-continuous, and continuous mean that the input gas flows were discontinuously controlled in each step, continuously controlled only for the only interface region between steps, and continuously changed during the whole process, respectively.

Table 1. Process conditions numbered in Fig.2.(C_3H_8-$SiCl_4$-H_2/Ar system)

Conition	C_3H_8 (sccm)	$SiCl_4$ (sccm)	Carrier H_2 (sccm)	ATM H_2 (slm)	ATM Ar (slm)
1	17	65	213	1.78	0
2	50	65	213	1.78	0
3	600	33	107	0.1	4
4	300	65	213	0.1	6
5	17	65	213	2	0
6	300	46	150	2	2
7	600	33	107	2	4
8	600	33	107	0	6

Fig. 3 shows SEM micrographs from the fracture surfaces of the specimens which were deposited in three different fashions. As shown in the Fig. 3a, the adhesion of interfaces between the layers is not so good in the case of FGMs deposited in a stepwise fashion. Hence, as shown in the Fig. 3b and 3c, the adhesion state is good for both FGMs in a continuous and a semi-continuous fashion. Judging from the SEM micrographs, interfaces of semi-continuously deposited specimen look better than those of continuously deposited one, in contrast with our expectation.

Thermal Conductivity

Thermal conductivities of various specimens were obtained from the thermal diffusivity measurement. Table 2 shows the thermal diffusivity and conductivity data. Unexpectedly, stepwise FGMs show the lowest value of conductivity, even lower than that of

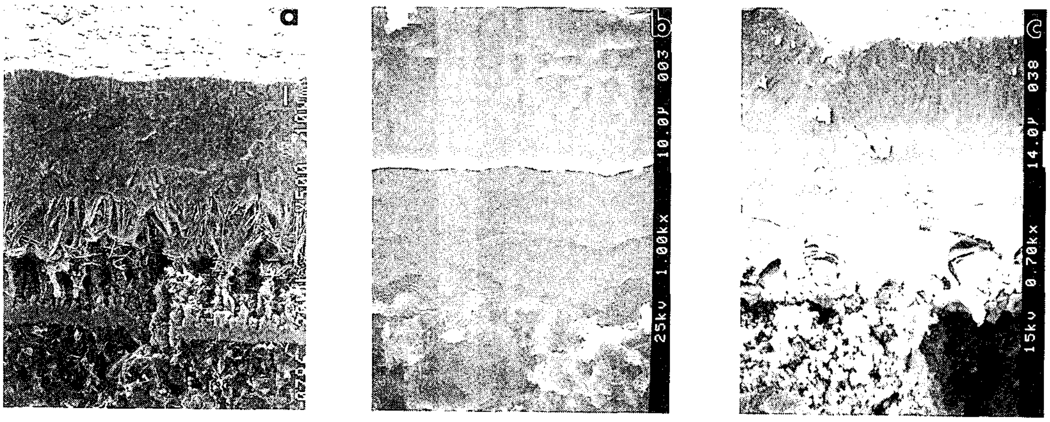

Fig. 3. SEM micrographs from the fracture surfaces of the specimens which were deposited in three different fashions.
(a) stepwise fashion, (b) continuous fashion, (c) semi-continuous fashion.

Table 2. The measured thermal conductivities of various specimens.

Sample	Frequency (Hz)	Thermal diffusivity (cm^2/s)	Thickness (μm)	Thermal conductivity (J/cm s℃)
Graphite	5	0.870	236	1.116
Stepwise FGMs	6	0.522	230	0.718
Semi-continuous FGMs	3	0.970	115	2.836
SiC(non-FGMs)	5	1.156	50	3.150

graphite. This would be caused by the presence of gaps in the interfaces in the FGMs deposited in a stepwise fashion. The air pocket in the gap may decrease the thermal conductivity. Semi-continuously deposited specimen shows the value between graphite and SiC. This means adhesion state of interface is good and the value is in good accordance with theoretical one.

CONCLUSIONS

Thermodynamic computer simulation program was completed with stoichiometric algorithm. In practice, the computer simulation data were well matched with the ones from experiment. The interfacial adhesion of the deposited FGMs in a semi-continuous fashion was the best of all. Thermal conductivity of FGMs deposited in a stepwise fashion was the lowest because porous layers were existed at the interfaces, however; their mechanical strength would be low. In overall judgment, the best way to deposit the FGMs would be a semi-continuous fashion and the specimen deposited in that way showed the expected thermal properties which is under our control.

ACKNOWLEDGMENTS

This study is supported by Korean Ministry of Education through Research Fund in 1995.

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