

Surface and interface characteristics of SiC coatings by chemical vapor deposition

RONG-JUN LIU*, CHANG-RUI ZHANG, XIAO-YANG LIU, XIN-GUI ZHOU, YING-BIN CAO

Key Laboratory of Advanced Fibers & Composites, College of Aerospace & Materials Engineering, National University of Defense Technology, Chang sha 410073, People's Republic of China
E-mail: Rongjunliu@163.com

SiC advanced materials grown by chemical vapor deposition (CVD) have many outstanding properties such as ultra-pure (>99.9995%), unparalleled wear and corrosion resistance, homogeneity, low CTE, fine grained microstructure, high thermal conductivity, chemical and oxidation resistance, cleanability, mirror-like surface finishes polishability as well as thermal and dimensional stability. These superior properties make CVD SiC very appropriate for high temperature structural materials, high temperature semiconductor and reflective optics materials [1–4].

SiC coatings (films) have been grown by many investigators using CVD techniques in the past years and almost all of the research has focused on the following issues [5–10]: (a) process conditions such as deposition temperature, pressure, flow rate ratio of carrying gas to diluent gas, (b) thermodynamic or kinetic study of CVD SiC, (c) SiC crystal growth mechanism. However to date has seen no reports on the difference of structure and composition between the surface and interface in CVD SiC coatings. The current work studied the surface structures of CVD SiC coatings as well as the microstructure of the interface between the SiC coatings and the substrates.

CH_3SiCl_3 (MTS) was used as precursor in the experiments because it has a 1:1 molar ratio of silicon to carbon, therefore, it can deposit stoichiometric SiC. A hot-wall type vertical CVD reactor was used for the present work, MTS was carried out by H_2 , Ar was used as diluent and protective gas, the flow rate of H_2 and Ar was 300 and 100 ml/min, respectively. All depositions were performed at temperature of 1100 °C and the total pressure was controlled at less than 5 kPa by a vacuum pump. Graphite and SiCp/SiC composites by PIP (precursor-infiltration-pyrolysis) process were used as deposition substrates. Detailed experiment procedures have been reported in a previous work [11].

The surface and interface microstructures of CVD SiC coatings were observed by scanning electron microscopy (SEM), the crystal structures and preferred orientation were characterized by an X-ray diffractometer (XRD). Chemical compositions of the as deposited coatings were analyzed by energy-dispersive X-ray spectroscopy (EDS).

Fig. 1 shows typical cross-sectional SEM image of CVD SiC coatings on graphite (Fig. 1a) and SiCp/SiC

(Fig. 1b) substrates. Both graphite and SiCp/SiC substrate bond well with the CVD SiC coatings. Because there are many micro-pores in the graphite and SiCp/SiC substrates, SiC particles can infiltrate into the substrates during CVD process, which contribute to the adhering of the coatings to the substrates. Also, it can be noted that CVD SiC coatings are very dense whether the substrate is graphite or SiCp/SiC.

Fig. 2 gives the surface and interface morphology of SiC coatings deposited on SiCp/SiC substrate. The SiC coatings were removed from SiCp/SiC substrate by mechanical method, therefore, it will produce cracks in the interface as shown in Fig. 2b. It can be seen that the SiC particles on the surface (Fig. 2a) are very large and have well-developed pyramid (faceted) structures, the grain shape of pyramid can indicate that SiC coatings have (111) preferred orientation; however, the crystals on the interface are ultra-fine.

Fig. 3 shows surface and interface XRD patterns of SiC coatings (the as-deposited coating is the same as that shown in Fig. 2). Although (111) plane is the preferred orientation in these two patterns, it is to be noted that there is great difference between the surface and interface XRD peaks. Firstly, there is a small quantity of α -SiC in the surface coatings; however, the interface coatings are composed of β -SiC. Secondly, the peaks of (220) and (311) of the surface coatings are stronger than that of the interface coatings.

Fig. 4 shows the cross-sectional SEM images of CVD SiC coatings, the thickness of the as-deposited coatings are about 200 μm . Three typical sites on the as deposited coating's cross-section were chosen and their chemical compositions were analyzed by EDS method. Block A is near the surface, block B is in the middle of the as deposited coating's cross-section and block C is close to the interface. The results of EDS are shown in Fig. 5, which indicates that the as deposited coatings are approximately stoichiometric near the interface (block C). At block A, C:Si atom ratio is bigger than 1, as the site go to block B, the percentage of C atom decreases and the Si atom content increases, when the site is near to the interface, the C:Si atom ratio approaches 1:1.

From Figs 2–5, it can be noted that the structure has the composition of the coatings that are different at the surface and at the interface. At the surface of the as deposited coatings, the morphology shows faceted

*Author to whom all correspondence should be addressed.

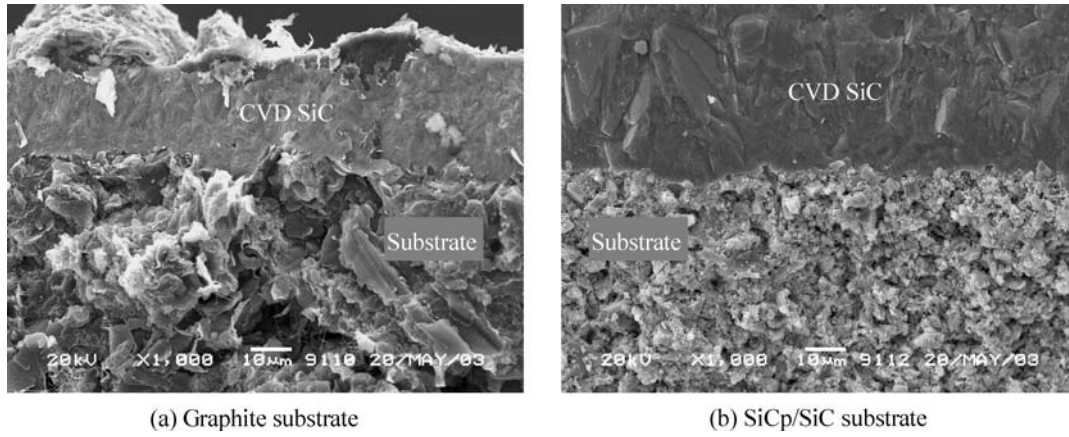


Figure 1 Cross-sectional SEM images of CVD SiC coatings and substrates.

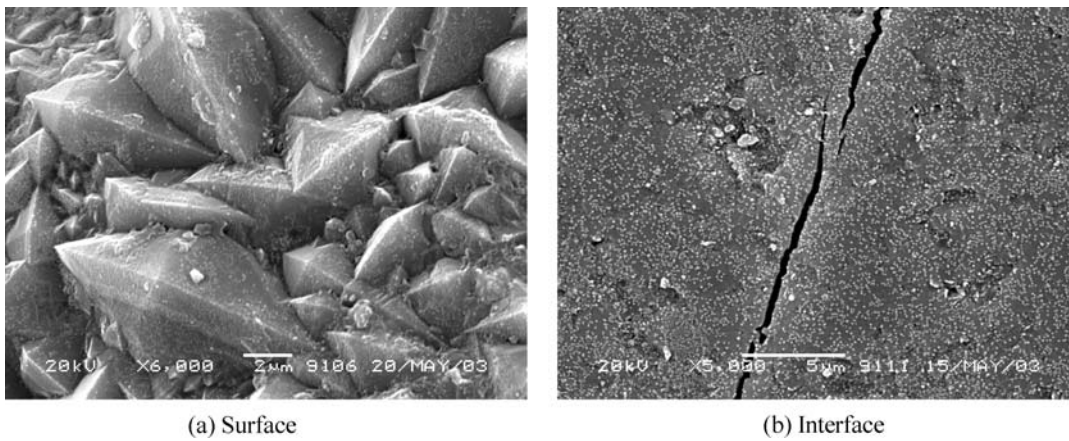


Figure 2 Surface and interface SEM image of CVD SiC coatings.

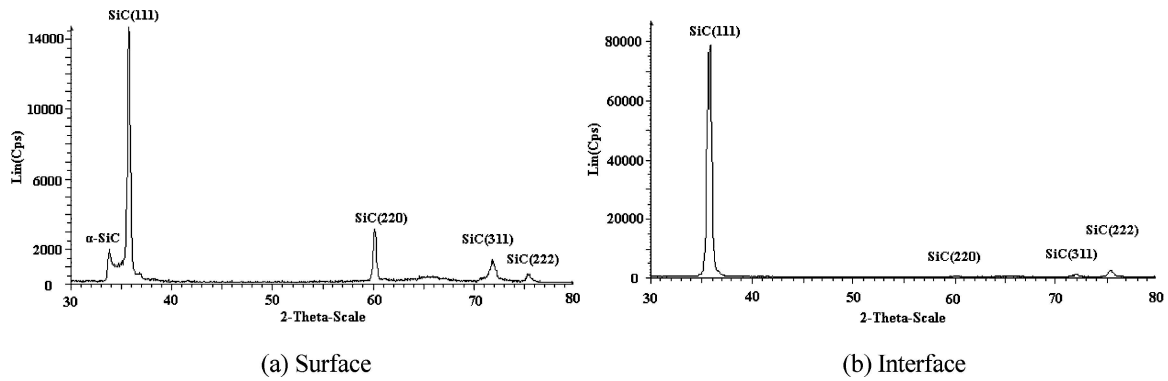


Figure 3 Surface and interface XRD patterns of CVD SiC coatings.

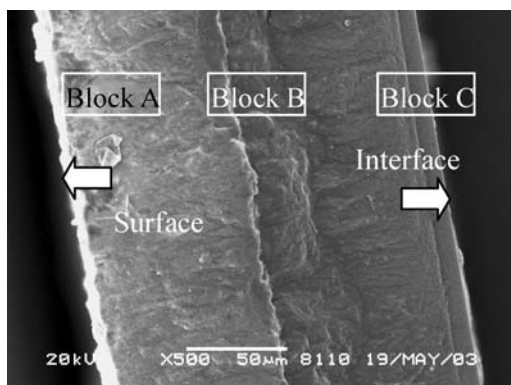


Figure 4 Cross-sectional SEM images of CVD SiC coatings.

structure, the crystal structures exhibit a trace of α phase in addition to β phase, the appearance of α -SiC is due to the excessive carbon atom, which can be seen in the data of Fig. 5. Also, in the XRD pattern of the surface, (220) plane increased drastically. The microstructure of the surface affects the preferred orientation; Kim and his co-worker reported that the development of (220) plane is associated with the formation of a faceted structure [12]. At the interface of the CVD SiC coatings, the morphology is smooth and ultra-fine. The coating consists primarily β -SiC, and is approximately stoichiometric near the interface.

CVD process is very complicated and may be divided into the following stages [6, 13]: (1) transport

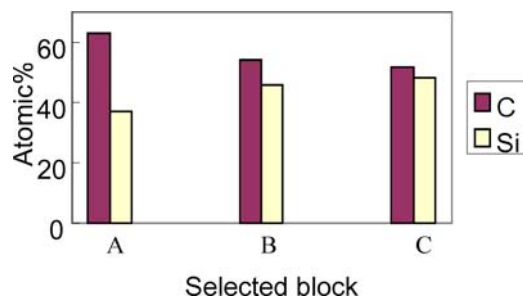


Figure 5 C:Si atom ratio at different selected blocks.

of reactant species to the vicinity of the substrate; (2) diffusion of reactant species to the substrate surface; (3) adsorption of reactant species; (4) surface diffusion, dissociation, inclusion of coating atoms into the growing surface, and formation of by-product species; (5) de-adsorption of by-product species; (6) diffusion of by-product species into the bulk gas; (7) transport of by-product species away from the substrate. This theory successfully explains the deposition process of coatings (films), however, it cannot interpret the difference of microstructure at the interface and surface. We suggest that an important step exists in the deposition process of SiC coatings; we call it the solid phase diffusion step.

The solid phase diffusion step can be explained as follows: the deposition of SiC coatings from MTS precursor results in SiC(s), C(s) (there is no excessive Si(s) in our experiments); as the deposition proceeds, the deposited SiC coatings are still undergoing crystallization, C(s) phase will diffuse toward the surface of the SiC coatings, therefore, the interior of the coating is composed of β -SiC, whereas the surface of the as-deposited coatings exhibit a trace of α phase in addition to β phase due to the excessive C(s).

In summary, due to solid phase diffusion step existing in the chemical vapor deposition of SiC coatings, the structures as well as element compositions between the

surface and interface are different from each other. At the surface of the as-deposited coatings, the morphology shows faceted columnar structure, the crystal structures exhibit a trace of α phase in addition to β phase. At the interface of the CVD SiC coatings, the morphology is smooth and ultra-fine, its crystal structures consist primarily β -SiC, and the as-deposited coatings are approximately stoichiometric.

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