Surface & Coatings Technology 334 (2018) 78–83

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Preparation of silicon carbide coating by chemical vapor deposition by using hexamethyldisilylamine precursor

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ARTICLE INFO

Keywords:
SiC
Coating
CVD
Crystal
Stacking faults
Twin

ABSTRACT

Silicon carbide (SiC) coating is deposited on C/C composite substrate for the first time by chemical vapor deposition (CVD) with hexamethyldisilylamine (HMDS, $C_6H_{19}NSi_2$) as precursor and N_2 as carrier gas in an intermediate deposition temperature range. The effects of deposition temperature on phase constitution, surface morphology and deposition rate of the coating are investigated by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The coating exhibits a β-SiC (3C) phase at 1010 °C, 1060 °C and 1100 °C, coexistence of both α-SiC (2H) and β-SiC (3C) phases at 1130 °C and 1180 °C, as well as a single β-SiC (3C) phase again at 1220 °C. The morphology and microstructure of coating change significantly with deposition temperature. The change of phase constitution and surface morphologies are closely linked to nucleation, growth and defects formation in SiC crystals during CVD process.

1. Introduction

Due to the low density, high specific strength, high thermal conductivity and low thermal expansion coefficient, C/C composites are widely used in aerospace and aviation of extremely high temperature environments [1–4]. C/C composites also exhibit a great potential as biomaterials due to the low elastic modulus, high corrosion resistance and good biomechanical compatibility [5,6].However, the drawbacks of hydrophobic surface and “black skin effect” of C/C composites greatly limit their further application as biomedical applications, especially in the artificial joints and other wear-resistant implants. For these reasons, C/C composites are often modified by the silicon-containing coating such as SiC to improve the surface bioactivity, wear resistance and service life [7,8]. This is ascribed to the fact that Si is one of the most essential elements in human body that can combine mucopolysaccharide and proteins and can maintain the activity of prolylhydroxylase in the collagen [9–12].

SiC is widely used as protective coating ascribed to its outstanding thermal stability, high hardness and good thermal conductivity etc. [13]. In addition, SiC is biologically nontoxic and is a promising biomaterial [14–16]. In general, SiC coating can be prepared by carbothermal reduction [17], pack cementation technique [18,19] or chemical vapor deposition (CVD) process [20–23]. Carbothermal reduction method is complex and requires high reaction temperature (≥ 1400 °C) [17].Coating from pack cementation technique is generally characterized by residual silicon in coating [18–19]. CVD is one of the most widely used methods in material preparation with the advantages of low deposition temperature, simple operation, easy maintenance and uniform coating etc. [20–23]. The precursor used commonly for SiC coating is methyltrichlorosilane (MTS, CH_3SiCl_3). However, the product of chlorine hydride gas is poisonous and harmful to the equipment. Since hexamethyldisilylamine (HMDS, $C_6H_{19}NSi_2$) is non-corrosive and non-toxic, it has been widely used as a precursor to produce SiC coating on many substrates such as SiC [24], Si [25] and etc. [26–27]. In addition, the decomposition temperature of HMDS is much lower than the other traditional precursors. Therefore, in this paper, SiC coating is prepared by CVD with HMDS as the precursor and N_2 as carrier gas. The morphology, microstructure and phase constitution are investigated in details at various temperatures.

2. Experimental

Substrate disc (φ10mm × 3 mm) of C/C composites with density of 1.75 g/cm^3 is used in this paper. A cold-wall horizontal CVD reactor is

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https://doi.org/10.1016/j.surfcoat.2017.11.017
Received 30 April 2017; Received in revised form 13 October 2017; Accepted 5 November 2017

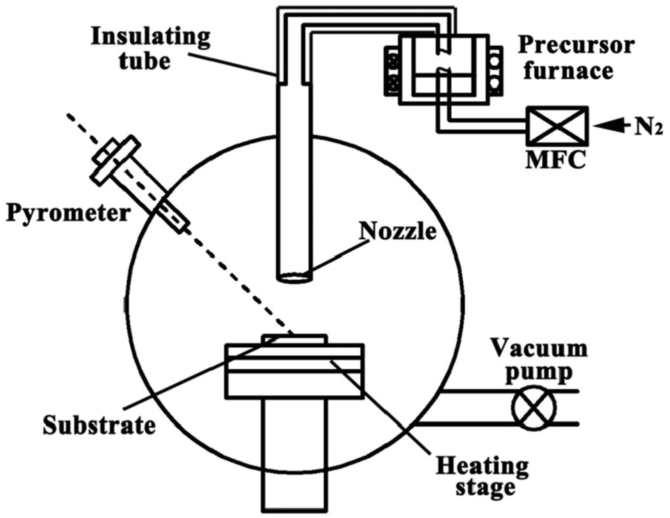

Fig. 1. The schematic figure for chemical vapor deposition reactor used in the present research.

used as shown in Fig. 1, where the substrate disk is locally heated by using a molybdenum wire from the bottom. Hexamethyldisilylamine (HMDS, $C_6H_{19}NSi_2$, ≥ 99.0% (GC)), the precursor gas is kept at a constant temperature of 50 °C and is carried into the CVD chamber by using N_2(99.99%). Ratio between precursor gas and carrier gas is kept to be 1:1 with the total pressure fixed at 450 Pa. Deposition temperature is a key factor to the characteristic of coating. From the previous research, CVD processes by using HMDS precursor was either performed at relatively low temperature range (760–900 °C) [24] or extremely high temperature (higher than 1300 °C) [25], and few study was carried out in the intermediate temperature range. In this research, deposition is carried out at 1010 °C–1220 °C for 2 h in all tests.

The crystal phase of coating is identified by using X-ray diffraction (XRD, Rigaku Corporation D/MAX-RA, CuK_{α} radiation). The surface and cross-sectional morphologies of coating are observed by scanning electron microscopy (SEM, Nova NanoSEM 230). Microstructure of coating is observed by the transmission electron microscopy and high-resolution transmission electron microscopy (HRTEM, Titan G2 60–300).

3. Results and discussion

Fig. 2 shows the XRD patterns of SiC coatings prepared at temperatures from 1010 °C to 1220 °C. The strong diffraction peaks at 2θ of 35.6° and 60.0° at 1060 °C and 71.8° at 1100 °C indicate the dominant β-SiC (3C) phase in the coating. With increasing temperature from 1010 °C to 1100 °C, the intensities of β-SiC (3C) peak increase and the microstructure of the coating vary from a random texture into a (111) preferred one (Fig. 2). Furthermore, α-SiC (2H) phase with diffraction peaks at 2θ of 33.5°, 38.2° and 49.8° is observed to co-exist with the β-SiC (3C) at 1130 °C and 1180 °C as shown in Fig. 2(d) and Fig. 2(e), respectively. With deposition temperature increasing to 1220 °C, single β-SiC (3C) phase is observed again as shown in Fig.2 (f). From above results, in the present condition, it is considered that SiC coating is formed by decomposition of HMDS as:

$$C_6H_{19}NSi_2\,(g) \rightarrow 2SiC\,(s) + 4C\,(s) + 8H_2\,(g)\uparrow + NH_3\,(g)\uparrow \quad (1)$$

Surface morphologies of SiC coating at different deposition temperatures are observed by using SEM as shown in Fig. 3 and Fig. 4. Fig. 4 is the corresponding amplified images on the selected regions in Fig. 3(d), (e) and (f), respectively. It can be seen in Fig. 3(a) that the coating is smooth at 1010 °C, in which some spherical SiC particles are observed. At the same time, the exposed carbon fibers are visible as indicated by the white arrows, indicating that the coating is very thin.

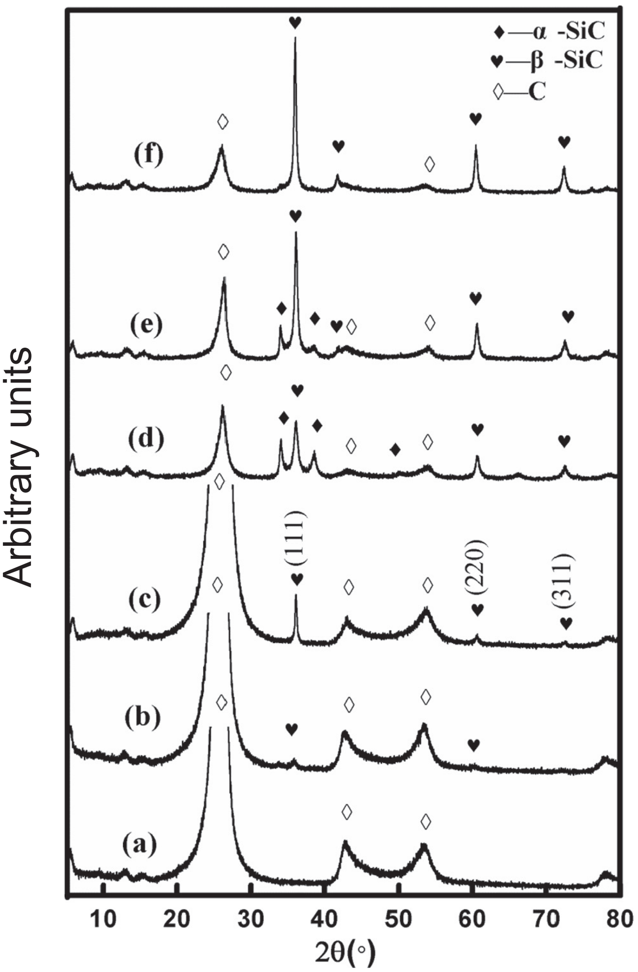

Fig. 2. XRD patterns of SiC Coatings at deposition temperatures of (a) 1010 °C, (b) 1060 °C, (c) 1100 °C, (d) 1130 °C, (e) 1180 °C and (f) 1220 °C for 2 h.

With the deposition temperature increasing to 1060 °C (Fig. 3(b)), the coating becomes rougher and the substrate is completely covered with thick SiC at 1100 °C (Fig.3(c)). With the further increase of temperature from 1130 °C to 1220 °C, the surface profile of the film varies into a large "cauliflower-like" structure, characterized by more and more boundaries or cracks in the "cauliflower-like" structures (Fig. 3(d)–Fig. 3(f)). From Fig. 4(b), it can be seen that the cauliflower-like particles under SEM are composed of "needle-flake" structure. The "needle-flake" structure grows gradually. At the same time, the gap between the "cauliflower-like" particles becomes smaller with increasing deposition temperature.

The surface roughness of sample surface before and after CVD at various temperatures is shown in Fig. 5. Due to the brittle nature of pyrocarbon matrix and the presence of carbon fiber, the C/C composite disc shows a relatively rough surface even after the careful machining. With increasing deposition temperature from 1010 °C to 1100 °C, the sample surface becomes smoother possibly ascribed to the even coverage of SiC on the substrate (Fig. 3 (a–c)). With further increasing deposition temperature, the sample surface turns rougher due to the presence of "cauliflower-like" structure (Fig. 3 (d–f)).

The cross-sections of SiC coating in various conditions are also observed by SEM (Fig. 6). From cross-section morphologies of coating at 1010 °C and 1220 °C, the interfaces between the coating and the substrate are relatively compact, and no obvious crack or spalling between the substrate and coating is observed.

Fig. 7 shows the bright-field TEM image and selected area diffraction (SAED) patterns of the SiC coating at 1180 °C. SAED pattern of the