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Effects of oxidation cross-linking and sintering additives (TiN, B) on the formation and heat-resistant performance of polymer-derived SiC(Ti, B) films

Xiaohui Xu [a,b,c], Yu Mao [a,b], Fen Chen [a,b], Rongqian Yao [a,b,c,*], Zude Feng [a,b], Lifu Chen [a,b], Ying Zhang [a,b]

[a] Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, China
[b] Fujian Provincial Key Laboratory of Advanced Materials, Xiamen University, Xiamen 361005, China
[c] Shenzhen Research Institute of Xiamen University, Shenzhen 518057, China

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ABSTRACT

Effects of oxidation cross-linking and sintering additives (TiN, B) on the microstructure formation and heat-resistant performance of freestanding SiC(Ti, B) films synthesized from Ti, B-containing polycarbosilane (TiB-PCS) precursor were investigated. TiB-PCS green films were first cross-linked for 1 h, 2 h, 3 h and 4 h, respectively, and then pre-sintered at 950 °C. Finally, they were sintered at 1800 °C to complete the conversion from organic films to inorganic SiC(Ti, B) films. The results reveal that curing time has a great impact on the uniformity and density of SiC(Ti, B) films. TiB-PCS films cured for 3 h yield the best quality SiC(Ti, B) films, which are composed of β-SiC crystals, C clusters, α-SiC nano-crystals, a small amount of TiB_2 and B_4C. TiB_2 and B_4C are both steady phases which can inhibit abnormal growth of β-SiC, effectively reduce sintering temperature and help consume excess C from decomposition of amorphous SiOxCy. After high temperature annealing at 1500 °C, 1600 °C and 1700 °C in argon, SiC(Ti, B) films still keep excellent mechanical properties, which makes them attractive candidate materials for microelectromechanical systems (MEMS) used at ultra-high temperatures (exceeding 1500 °C).

1. Introduction

Over the past several decades, silicon carbide (SiC) has been gaining increasing popularity as an alternative material to Si, for microelectromechanical systems (MEMS) used in harsh environments [1–3]. SiC has favorable electronic characteristics, mechanical strength, corrosion resistance and thermal performance under high-temperature environment, all of which make it a promising candidate for high temperature MEMS sensors used in various fields such as automotive, aerospace, nuclear station, etc. [4–7]. So far, SiC films can be prepared by multiple methods, among which chemical vapor deposition (CVD), physical vapor deposition (PVD) and sputtering are most commonly used [8–12]. Besides, a novel approach to produce SiC, polymer precursor pyrolysis has drawn extensive attention [13–16]. Compared with CVD, polymer pyrolysis is able to get SiC films that not only have superior mechanical properties and oxidation resistance, but also match well with the substrate in thermal expansion coefficient and lattice constant.

When the temperature rises up to 1200 °C, SiC films deteriorate rapidly, with abnormal grain growth and notable deficiency [17,18]. This deterioration prevents further application of SiC films in ultra-high temperature environment. In order to overcome this problem, the polymer precursor route can be modified by two approaches. The first is chemical modification of precursors by using organics that contain other elements such as N and Al [17,19–22]. The other is doping, which is carried out by adding specific inorganic molecules or atoms to the precursor [23,24].

Our previous work has successfully produced polymer-derived freestanding SiC films which can avoid the significant difference of thermal expansion coefficient resulted from heteroepitaxial growth [13,17]. In addition, performance of SiC materials can be improved effectively with Ti, B as additives, including prominent improvement in density and resistance to elevated temperature, notable decrease of defects and fairly good antioxidant activity [18,25]. However, the formation mechanism of compact SiC(Ti, B) films is rarely mentioned, and two questions need to be answered. One is how the oxidative cross-linking process would influence

* Corresponding author at: Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, China.
E-mail address: rqyao@xmu.edu.cn (R. Yao).

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the formation and mechanical performance of SiC(Ti, B) films. The other one is how the existing form of Ti and B atoms would influence their heat-resistant properties.

In order to address these issues, SiC(Ti, B) films with different oxidation cross-linking treatments were investigated. Composition, morphology, microstructure and physical properties of the green and sintered films were presented to provide an elaborated understanding of relevant techniques. Additional experiments were conducted to find out the existing form of Ti and B atoms [25]. Also, high-temperature annealing treatments were carried out to demonstrate thermal shock resistance of SiC(Ti, B) films. All these works would present detailed high-temperature properties of SiC(Ti, B) films and guide the design of their microstructure and composition.

2. Experimental procedure

TiB-PCS samples employed in this study were synthesized in our laboratory. PCS samples (Si: 41.03 wt%, C: 43.24 wt%, O: 1.05 wt%) were synthesized by thermal decomposition of polydimethylsilane (PDMS) [26]. They are transparent solid with a number average molecular weight (Mn) of 1426 measured by Gel permeation chromatography (GPC) using an Agilent 1100 system (Agilent, Santa Clara, CA, USA) and a melting point of 215 °C. TiN (purity > 99%, Shanghai Longjin Metallic Material Co., Ltd., China) and boron (purity 94–96%, Shanghai Longjin Metallic Material Co., Ltd., China) powders were added with concentration of 0.74% and 0.26% on the basis of PCS mass, respectively. Size of all particles measured by Laser Particle Sizer (LS-603, OMEC, China) was reduced to d50 < 300 nm by ball milling. After being mixed, TiN, B powders and PCS/xylene solution were homogenized by ball milling and ultrasonic agitation processing. The xylene was removed afterwards completely by vacuum distillation at 110 °C to yield brown TiB-PCS precursors powder.

Prepared TiB-PCS precursors were put into the spinning device and deaerated for 3 h in the vacuum deaeration furnace under 250 °C. Then they were melt spun into green films. The thickness could be altered by adjusting the spinneret mouth size and spinning speed using a melt spinning machine (MMCH05, Chemat, Northridge, CA) under 220 °C at an extrusion rate of 0.3 mm/min [18]. The green films were then cross-linked in oxidative air (flow rate: 200 ml/min) with a heating rate of 3 °C /min to 100 °C and 10 °C /h to 180 °C and held for 1 h, 2 h, 3 h and 4 h at 180 °C, respectively. Subsequently, the cured TiB-PCS films were presintered in argon (flow rate: 200 ml/min) with a heating rate of 5 °C/min to 950 °C and held for 30 min. In this pyrolysis progress, the translucent cured films were converted into lustrous black ceramic films. After that, the films were finally sintered at 1800 °C in high-purity argon atmosphere (flow rate: 200 ml/min) at a heating rate of 40 °C/min and maintained for 10 min. In addition, SiC films without sintering additives were also produced in the same way, except that during the final sintering, SiC films were heated with a heating rate of 10 °C/min to 1200 °C and held for 2 h. SiC(Ti, B) films and SiC films were also annealed under argon atmosphere (flow rate of 200 ml/min) with a heating rate of 40 °C/min and held for 1 h at 1500 °C, 1600 °C and 1700 °C to evaluate their high-temperature microstructure and properties.

TiB-PCS green and cured films were examined using Fourier transform infrared spectrometer (Nicolet Avatar FTIR 360, USA). SiC(Ti, B) films with different oxidation cross-linking time were characterized by the following ways. Their composition and microstructure were examined by electron probe microanalysis (EPMA) (JXA-8100, JEOL, Japan), scanning electron microscope (SEM) (Model 1530, LEO, Germany), X-ray diffractometer (XRD) (X'pert PRO, Panalytical, Netherlands), Raman spectrometer (LabRam I, Dilor, France) and transmission electron microscope (TEM) (JEM-2100, JEOL, Japan) equipped with an energy dispersive spectrometer (EDS) (Inca X-Max, OXFORD, UK). Mechanical properties of SiC(Ti, B) films were tested by Microhardness Tester (HV-1000, Nboeo Detecting Instrument, China) and Universal Testing Machine (Sun 2500, Galdabini, Italy) according to American Society for Testing and Materials (ASTM) D3379-75 procedure.

3. Results and discussion

Fig. 1 shows the FTIR absorption spectra of TiB-PCS green films before and after cross-linking. The cross-linking time ranges from 1 h to 4 h. It is clear that after cross-linking, the absorption peak intensity of Si–H stretching at 2100 cm^{-1} is reduced, while the stretching of Si–C–Si at 1020 cm^{-1} is enhanced (due to the overlapping absorption of Si–O–Si stretching) [18,27–29]. Besides, absorption peak of C–O stretching at 1710 cm^{-1} appears after curing [18]. Therefore, it can be inferred that TiB-PCS reacts with oxygen during the cross-linking process. Si–H bonds are oxidized into Si–O–Si, and a small amount of $Si–CH_3$ is oxidized into C–O. It is worth noticing that the peak intensity of Si–H stretching is gradually reduced as curing time increases, indicating an increase in the extent of oxidation. This is also reflected in the enhancement of Si–C–Si stretching (overlapped by Si–O stretching at 1020 cm^{-1}) and the weakening of $Si–CH_3$ stretching (overlapped by Si–C stretching at 780 cm^{-1}) with cross-linking time increasing.

Table 1 shows the composition of freestanding SiC(Ti, B) films after pyrolysis measured by EPMA. As expected, it suggests that elemental composition (Si, C, O and Ti) is strongly affected by cross-linking time. All the films contain low amounts of Ti and O. As curing time rises, O content increases, while the C, Ti contents and C:Si ratio initially decrease and then slightly increase. The C:Si ratio of SiC(Ti, B) films cured for 3 h is calculated to be 1.139, which is the most close to stoichiometric ratio.

The structure and morphology of sintered SiC(Ti, B) films with different cross-linking time were studied by XRD, Raman and SEM analysis. Fig. 2 shows the XRD patterns of SiC(Ti, B) films cross-linked at 180 °C and sintered at 1800 °C. There are three main sharp peaks at $2\theta = 35.597°$, 59.977° and 71.777° assigned to (3 1

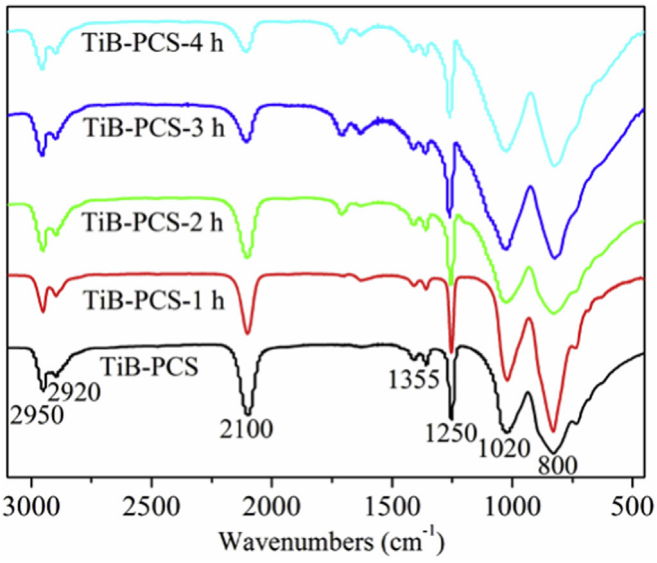

Fig. 1. FTIR absorption spectra of continuous freestanding TiB-PCS green films before and after oxidation cross-linking for different time. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)