Rare Metal Materials and Engineering
Volume 47, Suppl. 2, August 2018
Cite this article as: Rare Metal Materials and Engineering, 2018, 47(S2): 058-061.

Fabrication of Uniform ZrC Coating by Low Pressure Chemical Vapor Deposition: The in-situ Bromination Method

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Abstract: Bromination apparatus was designed and manufactured to accurately control the flow rate of $ZrBr_4$ vapor. Zirconium carbide (ZrC) coatings were deposited on graphite substrate at 1200 ℃ by low pressure chemical vapor deposition from the Zr-Br_2-C_3H_6-H_2-Ar system. The effects of gas composition (input C/Zr ratio) on the morphology and growth mechanism of ZrC coatings were investigated. The results show that the coating deposition process is controlled by the surface reaction kinetics at the input C/Zr ratio of 1.5, leading to a loose structure. When the input C/Zr ratios are 0.5 and 1, coating growth is dominated by diffusion kinetics, resulting in (200) preferential orientation with a dense columnar structure. Meanwhile, ZrC coating without free carbon is produced at the input C/Zr ratio of 0.5.

Key words: ZrC coating; ultra-high temperature ceramic; chemical vapor deposition; gas composition; growth mechanism

Chemical vapor deposition (CVD) of zirconium carbide (ZrC) coating, as one of the most promising coating techniques, can improve the oxidation and ablation resistances of materials containing thermal structure components such as C/C and C/SiC composites due to extremely high melting point (3540 ℃) and ablation resistance as well as low diffusion coefficient of oxygen[1]. Generally, CVD ZrC process is dominated by transmission and strict control of Zr-source precursor, because the stoichiometry, chemical purity, morphology, crystal structure and property of ZrC coating strongly depend on the input Zr/C ratio in gases[2-4].

Up to now, several methods have been developed to provide a controllable and stable Zr-source for preparing high-quality ZrC coatings, mainly involving two routes: sublimation of zirconium halide ($ZrCl_4$) [5-7] and reaction of halide vapor with Zr-metal[8, 9]. The former route suffers from condensation and agglomeration of halide vapor, so the flow rate of Zr-source to CVD chamber is neither reliable nor flexible. Therefore, some complicated facilities, such as a special powder feeder[10] and an impeller-driven vaporizer[11] have been prepared to improve the conventional vaporizer. Compared to the $ZrCl_4$ vapor route, the halogenation process is conveniently operable and cost-competitive without producing impurity. Particularly, bromine has high safety and reactivity as well as adaptable saturated vapor pressure at room temperature. The Japan Atomic Energy Agency has developed ZrC-coated fuel particles by bromide process from a fluidized bed chemical vapor deposition system[12]. However, ZrC coating has seldom been fabricated by low pressure chemical vapor deposition (LPCVD) using such process.

In this study, bromination apparatus was designed and manufactured to accurately control the flow rate of $ZrBr_4$ vapor, and the effects of initial gas composition on the morphology and growth mechanism of ZrC coatings were evaluated.

1 Experiment

ZrC coating was deposited by LPCVD from the Zr-Br_2-C_3H_6-H_2-Ar system in horizontal hot-wall apparatus. The self-made LPCVD system is shown in Fig.1,

Received date: August 25, 2017
Foundation item: National Key Basic Research Development Program of China (“973” Program) (2015CB655200); National Natural Science Foundation of China (91216302).
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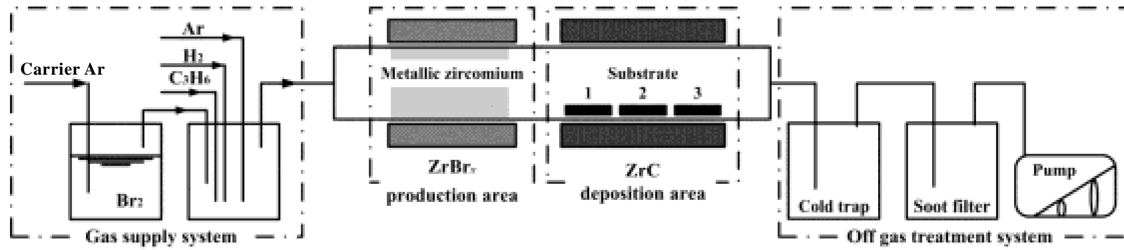


Fig.1 Schematic diagram of CVD apparatus

which consisted of four main parts: a gas supply system, a bromination furnace, a deposition furnace and an exhaust system. Bromine (Br_2, 99.5%) was reacted with Zr-metal particles to form $ZrBr_4$ vapor at 600 ℃. High purity propylene (C_3H_6, 99.9%) was the source for carbon. Purified hydrogen (H_2, 99.999%) was selected as the reducing agent for $ZrBr_4$ vapor, and argon (Ar, 99.999%) was used as the carrier of 0 ℃ Br_2 vapor and diluted gas. ZrC coatings were deposited on graphite slices (1.88 g/cm^3) at reduced pressure (5 kPa) and 1200 ℃.

Since the flow rate of $ZrBr_4$ was controlled by that of carrier Ar, the flow rate of carrier Ar was designed to be fixed. Therefore, the input C/Zr ratio was determined by the flow rate of C_3H_6. The designed gas compositions are listed in Table 1.

Crystalline phase of the coating was determined by X-ray diffraction (Siements D-500, Germany), and its microstructure was observed by scanning electron microscope (FESEM, HITACHI S-4800, Japan). Raman spectroscopy (Bruker, Senterra, Germany) was performed using an Ar^+ ion laser source at 532 nm.

2 Results and discussion

2.1 XRD analysis

The XRD patterns of as-deposited ZrC coating are shown in Fig.2a. The peak intensities of different diffraction planes of ZrC grains change with decreasing the input C/Zr ratio. The peak intensity of (200) plane is the same as that of (111) plane in ZrC-1 coating, while ZrC-2 and ZrC-3 coatings only have strong (200) peaks. There are no obvious free carbon peaks in all the three coatings, suggesting the deposits primarily consist of ZrC phase. As reported previously, the ZrC phase was generally not strictly stoichiometric, and co-deposited free carbon always functioned as a secondary phase in ZrC coating[11], which was thus analyzed by Raman spectroscopy. Raman spectra of all three coatings (Fig.2b), except for that of ZrC-3 coating, show two peaks corresponding to D-band and G-band of carbon[13, 14]. Accordingly, ZrC coating without free carbon can be prepared by this method at the input C/Zr ratio of 0.5.

2.2 Morphology analysis

The morphologies of as-deposited ZrC coatings are shown in Fig.3. ZrC-1 coating shows a loose structure, with obvious gaps and pores between protruding particles

Table 1 Designed gas composition for deposition of ZrC coating

Sample	Flow rate/mL·min^{-1}		Input C/Zr ratio
	H_2	Dilute Ar	
ZrC-1	300	300	1.5
ZrC-2	300	300	1
ZrC-3	300	300	0.5

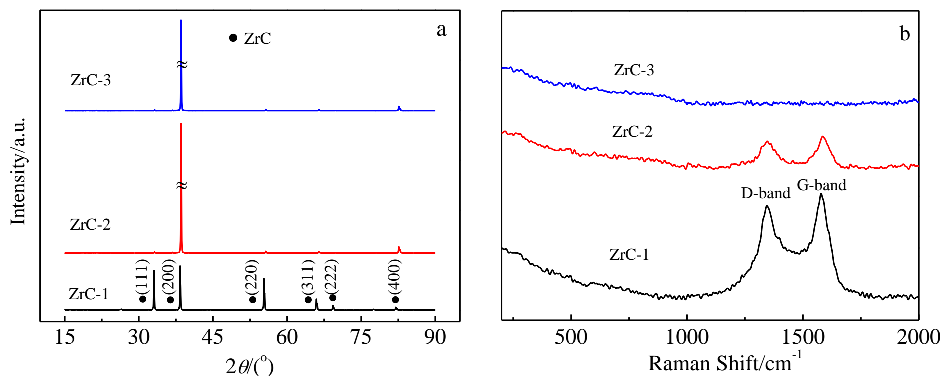


Fig.2 XRD patterns (a) and Raman spectra (b) of the as-deposited ZrC coatings

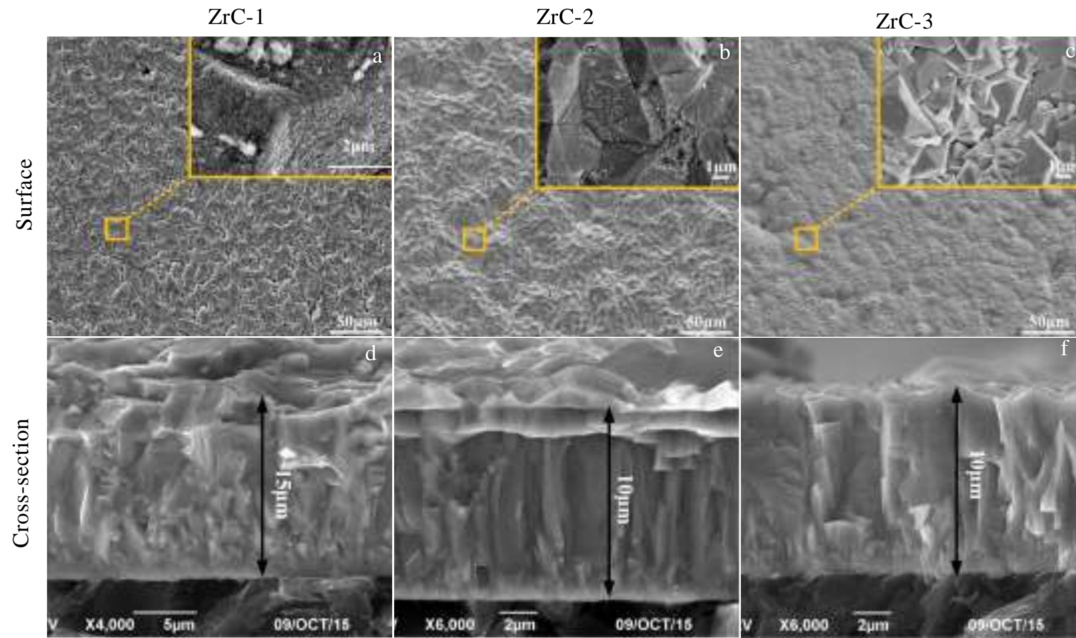
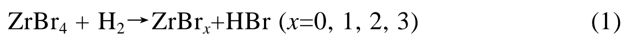


Fig.3 Microstructures of the as-deposited ZrC coatings

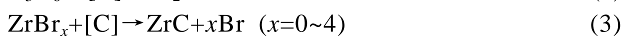
(Fig.3a). The cross-section image (Fig.3d) exhibits that the coating with a thickness of 15 μm is rather rough and disordered. With decreasing the input C/Zr ratio, the surfaces of ZrC-2 and ZrC-3 coatings are smooth, uniform and regularly shaped. ZrC-2 coating has a wavy structure (Fig.3b), whereas ZrC-3 coating exhibits a flat surface (Fig.3c). The corresponding cross-section images of ZrC-2 and ZrC-3 coatings (Fig.3e and 3f) show dense columnar grain structures both with 10 μm in thickness. The enlarged morphologies of the protruding particles are shown at the upper right corner of Fig.3. The surface of ZrC-1 coating comprises many agglomerated ZrC nanoparticles. Meanwhile, the surfaces of ZrC-2 and ZrC-3 coatings are stacked compactly by well-developed pyramid-like crystals. The morphological evolution indicates that gas composition significantly affects the growth mechanism of ZrC coating.

2.3 Growth mechanism

The CVD process of ZrC coating is controlled by chemical equilibrium and mass balance, with the key reactions described as follows:


$$ZrBr_4 + H_2 \rightarrow ZrBr_x + HBr \ (x=0, 1, 2, 3) \quad (1)$$

$$C_3H_6 \rightarrow [C] + H_2 \quad (2)$$


$$ZrBr_x + [C] \rightarrow ZrC + xBr \ \ (x=0\sim4) \quad (3)$$

$$Br + H_2 \rightarrow HBr \quad (4)$$

As suggested by the chemical reactions [Eqs. (1)~(4)], the preparation of ZrC was mainly controlled by the decomposition rate of carbon-containing species and the growth rate of ZrC crystals [15-17]. When CVD was conducted at the input C/Zr ratio of 1.5, the gas super-saturation of carbon-containing species exceeded that of zirconium-containing ones, which may induce rapid secondary nucleation and produce ZrC crystal nanoparticles. In this case, the deposition process was predominantly controlled by surface reaction kinetics. With decreasing the input C/Zr ratio, the deposited species tended to diffuse, sufficiently giving rise to the growth of ZrC crystals. As a result, the produced ZrC particles mutually fused and exhibited a compact, wavy structure in ZrC-2 coating. Under such condition, the deposition process was controlled by mass transport reaction mechanism. The precursor was more prone to gas supersaturation in the boundary layer as the input C/Zr ratio decreased to 0.5, which reduced the atomic diffusion capacity and then suppressed the growth of ZrC crystals. Consequently, ZrC-3 coating exhibited small pyramid-shaped crystals. Furthermore, C_3H_6 decomposed faster than $ZrBr_4$ did at 1200 ℃, so suitably excessive $ZrBr_4$ was beneficial to the reaction between C and Zr atoms and the formation of pure ZrC coating without free carbon.

3 Conclusions

1) The deposition process is controlled by surface reaction kinetics when the input C/Zr ratio is 1.5, whereas coating growth is dominated by diffusion kinetics as the ratio decreases to 0.5 and 1.

2) Given that ZrC coating without free carbon is produced at the input C/Zr ratio of 0.5, this method can be employed to prepare high-quality ZrC coating by accurately controlling gas composition.

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低压化学气相沉积制备 ZrC 涂层：原位溴化工艺

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摘　要：设计了一种溴化装置，用于合成并稳定控制 $ZrBr_4$ 蒸气的流量。采用低压化学沉积技术，以 Zr-Br_2-C_3H_6-H_2-Ar 为体系，于 1200 ℃ 在石墨基底上制备了 ZrC 涂层。研究了气体组分(源气 C/Zr 比)对 ZrC 涂层微观形貌及生长机制的影响。结果表明：源气 C/Zr 比为 1.5 时，涂层的沉积过程为以表面反应机制为主，ZrC 涂层较为疏松。源气 C/Zr 比为 0.5~1 时，扩散动力学是涂层的主要生长机制，所制备的 ZrC 涂层具有致密均匀 ZrC 柱晶结构，并沿(200)晶面择优取向。同时，源气 C/Zr 比为 0.5 时，制备的 ZrC 涂层无自由碳存在并具有近化学计量比。

关键词：ZrC 涂层；超高温陶瓷；化学气相沉积；气体组分；生长机制

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