Surface & Coatings Technology 281 (2015) 76–81

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Microstructure and mechanical properties of carbon–carbon composites modified by reactive diffusion treatment in niobium powder

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ARTICLE INFO

Article history:
Received 9 March 2015
Revised 25 August 2015
Accepted in revised form 10 September 2015
Available online 12 September 2015

Keywords:
Carbon–carbon composites
Powder Immersion Reaction Assisted Coating
Niobium carbide
Reactive infiltration
Flexural strength

ABSTRACT

Refractory carbide coatings are primary candidate materials for improving the high-temperature performance of carbon fiber-reinforced carbon matrix composite (C/C composites). In this paper, a niobium carbide coating was grown on the C/C composite surface employing a Powder Immersion Reaction Assisted Coating (PIRAC) method. 2D C/C composite plates were immersed into Nb powder and annealed at 800 to 1200 °C for up to 16 h. Metallic iodine was admixed to the metal powder to allow for Nb atoms transfer onto the C/C surface and into the pores by gas transport reaction. Following PIRAC treatment, several micrometer thick uniform conformant coatings were obtained consisting of a thin Nb-rich Nb_2C layer on the top surface and a thicker sub-stoichiometric NbC_{1-x} layer underneath. The coating growth was dominated by short-circuit diffusion with the activation energy of approximately 155 kJ/mol. At the lower PIRAC temperatures of 800–900 °C, surface coating growth was accompanied by the infiltration of the volatile Nb iodide and filling of inter-bundle pores with niobium carbide. This resulted in the reduction of residual porosity and an increase in flexural strength and elastic modulus. The greatest increase in specific strength (30%) was measured for C/C composites PIRAC treated at 900 °C, 16 h. No infiltration occurred at the higher temperatures, due to the rapid sealing of surface pores by the Nb carbide layer.

1. Introduction

Carbon fiber-reinforced carbon matrix composites (C/C composites) are promising materials for many structural applications due to their unique properties such as low density, high specific strength, high heat capacity, high thermal conductivity, low thermal expansion and good thermal shock resistance [1–3]. C/C composites are mostly used in aerospace industry, for aircraft brake disks, re-entry heat shields for space vehicles and missiles, rocket nozzles, etc. [2,4,5].

Carbon–carbon composites consist of ordered graphite fibers embedded in a carbon matrix. The carbon matrix is built-up on a fiber preform by chemical vapor infiltration (CVI) or by impregnation and pyrolysis of a thermosetting resin such as epoxy or phenolic resin. CVI fabrication of C/C composites often requires several processing steps and is very slow and expensive [6]. Resin-derived C/C composites, on the other hand, contain shrinkage voids and microcracks at matrix–fiber interfaces and between fiber bundles, and suffer from low interlaminar shear strength, especially 2-D composites with graphite fabric reinforcement. The residual porosity hinders the application of C/C composites in airtight structures (e.g. combustion chamber) since the fuel and/or combustion gas may leak through the open defects [7,8]. Another limitation to the high-temperature uses of C/Cs is their insufficient resistance to ablation and erosion in hot gases [9]. The high temperature performance of C/C composites can be significantly improved by coating with refractory carbides, such as HfC and TaC [10]. A decrease in ablation rate was reported for chemical vapor deposition TaC-coated C/C composites [11]. Similarly to TaC, niobium carbide, NbC, has a high melting temperature (~3500 °C) and high hardness that is retained at elevated temperatures. NbC was reported to exhibit low wear rates under dry sliding associated with high load carrying capacity [12,13]. At the same time, it is much lighter than TaC and has higher specific heat, which makes it an attractive candidate material as a high-temperature protective coating on C/C composites. NbC coatings were reported to protect carbon–carbon substrates from hot hydrogen [14,15].

The method of applying metal carbide coating on C/C composite substrate can have a large effect on its performance. For the coating to be adherent, it is desirable that the carbide layer is formed by reaction of the metal with the substrate. PIRAC (Powder Immersion Reaction Assisted Coating) seems an attractive method for growing such carbide layers on C/C composites. In PIRAC, the annealing of a ceramic part (SiC, Si_3N_4, etc.) immersed into a metal powder leads to the formation of the metal compound (silicide, carbide, etc.) coating via reactive interdiffusion at the ceramic/metal interface [16]. PIRAC was successfully used for the coating of graphite and diamond with Cr, Ti and Nb carbides [17–19] and for the coating of C/C composite with Cr carbides [19]. It

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http://dx.doi.org/10.1016/j.surfcoat.2015.09.020
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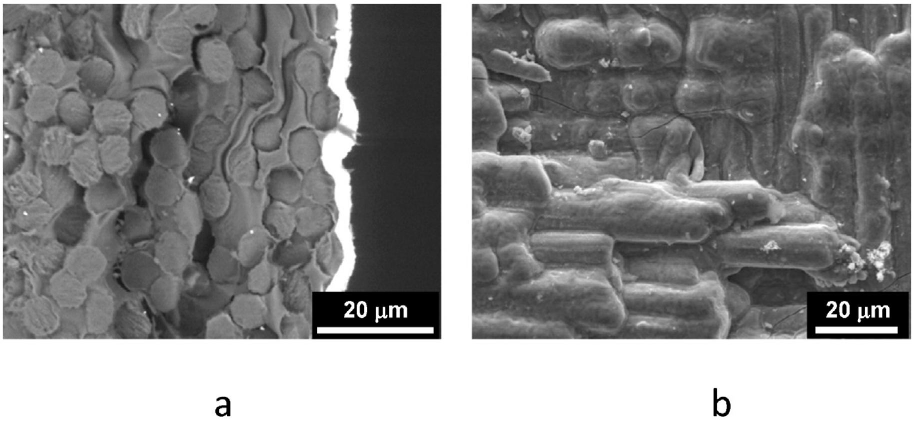

Fig. 1. SEM micrographs of PIRAC coating on C/C composite obtained by treatment in Nb–iodine powder at 900 °C, 16 h: a — cross-section, BSE image; b — top view, SE image.

has also been shown that the transport of metal atoms can be accelerated by adding a small amount of halogen forming volatile metal halides at the PIRAC treatment temperature [18–20]. PIRAC processing via this gas transport reaction provides the possibility of reactive infiltration of metal into the inherently porous C/C composites which will result in the filling of pores and make the material stronger and less permeable to hot gases in service.

In the present paper, carbon–carbon composites were PIRAC coated with niobium carbide, and the effect of processing conditions on the material microstructure and mechanical properties has been studied.

2. Experimental

2.1. Materials and specimen preparation

2D carbon–carbon composite plates (CF-226) with 60% fiber volume fraction and 8% open porosity were supplied by Schunk Kohlestofftechnik GmbH, Germany. The ~2 mm thick plates were cut into rectangular coupons 8 mm × 20 mm in size. To assess the feasibility of the proposed infiltration method for larger and complex shape parts, 250 mm × 300 mm rectangular specimens and 400 mm long tubes with 30 mm outer diameter and 2 mm wall thickness were used, too. Niobium (Nb) powder (99.8% purity, 100 mesh) was purchased from CERAC Inc.

For PIRAC coating, C/C composite coupons were immersed into Nb powder mixed with 1 wt.% metallic iodine and sealed inside double-walled Cr-rich steel containers, with small amounts of titanium and chromium powder placed between the walls. The containers with C/C composite coupons inside were furnace annealed at 800–1200 °C for up to 20 h. At the high annealing temperature, Cr and Ti acted as getters for O_2 and N_2, correspondingly, thus maintaining very low partial pressures of these gases inside the container. The infiltration of C/C coupons is realized by chemical vapor transport. The non-volatile Nb powder (the source) reversibly reacts with the transport agent (iodine) forming a volatile Nb iodide, NgI_4 [21]. Vapor pressure is gradually built-up and forces the NbI_4 vapor to penetrate into the voids of the C/C coupons (the sink). Here, Nb from the iodide reacts with carbon to generate niobium carbides. As a result, the concentration of gaseous Nb iodide inside the C/C coupons is reduced thereby creating the concentration gradient required for diffusive mass transfer from the source to the sink. Thus, unlike the classical chemical vapor transport method that is carried out in a temperature gradient [22,23], reactive PIRAC infiltration is an isothermal process where vapor flux is driven by the difference in the concentration of the gaseous transporting compound between the source and the sink.

2.2. Specimen characterization

C/C coupons (8 mm × 20 mm) were weighed before and after treatment in Nb powder on an analytical scale, and mass gain was calculated. The density and open porosity of PIRAC-treated specimens were measured by water immersion and water penetration methods, respectively. The microstructure of as-received and PIRAC treated C/C composites was characterized employing X-ray diffraction (XRD) and scanning electron microscopy (SEM). For XRD analysis, an automatic powder Philips PW-3020 diffractometer with a long-focus $Cu_{K\alpha}$ tube operating at 40 kV and 40 mA was used. Step scans were taken in the range of $2\theta = 25–75°$ with a 0.05° step and a 2 s exposure. SEM analysis was performed in a Philips XL-30 microscope equipped with LINK ISIS (Oxford Instruments, UK) energy-dispersive spectrometer (EDS).

The as-received and PIRAC treated C/C coupons were tested in three-point bending to determine flexural strength, σ_f (according to ASTM C1161). The tests were performed in an INSTRON testing machine at the cross-head speed of 0.1 mm/min with the support span of 16 mm.

3. Results and discussion

3.1. PIRAC coating microstructure and growth kinetics

A detailed microstructure characterization of PIRAC treated C/C composites was conducted on the 8 mm × 20 mm coupons. Qualitatively similar results were obtained on the larger (250 mm × 300 mm) plates

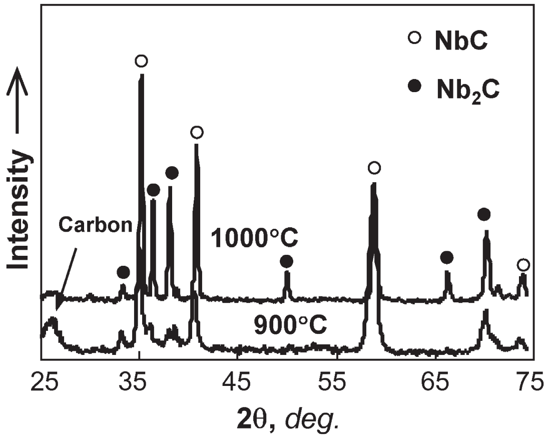

Fig. 2. XRD patterns taken from the surface of C/C composites PIRAC treated in Nb–iodine powder at 900 °C, 16 h and at 1000 °C, 16 h.