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Short communication

Oxidation resistance of aligned carbon nanotube–reinforced silicon carbide composites

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Abstract

Vertically-aligned carbon nanotube–reinforced SiC composites (VACNT/SiC) were prepared via a combined chemical vapor deposition/chemical vapor infiltration process. Thermal oxidation tests, showed the material to undergo virtually no mass loss up to 1400 °C in air, hence indicating excellent oxidation resistance of the composites within the target temperature range of advanced ceramics applications. Microstructural observation demonstrated complete absence of matrix cracks in the surface of VACNT/SiC. A large number of VACNTs having undergone pull-out were observed, a finding which indicated the tubes' survival after exposure to the oxidative environment of 1400 °C in air.

Keywords: B. Nanocomposites; D. SiC; D. Carbon; Oxidation resistance

1. Introduction

Improving the thermal oxidation resistance of ceramic matrix composites is a major scientific concern which has been explicitly emphasized in the case of carbon fiber reinforced silicon carbide composites (C/SiC). For the C/SiC, matrix micro-cracks caused by the thermal mismatch of matrix and fiber can act as diffusion channels for oxygen reaching- and severely oxidizing- the embedded fibers under the high operating temperature of 600–800 °C [1,2]. Carbon nanotubes (CNTs) have been proposed as reinforcing phase of protective coatings for improving the oxidation resistance of composites. In a notable example, Feng et al. showed that a double-layer coating consisting of SiC and CNT-doped SiC, prepared by chemical vapor infiltration (CVI), aided reduction of crack length and density in the SiC coating applied to carbon/carbon composites [3], hence greatly enhancing the material's oxidation resistance [4]. Gu et al. [5] found that the fracture strength of CNTs reinforced SiC composites (CNTs/SiC) prepared by CVI was an order of magnitude higher than bulk SiC's, reaching up to 20 GPa with an elastic modulus of 234 GPa. But oxidation resistance of CNTs/SiC composites has not been systematically studied. In this paper, static oxidation tests were employed to investigate the oxidation behavior of CNTs/SiC.

The present paper reports the fabrication and high temperature oxidation performance of vertically aligned carbon nanotube reinforced SiC composites (VACNT/SiC). Thermal oxidation tests were carried out by heating the composites from room temperature (RT) to 1400 °C, in air atmosphere, with a heating rate of 5 °C/min. The established behavior was compared to that of plain C/SiC, pristine CNT forest and carbon fibers having undergone identical oxidation treatments. The microstructures of surfaces and fractured sections of the composites were investigated by an scanning electron microscope (SEM).

2. Experimental procedure

VACNT forests were synthesized via the camphor-ferrocene catalytic CVD route described previously in [6]. The aspect ratio of the CNTs is approximately 1×10^4–2×10^4 with a

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diameter of 50–100 nm. Pieces of approximate dimensions of $2 \times 0.2 \times 1$ mm^3 (length × width × height) (Fig. 1a) were cut from the as-prepared forest, they were purified by rinsing with acetone, dried and then placed into the CVI furnace for subsequent infiltration of SiC matrix at *ca.* 1000 °C via the isothermal process described in [7]. And the volume fraction of CNTs reinforcement in the obtained composites was *ca.*15–20%. Investigations of the oxidation performance of resultant VACNT/SiC composites were carried out by heating the material from RT to 1400 °C for *ca.* 5 h, in air, with a heating rate of 5 °C/min. Oxidation tests were conducted in a STA 429 CD high temperature thermal analyzer (Netzsch-Gerätebau GmbH, Selb, Germany) with a 2 μg mass resolution. For comparison purposes, pristine VACNT forests, T-300™ carbon fibers provided by Toray Industries Inc. Japan and plain C/SiC composites prepared via identical CVI parameters as VACNT/SiC composites, were subjected to the same oxidation process. Surfaces of as-fabricated C/SiC and VACNT/SiC composites were polished using 1200 grit sandpapers for matrix crack observation. A number of samples were deliberately fractured using laboratory tweezers to allow observation of fractured surfaces' morphology. A Hitachi S-2700 (Hitachi Ltd., Tokyo, Japan) SEM was used for all microstructural observations.

3. Results and discussion

SEM micrographs in Fig. 1a and b demonstrate the morphology of as-grown VACNT forest pieces before infiltration and the growth pattern of nanotubes therein, respectively. As seen in Fig. 1b and the inset micrograph therein, the vertically oriented growth pattern is predominant at low magnification while inter-tube branching is evident at higher magnification. This effect, common to CVD-grown carbon nanotube forests [8] is responsible for the freestanding capacity of the material and for its potential, under certain conditions, to be drawn and twist-spun into CNT yarns [9]. Fig. 1c, a cross section of the pristine VACNT forest, demonstrates the open porosity of the forest, *i.e.* the empty space between neighboring nanotubes which was infiltrated with SiC matrix to obtain the VACNT/SiC composites. Fig. 1d shows a fractured section of the resultant composite; a great number of protruding MWCNT pull-out tips, all aligned, are observed. This retainment of the as-grown forest alignment following infiltration of the SiC matrix indicates that the forests' morphologies were unaffected by the CVI process.

The oxidation resistance of VACNT/SiC composites was investigated through thermogravimetric analysis (TGA), in air. Mass loss curves of pristine VACNT/SiC composites are plotted in Fig. 2; the corresponding behaviors of pristine forests, carbon fibers and plain C/SiC composites are also depicted, for comparison purposes. Four specimens were used in the oxidation tests for the four kinds of materials. It is observed that major mass loss commences at 550 and 630 °C, for the pristine forest and carbon fibers, respectively. The two materials appear to lose 100% of their initial mass, due to complete oxidation, at 610 and 760 °C, respectively. The plain C/SiC composites have a much more thermally stable behavior exhibiting only $12 \pm 2.2\%$ of mass loss up to 1400 °C; the effect starts at *ca.* 800 °C [10]. Most notably, the thermal stability curve for the VACNT/SiC composites appears essentially unvaried up to 1400 °C, indicating virtually complete absence of oxidation effects in the material up to this high

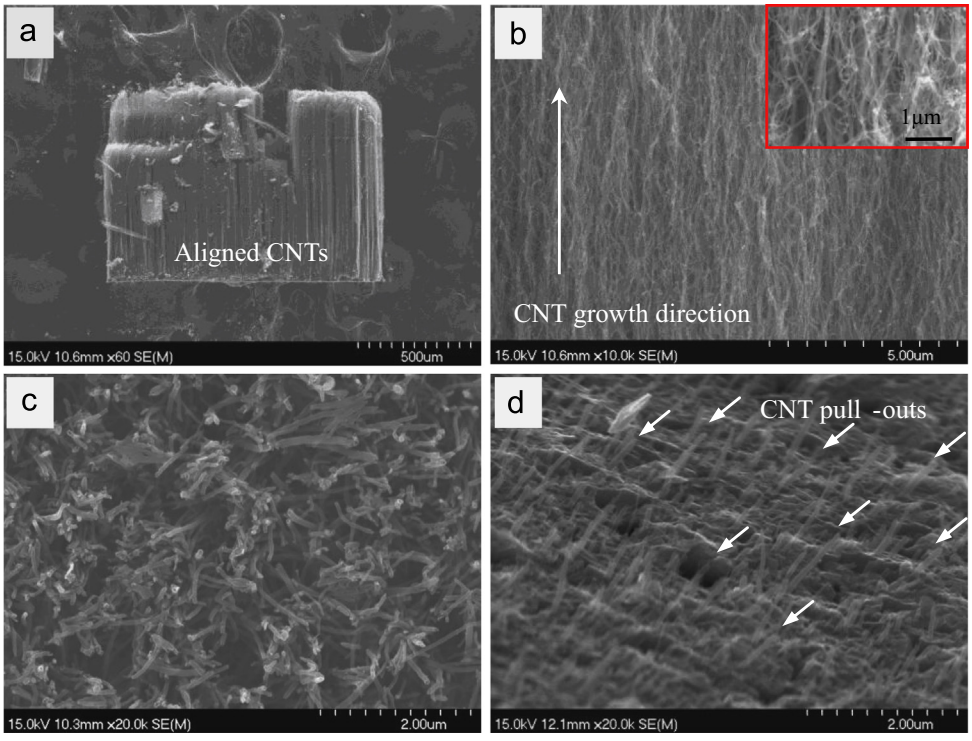

Fig. 1. SEM micrographs showing (a) the pristine VACNT forest piece, (b) vertical CNT alignment in the forest, (c) cross-section of forest showing open porosity and (d) numerous MWCNT pull-out tips in the fractured section of VACNTs/SiC composites.

temperature. It is a fact that some C and some Si must oxidize. But the oxidation of Si is a weight gain process ($Si \rightarrow SiO_2$) and oxidation of C is a weight loss process ($C \rightarrow CO_2$). To some extent, two oxidation mechanisms cancel each other out. Overall, it is a weight gain process. However, only the surface SiC was oxidized and the amount of oxidation is slight. So the weight gain in the TGA line is not obvious and it cannot be clearly observed.

For microstructural characterization, as-prepared C/SiC and VACNT/SiC composite specimens were resin-mounted and polished using 1200 grit sandpapers. Typical micrographs of the composites' polished surfaces are presented in Fig. 3, making possible a comparison of the matrix cracking density in the two types of composites. The typical VACNT/SiC morphology, shown in Fig. 3a was associated with almost complete absence of matrix cracking; opposite different behavior was noted in plain C/SiC composites where a repeatable transverse matrix cracking pattern associated with a *ca.* 100 μm spacing was observed on the specimen surface. In C/SiC, such cracks form during cooling from the high CVI processing temperature, due to the accumulation of internal thermal residual stresses (TRS) in the material stemming from the mismatch in coefficients of thermal expansion (CTE) between SiC matrix and carbon fibers. The cracks allow oxygen to diffuse inside the composite and oxidize embedded fibers, which is also the reason for the *ca.* 10% decrease in mass noted for plain C/SiC composites. Carbon fiber oxidation was also confirmed via SEM, as shown in locations indicated by arrows in the inset graph of Fig. 3b.

Although corresponding CTE mismatches exist between carbon tubes and matrix in VACNT/SiC composites as well, the cracking phenomenon in this material is believed to be masked as a result of the extreme inherent mechanical resilience of the forest [5], a property which allows them to deform enough to accommodate the TRS, hence preventing matrix cracking. Such absence of cracks also signifies absence of any diffusion channels available for oxygen to reach the embedded tubes, hence the excellent oxidation resistance of the material.

VACNT/SiC microstructure was characterized by SEM also following thermal oxidation tests, as shown in Fig. 4. A large part of the fracture section is shown in Fig. 4a, where the overall oxidized morphology can be conceived. The energy dispersive spectroscopy (EDS) spectrum in Fig. 4b shows that surface SiC was oxidized to viscous state silica, which is different from the typical CVI-SiC morphology. Fig. 4c, a higher magnification micrograph of the surface section indicated in Fig. 4a, reveals a great number of surfaces wherein tube tips originating from MWCNTs having undergone pull-out; the tubes are seen uniformly distributed across the fractured surface. An even higher magnification micrograph is shown in Fig. 4d, where pulled-out CNT tips are observed exhibiting absolutely no signs of structural degradation due to oxidation. This is in contrast to carbon fibers in plain C/SiC which suffered severe thermal oxidation (inset graph in Fig. 3b).

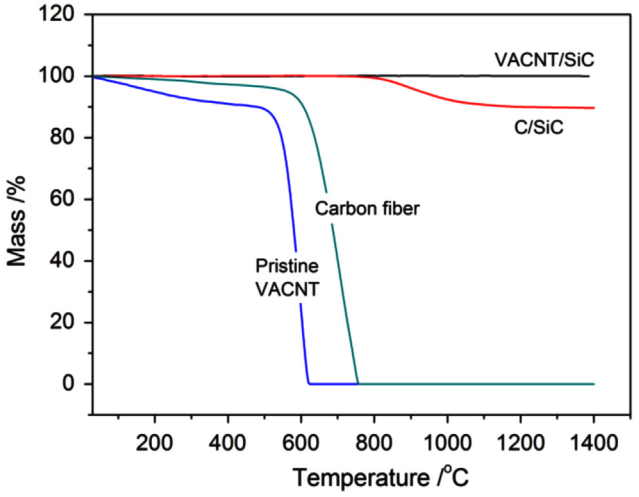

Fig. 2. Thermogravimetric curves of pristine VACNT forests, carbon fibers, plain C/SiC composites and VACNT/SiC composites, in air.

4. Conclusions

VACNT/SiC composites prepared by CVD/CVI exhibited excellent oxidation resistance up to 1400 °C in air, compared to C/SiC composites, a finding which unfolds the potential of the nanoscale-reinforced ceramic in a great number of advanced high temperature applications. Following thermal oxidation testing, only the surface SiC of the composites was found oxidized to silica whereas the embedded MWCNT forest structure retained original morphology and integrity, exhibiting complete absence of

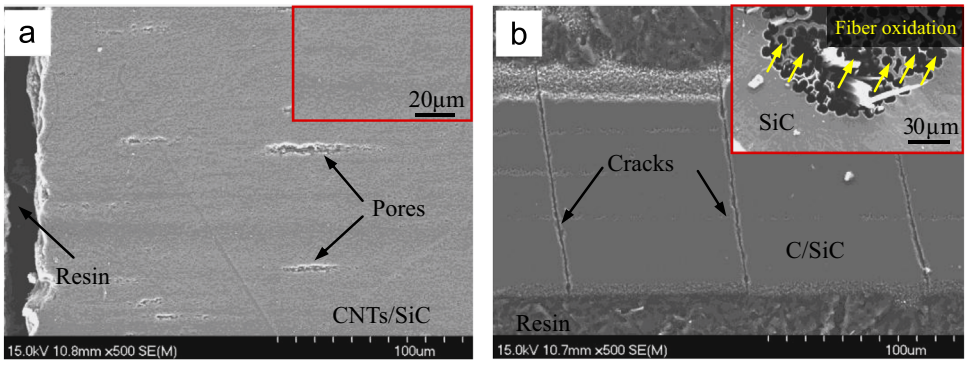

Fig. 3. SEM micrographs of the polished surface of (a) VACNT/SiC composite and (b) plain C/SiC composites prior to oxidation tests. Insets show higher magnifications of the surfaces of polished VACNTs/SiC and fiber oxidation through the cracked SiC matrix of C/SiC.

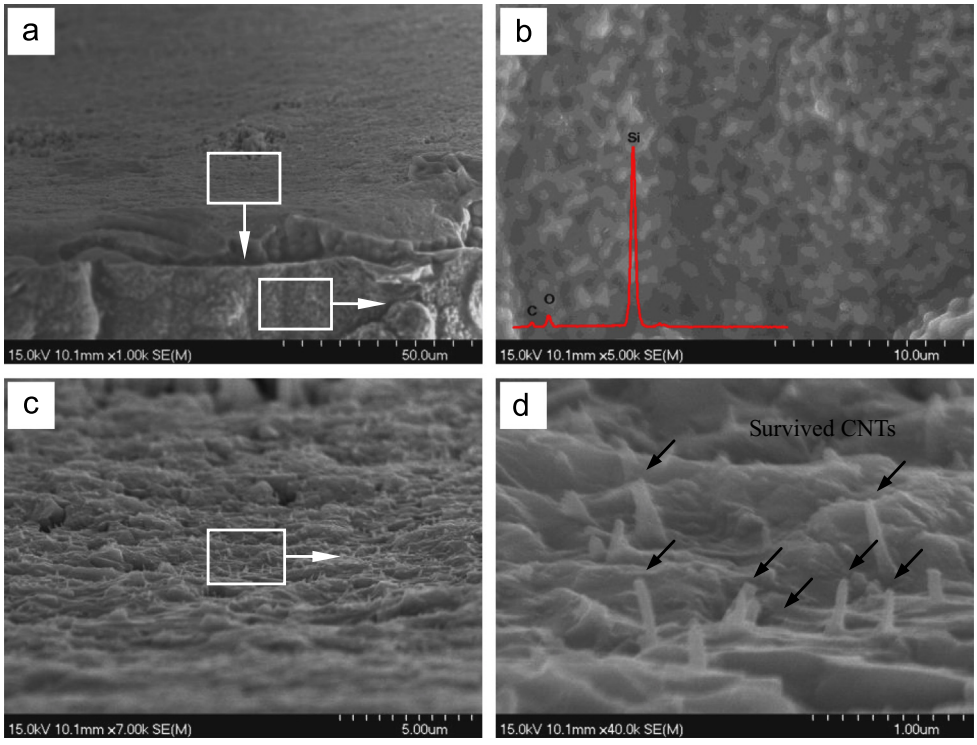

Fig. 4. SEM micrographs showing the fractured VACNT/SiC composites after oxidation: (a) the fracture section of the VACNT/SiC, (b) the surface of composite, where the SiC matrix was oxidized to viscous state silica, (c) a high magnification of the white rectangle in (a), in which plenty of CNT pull-outs were found, and (d) a high magnification of the white rectangle in (c), where the CNT pull-outs were clearly observed without apparent oxidation (black arrow).

oxidation due to the achievement of a crack-free SiC matrix providing effective isolation from high temperature oxidative environments.

Acknowledgments

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