ARTICLE IN PRESS

Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

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

Review article

Advances in oxidation and ablation resistance of high and ultra-high temperature ceramics modified or coated carbon/carbon composites

Xiaochao Jin[a], Xueling Fan[a,*], Chunsheng Lu[b], Tiejun Wang[a]

[a] State Key Laboratory for Strength and Vibration of Mechanical Structures, School of Aerospace Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[b] Department of Mechanical Engineering, Curtin University, Perth, Western Australia 6845, Australia

ARTICLE INFO

Keywords:
Carbon/carbon composite
Oxidation
Ablation
Coating
Matrix modification

ABSTRACT

Carbon/carbon (C/C) composites are considered as one of the most promising materials in structural applications owing to their excellent mechanical properties at high temperature. However, C/C composites are susceptible to high-temperature oxidation. Matrix modification and coating technology with ultra-high temperature ceramics (UHTCs) have proved to be highly effective to improve the oxidation and ablation resistance of C/C composites. In this paper, recent advances in oxidation and ablation resistance of C/C composites were firstly reviewed, with attention to oxidation and ablation properties of C/C composites coated or modified with UHTCs. Then, several new methods in improving oxidation and ablation resistance were discussed, such as by using nanostructures to toughen UHTCs coatings or carbon matrix and the combination of matrix modification and coating technology. In addition, relevant ablation tests with scaled models were also briefly introduced. Finally, some open problems and future challenges were highlighted in the development and application of these materials.

1. Introduction

The severe operating conditions in advanced aerospace applications, such as high temperature, fast speed and high stress, have an urgent need for new materials that can be used in a higher-performance thermal protection system [1,2]. Generally, temperature above 1600 °C and possibly exceeding 2200 °C in aerospace industries is described as an ultra-high temperature [3,4]. For example, the nozzle temperature of solid rocket motors can transiently increase from room temperature to 3000 °C, and temperature in the nose cones and leading edges of hypersonic vehicles may be over 1600 °C under atmospheric re-entry conditions [5–8]. Thus, materials for these areas must withstand ultra-high temperature and strong heat flux associated with large mechanical stress. Therefore, it is necessary to develop thermal protection materials endowed with good oxidation resistance, thermal shock resistance, and ablation resistance as well as dimensional stability [9,10].

Carbon/carbon (C/C) composites are considered as one of the most promising materials in ultra-high temperature structures due to their low density and coefficient of thermal expansion (CTE), high strength, fracture toughness and thermal conductivity, good thermal shock and ablation resistance, and high-reliability [11–13]. However, C/C composites are susceptible to oxidation at temperature of above 450 °C, which seriously limits their applications in oxygen-containing environments at ultrahigh temperature and high-speed gas flow [14–16]. To improve oxidation and ablation resistance of C/C composites, the available methods mainly include: (1) optimizing carbon fiber weave structures, (2) controlling pyrolytic carbon texture, (3) modifying carbon matrix, and (4) coating with anti-ablative ceramic layers. Among these methods, matrix modification and coating are the two most effective techniques.

Ultra-high temperature ceramics (UHTCs), based on carbides, nitrides, and borides from a group of IV_B and V_B transition metals in the periodic table, possess an excellent combination of high melting points (generally over 3000 °C) and mechanical properties, and they have caused more attention as potential candidate materials for extreme environments [17–20]. Here, it is worth noting that SiC can only be defined as high temperature ceramic (HTC), because its melting point (2700 °C) is lower than that (3000 °C) of UHTCs [19,21]. However, due to its superior performance, SiC still plays an important role in improving oxidation and ablation resistance of C/C composites. Thus, for simplicity, UHTCs in the following description refer to SiC and refractory compounds whose melting points are higher than 3000 °C. It has shown that, although UHTCs have good oxidation and ablation resistance, high thermal conductivity, modest thermal expansion, and high hardness and retained strength at high temperature [22–25], their applications in extreme environments are limited due to low fracture

* Corresponding author.
E-mail addresses: fanxueling@mail.xjtu.edu.cn, xlfanxjtu@163.com (X. Fan).

http://dx.doi.org/10.1016/j.jeurceramsoc.2017.08.013
Received 28 February 2017; Received in revised form 14 July 2017; Accepted 8 August 2017
0955-2219/

toughness, poor thermal shock resistance and damage tolerance [26].

Taking the advantages of these two kinds of materials into account, a better way to meet the requirements of a thermal protection system is to create C/C-UHTCs composites, i.e., the introduction of UHTCs into C/C. Experimental results showed that refractory carbides, nitrides and borides ceramics (such as SiC, ZrC, HfC, TaC, ZrB_2, HfB_2, HfN, etc.) could significantly enhance oxidation and ablation resistance of C/C composites [26–30]. Normally, there are two main methods of introducing UHTCs into C/C composites: (1) coating the C/C composites with UHTC layers, and (2) modifying carbon matrix with UHTCs. Over the past years, great advances have been made in developing a series of techniques that can largely improve oxidation and ablation resistance of C/C composites. However, to the best of our knowledge, there is still lack of a comprehensive review on these advances, and the purpose of this paper is to fill such a gap.

The paper is organized as follows. In Section 2, preparation, oxidation and ablation resistance of C/C composites are introduced. Sections 3 and 4 contribute to a thorough review on the oxidation and ablation properties of C/C composites coated or modified with UHTCs, respectively. In Section 5, some new progresses are reviewed, including UHTCs coatings or carbon matrix toughed by nanostructures and the combination of matrix modification and coating. Then, ablation tests with scaled models are briefly introduced in Section 6. Finally, several open problems and future challenges in the development of matrix modification and coating technologies are highlighted in Section 7, with a few of major directions in promoting the wide applications of C/C-UHTCs composites.

2. Preparation and properties of C/C composites

2.1. Preparation process

The preparation process of C/C composites is complex and expensive, which mainly concludes two steps: manufacturing reinforcement and densification.

Polyacrylonitrile (PAN)-based and pitch-based carbon fibers are the two most ones used in carbon reinforcement [31]. In some military and space equipment, rayon-based carbon fibers are also applied. The microstructures of reinforcements have an obvious effect on the densification process of C/C composites, and thus their mechanical, anti-oxidation and anti-ablation properties. There are three types of carbon fiber reinforcements: stacked non-woven layers, needled carbon fiber felts and carbon fiber textiles. Generally speaking, C/C composites with one-dimensional (1D) carbon fiber reinforcements can achieve a higher value of tensile strength in one direction. The interlaminate shear properties of C/C composites with 2D carbon fiber reinforcements might be weaken due to their low interfacial binding strength, and thus, the mechanical and physical properties of C/C composites are anisotropic. In contrast to 1D and 2D carbon fiber reinforcements, C/C composites with 3D carbon fiber reinforcements exhibit good integrity and isotropy [32–34]. Thus, most of the nose cones of missile warheads and high-reliability aircraft components prefer to use the latter to obtain a global stability performance.

The densification process has also an obvious effect on oxidation and ablation resistance of C/C composites. Liquid impregnation and carbonization and chemical vapor deposition/infiltration (CVD/CVI) are the two mainly used methods, as illustrated in Fig. 1, where CVI was developed based on the CVD technique [35,36]. Considering the high production cost and long manufacture period, several rapid densification techniques have recently developed based on traditional CVI processes [37–40].

According to the performance comparison between C/C composites and other high-temperature materials, C/C composites have the highest specific fast-rupture strength and a much wider range of applications [41,42], as shown in Fig. 2. The excellent physical and mechanical properties of C/C composites involve the low density, high mechanical strength, and good ablation resistance.

2.2. Oxidation and ablation resistance

C/C composites consist of carbon fiber, carbon matrix, and pyrolytic carbon (PyC), each of which is prone to react with oxygen. The inevitable existence of crystal defects, residual stress and impurity particles may lead to formation of active spots, which can easily adsorb oxygen and react with it. These characteristics make C/C composites susceptible to oxidation at a relatively low temperature. The oxidation mechanisms of C/C composites have been investigated in details [43,44]. Based on reaction temperatures, there are three kinds of oxidation in C/C composites: (1) when temperature is relatively low (< 600 °C), the oxidation process is caused by reaction between oxygen and active spots on carbon surface; (2) when temperature is between 600 °C and 800 °C, oxidation is dominated by the diffusion velocity of oxygen through the pore of C/C composites, with a rather different transition temperature due to different carbon materials; and (3) when temperature is over the transition temperature, oxidation is controlled by the diffusion velocity of oxygen in the boundary layer [43,44].

As an erosive phenomenon, ablation results in parts of a material being removed by coupled thermo-mechanical, thermo-chemical and thermo-physical interactions due to a combustion flame with high temperature, pressure and velocity [45,46]. Generally, oxyacetylene, arc-jet and plasma ablation tests are three main methods to measure the ablation properties of ablators [47]. In consideration of high cost of arc-jet and plasma wind tunnel tests, oxyacetylene ablation is the most often used method for evaluating the performance of thermal protection materials under hypersonic re-entry conditions. If not clearly specified, the ablation tests mentioned below were performed under an oxyacetylene flame.

The thermochemical ablation of C/C composites is of considerable importance to the thermal structure design of C/C parts at high temperature [48]. As shown in Fig. 3, the surface of C/C composites after ablation under high temperature flame can be divided into three regions: central, transitional and border regions. Ablation usually occurs at the interface between carbon fibers and matrix, and the latter has a lower ablation resistance than the former. The evolution process of microstructures in carbon matrix has shown that ablation firstly appears in the interfaces of PyC and active spots, where crystal defects and impurity particles exist [49–51]. The orientation of carbon fibers has also an obvious effect on the ablation resistance of C/C composites [52,53]. In terms of testing results, the performance of C/C composites with parallel ablation is better than that of vertical ablation. Parallel ablation is mainly controlled by block denudation while vertical ablation is dominated by particle denudation. In addition, different types of carbon display different ablated morphologies. In contrast to composites with smooth laminar carbon, rough ones have a higher graphitization degree and a lower ablation rate. The C/C composites with PyC and resin matrix have the highest ablation resistance, and PyC matrix works better than resin matrix [54]. Furthermore, ablation resistance increases with the increase of density and degree of graphitization of C/C composites [55,56].

Compared to oxyacetylene flame, a thermal spray system with high-velocity oxygen fuel can provide a hypersonic flow, in which temperature, pressure and speed are high enough to simulate a more realistic environment of hypersonic vehicles. Fan et al. [57,58] investigated the ablation behavior of C/C composites under hypersonic flowing propane flame provided by a high-velocity oxygen fuel system. Pores, chemical erosion and mechanical denudation can be observed in the central region. Scanning electron microscope (SEM) morphologies of C/C composites in different ablation regions are shown in Fig. 4, where the central region suffers much heavier ablation than the border region. That is, the central region has much higher temperature, chemical erosion and mechanical denudation. The microstructures of C/C composites indicate that, ablators under a hypersonic flowing propane