Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Comparison of microstructure and oxidation behavior of La-Mo-Si coatings deposited by two approaches

Changcong Wang, Kezhi Li*, Xiaohong Shi*, Caixia Huo, Qinchuan He

State Key Laboratory of Solidification Processing, Carbon/carbon Composites Research Center, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China

ARTICLE INFO

Keywords:
La-Mo-Si coating
Pack cementation
Plasma spraying
Porosity
Oxidation behavior

ABSTRACT

To investigate the effect of preparation methods on the La-Mo-Si (LMS) coatings, we developed a new LMS coating system using pack cementation (PC) and supersonic atmospheric plasma spraying (SAPS). Microstructure analysis showed that the SAPS-LMS coating possessed a higher porosity than that of the PC-LMS coating. Higher porosity can provide more channels to the oxidative and corrosive gasses to permeate the SAPS-LMS ceramic top-coat. After static oxidation for 150 h under 1773 K, the mass loss of SAPS-LMS coating (3.12 wt%) was much higher than that of the PC-LMS coating (0.05 wt%), and the parabolic rate constants presented faster oxidation kinetic in SAPS-LMS coating with respect to the PC-LMS coating. These results revealed that the protection effectiveness of SAPS-LMS coating was inferior to PC-LMS coating. Compared with SAPS-LMS coating, microscopic pores and cracks appeared in the PC-LMS coating with a thicker oxide film, which benefits from the formed La-Si-O-Al glass oxide with an excellent ability for crack healing. The reasons for poor antioxidant performance of SAPS-LMS coating are the higher volatility of La-Si-O glass containing Mo_5Si_3 and a weak interfacial interaction between coatings and substrate.

1. Introduction

Carbon/carbon (C/C) composites is recognized as one of the most promising materials (> 1873 K) for high-temperature applications where unique combination of properties such as lower density (< 2.0 g cm^{-3}), high strength, abrasion resistance, good thermal shock and creep resistance are desired [1–3]. However, when the temperature is above 673 K, the performance of C/C composites under aerobic environment are drastically degraded due to oxidation, which greatly limits its application [4,5]. Based on previous workers' experience, the introduction of an oxidation resistant coating contributes to protecting C/C composites from premature failure [4]. Unfortunately, crack initiation is inevitable due to the different thermal expansion coefficient (CTE) between the coatings and substrate, which will be good for the penetration of oxygen and eventually lead to the coating degradation. To deal with such thorny issues, multilayer coating systems with functional complementation have been developed [3,5,6]. SiC coating is usually employed as a transition layer between outer ceramic layer and substrate because of its excellent chemical compatibility with C/C substrate [3–6]. Recently, it is reported that LaB_6 modified $MoSi_2$-SiC (LMS) multiphase ceramic coating presents better oxidation resistant than the single SiC coating, owing to the formation of a coherent and adherent La-Si-O glass film, which can retard the oxygen diffuse inward and provide the long-lasting protection [6,7].

Numerous methods for coating preparation are commercially available, such as pack cementation (PC) [3,8], chemical vapor deposition (CVD) [9], sol-gel process [10], plasma spraying [6,11,12]. Among them, two common preparation techniques are PC and plasma spraying. Oxidation behavior of the as-prepared coatings is strongly dependent on the implemented technique and on the processing parameters resulting in different microstructures and compositions. As for PC-technique, it is generally known that it is a versatile process used for prepared silicide-based coatings, which is a kind of in-situ reaction between various material species under a relatively high temperature with inert gas shielding [13,14]. Chen et al. [15] utilized this concept to fabricate the $MoSi_2$-SiC coating on C/C composites by two-step PC process and investigate their oxidation resistance. The results showed that the coatings behaved similar to in-situ diffusion reaction and exhibited a dense structure with excellent oxidation resistance. Li et al. [16] studied the effect of rare earth La-element in $MoSi_2$ coating by the PC process. This paper evaluated the isothermal oxidation behavior of PC-LMS coatings at 1773 K, and substantiated the effect of rare earth elements in each sub-layer of the coating. Comparatively, plasma spraying is a kind of thermal spraying process,

* Corresponding authors.
E-mail addresses: likezhi@nwpu.edu.cn (K. Li), npusxh@nwpu.edu.cn (X. Shi).

http://dx.doi.org/10.1016/j.ceramint.2017.05.114
Received 7 April 2017; Received in revised form 14 May 2017; Accepted 15 May 2017

employing high temperature and high concentrated plasma as heating source [17,18]. In the spraying process, the rapid cooling with about 10^6 K/s for sprayed coating is an essential stage [19], and the cooling down of splats is accompanied by grain growth in the direction perpendicular to the substrate surface [20,21]. Wu et al. [12] reported the structural features and oxidation behaviors of $MoSi_2$ coating deposited by SAPS. The results showed that the mass loss of $MoSi_2$ coated specimen was relatively low after oxidation for 100 h at 1773 K, and the specimen could endure 11 thermal cycles between 1773 K and ambient temperature. Subsequently, Shi et al. [6] prepared a LaB_6-doped $MoSi_2$-SiC heterogeneous coating to elevate the antioxidant protective ability of C/C substrate. La as the permeable agent could increase the compactness of $MoSi_2$-SiC coating, and the dense La-Si-O glass layer covered surface to prevent the oxygen diffusion. Most previous researches have concentrated on the fabrication and performance of rare earth doped Mo-Si-based coating, but the systematic analysis for PC and plasma spraying method is rather deficient. Studying the structural characteristics of as-prepared coatings from different preparing techniques is significant for selecting an appropriate preparation technique in the future practical applications.

In the present work, two kinds of LMS coatings were prepared on C/C substrate by PC and SAPS. Their structural features and oxidation behaviors under non-isothermal and isothermal conditions were investigated in detail. The comparison of oxidation mechanisms was discussed simultaneously. More importantly, the obtained information is available for making primary assessment of varying methods, which will lay the foundation for their industrial application in the future.

2. Experimental procedure

2.1. Materials preparation

Two-dimension C/C composites (1.72 g cm^{-3}) were cut into small pieces with different sizes including 10 mm×10 mm×10 mm (for isothermal oxidation), 4 mm×4 mm×4 mm (for thermogravimetric analysis). These specimens were chamfered and polished sequentially using 180-mesh and 600-mesh sandpapers to eliminate the impurities on the specimen surface. Then they were ultrasonically cleaned with alcohol and dried for later use.

2.2. Coatings deposition

To relieve the thermal mismatch between the top-coating and substrate, the SiC coating was first obtained as a buffer layer on the C/C substrate surface. The preparation procedures of SiC coating has been reported in previous literature [22]. Schematic illustration of preparation process for PC-LMS and SAPS-LMS coatings is shown in Fig. 1, and the concrete steps are described in detail subsequently.

The PC-LMS coating was prepared by pack cementation using LaB_6 (5–15 wt%), $MoSi_2$ (50–70 wt%), SiC (20–30 wt%) and Al_2O_3 (5–10 wt%) as the precursor powders. Firstly, the feedstock powder was milled for 2–4 h to obtain a homogeneous mixture. Secondly, the pre-treated substrate was buried in the mixed powder in a graphite crucible, then the crucible was put into a graphite furnace. The furnace was heated to 2173–2373 K, and held for 2–4 h in Argon atmosphere. When the furnace temperature was naturally cooled to ambient temperature, the specimen was taken out from the crucible to obtain the PC-SiC coating.

The fabrication of SAPS-LMS coating mainly includes the feedstock preparation and coating deposition. Commercially available micron-sized $MoSi_2$ (50–70 wt%), SiC (20–30 wt%) and LaB_6 (5–15 wt%) are employed as feedstocks. Further processing for these feedstocks is necessary due to their irregular shapes which are difficult to use directly for spraying. Firstly, the mixed powder was treated by means of ball-milling with 6–8 h, and then spheroidized by spray drying technology. The obtained particles with smaller size (< 15 μm) and larger size (> 65 μm) were removed by standard sieves to meet the demands of spraying. The schematic diagram of SAPS is shown in Fig. 2. It can be seen that the parameters including the powder, spraying torch, plasma jet affect the properties of the coating. The phenomenon of heat and mass transfer occurred in the formation process of the coating [23]. The spraying parameters are as follows: current=400–450 A, voltage=100–150 V, carrier gas (Ar)=70–80 L/min, assisted gas (H_2)=1–3 L/min, powder feeding rate=4.5 r/min, spray distance (between the nozzle tip and the specimen surface) =100 mm, injection angle=90°, and the diameter of the spray nozzle was 5.5 mm.

2.3. Oxidation tests

Isothermal oxidation experiments were proceeded in static air at 1773 K in a high-temperature resistance furnace. The specimens were placed in a corundum crucible to monitor its oxidation behavior at high operating temperature. Similarly, the thermal shock test was conducted in an electric furnace between 1773 K and ambient temperature. After being oxidized for due time at 1773 K, the specimens were taken out and cooled down to room temperature. They were weighed at normal atmospheric temperature using a precision analytical balance with a sensitive of ± 0.1 mg. The mass change percentages (Δw_1) and mass change rate (Δw_2) were evaluated as the following Eqs. (1) and (2):

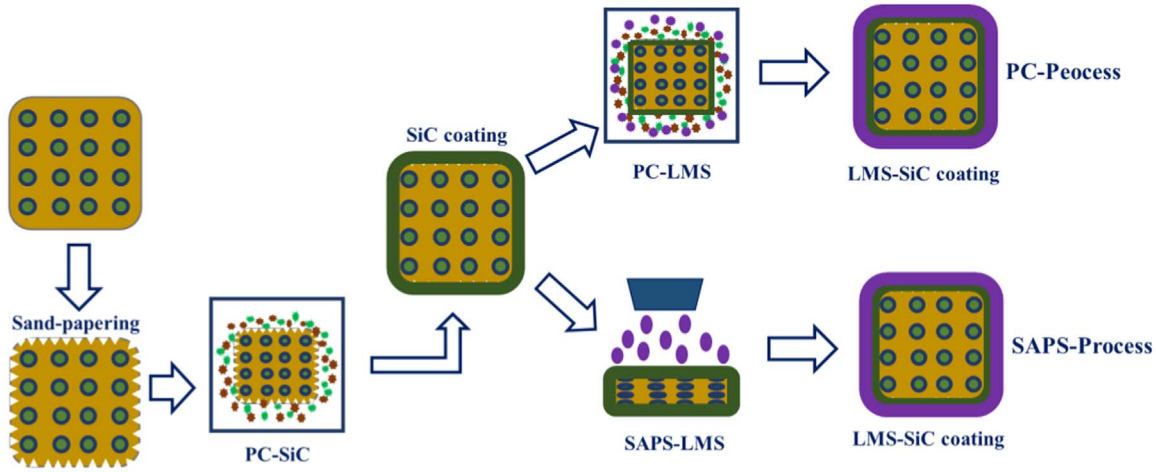

Fig. 1. Schematic preparation procedures of the LMS/SiC coating by PC and SAPS methods.