SiC/nano α -Al₂O₃ Double-Layer Coating on Graphite Component via Pack Cementation and Electrophoretic Deposition

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Abstract

Graphite and carbonaceous parts are being extensively employed in industrial and high-tech fields. Since these materials suffer from severe oxidation at elevated temperatures, it is vital to keep them safe from being damaged and corroded at high-temperature working conditions. In this study, a double-layer coating was prepared to achieve this aim. Primarily, SiC was coated on graphite samples via pack cementation method and then a layer of nano α -Al₂O₃ was coated on it through the electrophoretic deposition (EPD) method to improve the oxidation resistance at high temperatures. This alumina coating was further sintered only for 20 minutes at a relatively low sintering temperature of 1350 °C in a microwave furnace to densify and close the oxygen permeation paths. Finally, this double-layer fabricated coating could reduce the weight loss by oxidation about 50 times in comparison with the bare graphite. Regarding the excellent oxidation protection performance of this double-layer coating and its feasibility for production scale-up, it can be further investigated to protect various carbon-based engineering materials from oxidation at high temperatures.

Introduction

Engineered carbons like graphite, carbon fibers, and carbon-carbon composites are used in aerospace and other industries. Oxidation and evaporation are common problems for carbon materials, which limit their applications at high temperatures. The development of methods for protecting oxidation of carbon materials has been given considerable attention lately [1].

A wide variety of coatings are used as conventional techniques for the preservation of carbon products against oxidation, such as SiC [2], TiC [3], TiN [4], Si₃N₄[5], B₄C [6], SiO₂[7], ZrSiO₄[8], ZrO₂[9], HfC-ZrC-SiC [10], Al₂O₃[11], mullite[12], hexagonal-BN [13], LaB₆-MoSi₂-ZrB₂[14], MoSi₂-SiC[15], ZrB₂-ZrC-SiC [16] and ZrB₂[17].

The very common techniques of applying these ceramic coatings are the chemical vapor deposition (CVD) and pre-ceramic polymer pyrolysis[18], which are complex and expensive. Among the high-temperature ceramics, SiC has gained a lot of attention and is being extensively recruited for protecting graphite and C/C composites from oxidation because of its strong compatibility with the carbon substratum and the creation of a SiO₂ glass film, enjoying low oxygen permeability at high temperatures [19, 20].

At present, SiC coatings' preparation for protecting carbonaceous substrates have multiple methods, including pack cementation [21–23], laser-induced chemical decomposition (LICD) [24], and chemical vapor deposition (CVD) [25]. Several researchers have used pack cementation of SiC to reduce the thermal expansion variations between carbon-based substrates and coating[26]. Nevertheless, in the coating preparation process, the unavoidable mismatching of the thermal expansion coefficients between them is linked to crack development [27]. These micro-cracks are pathways for oxygen to reach the carbonaceous layers such as SiC. Therefore, the oxidation resistance of the SiC coatings should be

improved. Al_2O_3 has been widely used to provide oxidation shielding of C/C composites coated with SiC, thanks to its excellent corrosion resistance, good thermal stability, and low oxygen diffusion rate [28]. To coat alumina layers on different materials, abundant techniques such as atomic layer deposition [29], plasma spray [30], laser-cladding [31], and sol-gel [32] have been utilized, which are expensive and need special equipment. Thus, in the present work, the electrophoretic deposition technique was applied to obtain crack-free and uniform layers of $\alpha\text{-Al}_2\text{O}_3$ nanoparticles on the carbon layer. The EPD can be either used alone or in combination with other methods such as sol-gel for protective coatings of carbon parts [33].

In addition to coat complex pieces due to throwing power ability of EPD, this method has other advantages such as composite coatings of oxide-carbide ceramics with additives which are commonly used for their better performance. Moreover, EPD method is simple, low-cost, and low-temperature [34].

In order to further improve the efficiency of the coating and make it denser, microwave sintering was used, which is a suitable technique to densify ceramic materials. Despite SPS and HP techniques, microwave processing is cheap and enables to sinter complex shape samples. In addition, the sintering in a microwave is fast and requires lower working temperatures, as compared to traditional sintering techniques [35].

Material And Methods

Small pieces of graphite with a density of 1.75 g cm^{-3} (Cova GmbH) were used in this research. The pack cementation process was used in order to produce the first layer of graded SiC on graphite samples. Powder pack compositions were as follows: a) SiC (Good fellow) b) SiC with Si (Good fellow) and Al_2O_3 (Martinswerk, MR70) additives. Samples were conventionally heat-treated at 1650°C for 3 h in an argon protective atmosphere. Al_2O_3 (α phase, 99% grade, PL-A-AlO, Plasma chem, Germany) was used as the material for the final coating. The organic solvent used in this study was isopropanol purchased from Merck (931 k12707634) and used as received without any further purification. A gold-coated beaker and cubic carbon electrodes ($1 \times 1 \times 1 \text{ cm}^3$) were used as anode and cathode, respectively.

Suspensions containing 4 g lit^{-1} Al_2O_3 nanoparticles were prepared in isopropanol. The suspension was firstly sonicated for 15 minutes before being magnetically stirred at 400 rpm for 24 hours at room conditions. The prepared suspension underwent a second sonication for 15 minutes to break off any possible agglomeration. The EPD was conducted using a gold-coated beaker (50 mL) and carbon as anode and cathode at a constant voltage of 100 V, respectively. A regulated DC power supply (EICO 1030) was connected to the anode and cathode with a fixed distance of 1.5 cm. The gold coated beaker was washed with distilled water and acetone, and dried in air for a quarter. By trial and error approach, the optimum concentration and voltage values were obtained. In order to achieve crack-free alumina coating, a two-step deposition technique was applied (coating, drying in the air, and repeating this process for a second time). The total time of deposition was 8 min. After the deposition of alumina powder on the parts, the samples were heat-treated in a microwave furnace under a nitrogen atmosphere to ensure the

firm binding between the coated nanoparticles to improve their mechanical stability. The samples were heat-treated at 1350, 1450, and, 1550 °C for 10, 15, 20, and 60 min. The oxidation behavior of the samples was studied by an isothermal oxidation test in the air at 1500 °C in an electrical furnace.

The scanning electron microscopy (Hitachi. S4160) was used for the analysis of the deposition pattern of the obtained layers at an accelerating voltage of 20 kV. A WTW-inolab (Weilheim, Germany) conductivity meter was used to measure the conductivity of the prepared suspension. Also, the zeta potential and size distribution of Al_2O_3 nanoparticles were measured using a Malvern Zetasizer (3000 HAS, Malvern, U.K.). Furthermore, diffractometry (XRD) of the coated materials on the graphite substrate was performed with a Philips X-ray diffractometer (PW3710) 40 kV and 30 mA radiation and step size = 0.02.

Results And Discussion

The graphite parts were firstly coated with SiC through the pack cementation method. SiC was coated both without and with additives (alumina and Si). The latter was further coated with alumina nanoparticles via EPD and sintered in a microwave furnace at 1350 °C for 20 min in a nitrogen atmosphere. The sintering temperature of alumina nanoparticles in this work is lower than the conventional sintering temperature of this ceramic (above 1500 °C). In addition, microwave heat-treatment requires shorter durations in comparison with the ordinary sintering methods.

Figure 1a and b display the SEM images of the graphite sheet coated with SiC free of additives. The applied coating has a filamentous structure with obvious cavities. The SEM images of the other sample coated with SiC and the additives (Fig. 1C and d) also reveal a similar but morphology finer. The reason for the formation of such filaments is referred to evaporation and condensation processes [36, 37]. In the presence or absence of some additives such as Al_2O_3 , a series of chemical reactions at high temperatures occur and result in the evaporation of SiO. The resulting vapor diffuses to the substrate and reacts with it to form the filamentous structure of SiC after condensation. On the border between alumina nanoparticles and the SiC layer, the formation of SiO_2 becomes more probable, which results in an adjustment in the thermal expansion coefficient of these layers.

Figure 1e shows the X-ray diffraction pattern of the coating obtained from the cementation of 5 μm silicon carbide powder. Examining the X-ray diffraction pattern, it can be seen that the resulting coating is mainly composed of β -SiC phase besides a small proportion of α -SiC (shown by the blue arrows) and s. Huang and et al. [38] reported with increasing pack cementation temperature β -SiC phase transformed to stable α -SiC. Regarding the research conducted by Huang et, al.[39], the existence of α -SiC besides β -SiC enhances the resistance against oxidation of graphite parts. Although the graphite peaks are clearly observable, the SiC peak intensities are much smaller. The XRD pattern of the double-layer coating of SiC with additives and EPD deposited alumina is shown in Fig. 1 f. It can be perceived that the coating layer is composed of SiO_2 , SiC, and Al_2O_3 .

To coat alumina nanoparticles through the EPD method, 4 various liquids of methanol, ethanol, butanol, and isopropanol were employed. Among them, only with isopropanol, the alumina nanoparticles coating were successfully coated. After the alumina nanoparticles were dispersed in the electrolyte, the mixture was sonicated and stirred subsequently to form a homogeneous suspension. Moreover, the use of additives was limited due to the pore formation after sintering the final coating. The characteristics of the suspension employed for coating alumina nanoparticles are presented in the following table.

Table 1

Characteristics of 2-propanol-alumina nanoparticles suspension

Electrolyte	Zeta potential (mV)	Mobility ($\mu\text{mcm/V.s}$)	Electrolyte conductivity ($\mu\text{S/cm}$)
2-propanol	26.9	0.207	0.2

Alumina nanoparticles were coated on graphite parts that were previously coated with SiC containing additives by employing the setup illustrated in Fig. 2a. Figure 2b reveals the size distribution of alumina particles in the isopropanol suspension in the range of 200–400 nm with an average size of 323 nm. The SEM images of the final coating of alumina before and after sintering are depicted in Fig. 2c and d, respectively. Regarding the SEM images, after 20 min sintering at 1350 °C, the coating became denser and the cavities got closed.

In addition to the crack-free surface layer, other sensitive areas for multi-layer oxidation protective coatings are the graphite interface with the silicon carbide layer and the interface between SiC and alumina coating. To investigate these two interfaces, as well as the thickness of the oxidation protective layers, a scanning electron microscope image of the cross-section of the two oxidizing protective layers is demonstrated in Fig. 2e. One of the highlights of this image is crack-free interfaces, while due to the difference in the thermal expansion coefficient between alumina and silicon carbide [40], the interfacial cracks were expected. The absence of cracks can be attributed to the formation of an interlayer phase with an intermediate thermal expansion between alumina and silicon carbide after sintering. According to the corresponding XRD pattern of the two-layer structure of anti-oxidation coating (Fig. 1f), the presence of alumina, silicon carbide, and silica are confirmed. The formation of the silica phase can be related to the oxidation of silicon carbide, which is encouraged by the air trapped between the particles during the compacting of powders. Silica phase has a thermal expansion between alumina and silicon carbide [36] and the formation of it plays an important role in creating an interface without cracks between silicon carbide and alumina layers.

The isothermal oxidation curves of graphite, G/SiC,and G/SiC/Al₂O₃ are shown in Fig. 2 f. Bare graphite underwent dramatic corrosion and lost more than half of its weight in one hour as a result of oxidation. Coating SiC resulted in a great improvement in its oxidation resistivity at high temperatures. The addition of an alumina layer to the former coating could enhance the oxidation resistivity even more. For instance,

at 1 h, the weight loss of G/SiC/Al₂O₃ was fifty times smaller than that of the bare graphite. In the initial step (less than 1 h) the coated samples gain weight because of the formation of SiO₂, so this curve is drawn after 1 h. Also, the glassy and viscous SiO₂ phase can seal cracks at high temperatures [41]. By further heating, the negligible CO and CO₂ emissions from the coatings result in decreasing the weight of the samples. Since the alumina layer is very effective in improving oxidation resistance, in future work, the effect of thickness of SiC and Al₂O₃ and their composite layers on the oxidation resistance of the graphite layer will be considered.

Conclusions

The need to protect graphite and other carbonaceous engineering materials has urged scientists to protect them from oxidation in various working conditions. In this study, graphite was protected by a double-layer coating consisting of SiC and Al₂O₃. SiC was firstly coated on graphite through pack cementation and then Al₂O₃ was coated on it via the facile technique of EPD. The final coatings were sintered in a microwave furnace at 1350 °C only for 20 min, which enjoys a lower temperature and shorter duration as compared to the conventional sintering conditions. After heat-treatment, the double-layer coating demonstrated a dense filamentous morphology on the graphite substrate and could successfully decrease the weight loss of graphite during oxidation by 50 times in 1 h. This method can be converted to industrial-scale applications and preserve different carbonaceous engineering parts from oxidation at high temperatures.

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Figures

Figure 1

SEM images of (a) and (b) the SiC coating free of additives on the graphite parts (c) and (d) the SiC coating with alumina and Si additives on the graphite parts with different magnifications; XRD pattern of the (e) SiC coating without additives and (f) EPD deposited and sintered alumina on the graphite parts coated with alumina and Si additives.

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Figure 2

(a) Schematic illustration of alumina EPD on graphite parts; (b) alumina size distribution in the suspension; SEM images of alumina/SiC double-layer coating on graphite (c) before sintering and (d) after sintering at 1350 $^{\circ}\text{C}$; (e) SEM cross-section view of the double-layer coating on graphite; (f) weight loss of graphite, SiC coated graphite, and SiC/alumina double-layer coated graphite as a result of oxidation at multiple durations at temperature of 1500 $^{\circ}\text{C}$.

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