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Fast plasma sintering deposition of nano-structured silicon carbide coatings

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Abstract

Fast plasma sintering deposition of SiC nano-structured coatings was achieved using a specially designed non-transferred dc plasma torch operated at reduced pressure. Employing the Taguchi method, the deposition parameters were optimized and verified. With the optimized combination of deposition parameters, homogeneous SiC coatings were deposited on relatively large area substrates of $\Phi 50$ mm and 50×50 mm with a deposition rate as high as $20 \mu\text{m}/\text{min}$. Ablation test showed that such coatings can be used as oxidation resistance coatings in high temperature oxidizing environment.

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1. Introduction

Developments in some aerospace applications demand advanced structural materials with both high temperature strength and good oxidation resistance. For example, hypersonic vehicles with sharp aerosurfaces, such as engine cowl inlets, wing leading edges (LEs), and nosecones, have projected needs for 2300 to 2700 K materials which must operate in air and be re-usable [1, 2]. In some cases, the aerodynamic shape of the vehicle is required to be unchanged during the flight, thus zero-ablation behavior of the material is also needed. At temperatures higher than 2000 K, it is difficult to meet these requirements with a single material, and composites or bulk-coating systems are attractive solutions at present. The thermal environment involving severe aerodynamic heating, large aerodynamic forces and chemical reactions motivated the development of new thermal protection systems (TPS) [3]. State-of-the-art high temperature materials include carbon-carbon composites (CC), silicon carbide based composites (C/SiC) and ultra high temperature ceramics (UHTC) [4-6]. However, these materials are still not mature at present and are far from off-the-shelf condition. One of the biggest issues is the oxidation of TPS materials at high temperatures. To solve this problem, oxidation resistance coatings are suggested. Among the proposed materials, silicon carbide,

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owing to its excellent oxidation resistant property and good compatibility with base materials at high temperatures, is one of the most promising coating materials to protect CC or C/SiC from severe oxidation.

Chemical vapor deposition (CVD) is the most commonly used method for manufacturing SiC coatings [7, 8]. However, toxic feedstock and by-products generally exist in CVD SiC processing. On the other hand, with vapor phase depositions, the coatings formed usually have a columnar structure, which might create entrance channels for oxygen and result in the oxidation and subsequent failure of the coating in operation. Also, because of the mismatch of thermal expansion coefficients between SiC coating and C/C composites, cracks can easily develop at the coating-substrate interface. Considering these factors, nano-structured SiC coating formed by other methods would be preferable for improved coating quality. Compared with conventional technology, sintering of high-tech ceramics in thermal plasmas has the potential to drastically reduce the time period required for this process. In addition, plasma sintering offers the opportunity to restrain grain growth and to tailor heat transfer during the sintering process to obtain desirable structures and properties in the sintered materials [9].

In the Institute of Mechanics, Chinese Academy of Sciences, a specially designed non-transferred dc plasma deposition system was developed. Plasma generated at reduced pressure has shown good temporo-spatial stability. In this paper, fast plasma sintering of nano SiC coatings with such a dc plasma system is studied.

2. Experimental details

The geometric details of the specially designed dc plasma system can be found in ref. [10]. The torch has a set of inter-electrode inserts with floating potential and an abruptly expanded anode. The diameter of the torch exit is 60 mm. Large and stable plasma jets can be generated under almost a fixed arc length condition. That is, with the special torch structure, the arcing can only find its suitable attachment position on the anode surface within an almost fixed and narrow region at a given gas feeding condition and arc current. In this kind of torch, the change of arc column length caused by the movement of the arc root on the anode surface could generally be neglected compared with its long column passing through the inter-electrode insert. Thus, the fluctuation component of arc voltage originating from the length change of arc column can be kept generally at a negligible level [11]. Experimental results indicate that this kind of torch can generate plasma jet of laminar or turbulent flow state at atmospheric pressure by regulating the gas flow rate and arc current [12].

Table 1 Typical experimental parameters.

<i>Parameters</i>	<i>Values</i>
Input power (kW)	4.5 – 8
Plasma gas	Ar-H ₂
Hydrogen concentration (vol%)	0.5 - 6
Plasma gas flow rate (slm)	4.2 – 17.8
Chamber pressure (kPa)	0.5 – 6
Powder feeding rate (g/min)	0.2 – 1
Carrier gas flow rate (slm)	2 – 8
Substrate position (mm to torch exit)	10, 15, 20, 30 ,40
Substrate temperature (K)	673 – 1200
Deposition time (min)	10

To facilitate fast sintering, argon-hydrogen plasma was used to obtain a better heating and to eliminate surface impurities by reduction reaction. Nano-sized SiC powders (mean particle size of 50 nm) were fed into the torch by a modified fluidized bed powder feeder. Sintering deposition parameters, including substrate pretreatment condition, substrate temperature, chamber pressure, gas flow rate and hydrogen concentration were optimized based on the Taguchi method. Table 1 lists typical experimental parameters used in this research. Three kinds of graphite substrates were used, one had a square plate shape with the size of 50×50×3 mm and the other two were disk-

shaped with dimensions $\Phi 25 \times 4$ mm and $\Phi 50 \times 4$ mm respectively. The adhesion of coating depends on the substrate condition to a large extent. For SiC coatings deposited on CC or C/SiC materials, physical anchoring is the main adhesion mechanism. Therefore, a proper surface roughness of the substrate is needed. Deposition trials showed that good adherent coatings can be obtained using graphite substrate with pretreatment as follows: sand-blasted and ultrasonic cleaned, then heated to 800 K in ambient air for 30 minutes. In the deposition chamber, the substrate was first heated by Ar-H₂ plasma for 7 minutes before the powder was fed in.

A rotational substrate holder was used with rotary speed of 9 rpm. The temperature on the backside of the substrate was measured by a K-type thermocouple. Micro hardness of the deposited coating was measured using a micro Vickers tester. The surface roughness was measured by a surface profiler. The microstructures of the coatings were analyzed by field-emission scanning electron microscopy (FE-SEM). The phase was identified by x-ray diffractometry. The ablation behavior of the deposited coating was tested on a small arc-heating testing facility [13].

3. Results and discussion

3.1. Feedstock powder

Powder used as feedstock for fast plasma sintering deposition should be properly small, narrowly distributed, and have a good ability to flow. Only if the size of the powder is small enough can effective heat transfer from the plasma be expected. Because the residence time of the powder in the plasma is usually on the order of milliseconds, a powder that is too large cannot be fully heated. On the other hand, if the powder is too small, it is difficult to maintain a steady feed, as small powders tend to form large agglomerates due to large surface specific area and high surface energy. Furthermore, for a powder that is too small, because of its low inertia, it is difficult to gain enough momentum to penetrate into the plasma unless the carrier gas velocity is drastically increased. However, when the velocity of the carrier gas is too high, the plasma will be markedly disturbed and become unstable, which will certainly reduce the coating quality. The narrow size distribution of the source powder should also be emphasized. This is because the size distribution significantly affects the velocity of the powder before it is injected into the plasma. The difference in size might result in a drastic difference in mass, which will lead to totally different thermal histories of these particles.

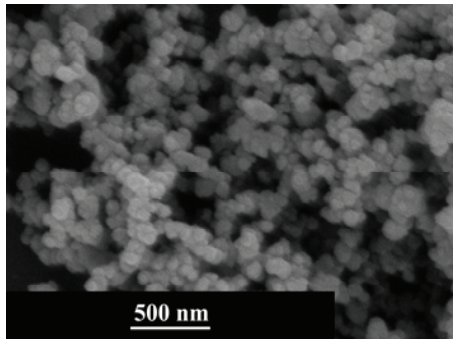


Figure 1 SEM micrograph of the feedstock SiC powder.

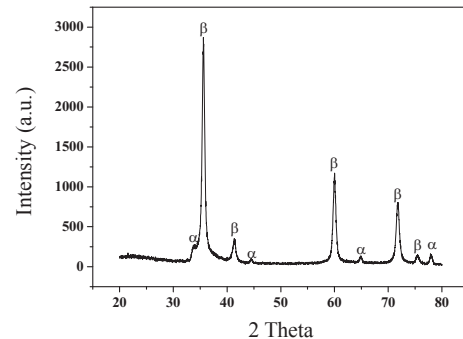


Figure 2 XRD pattern of the feedstock powder.

Figure 1 shows the SEM micrograph of the feedstock SiC powder used in this research. The mean size of the powder is 50 nm, and the size distribution is narrow. The shape of the powder is almost spherical. For such small sized powders, a relative large carrier gas flow rate is needed. In this research, a modified fluidized bed powder feeder was developed. There are two gas lines in the powder feeder: besides the normal carrier gas line, an additional argon jet was used to inject the powder into the torch. The additional injection of gas provides enough momentum to the feedstock powder without changing the carrier gas flow rate to maintain a controllable powder feeding rate.

XRD pattern of the feedstock powder shows that the powder is composed mainly of β -SiC with a small amount of α -SiC, as shown in figure 2.

3.2. Optimization of plasma sintering parameters

3.2.1. Substrate temperature control

Substrate temperature is one of the key parameters that affect coating quality in many thermal plasma coating processes, such as plasma chemical vapor deposition, plasma physical vapor deposition and thermal plasma spraying. In plasma sintering deposition, the injected powders are heated in the plasma plume and the sintering occurs at the substrate surface. Therefore, similar to normal pressureless sintering by ovens, the temperature is the most important parameter affecting the sintering process.

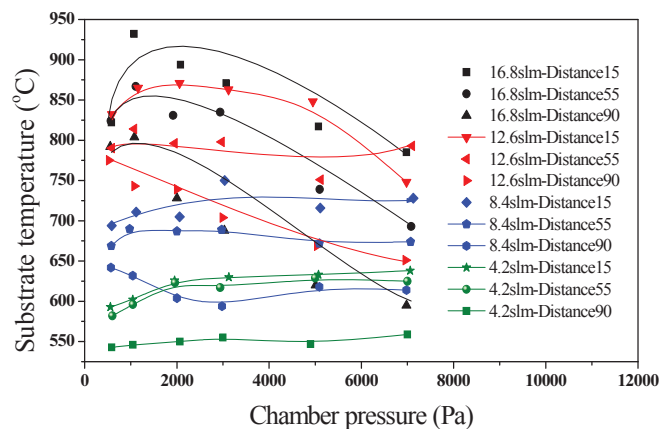


Figure 3 Substrate temperature evolutions on chamber pressure, gas flow rate and substrate position.

Figure 3 shows the dependence of substrate temperature on chamber pressure, plasma gas flow rate and substrate positions. It is interesting to see non-linear dependence of the substrate temperature on the chamber pressure at different plasma gas flow rates. The mechanism for such phenomena is closely related to the plasma flow state being laminar or turbulent. Previous research [14] showed that when the plasma gas flow rate is high, e.g. at 16.8 slm, the plasma transformed from laminar to turbulent flows at an elevated chamber pressure. When the chamber pressure is 500 and 1000 Pa, the overall uniformity of the plasma plume can be confirmed through fast imaging. Even when the exposure time of plasma plume is as short as 10^{-5} s, significant gradient in neither axial nor radius direction can be observed. With the increase in chamber pressure, the plasma plume becomes intensively twisted and changes to a fully developed turbulent state. At the same time, the length, together with the volume, of the plasma contracts at higher chamber pressures. At higher pressures, with the change in the arcing conditions, the temperature of the plasma increases, which leads to brighter zones in the high-temperature area. When the chamber pressure is kept constant, the decrease in gas flow rates also promotes the laminar flow.

Based on these facts, the result shown in figure 3 suggests that when the plasma is in laminar flow state, an increase of the substrate temperature with chamber pressure was observed because the length of the plasma plume is long enough to heat the substrate efficiently even at 90 mm from the torch exit. And the increase of chamber pressure leads to confined plasma jet with higher core temperature and higher heat transfer rate. On the other hand, when the plasma is in turbulent state, with the increase of chamber pressure, the twisted plasma jet becomes shorter and cannot heat the substrate effectively when the substrate is positioned relatively far from the torch exit.

3.2.2. Parameter optimization based on the Taguchi method

Based on preliminary experimental tryouts, the Taguchi method was employed to optimize plasma sintering deposition parameters of chamber pressure, substrate position, hydrogen concentration and arc current. The

parameters and levels are shown in Table 2. Other parameters were kept constant, such as the total gas flow rate to be 16.8 slm, etc. The micro-hardness of the coating was used to evaluate the coating quality where a higher micro-hardness is suggested to represent higher coating density. An $L_9(3^4)$ experimental design table was used to study the dependence of coating quality on the parameters listed above.

Table 2 Parameters and levels used in Taguchi method

Levels	Hydrogen concentration (vol%)	Arc current (A)	Chamber pressure (Pa)	Substrate position (mm)
1	2	80	1000	15
2	4	90	2000	25
3	6	100	4000	35

Range analysis shows that among the studied parameters, chamber pressure has the largest effect on the micro-hardness of the coating, followed by substrate position, arc current and hydrogen concentration. Highest micro-hardness was obtained at the combination of hydrogen concentration of 4%, arc current of 100 A, chamber pressure of 1000 Pa and the substrate position of 25 mm. The optimized parameter plan through direct analysis is similar to this combination except the substrate position was 15 mm.

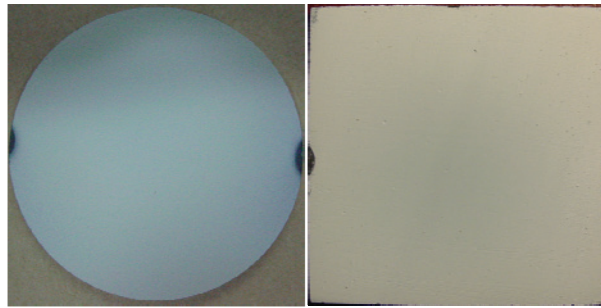


Figure 4 As deposited SiC coatings on $\Phi 50 \times 4$ mm and $50 \times 50 \times 3$ mm graphite substrates.

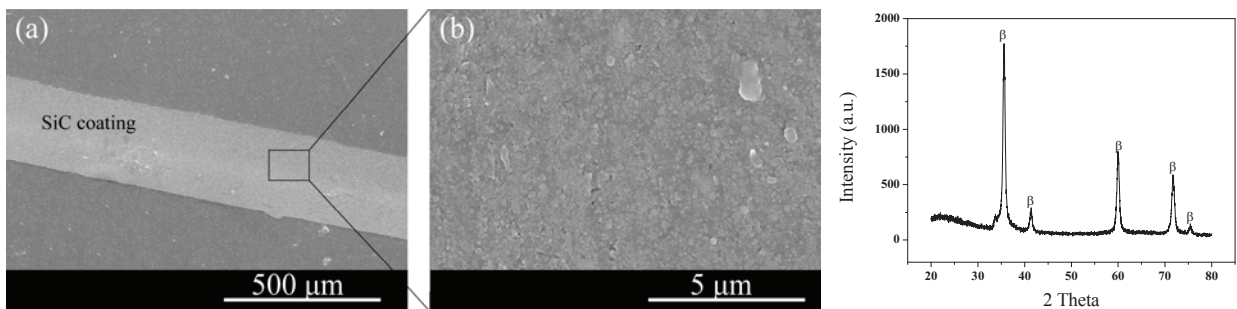


Figure 5 Cross sectional SEM image of a stand-off coating (a) and higher magnification image showing nano structure (b) and XRD pattern of the deposited coating (c).

With the optimized parameters, homogeneous SiC coatings were deposited on relative large surfaces shown in figure 4. In 10 minutes deposition, SiC coatings with thickness over $200 \mu\text{m}$ was prepared, which suggests a deposition rate as high as $20 \mu\text{m}/\text{min}$ was achieved. Figure 5 shows a stand-off coating and its microstructure, showing a dense packing of nano-structure. The grain of the coating is uniform with the size around 100 nm . Five XRD samples were taken from the center of the substrate to the edge, all of which show similar XRD patterns (Fig. 5 (c)). This shows that the coating was composed of pure β -SiC and the α -SiC existing in the feedstock powder was

not seen in the coating. This means that the deposition process is not a pure sintering process, chemical reduction of impurities and vapor deposition may also occur.

3.3. Ablation behavior of the coating

In order to evaluate the oxidation resistance property of the coating, deposited samples on $\Phi 25 \times 4$ mm substrate was tested in a small arc-heated material testing facility[13]. Gas mixture of 80% N_2 and 20% O_2 was used to simulate air composition. The total temperature of the flow is 2000 K with Mach number of 1.5. After 60 s ablation test, there is no crack or peel off of the coating observed. The graphite substrate was well protected under high speed oxidation flows. However, the color of the coating is somewhat changed from pale grey to white. This might be caused by nonstoichiometry when Ar- H_2 was used in the deposition process and further densification of the coating may also occur during the ablation test.

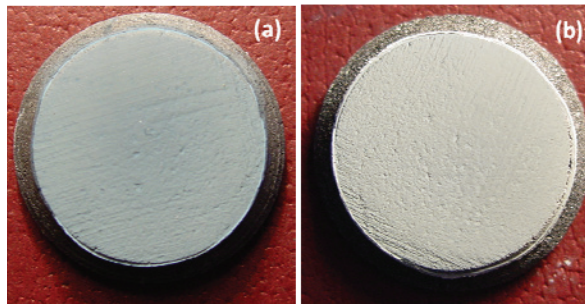


Figure 6 SiC coating before (a) and after (b) ablation under supersonic arc-heated N_2 - O_2 flow with stagnation temperature of 2000 K for 60 s.

4. Conclusions

Nano-sized SiC powders (mean particle size of 50 nm) were smoothly fed into a specially designed plasma torch by a modified fluidized bed powder feeder. With a temporo-spatially uniform Ar- H_2 plasma generated at reduced pressure, large area, fast sintering deposition of nano-structured SiC coating was achieved. Sintering deposition parameters, including substrate pretreatment condition, substrate temperature, chamber pressure, gas flow rate and hydrogen concentration were optimized based on the Taguchi method. With optimized parameters, 200 μm thick SiC coating was deposited on a 50 \times 50 mm graphite substrate uniformly in 10 minutes, with sintering deposition rate as high as 20 $\mu m/min$. XRD analysis showed that both the center and the edge of the obtained coating are in pure β phase. SEM observations of the coating cross-section confirmed that nano-structure was inherited from the original powder. With the help of such nano-structure, the interface between coating and substrate is clean and free of cracks. Ablation test showed that such coatings can be used as oxidation resistance coatings in high temperature oxidizing environments.

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