Received: 19 May 2020 | Revised: 16 September 2020 | Accepted: 18 November 2020

DOI: 10.1111/ijac.13671

International Journal of Applied Ceramic TECHNOLOGY

ORIGINAL ARTICLE

Preparation of aluminum oxide coating on carbon/carbon composites using a new detonation sprayer

Viacheslav Sirota[1] | **Viacheslav Pavlenko**[1] | **Natalia Cherkashina**[1] | **Marina Kovaleva**[2] | **Yurii Tyurin**[3] | **Oleg Kolisnichenko**[3]

[1]Belgorod State Technological University named after V. G. Shoukhov, Belgorod, Russia

[2]Belgorod National Research University, Belgorod, Russia

[3]E.O. Paton Electric Welding Institute NASU, Kyiv, Ukraine

Correspondence
Viacheslav Sirota, Belgorod State Technological University named after V. G. Shoukhov, Belgorod 308012, Russia.
Email: v-sirota@list.ru

Funding information
Russian Science Foundation, Grant/Award Number: 19-19-00316

Abstract

A new multi-chamber cumulative detonation sprayer (MCDS) was applied to fabricate an aluminum oxide coating on carbon/carbon composites. MCDS provides heating and acceleration of ceramic micropowders by means of combustible gas mixture detonation products with a frequency of 20 Hz and above. The ceramic aluminum oxide particle kinetic energy ensures the destruction of the weakened areas on the carbon-carbon composite material surface and the incorporation of these particles into the surface layer. The following powder particles decelerate on the already fixed particles and form a ceramic coating. The formed aluminum oxide coating is characterized by high hardness and low porosity (<1%). MCDS provides the formation of a high-quality ceramic layer, which can also serve as the basis for the formation of protective heat-resistant coatings.

KEYWORDS

Al_2O_3, carbon/carbon composites, formation mechanism, multi-chamber detonation sprayer

1 | INTRODUCTION

Carbon/carbon (C/C) composites contain carbon reinforcing elements in the form of discrete fibers, continuous filaments or bundles, felts, tapes, and fabrics with flat and three-dimensional weaving, volumetric frame structures.[1,2] The carbon matrix unites the reinforcing elements in the composite into a single whole, which allows perceiving external loads in the best possible way. The advantages of C/C are low density (1.3–2.1 t/m^3); high heat capacity, resistance to thermal shock, erosion and radiation; low friction and linear expansion coefficients; high corrosion resistance; a wide range of electrical properties (from conductors to semiconductors); high strength and stiffness. The best carbon fiber grades have a tensile strength of over 4.0 GPa and elastic modulus of about 240 GPa at a density of 1.75 g/cm^3, which favorably distinguishes them from other reinforcing fillers.[3] A unique feature of C/C composites is the 1.5–2.0 times increase in strength and increase in elastic modulus with increasing temperature. C/C products operate up to 2500°C in an inert atmosphere and vacuum.[4] C/C composites have found application in rocket production and chemical engineering, aviation and space technology, in sports equipment production, etc. The use of carbon-carbon composites in various technology branches allowed creation of new structures with significantly increased functional capabilities during operation under extreme conditions. C/C composites are mainly used in products that operate at temperatures above 1200°C–1500°C, which leads to increased requirements to protect the surface from oxidation.[5] The properties of C/C composites are changed in air with prolonged exposure to relatively low temperatures. There is also a tendency to burnout or oxidize with increasing temperature above 500°C in an oxidizing environment, and, as a result, there is a rapid decrease in strength due to an increase in porosity.[4–6]

In this regard, the development of technology and equipment for the application of protective coatings on the surface

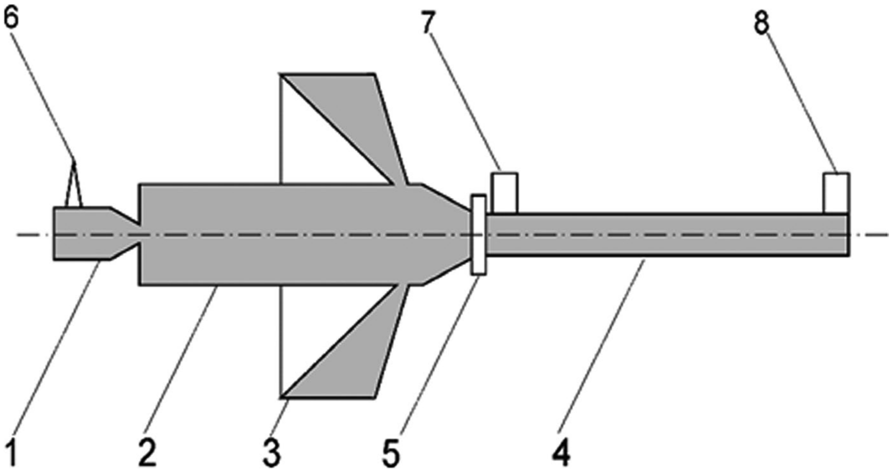

FIGURE 1 Equipment for deposition of the aluminium oxide coatings

of C/C composites products is a promising task at present. Various methods are used to create coatings, including pack cementation, slurry method, chemical vapor deposition, atmospheric plasma spraying, and thermal spray, etc.[7–10] All these methods require special preliminary surface preparation or the formation of a bonding sublayer between of coating material and substrate.[11]

The use of high-speed gas-thermal methods, which impart high kinetic energy to powder particles while reducing their temperature, is expedient for obtaining coatings on the carbon-carbon materials surface. The high speed of the powder particles, 3–4 times higher than the speed of sound, at a lower temperature thereof, allows to destroy fragile and weakened surface areas of the C/C composites, to embed and form coatings on dense microcrystalline areas, without oxidation and with high adhesion and cohesion. Such a coating can provide protective functions against high-temperature oxidation and form the basis for the manufacture of heat-shielding ceramic materials.

Coatings made of Al_2O_3 powders are widely used to protect surfaces exposed to aggressive working environments at high temperatures. The widespread use of alumina coatings may be due to their attractive service properties and low cost.[12,13] It is also known that aluminum oxide ceramics show sufficiently high heat-resistant properties in the range of operating temperatures of C/C composites.[14] While applying the aluminum oxide coating, also it is necessary to take account that the coating may be operated in thermo-cyclic environments, which puts high demands on adhesion strength and toughness of coatings.

The purpose of this work is to study the formation mechanism of ceramic aluminum oxide coatings on the surface of C/C composites. The deposition characteristics and the microstructure of the resultant coating were analyzed. Coatings were created from standard powders of aluminum oxide ceramics, which were heated and accelerated in a cumulative detonation sprayer.

The authors developed a new design of multi-chamber cumulative detonation sprayer (MCDS) unit for deposition of coatings. The essential difference of the MCDS from the detonation one is that it sums up the energies of products of detonation combustion of fuel gas mixtures from several specially profiled detonation chambers. The rate and temperature of the combustion products depend only on the parameters of filling of each chamber with the fuel gas mixture. In our previous work[15] the efficiency of the MCDS was compared to that of the best samples of a wide variety of units for thermal spraying of coatings, which provide a high velocity of spraying powder and minimal porosity of the resulting coating. The MCDS is advantageous over other units in that it requires a much lower consumption of fuel gases and electric power at the same quality of coatings. Pressure in the gas lines is not in excess of 0.4 MPa. Design peculiarities of the unit allow the spraying process to be performed without overheating of device's parts and without damaging them.

2 | EXPERIMENTAL PROCEDURE

Nanocomposite aluminum oxide coatings were obtained from AMPERIT 740.0 Al_2O_3 powder (dispersion size 5.6–22.5 μm) on the surface of C/C composites using a multi-chamber cumulative detonation sprayer (MCDS) with a barrel length of 500 mm (Figure 1).[15–20] The phase composition of Al_2O_3 powder is mainly represented by γ-Al_2O_3 (92.34%), α-Al_2O_3 (3.83%), and SiO_2 (3.83%).[17] In our previous work[18] a series of Al_2O_3 coatings have been prepared on steel substrate in the three modes at different nozzle lengths (300, 400, 500 mm) of MCDS. The dense ceramic layers with high hardness and low porosity have been prepared using MCDS with a nozzle length of 500 mm. The spray parameters used for deposition of aluminum oxide coatings are listed in Table 1.

The sprayer consists (Figure 1) of a prechamber for initiating the detonation process (1); the main cylindrical chamber (2), where the detonation combustion mode develops; an annular chamber with a slit exit into the cylindrical chamber (3). The detonation combustion mode of the combustible mixture is initiated by an automobile spark plug (6). The annular chamber (3) is used to compress the combustion products and create an additional jet, which "props" the detonation products in the cylindrical nozzle (4) from the main chamber (2). A dose of powder is fed into the nozzle through an annular gap (5) for acceleration and heating. The nozzle dimensions can be 16–20 mm in the inner diameter and 300–520 mm in length and are selected depending on the material properties of the sprayed powder. Sensors (7) and (8) are installed on the nozzle to measure the pressure and velocity of the combustion products. The narrowing of the working volume of a cylindrical chamber with a diameter of 24 mm to a nozzle with a diameter of 16 mm ensures the over-compression of the detonation burning mode. Subsequent compression of the combustion products occurs due to the energy of the annular chamber (3). The gas-dynamic process of detonation initiation in the annular chamber provides for the accumulation of combustion products along the axis of the central chamber, which significantly increases their speed, pressure and density in the nozzle. To acceleration and heating of the powder were produced the supply of a compact portion of powder to the nozzle, synchronization of powder injection and detonation initiation. To achieve high deposition efficiency, a valveless unit for dosing and supplying doses of powder to the nozzle has been developed.

A number of studies[15–20] have confirmed that the combustion rate products increase significantly when the second combustion chamber is connected. In this case, a longer flow of combustion products is formed in the barrel. The flow has two pressure maxima. Powder particles that are fed in front of the high velocity front of combustion products have a higher velocity.

The sprayed samples were sectioned and metallographically prepared through multiple steps of grinding and polishing. To study the microstructure and phase composition of aluminum oxide coatings, an optical inverted microscope Olympus GX51, an electron scanning microscope Quanta 200 3D equipped with EDX (SEM) and X-ray diffractometer Rigaku Ultima IV were used. The porosity of the composite coating was measured by the metallographic method with elements of the qualitative and quantitative analysis of the geometry of the pores using an optical inverted Olympus GX51 microscope. The images were registered in an optical microscope, in bright field, magnified 500×. The image acquisition of the structure of the studied layer was done using "SIAMS Photolab" programme. At least ten arbitrarily selected typical micrographs were analyzed for each experimental point. The hardness tests were carried out with an automatic microhardness analysis system DM-8 AFFRI by Vickers method with an indenter load of 300 g.

3 | RESULTS AND DISCUSSION

Figure 2 shows a typical cross-section of the aluminum oxide coatings on the surface of the C/C composites indicating the uniformity of the coatings. The coating thickness was about 400–450 μm. The structure of the coating presents many lamellae piled up one upon another, as shown in Figure 2. It was found that the coating porosity is less than 1%. Investigations of microhardness of the ceramic coating layer were carried out under loads of 300 g. The value of microhardness monotonically decreased from the maximal value (1300 ± 25 $HV_{0.3}$) on the surface to lower values deeper in the coating (950 ± 25 $HV_{0.3}$). X-ray phase analysis shows that the aluminum oxide coating consists of α-Al_2O_3, γ-Al_2O_3, and θ-Al_2O_3 (Figure 2B). Defects (gaps or voids) at the coating-substrate interface are formed during the preparation of thin sections due to chipping of solid particles and destruction of the substrate components.

The mechanisms of cohesion and adhesion for metal/ceramic coatings on metal substrates have been well studied to kinetic spray methods.[21–23]

However, the deposition behavior of the ceramic particles (the interaction of ceramic particle with the C/C composites substrate, deformation of the substrate surface, mechanisms of adhesion, etc.) on carbon/carbon composites is poorly understood.[24]

TABLE 1 Parameters employed for deposition of Al_2O_3 coating

Flow rate of fuel mixture components, m^3/h							
Oxygen	C_3H_8	Air	Barrel length, mm	Barrel diameter, mm	Spray distance, mm	Powder feed rate, g/h	Frequency, Hz
4.40[a]/ 4.00[b]	0.83[a]/ 0.82[b]	0.14[a]/ 0.25[b]	500	16	60	700	20

[a]Cylindrical form combustion chamber.

[b]Combustion chamber in the form of a disk.

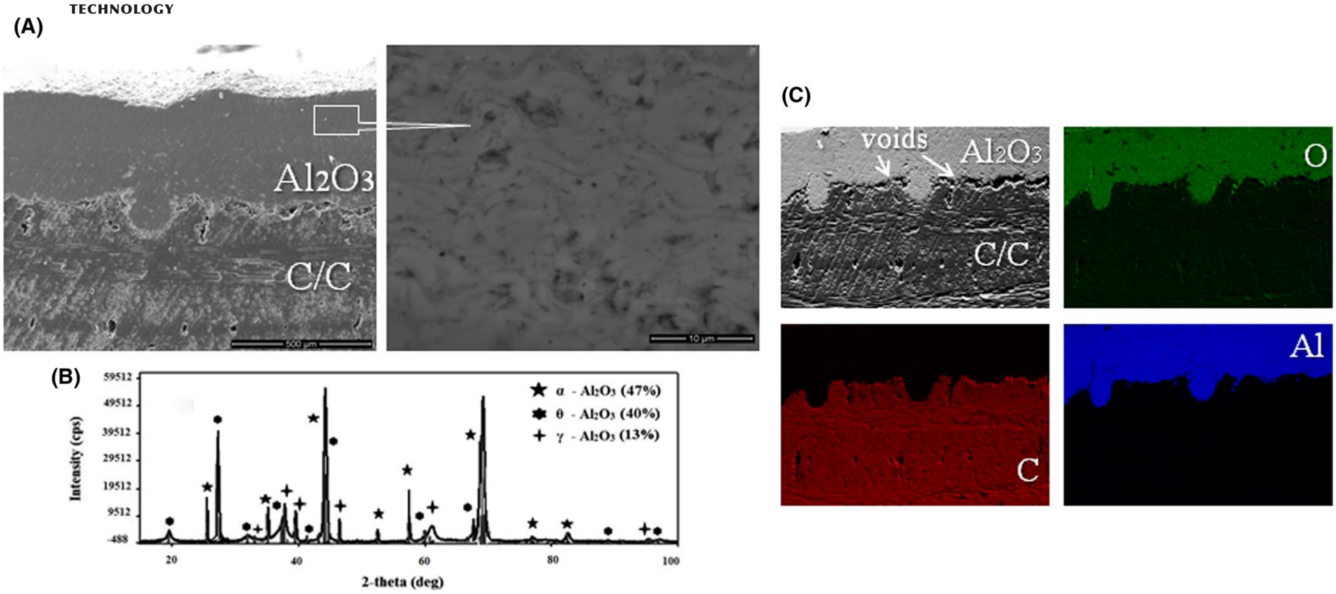

FIGURE 2 The aluminium oxide coating on C/C: cross-section SEM micrographs (A), X-ray pattern (B), SEM EDX element distribution maps [Color figure can be viewed at wileyonlinelibrary.com]

Coatings are built up from the individual particles that strike the substrate. The particles are fully and partially melted at the moment of impact. At the beginning of the coating build-up, particles impact directly onto the substrate. The phenomena occurring at this stage determines the adhesion of the coating to the substrate.[25]

Three different adhesion mechanisms are generally considered: diffusion, chemical, and mechanical.[26] Diffusion adhesion occurs when the temperature during coating application is sufficiently high and no oxide layer exists at the surface. Chemical adhesion requires that the impacting droplet melts the substrate, and a chemical compound of both liquids exists.[23] Mechanical adhesion takes place when the substrate is roughened, for example by grit blasting.[27,28] The first particles hitting the surface do not adhere immediately: rather, there is an induction period during which impacting particles clean and deform the surface and partially remove the components of the surface layer of the substrate. For this to occur, particle velocities must be higher than a critical velocity.[29]

The velocity of the powder material during the collision with the substrate is one of the key parameters determining the physicochemical parameters of the materials' interaction, as well as the possibility of high-quality coatings forming on the surface of C/C composites. These parameters determine the interaction features: the dispersed particle's material spreading dynamics, and the substrate material deformation degree.

Two piezoelectric pressure sensors of 014MI type have been used to monitor the pressure of combustion products at the multi-chamber cumulative detonation sprayer nozzle during the deposition process. The first sensor (7) (Figure 1) was fixed at a distance of ~60 mm from the annular chamber exit (3), directly at the entrance to the nozzle. The second sensor (8) was fixed at the nozzle exit. In the experiments, a nozzle 500 mm long and 16 mm in diameter was used. The distance between the sensor axes was 525 mm. The experiments were carried out using a combustible mixture of propane and oxygen in a stoichiometric proportion. The signal from the sensor was fed to the ADC "L-Card783" and was recorded on a computer using a programme PowerGraph 3.0.

The passage of the detonation wave between the sensors averages 0.25 ms, and the speed is 2100 ± 100 m/s. For the stoichiometric oxygen-propane mixture the value of the stationary detonation velocity corresponding to the Chapman-Jouguet conditions reaches 2450 m/s. The resulting speed is less due to energy losses during movement in a nozzle with a diameter of 16 mm and mixing air into the combustible mixture during the chambers filling of the between the pulses.

It was found that the use of MCDS makes it possible to form high-speed pulsed jets of heated ceramic alumina powders, which provide the ability to create high contact loads upon impact of discrete particles on the substrate surface, which makes it possible to deform ductile, destroy fragile substrate materials, and incorporate and mechanically fix dispersed particles.

Thus, the formation mechanism of aluminum oxide ceramic coatings is mechanical and based on the destruction processes of the most weakened part of C/C composites, which includes the carbon matrix and/or poorly fixed fiber segments, as well as the development of recesses at this place (Figure 4A).

In the impact zone, the material of the powder and substrate are strongly plasticized and deformed, which provides all the necessary conditions for the coating formation. Upon impact, part of the kinetic energy of the powder particle is spent on its deformation and the substrate deformation. When a liquid particle of aluminum oxide impinges on to a surface, about 80% of its kinetic energy is transformed into the energy of the viscous forces at the substrate surface, 20% of the kinetic energy is transformed into the energy at the surface and also could be stored as plastic strain energy in the substrate surface region and give rise to craters.[30]

The kinetic energy of the particle at the moment of impact concentrates on a small contact area between the deformed surface of the particle and substrate. The impact time is very short, which makes it permissible to assume that the main part of the energy is spent on heating of the particle and thin surface layers of the substrate in the contact zone. In addition, the dynamic impact of a particle on a substrate makes a significant contribution to the process of material deformation and coating formation.

The spraying torch moves over the substrate and the first layer is usually composed of 5–15 lamellae. The first 5 seconds of the deposition process ensure the formation of well separated areas of ceramic deposits in the surface layer. The process of mechanical fixing of heated ceramic particles takes place in the recesses.[31] It can be concluded (see Figure 2C) that the penetration of aluminum oxide particles into C/C composites occurs due to the destruction of the binding material between the carbon fibers. Such a mechanism of engagement provides high adhesion bond strength. Aluminum oxide ceramics do not chemically interact with carbon material (Figure 3), which excludes the possibility of adhesive bonding through the formation of chemical compounds.

In the subsequent 5 seconds the torch returns to the same spot and a high-speed powder jet impact on the surface ensures the formation of a continuous layer of ceramic coating that covers the entire surface (Figure 4B). The surface of the layer is subjected to cooling. The molten particles deform, become lamellated and solidify into columnar or fine-grained equiaxial crystals. During spraying of the next layer of coating, the torch also heats up the previously deposited material by convection. Additional heat fluxes result from solidification of the particles and their cooling down to the temperature of equilibrium. The final coating's thickness is reached in a few passes of the torch over the substrate. Thereafter, the coating is cooled down to room temperature.

Further, it is possible to form ceramic layers (Figure 4C) and layers from other materials on the obtained ceramic layer. In our preliminary currently unpublished study, a multilayer Al_2O_3/ZrB_2–$MoSi_2$ protective heat-resistant coating has been prepared on the surface of C/C composites using a multi-chamber cumulative detonation sprayer (Figure 5).

4 | CONCLUSIONS

In this study, a multi-chamber cumulative detonation sprayer was used to apply an aluminum oxide coating on the surface

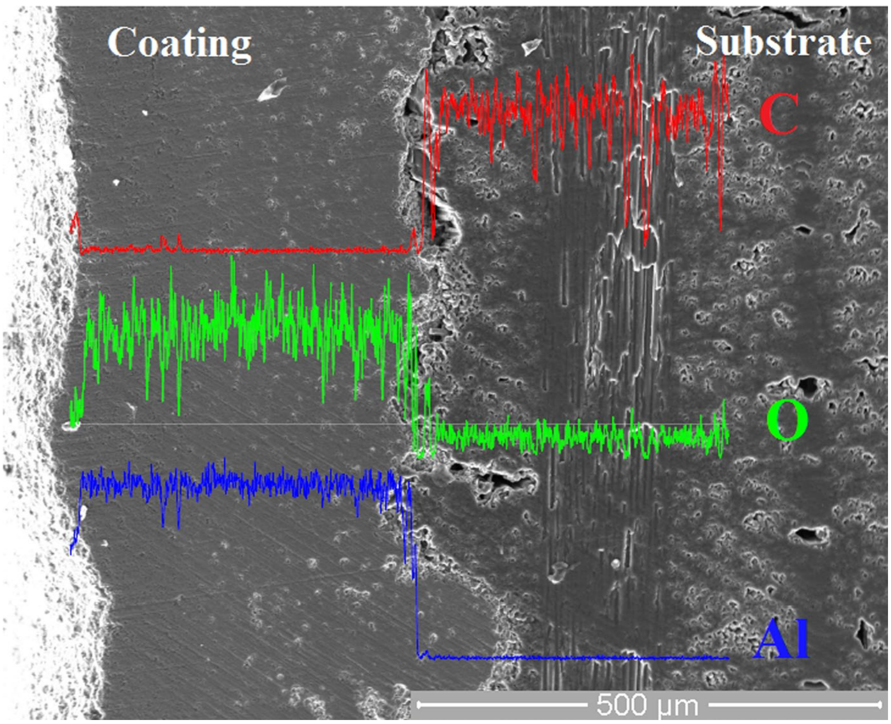

FIGURE 3 EDS line-scan of interface between aluminum oxide coating and C/C composite (across the white line) [Color figure can be viewed at wileyonlinelibrary.com]

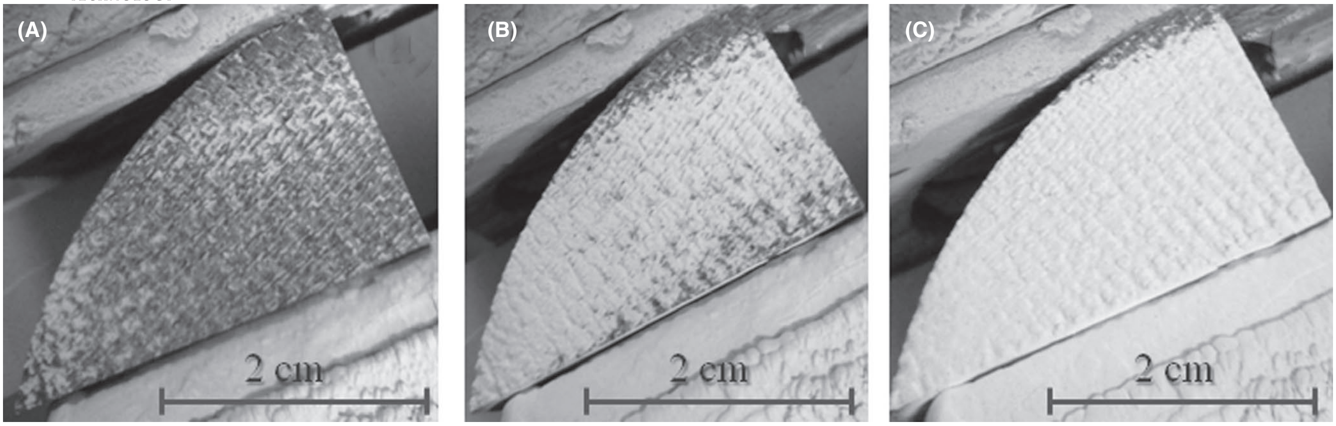

FIGURE 4 The formation of aluminum oxide coating on the surface of C/C composite: the creation of recesses and fixing of individual ceramic particles (A); the formation of bridges of ceramic particles (B); the formation of continuous ceramic coating (C)

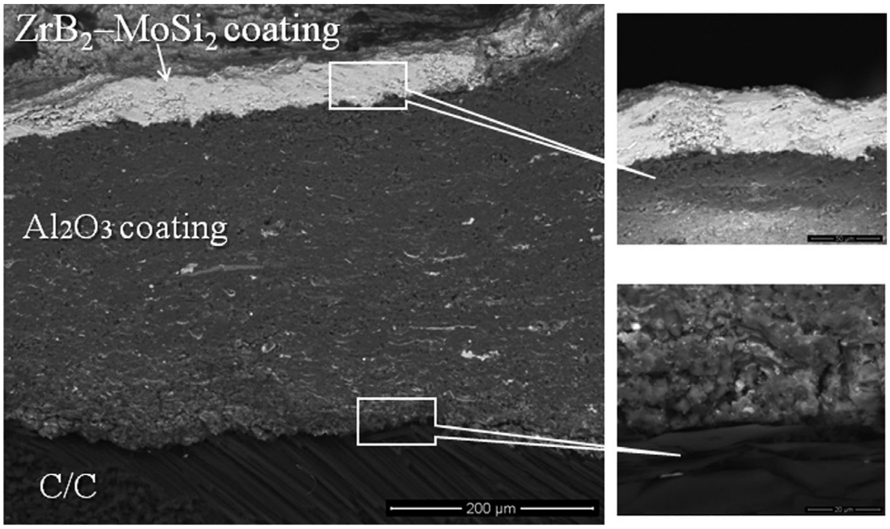

FIGURE 5 SEM micrograph plane view of the cross-section of the multilayer Al_2O_3/ZrB_2–$MoSi_2$ coating on the surface of C/C composites (back-scattered electron mode)

of carbon/carbon composites. The main results can be summarized as follows:

1. MCDS application allows the formation on the surface of C/C composites a dense hard aluminum oxide ceramic layer with a porosity of less than 1.0% and microhardness of 1300 ± 25 $HV_{0.3}$;
2. Based on the observations in this study, it can be concluded that mechanical interlocking is the main adhesion mechanism of alumina oxide coating to the surface of a carbon-carbon composites. Fragile materials on the surface of C/C composites (carbon matrix) are destroyed, which leads to the formation of voids and cavities. Discrete ceramic particles are broken and fixed in cavities, and they also provide the creation of a ceramic coating material:

It is commonly accepted that mechanical interlocking is the main adhesion mechanism of thermal spray deposits.

3. The results of the work open up prospects for the further development of a new technology for producing a high-quality ceramic layer that can improve the properties of carbon-carbon composites and can also serve as the basis for the formation of protective heat-resistant coatings.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Science Foundation, under grant No. 19-19-00316. The studies were carried out using the equipment of the Centre for High Technologies of BSTU and the Joint Research Center of Belgorod State National Research University «Technology and Materials».

ORCID

Viacheslav Sirota https://orcid.org/0000-0003-4634-7109

REFERENCES

1. Devi G, Rao K. Carbon-carbon composites - an overview. Def Sci J. 1993;43:369–83.
2. Sheehan JE, Buesking KW, Sullivan BJ. Carbon-carbon composites. Annu Rev Mater Sci. 2003;24:19–44.
3. Jacobson NS, Curry DM. Oxidation microstructure studies of reinforced carbon/carbon. Carbon. 2006;44:1142–50.
4. Lalit MM. High performance carbon–carbon composites. Sadhana. 2003;28:349–58.
5. Windhorst T, Blount G. Carbon-carbon composites: a summary of recent developments and applications. Mater Des. 1997;18:11–5.
6. Krenkel W, Berndt F. C/C–SiC composites for space applications and advanced friction systems. Mat Sci Eng A. 2005;412:177–81.
7. Zmij VI, Rudenkyi SG, Shepelev AG. Complex protective coatings for graphite and carbon-carbon composite materials. MSA. 2015;6:879–88.
8. Zhao J, Guo QN, Shi JL, Zhai GT, Lin L. SiC-Si-$MoSi_2$-oxidation protective coating for carbon-carbon composites. Surf Coat Technol. 2006;201:1861–5.
9. Huang J-F, Wang B, Li H-J, Liu M, Cao L-Y, Yao C-Y. A $MoSi_2$/SiC oxidation protective coating for carbon/carbon composites. Corros Sci. 2011;53:834–9.
10. Reu XR, Li HJ, Chu YH, Li KZ, Fu QG. ZrB_2-SiC gradient oxidation protective coating for carbon/carbon composites. Ceram Int. 2014;40:7171–6.
11. Shen Q, Shan J, Itoh T, Kitagawa K. Multi-layer coating of SiC, Al_2O_3 and glaze on C/C composites for oxidation resistance at high temperature. J Jpn Soc Powder Powder Metall. 2004;51:237–41.
12. Heimann RB. Applications of plasma-sprayed ceramic coatings. Key Eng Mater. 2006;122–124:399–442.
13. Pawlowski L. Strategic oxides for thermal spraying: problems of availability and evolution of prices. Surf Coat Technol. 2013;220:14–9.
14. Babin SV, Khrenov VV. Devepopment and investigation of protective coating for carbon-carbon. Nauchno-tekhnicheskij vestnik Povolgya. 2011;3:49–53. (In Russian).
15. Tyurin YU, Kolisnichenko O, Jia J, Vasilik N, Kovaleva M, Prozorova M, et al. Performance and economic characteristics of multi-chamber detonation sprayer used in thermal spray technology. Paper presented at: ITSC 2016. Proceedings of the International Thermal Spray Conference and Exposition; 2016 May 10–12. Shanghai, China: ASM International, 2016; p. 630–4.
16. Vasilik N, Tyurin YU, Kolisnichenko O. Method for gas-dynamic detonating speedup of powders and device for its implementation. RU Patent 2,506,341. 2012.
17. Kovaleva M, Tyurin YU, Vasilik N, Kolisnichenko O, Prozorova M, Arseenko M, et al. Effect of heat treatment on the microstructure and microhardness of nanostructural Al_2O_3 coatings. J Therm Spray Tech. 2014;23:1199–209.
18. Kovaleva M, Tyurin YU, Vasilik N, Kolisnichenko O, Prozorova M, Arseenko M, et al. Deposition and characterization of Al_2O_3 coatings by multi-chamber gas-dynamic accelerator. Surf Coat Technol. 2013;232:719–25.
19. Kovaleva M, Tyurin YU, Vasilik N, Kolisnichenko O, Prozorova M, Arseenko M, et al. Effect of processing parameters on the microstructure and properties of WC–10Co–4Cr coatings formed by a new multi-chamber gas-dynamic accelerator. Ceram Int. 2015;41:15067–74.
20. Kovaleva M, Prozorova M, Arseenko M, Tyurin Y, Kolisnichenko O, Yapryntsev M, et al. Zircon-based ceramic coatings formed by a new multi-chamber gas-dynamic accelerator. Coatings. 2017;7:142.
21. Assadi H, Gartner F, Stoltenhoff T, Kreye H. Bonding mechanism in cold gas spraying. Acta Mater. 2003;51:4379–94.
22. Yuan L, Luo F, Yao J. Deposition behavior at different substrate temperatures by using supersonic laser deposition. J Iron Steel Res Int. 2013;20:87–93.
23. Chandra S, Fauchais P. Formation of solid splats during thermal spray deposition. J Therm Spray Tech. 2009;18:148–80.
24. Li C, Zhang L, Guo Z. Investigation on interface of oxidation resistance coating of carbon-carbon composite. Acta Mat Compos Sinica. 1993;10:53–9.
25. Pawlowski L. The Science and Engineering of Thermal Spray Coatings. Chichester: Wiley; 2008.
26. Fauchais P. Understanding plasma spraying: an invited review. J Phys D Appl Phys. 2004;37:R86–R108.
27. Mellali M, Grimaud A, Léger AC, Fauchais P, Lu J. Alumina grit blasting parameters for surface preparation in the plasma spraying operation. J Therm Spray Technol. 1997;6(2):217–27.
28. Bahbou F, Nylen P. Relationship between surface topography parameters and adhesion strength for plasma spraying. Paper presented at: ITSC 2005. Proceedings of the International Thermal Spray Conference and Exposition. Basel, Switzerland: ASM International; 2005 May 2-4.
29. Klinkov SV, Kosarev VF. Measurements of cold spray deposition efficiency. J Therm Spray Technol. 2006;15(3):364–71.
30. Sobolev VV, Guilemany JM, Nutting J, Miquel JR. Development of substrate-coating adhesion in thermal spraying. Int Mater Rev. 1997;42:117–36.
31. Tiwari R, Herman H. Incorporation of reinforcements in spray formed MMCs. Scr Metall Mater. 1991;25:1103–7.

How to cite this article: Sirota V, Pavlenko V, Cherkashina N, Kovaleva M, Tyurin Y, Kolisnichenko O. Preparation of aluminum oxide coating on carbon/carbon composites using a new detonation sprayer. *Int J Appl Ceram Technol.* 2021;18:483–489. https://doi.org/10.1111/ijac.13671