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# STRUCTURE AND PHASE COMPOSITION OF $ZrB_2$–SiC–AlN PLASMA COATINGS ON THE SURFACE OF C/C–SiC COMPOSITE MATERIAL

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The process of protective plasma $ZrB_2$–SiC–AlN coating deposition on the surface of C/C–SiC composite material was studied. Coating was sprayed using subsonic Ar/$N_2$-plasma jet and supersonic jet of air-gas plasmatron. The role of interphase phenomena occurring during plasma spraying in the volume of particles of $ZrB_2$–SiC–AlN composite powder in formation of the coating layer was established. It is shown that the composition and velocity of the plasma spray jet affects the structure and phase composition of the forming $ZrB_2$–SiC–AlN coating. Resistance of the produced coatings to thermal cyclic heating was tested by a flame jet of oxygen-propane-butane torch. Coating of 400 μm thickness showed concervation of protective properties after 15 thermal cycles. Effect of thermal cyclic heating on formation of a three-zone structure in the protective coating, as a result of oxidation process was studied. Its texture and phase composition was examined by XRD and MXRD techniques. It is found that the surface layer of the coating after thermal cyclic heating consists of $Al_2SiO_5$-based matrix with submicron $ZrO_2$ inclusions. 25 Ref., 3 Tables, 9 Figures.

***Keywords:*** *plasma spraying, protective coating, composite material, ultra high temperature ceramics, microstructure, phase composition, interphase interaction, oxide microinclusions*

Composite materials (CM), consisting of carbon matrix, strengthened with fibers of carbon or silicon carbide (C/C, C/SiC, C/C–SiC), have a series of high service characteristics due to combination of high-temperate strength, high thermal conductivity, low values of CTE, resistance to thermal shocks and ablation wear. This promoted an interest to their practical application, including in aerospace industry in manufacture of parts of rockets and space vehicles [1–5]. A disadvantage of these materials lies in small value of heat resistance, which limits their application in temperatures above 500 °C, and resistance to erosion wear at high temperatures.

In this connection it is relevant to develop the compositions and techniques for deposition on C/C and C/C–SiC CM coatings providing reliable operation of parts and assemblies of aerospace equipment under extreme conditions of their operation.

Efficiency of service and life time of protective coatings on C/C and C/C–SiC CM is determined by level of fulfillment of a complex of the next requirements:

- corrosion resistance in oxidizing medium at heating to 2000 °C including under conditions of cyclic heating;
- resistance to variable thermal loads in thermal fatigue and thermal shock mode;
- presence of thermal barrier properties for protection of substrate from CM;
- resistance to erosion wear (ablation) under effect of high-temperature gas jet;
- ensuring the necessary level of mechanical characteristics of material of substrate from CM.

In realizing the requirements mentioned above the method and technology of formation of protective coatings of specific composition shall provide regulation of adhesion strength of coating with substrate from CM (at substrate-coating interface) as well as cohesion strength of layers of the formed coating and products of its interaction with environment, generating under its operation.

A series of review papers considers the experience of development of compositions for coatings of such designation as well as technologies of their deposition accumulated in the recent time in RF, Western Europe, USA and PRC. The analysis of these reviews shows a variety of compositions of investigated coatings, covering refractory oxides ($ZrO_2$, $HfO_2$), carbides (TiC, TaC, ZrC, HfC), borides ($ZrB_2$, $HfB_2$, $TiB_2$, $B_4C$), silicides ($MoSi_2$, $TiSi_2$), nitrides ($Si_3N_4$, BN), including their combinations referred to a class of ultra high temperature ceramics (UHTC), namely $ZrB_2$–SiC, $HfB_2$–SiC, etc. [6–10].

A list of presented methods and technology of coating deposition for protection of CM based on carbon and results of their application includes:

- deposition of powder suspensions from components of coating with next annealing;
- deposition of SiC, SiC–ZrC–SiC etc., layers using CVD method;
- plasma spraying;
- impregnation by polymer followed by pyrolysis (PIP);
- sol-gel method;
- thermal diffusion deposition (for example, siliciding C/C)

as well as processes consisting of combination of these technologies. For example, it is formation on C/C CM surface of SiC underlayer by siliciding method with next application of a layer of suspension from $ZrB_2$–SiC and annealing in inert medium and production of SiC upper layer using CVD method. However, usage of the combined CVD technologies and deposition of suspensions are related with long (2–10 h) spreading procedures of heat treatment in vacuum or protective medium at 1000–1150 °C.

The plasma spraying method differs from other by absence of the stages of high-temperature and long-term heat treatment, necessary for formation of adhesion forces with substrate surface and inner cohesion strength of coating layer. Not the least is the possibility of formation in plasma spraying of the layers of several millimeters. This allows using it for manufacture of free-standing products from the materials being sprayed.

The widest complex of investigations in the field of plasma spraying of $ZrB_2$–SiC-based coatings in a chamber with vacuum, increased pressure, inert medium was carried out in Italy by Rome University «La Sapienza» and Centro Sviluppo Materiali S. p.A. [11–16] staff members. The investigation was carried out for determination of effect of coating annealing on air at 1200, 1400, 1600 and 1800 °C during 10 h on phase composition and coating oxidation, effect of coating heat treatment at 1800 °C during 160 and 1800 s on structure and phase composition of $ZrB_2$–SiC at $ZrB_2$–SiC relationship variation [11–17]. One of the important results of their investigations is determination of efficiency of performance of «passivating» annealing stage for $ZrB_2$–SiC coating at 1100 °C during 6 h. This allows rising coating resistance to oxidation followed by heating to 1600 °C [13].

Experiments on coating deposition on C/C–SiC CM surface using plasma spraying in air were carried out in PRC with formation of double-layer coatings of $Er_2SiO_8/LaMgAl_{11}O_{19}$ and $Yb_2SiO_5/LaMgAl_{11}O_{19}$ characterizing with high oxidation resistance [18, 19].

The task of the present work lied in investigation of effect of thermal cyclic heating in air on phase and structure state of plasma coating of composite powder (CP) $60ZrB_2$–20SiC–20AlN (wt.%) sprayed on a substrate from C/C–SiC CM using atmospheric plasma spraying method.

Composite ceramics based on $ZrB_2$ of specified composition was developed by staff members of IPM of NASU and the process of high-temperature oxidation of its hot-pressed samples at temperatures to 1650° during 5 h [20] was investigated.

**Methods and materials.** Composition of CP and technology of its manufacture from mechanical mixture of $ZrB_2$, SiC, AlN components by granulation method on a couplant from polyvinyl alcohol was developed by IMP of the NAS of Ukraine.

The initial powders of $ZrB_2$, SiC, AlN for CP manufacture were of around 99.5 % purity with particle size 0.5–1.0 μm. Figure 1 shows appearance and structure of powder particles, a histogram of distribution of its grain-size composition is given in Figure 2.

A plate of C/C–SiC CM of 20×20×5.7 mm size was used as a substrate for spraying. Before spraying its surface was sandblasted.

Two methods of plasma spraying in open atmosphere (in air medium) were used for coating deposition in this work. They differ by composition of plasma gas ($Ar/N_2$, air), plasmatron power (24 and 82 kW,

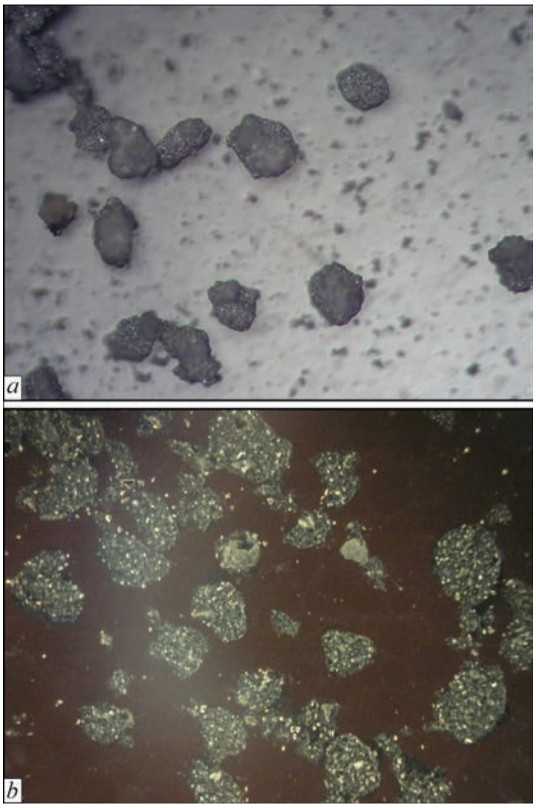

**Figure 1.** Appearance of $60ZrB_2$–20SiC–20AlN (wt.%) powder (*a*) and structure of particles in polarized light (*b*)

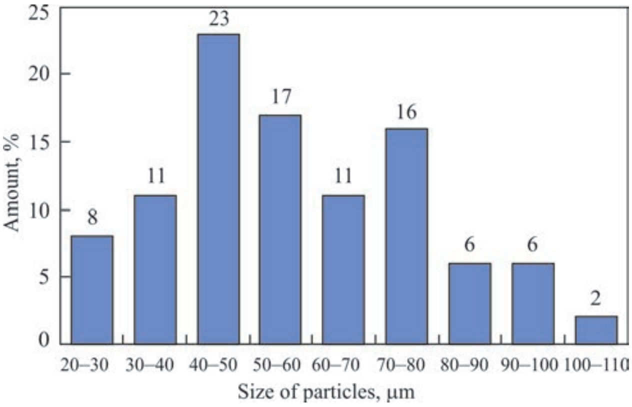

**Figure 2.** Histogram of distribution of grain-size composition of $60ZrB_2$–20SiC–20AlN powder (wt.%)

respectively) and velocities of plasma jet (sub and supersonic), (PS — subsonic $Ar/N_2$ plasma spraying; SAGPS — supersonic air-gas plasma spraying).

Application of program for computer simulation of a process of plasma powder spraying CASPSP [21] and available experimental data on velocities of particles under conditions of plasma spraying using similar gases [22] allowed carrying out evaluation of velocities of $ZrB_2$–SiC–AlN CP particles of selected composition and duration of time of their staying in plasma jet — $\tau_p$ taking into account their diameter — $d$ and spraying distance — $h$.

Acceleration and heating of spray particle under effect of plasma jet depend on its size and density.

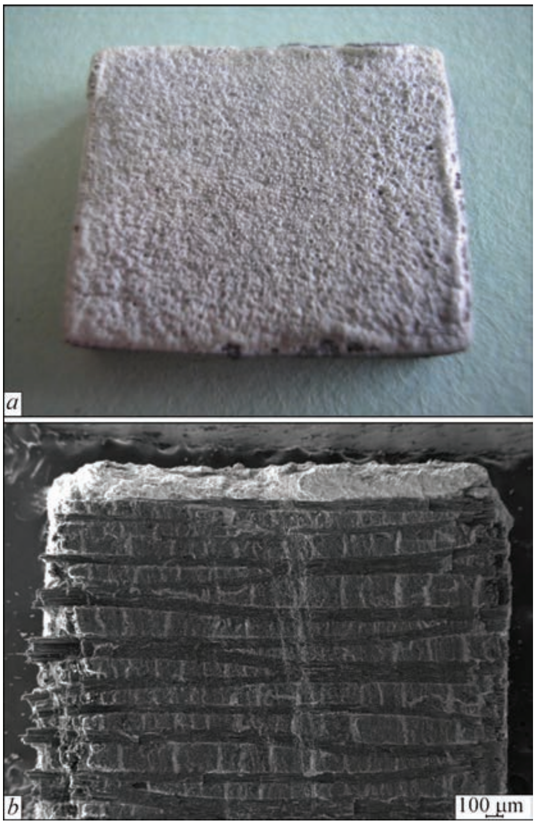

**Figure 3.** Appearance of surface (*a*) and section (*b*) of sample with plasma coating $ZrB_2$–SiC–AlN after 15 cycles of heating

Converting $60ZrB_2$–20SiC–20AlN wt.% composition in vol.% we get CP $43ZrB_2$–28.5SiC–28.5AlN (vol.%) and volume density of such composition is 4.4 g/cm$^3$ (without binder consideration).

The results of carried calculations provided a complex of characteristics of conditions of plasma atmospheric spraying at subsonic and supersonic modes of plasma jet flow used for coating deposition:

● subsonic: plasma gas — $Ar/N_2$, $T_{pl} \sim 10000$ K, $W_{pl} \sim 600$ m/s, $W_p \sim 100$–130 m/s, $\tau_p$ ($d = 60$ μm, $h = 100$ мм) ~ 1,5 ms;

● supersonic: plasma gas — air $T_{pl} \sim 6000$ K, $W_{pl} \sim 2500$ m/s, $W_p \sim 300$–350 m/s, $\tau_p$ ($d = 60$ μm, $h = 180$ mm) ~ 0,5 ms.

A calculation time of complete staying in plasma jet volume of $ZrB_2$–SiC–AlN CP particles of 40–80 μm size under conditions of subsonic spraying makes 0.5–3.0 ms, at supersonic it is 0.2–1.5 ms.

Resistance of protective coating on C/C–SiC CP surface to high-temperature cyclic loads is one of the most important its functional characteristics.

Thermal cyclic heating of the sample with 400 μm thickness coating was carried out with the help of jet of oxygen-propane-butane flame of GN-2 torch. Temperature of flame made around 2000 °C, distance from torch tip to sample surface was 70–80 mm. In a mode of cyclic heating the sample was heated for 2 min reaching an incandescence state during 10 s with next cooling in air during about 10 min before following heating.

Appearance of surface and section of the sample with $ZrB_2$–SiC–AlN coating produced by SAGPS method, after 15 cycles of heating (Figure 3), indicate the absence of indices of coating failure and preservation of its protective properties under conditions of used mode of its heat resistance testing.

**Results of investigation**. Microstructure of coatings from $ZrB_2$–SiC–AlN CP sprayed on C/C–SiC CM (Figure 4), is characterized with heterogeneity, high density, absence of defects and delaminations at boundary with the substrate.

In coatings' structure it is possible to determine the alternating areas of light and darker phases (probably, mixture of several phases), at that separate areas of the coatings demonstrate a lamellar-like structure. The difference in the structure of coatings produced by sub- and supersonic plasma spraying methods, determined at metallographic examination, lies in relationship of visible area of light and dark phases. Portion of dark phase prevails in the case of supersonic spraying. Structure of dark phase has a glass-like nature.

The results of X-ray structural phase analysis (XRD) of sprayed coatings (Figure 5) showed that interaction of the components of initial powder (Figure 5, *a*) with environment (air) and between them-

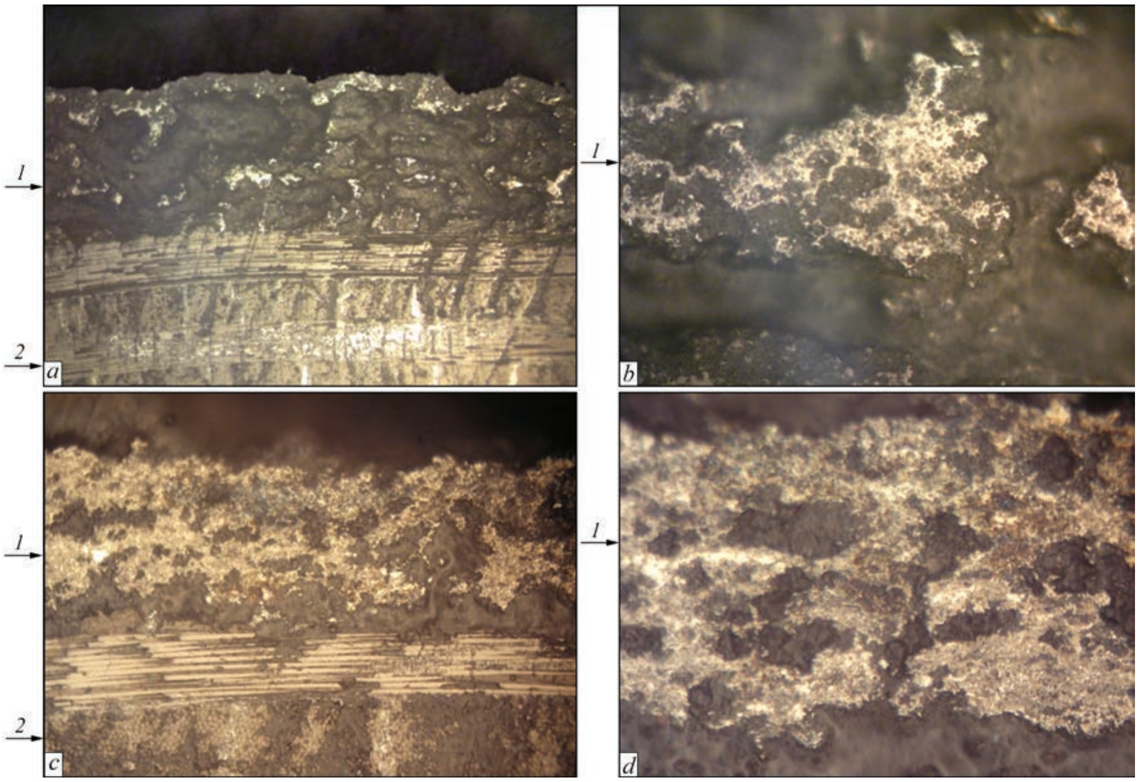

**Figure 4.** Microstructure of plasma coatings of $60ZrB_2$–20SiC–20AlN (wt.%) CP obtained by methods of subsonic (*a*, *b*) and supersonic (*c*, *d*) spraying: *1* — coating; *2* – C/C–SiC substrate (*a* — ×100; *c* — ×200; *b*, *d* — ×400)

selves takes place during the process of plasma spraying, due to what there is formation of oxide phases in the deposited material. Thus, in the coating produced by method of subsonic plasma spraying (Figure 5, *b*) this is $ZrSiO_4$, $Al_2SiO_5$ and $ZrO_2$ (Figure 5, *b*). Use of supersonic spraying method (Figure 5, *c*) $ZrSiO_4$ phase is not found in the initial deposited coating, however, a «halo» can be observed on X-ray pattern in 24–29° angle interval. It indicates presence in the coating of amorphous phase (Figure 5, *c*), as may be supposed $SiO_2$, as a product of $ZrSiO_4$ decomposition.

A comparison of intensity of X-ray reflections $ZrB_2$, SiC, AlN of the initial powder and coatings indicate significant decrease of $ZrB_2$ content as a result of its oxidation during spraying process.

Joint consideration of the results of metallographic examinations and XRD of the initial coatings (Figures 4, 5) obtained by different methods of plasma spraying allows making a conclusion that amount of oxide phases observed in the coatings produced using subsonic plasma jet is more considerable. A reason for this is apparently lower velocity of particle movement and, respectively, larger time of particle staying in the oxidation zone.

Most probably, the oxide phases ($ZrO_2$, $Al_2SiO_5$) on the section are dark colored and metal-like ($ZrB_2$, SiC, AlN) are light.

Only oxide phases, namely $ZrO_2$ (in form of tetragonal and monoclinic modifications) and $Al_2SiO_5$ were found in both cases (Figure 6, *a*, *b*) at X-ray structural phase analysis of the coatings after thermal cycling in the surface layer. Amorphous phase, which was found in the initial coating at SAGPS, is absent in this case.

Since components of the initial powder ($ZrB_2$, SiC, AlN) were not found in the surface layer of these coatings, the analysis of separated from substrate and refined SAGPS-coating (Figure 6, *c*) was carried out. All three phases were found at that, however, in smaller amount than in the initial coating (Figure 5, *c*).

Examination of chemical composition of the separate structural constituents of the coating in initial state and after thermal cycling was performed using a method of scanning electron microscopy together with X-ray spectrum microanalysis (MXRD) (Figures 7, 8). At that a surface layer of the coatings as well as transverse section along all its thickness were analyzed. Content of the elements included in CP composition (B, C, N, Al, Si, Zr) and oxygen, was determined by scanning of five-seven segments of 50×50 μm size and averaging at all area (Figure 8, *b*) of surface layer of the coating or its segment (Figure 7, *b*, Table 1). The analysis of content of structural constituents was carried out locally using electron probe of 1.5 μm size (Tables 2, 3).

Thus, it is determined that in process of plasma spraying due to oxidation of $ZrB_2$–SiC–AlN CP particles the relative amount of Al, Si and Zr in comparison with initial powder reduce and content of oxygen

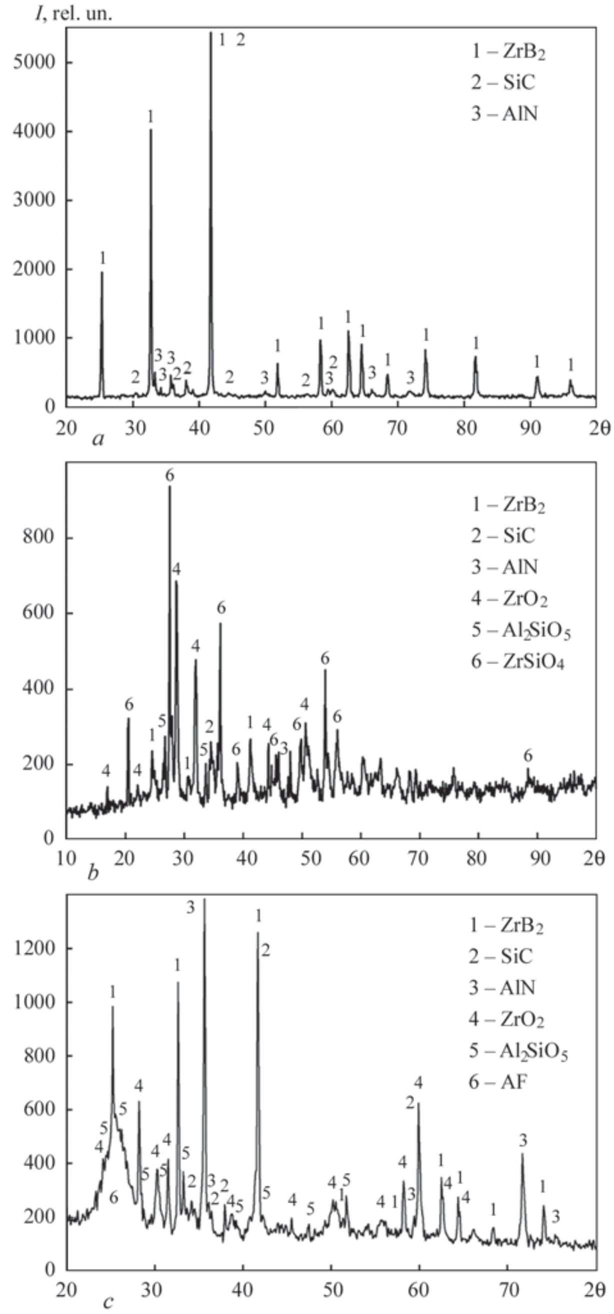

**Figure 5.** X-ray patterns of initial powder (*a*) and coatings obtained by methods of subsonic (PS) (*b*) and supersonic (SAGPS) (*c*) plasma spraying

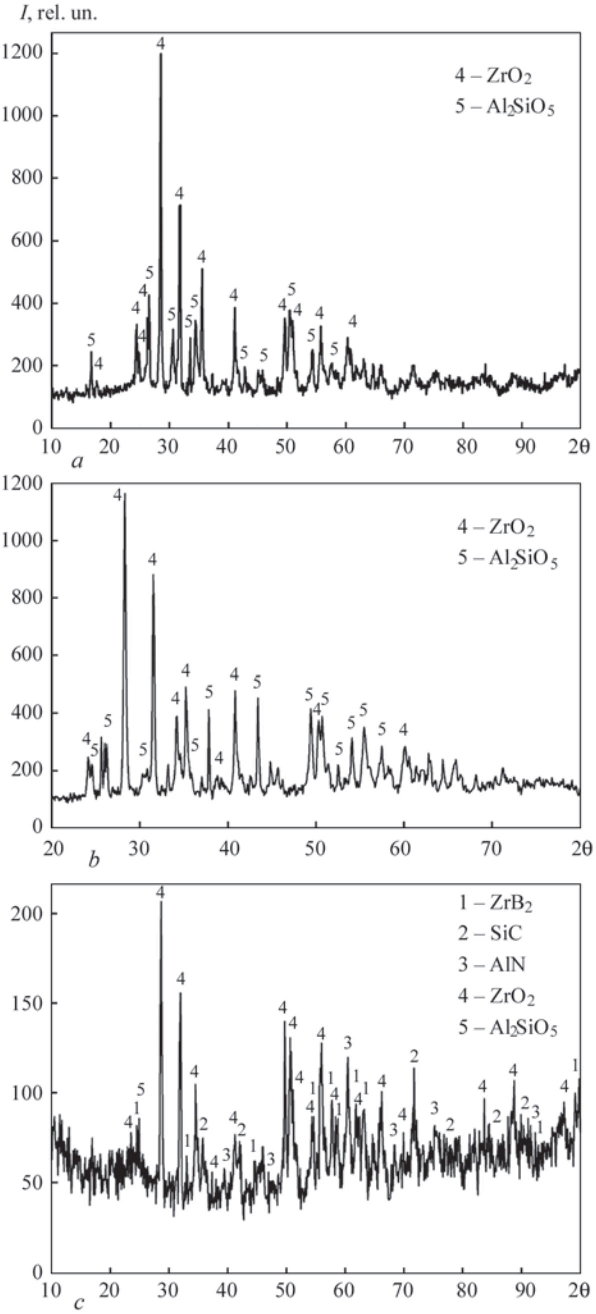

**Figure 6.** X-ray patterns of plasma coatings of $60ZrB_2$–20SiC–20AlN (wt.%) CP on surface of C/C–SiC CM after thermal cycling: *a* — PS-coating, surface layer; *b* — SAGPS-coating, surface layer; *c* — SAGPS-coating, composition averaged on all thickness

reaches around 30 wt.%. As a result of thermal cycling the phases containing B, C and N on the surface of coating are absent and amount of oxygen in the subsurface layer rises to 48 % (Table 1). Local analysis of composition of plasma coating after thermal cycling along its depth demonstrates reduction of oxygen content from 48 to 30 wt.% (spectra 1–4, Figure 8, *a*). The results of MXRD (Tables 2, 3) on the one hand completely prove XRD results, namely presence of $ZrO_2$, $Al_2SiO_5$ and $ZrSiO_4$ oxide phases in the coatings, and on the other hand allow assuming presence of amorphized boron silicate ($B_2O_3 \times SiO_2$) phases as well. It is determined that thermal cycling process promotes structural changes of the surface layer to a depth (Figures 3, *b* and 8, *a*), sizes of which are determined by temperature mode set in coating volume at its thermal cycling heating.

**Analysis of obtained results.** Formation of a protective coating layer on the surface of C/C–SiC CM takes place under conditions of atmospheric spraying of $60ZrB_2$–20SiC–20AlN (wt.%) CP.

The peculiarity of the process of plasma spraying of coating from $ZrB_2$–SiC–AlN CP is formation at heating in a plasma jet of particles being sprayed,

**Table 1.** Total content of elements of SAGSP-coating, wt.%

| Element | Powder | Coating in initial state* | Coating after thermal cycling** |
|---|---|---|---|
| B | 11.55 | 21.58±4.71 | 2.01 |
| C | 5.99 | 16.77±3.95 | 2.02 |
| N | 6.84 | 1.90±1.33 | 0.00 |
| O | 0.20 | 33.16±6.98 | 47.73 |
| Al | 15.16 | 6.25±1.36 | 19.28 |
| Si | 14.01 | 7.26±0.89 | 9.39 |
| Zr | 48.75 | 12.34±2.54 | 17.40 |

*Averaged composition on all thickness (Figure 7, *b*, points 1, 2–5)
**Composition of surface layer averaged on area 600×600 μm (Figure 8, *b*, spectrum 1).

consisting of a mixture of $ZrB_2$, SiC, AlN melts. Ordanyan S. S. with colleagues when studying $ZrB_2$–SiC phase diagram carried out heating of $ZrB_2$ and SiC mixture to a stage of co-melting at 2900 °C and did not find at that interaction of these melts. On the other hand in $ZrB_2$–SiC system they determined existence of eutectics, namely 77 % of SiC [23], at 2270 °C. It is assumed that its presence prevents the phenomenon of SiC decomposition in heating that provides co-melting of $ZrB_2$ and SiC at plasma spraying [15].

The fact of $ZrB_2$–SiC CP transition under conditions of plasma spraying into melting stage was experimentally determined by staff members of Rome University «La Sapienza» and Centro Sviluppo Materiali S. p.A [12]. It is indicated by type of obtained deformed particles of melt, i.e. splats, and effect on them of plasma spraying modes.

In this connection it is possible to state that formation of coating layer from $ZrB_2$–SiC–AlN CP under used conditions of plasma spraying is carried out by means of cooling and solidification on C/C–SiC surface CM of particles of a melt from mixture of components of ZrB, SiC, AlN CP, passing the stages of melting and interphase interaction, including with formation of oxidation products ($ZrO_2$, $SiO_2$, $Al_2O_3$).

The level of development of this process in a disperse medium of plasma jet depends on dimensions of particles of sprayed powder determining position of trajectory of their flight in a jet volume.

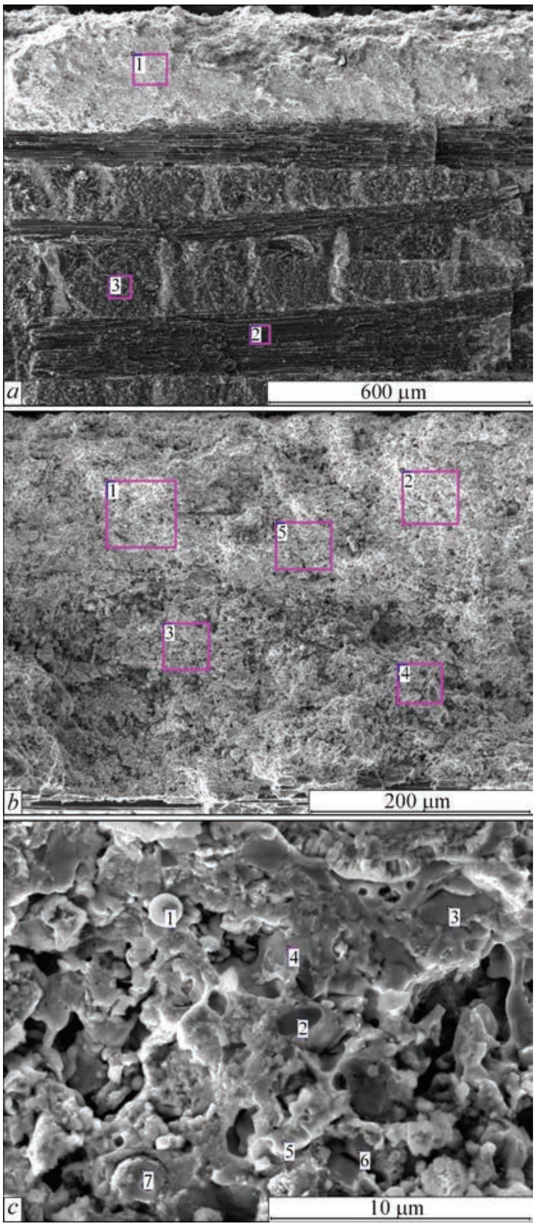

**Figure 7.** Electron micrograph of initial plasma SAGPS-coating of $ZrB_2$–SiC–AlN CP on surface of C/C–SiC CM: *a* — section of sample with plasma coating (1 — coating; 2 — carbon fiber; 3 — C/C–SiC CM); *b* — coating section, general view; *c* — structural elements on coating fracture (decoding the composition on spectra 1, 2 etc. in Figure 7, *b*, *c*, presented in Tables 1, 2)

**Table 2.** Content of elements (at.%) in structural constituents of initial plasma SAGPS-coating

| Element | Number of spectrum (Figure 7, *c*) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| B | 4.8 | 0.0 | 55.4 | 0.0 | 0.0 | 0.0 | 52.5 |
| C | 7.1 | 42.0 | 6.4 | 0.6 | 0.0 | 2.2 | 5.1 |
| N | 2.9 | 1.1 | 1.1 | 0.0 | 0.0 | 46.7 | 0.6 |
| O | 60.4 | 2.4 | 10.3 | 76.9 | 71.4 | 10.6 | 13.6 |
| Al | 0.5 | 0.9 | 0.1 | 2.7 | 14.8 | 38.8 | 0.3 |
| Si | 0.2 | 51.6 | 0.2 | 7.4 | 7.2 | 0.9 | 0.6 |
| Zr | 30.0 | 2.0 | 26.5 | 8.9 | 0.3 | 0.8 | 27.3 |
| Main phase | $ZrO_2$ | SiC | $ZrB_2$ | $ZrSiO_4$ | $Al_2SiO_5$ | AlN | $ZrB_2$ |

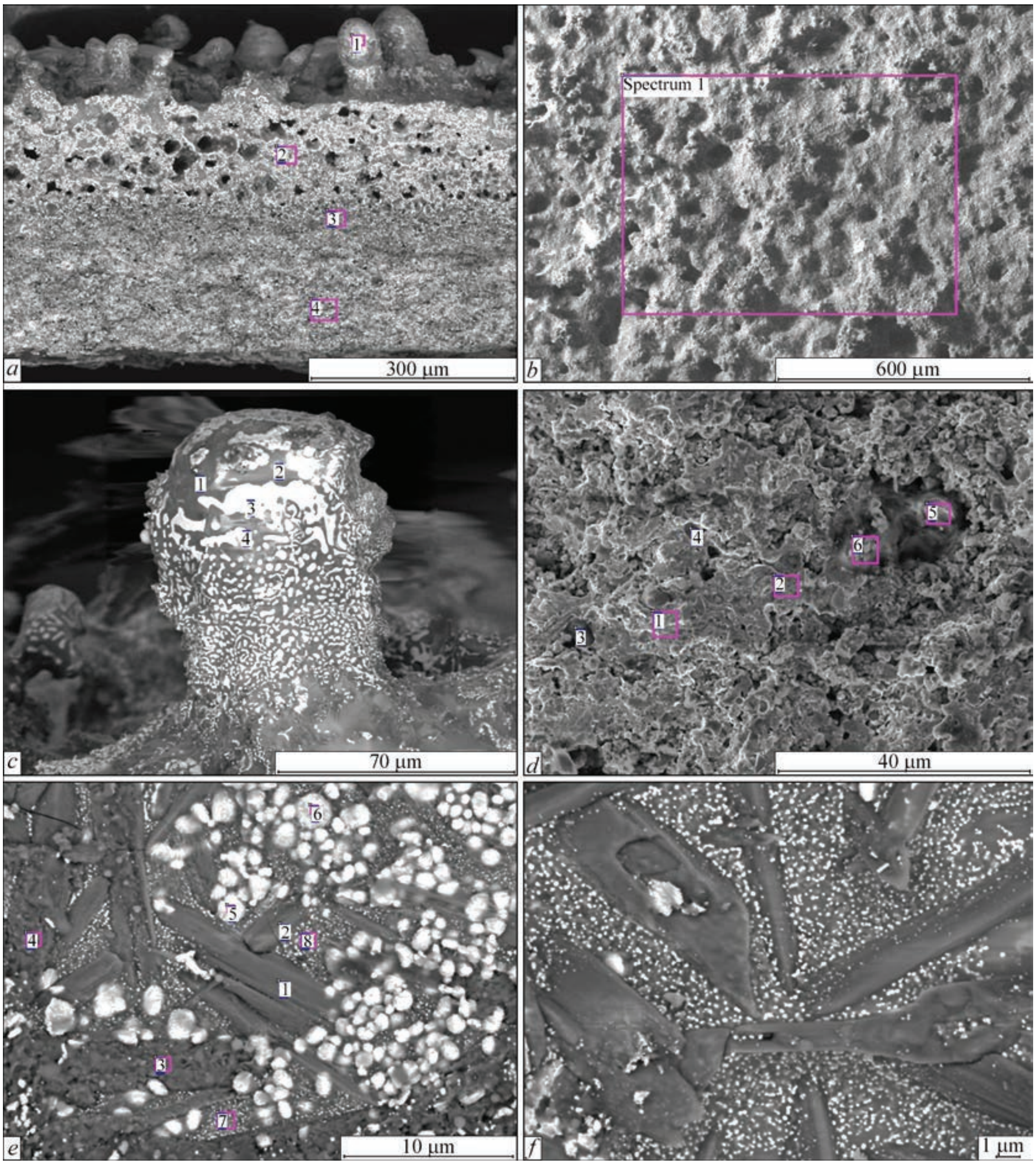

**Figure 8.** Electron micrograph of plasma SAGPS-coating of $ZrB_2$–SiC–AlN CP on surface of C/C–SiC CM after thermal cycling: *a* — section of sample with plasma coating; *b* — general view of coating surface; *c* — buildup on surface; *d* — coating section, general view; *e*, *f* — structure elements on coating surface

In a period of movement of particles of sprayed metal under conditions of atmospheric plasma spraying their interaction with environment oxygen and formation of products of their oxidation, that, in particular, is determined during deposition of coating from $ZrB_2$ [14], is inevitable.

When particles reach the substrate surface the effect of impact pressure results in deformation of

**Table 3.** Content of elements (at.%) in structural constituents of SAGSP-coating after thermal cycling

| Element | Number of spectrum (Figure 8, *d*) | | | | | | | | Number of spectrum (Figure 8, *c*) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 1 | 2 | 3 | 4 |
| B | 1.2 | 1.5 | 1.8 | 0.0 | 1.7 | 0.9 | 3.2 | 0.0 | 0.0 | 0.0 | 0.0 | 2.6 |
| C | 0.7 | 0.7 | 0.5 | 0.4 | 1.8 | 2.8 | 2.1 | 0.9 | 1.6 | 0.6 | 4.3 | 3.7 |
| N | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| O | 69.6 | 61.1 | 65.4 | 67.7 | 71.9 | 71.1 | 51.6 | 72.4 | 62.1 | 61.3 | 73.0 | 62.0 |
| Al | 21.7 | 24.4 | 26.6 | 26.6 | 3.7 | 3.6 | 21.0 | 10.6 | 27.0 | 21.6 | 0.2 | 0.6 |
| Si | 6.5 | 6.7 | 5.1 | 4.6 | 3.0 | 2.0 | 16.0 | 12.5 | 13.2 | 16.2 | 0.1 | 0.0 |
| Zr | 0.1 | 0.3 | 0.2 | 0.2 | 17.3 | 18.9 | 4.2 | 2.4 | 2.6 | 0.1 | 34.0 | 30.2 |
| Main phase | $Al_2SiO_5$ | | | | $ZrO_2$ | | Mixture $Al_2SiO_5$ and $Al_2O_3$ | | $Al_2SiO_5$ | | $ZrO_2$ | |

sprayed particle with formation of splats. Simultaneously, there is oxidation of surface of particles forming the coating.

The size of splats, their thickness, determining the cooling rate of their material, is related with value of impact pressure, which is determined by particle velocity and its density. Thus, in the case of application of method of plasma subsonic spraying for $60ZrB_2$–20SiC–20AlN CP particles of 60 μm size the impact pressure makes 50–75 MPa and at supersonic method it is 400–500 MPa. In both cases it exceeds the indices used in technology of hot pressing of UHTC of similar composition (48 MPa) [20].

Thus, considered above circumstances of formation of coatings from UNTC of $ZrB_2$–SiC–AlN CP during plasma spraying in air using operations of preliminary heating of C/C–SiC CM surface being sprayed show that the process takes place by means of fast heating of the particles on initial length of plasma jet up to complete melting of material of all components with formation of particles from mixture of $ZrB_2$, SiC and AlN melts not interacting with each other. The processes of interphase interaction of particle surface with ambient oxygen-containing medium develop at the stage of movement of these particles into the volume of plasma jet with variable values of its temperatures, velocities and composition of environment. This results in formation of oxidation products, recirculation of these products into the particle volume that causes their interphase interaction with formation of complex compounds. Presence of silicate phases $Al_2SiO_5$ and $ZrSiO_4$ in the structure of initial coating indicate the processes of oxidation in a volume of spray particles at interaction with environment in time of its movement in plasma jet as well as interphase phenomena into a volume with mullite phases and zircon synthesis.

Described scheme of the process of formation of composition and structure of initial plasma coating is proved by data of XRD of spray powder and coating (Figure 5). Absence of boron-containing phases is apparently related with temperature mode of particle heating, promoting transition of $B_2O_3$ into gas or amorphous phase. Found amorphous phase can be also related with appearance of silicate Al–Si–O phase.

During cyclic heating of coating surface there is formation in its volume a temperature field related with heating mode, power of heat source, thermal physical properties of coating and substrate, sample and coating sizes. Pattern of temperature distribution determines the development of phase transformations over coating thickness.

The coating, presented in Figure 8, *a*, consists of three zones. Formation of pores in the upper part of coating layer (Figure 8, *a*) is connected with temperature fields formed in coating volume during thermal cycling process. The reason for appearance of pores is change in coating material volume taking place in oxidation of $ZrB_2$ according to reaction $ZrB_2 + 2.5O_2 = ZrO_2 + B_2O_3$. At that there is formation of 1 g/mole of $ZrO_2$ and 1 g/mole of $B_2O_3$, which have volume of 22.4 $cm^3$ and 38 $cm^3$. That results in increase of initial volume of $ZrB_2$ component to 60.4 $cm^3$ or in 3.3 times. Active evaporation of $B_2O_3$ and formation of porous structure of this layer occur in subsequent coating heating to 1100 °C. Thickness of porous coating layer is approximately 150 μm that is obviously related with value of depth of its heating in thermal cycling to around 1100 °C . Vapors of $B_2O_3$ come out from the coating forming the channels (Figure 8, *c*) and entrailing the material of aluminum silicate melt $Al_2SiO_5$ with appearance of buildups on the surface (Figure 8, *c*).

Examination of thin structure of surface and coating section (Figure 8, *e*, Table 3) showed the presence of high-disperse (0.1–2.0 μm) inclusions of $ZrO_2$-phase in $Al_2SiO_5$ matrix phase. It can be explained following form presence of quasi-binary system of phase equilibrium $Al_2SiO_5$–$ZrO_2$, where transition of $ZrO_2$ in $Al_2SiO_5$ melt is shown [25] (Figure 9).

In respect of this the process of thermal cycling leads to precipitation of more refractory phase $ZrO_2$

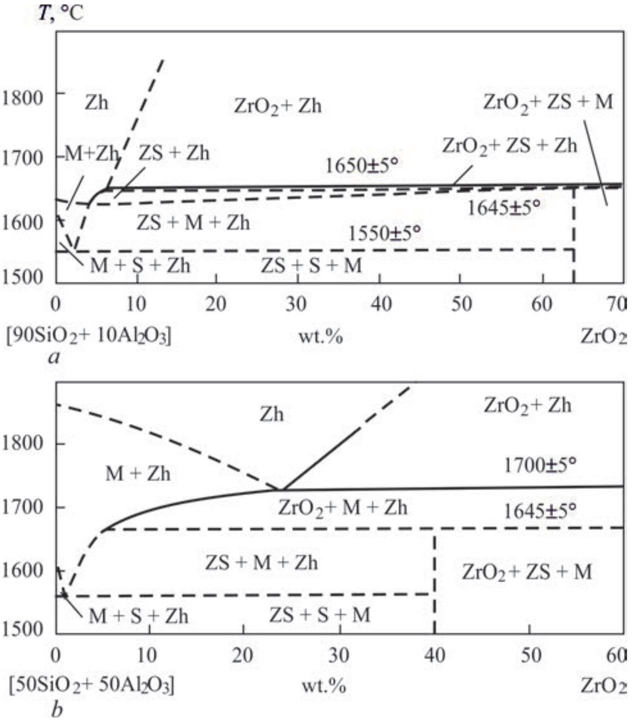

**Figure 9.** Diagram of state of several sections of particular triple system $3Al_2O_32SiO_2$–$ZrO_2$–$SiO_2$ (on Quercshi and Brett): *a* — section [$90SiO_2$ + $10Al_2O_3$] – $ZrO_2$; *b* — section [$50SiO_2$ + $50Al_2O_3$–$ZrO_2$]; C — crystobalite; M — mullite

from $Al_2SiO_5$ matrix, having melting temperature 1850 °C.

Presence of porosity and $ZrO_2$ inclusions shall assist decrease of heat conductivity of coating material in this zone that allows it performing functional characteristic of thermal protection from external heat source.

Content of the second below zone of the coating of around 100 μm thickness following the analysis results includes $ZrO_2$, $Al_2SiO_5$ and $B_2O_3$ and has dense structure that indicates its formation under conditions of temperatures below 1100 °C. Presence of a liquid phase $B_2O_3$ (probably triple alumoborosilicate phase $Al_2O_3 \times SiO_2 \times B_2O_3$), impregnating the coating layer, provides density and protective properties [24].

Lower coating zone, adjacent to surface of substrate — CM C/C–SiC of around 150 μm thickness, corresponds on composition to the coating in the initial sprayed state, i.e. $ZrB_2$–SiC–AlN with oxide inclusions.

Thus, under these experimental conditions with performance of thermal cycling heating there was formed a three-layer coating consisting of $Al_2SiO_5$–$ZrO_2$ porous external layer; intermediate dense one, having protective properties of $Al_2SiO_5$–$ZrO_2$ layer, containing $B_2O_3$, and a layer in contact with C/C–SiC base, consisting of components of initial plasma coating — $ZrB_2$, SiC, AlN with presence of products of their oxidation.

**Conclusion.** Formation of protective coating on surface of C/C–SiC CM under conditions of atmospheric (in open air) plasma spraying using composite powder (CP) $60ZrB_2$–20SiC–20AlN (wt.%) takes place by means of heating of CP particles during movement in volume of plasma jet to melting stage in related processes of their interaction with environment and interphase phenomena in the volume of composite $ZrB_2$–SiC–AlN particle with their next deformation and laying on the surface of C/C–SiC base under effect of impact pressure.

Composition of sprayed plasma $ZrB_2$–SiC–AlN-coating depends on level of heating of CP particles and development of interphase interaction of their components ($ZrB_2$, SiC, AlN) with high-temperature gas medium ($O_2$, $N_2$, Ar) as well as into a volume of particles between their components. Time of staying of CP particles in the plasma jet and dynamics of the processes of their heating and acceleration are caused by the parameters of the process of plasma spraying (composition and consumption of plasma gases, plasmatron power, spraying distance).

Experimental work on atmospheric plasma spraying of coatings from CP $60ZrB_2$–20SiC–20AlN on surface of C/C–SiC CM was carried out using subsonic plasma jet obtained at plasmatron power 24 kW and plasma gas Ar/$N_2$ , and supersonic plasma jet forming at plasmatron operation of 82 kW power with air as plasma gas.

A calculation-theoretical evaluation of the main characteristics of the process of plasma spraying of coating from $60ZrB_2$–20SiC–20AlN CP (wt.%), having 4.4 g/cm$^2$ calculation density of particle material, such as temperature and velocity of plasma jet, velocity of particles of average diameter (60 μm), time of their spraying in plasma jet was carried out using CASPSP program for computer simulation of process of plasma spraying. In the case of parameters of subsonic and supersonic plasma spraying used in the experiments performance the approximate calculation values of the temperature of plasma jet made 10000 and 6000 °C , jet velocity — 600 and 2500 m/s, time of staying of spray particles in jet volume — 0.5–3.0 and 0.2–1.5 ms, respectively.

The calculation value of impact pressure in particle impact on substrate made 47–75 and 400–500 MPa, respectively.

XRD data of coatings obtained under conditions of atmospheric plasma spraying in comparison with XRD of initial $60ZrB_2$–20SiC–20AlN CP indicate appearance in the coatings of new phase-products of interaction of sprayed particles with environment oxygen ($ZrO_2$, $Al_2SiO_5$, $ZrSiO_4$). This phenomenon was absent in the case of application of the technology of plasma spraying of $ZrB_2$–SiC coating in closed chambers with controlled medium [11].

Analysis of the results of XRD and optical metallography allowed determining some difference of phase composition of the coatings, obtained using plasma jet with subsonic and supersonic flow velocity.

Testing the heat resistance of $ZrB_2$–SiC–AlN-coating by means of cyclic heating by oxygen-propane-butane torch flame and following air cooling were carried out for 15 cycles, without failure and delaminations of coating of around 400 μm thickness.

Three-zone structure of plasma $ZrB_2$–SiC–AlN-coating with change of content of oxygen deep inside the coating from 50 to 30 wt.% is formed under effect of thermal cyclic heating. An upper zone consists of mullite $Al_2SiO_5$ being a matrix constituent of the coating with multiple $ZrO_2$ inclusions of submicrone size and has porosity formed as a result of evaporation of initially formed sections of $B_2O_3$ phase. A middle zone contains a mixture of $ZrO_2$ phases and silicates (or borosilicates) and $Al_2O_3$–$SiO_2$–$B_2O_3$ system. It is characterized with high density and resistance to $O_2$ diffusion that determines its protective properties. A lower zone located in contact with C/C–SiC CM surface corresponds on composition to initial sprayed coating $ZrB_2$–SiC–AlN with inclusions of oxide phases — its oxidation products.

High-temparature resistance testing of plasma $ZrB_2$–SiC–AlN coating under conditions of cyclic heating with oxygen-propane-butane torch flame during 2 min with cooling on air showed that the coating conserved integrity and its protective properties after 15 cycles of heating.

1. Sorokin, O.Yu., Grashchenkov, D.V., Solntsev, S.St., Evdokimov, S.A. (2014) Ceramic composite materials with high oxidation resistance for perspective aircrafts (Review). *Trudy VIAM*, 06–08 [in Russian].
2. Roger, R., Naslain, R. (2005) Fiber-reinforced ceramic matrix composites: state of the art, challenge and perspective. *Composites*, 5(**1**), 3–19.
3. Krenkel, W., Berndt, F. (2005) C/C–SiC composites for space applications and advanced friction systems. *Mat. Sci. and Engng. A*, **412**, 177–181.
4. Heidenreich, B. (2007) Carbon fibre reinforced SiC materials based on melt infiltration. *Proc. of 6th Int. Conf. on High Temperature Ceramic Matrix Composites* (HTCMC 6).
5. Kumar, S., Chandra, R., Kumar, A. et al. (2015) C/SiC composites for propulsion application. *Composites and Nanostructures*, 7(**4**), 225–230.
6. Tkachenko, L.A., Shuvalov, A.Yu., Berlin, A.A. (2012) High-temperature protective coatings of carbon materials. *Neorganicheskie Materialy*, 48(**3**), 261–271 [in Russian].
7. Lebedeva, Yu.E., Popovich, N.V., Orlova, L.A. (2013) High-temperature protective coatings for composite materials based on SiC. *Trudy VIAM*, **12**, 1–7 [in Russian].
8. Xiang Yang, Chen Zhao-hui, Cao Feng (2014) High-temperature protective coatings for C/SiC composites. *J. of Asian Ceramic Societies*, 2(**4**), 305–309.
9. Sufang Tang, Jingyi Deng, Shijun Wang et al. (2007) Ablation behaviours of ultra-high temperature ceramic composites. *Mat. Sci. and Engng. A*, **465**, 1–7.
10. Marschall, J., Pejakovic, D.A., Fahrenholtz, W.G. et al. (2009) Oxidation of $ZrB_2$–SiC ultrahigh-temperature ceramic composites in dissociated air. *J. of Thermophysics and Heat Transfer*, 23(**2**), 267–278.
11. Valente, T., Bartuli, C., Visconti, G., Tului, M. (2000) Plasma sprayed ultra high temperature ceramics for thermal protection systems. In: *Proc. ITSC'2000*, 837–841.
12. Bartuli, C., Valente, T., Tului, M. (2001) High temperature behavior of plasma sprayed $ZrB_2$–SiC composite coatings. In: *Thermal Spray 2001: New Surfaces for a New Millenium*. Ohio, USA, 259–262.
13. Bartuli, C., Valente, T., Tului, M. (2002) Plasma sprayed deposition and high temperature characterization of $ZrB_2$–SiC protective coatings. *Surfaces and Coating Technology*, **155**, 260–273.
14. Tului, M., Ruffini, F., Arezzo, F. et al. (2002) Some properties of atmospheric air and inert gas high-pressure plasma sprayed $ZrB_2$ coatings. *Ibid.*, **151-152**, 483–489.
15. Tului, M., Marino, G., Valente, T. (2006) Plasma spray deposition of ultra high temperature ceramics. *Ibid.*, **201**, 2103–2108.
16. Tului, M., Lionetti, S., Pulci, G. et al. (2008) Effects of heat treatments on oxidation resistance and mechanical properties of ultra high temperature ceramic coatings. *Ibid.*, **202**, 4394–4398.
17. Tului, M., Lionetti, S., Pulci, G. et al. (2010) Zirconium diboride based coatings for thermal protection of re-entry vehicles: Effect of $MoSi_2$ addition. *Ibid.*, **205**, 1065–1069.
18. Zou, B., Khan, Z.S., Fan, X. et al. (2013) A new double layer oxidation resistant coating based on $Er_2SiO_8/LaMgAl_{11}O_{19}$ deposited on C/SiC composites by atmospheric plasma spraying. *Ibid.*, **219**, 101–108.
19. Zou, B., Khan, Z.S., Gu, L., Fan, X. et al. (2012) Microstructure, oxidation protection and failure mechanism of $Yb_2SiO_5/LaMgAl_{11}O_{19}$ coating deposited on C/SiC composites by atmospheric plasma spraying. *Corrosion Sci.*, **62**, 192–200.
20. Grigoriev, O.N., Panasyok, A.D., Podchernyaeva, I.A. et al. (2018) Mechanism of high-temperature oxidation of composite ceramics based on $ZrB_2$ of $ZrB_2$–SiC–AlN system. *Poroshk. Metallurgiya*, **1/2**, 93–98 [in Russian].
21. Borisov, Yu.S., Krivtsun, I.V., Eritt, U. (2000) Computer modelling of plasma spraying process. *The Paton Welding J.*, **12**, 40–50.
22. Petrov, S.V., Karp, I.N. (1993) *Plasma gas-air spraying*. Kiev, Naukova Dumka [in Russian].
23. Ordanyan, S.S., Dmitriev, A.I., Moroshkina, E.S. (1987) Interaction of SiC with $ZrB_2$. *Izv. AN SSSR. Neorganicheskie Materialy*, 1752–1754 [in Russian].
24. Krivoshein, D.A., Maurakh, M.A., Dergunova, V.S. et al. (1980) Mechanism of formation of glass-like films on surface of material of $ZrB_2$–ZrC–SiC–C system in its oxidation. *Poroshk. Metallurgiya*, **8**, 58–62 [in Russian].
25. Toropov, N.I., Barzakovsky, V.P., Lapin, V.V. et al. (1972) *State diagrams of silicate systems*: Handbook, Issue 3. Leningrad, Nauka, 290–293 [in Russian].

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