

Pulsed vacuum-arc evaporation of the $\text{ZrB}_2\text{--SiC}$ composite for obtaining amorphous Zr--B--Si--C--(N) coatings

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The possibility of depositing amorphous coatings of the Zr--B--Si--C(N) system by pulsed vacuum-arc deposition using a composite $\text{ZrB}_2\text{--SiC}$ cathode is demonstrated. The pulsed character of the deposition mode provided a minimal thermal load, formation of homogeneous coatings with a low fraction of droplet phase, and their amorphous state.

Keywords: amorphization, heat-resistant coatings, zirconium diboride, silicon carbide.

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Composites of the $\text{ZrB}_2\text{--SiC}$ system are actively studied in the form of both bulk materials [1] and coatings [2]. In the field of aerospace engineering, materials based on this system are considered as barrier layers providing protection against oxidation and ablation [3], while in nuclear power engineering they are used as absorbing materials and diffusion barrier layers [4]. Service life of such layers is determined by low diffusion mobility of the coating-material components. One of the ways to reduce diffusion coefficients and increase chemical inertness of the coatings is to make them amorphous. An amorphous material structure devoid of extended grain boundaries is able to provide high barrier and corrosion characteristics. In this regard, developing and studying amorphous modifications of coatings based on the Zr--B--Si--C system become relevant. This paper considers specific features of the phase formation and elemental composition of this-system coatings obtained by the pulsed vacuum-arc method.

Cathodes for deposition were fabricated by spark plasma sintering from a mixture of ZrB_2 (80 vol.%) and SiC (20 vol.%) powders (the powder fraction was 14–20 μm) on a Labox-650 setup (at the temperature of 1600 °C, isothermal holding time of 300 s, pressure of 50 MPa, heating rate of 1.67 °C/s, in vacuum). Prior to sintering, the samples were mixed in a ball mill at the drum rotation speed of 0.73 s^{−1}, ratio of grinding bodies mass to the powder mass of 6:1, and mixing duration of 2.88 · 10⁴ s (8 h).

The Zr--B--Si--C coatings were deposited by the pulsed vacuum-arc method at the 300 mm source-to-substrate distance, 30 Hz pulse generation frequency, ~ 2 J pulse energy, and 1.08 · 10⁴ s (3 h) deposition time in a residual vacuum atmosphere of 6.67 · 10^{−3} Pa on the WC-6 (WC–Co (6 wt.%)), EC-61 (Inconel 718) and WC-96 (vacuum–dense Al_2O_3) substrates. Prior to deposition, the substrates were pre-washed with isopropyl alcohol in an ultrasonic bath at 40 °C for 20 min. The Zr--B--Si--C--N

coatings were deposited under similar conditions but in the N_2 atmosphere at 5.33 · 10^{−2} Pa.

The morphology, structure, and phase and elemental compositions of the coatings were examined by scanning electron microscopy (SEM) (Vega 3SB, Tescan, Czech Republic), transmission electron microscopy (TEM) (JEM-2100, JEOL, Japan), X-ray phase analysis (Ultima 4, Rigaku, Japan) based on the CoK_α radiation, and X-ray photoelectron spectroscopy (XPS) (PHI-5500, Physical Electronics, USA). To obtain depth concentration profiles, we used etching with 2 keV Ar ions at the raster of 2 × 2 mm and etching rate of about 10 nm/min.

Material of the sintered cathodes consisted of two phases: a ZrB_2 matrix and SiC arbitrary-shaped inclusions, which is confirmed by the surface image (Fig. 1, *a*) and peaks revealed in the diffraction pattern (Fig. 1, *b*). The observed broadening of reflections in the sintered compact diffraction pattern (the ZrB_2 101 reflection half-width increased from 0.22 to 0.44°) may be caused by the formation of linear defects under the load applied during sintering.

The deposited coatings contained an insignificant amount of the droplet phase (droplet density of 12.4 μm^{-2} ; [supplementary materials](#) available online have shown that the droplet density for similar coatings obtained by using a stationary arc is 48.9 μm^{-2}) (Fig. 2, *a*), which is explained by a decrease in the cathode thermal load in the process of deposition. Thickness of the Zr--B--Si--C and Zr--B--Si--C--N coatings was about 1.3 μm (Fig. 2, *b*). The coatings are amorphous: the TEM images do not exhibit crystalline structure, electron-diffraction pattern demonstrates only a halo (Fig. 2, *c*), and diffraction patterns show only the substrate peaks and halo in the range of small diffraction angles (Fig. 2, *d*).

Amorphization of the system during deposition may be explained by the Inoue's rule for the bulk amorphous material formation [5]: all the system components have negative mixing enthalpies [6] (the infographics is given in

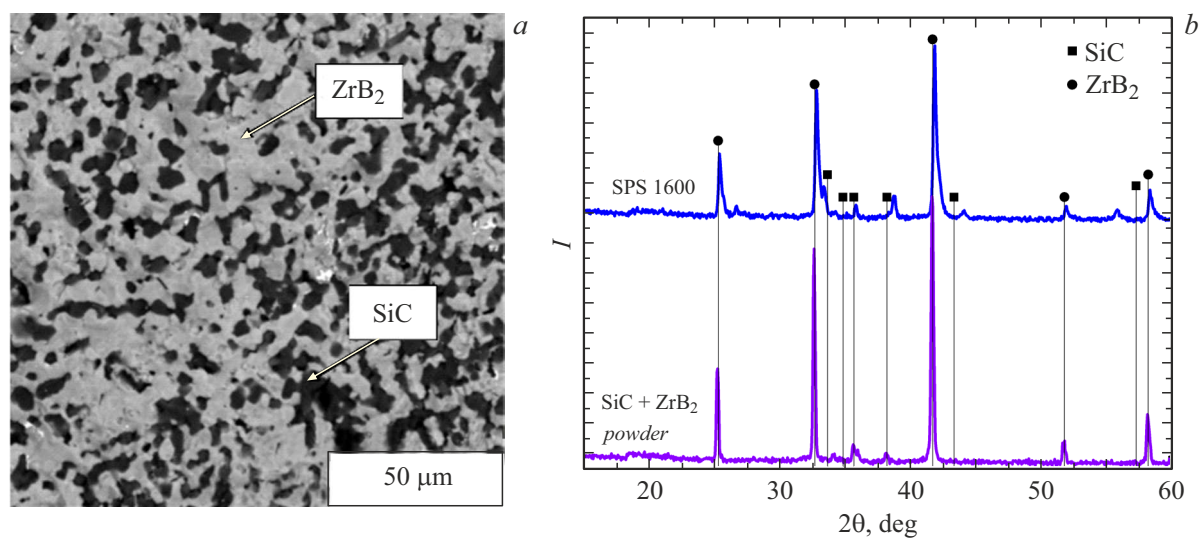


Figure 1. SEM image of the sintered cathode surface obtained in the backscattered-electron mode (a), and diffraction patterns of the initial powder mixture ($\text{SiC} + \text{ZrB}_2$) and sintered compact (SPS 1600) (b).

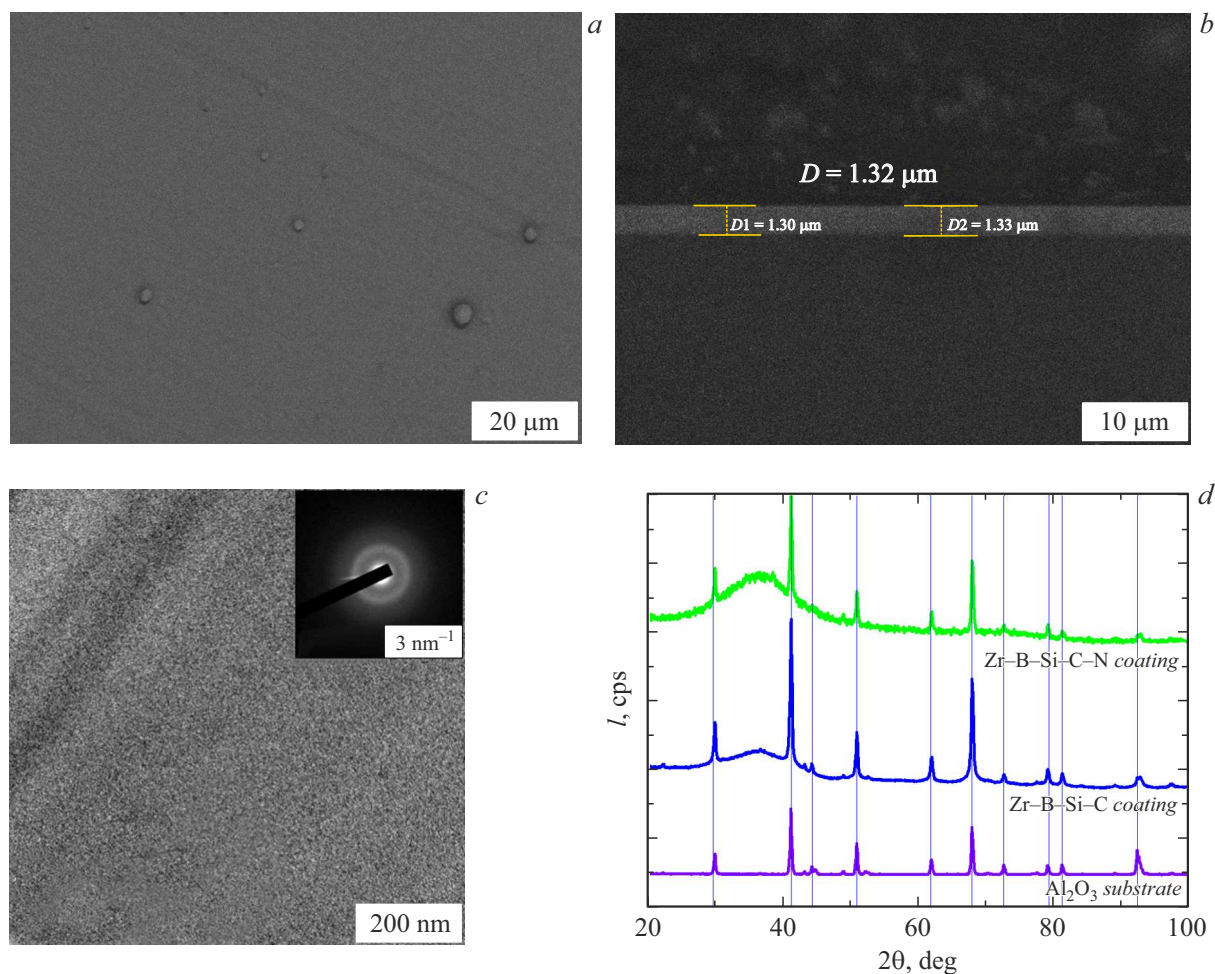


Figure 2. Typical SEM images of the surface (a) and end face (the coating thicknesses are indicated) (b), TEM image and electron diffraction pattern of the depicted area (c), and diffraction patterns (d) of the Zr-B-Si-C-N coatings.

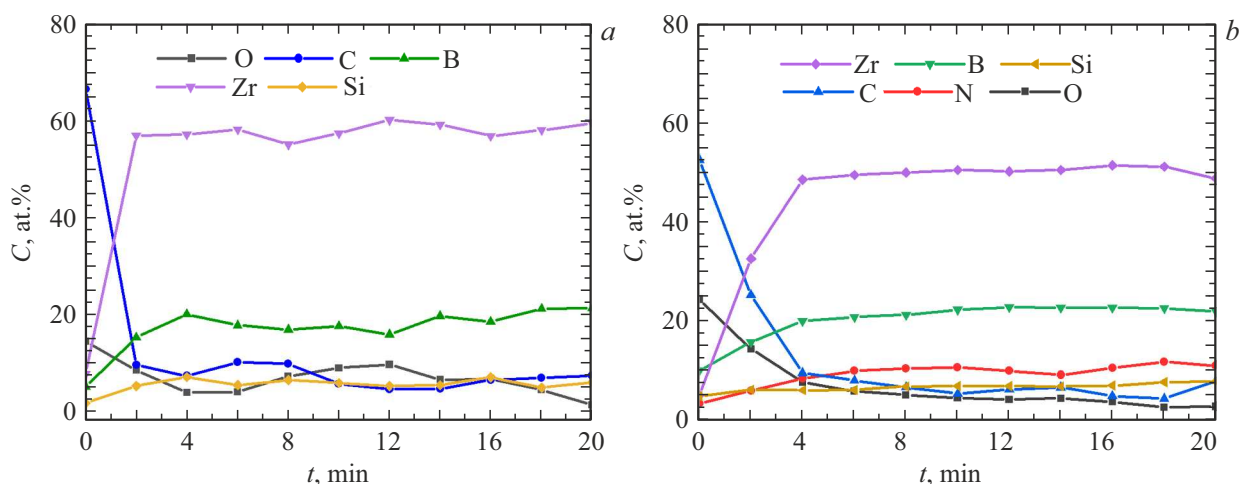


Figure 3. Elemental concentration profiles in the Zr-B-Si-C (a) and Zr-B-Si-C-N (b) coatings (etching rate was 10 nm/min).

the supplementary materials), and the system cooling rate during the plasma flow condensation on the substrate is hundreds of degrees per second [7]. The pulsed deposition mode provides reducing the substrate heating and avoiding crystallization of the amorphous coating.

Elemental compositions of the coatings were assessed based on XPS concentration profiles of the elements (Fig. 3), since the presence of light elements (boron, carbon, silicon) in the cathode and coatings limits the application of energy-dispersive spectroscopy for quantitative assessment of elemental composition. Compositions of the coating and sputtered cathode exhibit a significant difference: a higher content of Zr and low concentration of B, C and Si. This may be connected with several factors. First, the ratio between elements in plasma may differ significantly from that in the cathode. This is typical of borides, carbides and silicides. For instance, paper [8] showed that, in the case of the Zr-76% Si cathode, plasma predominantly contained the Zr^{2+} ions (73 at.%), while paper [9] demonstrated that in the case of the SiC cathode the Si ion content in plasma was 60 at.%. Second, kinetic energy of the B, C and Si ions will be, due to their smaller mass, significantly lower than that of Zr at equal velocities, which impedes ions of lighter elements from reaching the substrate surface because they lose their energy in collisions with residual gas atoms.

High-resolution X-ray photoelectron spectra of the Zr-B-Si-C and Zr-B-Si-C-N coatings confirm active interaction of the coating components with each other. In the $Zr3d$ spectrum, three doublets are distinguished for both coatings: the first one at 179.1–179.3 eV corresponds to ZrB_2 , ZrC [10]; the second one is located at 179.5–180.4 eV which is close, as per reference data, to the Zr-N, Zr-Si bonds (180.9 eV [11]); the third one at 182.4–182.6 eV corresponds to ZrO_2 . In the $Si2p$ spectrum for the Zr-B-Si-C coating, one doublet was revealed at 98.8 eV. This energy belongs to the silicide range [12]. Additional peaks in the Zr-B-Si-C-N coating at 100.9 and 102.6 eV correspond to mixed bonds Si-Si/Si-O/Si-N. For $B1s$,

one peak is observed at 187.5–187.7 eV, which corresponds to boride ZrB_2 (187.9 eV) [13]. For $C1s$, the carbide peak binding energy (E_b) is of 282.5–282.7 eV, which may correspond to the Si-C-Zr mixed bond. The E_b reference values are as follows: 283.0 eV in SiC [14], 282.1 eV in ZrC [15]. The $N1s$ spectrum exhibits one peak at $E_b = 397.1$ eV, which may mean bonds Si-N (397.4 eV) [16] and Zr-N (397.7 eV) [11]. The Si and Zr spectra also contain doublets indicating binding with nitride.

The absence of significant heterogeneity of the coating elemental composition, which was observed in the cathode, is caused by that the characteristic size (about 100 μm) of the cathode spot where the material transforms into vapor is larger than the size of filler (SiC in Fig. 1, a). The cathode SEM images after deposition are given in supplementary materials.

Thus, the study has shown the possibility of obtaining amorphous coatings based on the Zr-B-Si-C-(N) system by the method of pulsed vacuum-arc deposition. The pulsed mode enabled minimizing the thermal load on the substrate and cathode, which ensured formation of uniform coatings with a low droplet phase content. By analyzing the coating structures, we have demonstrated their amorphous state caused by formation of a complex network of chemical bonds (Zr-B, Zr-C, Si-C, and also Zr-N and Si-N in the presence of nitrogen) and high rate of the plasma flow cooling. The observed deviation of the coating elemental compositions from that of the cathode, that is, enrichment with zirconium, is explained by peculiarities of the plasma formation and ion transfer.

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Conflict of interests

The authors declare that they have no conflict of interests.

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