Cathodic arc-PVD Zr-B-Si-C-Ti-(N) coatings

I V Blinkov, D S Belov, V M Shestakova, A V Chernogor, B Yu Kuznetsov and A I Laptev

National University of Science and Technology «MISiS», 119049, 4, Leninskiy prospect, Moscow, Russia

E-mail: biv@misis.ru

Abstract. Arc-PVD coatings Zr-B-Si-C-Ti-N and Zr-B-Si-C-Ti were obtained using combined evaporated ZrB₂-SiC-Ti cathodes in a residual atmosphere of N₂ and Ar. Their structure and composition were investigated. The Zr-B-Si-C-Ti-N coating has a predominantly amorphous structure, formed mainly on the basis of nitride, carbide, boride phases and complex compounds Zr, Si, Ti. The Zr-B-Si-C-Ti coating is characterized by an amorphous-nanocrystalline structure. The amorphous component of this coating is formed mainly by phases based on Zr and Si. The nanocrystalline structure is formed by a complex carbide (Zr, Ti) C.

1. Introduction
Thermal spray coatings ZrB₂ – SiC are being investigated to study the possibility of their application for protection against high-temperature oxidation of structural materials [1, 2]. However, the high porosity of coatings, low adhesive strength with the substrate, realized by this method, do not make it possible to consider them as simultaneously increasing the wear-resistant characteristics of rubbing structural elements operating in an oxidizing environment at high temperatures. This work is devoted to studying the possibilities of forming coatings of this system by the arc-PVD method, which is widely used to create coatings with a variety of functional properties, making it possible to use them as wear-resistant in various operating conditions [3].

2. Experimental details
The coatings were deposited on substrates made of WC – 6 wt.% Co alloy and EK61 heat-resistant nickel-based alloy by the arc-PVD method. The evaporated cathode was made of a combined cylindrical powder composite insert ZrB₂ (80 vol.% or 88.4 wt.%) - SiC (20 vol.% or 11.6 wt.%) 58 mm in diameter and 15 mm in height, prepared by the spark plasma sintering method, which was pressed into a metal base made of titanium (titanium alloy, Ti ~ 99.7 wt.%) with a diameter of 62 mm. The current and voltage of the evaporating arc were 110A and 20V. A negative bias potential of 120V was applied to the substrate. The partial pressure of nitrogen during the formation of coatings Zr-B-Si-C-Ti-N was 0.8 Pa. The argon pressure during the deposition of Zr-B-Si-C-Ti coatings was 0.4 Pa.

The phase and elemental composition, characteristics of the coatings structure were investigated by the X-ray diffractometry methods using a sliding X-ray beam and micro X-ray spectral analysis. Their structure was studied using a transmission electron microscope (TEM). The binding energy of the coating elements was analyzed using X-ray photoelectron spectrometry.
3. Results and discussion

The elemental composition of the formed coatings is given in the table 1.

| Residual atmosphere | Element content, at. % |
|---------------------|-----------------------|
|                     | N  | C  | B  | Si | Zr | O  | Ti |
| N₂                  | 24,0 | 22,4 | 18,4 | 18,0 | 11,4 | 3,0 | 2,8 |
| Ar                  | -  | 33,8 | 23,6 | 18,4 | 15,1 | 3,1 | 6,0 |

Figure 1 shows images of the coatings end fractures. They have a monolithic structure. Fractographic studies indicate a different destruction mechanism of the obtained samples. For the Zr-B-Si-C-Ti-N coating, it occurs by a brittle cleavage mechanism with a characteristic feature - the formation of intergranular facets in the microrelief. The destruction of the Zr-B-Si-C-Ti coating is viscous. It is accompanied by the merging of microvoids with the pits formation of a fibrous-banded fracture in the microrelief [4].

![Figure 1. Images of the coatings end fracture Zr-B-Si-C-Ti-N (a) and Zr-B-Si-C-Ti (b).](image)

Diffraction patterns of the obtained coatings Zr-B-Si-C-Ti-N and Zr-B-Si-C-Ti are shown in figure 2. It follows from them that the composition of the coatings predominantly contains X-ray amorphous phases. An approximate estimate based on the ratio of the areas under the halo and diffraction lines from crystalline phases indicates the degree of amorphization of the coating structure at 88% and 75%, respectively, for the first and second coating compositions.

The images of the coatings structure (figure 3) and the electron diffraction patterns obtained by the TEM method confirm the results of X-ray diffraction analysis on the predominantly amorphous structure of both coatings compositions and the greater degree of amorphization of the Zr-B-Si-C-Ti-N coatings. TEM images indicate elemental and phase heterogeneity of the coatings. They can be judged by the different background shade of coatings areas, shown in the figure 3. Dark areas correspond to phases based on heavier elements, and light - on lighter ones [5]. The sizes of the regions of structural heterogeneity of the coatings vary from 1 to 10 nm and from 1 to 50 nm for the Zr-B-Si-C-Ti-N (a) and Zr-B-Si-C-Ti coatings, respectively. Their clear periodicity is not observed. The EDS analysis showed that the phases in the light areas (area 1) are formed mainly by Si and Zr elements, and the phases in the dark areas (area 2) are formed by Ti.
Figure 2. Diffraction patterns: Zr-B-Si-C-Ti-N (a) and Zr-B-Si-C-Ti (b).

Figure 3. TEM images and electron diffraction patterns of the cross-section of the coatings structure Zr-B-Si-C-Ti-N (a, b) and Zr-B-Si-C-Ti (c, d).
Moreover, high-resolution figures show that it is the dark regions in the structure of the Zr-B-Si-C-Ti coatings that are characterized by a crystalline structure with a crystallite size of ~ 10 nm located in an amorphous matrix. Taking into account the obtained electron diffraction patterns, these phases have an fcc structure and can be assigned to titanium and zirconium carbides, or to complex carbide (Zr, Ti) C.

The XPS study of the Zr-B-Si-C-Ti-N coating indicates that the maximum of the Zr3d spectral line corresponds to 180.0 eV, which belongs to zirconium carbide. The Si2p spectrum contains a line with an energy of ~ 101.1 eV. This value is in the range of reference values for SiC (100.2 eV) and Si3N4 (101.8 eV) and corresponds, apparently, to silicon carbonitride. The Ti2p spectrum consists of one doublet, $E_b$ (Ti2p3) - 454.7 eV, that is slightly lower than for titanium nitride (454.9 eV). Perhaps this is determined by the formation of Ti-Ti, Ti-B bonds. The spectrum of boron B1s is located at $E_b$ 188.2 eV, which characterizes the energy of Zr-B bonds.

In the Zr-B-Si-C-Ti coating for the Ti2p spectrum, a peak of 454.8 eV is observed, which can be interpreted as titanium with a mixed type of Ti-Ti, Ti-C bond. The spectrum of Zr3d + B1s contains a peak at 179.7 eV, which corresponds to zirconium carbide. The presence of a boron peak with an energy of 188.2 eV can be explained by the presence of Zr – B bonds. The Si2p spectrum has two peaks: 99.9 and 101.1 eV. The main peak at 99.9 eV can be attributed to silicon carbide with a small fraction of Si – Si bonds. The second peak exceeds the SiC reference value (100.2 eV), so it can be attributed to SixOyCz, which is consistent with the presence of oxygen in the coating.

4. Conclusions
Coatings were obtained in the Zr-B-Si-C-Ti-N and Zr-B-Si-C-Ti systems by vacuum arc evaporation of ZrB2-SiC-Ti combined targets in a residual atmosphere of N2 and Ar. The Zr-B-Si-C-Ti-N coating has a predominantly amorphous structure, formed mainly on the basis of nitride, carbide, boride phases and complex compounds Zr, Si, Ti. The Zr-B-Si-C-Ti coating is characterized by an amorphous-nanocrystalline structure. The amorphous component of this coating is formed mainly by phases based on Zr and Si. The nanocrystalline structure is formed by a complex carbide (Zr, Ti) C. The increased degree of the structure amorphization of the Zr-B-Si-C-Ti-N coatings can be associated with a higher cooling rate of the forming coating due to the higher thermal conductivity of the residual nitrogen atmosphere as compared to argon.

Acknowledgments
The research was supported by the Russian Foundation for Basic Research, the project № 18-03-00321 A.

References
[1] Yang X, Wei L and Song W 2013 Composites Part B: Engineering 45 1391–6
[2] Wang D, Zeng Y and Xiong X 2014 Ceramics International 40 14215–22
[3] Krella A 2020 Coatings 10 921–34
[4] RD 50-672-88 Strength tests and calculations. Classification of fractures of metals 2018 (M.: Standartinform)
[5] Williams D B and Carter C B 2009 Transmission Electron Microscopy 407–17