Structure and properties of the surface layer of «Ti/SiC-ceramic» system irradiated by low-energy pulsed electron beam

A A Leonov1, E E Kuzichkin1, V V Shugurov2, A D Teresov2, M P Kalashnikov1, M S Petyukevich1, V V Polisadova1 and Yu F Ivanov2

1National Research Tomsk Polytechnic University, 30 Lenin Ave., Tomsk, 634050, Russia
2Institute of High-Current Electronics SB RAS, 2/3 Akademichesky Ave., Tomsk, 634055, Russia

E-mail: laa91@tpu.ru

Abstract. The results of the investigation of evolution structural phase states of the surface layer «film (Ti)/substrate (SiC-ceramics)» system subjected to processing with an intense pulsed electron beam are presented (Ti film 0.5 μm thick was deposited on the surface SiC ceramic). Samples of SiC ceramics obtained by SPS-sintering were used. Irradiation with an intense pulsed electron beam of submillisecond duration was carried out at the «SOLO» device under the condition: energy density of the electron beam of 15 J/cm², pulse duration of 200 μs, quantity of pulses – 20 and 30. The X-ray diffraction analysis of the treated electron beam «Ti/SiC» system showed that under the specified irradiation regime the phase composition formed in the surface layer and the volume fraction of the phases depend on the quantity of irradiation pulses. At 20 pulses, following phase composition of the surface layer was formed: SiC – 18.5 %, TiC – 36.6 %, Ti5Si3 – 44.9 %; at 30 pulses, a phase relationship: SiC – 81.6 %, TiC – 12.7 %, Si – 0.5 %, C – 5.2 %. Scanning and transmission electron microscopy revealed, that irrespective of the quantity of pulses of the electron beam, takes place the formation of a surface layer with a globular structure, formed as a result of melting of the titanium film, which contains a droplet fraction. The particles of the drop fraction had a submicro-nanocrystalline structure and were enriched mainly by titanium, silicon and carbon atoms. It was established that electron beam treatment with 30 pulses leads to formation of round-shaped regions on the surface of irradiation, the microhardness of which varies from 55 GPa to 96 GPa, which is several times the microhardness of the initial SiC ceramic (36 GPa). It was suggested that these regions were formed as a result of electron beam treatment of the surface layer, which contains a drop fraction.

1. Introduction
Silicon carbide is referred to a family of non-oxide ceramics and which is widely used construction materials in engineering, nuclear power engineering, defense industry enterprises for the manufacture of light armor and in microelectronics [1, 2]. To improve the technical characteristics of ceramic materials, a submicro- and nanocrystalline state is formed [3-6]. This is especially important for superhard ceramic materials, because this allows localizing plastic deformation at the submicron-scale level. This insure a uniform distribution of elastic stresses and increase the nucleation and initiation
energy of critical stress concentrators [3]. The method for modifying the material surface with intense pulsed low-energy (to 30 keV) electron beams of micro- and submillisecond exposure duration is referred to the modern microstructure regulation approach. It is shown that the effect of such beams on metals, alloys, cermet and ceramic materials is accompanied with the formation of an amorphous, nano and submicroncrystalline structure in the surface layer of the product [7, 8]. Significant changes in the structural-phase state in the surface volume of the material lead to an essential increase in physicochemical, electrophysical and strength properties, which is unattainable with traditional methods of surface treatment [6-8]. The purpose of this work was the formation of surface alloys of the "Ti/SiC-ceramic" system, which are practically impossible to obtain by traditional metallurgy methods because of the low mutual solubility of the components in the solid state and the significant difference in the melting points.

2. Samples and investigation methods

SiC powder with particle sizes (0.9-4.0 μm) and nanopowder of the same composition (particle size 60 nm) were used to create ceramic samples. SiC nanopowder (NEOMAT, with specific surface area of 32 m²/g) in an amount of 3 wt.% was added to the base powder. The main phase of the SiC powder used was a polytype with hexagonal unit cell SiC-6H; in a small amount there was a polytype with rhombohedral unit cell SiC-15R. Samples produced in the form of tablets with diameter of 14 mm and thickness of 3 mm were obtained by SPS-sintering [9] (SPS 515S, SPS SYNNEX). Sintering mode: sintering temperature 2100 °C, pressure up to 70 MPa and sintering time 10 min. After sintering, to conduct complex studies, the samples were subsequently ground and polished to a mirror state. The formation of the «film (Ti)/substrate (SiC-ceramics)» system was carried out on «KVINTA» unit (Institute of High Current Electronics SB RAS) by vacuum electric arc spraying of a target of technically pure titanium of the VT1-0 grade with plasma assistance («PINK» plasma generator) [10]. The thickness of the titanium film is 0.5 μm. The modification of the «film (Ti)/substrate (SiC-ceramics)» system was carried out with an intense pulsed electron beam at the «SOLO» (Institute of High Current Electronics SB RAS) setup with beam parameters: the accelerated electron energy U=18 keV, electron beam energy density $E_s = 15 J/cm^2$ for a pulse duration of $\tau = 200 \mu s$ and quantity of pulses $n = 20$ and 30 (the pressure of the residual gas (argon) in the working chamber is $10^{-2}$ Pa) [5-7].

Investigations of the structural-phase state of the modified surface layer of ceramics before and after the effect of the electron beam were carried out using the equipment of the Nano-Center TPU – scanning electron microscopy (JSM-7500FA, JEOL), transmission electron microscopy (JEM-2100F, JEOL) and X-ray diffractometer (XRD-7000S, Shimadzu). The mechanical characteristics of the modified layer were studied by microhardness using the Vickers diamond pyramid (PMT-3M, LOMO).

3. Results and considerations

Scanning electron microscopy has established that a titanium film formed on the surface of SiC ceramic is characterized by the presence a lot of amount of oval-shaped particles of the droplet fraction (figure 1). The sizes of drops are changing from tens nanometers to units of micrometers. Energy-dispersive X-ray spectroscopy (EDS) shown that droplets are formed preferably of titanium atoms (figure 1, table).

Irradiation of the «film (Ti)/substrate (SiC-ceramics)» system with an intense pulsed electron beam, irrespective of the quantity of pulses of the electron beam, is accompanied by the formation of a surface layer with a "smoothed" topography. On it educe areas of light contrast, formed as a result of the melting of a titanium film containing a droplet fraction (figure 2a). The specific regions have a submicro-nanocrystalline structure, which is detected by scanning electron microscopy (figure 2b).
The EDS method established that the areas of light contrast are enriched with titanium, silicon and carbon atoms (figure 3c, table); the space separating these areas is enriched with silicon and carbon atoms (figure 3b, table).

**Figure 1.** The structure of surface of the «film (Ti)/substrate (SiC-ceramics)» system before irradiation with an intense pulsed electron beam. Areas are marked and numbered for which the elemental composition (table) is determined.

| Range | C, at.% | Si, at.% | Ti, at.% |
|-------|---------|---------|---------|
| Range 1 | 0.04 | 0.57 | 99.39 |
| Range 2 | 0.01 | 0.95 | 99.04 |
| Range 3 | 2.47 | 4.57 | 92.96 |

Investigation of the elemental composition and defective substructure of the cross-section of the surface layer of an electron beam-modified of the «film (Ti)/substrate (SiC-ceramics)» system was carried out by scanning electron microscopy (brittle fracture method) and transmission electron microscopy (transverse foil method). In figure 4 (scanning electron microscopy) and figure 5 (transmission electron microscopy) presents characteristic images of the structure of cross-section of the ceramic. See distinctly that the droplet fraction has a nanocrystalline structure, the crystallite size of which varies from 20 nm to 150 nm (figure 5a). The crystallite sizes forming the deposited titanium film vary from 150 nm to 180 nm at a film thickness of \(\approx 200 \text{ nm} \) (figure 5c).

The EDS method revealed the distribution of the main elements of the modified layer of ceramic (figure 6). Analyzing the results presented in this figure, we can note the following. First, titanium is present in the surface layer with a thickness of \(\approx 15 \text{ μm} \), at a thickness of a drop of deposited titanium (figure 6a, drop is indicated by an arrow) \(\approx 11 \text{ μm} \). Consequently, the thickness of the Ti-doped SiC-ceramic layer reaches 4 μm.
Figure 3. Structure of the «film (Ti)/substrate (SiC-ceramics)» system irradiated with an intense pulsed electron beam at 30 pulses – image of the area (a); obtained in X-ray beams of silicon (b) and titanium (c) atoms; the table shows the elemental composition of the areas marked in (a).

| Range | C, at.% | Si, at.% | Ti, at.% | Fe, at.% |
|-------|---------|----------|----------|----------|
| Range 1 | 47.11   | 6.17     | 46.26    | 0.47     |
| Range 2 | 47.53   | 5.65     | 46.07    | 0.76     |
| Range 3 | 69.54   | 28.56    | 1.61     | 0.28     |

Secondly, the drop has a multielement composition (titanium, carbon and silicon atoms are present). Consequently, irradiation of the «film (Ti)/substrate (SiC-ceramics)» system with an intense electron beam is accompanied by the diffusion of ceramic elements into the deposited coating. Thus, it can be assumed that the droplet has a multiphase composition (titanium and silicon carbides, silicides and silicocarbides of titanium).

The phase composition of the «film (Ti)/substrate (SiC-ceramics)» system, treated with an electron beam, was studied by X-ray diffraction analysis. Established that under the selected irradiation regime the phase composition formed in the surface layer and the volume fraction of the phases depend on the quantity of irradiation pulses. At 20 pulses, following phase composition of the surface layer was formed: SiC – 18.5 %, TiC – 36.6 %, Ti₅Si₃ – 44.9 %; at 30 pulses, a phase relationship: SiC – 81.6 %, TiC – 12.7 %, Si – 0.5 %, C – 5.2 %.

It should be noted that the method of formation of nonequilibrium surface alloys was realized for the first time in the eighties of the last century using a nanosecond laser [11, 12] and nanosecond (~50 ns) low-energy high-current electron beams [13-16]. In the following years for liquid phase mixing of the film-substrate systems along with the nanosecond laser beam [17] used low-energy high-current pulsed electron beams [18], powerful ion beams [19], compression plasma flows [20] and...
plasma beams [21]. In most experiments, the thickness of the deposited film varied from 100 nm to 700 nm, with the thickness of the doped layer varying from 2 μm to 5 μm.

Figure 5. The structure of the transverse foil of the «film (Ti)/substrate (SiC-ceramics)» system irradiated with an electron beam at 20 pulses; a – structure of the modified droplet layer (arrow indicates the irradiation surface); b – structure of the modified layer of droplet (1) and the substrate (2); c – structure of a titanium film. Transmission electron microscopy.

Figure 6. Structure of the surface layer of the «film (Ti)/substrate (SiC-ceramics)» system irradiated with an intense electron beam at 30 pulses – a (arrow indicates the particle of the drop fraction); dependence on distance from surface of irradiation of the concentration δ of basic elements in surface layer of the «film (Ti)/substrate (SiC-ceramics)» system, modified by an electron beam – b. The EDS analysis was carried out along the line indicated on (a).

Mechanical properties of the «film (Ti)/substrate (SiC-ceramics)» system modified with an intense pulsed electron beam were investigated by determining the microhardness of the irradiation surface. It was established that the microhardness of droplet fraction particles after irradiation with an electron beam at a pulse quantity of 30, varies from 55 GPa to 96 GPa, which is several times the microhardness of the SiC ceramic (36 GPa). It is assumed that such high values of microhardness are
due to the formation of a nanocrystalline multielement multiphase state formed as a result of saturation of titanium droplets with carbon and silicon atoms.

4. Conclusion
By means of vacuum electric arc spraying of a target of technically pure titanium of the VT1-0 grade with plasma assistance («PINK» plasma generator) on polished surface of SiC-ceramic sintered by SPS-method (base – particles of SiC powder with size (0.9–4.0) μm + 3 wt.% of SiC particles with a particle size of 60 nm), thickness 0.5 micron titanium film was formed containing particles of a droplet fraction of micron sizes. It is shown that irradiation of the «film (Ti)/substrate (SiC-ceramics)» system with an intense pulsed electron beam (15 J/cm², 200 μs, 0.3 s⁻¹, 20 and 30 pulses) leads to the formation of a surface layer, having a multielement multiphase structure of the submicro-nanocrystalline range. The mutual diffusion the atoms of film and substrate have been revealed. The thickness of titanium-doped layer of ceramic reaches 4 μm. The thickness of titanium droplets doped with carbon and silicon reaches 10 μm. It was established that the microhardness of droplet fraction particles after irradiation with an electron beam, varies from 55 GPa to 96 GPa, which is several times the microhardness of the SiC ceramic (36 GPa). It is obvious that such high values of microhardness are due to the formation of a nanocrystalline, multielement, multiphase state formed as a result of saturation of a titanium drop by carbon and silicon atoms during irradiation with an intense pulsed electron beam.

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