Plasma diagnostics during deposition of Zr-B-N coatings by magnetron sputtering of UHTC ceramic in DCMS and HIPIMS modes

A D Sytchenko and Ph V Kiryukhantsev–Korneev

National University of Science and Technology “MISiS”, 4 Leninsky Ave., Moscow, 119049, Russia

E–mail: kiruhancev–korneev@yandex.ru, alina–sytchenko@yandex.ru

Abstract. In this work, plasma diagnostics during the deposition of Zr-B-N coatings by DCMS and HIPIMS methods were carried out, the structural characteristics and growth rates of the obtained coatings were investigated; the regularities of the influence of the working atmosphere on the composition of the plasma, as well as on the thickness and growth rate of the coatings are revealed. It was found that the introduction of nitrogen leads to a decrease in the concentration of Zr and B ions in the plasma, as a result of which the growth rate of the coatings decreases. Note that, when using the DCMS method, predominantly argon plasma is observed, while with HIPIMS, the plasma is characterized by a large number of metal ions.

1. Introduction

Ultra-high-temperature ceramics (UHTC) (ZrB₂, ZrN, TaC, etc.) provide high stability at temperatures exceeding 2000°C and are promisingly used both as possible materials for heating elements and thermal protection systems and as coatings for materials exposed to exposure to high temperatures [1]. ZrB₂ based coatings are attracting attention due to their low resistivity (4.6 µOhm-cm), high melting point (3220°C), and excellent chemical inertness [2, 3]. For ZrB₂ coatings, there is a wide range of hardness ranging from 16 to 54 GPa. In work [4], extremely high values of hardness above 45 GPa were obtained for the ZrB₂ coatings; the modulus of elasticity and elastic recovery was 350–400 GPa and 70%, respectively. Coatings based on ZrN are characterized by hardness of 20–35 GPa, an elastic modulus of 350–450 GPa, and high corrosion resistance [5-7].

It is known that the introduction of nitrogen improves the diffusion-barrier properties and thermal stability of ZrB₂ coatings due to the transformation of the structure from crystalline to amorphous [8, 9]. An increase in the nitrogen content leads to a slight decrease in the hardness of the coatings; however, their corrosion resistance improves [10, 11].

The most common method for producing Zr-B-N coatings is direct current magnetron sputtering (DCMS) [9-11]. The main disadvantage of such coatings is their low adhesive strength. The use of the method of high-power pulsed magnetron sputtering (HIPIMS) by increasing the plasma density, leading to ionization of atoms of sputtered material and an increase the energy of ions in flow, makes it possible to improve the adhesion strength of coatings [12]. HIPIMS uses pulsed power at a very high peak density, which provides ionization of the sputtered particles up to 90% [13]. The use of the HIPIMS technology leads to an increase in the density of coatings, as a result of which the mechanical...
and tribological characteristics, as well as the resistance to corrosion, increase [14, 15]. Much attention is paid to studying the composition and degree of plasma ionization using the DCMS and HIPIMS methods [16, 17].

The aim of this work is to study plasma in the process of deposition of Zr-B-N coatings by DCMS and HIPIMS methods with varying N2 content in a gas atmosphere, to study the composition and structure of the coatings obtained.

2. Experimental Part

The deposition of coatings by the HIPIMS method was carried out on a modernized magnetron sputtering installation based on the UVN-2M vacuum system (Russia). For sputtering, a ZrB2 target obtained by the method of self-propagating high-temperature synthesis was used. Magnetron sputtering of target was carried out under in direct current mode (DCMS) using a Pinnacle Plus 5x5 (Advanced Energy) power supply equipped with an arc suppression system and allowing automatic maintenance of the specified electrical parameters. The current and voltage were 2 A and 400-500 V. The HIPIMS process was carried out with the following parameters: average power of 1 kW, peak power of 70 kW, peak current of 130 A, frequency of 100 Hz, pulse duration of 200 μs. The working pressure in the vacuum chamber was 0.1-0.2 Pa. Deposition by DCMS and HIPIMS methods were carried out in Ar (99.999%), N2 (99.999%), and an Ar + 15% N2 gas mixture. The coatings were deposited within 15-40 minutes. Si (100) of the KEF – 4.5 type and HSS steel R18 were used as model substrates. Substrates were cleaned in isopropyl alcohol on a UZDN-2T unit with an operating frequency of 22 kHz for 3 min. Immediately before the deposition of coatings, the substrates were etched with argon ions in a vacuum chamber for 10 min using a slot-type ion source.

PlasmaScope Horiba JY optical spectrometer was used for plasma diagnostics. To decode the spectra, we used the PlasmaScope and Quantum XP program databases from Horiba JY. Structural studies of the coatings were carried out by scanning electron microscopy (SEM) on an S-3400N complex with a NORAN 7 attachment for energy dispersive spectroscopy (EDS) manufactured by Hitachi (Japan).

3. Results and Discussion

The plasma spectra obtained during the deposition of coatings by the DCMS method in an environment of 100% Ar, Ar + 15% N2, and 100% N2 are shown in figure 1. It can be seen that the most intense peaks in the 700 - 850 nm range correspond to argon in the spectra recorded by DCMS deposition in Ar. There is also a peak at a wavelength of 249 nm corresponding to B. No Zr peaks were found, which may be due to the fact that Zr is in the atomic state in the plasma. It is known that at DCMS the plasma mainly consists of gas ions (Ar+) [18, 19]. With the introduction of 15% N2, additional peaks of N are detected at 315 and 337 nm. The transition to reactive sputtering in 100% N2 led to a radical change in the plasma spectra: high-intensity peaks of N were observed, which indicates a high degree of nitrogen ionization. The dependences of the intensities of lines B, Zr, and N on the composition of the working gas were also plotted (figure 1). Plasma boron and zirconium concentrations gradually decreased with increasing nitrogen concentration. The composition of the plasma and the degree of ionization of metallic and non-metallic elements directly affect the composition and growth rate of coatings (table 1). According to the EDS data, the coating obtained in Ar (DCMS) had the following composition: 24 at.% Zr and 76 at.% B. With the introduction of nitrogen into the working atmosphere, a regular decrease in the concentration of Zr and B to 11 and 45 at.% was observed, and an increase in the N content up to 44 at%. The data obtained correlate well with the results of plasma spectroscopy.

In figure 2 (a) shows SEM images of cross-sections of coatings obtained by the DCMS method. The thicknesses and growth rates determined by their micrographs are listed in table 1. The Ar coating had a thickness of 0.78 μm and a growth rate of 52 nm/min.
Figure 1. Plasma spectra recorded during coating deposition by DCMS method.

Table 1. Composition, thickness, deposition rate of coatings obtained by DCMS method.

| Atmosphere   | Composition (at.%) | Thickness (μm) | Growth rate (nm/min) |
|--------------|--------------------|----------------|----------------------|
| Ar           | Zr 24, B 76, N -   | 0.78           | 52                   |
| Ar + 15% N₂  | Zr 18, B 61, N 21  | 0.75           | 49                   |
| N₂           | Zr 11, B 45, N 44  | 0.60           | 20                   |

Figure 2. Cross-section SEM images of coatings obtained by DCMS (a) and HIPIMS (b).
The introduction of a small proportion of N$_2$ into the working atmosphere led to a decrease in the thickness and growth rate by 4-6%. This phenomenon may be associated with a decrease in the concentration of Zr and B ions in the plasma. Deposition of coatings in 100% N$_2$ reduced the thickness of the coatings and the growth rate to 0.60 $\mu$m and 20 nm/min. The sharp drop in the growth rate by 60% is probably due to the difficulty of nitrogen atoms ionization compared to argon.

The presence of exclusively nitrogen ions in plasma can lead to target poisoning and the formation of a nitrogen-containing layer on its surface [19].

The results of plasma spectroscopy during deposition of coatings by the HIPIMS method are shown in figure 3.

![Figure 3. Plasma spectra recorded during coating deposition by HIPIMS method.](image)

It can be seen that the total intensity of the lines in the spectra decreases with the introduction of nitrogen into the composition of the reaction gas. The strongest line in the spectrograms, observed at the position of 339 nm, corresponds to Zr. According to the basic data, a first-order boron line is observed at a wavelength of 249 nm. Argon peaks were observed in the range 650-850 nm. With the introduction of 15% N$_2$, a slight decrease in the concentration of Zr and B was observed. There were no peaks corresponding to N. When passing to sputtering in 100% N$_2$, the concentration of target...
elements in the plasma sharply decreased and amounted to 4-8 arb. units; peaks of N have been detected at positions 315, 391, 423, and 567 nm. It can be concluded that the introduction of nitrogen reduces the degree of ionization of metal elements.

Table 2 shows the elemental composition of the Zr–B–N coatings obtained by the HIPIMS method with varying gas flow rates.

| Atmosphere | Composition (at.%) | Thickness (Si substrate) (μm) | Thickness (R18 steel substrate) (μm) | Growth rate (nm/min) |
|------------|--------------------|-------------------------------|-------------------------------------|---------------------|
| Ar         | Zr 28.9  B 71.1     | 0.80                          | 1.60                                | 40                  |
| Ar + 15% N₂ | Zr 12.5  B 38.0  N 49.5 | 1.40                          | 1.50                                | 37                  |
| N₂         | Zr 18.2  B 13.0   N 68.8 | 0.50                          | 0.10                                | 2.5                 |

The concentration of Zr and B for the coating obtained in Ar was 28.9 and 71.1 at.% respectively. With the introduction of 15% N₂ into the working atmosphere, a decrease in the concentration of zirconium to 12.5 at.% and boron up to 38.8 at.%, which is in good agreement with the analysis of the plasma spectra. The nitrogen concentration was 49.5 at.%. Upon deposition in 100% N₂, a decrease in the concentration of Zr and B by ~40 and ~80% compared with the nitrogen-free sample was observed.

According to micrographs (figure 2 (b)), the thicknesses of the coatings obtained on silicon in 100% Ar, Ar + 15% N₂ were 0.8, 1.4 and 0.5 μm, respectively (table 2). The thicknesses of the coatings obtained on R18 steel were 1.60 μm (100% Ar), 1.50 μm (Ar + 15% N₂) and 0.10 μm (100% N₂). The difference in the values of the thicknesses according to the SEM (coatings on Si) and GDOES (coatings on steel) data can be explained by the higher roughness of the R18 substrate, high stresses, delamination, and redeposition of the coating in the case of a Si substrate. Therefore, the growth rate was estimated for coatings deposited on the steel. The growth rates of the coatings were 40, 37 and 2.5 nm/min for the samples prepared in a medium of 100% Ar, Ar + 15% N₂ and 100% N₂, respectively. A decrease in the thickness and growth rate upon the introduction of 15% N₂ is associated with an insignificant change in the concentration of Zr and B in plasma, as well as with target poisoning. With an increase in the nitrogen content in the gaseous medium, as a result of a decrease in the concentration of target elements in the plasma, a decrease in the growth rate by ~15 times was observed. It is known that with an increase in the pressure of the reaction gas, the growth rate of coatings decreases [20]. Thus, poisoning of the target had a very strong effect on deposition in the HIPIMS mode compared to DCMS. The growth rate of the coatings differed by 10 times.

Note that when using both the DCMS and HIPIMS methods with the introduction of nitrogen, a regular decrease in the concentration of Zr and B in the plasma is observed, which leads to a decrease in the growth rate of the coatings. However, significant differences in the composition of the plasma were revealed when using the deposition method data. This difference is clearly seen when comparing figure 1 and 3. In DCMS, the plasma consists mainly of ions of gaseous elements (Ar, N). Whereas when using the HIPIMS method, metal elements (Zr) have the maximum intensity. Note that, ongoing from DCMS to HIPIMS, the emission of Zr and Ar particles increases significantly, which indicates a high ionization of metal and gas particles [21]. The decrease in the growth rate during the transition from DCMS to HIPIMS can be associated with the effect of self-sputtering, as well as with a decrease in the total sputtering time in pulsed regime of HIPIMS [22, 23].

4. Conclusion
Zr-B-N coatings were obtained by methods of DCMS and HIPIMS in a medium of 100% Ar, Ar+15% N₂ and 100% N₂. Plasma spectra were recorded during the deposition of the coatings; the
resulting coatings were examined in terms of their composition and structure. The results of plasma spectroscopy showed that when coatings are prepared by the DCMS method in an inert gas, the plasma consists mainly of argon. While at HIPIMS, metal ions predominate in the plasma. In both cases, with the introduction of nitrogen into the composition of the gas medium, the concentration of zirconium, boron, and argon in the plasma decreased. When deposited in 100% N₂, the plasma contained mainly nitrogen ions. It should be noted that the coatings obtained by the HIPIMS method showed a lower growth rate compared to the DCMS.

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