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F. I. Panteleenko, a member-correspondent. NAN B, Ph. D., Professor,
V. A. Okovity, Ph. D**., O. G. Devoino**, Ph. D., Professor, **A. S. Volodko,**
V. A. Sidorov, Ph. D., associate Professor, **V. V. Okovity**
Belarusian National Technical University, Minsk, Belarus
Tel. / Fax+375 17 293-95-99, **E-mail:** *niil_svarka@bntu.by*
V. M. Astashinsky, a member-correspondent. NAS B, D. Phys. - math. n., prof.
A. V. Lykov
Institute of Heat and Mass Transfer of the National Academy of Sciences of Belarus,
Minsk, Belarus
Tel. / Fax +375 17 284-24-91, **E-mail:** *ast@hmti.ac.by*

THE FORMATION OF THE MULTILAYER PLASMA-BASED COATING COMPOSITIONS OF THE OXIDE

The article presents the results of studying the process of deposition of multilayer composite plasma oxide coatings and optimizes the technological parameters of the deposition of multilayer plasma coatings based on hafnium oxide stabilized with yttrium oxide. A gradient plasma coating with a smooth change in physical and mechanical properties has been developed. The technologies of plasma spraying in air (APS) and in vacuum (VPS) were used. HfO2 with 15% Y2O3 was chosen as a ceramic powder for spraying, since after spraying this powder, the maximum amount of the tetragonal phase (up to 99%) remains in the coating, which has a major effect on the heat-shielding properties. Nickel-based alloy was selected as the sublayer. including 25 wt. % chromium, 10 wt. % aluminum and 0.5 wt. % yttrium.
Keywords: *multilayer plasma coatings, zirconium dioxide, thermomechanical stresses, residual stresses, technological modes of coating deposition, crystal lattices*

Ф. И. Пантелеенко, В. А. Оковитый, О. Г. Девойно, А. С. Володько, В. А. Сидоров, В. В. Оковитый, В. М. Асташинский, А. В. Луков

ФОРМИРОВАНИЕ МНОГОСЛОЙНЫХ ПЛАЗМЕННЫХ ПОКРЫТИЙ НА ОСНОВЕ ОКСИДА

В статье представлены результаты исследования процесса нанесения многослойных композитных плазменно-оксидных покрытий и оптимизированы технологические параметры нанесения многослойных плазменных покрытий на основе оксида гафния, стабилизированного оксидом иттрия. Разработано градиентное плазменное покрытие с плавным изменением физико-механических свойств. Использовались технологии плазменного напыления на воздухе (APS) и в вакууме (VPS). В качестве керамического порошка для напыления был выбран HfO2 с 15% Y2O3, поскольку после напыления этого порошка в покрытии остается максимальное количество тетрагональной фазы (до 99%), что оказывает существенное влияние на теплозащитные свойства. В качестве подслоя был выбран сплав на основе никеля. включая 25 мас. % хрома, 10 мас. % алюминия и 0,5 мас. % иттрия.
Ключевые слова*: многослойные плазменные покрытия, диоксид циркония, термомеханические напряжения, остаточные напряжения, технологические режимы нанесения покрытий, кристаллические решетки*

1. Introduction.

The main method used for the deposition of zirconium dioxide coatings is plasma sputtering (up to 90% of developments) [1-5]. Nevertheless, the predominant spread of plasma sputtering remains, primarily due to its high performance and versatility, which allows applying metal and ceramic materials of a given chemical and phase composition. In general, the coating is a multi-layer system that includes a metal sublayer, an outer ceramic layer, and transition ceramic layers [6-8]. The main reason for the destruction of plasma coatings is the thermomechanical stresses that occur during heat changes in engines, due to the mismatch of

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the thermal expansion of the base metal and the ceramic layer, as well as the uneven distribution of the temperature field in the coating. Thermomechanical stresses are aggravated by the action of residual stresses that occur in the coating during deposition, and are weakened by the effects of plasticity and creep that are realized in the metal sublayer [9-11]. The significant structural sensitivity of the properties of zirconium dioxide-based coatings requires strict reproducibility of the results. This imposes particularly strict restrictions on the quality of the materials used and the accuracy of maintaining the technological modes of coating application[12-18]. Hafnium oxide was chosen for use as a powder for heat-shielding coatings along with zirconium dioxide due to their similarity in structural modification, lattice, chemical and physical properties, and its increased temperature of structural transformations.

The similarity of Hf+4 and Zr+4 cations leads to the formation of identical metastable phases during rapid quenching. The differences in the crystal lattices of ZrO_2 and HfO_2 are very small, due to the equivalent valence band and the almost equivalent ionic radii of Zr+4 and Hf+4.For this reason, the ZrO_2 - HfO_2 system can form continuous substitution solutions, and it is possible to isolate the X-ray diffraction patterns of ZrO_2, HfO_2 in solid solutions only by using extremely high resolution of the X-ray diffraction method.

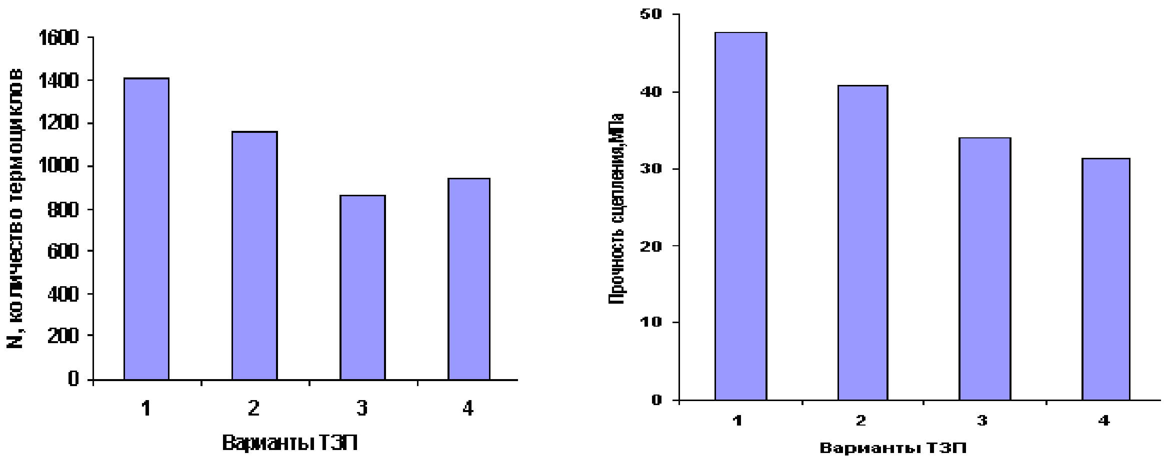
The similarity between ZrO_2-Y_2O_3 and HfO_2-Y_2O_3 in the equilibrium phase diagrams also extends to the formation of non-equilibrium phases. All the considered compositions of hafnium dioxide, partially stabilized by yttrium oxide under rapid cooling, show one metastable t 'phase, with a microstructure equivalent to the pure t' phase. In addition, the temperature of phase transformations during the transition of tetragonal phase to monoclinic with increasing Y_2O_3 concentration decreases, and when the concentration of HfO_2 increases, making the system HfO_2 - Y_2O_3 in the equilibrium phase diagrams also extends to the formation of non-equilibrium phases. All the considered compositions of hafnium dioxide, partially stabilized by yttrium oxide under rapid cooling, show one metastable t 'phase, with a microstructure equivalent to the pure t' phase. In addition, the temperature of phase transformations during the transition of tetragonal phase to monoclinic with increasing Y_2O_3 concentration decreases, and when the concentration of HfO_2 increases, making the system HfO_2 - Y_2O_3 promising for obtaining coatings with desired properties. Taking into account the above, it is assumed that the use of HfO_2-Y_2O_3 will allow obtaining coatings with a resource exceeding the resource of ZrO_2-Yb_2O_3 and ZrO_2 - CeO_2 coatings. Improving the properties of heat-protective coatings is also carried out by changing the structure of the ceramic layer of the heat-protective coating, by creating gradient layers. Gradient layers combine the heat resistance of ceramics with the ductility of metals. A gradual change in the microstructure without sharp interfaces, a smooth change in the microhardness and the convergence of the elastic modulus of the ceramic and metal layers leads to an increase in the strength of the coating and its durability.

Hafnium oxide was chosen for use as a powder for heat-shielding coatings along with zirconium dioxide due to their similarity in structural modification, lattice, chemical and physical properties, and its increased temperature of structural transformations. The similarity of Hf+4 and Zr+4 cations leads to the formation of identical metastable phases during rapid quenching. The differences in the crystal lattices of ZrO_2 and HfO_2 are very small, due to the equivalent valence band and the almost equivalent ionic radii of Zr+4 and Hf+4. All the considered compositions of hafnium dioxide, partially stabilized by yttrium oxide under rapid cooling, show one metastable t 'phase, with a microstructure equivalent to the pure t' phase. In addition, the temperature of phase transformations in the transition of tetragonal phase to monoclinic with increasing Y_2O_3 concentration decreases, and when the concentration of HfO_2 increases, making the system HfO_2 - Y_2O_3 promising for obtaining TZP with desired properties. Taking into account the above, it is assumed that the use of HfO_2-Y_2O_3 will allow to obtain a TP with a resource exceeding the resource of ZrO_2-Yb_2O_3 and ZrO_2 - CeO_2 coatings.

2. Formation of a multi-layer coating.

A gradient plasma coating with a smooth change in physical and mechanical properties has been developed (Figure 1). In this case, the technologies of plasma spraying in air (APS) and in vacuum (VPS) were used. HfO_2 with 15% Y_2O_3 was chosen as the ceramic powder for spraying, since after spraying this powder, the maximum amount of the tetragonal phase (up to 99%) remains in the coating, which has the main effect on the heat-shielding properties. A nickel-based alloy is selected as the sublayer. including 25 wt. % chromium, 10 wt. % aluminum and 0.5 wt. % yttrium. Figure 2a shows a five-layer coating, sprayed from ceramics based on ZrO_2-20 wt. % CeO_2-NiCrAlCe (×400). Figure 2b shows a five-layer coating, sprayed from ceramics based on HfO_2-15 wt. % Y_2O_3 - NiCrAlY (×400). As noted, two types of coatings were sprayed for comparative analysis :

a) a five-layer coating, sprayed according to the source technology [9-13], Figure 2a. The coating includes a ceramic layer of ZrO_2-CeO_2-100 microns, intermediate layers of 80 % (ZrO_2 - CeO_2) – 20% NiCrAlCe - 100 microns, 50% (ZrO_2 - CeO_2) – 50% NiCrAlCe-100 microns and 20% (ZrO_2 - CeO_2) – 80% NiCrAlCe - 100 microns, as well as a sublayer of NiCrAlCe-100 microns. The NiCrAlCe sublayer and the two intermediate layers closest to the substrate, 20 % (ZrO_2 - CeO_2) – 80% NiCrAlCe and 50% (ZrO_2 - CeO_2) – 50% NiCrAlCe, were applied in vacuum at reduced pressure, with a gradual increase in it with an increase in the amount of ceramics in the mechanical mixture.



a **b**

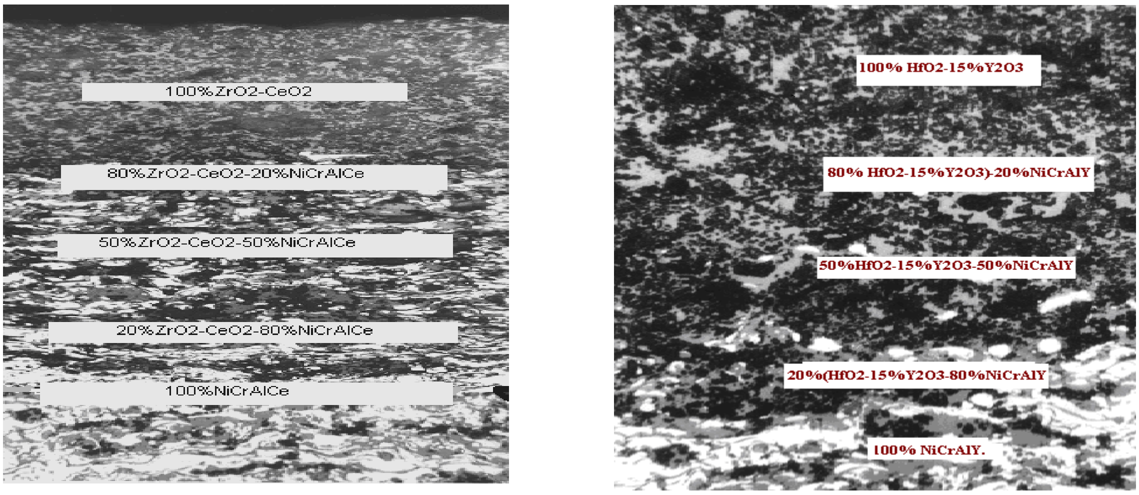
Figure 1. Production of multilayer coatings (1 -- HfO_2-15 wt. % Y_2O_3-NiCrAlY; 2-HfO_2-25 wt. % Y_2O_3-NiCrAlY; 3 -- ZrO_2-20 wt. % CeO_2- NiCrAlY ; 4 – ZrO2-25 wt. %CeO_2 - NiCrAlY): a-heat resistance; b-transparency of the greenhouse.

The two upper layers were sprayed in air (APS) with intensive cooling;b) the five – layer coating (Figure 2b) includes a ceramic layer of HfO_2 - 15% Y_2O_3 – 100 microns, intermediate layers of 80 % (HfO_2- 15% Y_2O_3) - 20% NiCrAlY – 100 microns, 50 % (HfO_2– 15% Y_2O_3) - 50% NiCrAlY – 100 microns and 20 % (HfO_2 – 15% Y_2O_3) - 80% NiCrAlY - 100 microns, as well as the NiCrAlY sublayer-100 microns. The NiCrAlY sublayer and the two intermediate layers closest to the substrate, 20 % (HfO_2 – 15% Y_2O_3) – 80% NiCrAlY and 50% (HfO_2

– 15% Y_2O_3) – 50% NiCrAlY;), were applied in vacuum at reduced pressure, with a gradual increase in it with an increase in the amount of ceramics in the mechanical mixture. The top two layers were sprayed in air (APS) with intensive cooling.

The gradient ratio of ceramics and nickel-based alloy in the intermediate layers was created according to the prototype scheme. The adhesion strength was determined on the Instron installation. The quantitative estimates of the parameters were determined as averaged over five dimensions. The coatings were cyclically tested in a furnace at 1300 °C. The temperature in the furnace was measured with a platinum thermocouple and maintained within 1300°C ± 10°. The cycle consisted of heating for 10 minutes, holding at 1300 °C for 60 minutes, and sixty minutes of cooling to 300 °C. For every 10 cycles, samples were removed from the furnace for testing when the temperature dropped to 300 °C. The tests continued until the destruction of the ceramic coating, which was assumed to be the formation of a crack visible to the naked eye.

Data for heat resistance and adhesion strength of the coatings obtained on the technology presented in [9-13] and can be shown in figures 1A and b. According to figure 1A gradient (five-layer) coating of powders HfO_2 – 15 % Y_2O_3 and HfO_2 – 25 % Y_2O_3, developed



a **b**

Figure 2. Five-layer coating, sprayed from ceramic: a-based ZrO_2 - 20 мас. % CeO_2 – NiCrAlCe; b- HfO_2 - 15 мас. %Y_2O_3 - NiCrAlY(×400)

by the authors, showed the thermal stability of the 1.2 - 1.3 times higher compared to the same bilayer. In comparison with gradient coatings made of ZrO_2 powders-20 wt. % CeO_2 and ZrO_2 - 25 wt. % CeO_2 efficiency increased by 1.4-1.5 times. The adhesion strength of gradient (five-layer) coatings made of HfO_2 – 15% Y_2O_3 and HfO_2 – 25% Y_2O_3 powders is 1.6 - 1.7 times higher in comparison with gradient coatings of ZrO_2 - 20 wt. % CeO_2 and ZrO_2 - 25 wt. % CeO_2 (Figure 1b)

3.Conclusion.

Criteria for obtaining high-quality multilayer plasma coatings based on hafnium oxide stabilized with yttrium oxide are developed. The application modes of the material based on hafnium oxide stabilized with yttrium oxide were optimized to obtain the maximum content of the tetragonal phase in the coating. Improving the properties of heat-protective coatings was carried out by creating gradient layers. Gradient layers combine the heat resistance of ceramics with the ductility of metals. A gradual change in the microstructure without sharp interfaces, a smooth change in the microhardness and the convergence of the elastic modulus of the ceramic and metal layers leads to an increase in the strength of the coating and its durability. Gradient (five-layer) coatings sprayed from HfO_2-15% Y_2O_3 and HfO_2-25% Y_2O_3 powders according to the technology developed by the authors showed heat resistance 1.2-1.3 times higher compared to two - layer coatings sprayed from the same powders and 1.4 - 1.5 times higher compared to gradient coatings sprayed from ZrO2-20 wt powders. % CeO_2; ZrO_2-25 wt. % CeO_2. The adhesion strength of gradient (five-layer) coatings sprayed from HfO_2-15% Y_2O_3 and HfO_2 - 25% Y_2O_3 powders is 1.3 - 1.4 times higher compared to two - layer coatings sprayed from the same powders and 1.6-1.7 times higher compared to gradient coatings sprayed from ZrO_2-20 wt powders. % CeO_2; ZrO_2-25 wt. % CeO_2

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