Formation and investigation of plasma nanostructured hafnia coatings

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Abstract. Nanostructured coatings HfO₂-9wt%Y₂O₃ were obtained by plasma spraying in vacuum using supersonic nozzle creating Prandtl-Mayer expansion fan. The coatings were investigated by scanning electron microscopy, X-ray diffraction analysis, and synchronous thermal analysis (differential scanning calorimetry, thermogravimetric analysis, and differential thermogravimetric analysis) in the temperature range of 40÷1600°C. The coatings are predominantly characterized by the nanostructured globular structure. Thermal analysis showed a peak corresponding to the exothermic reaction in the temperature range of 1400÷1600 °C, accompanied by a mass loss. c-HfO₂ phase remained in the coating after thermal analysis with a decrease in the lattice parameter from 5.18 Å to 5.13 Å.

1. Introduction
Hafnia is a perspective material for the thermal barrier layer of the thermal barrier coating due to its similarity with zirconia and its elevated temperatures of phase transitions. Hafnia has a lower thermal conductivity than zirconia and shows lower sintering rates due to lower partial oxygen pressures for transition of the ionic conductivity to electronic conductivity compared to zirconia [1-5]. In [6] it was shown that the thermal stability of the HfO₂-7.5wt%Y₂O₃ coating increases by at least 100°C compared to the coating of ZrO₂-8wt%Y₂O₃. However, the disadvantage of hafnia use is a lower coefficient of thermal expansion in comparison with zirconia.

Nanostructured coatings are characterized by more homogeneous distribution of pores therefore their influence on the coating structure is less destructive [7, 8]. In addition, the presence of nanopores can contribute to an effective damping of the volume changes in the coatings when the operating temperature changes. Also, the nanostructured coating can have better thermal insulation properties due to the increase in the number of boundaries that promote the scattering of lattice phonon waves.

One of the methods to obtain a nanostructured coating by plasma spraying is the formation of rarefaction waves in Prandtl-Maier expansion fan in vacuum. An abrupt expansion of the vapor phase in Prandtl-Maier expansion fan contributes to condensation of nanoparticles of the deposited material [10, 11]. The Prandtl-Mayer expansion fan is a supersonic gas flow with a continuous increase in speed [9]. It can be obtained when the freely expanding gas jet flows around a convex corner into a region of reduced pressure. In this case, in the strongly underexpanded gas jet a shock wave (so-called “first barrel”) appears. Inside barrel-shaped shock wave the flow coincides with the flow in the jet...
outgoing into vacuum. When the supersonic flow is turned in the Prandtl-Mayer flow at angles of the order of several tens of degrees, the local flow parameters (static pressure and temperature) drop sharply. In the vicinity of the corner of the turn the cooling of the spraying material vapor phase occurs faster. The static pressure also falls faster than inside the nozzle.

In this work a nanostructured hafnia coatings formed by plasma spraying in vacuum using a supersonic nozzle creating a rarefaction waves in a Prandtl-Mayer expansion fan were investigated by scanning electron microscopy and thermal analysis.

2. Experimental setup and characterization techniques
Hafnia coatings with the thickness up to 60 µm were obtained on samples of bronze alloy (1wt%Cr) with a diameter of 30 mm and a thickness of 2 mm. The coatings were formed by DC plasma torch with a power up to 10 kW in VS-2 setup of Keldysh Research Center under conditions of dynamic vacuum (the pressure ~ 120 Pa) in the chamber. Plasma spraying was carried out using the powder of HfO<sub>2</sub>-9wt%Y<sub>2</sub>O<sub>3</sub> with a particle size of 10-40 µm. A supersonic nozzle of plasma torch was equipped with two turning sections creating Prandtl-Mayer expansion fan: the first by 6 and the second by 27 degrees. Such parameters of the nozzle lead to the condensation of hafnia nanoparticles as a result of cooling the vapor phase of the sprayed material in the vicinity of the turning sections. The consumption of the plasma-forming gas (N<sub>2</sub>) was 0.87 g/s, the powder consumption was 0.23 g/s. The arc current was 120 A, and the voltage was 60 V. The spraying process was carried out by reciprocating displacement of the plasma torch along the rotating holder with the samples.

The coatings were investigated using a Quanta 600 scanning electron microscope (SEM), X-ray diffractometer (Empyrean PANalytical, CuKα radiation), and synchronous thermal analysis (NETZSCH STA449F 1 Jupiter). The coating was studied by thermal analyzer in a corundum crucible in the temperature range of 40-1600°C at a rate of 5 °C/min. The protective and purge gases were argon with the flow of 50 ml/min and air with a flow of 50 ml/min.

3. Results and discussion
The study of hafnia coatings surface showed the presence of several types of particles (Figure 1 (a)): deformed planar particles with size up to 30 µm, smaller fragments of particles formed in a collision with the surface of superheated powder particles, the particles in the form of disks with hole in the centre obtained as a result of a collision with the surface of the particles with a molten shell and a solid centre. Between big particles there are regions containing particles with size of 2 ÷ 5 µm that mainly have the form of flat discs with uneven edges, and submicron particles (Figure 1 (b)). Submicron particles prevailing in the structure of the coating are represented in the form of globules with a size of 0.2 ÷ 0.4 µm (Figure 1 (c,d)), which are formed mainly of nanoparticles (Figure 1 (d)).

It can be assumed that the presence of nanostructured globules in the structure of the coating is due to formation of rarefaction waves in the Prandtl-Mayer expansion fan in the nozzle of the plasma torch. In this case, the central part of the nozzle contributes predominantly to the formation of the deformed particles but the peripheral part of the nozzle with turning sections contributes to the formation of predominantly nanoparticles in the coating structure.

The hafnia coating was investigated using synchronous thermal analysis including differential scanning calorimetry (DSC), thermogravimetric analysis (TG), and differential thermogravimetric analysis (DTG). In figure 7 the graphs of DSC, TG and DTG on temperature are presented. The sample for analysis was obtained by scraping down the coating from the substrate.

Synchronous thermal analysis did not show significant mass changes in the temperature range from 30 to 1200 °C that indicates the stability of the chemical compound in this temperature range, see figure 2 (1). In DTG curve, a small peak corresponding to a decrease in mass can be noted at a temperature of 210 °C, see figure 2 (2). It can be associated with the release of gases from the coating (water vapor, CO<sub>2</sub>). Small peaks on the curves of DSC, TG, and DTG corresponding to a slight increase in mass and exothermic reaction at the temperature of about 700 °C can be associated with oxidation of residual carbon on the surface of the coating. At a temperature of more than 1300 °C, the
mass decreases by 2%. In this temperature region there is also a peak in the DSC graph corresponding to the exothermic reaction completed by 1600 °C, see figure 2 (3). The temperature corresponding to the maximum of this peak, according to the DTG graph, is ~ 1412 °C. This peak can be associated with changes in the crystal structure; for example, redistribution of the stabilizing oxide (yttria) and partial release of it from the hafnia crystal lattice, because the sprayed powders often have an uneven distribution of the stabilizer, which is then partially retained in the coating structure.

**Figure 1.** SEM images of HfO$_2$-9wt%Y$_2$O$_3$ coating surface: a) The morphology of the coating, b) the structure of coatings in the regions between the big particles, c) the globular structure at higher magnification, and d) nanostructured particles.

1 - Deformed particles in the form of disks, 2 - fragments of molten particles in the structure, 3 - particle in the form of discs with a hole in the center.

X-ray diffraction analysis of the coating after thermal analysis showed that the cubic modification of hafnia remained in the coating with the crystal lattice parameter $a \approx 5.14$ Å. The parameter $a$ was 5.18 Å before the thermal analysis. A decrease in the parameter $a$ may indicate partial losses of yttria from the crystal lattice of hafnia. It may also be due to a decrease of imperfections and internal stresses in the coating caused by a strong deformation of the hafnia particles sprayed at supersonic speeds. The parameter $a \approx 5.18$ Å corresponds to a 9wt% yttria content, which confirms the distortion of the crystal lattice in the coating prior to thermal analysis [12].
Figure 2. Graphs of thermogravimetric analysis (TG) (1), differential thermogravimetric analysis (DTG) (2) and differential scanning calorimetry (DSC) (3) on temperature.

The peak on the DSC graph in the temperature range from 1400 to 1600 °C can also be related to the crystallization of the amorphous component in the coating, the presence of which can be caused by high rates of spraying and cooling.

4. Conclusions
Nanostructured coatings of HfO$_2$-9wt%Y$_2$O$_3$ with a thickness of up to 60 µm were obtained by plasma spraying in vacuum using supersonic nozzle creating rarefaction waves in the Prandtl-Mayer expansion fan. The coatings are predominantly characterized by a globular structure that consists of nanoparticles. Thermal analysis of the coatings showed the presence of a peak corresponding to the exothermic reaction in the temperature range 1400÷1600 °C accompanied by a mass loss that may be due to the partial release of the stabilizing oxide, its redistribution, and reduction of defects and internal stresses in the coating. X-ray diffractometry showed the stability of the cubic structure of hafnia after thermal analysis with a decrease in the lattice parameter $a$ from 5.18 Å to 5.13 Å.

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References
[1] Zhu D, Miller R A Surf. Coat. Technol. 1998 108–109 114–20
[2] Winter M R, Clarke D R Acta Mater. 2006 54 5051–59
[3] Singh J, Wolfe D E, Miller R A, Eldridge J I, Zhu D M J. Mater. Sci. 2004 39 1975–85
[4] Stöver D, Pracht G, Lehmann H, Dietrich M, Döring J E, Vaßen R J. Therm. Spray Technol. 2004 13(1) 76–83
[5] Ibigazne H, Alpirine S, Diot C J. Mater. Sci. 1995 3 938–51.
[6] Matsumoto K, Itoh Y, Kameda T Sci. Technol. Adv. Mater. 2003 4 153–158
[7] Wang Y, Bai Y, Yuan T, Chen H Y, Kang Y X, Shi W J, Song X L, Li B Q Surf. Coat. Technol. 2017 319 95-103
[8] Liu C, Zhang Z, Jiang X, Liu M, Zhu Z Trans. Nonferrous Met. Soc. China 2009 19 99–107
[9] Schetz J A, and Fuhs A E 1999 Fundamentals of Fluid Mechanics. 3rd Edition (John Wiley & Sons)
[10] Polyanskiy M N, Savushkina S V J. Surf. Invest.: X-Ray, Synchrotron Neutron Tech. 2014 8 144–48
[11] Borisov A M, Vostrikov V G, Polyansky M N, Romanovsky E A, Savushkina S V, Suminov I V, Tkachenko N V J. Surf. Invest.: X-Ray, Synchrotron Neutron Tech. 2015 9 248–52
[12] Stacy D W, Wilder D R J. Am. Ceram. Soc. 1975 58 285–88