Thermo-barrier nanostructure microplasma coatings of ZrO₂

M S Dorofeeva¹, T I Dorofeeva², B P Gritsenko², V P Sergeev²

¹National Research Tomsk State University, 30 Lenin Ave, Tomsk, 634050, Russia
²Institute of Strength Physics and Materials SB RAS, 2/4 Akademicheskii Ave., Tomsk, 634055, Russia

E-mail: dorofeevatomsk@gmail.com

Abstract. This work shows the formation of oxide ceramic coating ZrO₂. The coating is formed on a copper substrate in the series of layers. Two different methods are used for deposition of metallic layers: vacuum arc deposition (PVD) and magnetron sputtering. The last metal layer is converted into oxide by microplasma oxidation. As a result, microplasma nanostructured coating is formed on the surface. Morphology and elemental composition of these coatings are investigated by means of a scanning electron microscope with attachment for element analysis. Thermocyclic stability of coatings is determined. Thermal cycling tests for the coatings have demonstrated promising results of lifetimes more than 1000 cycles.

1. Introduction

The internal cavities of rocket engine nozzles should have high thermal cycling stability. So the traditional coatings with laminar layers are difficult to meet the increasing demand for applications such as aerospace industry. Development of multilayer thermo-barrier nanostructure coatings, which are capable to maintain thousand-degree temperature drops without destruction, for space technologies is an urgent problem of present days. To do this, heat-shielding coatings of zirconium dioxide are deposited. Zirconium ceramics occupies a leading place among refractory construction materials [1]. Zirconium dioxide retains high mechanical properties up to a temperature of 3173 K [2]. Many of technologies of coatings deposition do not allow to obtain coatings with the desired quality. In this paper, a combination of well-known methods was used to achieve the desired effect (PVD, magnetron deposition, microplasma oxidation) [3-5]. Researches in the field of synthesis of functional ceramic coatings have developed a technique for formation of a unique thermo-barrier nanoporous layered oxide ceramic coating on a copper substrate.

The main method in this paper is microplasma oxidation. This method allows to form oxide ceramic coatings on the surface with increased physical mechanical properties. This work aims to study possibilities of increasing the thermal cycle stability of ZrO₂ coatings by optimizing the modes of microplasma treatment.

2. Experimental procedure

As a substrate were samples of copper. Samples (size 30×20×2 mm) were made from M1 grade copper sheet. The working surface of samples was polished to a roughness Ra=0.08 µm.

Titan is sprayed on a copper substrate (PVD method), and then zirconium is sprayed (magnetron deposition) step by step. Then the sample is exposed to microplasma influence in an electrolyte solution (sodium metasilicate – 70 g/l and alkali – 6 g/l. Operation parameters of microplasma regime:
voltage – 350 V, pulse duration of voltage – 200 mks Process time varied from 6 to 10 minutes As a result, zirconium transforms into zirconium dioxide, and the porous ceramic coating is formed on the surface. These coatings have high adhesion and contain compounds from elements of material substrates (zirconium dioxide) and elements of electrolyte (silicon oxide).

Morphology and composition of the obtaining coatings were researched by means of electron microscope LEO EVO-50XVP (Carl Zeiss, Germany) with option for element analysis Oxford INCA Energy X-act and INCA Wave. The structure-phase state of the coatings was studied through X-ray structural analysis of diffractograms recorded with a DRON-7 diffractometer. To test for thermal-cyclic resistance the coated specimens were heated in a furnace up to 1000°С for 90 sec with the following shock cooling down to the room temperature in water.

3. Results
Smooth uniform light gray coatings are formed during microplasma treatment (figure 1).

Figure 1. Photos of a samples surface with oxide ceramic coatings after microplasma oxidation.

Time of microplasma process does not affect color and uniformity of coating. The coating thickness was 54.7 µm after microplasma process for 6 min and 58.2 µm after microplasma process for 10 min. Further increase of processing time leads to rising of silicate formations on the surface; coating thickness does not increase almost.

The formed oxide ceramic coating morphology is introduced in surface photos (figures 2-3).

Figure 2. Electron microscopy (SEM) image of surface samples with oxide ceramic coating (microplasma process time – 6 min).

Porous oxide ceramic coatings with pore sizes of about 1 µm are formed on the surface (figure 2). The number of pores and pore sizes are reduced with increasing microplasma process time to 10 minutes (figure 3). The surface roughness increases at the same time.
The elemental composition of the coating is shown in the table 1.

Table 1. The elemental composition of the coatings.

| Element | Concentration, at.% |
|---------|---------------------|
|         | treatment time 6 min. | treatment time 10 min |
| O       | 72.15                | 73.27                   |
| Si      | 6.75                 | 11.25                   |
| Zr      | 31.09                | 25.48                   |

As can be seen, the main structural oxide is zirconium oxide – about 30% in both cases. As the processing time increases, the number of silicon atoms that make up the coating from the solution increases. The compounds of silicon (12%) along with zirconium dioxide includes in the coating composition. Titanium compounds cannot be diagnosed in the surface layer, indicating a lack of breakdown of the film of the deposited zirconium in the period of micro-plasma oxidation.

The structural-phase state of coatings was studied by x-ray structural analysis (RSA) obtained using the diffractometer DRON-7.

The coating composition contains monoclinic and tetragonal zirconium oxide. The monoclinic phase was 18% vol. in the coating. The tetragonal phase was 72% vol. in the coating. Silicon oxide is contained in the X-ray amorphous state in the coating. Silicon oxide stabilizes the zirconium dioxide in case thermal stress.

4. Discussion
The formed nanoporous ceramic coatings have been analyzed on thermal-cycle durability. The resistance of coatings to cracking and delamination during temperature change was determined by the results of thermal cycling of samples in the following modes: heating of the sample up to 1000°C at a speed of 20 deg/sec, hold for 1 minute at this temperature, forced cooling at a speed of 20 deg/sec to room temperature. Taking photos of the sample surface from the coating side using a special Microscope DCM 500 camera on the optical microscope BMG-160, the data were recorded directly in the computer. The cycle duration was 5 min. The tests were stopped when about 50% of the coating was destroyed. The number of cycles that the coatings withstood during these tests was taken as the value of their thermal cycling resistance (TCR).

Dynamics of transformations at thermo cyclic loading is reflected in surface photos (figures 4-5). The coating becomes dark after the first cycles (regardless of the time of the microplasma process).
The uniformity of the coating remains until the 40th cycle (treatment time – 10 min) (figure 4). Small parts at the coating after the 44th cycle start to peel; there are copper sites after the 58th cycle. Further there are no visible changes until the 63rd cycle; at the 70th cycle the number of copper sites increases. As a result, more than 50% of the coating preserves at the 95th cycle.

![Figure 4. Photos of a sample surface with oxide ceramic coatings after thermocyclic tests: 5, 8, 22, 57, 70, 95 cycles (microplasma process time – 10 min).](image)

The sample 2 (figure 5) showed lower results (microplasma treatment time – 6 min). The uniformity of the coating remains until the 10th cycle. Copper appears on the 13th cycle. More than 50% of the coating is destroyed by the 70th cycle. In addition, the base is strongly deformed during thermal cycling tests.

![Figure 5. Photos of a sample surface with oxide ceramic coatings after thermocyclic tests: 1, 6, 12, 44, 68, 75 cycles (microplasma process time – 6 min).](image)

The resistance of the coating to thermal cycling loads increases with the increase in the time of microplasma treatment. This may be due to an increase in the content of silicon oxide in the coating.

5 Conclusion

Thus, the combination of three processing methods of surface treatment (vacuum arc deposition, magnetron deposition, and microplasma oxidation) has allowed creation of the new unique thermo-barrier oxide ceramic coating with the raised thermal stability owing to formation of a nanoporous layer structure. The main oxide coating is formed under conditions of microplasma discharge in the electrolyte solution. The following treatment conditions have been determined: voltage no higher than 300 V, time of 10 min, and electrolyte composition (alkali content no higher than 0.6 g/liter) under the microplasma action to obtain zirconium dioxide modified by silica. Similar coatings can be used on an interior sheeting of a nozzle in explosive motors for the space industry.
Acknowledgments
The work was supported within the scope of the basic scientific research of state academies of sciences for 2013-2020.

References
[1] American Ceramic Society 2009 Progress in Thermal Barrier Coatings (New Jersey: John Wiley and Sons) p 628
[2] Torben Fiedler, Martin Bäker and Joachim Rösler Surf. Coat. Tech. 2017 332 30
[3] Fedorischeva M V, Kalashnikov M P, Sergeev V P and Neufeld V V 2014 Bulletin of the Russian Academy of Sciences. Physics 78 710
[4] Hongbo Guo, Shengkai Gong and Huibin Xu Mater. Sci. Eng. A 2002 325 261
[5] Mamaev A I, Borikov V N, Mamaeva V A and Dorofeeva T I 2005 Protection of Metals 41 254