About properties of ZrO₂ thermal protective coatings obtained from spherical powder mixtures

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Abstract. It is developed the technology of high-energy plasma spraying of the zirconium dioxide (ZrO₂) thermal protective coating on the basis of ZrO₂ tetragonal and cubic phases with the spheroidal grain shape and the columnar substructure, with the total porosity \( P = 4 \% \), the hardness \( HV = 12 \) GPa, the roughness parameter \( R_u \approx 6 \) \( \mu \)m, the thickness 0.3–3 mm. As a sublayer it is used the heat-resistant coating of “Ni-Co-Cr-Al-Y” system with an intermetallic phase composition and the layered microstructure of the grains.

1. Introduction

In the course of technology development the up-to-date method of high-energy plasma powder spraying has been used. To create the zirconium dioxide thermal protective coating with improved performance properties the IPME RAS and the NPC “Tribonika” have updated the technology of plasma powder spraying through the use of plasmatron (capacity 50–70 kW), the design of which is improved via the incorporation of the sectionalized insert and the loop scheme of powder mixture introduction. The plasmatron modernization has allowed to stabilize the arc current and to increase the plasma flow energy characteristics (mass-average velocity of plasma jet \( V = 1200–2400 \) m/s, temperature of plasma flow \( T = 6500–7000 \) K) [1]. So, the advantage of high-energy plasma spraying is the heating effectiveness increase of powder mixture when passing through plasma flow and this increase contributes to the fusion of powder particles edges and to their spheroidizing.

2. Researches technique

The targets of researches were the ZrO₂ thermal protective coatings on the intermetallic sublayer of “Ni-Co-Cr-Al-Y” system [2, 3], which are formed in spherical ZrO₂ powder mixtures with different content of yttrium oxide stabilizing additive: 1 – powder mixture (ZrO₂ + 7 % Y₂O₃) in solid spherical particles; 2 – powder mixture (ZrO₂ + 5.5 % Y₂O₃) in hollow microspheres; 3 – powder mixture (ZrO₂ + 16 % Y₂O₃) in hollow microspheres.

The phase composition of coatings has been examined by X-ray structural analysis using the diffractometer “Drone-3M”. The metallographic examinations were carried out on the scanning electron microscope “VEGA TESCAN II”. The Vickers hardness (HV) measurements have been performed with the use of the ultrasonic hardness tester with the load on indenter 1 N in accordance with GOST 9450-76 Standard. The coating surface roughness (\( R_u \) parameter) has been determined using the profile meter TR 200 in accordance with GOST 2789-73 Standard. The strength of coatings under formation has been evaluated by scratch hardness testing with diamond indenter (Rockwell) on
the automated installation Revetest RST with the indenter displacement speed 1mm/min and with the continuous load increase on it from 0 to 200 N. The coatings porosity has been determined by the use of mathematical processing methods (software «Good Grains») and also of electronic and microscopic pictures of coatings cross sections.

3. Results of researches
When developing the heat-resistant coating the powder mixture of NiCr20Co20Al13 grade with particles dispersion 40/100 µm has been selected. By X-ray structural analysis it was established that the main phase of the powder mixture is an intermetallic compound β-(Ni, Me)Al. In case of high-energy plasma spraying the coating is formed with two-phase intermetallic composition: β-(Ni, Me)Al + γ’-(Ni, Me)2Al. The γ’-phase formation in the coating is a result of the phase transformation β→γ’ running due to the high-temperature effect of plasma flow. The obtained intermetallic sub-layer has the thickness of ~150 µm with a size of internal pores of 5–10 µm, the hardness HV = 7.5 GPa and the surface roughness Ra = 4.6 µm.

The powder mixture obtained by plasma technology and consisting of solid spherical particles (figure 1(a)) and of hollow microspheres (figures 1(b), 1(c)), has a greater spread of particle size distribution. The main defects are particles of irregular shape with a cut, ellipsoid granules and particles from the chipped surface of the shell (figure 1(a)). On the particles surface of coarse fraction (~90–100 µm) there are the accumulations of micro-particles. Large particles have a microstructure of grains in the form of polyhedra with well-developed subgrain structure inside (figures 1(b), 1(c)).

![Figure 1](image1.png)

**Figure 1.** Microstructure: (a) – of powder mixture particles (ZrO2 + 7 % Y2O3) in solid spherical particles (x500); (b) – of powder mixture particles (ZrO2 + 5.5 % Y2O3) in hollow microspheres (x1000); (c) – of powder mixture microspheres (ZrO2 + 16 % Y2O3) in hollow microspheres (x1000).

When forming an external ceramic layer the spherical powder mixtures have been used with maximum particles size ~100 µm. By X-ray structural analysis it is determined that the powder had a phase structure on the basis of tetragonal phase (T)-ZrO2. In case of high-energy plasma spraying the two-phase coating is formed from the tetragonal (T)-ZrO2 phase and the cubic (K)-ZrO2 phase (~10 %). Figure 2 shows the ceramic coating microstructures with columnar grains ZrO2 size in cross section ~100–200 nm. In coating cross section are visible the layers (thickness ~2.5 µm) with a columnar structure of grains. The cross dimension of columns is in the interval from 0.1 to 1µm. The physical-mechanical characteristics of coatings, obtained in different powder mixtures are given in table 1.

At present time high demands are required to the life-time of thermal protective coating with a view to the possibility of its premature destruction under high operating temperatures (up to 1100 °C). To increase the coating reliability the great importance is to solve the problem to enhance its adhesion strength with a basic material, since the coating performs its protective function while the coating maintains its integrity. In terms of failure mechanism more preferable is the cohesive nature of failure, accompanied by partial or fragmentary detachment and which promotes the extension of coating life cycle.
Figure 2. Cross section of zirconium dioxide thermal protective coating, formed from the powder mixture: (a) – (ZrO$_2$ + 7 % Y$_2$O$_3$); (b) – (ZrO$_2$ + 5.5 % Y$_2$O$_3$); (c) – (ZrO$_2$ + 16 % Y$_2$O$_3$) on intermetallic sublayer of «Ni-Co-Cr-Al-Y» system (x20 000).

Table 1. Physical-mechanical characteristics of thermal protective coatings formed in different powder mixtures

| Coating material | Porosity, % | Surface roughness $R_a$, $\mu$m | Hardness HV, GPa |
|------------------|-------------|---------------------------------|-----------------|
| Coating in spherical solid powder (ZrO$_2$ + 7 % Y$_2$O$_3$) | 4.1 | 6.3 | 12 |
| Coating in powder of hollow microspheres (ZrO$_2$ + 5.5 % Y$_2$O$_3$) | 4.7 | 7.5 | 9.65 |
| Coating in powder of hollow microspheres (ZrO$_2$+16 % Y$_2$O$_3$) | 2.1 | 7.6 | 9.45 |

In case of adhesive bond violation with the substrate under a great detachment (from the substrate), the access for aggressive medium opens and the destruction of a basic material begins. For the coating, obtained from the solid spherical powder, in case of scratch hardness testing, the low-amplitude acoustic signal, caused by the process of fragmentary micro-shearing is registered. With the growth of indenter depth penetration under increased load the signal amplitude practically does not change and this fact shows the cohesive nature of failure. Even at a maximum load (200 N) there is no violation of the adhesive bond and there is no coating detachment from the substrate.

4. Conclusions
As a result of researches performed is developed the zirconium dioxide thermal protective coating of enhanced thickness (0.3–3 mm), which is formed on an intermetallic sublayer of “Ni-Co-Cr-Al-Y” system in spherical powder mixtures with a different content of yttrium oxide. This coating and intended for parts protection working at high temperatures (up to 1000 °C).

The developed thermal protective coating has been put to an evaluation test at the NPC “Tribonika” (Nizhny Novgorod city, Russia) as part of repair and recovery technology to extend the service life of working and guide blades of SGT 800 Siemens gas turbine (for “Cityenergo” LLC, Moscow).

References
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