Advanced functional coatings deposited using supersonic atmospheric plasma spraying

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Abstract. This paper presents the latest results of the ITAM team’s work in the development of the supersonic version of a spraying DC plasma torch «PNK-50» and demonstrates possibilities of Supersonic-APS method. Increasing the speed of the plasma flow to the level of 2000–2500 m·s⁻¹ has allowed deposition of functional coatings with outstanding properties. Thus, using the low-enthalpy (low-temperature) S-APS regime, low porosity (P = 0.3–1.6%) wear-resistant coatings from powder materials of NiCr alloy and WC/CoCr carbide composite were obtained, demonstrating characteristics previously available only to high-speed HVOF and DS methods. The use of the high-enthalpy (high-temperature) regime of S-APS provided spraying of refractory yttria stabilized zirconia (YSZ) oxide coatings with porosity of only 2.5% using conventional powder feedstock. The methods of SPS and LPPS made it possible to obtain advanced coatings of YSZ ceramics: thermal barrier coatings (TBC) with a columnar structure and high-density gas-tight coatings. Also ceramic coatings with a pronounced bimodal surface profile were obtained demonstrating super-hydrophobic effect.

1. Introduction

The development of thermal spraying (TS) methods over the past decade has been associated with an increase in the velocities of the sprayed particles in order to improve coating characteristics such as density, hardness, adhesive strength, corrosion resistance, etc. The reference methods in this area are high velocity oxygen/air fuel (HVOF/HVAF) and detonation spraying (DS), in which gas jet achieves a velocity of 2000–2500 m·s⁻¹ providing acceleration of particles of the deposited material up to 600–800 m·s⁻¹ and above [1, 2]. Conventional plasma spraying provides high temperatures (usually higher than 1800-2000°C) and low velocities (100–400 m·s⁻¹) of particles. This allows the application of high-quality coatings of refractory materials, such as oxides, but metal-based coatings almost always have high porosity. Figure 1 shows a comparison of the basic thermal spray methods based on the speeds and temperature of the sprayed particles of the material.

However, advances in the development of supersonic atmospheric plasma spraying (S-APS) equipment in recent years have demonstrated that this method is capable of providing comparable parameters for particles of the dispersed phase and the quality of coatings as in HVOF and DS methods. In addition, in recent years, plasma spraying of suspensions and liquid precursors (SPS and
LPPS) has developed intensively [3, 4], in which the formation of coatings of small particles (0.1–3 μm) requires an increase in their velocity above 1000 m·s⁻¹.

Figure 1. Comparison of thermal spray methods in terms of sprayed particles temperature and velocity: APS – atmospheric plasma spraying, S-APS – Supersonic APS, HVOF – high velocity oxy-fuel spraying, DS – detonation spraying, CDS – cold dynamic spraying.

2. Supersonic DC plasma torch «PNK-50»

The PNK-50 industrial air plasma torch (ITAM SB RAS) was modified using the convergent-divergent (de Laval) nozzle in the plasma torch channel [5]. The plasma discharge chamber of the plasma torch is an expanding channel, formed by electrically isolated sections of the interelectrode inserts. A key element in the design of the plasma torch is the original node of the annular input and gas-dynamic focusing of the powder. This injection scheme provides injection of the sprayed powder into the axial high-temperature and high-speed part of the plasma flow, which significantly increases the efficiency of heating and acceleration of particles, the deposition performance. Figure 2 shows the plasma torch operation in a supersonic mode, in which the diamond jet structure of the plasma flow is clearly visible. In the lower part of the figure, the calculated distributions of the velocity and temperature of the plasma flow on the jet axis are shown. The developed equipment allowed to raise the average speed of the sprayed particles to 700–750 m·s⁻¹ using metal powders of 15–45 microns in size.

3. Coatings

This section will present a comparison of the coating structures of various materials obtained in subsonic (conventional APS) and supersonic (S-APS) modes of the plasma torch. For spraying metal-based coatings (NiCr, WC/CoCr), spraying regimes with a low gas enthalpy were used to prevent substantial overheating of metals above the melting point, which is 1200–1600°C. In the deposition of YSZ oxide coatings, on the contrary, regimes with a high enthalpy of flow were used to melt the high-temperature material. The main attention was paid to the porosity of the resulting metal, composite and ceramic coatings.
3.1. Wear resistant NiCrSiBC coatings

Spraying of the coatings was carried out using the powder of the self-fluxing alloy of the PR-HH16SR3 grade of the 20–63 µm fraction used to create wear-resistant, corrosion-resistant, heat-resistant coatings. Nickel in these alloys provides corrosion resistance to acidic (under normal conditions) and alkaline media (even at elevated temperatures). Chromium is added to increase corrosion resistance. Chemical compounds of nickel with boron (nickel borides) and chromium with boron and carbon (borides and chromium carbides) contribute to an increase in hardness and, as a result, wear resistance of coatings.

Figure 2. Plasma torch PNK-50 operating in supersonic regime during spraying WC/CoCr coating (a). Visualization of diamond jet structure of supersonic flow (b) and calculated gas velocity and temperature distribution along the plasma jet (c).

Figure 3. Comparison of NiCrSiBC coatings deposited using conventional (subsonic, left) and supersonic (S-APS, right) plasma spraying.
As can be seen, the NiCrSiBC coatings obtained in the supersonic mode have a significantly more dense structure, the porosity of the coatings decreased from 4.6 to 1.6%, which positively affects the corrosion resistance of the material. In addition, the microhardness of NiCrSiBC coatings increased from 560 HV0.3 to 680 HV0.3 when going from subsonic to supersonic spraying.

3.2. Wear resistant WC/CoCr coatings
Tungsten carbide is a material with high hardness and high wear-resistant properties. WC coatings have high strength properties, as well as high corrosion resistance. Today tungsten carbide coatings are the best alternative to electrolytic chrome plating.

![Figure 4. Comparison of WC/CoCr coatings deposited using conventional (subsonic, left) and supersonic (S-APS, right) plasma spraying.](image)

Figure 4 shows a comparison of the structures of coatings obtained from WC/10Co4Cr powders 15–45 µm in size with the use of subsonic and supersonic spraying regimes. The use of S-APS mode allowed to significantly reduce the porosity of the coating from 8 to 0.3%, this low value corresponds to the level of HVOF/HVAF technologies. In addition, the supersonic coating has a more uniform microstructure, and the average hardness is 1132 HV0.3.

3.3. Dense YSZ coatings
APS coatings of YSZ oxide ceramics usually have a high porosity of 10–20% or more. Such coatings have low thermal conductivity and are used as heat-shielding layers. At the same time, many tasks require dense ceramic coatings that protect parts from corrosion in gas and liquid media.

In figure 5, one can see that S-APS in the high-enthalpy mode allows to spray not only metallic materials, but also the most refractory, for example YSZ. Supersonic coating has a porosity of only 2.5%, which is significantly lower than typical values for plasma coatings. It is interesting to note that, despite the decrease in the porosity of almost 5 times compared with the subsonic mode, the surface roughness of the coating practically did not change and amounts to 10 µm.

3.4. Suspension and Liquid Precursor Plasma Spraying
The microstructure of coatings LPPS and SPS is fundamentally different from the layers obtained by powder coating. The LPPS coating has a columnar structure similar to the coatings obtained by the gas phase deposition (PVD) method [6]. The width of the pillars is 30–60 µm, quasi-regular vertical faults intersecting the entire thickness of the coating are observed in the structure. Pictures taken at high magnification show that the structural elements of the coating mainly have a size of 0.2–1 µm,
which corresponds to the size of material particles colliding with the substrate. The porosity of the coating is 11.8%.

![SEM Image](image1.png)

Figure 5. Comparison of YSZ coatings deposited using conventional (subsonic, left) and supersonic (S-APS, right) plasma spraying.

The SPS coating has a low porosity of 1.4%, has a dense structure with pores that do not exceed 2 microns in size. The more dense structure of the SPS coating is associated with a high average particle size of the agglomerate particles in suspension – 1–5 microns. At the same time, there are no unmelted particles in the coating, which indicates a sufficient thermal power of the plasma jet (figure 6). The characteristic size of the coating structure (thickness splats) is 1–3 microns.

![SEM Image](image2.png)

Figure 6. Microstructure of YSZ coatings produced using liquid feedstock materials – solution precursor (LPPS, left) and suspension (SPS, right).
3.5. Superhydrophobic coatings with bimodal surface profile

Obtaining superhydrophobic properties of the material can be achieved by forming a regular bimodal (two-level) structure of micro- and nano-asperities [7] on its surface (figure 7a). Such a surface structure can be obtained by the method of atmospheric plasma spraying using micropowders (size 20–80 μm) and liquid materials in the form of precursor solutions and suspensions (particle size 50–100 μm). In figures 7b and 7c shows an example of a coating prepared using a PNK-50 plasma torch. The microrelief of the coating is formed using powder spraying, while the nanorelief is formed using liquid-phase spraying of LPPS precursor solutions. The use of such an approach made it possible to increase the contact wetting angle of the surface of oxide ceramics from 11 to 145 degrees.

Figure 7. Production of bimodal surface profile using plasma spraying of micro-scale layer (powder) and subsequent spraying of nano-scale layer (LPPS) (a). SEM image of bimodal surface structure (b). Demonstration of superhydrophobic effect of deposited ceramic coatings: still water droplets (c) and rebound of falling water droplet (d).

4. Conclusion

The possibilities of improving the quality of functional coatings using the supersonic plasmatron PNK-50 developed in ITAM SB RAS are demonstrated. Increasing the speed of the particles of the sprayed powder material to 700–750 m·s⁻¹ makes it possible to obtain protective wear-resistant NiCr and WC/CoCr coatings with low porosity P = 0.3–1.6%. The use of the high-enthalpy (high-temperature) regime of S-APS provided spraying of refractory yttria stabilized zirconia (YSZ) oxide coatings with porosity of only 2.5% using conventional powder feedstock. The methods of SPS and LPPS made it possible to obtain advanced coatings of YSZ ceramics: thermal barrier coatings (TBC) with a columnar structure and high-density gas-tight coatings. Subsequent use of powder and liquid-phase plasma spraying allowed to form a pronounced bimodal surface profile demonstrating superhydrophobic effect.

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