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MODIFICATION METHODS WITH HIGH ENERGY THE IMPACTS OF MULTILAYER PLASMA COATINGS ON BASIS OF CERAMICS

The article discusses processing methods using highly concentrated energy flows that effectively affect the structure of multilayer plasma coatings with subsequent modification of the structure and without changing the operational properties of the base. is thermal, associated primarily with the thermalization of the kinetic energy of the particles and contributing to the heating of the resulting near-surface layer. Even despite the high melting temperatures of the materials of the coatings under study, high-energy treatment ensures their melting with the formation of a melt above their melting temperature. The high temperature gradient that arises in the molten layer of the formed coating, accompanied by the mechanical effects of flows on the melt surface and the pressure of the shock-compressed layer, as well as the development of a number of hydrodynamic instabilities at the phase boundaries, contributes to the mixing of the resulting molten layer, which in its turn turn and contributes to the homogenization of the elemental composition. High temperatures in the melt also lead to partial evaporation of the atoms of the processed material, as a result, the ratio of oxygen and metal in the resulting coating changes slightly.

Keywords*: ceramic-metal plasma coatings, high-energy flows, treatment distance, molded structures, surface layers, compression plasma, laser treatment*

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СПОСОБЫ МОДИФИЦИРОВАНИЯ ВЫСОКОЭНЕРГЕТИЧЕСКИМИ ВОЗДЕЙСТВИЯМИ МНОГОСЛОЙНЫХ ПЛАЗМЕННЫХ ПОКРЫТИЙ НАОСНОВЕ КЕРАМИКИ

В статье рассмотрены способвы обработки при помощи высококонцентрированных потоков энерги, которые эффективно воздействуют на структуру многослойных плазменных покрытий с последующей модификацией структуры и без изменения эксплуатационных свойств основы.

Одним из самых основных эффектов при воздействии высококонцентрированных потоков энерги на обрабатываемую поверхность покрытий является тепловой, связанный в первую очередь с термолизацией кинетической энергии у частиц и способствующий нагреву полученного приповерхностного слоя. Даже несмотря на высокие температуры плавления материалов исследуемых покрытий при высокоэнергетической обработке обеспечивается их плавление с формированием расплава выше температуры их плавления. Возникающий при этом в расплавленном слое сформированного покрытия высокий градиент температур, сопровождающийся механическими воздействиями потоков на поверхности расплава и давлением ударно-сжатого слоя, а также развитием целого ряда гидродинамических неустойчивостей на границах фаз, способствует перемешиванию полученного расплавленного слоя, что в свою очередь и способствует гомогенизации элементного состава. Высокие температуры в расплаве также приводят к частичному испарению атомов обрабатываемого материала, в результате незначительно меняются соотношении кислорода и металла в получаемом покрытии.

***Ключевые слова**: металлокерамические плазменные покрытия, высокоэнергетические потоки, дистанция обработки, сформованные структуры, поверхностные слои, компрессионная плазма, обработка лазером.*

1. Introduction. Plasma wear-resistant powder coatings are widely used in modern technology. The use of high temperatures and energy densities allows coatings of refractory materials that are difficult to melt with other traditional thermal spray processes. In addition, the effective use of wear-resistant coatings can be significantly improved by applying a subsequent modifying effect on their structure. When processing wear-resistant plasma coatings with high-energy effects, their sources have a number of advantages: firstly, locality and a high concentration of input energy, which makes it possible to act on the necessary area of the formed wear-resistant coating, thereby not disturbing, due to the general heating of its entire volume, microstructure and required properties; secondly, the possibility of strict control of all the parameters of the impacts, which make it possible to form the structure of the created layer, regulate its roughness and the necessary geometric dimensions, and obtain the necessary parameters of wear resistance, total porosity, and hardness [1-5]. However, one should always keep in mind the ability of a high-energy modification to change and redistribute residual stresses in the formed coating, especially at small coating thicknesses.

2. Methods for modifying multilayer plasma coatings by high-energy effects.

The main methods of effectively influencing the structure of plasma coatings with subsequent modification of the structure and without changing the operational properties of the base are their processing using highly concentrated energy flows. The main types of such subsequent processing of coatings include: melting of the formed coatings using a plasma installation; treatment with short-term pulses of compression plasma; subsequent reflow using laser beam radiation [6-8]. After the plasma reflow process, the formed coatings significantly increase the size of the main phase of the resulting solid solution, which leads to a decrease in microhardness. At the same time, porosity also decreases, and macrohardness increases accordingly. All of the above factors (a decrease in total porosity with a corresponding activation of diffusion processes) during plasma treatment lead to a fairly dense coating with high characteristics of both cohesive and adhesive strength. But the main drawback of this technology is the presence of a zone of thermal influence on the corresponding base metal of the product, which is why massive and overall coatings are subjected to the process of melting [9]. The disadvantage mentioned above is not observed when the formed plasma coatings are processed by the action of pulses of a compression plasma jet. Usually, plasma injectors equipped with a coaxial system of electrodes serve as sources of pulsed flows under such influences. It was this treatment that was carried out on the formed surface of the HSC (heat-shielding coating) (Ni-Cr-Al-Y-ZrO_2 - 8% Y_2O_3) on the parts of gas turbine blades [10]. In this process, nitrogen was used as a plasma-forming gas; the forged heat flux is not able to propagate in depth to a very large value. And therefore, from the surface, the resulting plasma coating structure has the form of a molten layer with a thickness of about 10 microns. The transformed layer formed after exposure is evenly distributed on the surface and, accordingly, clogs the pore outlets. The conditions obtained under the influence of pulses of a compression jet, which is a high-speed thermal shock with further instantaneous cooling over the entire surface of the resulting coating, largely form thermal stresses and lead to the corresponding fragmentation of the surface. That is why plasma coatings with very low thermal conductivity, such as, for example, oxide HSC, become much more efficient and workable under high-temperature conditions. In the process of thermal cycling of a number of parts (as a rule, parts of aircraft engines, such as gas turbine blades, combustion chambers, nozzles) [11–14], they are deformed, but without destruction due to general fragmentation and the resulting closure of pore exits, which is significantly reduces the gas permeability of the resulting coating. All this makes it possible to perform layer-by-layer processing of sprayed coatings containing formed pores with their gradual melting over the entire thickness due to an increase in the thermal conductivity of the previous treated layers and overheating of the still untreated subsequent deep layers [15]. This leads to a significant increase in the efficiency of the most used HSC. A structure of surface layers with increased heat resistance and coating layers bordering the substrate with high operational characteristics of cohesion and adhesion is formed. The sources [10] considered the effect of exposure to compression plasma flows on the combinatorics of plasma coatings consisting of many layers (sublayers (Ni-Al, Ni-Cr) and outer layers of oxides (Al_2O_3, TiO_2, ZrO_2) formed on thin substrates of aluminum. Conducted high-energy impacts modify the near-surface layer. The analysis of the elemental and phase composition of ceramic coatings was carried out, their microstructure and mechanical characteristics were considered, which made it possible to establish the regularities of the effect of compression plasma on such types of coatings. One of the most basic effects when a compressive plasma flow acts on the treated surface of coatings is thermal, which is associated primarily with the thermalization of the kinetic energy of plasma particles and contributes to heating the resulting near-surface layer. Even despite the high melting temperatures of the materials of the coatings under study: 2715 C - (ZrO_2), 2072 C - (Al_2O_3), 1843 C - (TiO_2) - when heated by a compression plasma flow, their melting is ensured with the formation of a melt above their melting temperature. The high temperature gradient (~105 K/m) arising in this case in the molten layer of the formed coating, accompanied by the mechanical effects of the plasma flow on the melt surfaces and the pressure of the shock-compressed layer, as well as the development of a number of hydrodynamic instabilities at the phase boundaries, contributes to mixing of the resulting molten layer, which in turn contributes to the homogenization of the elemental composition. High temperatures in the melt also lead to partial evaporation of the atoms of the processed material, as a result, the ratio of oxygen and metal in the resulting coating changes slightly. Nevertheless, it does not lead to a violation in the stoichiometry of the compositions of the modified ceramic oxide phases. According to the equilibrium diagrams of the state of binary systems, Zr-O, Al-O and Ti–O, zirconium oxide ZrO_2 has a fairly wide region of homogeneity, which begins at oxygen concentrations of about 40% atomic fractions, while Al_2O_3 and TiO_2 oxides can exist in narrower concentration ranges. Therefore, the use of coatings based on zirconium oxides ZrO_2 are more preferable due to the preservation of the oxide modification of the surface layer even after the use of compression plasma flows, not excluding repeated exposures leading to a change in the ratio of metal and oxygen atoms. Partial evaporation of atoms from the formed melt and hydrodynamic mixing of the resulting molten layer contribute to a decrease in the concentration of impurity atoms found in coatings during investigation. The formed surfaces of coatings based on oxides are characterized by increased roughness, this is due to the sintering of individual particles of powder material during the formation of plasma coatings (Figure 1 a). After high-energy exposure to compressive plasma flows, intense hydrodynamic mixing of the melts occurs, which, due to the surface tension forces, smoothes the surfaces after crystallization (Figure 1 b). At the same time, the high cooling rate of the melt, due to intense heat removal to the unmelted part of the samples, leads to rapid crystallization of the melt, as a result, the crystallized solid phase has a high level of mechanical stresses, which leads to the appearance of a network of surface cracks. The number of cracks, as well as their spatial localization, as well as their average size, do not depend on the type of plasma coating being processed. An analysis of the microstructure of the coatings formed after exposure to compression plasma was carried out. He showed that the depth near the molten layer is on the order of 6–10 μm for plasma coatings based on aluminum oxide (Al_2O_3) powder material, and on the order of 10–15 μm for coatings based on zirconium oxide (ZrO_2). The increase in the depth of the molten layer of coatings based on ZrO_2 is due to its lower thermal conductivity (3–5 W/m K) in comparison with Al_2O_3 (40 W/m K). For coatings based on aluminum oxide powder material, the heat flux is more intensively removed to the unmelted volume and, accordingly, contributes less to heating in the near-surface region. The crystallized layer of the formed coating is characterized by the almost absence of pores, as well as longitudinal cracks, which are usually present in the coating after formation, it turns out that as a result of the impact of the compression plasma flow, a significant compaction of the near-surface layer occurs. It should be noted that the intermediate layer based on nickel-aluminum and nickel-chromium powder materials does not change its composition and thickness even after exposure to a compression plasma flow.

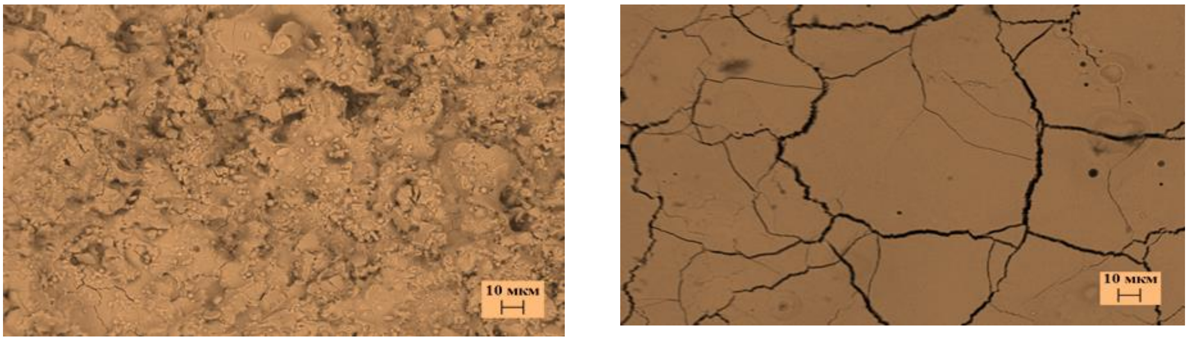

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Figure 1. Areas of the surface of the coatings: a - before and b - after processing compression plasma (magnification ×1000)

This is due to the fact that the thickness of the outer oxide layer is approximately several hundred micrometers, due to which the thermal effect when exposed to the plasma flow on the sublayer is negligible. In the practical use of multilayer composite plasma coatings, coatings based on M rabbits (Ni-Cr-Y-Al) are optimal, since this sublayer contains elements of both the oxide layer (yttrium) and substrate elements (aluminum). In this case, the conjugation of the sublayer with the oxide layer and the substrate leads to an increase in the required adhesion strength and prevents the layers from peeling off under external influence. While maintaining the elemental composition within the required homogeneity of the existence of oxide phases, it stabilizes the phase composition of plasma coatings after exposure to compression plasma flows. In the case of plasma coatings based on ZrO_2, in which two modifications (monoclinic and cubic) are simultaneously present in the initial state, the volume content of the monoclinic modification decreases. This contributes to an increase in the wear resistance of the coating itself due to the homogeneity of the phase composition and a decrease in the level of internal stresses at the phase boundaries. Changes in the structure in the near-surface layer of the formed coatings after exposure to compression plasma flows also contribute to the modification of their mechanical properties. Smoothing the surface, increasing the density of the crystallized layer and the absence of pores and macrocracks makes it possible to improve the mechanical properties of the surface, as evidenced by the decrease in the friction coefficient. The presence of surface cracks in the remelted layer (Figure 71 b) negatively affects the change in the friction coefficient, leads to its increase. They can be initiators of internal stresses, which can lead to the destruction of the formed coatings and an increase in the intensity of abrasive wear. Such destruction during tribological testing of the surface can occur when modifying coatings based on Al_2O_3, for which an increase in the friction coefficient was recorded. For coatings based on ZrO_2, a hardened layer based on zirconium nitride (ZrN) is formed on the surface. They are characterized by a decrease in the coefficient of friction after treatment using compression plasma. X-ray spectral microanalysis from the surface provides the following data on the percentage in atomic fractions of elements in the near-surface layer - 56.1% O2 and 27.3% Zr, 9.3% Y; 2.4% N. The presence of nitrogen is explained by the introduction of a plasma-forming substance into the near-surface layer. The ratio of elements under the influence of compression plasma changes and this is caused by partial evaporation of oxygen atoms with a decrease in concentration. High-energy treatment forms a surface relief characteristic of a remelted or crystallized layer with an extensive network of microcracks (from 20 to 80 μm) and a fine-mesh substructure (average cell size at the level of 200–400 nm) due to rapid crystallization near the melt and the creation of thermoelastic stresses in top layers of the coating. In sources [11- 13], for high-energy processing of TRC based on partially stabilized zirconia, CO2 lasers were used: repetitively pulsed (pulse energy density from 90 to 250 J/cm2, wavelength 9.25 μm) and continuous operation (power 800 W, wavelength 10.6 μm, spot diameters 4; 5 and 7 mm). After processing using a pulsed CO_2 laser, almost 100% of the tetragonal modification is formed in the plasma coating, there is no monoclinic modification of ZrO_2.

Rapid cooling as a result of laser processing equalizes the concentrations of yttrium oxide in the coating volume and starts the suppression of diffusion processes, this redistributes yttrium oxide and forms the complex oxide $Y_{0.15}Zr_{0.85}O_{1.93}$. In the heat-affected zone, 3 regions are formed, which is associated with a decrease in the cooling rate of the material with distance from the surface due to insufficient thermal conductivity of zirconium dioxide. The thinnest, microcrystalline, amorphous structure of tetragonal zirconium dioxide formed directly at the very surface. In the center of the zone, thin dendrites are distinguished, approximately 0.01 μm in size and up to 0.05 μm in length, while the layer thickness is approximately 2-3 μm. Further, a larger and more pronounced crystalline structure is observed with rather large grains of tetragonal gray zirconium dioxide (0.05-0.1 μm) and thin light grains (0.008-0.016 μm) of the complex oxide $Y_{0.15}Zr_{0.85}O_{0,\ 93}$. The formation of complex oxides is explained by the redistribution (segregation) of the stabilizer occurring in this area and by the fact that, during crystallization, its excess is displaced from the outer region into this zone. The approximate thickness of this layer is about 3-4 microns. In the region of the largest value, tetragonal zirconium dioxide (about 10-20 μm) has two modifications: large inclusions (modifications 17-923 about 0.1-0.2 μm) and small inclusions (modifications 14-534 less than 0.01 μm). When a cw CO_2 laser is used for modification, the main regularities are preserved when the structure of the formed coating changes. However, the heat-affected zones (HAZ) have a much greater depth and the formed cracks propagate not only through the HAZ, but also further into the treated coating. The resulting structure of the transformed layer during high-energy processing with a pulsed CO_2 laser is preferable for the appointment of heat-protective coatings. This was shown by the results of thermal cycling, in HSC treated with a pulsed laser, the number of thermal cycles is 1.5 times more (483) than in coatings without treatment, and 1.4 times higher than in coatings treated with a continuous CO_2 laser. In [10–13], Al_2O_3–TiO_2 coatings obtained by plasma spraying onto a carbon steel substrate were treated with a laser, and the effect of laser remelting on the microstructure and wear resistance of plasma sprayed Al_2O_3–TiO_2 coatings was studied. The powder sublayer consists of 80 wt.% Ni - 20 wt. % Cr, the main parameters of plasma deposition are as follows: current - 500 A, voltage - 68 V, Ar primary gas - 40 l / min, He secondary gas - 20 l / min, spray distance - 120 mm, and spray thickness - about 50 microns. The surface ceramic coating powder consists of 60 wt.%

Al_2O_3 and 40 wt.% TiO_2, the main parameters of plasma spraying are as follows: current - 585 A, voltage - 70.6 V, primary Ar - 40 l/min, secondary He - 20 l/min, spray distance - 120 mm, spray thickness - 300-400 microns. Laser remelting was carried out with a high-energy pulsed laser (type HAN'S-LASER YAG W200B) with a spot diameter of 4 mm, a single-pulse power of 8 kW, and a scanning speed of 8 mm/s. The microstructure and phase composition of plasma-sprayed and laser-remelted coatings were analyzed using scanning selective microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD). The microhardness and adhesive strength of the two coatings were measured using a microhardness tester and an electronic universal tensile testing machine. The wear resistance of the two coatings was tested using a slurry rubber wheel abrasion tester, and the wear behavior was also studied by SEM. to the right, the bonding layer and the ceramic coating are alternately located. The coating has a typical plasma-sprayed lamellar structure and contains many pores and cracks (Figure 2 a). Laser remelting makes it possible to effectively reduce the pores and microcracks of the plasma-sprayed coating, and the coating itself has become much denser. In addition, lamellar defects of the plasma-sprayed coating were erased and fine equiaxed grains with a uniform distribution were obtained (Figure 2 b). Thus, the compactness of the plasma-sprayed coating has been greatly improved by laser remelting. The plasma-sprayed coating has a porous microstructure and a microhardness value in the range from 460 to 630 HB (Figure 2 a). The laser remelted coating has a dense microstructure and a microhardness value in the range from 980 to 1000 HB (Figure 2b). Obviously, laser remelting leads to a significant increase in microhardness (more than 50%) and a homogeneous dense microstructure (very uniform microhardness).

X-ray diffraction analysis was carried out on the plasma-sputtered coating and the laser-remelted coating. The microstructure of the plasma-sprayed coating mainly consists of α-Al_2O_3, γ-Al_2O_3 and $TiAl_2O_5$, while the laser remelt coating consists only of α-Al_2O_3 and $TiAl_2O_5$. Obviously, the metastable γ-Al_2O_3 phase transforms into the stable α-Al_2O_3 phase due to remelting and recrystallization of the plasma-sprayed coating during laser remelting. Therefore, it is possible to increase the hardness and wear resistance of the coating using laser remelting. The laser remelted coating becomes much denser, and then its microhardness and adhesive strength are greatly improved. Laser remelted coating has better wear resistance compared to plasma sprayed coating, and the main wear mechanism responsible for wear is wear of micro-cracks and cracks.

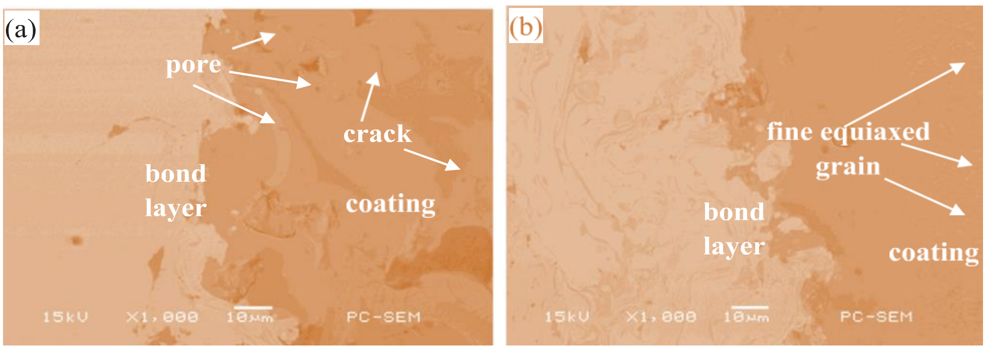

Figure 2 - Cross section of SEM images of coatings: (a) plasma spraying; (b) laser remelting

3. Conclusion

Based on the review of methods for modifying high-energy plasma coatings based on ceramics, it can be stated that these coatings have a number of significant defects, such as high residual porosity, lamellar structure, and not always sufficient adhesion. Subsequent high-energy processing, as a surface hardening technology, is an effective way to eliminate these defects and improve the quality of the plasma-welded coating. Our studies allowed us to state that when the resulting wear-resistant plasma coatings are exposed to compression plasma flows, the following processes take place. The high amount of energy transferred by the plasma flow to the coating contributes to the melting of the surface layer with a thickness of 10–70 μm, depending on the coating material being processed. When exposed to a plasma flow, a certain part of the coating material can be removed due to the ablation effect. Moreover, the amount of material removed will increase with an increase in the energy transferred to the coating by the plasma flow. Under the influence of the pressure of the plasma flow, liquid-phase mixing will occur in the molten coating layer. At the last stage, the surface layer of the coating hardens under conditions of ultrafast cooling. It turns out that the phase and elemental composition of the surface layer of the coating changes significantly. A layer is formed in the coating, which contains elements of the coating and plasma-forming gas. And in the case of multi-stage processing of the "coating-base" system, a layer is formed that contains elements and coatings, and bases and plasma-forming gas.

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