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Multi-Layers Composite Plasma Coatings Based on Oxide Ceramics and M-Croll

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Abstract. The paper considers the influence of the parameters of the plasma spraying process on the technological characteristics of multilayer coatings based on nickel-chromium, nickel-chromium-aluminum-yttrium materials, oxide ceramics, intended for operation at high temperature and additional dynamic loads. The design of plasma coatings during their application (with subsequent high-energy processing) under such conditions requires a comprehensive solution – both the use of high-quality powder ingredients and the optimization of technological parameters. The plasma process of applying powder materials has been improved to obtain the maximum values of their utilization factors. The technological characteristics that affect the properties of plasma coatings are optimized, namely: the flow rates of the plasma-forming and materials-transporting gases, the flow rate of supplied powder materials, the current and voltage of the electric arc of the plasma torch, the distance from the plasma torch nozzle exit to the substrate. The paper presents the results of studies of the structure of coatings, performed using scanning electron microscopy. Their analysis has made it possible to form general regularities obtained by the action of radiation of compression plasma flows on coatings formed by air plasma. The considered structures are created using the processes of melting, compaction and high-speed cooling of plasma coatings. The main optimization indicators are the maximum local compaction and spillage of the obtained compositions with the absence of defects and destruction from the impact of compression plasma flows. The main effect during the action of radiation of a compression plasma flow on previously formed coatings is thermal. It contributes heating of the near-surface layer. When the coating is exposed to radiation of compression plasma flows, a remelted layer of oxides with a thickness of about 12–15 μm is created, smoothing the relief of the formed surface and creating a network of cracks on the surface, diverging into the depth of the coating. The liquid-phase processes occurring in the molten phase of the near-surface layers after exposure to compression plasma radiation change the structure of the layers and contribute to the modification of their mechanical properties. By smoothing the surface, increasing the density of the surface crystallized layer and minimizing macro-defects – pores or macrocracks – the mechanical characteristics of the coatings increase.

Keywords: plasma torch, technological modes, optimization process, powder utilization factor, radiation of plasma compression flows, modification of near-surface layers, operational parameters

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Многослойные композиционные плазменные покрытия на основе оксидной керамики и м-кролей

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Реферат. Рассмотрено влияние параметров процесса плазменного напыления на технологические характеристики многослойных покрытий на базе материалов никель-хром и никель-хром-алюминий-иттрий, оксидной керамики, предназначенных для эксплуатации при высоких температурных и дополнительных динамических нагрузках. Конструирование плазменных покрытий при их нанесении (с последующей высокоэнергетической обработкой) в таких условиях требует комплексного решения – как применения качественных порошковых ингредиентов, так и оптимизации технологических параметров. Усовершенствован плазменный процесс нанесения порошковых материалов для получения максимальных значений их коэффициентов использования. Оптимизированы технологические характеристики, оказывающие влияние на свойства плазменных покрытий, а именно: величины расходов плазмообразующего и транспортирующего материалы газов, расход подаваемых порошковых материалов, ток и напряжение электрической дуги плазменной горелки, расстояние от среза сопла плазмотрона до подложки. В статье приведены результаты исследований структуры покрытий, выполненных с применением растровой электронной микроскопии. Их анализ позволил сформировать общие закономерности, получаемые при воздействии излучения компрессионных плазменных потоков на сформированные воздушной плазмой покрытия. Рассмотренные структуры созданы при помощи процессов плавления, уплотнения и высокоскоростного охлаждения плазменных покрытий. Основные показатели оптимизации – максимальное локальное уплотнение и проплавление полученных композиций с отсутствием дефектов и разрушений от воздействия потоков компрессионной плазмы. Главный эффект при воздействии излучения компрессионного плазменного потока на ранее сформированные покрытия – тепловой. Он способствует нагреву приповерхностного слоя. При действии на покрытия излучения компрессионных плазменных потоков создается переплавленный слой оксидов толщиной порядка 12–15 мкм, сглаживающий рельеф сформированной поверхности и создающий на поверхности сетку трещин, расходящихся в глубину покрытия. Происходящие в расплавленной фазе приповерхностных слоев жидкофазные процессы после воздействия излучения компрессионной плазмы изменяют структуру слоев и способствуют модификации их механических свойств. Благодаря сглаживанию поверхности, увеличению плотности поверхностного закристаллизованного слоя и минимизации макродефектов – пор или макротрещин – повышаются механические характеристики покрытий.

Ключевые слова: плазменная горелка, технологические режимы, процесс оптимизации, коэффициент использования порошка, излучение плазменных компрессионных потоков, модификация приповерхностных слоев, эксплуатационные параметры

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Introduction

The design of new ceramic composites is based on the need to further improve the properties of plasma coatings for operation under high-temperature operation and under conditions of intense wear [1–5]. The process of plasma spraying is one of the most widespread methods of deposition of coatings from ceramics and especially oxide ceramic materials in production [6–9]. This method of creating coatings is universal, since using one apparatus in the appropriate modes, various materials can be applied to surfaces and a number of restorative and hardening technologies can be implemented. It makes it possible to manufacture a wide range of parts with minimal costs for technological equipment [10]. The effectiveness of protection against failure of mechanisms at high energy loads is limited by the impact resistance of the materials used. Spacecraft protection is based on the use of high-strength materials with minimal density, high viscoplasticity and hardness [1, 3]. The effectiveness of protection is characterized by the ability to absorb kinetic energy, determined by the impact resistance of the materials used. Sufficient ductility and strength characteristics are important elements for extending service life. An increase in hardness indicators corresponds to a decrease in viscosity and plasticity indicators, which causes brittle fracture processes. The formed gradient plasma coatings with a ceramic outer layer and a metal substrate are characterized by high impact strength. One of the most frequent defects in the plasma deposition of oxide ceramics is the flaking of the created coatings [11]. It is associated with a large difference between the values of the thermal expansion coefficients of the oxide layer and the substrate metal. Metal sublayers serve for possible smoothing of the values of the temperature coefficients of linear expansion [12–17]. When choosing substrate materials, it is also necessary to ensure a high level of adhesive strength at the interface [17–21]. The main functional task of the sublayer in the created plasma coatings is the maximum plastic relaxation of the stress index, which is created during an incompatible change in the volumes of metal and ceramics in the case of heating and cooling of the created coating. The operational ductility of alloys decreases due to a complex of high-temperature oxidation processes, since the ceramic layer is gas-permeable; therefore, the sublayer materials must have high thermal resistance [20]. Accordingly, the binder sublayer must solve two main problems:

1) maintain the required level of plasticity in the operating range of operating temperatures;

2) maintain its heat resistance. It is difficult to solve these problems comprehensively.

The optimization of the phase and chemical composition of the alloy obtained is required. Therefore, the main goal of the ongoing research is to optimize the technological characteristics of the plasma process for the deposition of multilayer structures on substrates that reproduce products used for protection against high-temperature damage.

Optimization of technological characteristics of the process of deposition of multilayer gradient coatings

When implementing plasma spraying, a number of factors affect the properties of the coatings being formed. The main ones are: the consumption of the plasma-forming and carrier gas of the powder material, the consumption of the sprayed materials, the current and voltage of the electric arc of the plasma torch, the distance from the plasma torch nozzle exit to the base, and the speed of the substrate. As an example (Fig. 1) the results of the optimization of the process of plasma formation of layers based on oxide ceramics (zirconium dioxide stabilized with yttrium oxide) with intermediate metal layers (nickel-chromium and nickel M-Croll), which under the specified sputtering conditions are characterized by the corresponding coefficients of the use of the powder material, are presented (KIP, %).

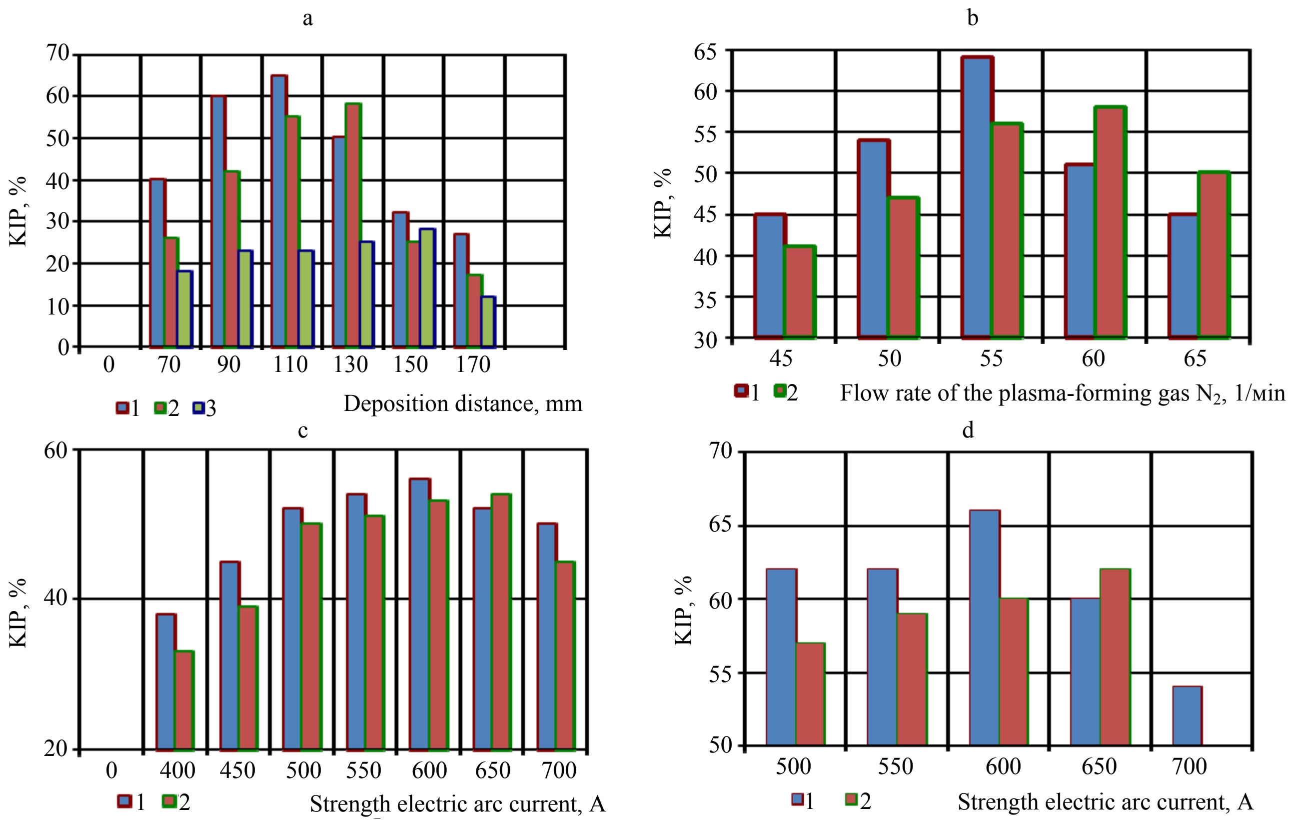

Fig. 1. Dependencies KIP of the technological characteristics of the spraying process:
a – deposition distance *L*, mm, for powders ZrO_2–Y_2O_3 (1 – with a fraction of 50–63 microns; 2 – fraction of 63–80 microns; 3 – with a fraction of 80–100 microns; I = 500 A; R_N = 45 l/min; R_{por} = 4.5 kg/h);
b – flow rate of the plasma-forming gas N_2 for ZrO_2–Y_2O_3 powders (M-Croll sublayer) (1 – with a fraction of 40–63 microns; 2 – with a fraction of 63–80 microns; L = 100 mm; I = 500 A; R_{por} = 4.5 kg/h); c – strength electric arc current *I*, A, for ZrO_2–Y_2O_3 powders (nichrome sublayer) (1 – with the flow rate of plasma-forming gas N_2 R_N = 55 l/min; 2 – with R_N = 50 l/min; L = 100 mm; R_{por} = 4.5 kg/h, with a fraction of 40–63 microns); d – strength electric arc current *I*, A, for powders ZrO_2–Y_2O_3 (M-Croll sublayer) (1 – with the flow rate of the plasma-forming gas N_2 R_N = 55 l/min; 2 – with R_N = 50 l/min; L = 100 mm; R_{por} = 4.5 kg/h, with a fraction of 40–63 microns)

In the case of small sputtering distances, the particle does not have time to heat up and reaches the substrate at a temperature <t_{pl}. In our case, an increase in the KIP to values L = 100 mm for powder material ZrO_2–Y_2O_3 with a fraction of 40–63 μm and to values of L = 110 mm with a fraction of 63–80 μm with a further increase in the distance, the particle melts, being in the jet for a long time, and is sprayed when hitting the substrate. This causes the KIP to fall [15]. When the electric arc current and plasma gas flow rates increase to certain values (Fig. 1b–d), a corresponding correlation of the instrumentation occurs, since these characteristics affect the degree of penetration of the powder material [11–14]. With their further increase, overheating and splashing occurs when it hits the substrate; therefore, KIP decreases. As the N_2 flow rate increases, the current maximum KIP values decrease.

The morphology of the coating surface, changed by the flows of compression plasma

Under the action of compression plasma flows on multilayer gradient coatings formed on substrates and consisting of a solid layer of the oxide phase ZrO_2–Y_2O_3 and viscous sublayers (Ni–Cr–Al–Y; Ni–Cr), the surface layer changes. Analysis of the obtained microstructures and mechanical properties made it possible to construct schemes for the effect of compression plasma on these coatings. The main defining effect of the compression plasma flow on the formed surface of the coatings is thermal, which promotes overheating of the layer near the surface. Heating by a flow of compression plasma ZrO_2–Y_2O_3 ensures its melting, despite the high melting temperatures of the material 2715, the resulting melt is heated above the melting temperature. High characteristics of the temperature gradient (~105 K/m) in the molten layer of the formed coating, accompanied by the mechanical effect of plasma flows on the surface of the resulting melt, pressure in the shock-compressed layer and the development of hydrodynamic effects create instability at the boundaries of intermediate phases during mixing of the molten layer and promote homogenization at its elemental composition. According to the equilibrium diagram of binary systems of elements Zr–O, zirconium oxide ZrO_2–Y_2O_3 creates a wide range of homo geneity (from the oxygen concentration of about 40 % atomic fractions). Therefore, plasma coatings based on zirconium oxide ZrO_2–Y_2O_3 are more preferable due to the possibility of maintaining the oxide modification of the surface layer after exposure to a compressive flow of compression plasma and even after repeated exposure, which, as mentioned above, creates a change in the ratio of metal and oxygen atoms. In addition, with partial evaporation of melt atoms and hydrodynamic stirring of the melt layer, the concentration of atoms in technological impurities, which are always present in the obtained coatings, decreases. The surface of coatings based on metal oxides is characterized by increased roughness, combining sintering of individual powder particles when creating a coating (Fig. 2). After the action of the compressive compressive plasma flow, the composition of the melt is hydrodynamically mixed, and this, due to the forces of surface tension, leads to the leveling of the surface after the crystallization process (Fig. 2). High values of cooling rates in melts due to intensive heat removal to the unmelted part of the samples leads to rapid crystallization; as a result, high mechanical stresses are created in the crystallized solid phase, which causes the formation of surface cracks.

As a rule, the quantitative values of cracks, their location in space and average dimensions do not depend on the coating being treated. For the practical use of multilayer plasma coatings, coatings with a viscous layer based on Ni–Cr–Y–Al, including elements of a single-layer solid oxide (yttrium), are optimal and a support element (aluminum). The diffusion bonding of the intermediate layer with the outer oxide layer and the substrate can increase the adhesion parameters and exclude delamination of individual layers under external influences. Changes in structures in the near-surface layer of the created coatings after exposure to radiation of compression plasma flows lead to a change in their mechanical properties. The effect of surface leveling, an increase in the density of the crystallized layer. the absence of macrodefects, such as pores and macrocracks, makes it possible to increase the mechanical properties of the formed surfaces, as evidenced by a decrease in the coefficient of friction.

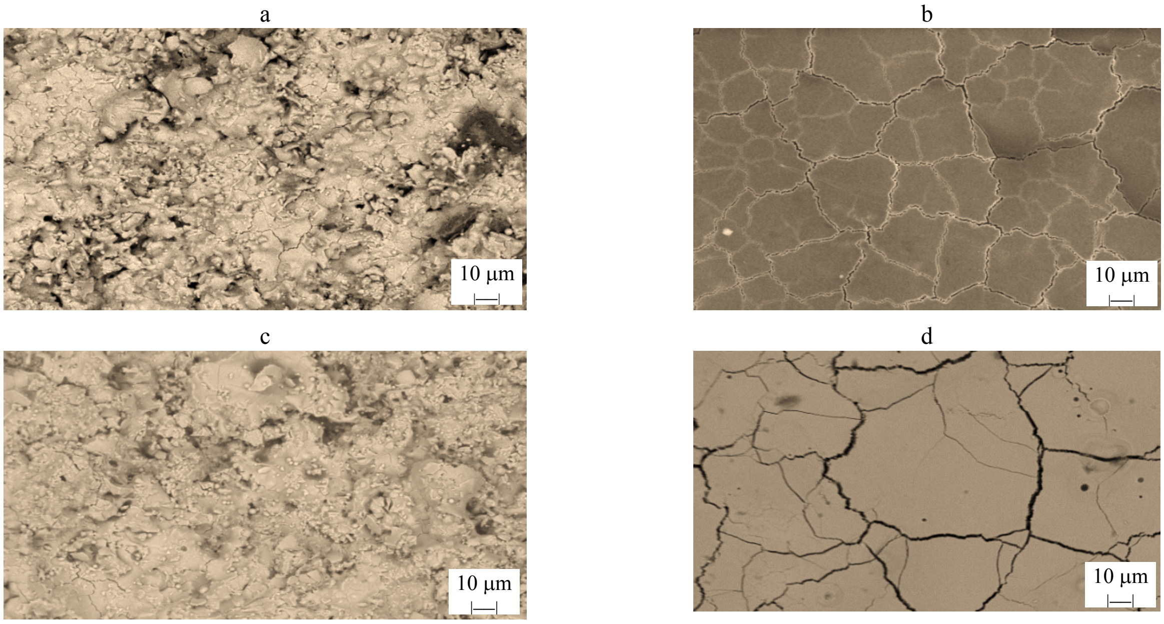

Fig. 2. SEM-image of the surface of the formed coatings before and after the compression plasma flow:
a; b – using a NiCr sublayer and an upper ZrO_2–Y_2O_3 layer; c, d – using the NiCrAlY sublayer and the upper ZrO_2–Y_2O_3 layer;
a, c – after the deposition process; b, d – after the teatment with a compression plasma flow (×1000 increase)

The presence of surface cracks in the treated layer adversely affects the change in the coefficient of friction and leads to its increase. They can be a source for creating internal stresses, which lead to the destruction of the resulting coatings and an increase in their abrasive wear. At the same time, coatings based on zirconium oxide ZrO_2–Y_2O_3, with a formed hardened layer based on zirconium nitride ZrN, have a reduced coefficient of friction after exposure to compressive compression plasma currents.

CONCLUSIONS

1. The design and creation of new systems of multilayer plasma coatings based on new powder materials or integrated technologies is necessary for the further advancement of technologies using plasma in modern conditions due to an increase in dynamic loads, an increase in operating temperatures, price and environmental requirements for technological equipment. The technologies considered in the article for the formation of metal-oxide coatings using plasma spraying in air and subsequent modification using compression plasma flows are precisely designed to solve these problems. As a result of the research carried out, the optimization of the modes of plasma spraying of multilayer oxide layers was carried out, their properties, morphology and microstructure of the created surfaces were determined, and the layers after exposure to compressive compressive plasma flows were investigated. In the process of plasma spraying, the properties of the formed coatings are influenced by a number of parameters that have been optimized.

2. The most important of them are: the consumption of plasma-forming and transporting gases, the consumption of the sprayed material, the current and voltage of the plasma torch electric arc, the distance from the outlet of the plasma torch nozzle to the substrate, the velocity of the substrate relative to the plasma torch. The results of the study of the morphology, structures and compositions of the created coatings, using a scanning electron microscope, are presented. The analysis of the structures created for the coatings made it possible to assess the regularities of their formation under the influence of a compressive compressive plasma flow. It is shown that the resulting effects from compression flows on the created multilayer metal-ceramic coatings are modified in the near-surface layer to a depth of 15–20 microns, its melting and crystallization occurs, leading to an increase

in density. The occurring liquid-phase processes accompanying the melting of layers at the surface change the morphological properties of the formed surface due to a decrease in the quantitative values of roughness. This changes the mechanical and tribological characteristics of the formed coatings, leading to a decrease in friction coefficients and an increase in wear resistance parameters.

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