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REGULAR ARTICLE

Influence of Laser Thermal Cycling on the Structure Evolution and Tribological Properties of Plasma Coatings

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The paper presents a comprehensive study of the structure and properties of plasma eutectic coatings after thermocyclic treatment (TCT). It is shown that such treatment significantly increases the adhesive and cohesive strength of coatings. It has been found that the wear resistance of two-layer coatings in the entire temperature range is higher than for single-layer ones. This is primarily due to the increase in adhesive properties, a decrease in the hardness gradient along the coating depth, and an increase in the thermal stability of the coating due to the barrier properties of the boride-alloyed layer. By controlling the size of the dispersed crystals of the penetration phases along with the state of the metal matrix, it is possible to select such TCT modes at which the coatings can acquire optimal tribological properties. It was found that the wear resistance of the original plasma coating and after thermal cycling is approximately the same, which can be explained by the complete decomposition of solid metastable structures and intensive oxidation of the coatings due to their porosity. It is shown that the wear resistance of two-layer coatings is higher than that of single-layer coatings in the entire temperature range, which is primarily due to the increase in adhesion properties and increased thermal stability of the coating due to the properties of the layer doped with borides.

Keywords: Wear resistance, Thermocyclic treatment, Plasma coating, Wear, Adhesive strength, Laser melting, Eutectic alloys.

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1. INTRODUCTION AND RESEARCH OBJECTIVES

The deposition of protective gas-thermal coatings to working surfaces is one of the most effective ways to protect parts and mechanisms from various types of wear. Among the materials that are widely used for spraying, eutectic alloys based on iron are of particular interest. During gas-thermal spraying of such powder materials, when crystallization proceeds at rates of 104-106 °C/s, coatings with a eutectic, microcrystalline, or amorphous structure are formed [1]. The phases and structures formed at such cooling rates are in a metastable, unbalanced state, which should contribute to their structural self-organization during friction [2-5].

However, the stability of such coatings, especially under dynamic loads, as well as operation at high temperatures in the heat exchange mode, is usually low as a result of their fragility, porosity, low adhesive strength, large gradient of properties, and the occurrence of diffusion processes at the coating-substrate interface [6, 7].

There are many ways to increase the adhesion strength of gas-thermal coatings. In order to increase the adhesion strength of the plasma coating to the base, diffusion annealing at 1000-1100 °C is widely used, which is associated with high energy consumption and undesirable overheating of the steel base. An effective increase in adhesion properties can be achieved by diffusion annealing of plasma coatings in the thermal cycling mode [8-10]. Thermal cycling treatment (TCT) in the temperature range covering polymorphic transformations leads to an intensification of phase transformations. In works [11, 12], the processes occurring in gas-thermal coatings during high-temperature annealing, as well as during reflow, have been investigated.

With these methods for increasing the adhesion strength of coatings, however, the non-equilibrium state of the structure (metastable phases, supersaturated solid solutions of the phases penetrating into the matrix), which is favorable during friction, is lost. At the same time, it is known [13] that if the structure is unstable under given loading conditions, i.e., capable of restructuring, then the energy of deformation by friction is dissipated into favorable relaxation processes, and the resistance to wear increases. The use of furnace volumetric heating during isothermal and thermocyclic annealing, which is characterized by the inertia of heating and cooling, does not allow simultaneously ensuring an increase in adhesion strength and maintaining a certain level of the initial non-equilibrium state of the plasma coating.

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In this regard, the work used the TCT of coatings with a laser, as well as the preliminary deposition of barrier boride layers before spraying, which limits the mutual diffusion of coating and substrate elements and the degradation of their structure.

2. RESEARCH METHODOLOGY

For coatings, powders of eutectic alloys of the 12Kh18N9T–TiB2–VC (VTN) and 12Kh18N9T–TiB2–CrB2 (KhTN) systems were used, the chemical composition of which is given in [14].

The deposition was carried out on substrates made of low- and medium-carbon steels and 12Kh18N9T steel. Protective barrier layers were obtained by laser alloying from plaster containing amorphous boron and boron carbide. The thickness of the coating was from 100 to 200 μm.

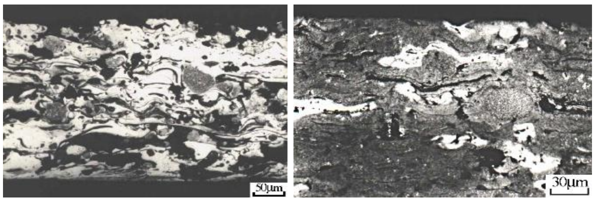
The microstructure of the coatings was studied metallographically, and the microhardness was determined on an M-400 device of the company "Leso Corporation" with automatic loading. The distribution of elements in the coating was studied using a scanning electron microscope-analyzer "Samscan-4DV" with the software and mathematical support. Tribotechnical tests were conducted on a friction machine at loads of 1-3 MPa, sliding speeds of 0.1-1.9 m/s, and temperatures of 20-800 °C. The ZhS6K alloy was chosen as a counterbody.

Thermocyclic treatment in the temperature range of 900 ↔ 500 °C was carried out on a laser installation "LATUS-31". The temperature of the upper limit of the cycle was chosen based on the previously constructed phase equilibrium diagrams, and it was 0.75 of the melting temperature. Such a temperature ensures the absence of morphological changes in the eutectic crystals of the penetration phases, but can significantly affect the decomposition of the metal base of the matrix, the coagulation of dispersed crystals in the penetration phases contained in the "white" regions, as well as the diffusion processes in the steel substrate-coating transition zone. The number of thermal cycles was chosen with taking into account the aim to obtain levels of a structural state approaching the equilibrium one [11]. Thus, the selected temperature and quantitative modes of TCT made it possible to influence the diffusion processes at the substrate-coating boundary, structural state, and the thermodynamic equilibrium of white regions.

3. RESEARCH RESULTS AND DISCUSSION

In the sprayed eutectic coatings, weakly etched regions called "white", unmelted or partially melted powder particles, and a small number of pores are observed(Fig. 1, a). Noteworthy is the relatively small porosity of the coatings (about 10 %). White regions probably arise due to the rapid crystallization of liquid droplets on a cold substrate. Such regions have high chemical resistance and practically do not interact with a reagent that reveals the structure of the alloy before spraying, which determined their name.

For both systems of eutectic coatings from VTN and KhTN, starting from three thermal cycles, a noticeable decrease in the boundaries between white regions and their disintegration are observed. In the KhTN coating after three TCTs, the number of gray regions, i.e., white regions that have partially disintegrated, increases(Fig. 1, b). Upon increasing the number of thermal cycles to five, a higher degree of disintegration of white regions takes place accompanied by the separation of dispersed particles from the penetration phases in them. At the same time, coagulation and coalescence processes occur, which leads to an increase in the size of the separated particles and the appearance of a solid solution with a significantly smaller number of the penetration phases.



a b

Fig. 1 – Structure of the plasma coating KhTN: a – original (sprayed); b – after five times thermal cycling

The kinetics of changes in the properties of the coating structure components depending on the number of thermal cycles is given in Table 1. A decrease in microhardness is observed for both main structure components, which is associated with the decomposition of the supersaturated solid solution of the base. It should be noted that the microhardness of the eutectic regions decreases only after four thermal cycles. It can be assumed that the specified decrease in microhardness is caused by the decomposition of the metal matrix, and the occurrence of coagulation processes with the increasing number of thermal cycles does not lead to a significant decrease in microhardness. For white regions, a constant decrease in microhardness with the increasing number of thermal cycles is characteristic. However, after six cycles, the microhardness of the white and eutectic regions becomes almost equal. The microhardness of the coating after such treatment is somewhat lower than that of the deposited one without subsequent TCT but higher than that of the laser-melted one.

Table 1 – Microhardness and volume content of structure components of plasma coating from the eutectic VTN alloy

Structure component	Content of structure component, vol%	Microhardness H100, MPa					
		Before TCT	Number of TCT cycles				
			2	4	6	8	10
Eutectic regions	12 – 14	9750	9100	8740	7800	7150	7175
White regions	70 – 80	1340	10250	9100	7750	6800	6780

Further increase in the number of treatments leads to a decrease in the microhardness of the white regions compared to the eutectic component. This is probably due to the coagulation of the penetration phases in the white regions, which leads to a decrease in their strength.

Thermocyclic treatment is accompanied by the development of relaxation processes, which increase the plasticity of the deposited coatings, confirmed by the absence of cracks on the microhardness measurement prints, and is consistent with the data of other studies. Thus, it has been shown that annealing of gas-thermal coatings increases the elastic modulus of white regions and the plasticity of both white regions and eutectic components [10]. Based on this, it made it reasonable to examine porosity, adhesion strength to the substrate, and diffusion processes in the plasma coating after 2-6-fold TCT, when the relatively high microhardness of the white regions and the coating as a whole is still maintained.

The findings listed in Table 2 evidence that thermal cycling reduces porosity and increases the adhesion strength of the plasma coating compared to the original ones without TCT. The increase in the adhesion and cohesion properties of the deposited coating is due to the intensification of diffusion processes under TCT. When studying the microstructure obtained in the "phase contrast" mode, a gray zone with a thickness of 1.5-2 μm was detected, adjacent to the substrate side at the interface with the matrix. To identify the state of the chemical elements in this zone, special studies were conducted using the "Digimap-M" program. It was revealed that the coatings contain a large amount of vanadium. It diffuses to the coating-substrate interface and interacts with iron or iron and chromium simultaneously.

Table 2 – Dependence of microhardness, porosity, and adhesion strength to the 12Kh18N9T substrate on the treatment of plasma coating from VNT

Treatment	Micro-hardness, H100, MPa	Porosity, %	Adhesive strength to the substrate, MPa
Plasma spraying	12400	10 – 2	16 – 20
Plasma spraying and 4 TCTs	10050	7 – 9	90 – 100
Plasma spraying on the barrier layer	11750	7 – 9	30 – 40*
Plasma spraying on the barrier layer and 4 TCTs	10200	5 – 7	120 – 150
Laser melting	8250	0.5 – 1	400 – 450

* The adhesion strength of the plasma coating to the barrier boride-alloyed layer

To determine the quantitative composition of chemical elements in the coating-substrate system, a micro X-ray spectral analysis was performed for five points along the length of the segment perpendicular to the coating-substrate interface with an interpoint distance of 20 μm. The probe location was 2.5 μm in diameter and 1.5 μm in depth. For the targeted penetration of the probe into the studied phases, the SEM phase contrast mode was used. The chemical composition of the analysis points was determined using computer programs. According to the quantitative analysis data, histograms of the distribution of elements were constructed (Fig. 2).

Analysis of the distribution of elements at the coating-substrate/boundary indicates that TCT causes joint mass transfer of vanadium, titanium, chromium into the substrate and iron and manganese from the substrate into the coating. The coating-substrate boundary becomes blurred and represents solid solutions of these alloying elements in iron, as evidenced by the data on the chemical composition and microhardness.

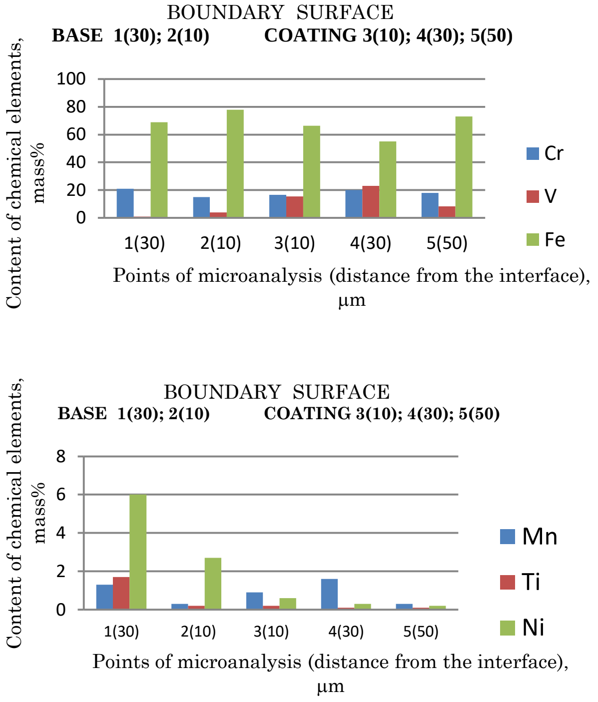


Fig. 2 – Histograms of the distribution of elements in the plasma coating from VTN and the 12Kh18N9T substrate before and after four-fold TCT

As follows, the selected TCT mode (4-6 thermal cycles) allows one to increase the adhesive properties and plasticity of the coating, reduce its porosity, and simultaneously maintain a relatively high microhardness.

However, the intensification of TCT diffusion processes leads to an increase in adhesion, and with its prolonged exposure – to the degradation of the initial structure and phase composition. In this regard,

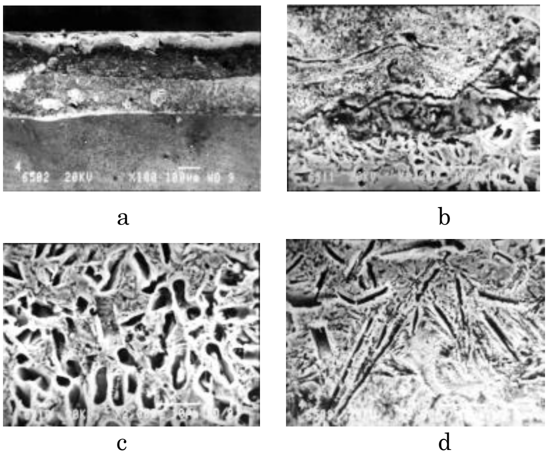

a
b
c
d

Fig. 3 – Microstructures of the two-layer coating after tribological tests at 850 °C: a – general view, ×50; b – transition zone between plasma VTN and boride-alloyed coatings, ×2000; c – microstructure of the boride-alloyed layer, ×2000; d – transition zone between the boride-alloyed layer and the base (steel 12Kh18N9T), ×2000

we conducted a study of the properties of a two-layer coating containing a barrier boride-alloyed layer deposited by laser(Fig. 3).

These studies have shown that the barrier layers are a structure of the eutectic type based on the Fe-B-C system(Fig. 3, c). The nature of this structure and the degree of its non-equilibrium depend on the laser processing mode. The layer microhardness is 6000-9000 MPa. It was experimentally established that the adhesion strength of the plasma coating to the alloyed layer is higher than that to the steel substrate (Table 2). Probably, the low melting point of the alloyed layer (low-melting eutectic Fe – Fe2B) and its melting during spraying contribute to the chemical interaction of the plasma coating with the layer. In addition, the non-equilibrium state of the laser-assisted boride-alloyed layer contributes to increased adhesion of the plasma coating.

X-ray spectral analysis of samples with a two-layer coating subjected to 50-fold TCT did not reveal any mutual diffusion of elements of the eutectic coating and the barrier layer. Only diffusion of boron into the plasma coating, as well as into the substrate from the barrier layer and iron into this layer was observed. The limited mass transfer processes in the working coating also contribute to the preservation of its high performance properties[17, 18].

The microstructures of the coating after high-temperature friction and wear tests also confirm the absence of interaction of the barrier layer with the plasma coating and indicate the thermal stability of the two-layer coatings(Fig. 3, b). Friction and wear tests of plasma coatings in the initial state and after TCT showed their different resistances to wear. TCT allows for changing the structural state and thermodynamic equilibrium of white regions along with increasing the number of regions with a more plastic eutectic structure (Table 3). Such a structure can absorb a significant portion of energy and relax friction stresses to a greater extent. The reduction in brittleness and increase in plasticity of the coating after TCT increases its ability to form secondary structures(Fig. 3, a), which indicates its favorable tribological properties[9].

After TCT, continuous oxide films are formed on the friction surfaces of coatings, whereas on coatings without TCT, films are formed in the form of separate regions. The prerequisite for this may be a decrease in the corrosion resistance of white regions during their disintegration. The wear resistance of the KhTN coating after TCT increases more significantly compared to that of the VTN coating along with a decrease in the friction coefficient.

Table 3 – Wear resistance of 12X18H9T steel with eutectic coating from VTN, depending on the treatment

Processing type	Wear, mg/cm^2 per 10^3 m		Friction coefficient	
	293 K	873 K	293 K	873 K
Plasma spraying	54,10	36,40	0,64	0,25
Plasma spraying + 4TCT	28,35	32,50	0,43	0,20
Plasma sputtering on a boride layer + 4TCT	24,30	12,35	0,38	0,11

4. CONCLUSIONS

Some plasma eutectic coatings after laser thermal cycling treatment have been investigated. Tribological tests at high temperatures have found that the wear resistance of the original plasma coatings and after thermal cycling is approximately the same. This can be explained by the complete decomposition of solid metastable structures and intense oxidation of the coatings due to their porosity.

The test results also showed that the wear resistance of two-layer coatings is higher than that of single-layer coatings over the entire temperature range. This is primarily due to increased adhesion properties, reduced hardness gradient along the coating depth, and increased thermal stability of the coating due to the barrier properties of the boride-alloyed layer.

Thus, by controlling the size of the dispersed crystals of the penetration phases and simultaneously the state of the metal matrix, it is possible to select such TCT parameters at which plasma coatings can reach high adhesive-cohesive strength with a simultaneous increase in tribological properties.

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Вплив лазерного термоциклювання на еволюцію структури і триботехнічні властивості плазмових покриттів

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У роботі проведено комплексне дослідження структури та властивостей плазмових евтектичних покриттів, після термоциклічної обробки (ТЦО). Показано, що така обробка суттєво підвищує адгезійно – когезійну міцність покриттів. За результатами проведених досліджень встановлено, що стійкість проти спрацювання двошарових покриттів у всьому діапазоні температур вища ніж для одношарових. Це в першу чергу зумовлене підвищенням адгезійних властивостей, зниженням градієнту твердості по глибині покриття, підвищенням термостабільності покриття завдяки бар'єрним властивостям легованого боридного прошарку. Керуючи величиною дисперсних кристалів фаз проникнення і одночасно станом металевої матриці, можна підібрати режими ТЦО, при яких покриття отримують оптимальні триботехнічні властивості. Було виявлено, що зносостійкість вихідного плазмового покриття та після термоциклування приблизно однакова, що можна пояснити повним розкладанням твердих метастабільних структур та інтенсивним окисленням покриттів за рахунок їх пористості. Показано, що зносостійкість двошарових покриттів вища, ніж одношарових у всьому діапазоні температур, що пов’язано насамперед із підвищенням адгезійних властивостей та підвищенням термічної стійкості покриття за рахунок властивостей шару, легованого боридами.

Ключові слова: Зносостійкість, Термоциклічна обробка, Плазмове покриття, Зношування, Адгезійна міцність, Оплавлення лазером, Евтектичні сплави.