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Operating properties of the coating, depending on the composition during plasma-chemical modification

D O Bondarenko and V V Strokova

Belgorod State Technological University named after V G Shoukhov, 46, Kostukov Street, Belgorod, 308012, Russia

E-mail: di_bondarenko@mail.ru

Abstract. Compositions of protective and decorative coatings on the basis of a mixture of high alumina refractory, liquid glass and dyeing salts of metals are developed. The color of the coatings depends on the type of dyeing salt and the concentration of the aqueous solution. Data on the effect of the composition on the operational properties of vitreous coatings obtained by the method of plasma-chemical modification are presented. The increased content of aluminium and silicon oxides provides an improvement in a number of characteristics such as microhardness, heat resistance, water resistance and acid resistance, which are essential in the formation of protective and decorative coating. It is established that at the rate of plasma jet passage up to 15 mm/s a protective-decorative coating with uniform texture is formed, at the rate of plasma jet passage 20 mm/s and more the coating represents a hilly surface with separate and congested deformed drops of frozen melt.

1. Introduction

Currently, the issue of biological corrosion is acute at the enterprises of agro-industrial complex. This problem is being addressed through disinfection, rehabilitation and preventive maintenance of the premises. Chemical methods of pathogenic microflora control are widely used, but frequent treatment of buildings' surfaces structural elements and structures with caustic substances leads to their gradual degradation under the influence of corrosive acids, washout of soluble substances, as a consequence - formation of additional porosity of materials, microcracks, etc. Development of bio-resistant composite materials, which are able to withstand the main agents of corrosion, taking into account the degree and dynamics of corrosion at the enterprises of agro-industrial complex, makes it possible to reduce the destructive impact of microorganisms [1-2].

Plasma-chemical modification of composite materials is an energy-saving, high-performance, efficient and environmentally friendly technology for obtaining vitreous coatings with increased technical and operational parameters, such as microhardness, water resistance, acid resistance, alkali resistance, etc. [3-5]. Glass is a corrosion-resistant and weather-resistant material that does not collapse under the influence of strong and weak organic, mineral and bioacids, salts, as well as fungi and bacteria. In this regard, the development of compositions of protective and decorative coatings on concrete products with the use of plasma melting is urgent.

2. Materials and methods

In order to study the possibility of obtaining a coating modified with low-temperature plasma, the main raw materials used were high alumina refractory breakage and liquid sodium glass. Dyeing salts of



cobalt, nickel and copper metals were used to expand the color characteristics of protective and decorative coating.

Before plasma melting, a heat-resistant powder was prepared on the basis of high alumina refractory by grinding a battle in a ball mill with subsequent sifting (0.25-0.63 mm). The powder was mixed with an aqueous solution including 5 % and 10 % liquid sodium glass with a density of 1.4 g/cm³ in a propeller stirrer to obtain a homogeneous suspension. The suspension was taken as a basis, divided into several parts and added the necessary amount of dyeing salts of metals. Then, they sprayed and dried the face of the composite material. The applied layer was evenly absorbed into the surface. Plasma-chemical modification was carried out on a specially mounted stand with adjustment of plasma treatment speed. The high-temperature source was the multifunctional portable plasma complex "Gorynych". For formation of plasma jet we used plasma-forming liquid, which is 50-% water-alcohol solution. Parameters of plasma-tron operation: current 6 A, voltage 140-160 V, plasma jet temperature 6000 °C.

To assess the dependence of microhardness of the protective-decorative coating on its composition after plasma treatment of samples, the melted surface of the coating was cut off with a diamond disk with subsequent pouring of irregularities with epoxy resin. After hardening of epoxy resin, surface grinding was performed. The prepared coating layer was tested for microhardness with the help of a Vickers hardness tester Nexus 4504-IMP with a test load of 0.1 kgf/0.98N.

In order to study the temperature resistance of the samples, which have the temperature of 20±1 °C, they were heated successively in the thermo cabinet at the temperatures of 90-150 °C. After heating the samples were immersed in water with the initial temperature of 15±1 °C. Thermal resistance was estimated by the temperature difference at which microcracks appear on the front surface of the protective and decorative coating.

Water resistance of the protective and decorative coating was determined by the standard method in accordance with the requirements of GOST 10134.1-82. Water resistance and acid resistance of the protective and decorative coating were determined according to the standard method in accordance with the requirements of GOST 10134.1-82 and GOST 473.1-81. Surface texture, color and shine were determined by organoleptic method.

3. Results and Discussion

Plasma-chemical modification was carried out on the stand at plasma jet speeds of 5 mm/s, 10 mm/s and 25 mm/s. The speed of plasma processing is one of the main technological factors forming the texture of the decorative coating. Thus, at a speed of up to 15 mm/s, a decorative coating with a uniform texture is formed, and at a speed of 20 mm/s and more, the coating is a hilly surface with separate and congested deformed droplets of frozen melt (Figure 1).

Under the influence of high temperatures of plasma jet in the protective-decorative coating there is an impoverishment of calcium and sodium oxides, enrichment with aluminum and silicon oxides (Table 1). The increased content of aluminum and silicon oxides will improve a number of operational properties, such as microhardness, heat resistance, water resistance and acid resistance, which are the main in the formation of protective and decorative coating.

Table 1. Chemical composition of protective-decorative coating

Title	Chemical composition, wt. %						
	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃
	Based on high alumina refractory:						
prior to processing	1.59	95.05	2.38	0.18	0.73	0.02	0.05
after processing	2.09	95.95	1.45	0.13	0.33	0.01	0.04
	Based on high alumina refractory and liquid glass (5%)						
prior to processing	8.94	82.79	2.32	0.17	5.91	0.02	0.05
after processing	9.45	83.89	1.82	0.12	4.67	0.01	0.04

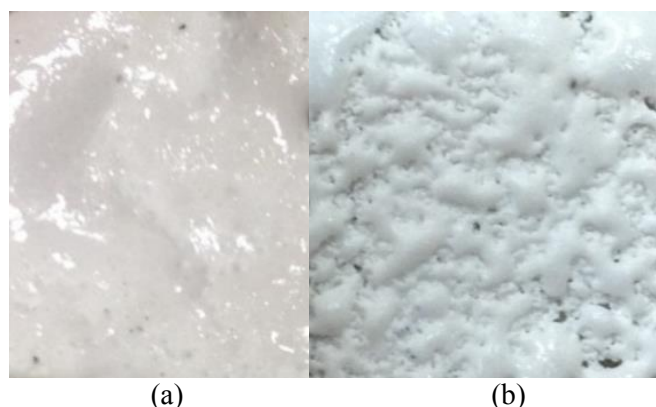


Figure 1. Macrostructure of decorative coating at plasma processing speed: (a) 10 mm/s (smooth surface); (b) 25 mm/s (textured surface).

6 compositions of protective-decorative coatings were developed for the studies (Table 2). The microhardness of the coating determines its durability. Composite material can be subjected to various impacts and scratches during operation, as well as during its periodic cleaning if necessary from contamination. The hardness of glasses and glass-crystalline materials depends on many factors, the main of which are chemical and mineralogical composition, thermal past of the material, in particular, hardening, the value of internal stresses, etc. As it is known, hardness is also influenced by the radius of the protective-decorative coating of cations. Thus, Ca^{2+} cation increases microhardness in glasses and glass-crystalline materials in comparison with Na^+ cation, increase of content in Na^+ cation coating contributes to decrease of microhardness. In addition to various modifications of aluminum oxide, the protective and decorative coatings under study contain calcium oxide (composition 1, Table 2) and sodium and silicon oxides (composition 2-6, Table 2). With the increase in the content of sodium liquid glass microhardness decreases, which is due to the increased content of sodium oxide in the protective-decorative coating.

Table 2. Dependence of the protective and decorative coating characteristics on the composition

Composition	Glass coating, %		Metal dyeing salts (water solutions, %)			Microhardness, HV	Color of coating
	Fire-resistant fraction 0.25–0.63 mm	Liquid glass	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$		
1	100	–	–	–	–	2510	white
2	95	5	–	–	–	887	white
3	95	5	1.5	–	–	856	blue
4	95	5	–	1.5	–	708	green with brown and yellow inclusions
5	95	5	–	–	1.5	1300	white with pink inclusions
6	90	10	–	–	–	702	white

During plasma-chemical modification, the metal dyeing salts, located in a thin layer on the front surface of the decorative coating, decompose to form metal oxides. Metal oxides diffuse into the surface layer of the coating, changing its chemical composition. The effect of thermodiffusion, which changes the chemical composition of the protective-decorative coating leads to changes in microhardness in

comparison with protective-decorative coatings without dyeing metal salts. The most effective are the dyeing salts of copper, which increased the microhardness of the coating by almost 1.5 times.

Chemical stability is one of the most important indicators characterizing the safety and decorative coating. The protective and decorative coating can be exposed to a variety of corrosive media during operation. As the temperature increases, the chemical attack on glass and glass-crystalline materials increases significantly, which can significantly reduce the aesthetic properties of the composite. The main indicators of chemical stability include water resistance and acid resistance.

As follows from the results obtained (Table 3), water resistance of protective and decorative coating on the basis of high alumina refractory refers to the II hydrolytic class. Water resistance of protective and decorative coating on the basis of high alumina refractory, liquid glass and dyeing salts belongs to the III hydrolytic class. This is explained by the presence of increased content of sodium oxide in the composition of the composition by the introduction of sodium liquid glass into the coating.

The coating is considered to be acid-resistant if there is no border on the front surface that is visible to the naked eye due to the change of color or shine of the coating. The analysis of the obtained results (Table 3) allows us to conclude that all the protective and decorative coatings under study, except for composition 6, are acid-resistant. Protective and decorative coating (composition 6) compared to all other coatings under study, contains twice as much sodium liquid glass as is due to relatively low acid resistance.

Materials are thermocycled during operation, which contributes to the accumulation of both protective and decorative coatings and at the base of constant and temporary stresses, the formation of cracks in the coating and its spontaneous separation. In this regard, heat resistance is an important performance indicator that affects the durability of the composite.

In the case of plasma-chemical modification, the high thermal stability of the raw material (Table 3) ensures high adhesion strength and frost resistance of the composite. In turn, the value of thermal stability depends on many factors: the porosity of the material, the presence of two or more phases, the value of thermal conductivity.

Table 3. Chemical composition of protective-decorative coating

Compos ition	Glass coating, %		Metal dyeing salts (water solutions, %)			Water resistance		Acid resista nce	Heat resist ance, °C
	Fire-resistant fraction 0.25– 0.63 mm	Liquid glass	CoCl ₂ ·6H ₂ O	NiCl ₂ ·6H ₂ O	CuCl ₂ ·2H ₂ O	0.01n HCl, ml.	Hydrol ytic class		
1	100	–	–	–	–	1.04	2	No	146
2	95	5	–	–	–	2.48	3	change	138
3	95	5	1.5	–	–	3.25	3	in	135
4	95	5	–	1.5	–	2.94	3	color	132
5	95	5	–	–	1.5	3.01	3	or gloss	141
6	90	10	–	–	–	3.43	3	subtle change in color	122

Plasma-chemical modification of the front surface of composite finishing materials was made in order to obtain protective and decorative coatings, which significantly improve its aesthetic properties. The coatings are non-porous and will protect the composite from penetration of aggressive media and thus prevent corrosion of the matrix.

4. Conclusion

Influence of plasma treatment speed on formation of protective-decorative coating and texture of concrete face surface is investigated. It is established that at a speed of up to 15 mm/s a protective and

decorative coating with a uniform texture is formed, at a speed of 20 mm/s and more the coating is a hilly surface with separate and time deformed droplets of frozen melt.

It is shown that under the influence of high temperatures of plasma jet in the protective and decorative coating there is a depletion of calcium and sodium oxides, enrichment with aluminum and silicon oxides. The increased content of aluminum and silicon oxides provides an improvement in a number of operational properties, such as microhardness, heat resistance, water resistance and acid resistance, which are essential in the formation of protective and decorative coating.

Glass protective-decorative coatings can compete with paints and varnishes in terms of their aesthetic qualities. They have a beautiful appearance, have a high hardness and wear resistance, and in the case of the use of dyeing salts of metals (without additional costs for dyes) can obtain additional decorative effect. The coatings are cost effective and durable.

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