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Plasma-Chemical Modification of Facing Composite Material on the Basis of Hollow Glass Microspheres with Decorative Protective Coating

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Abstract—The paper considers plasma-chemical modification of facing composite material on the basis of hollow glass microspheres with decorative protective coatings. It is shown that the technology of obtaining decorative protective coating by the method of plasma reflow is highly efficient and energy-saving, which will allow competition with traditional technologies and significantly reduce the cost of finishing work. Compositions of decorative protective coatings based on high-alumina refractory and liquid glass have been developed. It was revealed that the use of high-alumina refractory crushed material in the intermediate layer makes it possible to reduce the number of microcracks and eliminate the consequences of high-temperature impact on the matrix of fine-grained concrete. The positive effect of hollow glass microspheres on the minimization of thermal shock was established. The results of the investigation of the effect of plasma-chemical modification on the phase composition and structural features of the facing composite material on the basis of hollow glass microspheres with a decorative protective coating are presented. The regularity of layer-by-layer variation of the phase composition and the macro- and microstructure of the decorative protective coating of the facing composite material is established. It is shown that the upper layer is represented by Na–Ca–Al–Si glass, the middle glass ceramic layer is represented by the glass phase and α and β modifications of aluminum oxide, and the lower dehydration layer is represented by dehydration products of hydrosilicates and α and β modifications of alumina. High-temperature action of the plasma jet intensifies thermal diffusion, which in turn leads to a redistribution of oxides along the thickness of the decorative protective coating.

Keywords: blister composite, plasma-chemical modification, decorative protective coating, hollow glass microspheres, alumina modifications

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INTRODUCTION

At present, in modern home building, a great amount of attention is paid to decorating front facades of buildings and constructions. Facing materials such as silicone coatings, polymer cement compositions, water-based paints, and other organic and organomineral compositions are used [1]. However, these coatings are nondurable and highly expensive.

Unlike organic coatings, vitreous decorative protective ones have a high microhardness and chemical stability and low abrasion. The plasma reflow of the front surface of facing composite materials is a more effective technological solution compared with traditional technologies; this method allows not only reducing energy costs but also significantly improving aesthetic and consumer properties [2–12].

Effective heat insulation materials are also used in modern home building to save energy [13, 14]. Using hollow glass microspheres (HGM) in the composition of lightweight concrete makes it possible to obtain efficient wall heat insulation materials [15, 16].

The aim of this work is to develop facing composite materials obtained by plasma-chemical modification on the basis of HGM with decorative protective coating.

EXPERIMENTAL

The phase composition of coatings was determined by the X-ray diffraction (XRD) method by means of a Thermo Fisher Scientific ARL X'TRA diffractometer in the 2θ range of 4°–64° with Cu anode and K_α radiation and the voltage of 40 kV using the Crystallo-

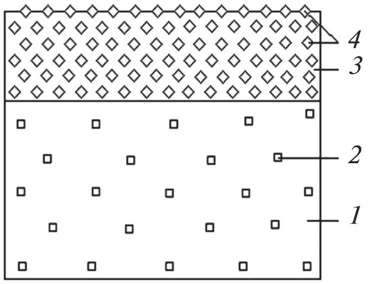

Fig. 1. Structure of composite lining material with a decorative protective coating before plasma-chemical modification: (*1*) composite lining material; (*2*) filler (quartz sand, PSM); (*3*) hydrated Portland cement; (*4*) filler (crushed high-alumina refractory).

graphica Search-Match Version 2.0.3.1 software program. The content of components in the decorative protective coating after the plasma-chemical modification was determined by X-ray fluorescence analysis using a WorkStation RL 9900 spectrometer with Co anode and K_α radiation and the voltage of 60 kV. The XRD patterns were treated using the DIFWIN software program. The XRD patterns were decoded using the ASTM database and a demo version of the Match program (Phase Identification from Powder Diffraction) created by Crystal Impact.

The microstructure of the coating matrix was determined using a MIRA 3LM energy dispersive spectrometer for the electron probe microanalysis. This spectrometer allows one to analyze samples with a thickness of more than 100 nm by fast and accurate quantitative analysis using the modified Cliff–Lorimer algorithm.

The fusion was carried out with a speed of passage of the plasma jet on the front surface of 10 and 20 mm/s using a Gorynych electric-arc plasma torch. The temperature of the plasma jet at the point of the contact with the front surface was 6000°C. After the plasma reflow of the samples with the decorative protective coating based on a high-alumina refractory and liquid glass, a layer-by-layer coating sanding was performed using an IsoMet 5000 (BUEHLER®) machine for the section preparation. The phase composition of each sanded layer located above the high vitreous amorphous layer was studied.

The surface temperature after the plasma-chemical modification was determined using a Promin optical pyrometer. The distribution of temperatures in the surface layers was determined using platinum-rhodium thermocouples.

The following compositions of the decorative protective coatings are developed:

—Portland cement: crushed high-alumina refractory with the fractional composition of 0.25–0.63 mm with the cover of crushed high-alumina refractory with the fractional composition of 0.63–0.8 mm in the mass ratio of 1 : 3;

—Portland cement (mixed with a 5% aqueous solution of liquid glass): crushed high-alumina refractory with the fractional composition of 0.25–0.63 mm in the mass ratio of 1 : 3 with the cover of crushed high-alumina refractory with the fractional composition of 0.63–0.8 mm wetted by the mixture of liquid glass with coloring metal salts in the amount of 1.5–3.0 wt %.

A set of samples of the facing composite materials with the filler made of a mixture of quartz sand and HGM with the decorative protective coatings was prepared for the plasma reflow. A form was filled with a solution based on Portland cement and the mixture of quartz sand and HGM by 3/4; then the 1/4 of the layer of the decorative protective coating based on crushed high-alumina refractory with different fractional composition was added (Fig. 1). At the formation, the surface of the samples was covered with the crushed high-alumina refractory with a certain fractional composition wetted by the liquid glass with coloring metal salts. Then, this layer was compacted to achieve a sufficient contact between the samples and coating [12].

The plasma reflow of the composite material using an electric arc laboratory setup of low-temperature plasma was carried out at the temperature of the

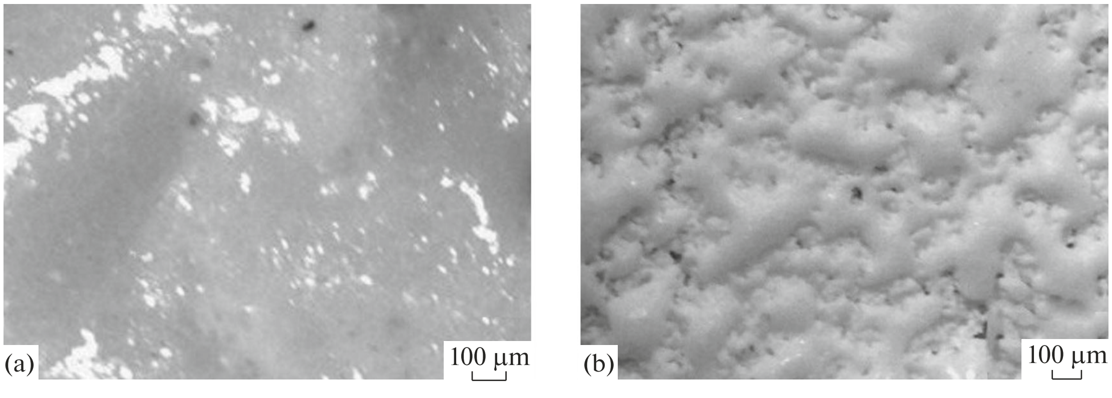

Fig. 2. Macrostructure of the decorative protective coating at speed of passage of plasma jet of (a) 10 and (b) 20 mm/s.

plasma jet of 6000°C after the solidification of samples for 28 days.

Scanning electron microscopy using a TESCAN MIRA 3 LMU high-resolution microscope was applied to study the microstructure of the fused area after the reflow of the surface layer of the facing composite material with the filler made of the mixture of quartz glass and HGM with the decorative protective coating based on the mixture of the crushed high-alumina refractory and liquid glass.

The samples with the decorative protective coatings without coloring metal salts were reflowed at different rates of passage of the plasma jet over the surface of 2, 5, 10, 15, and 20 mm/s.

RESULTS AND DISCUSSION

Figure 2 presents the microstructure of the decorative protective coating at the rates of passage of the plasma jet of 10 and 20 mm/s.

The surface texture of the decorative protective coating significantly depends on the rate of passage of the plasma jet. A flat coating is formed at the rate of passage of 10 mm/s, and a coating with a bumpy surface is formed at the rate of passage of 20 mm/s. This is explained by the value of the surface tension of the melt and the coating thickness. When the coating thickness is small (~200–500 μm), a bumpy surface is formed under the action of surface tension forces. With the accumulation of the melt (thickness greater than 1000 μm), the surface tension forces are not enough to congregate the melt.

The hollow glass microspheres have a positive effect on the minimization of the thermal shock of the plasma jet at the plasma-chemical modification. They make possible the elimination of the microcrack zone together with the decorative protective coating based on crushed high-alumina refractory with liquid glass (Fig. 3).

The microstructure of the composite material with the decorative protective coating after the treatment with the low-temperature plasma is given in Fig. 4.

The high temperatures of the plasma jet (~6000°C) melted the crystalline phases of the surface layer. The fused top layer of the decorative protective coating after the plasma-chemical modification was amorphous (Fig. 5).

The surface layer warmed to 2100°C; the temperature of the glass ceramic layer reached 1600°C. At the depth of 1500 ± 50 μm, where the matrix with the HGM is located, the layer warmed up to 400°C. At this temperature, partial dehydration processes occur; as is known [17], ettringite dehydrates in the temperature range of 100–150°C.

Corundum melts at the temperature of 2050°C. The amorphous zone consists of Na–Ca–Al–Si glass with an increased content of sodium and aluminum oxides and without crystalline impurities. This is

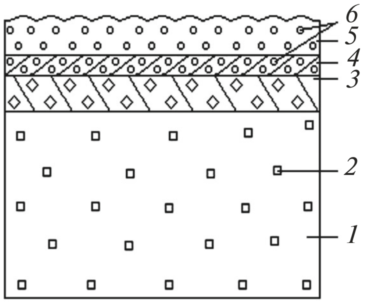

Fig. 3. Structure of composite lining material with a decorative protective coating after plasma-chemical modification: (*1*) composite lining material; (*2*) filler (quartz sand, PSM); (*3*) unmelted dehydration zone of decorative protective coating; (*4*) glass ceramic zone; (*5*) amorphous zone; (*6*) gas inclusions.

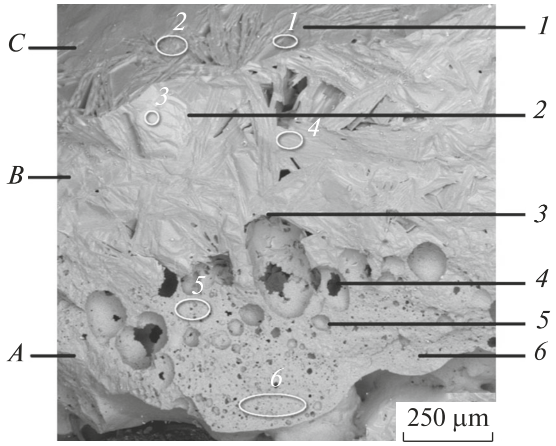

Fig. 4. Microstructure of the facing composite material with decorative protective coating after plasma-chemical modification: (*A*) matrix with PSM; (*B*) decorative protective coating based on Portland cement and a mixture of crushed refractory of the fraction of 0.25–0.63 mm with liquid glass at a ratio of 1 : 3; (*C*) amorphous zone, (*1*) decorative protective coating; (*2*) glass ceramic zone; (*3*) dehydration zone; (*4*) pores; (*5*) PSM.

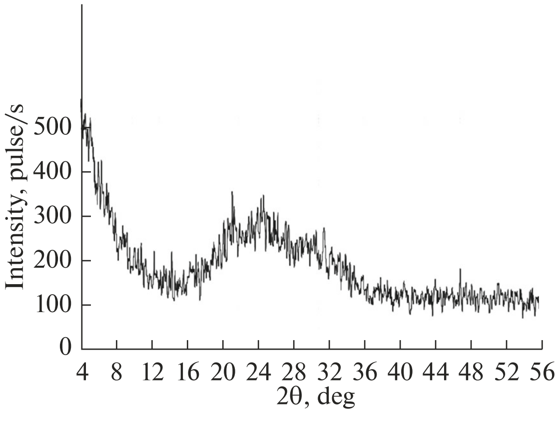

Fig. 5. Powder X-ray diffraction pattern of melted zone.

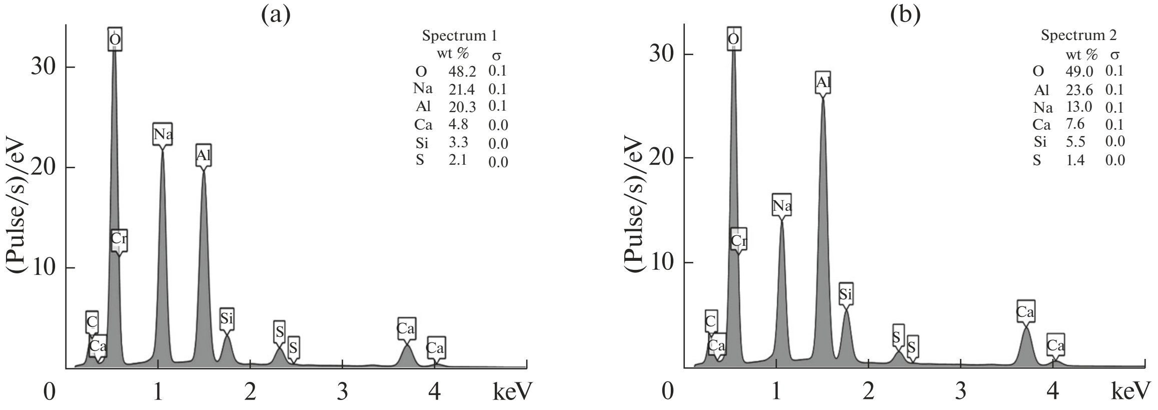

Fig. 6. Energy dispersive spectra of the amorphous zone of decorative protective coating represented by Na–Ca–Al–Si glass (the speed of the plasma jet is 10 mm/s).

explained by the fact that the top layer is covered with the crushed high-alumina refractory with the liquid glass in the ratio of 1 : 1.

The melt formed on the front surface of the facing composite material at the plasma-chemical modification has a high viscosity. In a short cooling time, the relaxation processes cannot occur fast enough. According to the XRD data, the amorphous phase does not contain the crystalline phases and it is silicate glass with areas of inhomogeneity with a high content of Na^+ and Al^{3+}, which is confirmed by the energy dispersion spectra of the studied areas (Fig. 6).

The X-ray diffraction analysis of the glass ceramic area allowed us to identify the α-Al_2O_3 (PDF cards nos. 5-712 and 38-470) and β-Al_2O_3 (PDF cards nos. 51-769 and 31-1263) modifications (Fig. 7). The data are in agreement with the data of other authors [18].

In addition to the main crystalline phase (α-Al_2O_3), the β-Al_2O_3 phase with the composition of $Na_2Al_{22}O_{34}$ ($Na_2O_{11}Al_2O_3$) was found in the glass ceramic layer. The β-Al_2O_3 modification forms owing to the existence of Na_2O and CaO, which are present in the crushed high-alumina refractory, in the coating composition (Fig. 8).

As was noted, the thermodiffusion processes leading to the redistribution of oxides over the thickness of the decorative protective coating intensify under the high-temperature influence of the plasma jet (Fig. 9).

The redistribution of aluminum, sodium, calcium, and silicon oxides over the thickness of the decorative protective coating occurs.

CONCLUSIONS

1. The regularity of the layer-by-layer change in phase composition and micro- and macrostructure of the decorative protective coating of the composite facing materials was established. It was found that top amorphous, middle glass ceramic, and bottom dehydration areas were formed.

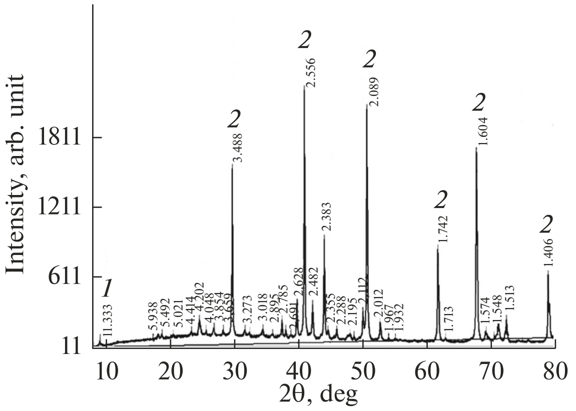

Fig. 7. Powder X-ray diffraction pattern of glass ceramic layer of the decorative protective coating: (*1*) α-Al_2O_3; (*2*) β-Al_2O_3 ($Na_2Al_{22}O_{34}$).

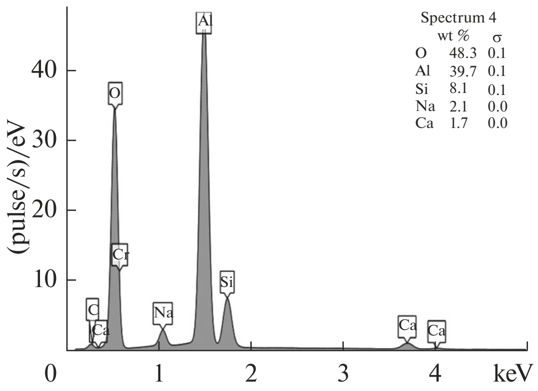

Fig. 8. The energy dispersion spectrum of the inhomogeneity region with increased Al_2O_3 content (the speed of the plasma jet is 10 mm/s).

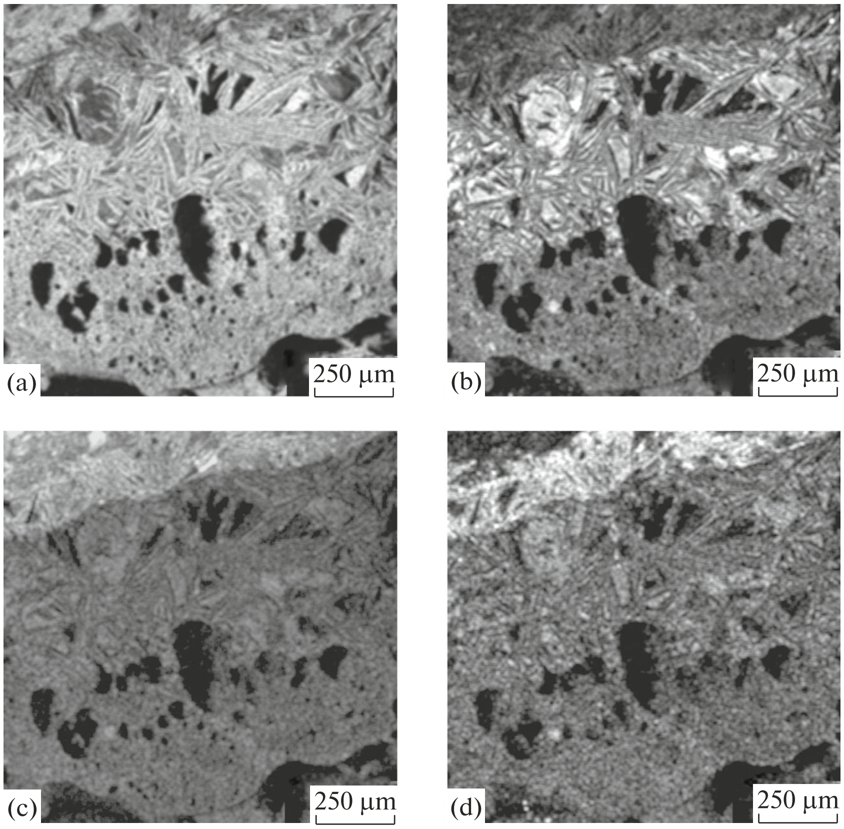

Fig. 9. Distribution of Al (a), Si (b), Na (c), and Ca (d) along the thickness of the facing composite material with a filler made from a mixture of quartz sand and PSM with a decorative protective coating after plasma-chemical modification.

2. The phase composition of the decorative protective coating was studied. It was shown that the top amorphous area is Na–Ca–Al–Si glass, the average glass ceramic area consists of α-Al_2O_3, β-Al_2O_3, and the amorphous phase, and the lower dehydration area includes α- and β-Al_2O_3 modifications and dehydration products of Portland cement.

3. It was established that using HGM together with the mixture of crushed high-alumina refractory with liquid glass eliminates the effects of thermal shock and microcracks in the surface layer of the facing composite material at its plasma-chemical modification.

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