Further development of the possibility of creating composite coatings from ash microspheres on a steel basis

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Abstract: *The article is devoted to the solution of an important scientific and technical problem of development of new composite coatings with the use of industrial waste of thermal power plants – aluminosilicate empty microspheres. The analysis of existing technologies showed the prospects for the use of electric arc spraying, which will expand the scope of compositions. All-drawn wires of* ER346 (Cв-08) *and* 1066 (65Г) *brands were used for coating, ash fillers of aluminosilicate composition were used as fillers. The effectiveness of ash microspheres for the formation of coatings is confirmed by the results of hardness measurements. Coatings filled with ash microspheres have increased Vickers hardness by 7… 22%. The use of ash slags in new technologies is a promising practical area, the implementation of which will help in the search for scarce minerals.*
Keywords*: ASH MICROSPHERES, SPRAYED COATINGS, ELECTRIC-ARC SPRAYING, THERMAL POWER PLANTS.*

1. Introduction

The efficient operation of Ukrainian thermal power plants is accompanied by the release of large amounts of fuel waste, the mineral components of which are converted into ash slag. Ash slag accumulates in ash dumps, which has a negative impact on the environment. Therefore, the issue of fuel waste disposal is very acute. As a result of combustion of coal particles at temperatures of 1600… 1800 ° C complex silicates are formed, which in the process of melting under the action of dissolved gases are transformed into spherical droplets (microspheres) with a gaseous atmosphere in the middle, which includes nitrogen, oxygen, and carbon monoxide [1].

Aluminosilicate hollow microspheres (ASHM) are the product of light fraction processing of fly ash in thermal power plants, after capture by electrostatic precipitators from the flue gas composition.

The combination of these unique properties makes the possibilities and prospects of using these microspheres in the oil, gas, chemical industry, automotive industry, refractory ceramics and construction unlimited. Microspheres are a valuable raw material, which is actively used by mining companies and construction industry companies in their technologies, as well as for the production of composite materials.

In the work [2] the authors analyzed the activities of Burshtyn, Prydniprovska, Trypillya, Kryvyi Rih and Chernihiv TPPs with the production of ash microspheres and their promotion in the industrial markets of Ukraine, Germany, Italy, Slovakia, Kazakhstan, Korea, Netherlands, Moldova, Romania and Romania. Their chemical composition directly depends on the mineral components of coal, in particular the presence of clay minerals, hydromica, quartzite and the content of quartz, pyrite, dolomite, magnesite, siderite, which undergo complex chemical and phase transformations during production processes [3].

The addition of ash microspheres to the composition of dry building mixtures and refractories gives them reduced density and thermal conductivity, the ability to dampen dynamic vibrations and vibrations, chemical inertness, which causes their use in solvents, organic liquids, acids, alkalis, water. Materials manufacturing technologies are low-temperature and are based on high fluidity, compact laying of ash microspheres, their ability to inhibit shrinkage processes during curing and polymerization of mixtures. However, it is possible to expand the areas of application and give the materials new operational properties by combining metallic and non-metallic components in one composition, which will require the introduction of high-temperature technologies.

Theoretical prerequisites for the creation of such compositions are scientific ideas about the physico-chemical processes of joining glass or ceramics with metals [4, 5], the formation of polydisperse composite media using non-metallic microspheres [6, 7] and own developments of the authors of the article on the scientific and technical bases of applying electric arc coatings filled with empty glass microspheres on a steel surface [8]. Due to the convenience and energy efficiency of electric arc spraying is considered a promising high-temperature method by which metal coatings can be applied metal-glass or metal-ceramic coatings up to 1.5 mm thick, as evidenced by [9]. The fine-grained structure of the coatings is formed during the melting of solid welding wires due to the occurrence of an electric arc between them and the transfer of compressed gas droplets on the spray surface. The experiments considered in [8, 9] include the addition of dispersed nonmetallic particles to the electric arc zone, but the use of ash microspheres in high-temperature technologies, in particular in electric arc spraying, has not yet been studied. Identifying differences and establishing patterns of formation of the structure of new dispersed coatings can be useful for the development of methods of protection of parts and mechanisms in mechanical engineering, energy, chemical industry.

The aim of the work is to experimentally prove the possibilities of using ash microspheres as a part of composite electric arc coatings on a steel surface and to establish the regularities of their structure formation.

2. Materials and Methodology

Experimental work included the formation on a substrate of carbon steel grade A284Gr.D (Ст3) (GOST 380-2005) two types of composite coatings, which used solid wires of the most affordable and inexpensive steels, capable of structural-phase transformations during thermodeformation treatment. These are wire of spring-spring steel of ferrite-perlite structure of brand 1066 (65Г) (GOST 14959-79) and low-carbon welding wire of brand ER346 (Св-08) (GOST 2246-70). Aluminosilicate hollow microspheres (ASHM) "Pinosphere" of MPk200-400 brand (manufacturer – LLC "Microspheres Production Association", Ukraine) are used as fillers, which are used in technologies of thermopanels, textured paints, etc. Aluminosilicate microspheres (TU 5717-001-11842486-2006) were used in the research, the chemical composition of which: SiO_2 – 74,9%; Al_2O_3 –13,9%; K_2O – 2,8%; Na_2O – 1,9%; Fe_2O_3 – 0,9%; CaO – 1,2%; FeO – 0,6%; TiO_2 – 0,2%. A general view of the microspheres is shown in Figure 1.

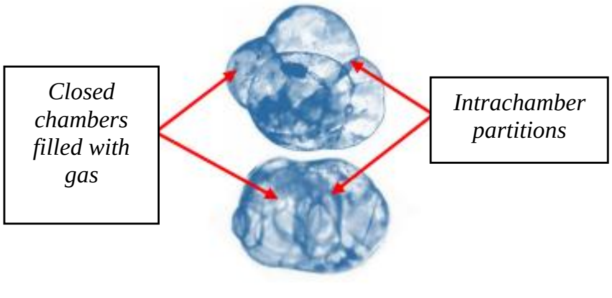

Fig. 1. *A general view of the microspheres*

ASHM are light gray solid bulk particles with a bulk density of 50… 60 kg/m3 and a dispersion of 200…400 μm. Optical microscopes MMP-2P and BIOLAM-I (БІОЛАМ-І); scanning electron microscope JSM-7610F were used for researching of structure. X-ray diffraction analysis by DRON-3.0 (ДРОН-3.0) in molybdenum radiation $Mo_{k\alpha}$ = 0.071069 nm with U = 40 kW, 40mA were used to study morphological characteristics.

The coating with a thickness of 1.0…1.5 mm was applied on one side to the pre-treated by jet-abrasive treatment of the steel plate with a size of 3×10×140 mm. Technological modes of electric arc spraying are selected in accordance with the recommendations of the authors [9]: current strength – 80; 120; 160 A; air pressure – 0.4; 0.5, 0.6 MPa; consumption of microspheres – 150 g/min; wire feed speed – 4.2 m/min; distance from the nozzle to the spray surface – 80 mm.

The topography of the sprayed surface was studied by electron microscopy, the phase composition was studied on samples separated from the substrate by X-ray diffraction. The chemical composition of the microregions around the microspheres was studied using micro-X-ray spectral analysis using a microscope-microanalyzer REMMA-102-02 (PEMMA-102-02). The volumetric content of the microsphere coatings was determined by spot analysis with the processing of digital microphotographs.

Hardness (HV_5) was determined according to DSTU ISO 6507-4: 2008 (ДСТУ ISO 6507-4:2008) on a Vickers device with a load of 5 kg.

3. Results and discussion

The chemical composition of microspheres was investigated by X-ray diffraction analysis, which proved the general amorphous nature of microspheres, but showed the presence of α- and β-cristobalite, α- and β-quartz, and crystalline modifications of Al2O3 on diffractograms (Table 1).

Table 1: *Results of X-ray diffraction analysis of ASHM*

Reflection angle, 2θ, °	Interplanar distance, d, Ȧ	Crystal modifications
16.7	2.447	γ-Al_2O_3
16.9	2.4189	SiO_2 (α- cristobalite)
17.05	2.397	γ-Al_2O_3
19.45	2.1036	α-Al_2O_3
20.45	2.00183	γ-Al_2O_3
20.65	1.9826	γ-Al_2O_3
22.3	1.837	SiO_2 (β- quartz)
22.55	1.817	SiO_2 (α- quartz)
22.75	1.8016	SiO_2 (α-кварц)
24.95	1.645	SiO_2 (β- cristobalite)
26.275	1.563	SiO_2 (β- quartz)
29.35	1.402	γ-Al_2O_3
30.00	1.372	γ-Al_2O_3

By means of optical analysis of microspheres, the ideal sphericity of experimental particles was established, the Gaussian distribution of which by diameter are: 80% – 200… 300 μm; 20% – 300… 400 microns.

The problem of energy saving in recent years is one of the main for all developed economies. In this regard, one of the revolutionary solutions for heat preservation can be considered liquid ceramic coatings, which at a thickness of 2…3 mm provide the same thermal insulation effect as a layer of mineral wool with a thickness of 50 mm. The method relates to the field of obtaining coatings with high strength characteristics, heat, fire and weather resistance characteristics for the protection of pipelines of heating systems and air ducts of air heating and ventilation systems.

Variation in the values of current and air pressure during application of the composite coating makes it possible to obtain samples with different fillings of microspheres: from 10 to 25%. Experimental work has shown the tendency of aluminosilicate hollow microspheres to form conglomerates and a high percentage of material loss by spraying (more than 50%), which does not allow accurate calculation of dosage and exact volume content and presents certain technological difficulties.

A schematic representation of a steel-based composite coating with the addition of aluminosilicate hollow microspheres is shown in Figure 2.

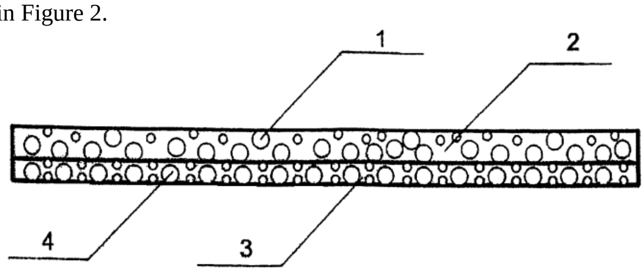

Fig. 2. *Scheme of coating with aluminosilicate microspheres: 1– microspheres; 2 - acrylic latex; 3 - layer with empty microspheres; 4 - aluminosilicate microspheres are covered with metal*

Sprayed coatings based on ER346 (Св-08) and 1066 (65Г) will have a similar polydisperse porous structure (Figure 3) with spherical inclusions, which according to the results of RSA do not undergo phase transformations. The intensity on the X-ray diffraction patterns of Fe [111] indicates that the microspheres acquire the effect of surface metallization due to envelope of dispersed molten metal, which when cooled on a steel substrate is cooled to form microvolumes with spherical inclusions.

The number of microspheres on the surface can be seen with the help of photographs of microstructures taken with the JSM-7610F scanning electron microscope. Since aluminosilicate hollow microspheres are not conductive, they are lighter in structure (figure 2, b, d).

No new chemical compounds are formed on the interface between the steel matrix and the microspheres, which shows the absence of interfacial interaction processes during electric arc spraying, which is also confirmed by the results of micro-X-ray spectral analysis. In figure 4, as an example, shows a spectrogram from the surface of the microsphere in the coating based on ER346 (Св-08).

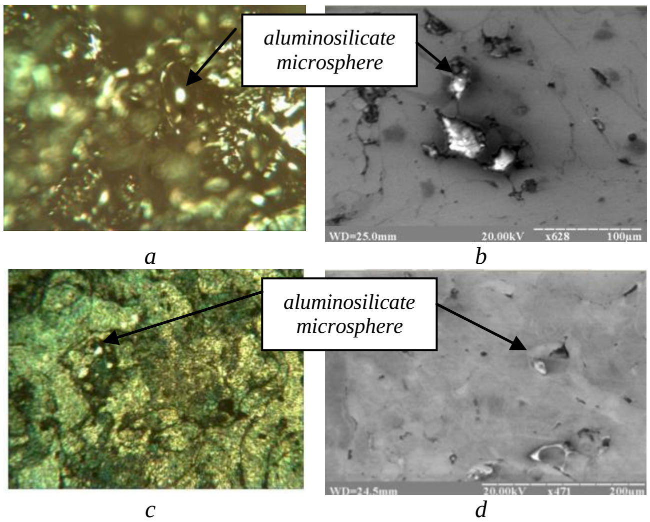

Fig. 3. Optical micrographs of coatings filled with APHM:
a – transverse section (× 150) of the composition of ER346 (Св-08);
b – transverse section (× 628) of the composition of ER346 (Св-08);
c – surface topography (× 150) of the composition with 1066 (65Г);
d – surface topography (× 471) of the composition with 1066 (65Г)

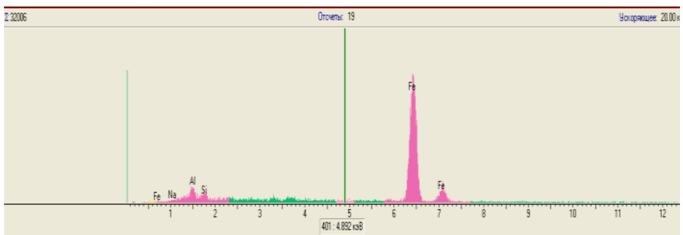

Fig. 4. *Spectrogram of aluminosilicate microsphere*

The results of research were compared to the features of the structure of electric arc coatings filled with glass microspheres and powders [10]. It was determined that the structure of the experimental coatings, in contrast to metal-glass compositions, is not associated with liquation processes in ASHM: short-term exposure to the arc jet in the walls of microspheres does not form glass phase, which will strengthen adhesive and cohesive bonds.

The effect of filling electric arc coatings with ash microspheres was determined by the results of hardness measurements HV_5 (Table 2), the measurement error did not exceed ± 10%.

Table 2: *Results of X-ray diffraction analysis of ASHM*

Material	Coating without filler	Coating with ASPM (volume 18%)	Hardness gain,%
ER346 (Св-08)	2.10	2.56	21.9
1066 (65Г)	2.50	2.70	7.4

Comparison of the results with coatings without filler showed an increase in hardness by 7… 22%, which can be explained by the formation of microstresses around the spherical inclusion in the hardening structure of the steel matrix, which arise due to differences in linear expansion coefficients.

Prospects for further work are related to the study of their physical and mechanical properties.

The use of ash microspheres in the technologies of functional coatings will have a significant economic and social effect, while associated with the creation of new compositions using cheap material resources and identifying ways to dispose of waste thermal power plants. The obtained coatings can be used in the chemical industry, energy, shipbuilding and mechanical engineering.

The research results reveal the regularities of structure formation of ER346 (Св-08) and 1066 (65Г) coatings with the addition of aluminosilicate ash microspheres deposited on steel substrate with A284Gr.D (Ст3) by electric arc method, which is aimed at solving the current scientific and technical problem of developing new coatings for industrial waste power plants. The use of ash slag in new technologies is a promising practical area, the implementation of which will help in the search for scarce minerals.

4. Conclusions

1. The possibility of adding to the composition of electric arc coatings with ER346 (Св-08) and 1066 (65Г) ash microspheres of aluminosilicate composition in a volume of 10…25% has been experimentally proved.

2. Regularities of formation of structure of composite coatings on steel substrate with A284Gr.D (Ст3) are determined: when spraying microspheres, they are enveloped by dispersed drops of molten metal, but will retain spherical shape, microcrystalline structure, phase and chemical composition; no new phases are formed on the interface between the wall and the steel matrix.

3. The efficiency of ash microspheres for the formation of coatings is determined by increased by 7… 22% Vickers hardness, as well as by economic and social values.

5. References

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