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ИССЛЕДОВАНИЕ ЭЛЕКТРИЧЕСКИХ СВОЙСТВ ЭПОКСИДНОГО КОМПОЗИТА С УГЛЕРОДНЫМИ НАПОЛНИТЕЛЯМИ

Проведено исследование основных физических свойств углеродных наполнителей. Исследовано влияние вида и со-

держания углеродного наполнителя на электрические и диэлектрические свойства эпоксидного композита. Показано, что при увеличении концентрации наполнителя в полимерной матрице растет величина диэлектрической проницаемости, а перколяционный порог для систем эпоксидная смола – углеродный наполнитель колеблется в пределах ~1–5 мас. %.

Ключевые слова: углеродные нанотрубки, эпоксидный композит, терморасширенный графит, удельное сопротивление, диэлектрическая проницаемость.

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INVESTIGATION OF SURFACED PRESS MOLDS MADE ITS WORKING RESOURCE

Показано, що при ремонті і виготовленні виробів необхідне зміцнення поверхонь, працюючих при термоциклічних навантаженнях в хімічно агресивних середовищах. Проведено дослідження структурної неоднорідності наплавленого металу і її вплив на працездатність прес-форм. Проаналізовано всі варіанти наплавлення способом плазма-МІГ наплавлення і на основі проведених досліджень прийняте оптимальне рішення, що дозволяє істотно підвищити швидкість кристалізації наплавленого металу.

Ключові слова: плазма-МІГ наплавлення, порошковий дріт, структурна неоднорідність наплавленого металу, працездатність прес-форм.

1. Introduction

One of the most important tasks of industrial production in Ukraine is to improve the quality of products, reduce labor, energy and materials. The possibility of using different methods of surfacing for the purpose of repairing and obtaining surfaces of tools and parts operating under extreme conditions has a great importance [1]. Such products include press molds for the production of glass insulators, as well as equipment for hot working with non-ferrous metals [2]. The working surface of the press mold is exposed not only to high temperatures and their sudden drop, but also to the chemical attack of the corrosive medium. Therefore, to restore worn surfaces, special attention is paid to both the composition and structure of the weld metal and its high-quality application to the surface of the product. With the help of the conducted researches it is possible to reduce the probability of cracks formation in the deposited layer by means of plasma-MIG surfacing.

2. The object of research and its technological audit

The object of research is the repair of press molds with the help of plasma-MIG surfacing.

Plasma-MIG process with the use of a flux-cored wire ensures maximum uniformity of the deposited layer and its specified chemical composition in one pass. This is explained by the features of the process, which allows to get a shallow and wide weld pool. However, when repairing previously welded press molds that have worn out their working life, a new layer of surfacing material is applied after machining by the plasma-MIG method on the previously treated surface (in the manufacture) with the thermal action of the plasma. Therefore, the weld metal on the repaired press molds wears out unevenly, has different structure and hardness, which is characteristic of multilayer surfacing of alloyed steels. This shows that research in this direction is necessary.

3. The aim and objectives of research

The aim research is investigation of the structural heterogeneity of the weld metal and its effect on the operability of the press molds to ensure uniform hardness over the section of the welded metal layer.

To achieve this aim, it is necessary to perform the following tasks:

1. To establish, with what step it is necessary to conduct surfacing at restoration of the press molds working at thermocyclic loadings.

2. To experimentally prove that the plasma-MIG surfacing should be carried out at the minimum possible current to increase the rate of crystallization of the weld metal.

4. Research of existing solutions of the problem

The greatest way to manage the storage and quality of surfacing is a combined method – plasma-MIG surfacing. In [3, 4], the expediency of using a flux-cored wire as an electrode, which is melted, fed into the combustion zone by a cylindrical plasma arc, is proved. This greatly expands the possibilities of plasma processes.

The reinforcement of surfaces during the repair and manufacture of products operating under thermocyclic loadings in chemically aggressive environments causes considerable difficulties, due (in the first place) to the exact observance of the composition of the deposited material [2]. This can be achieved by applying a method of plasma surfacing with axial feeding of a cored wire [3].

As is known, press molds for the formation of glass insulators operate under heavy industrial conditions. A number of materials are recommended for use in high-temperature and thermocyclic loadings [4, 5]. However, some of them, for example stellite, are quite expensive, since they contain a large amount of cobalt. A number of alloys contain a significant amount of nickel, tungsten and molybdenum, so their use in industry also has a limited area.

In [1, 6], steel is proposed for surfacing a mold of glass production of the type 2X13H12FC2P2. Despite the economical use of nickel in this steel, its resistance to thermocyclic loads is slightly lower than that of nickel-based alloys. This steel is taken as a basis.

It is known that the material for press mold surfacing, other than heat resistance, must have a sufficiently high thermal conductivity [6]. The most widely used in recent years are surfacing materials, the thermal conductivity of which increases with increasing temperature and reaches a maximum value at a temperature of 500 °C. The high-temperature austenitic nickel-based surfacing materials fully possess this property. The surfacing materials must also have a number of technological properties, namely [2, 6]:

- ensure a good formation of the weld bead;
- good separation of the slag crust;
- the lowest possible rate of crack formation in the weld metal; Good workability by cutting.

Alloys based on aluminum, magnesium, copper, iron, nickel, cobalt, and chromium are most often used as surfacing materials used to restore and strengthen products operating at high temperatures [1, 6].

In work [7], comparisons of glass and plastic are considered, which can be extended on the basis of the manufacturing method. The two main ways of producing press molds are injection molding of plastics and the formation of precision glass. To date, the market has more than 200 different types of molded glass for press molds, while only a few optical types can be chosen.

In work [8], the characteristics of microray plasma-arc powder surfacing for the restoration of press molds, as well as the study of the main technological parameters are considered. Factors of influence on durability formation are discussed and several typical applications of this new and advanced technology are listed.

In [9], the stages of the restoration system from the beginning to the achievement of the desired surfacing are considered. Creation of advanced systems based on the absolutely automatic filling of the MIG through robotics, advanced information technologies, production recovery technologies, and control by monitoring pre-processing and optimization in order to minimize time is proposed and implemented. The main stages of these systems include:

- 1) use of a visual sensor;
- 2) rearrangement of a curved surface based on contour data and a combined model of CAD objects;
- 3) construction of a model of recovery production on the basis of a model of CAD material objects and design of recovery production process;
- 4) redesign of the machine parts using the MIG surfacing technology.

In work [10], a new advanced technology of plasma-MIG surfacing is considered. The characteristics of surfacing and used equipment are briefly described in the study of the main technological parameters, factors of influence on the formation of a wear-resistant surface are discussed. Also there are listed a few typical applications of this new and advanced technology.

Thus, the results of the analysis lead to the conclusion that the wear of the surface layer of press molds for glass is uneven often has a striped wear. The cause of this wear can be the presence of weld metal sections with different structure and hardness. Such areas are observed with multilayer surfacing of alloyed steels.

5. Methods of research

The plasma-MIG method consisted of welded samples of a developed flux-cored wire. Samples were surfaced into 2 layers with different overlapping of adjacent rollers at a welding step of 8, 12, 16 mm.

In all cases of surfacing, a martensitic-austenitic structure of the weld metal is observed. And in the structure of all samples – the general pattern: at the edges of each deposited roller (along the entire perimeter), the austenite is larger than in the central regions of the cross section of the roller. In the center it is located in small layers between the martensite, on the edge – by large islands. However, in the center of the weld bead the ratio of martensite and austenite is different, and the morphology of these structural components in individual micro-sections is also differed. This is explained by the instability of the thermal cycle of surfacing, which in turn affects not only the rate of cooling of the metal, but also its chemical composition in individual microvolumes.

On samples with different deposition rates, the microhardness of the site enriched with austenite is slightly below the microhardness of the entire layer (4.4 and 5.2 kN/mm², respectively); microhardness of the structural constituents – martensite 4.5...4.8 kN/mm², austenite 2.8...3.0 kN/mm².

In order to identify the microchemical and structural inhomogeneities in the joints, the etching technique of the samples in copper solutions of various concentrations and solutions of picric acid with synthol is used. The latter technique is also used to reveal the primary structure of the weld bead. The secondary structure of the roller is examined after pickling the polished samples in nital.

This heterogeneity of the structure and the uneven distribution of hardness in the weld metal is the result of the thermal action of the arc when the next rollers are overlaid next to the previous one with partial overlapping. And the heating temperature of a certain area in the previous roller by its intersection depends on its location relative to the line of fusion of the rollers.

To determine the effect of the structure on the tendency to cracking, a metallographic analysis of a sample cut from the working layer of the welded press mold after its operation is carried out. The structure of the weld metal is a coarse-needle martensite with islands of residual austenite. It should be noted that the structure of this sample is coarser than that of samples surfaced in laboratory conditions, and the surface layer is damaged by cracks. There are many microcracks appearing as a result of the swell.

6. Research results

The results of metallographic studies confirm the presence of the following structural components in the weld metal: residual austenite, martensite and eutectic, which is formed at the boundary of the primary structure (Fig. 1). Analysis of the results of studies of chemical heterogeneity in a weld metal sample shows that in samples cut from press molds in service, chemical heterogeneity is associated with the presence of various structural components. In the output samples, the nature of chemical inhomogeneity is similar. One of the reasons for the appearance of cracks in the weld metal can be the formation of separate wide border zones near the surface, which was in direct contact with the hot metal while the press mold was operating.

Researches have shown that to provide uniform hardness over the section of the welded layer, the surfaced metal should be kept at a minimum step.

In order to reduce the width of the eutectic sections, it is allocated along the grain boundary, and hence the probability of crack formation in the deposited layer, surfacing should be carried out at a minimum current. This makes it possible to substantially increase the rate of crystallization of the deposited metal [2].

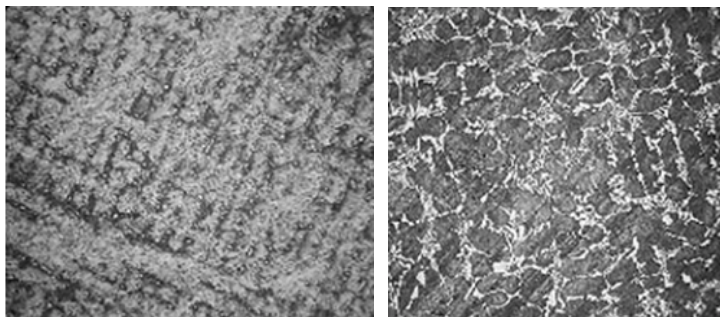


Fig. 1. Microstructure of test samples

Chemical composition of weld metal: Cr – 12.2–13.2 %; Ni – 11.4–11.9 %; Mn – 0.8–1.2 %; Cu – 1.9–2.1 %; Al – 0.8–1.2 %; Be – 0.6–0.8 %.

In the case of plasma-MIG surfacing of the developed flux-cored wire, the following welding technological parameters are obtained at the optimum operating mode:

- deposition coefficient $\alpha_H=16-19$ g/A·h;
- loss on burning and spraying $\psi_{B,S}=4-5$ %;
- yield of a suitable metal $K_V=91$ %.

The weld metal is satisfactorily processed with a carbide tool and has sufficient wear resistance to maintain the required profile of the press mold during its operation.

Surfacing is carried out using the developed equipment (Fig. 2) that provides:

- optimal conditions for the process (both for plasma surfacing in automatic and semi-automatic modes);
- increase in surfacing productivity;
- improvement of the quality of the weld metal (due to a decrease in the share of the base metal);
- liquidation of burning of a flux-cored wire shell at simultaneous cheapening of existing unit.

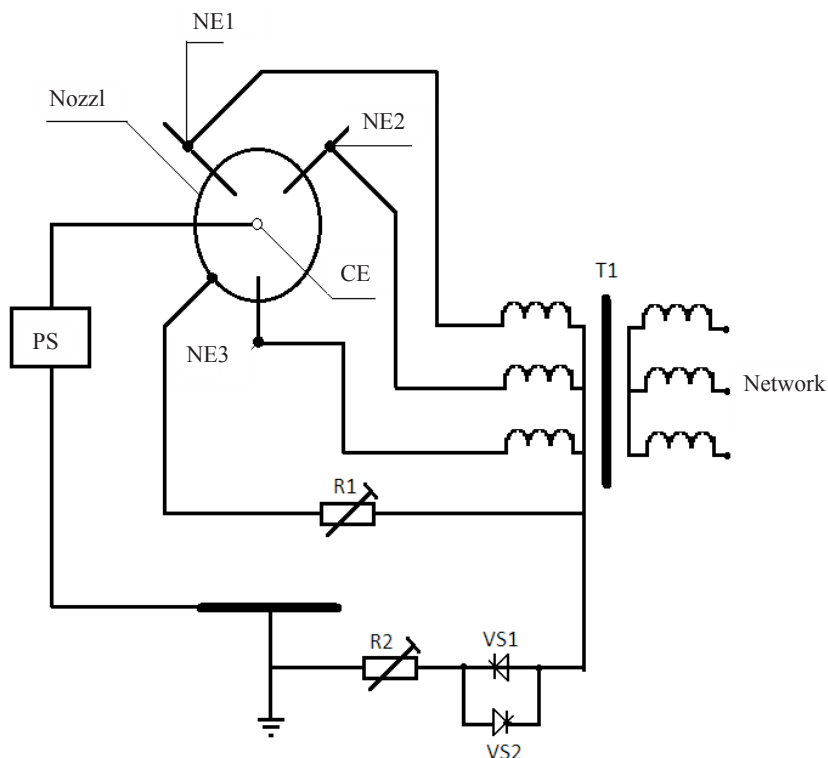


Fig. 2. Schematic diagram of the developed unit for plasma-MIG surfacing with flux-cored wire: IP – power source; NE1, NE2, NE3 – nonconsumable electrode; CE – consumable electrode; T1 – three-phase transformer; R1, R2 – resistors; VS1, VS2 – diodes

The aim is achieved by using a three-phase power transformer as the power source of the plasma arc. The supply of a plasma arc with a variable three-phase current allows one to abandon the rectifier [11, 12].

When the unit is in operation, the three-phase arc electrode is evenly heated, which melts. This allows to use the unit not only for automatic, but also for semi-automatic welding – surfacing, when the consumable electrode is not rectilinear, and the unit of melting device on a hand burner is not possible. On the surface of the electrode,

which melts periodically, the active spots of the arcs are appeared that increases the efficiency of consumable electrode heating, accelerates its melting, and leads to an increase in the fraction of the electrode metal in the deposited roller [11, 12].

A decrease in the penetration depth of the base metal is also facilitated by the fact that the current of the arc burning between the consumable electrodes and the product is small, and a stream of highly ionized gas from the arcs, burning inside the plasma torch, leaves the nozzle of the plasma torch. This leads to the fact that the arc of the consumable electrode burns under conditions of forced ionization with an excess of free charge carriers. Under these conditions, it is possible to expand it, cover an arc of a larger surface area of the deposited product, and reduce the density of heat flow into the product. As a result, a weld bead of a large width with a shallow penetration depth of the base metal is obtained [13].

When conducting surfacing works with flux-cored wires, air of industrial premises is polluted with various kinds of harmful to human health secretions. The composition and amount of harmful substances is determined, as a rule, by the composition of the core of the powder wires. To determine the concentration of harmful substances in the air of the working area, a number of studies is carried out, in which the amount and composition of harmful emissions formed during surfacing with a developed flux-cored wire is determined. The air is removed by aspiration using the rotameter ИПУ-4 (Russia). The results of the conducted researches show that the developed flux-cored wire for the plasma-MIG process of welding of press molds along with high technological parameters has good environmental indicators.

7. SWOT analysis of research results

Strengths. It should be noted that the obtained results increase the working capacity of press molds. The use of the obtained data allows conducting surfacing with such step, in which uniform hardness of the welded metal layer along the section is ensured.

Weaknesses. The weaknesses of this research are that the necessary calculations to ensure uniform hardness over the section of the welded metal layer are laborious.

Opportunities. When the research results are implemented at the enterprise, the working capacity of the press molds is increased, which means that there will be less labor, energy and material costs for the production of new press molds.

Threats. The threats in implementing the research results are related to two main factors. The first of these is the material cost of materials to achieve the required hardness and ensure the necessary performance. The second factor – when conducting surfacing works with flux-cored wires, air of industrial premises is polluted with various kinds of harmful to human health secretions. Therefore, the use of rotameters is necessary.

8. Conclusions

1. It has been established that when restoring press molds working under thermal cyclic loads, to ensure uni-

form hardness over the cross-section of the welded metal layer, the surfacing should be carried out with a minimum step in the optimum operating regime: $\alpha_H=16-19$ g/A·h. $\psi_{B,S}=4-5$ %; $K_V=91$ %

2. It has been experimentally proved that in order to reduce the width of the eutectic sections that is distinguished along the grain boundaries, and hence also the decrease in the probability of crack formation in the deposited layer, the plasma-MIG surfacing on the developed unit should be carried out at the lowest possible current $I=75-90$ A.

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ИССЛЕДОВАНИЕ НАПЛАВЛЕННЫХ ПРЕСС-ФОРМ, ОТРАБОТАВШИХ СВОЙ РАБОЧИЙ РЕСУРС

Показано, что при ремонте и изготовлении изделий необходимо укрепление поверхностей, работающих при термо-

циклических нагрузках в химически агрессивных средах. Проведено исследование структурной неоднородности наплавленного металла и его влияние на работоспособность пресс-форм. Проанализированы все варианты наплавки способом плазма-МИГ наплавки и на основе проведенных исследований принято оптимальное решение, позволяющее существенно повысить скорость кристаллизации наплавленного металла.

Ключевые слова: плазма-МИГ наплавка, порошковая проволока, структурная неоднородность наплавленного металла, химическая неоднородность.

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INVESTIGATION OF THE INFLUENCE OF ORGANOMINERAL ADDITIVES ON THE COLLOID-CHEMICAL PROPERTIES OF GEOCEMENT DISPERSION

Наведено результати впливу органімінеральної добавки на колоїдно-хімічні властивості геоцементної дисперсії. Оптимізовано склад органімінеральної добавки і визначено області допустимих концентрацій її складових. Встановлено, що зміни величин інших вихідних параметрів прив'язані до зміни умовної в'язкості. Кількісне вираження вихідних параметрів знаходиться в межах: $\rho = 1,571 - 1,766 \text{ г/см}^3$, $\cos\Theta = 0,50 - 0,67$, поверхневий натяг $\sigma = 114 - 128 \text{ мН/м}$, роботи адгезії, змочування і когезії, відповідно, $184 - 204 \text{ мН/м}$, коефіцієнти змочування і розтічності $-0,77 - (-)0,84$, $-37 - (-)55 \text{ мН/м}$.

Ключові слова: геоцементна дисперсія, оптимізація складу органімінеральної добавки, колоїдно-хімічні властивості.

1. Introduction

In recent years, materials based on alkali-activated binders – geocements or alkaline hydroaluminosilicates – have become increasingly popular. In general, the main properties of the binders themselves are considered: the processes of structure formation, strength, frost resistance, etc. [1–12]. Occasionally, publications aimed at studying special properties (heat resistance, fire resistance, corrosion resistance, etc.) of geocement materials [13–23], including properties of protective coatings – adhesion, technological viscosity, etc., can be found occasionally [24]. However, in these publications, the authors do not at all concern the study of the colloidal-chemical properties of geocement binders, as the basis for obtaining highly filled composites. Therefore, the studies considered in this paper are relevant and are aimed at studying the influence of mineralogical on the colloidal-chemical properties of geocement dispersions.

2. The object of research and its technological audit

The object of research is the geocement dispersion of the heulandite-clinoptilolite composition of the structural formula $\text{Na}_2\text{O} \times \text{Al}_2\text{O}_3 \times 6\text{SiO}_2 \times 20\text{H}_2\text{O}$, modified with an organomineral additive. This additive consists of:

– redispersible in water dispersion powder of the terpolymer of ethylene, vinyl laurate and vinyl chlo-

ride – Vinnapas RI-551Z (Vinnapas 8031 H, Wacker Polymer Systems, Germany);

– microcalcite fraction of 2 microns (Nigtas, Turkey);
– aluminate cement Istra 40 (HeidelbergCement, Germany), taken in certain quantitative relationships. Positive from the use of organomineral additives, in addition to elasticity, hydrophobicity and strength, is the improvement of the colloidal-chemical properties of geocement dispersion, namely:

- wetting contact angle;
- surface tension;
- works of adhesion, cohesion and wetting;
- coefficients of wetting and spreading.

For investigations in this work, a geocement dispersion of the composition $\text{Na}_2\text{O} \times \text{Al}_2\text{O}_3 \times 6\text{SiO}_2 \times 20\text{H}_2\text{O}$, obtained on the basis of metakaolin, microsilica, and sodium soluble glass is used. Optimization of the composition of the organomineral additive that affects the colloidal-chemical properties of the geocement dispersion is carried out using a three-factor simplex-center method of experiment planning in the mathematical environment of Statistica 12.0.

The number of additives is chosen as the variable factors, %: RI-551Z (factor X1), CaCO_3 (factor X2) and AC (factor X3), the changes of which are given in Table 1. As the output parameters are chosen: conditional viscosity, density, wetting angle, surface tension, work of adhesion, cohesion and wetting, wetting and spreading coefficients.