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COATINGS AND ENAMELS

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GLASS CERAMIC PROTECTIVE COATINGS FOR GASOSTATIC TREATMENT OF HEAT-RESISTANT NICKEL ALLOYS

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It is shown that glass ceramic coatings can be created in the system BaO–Al_2O_3–SiO_2 for high-temperature gasostatic treatment of heat-proof nickel alloys. The physical-chemical and technological properties of glass ceramic coatings are investigated and it is shown that they can be effectively used during gasostatic treatment of nickel alloys.

Key words: synthesis, glass ceramic coating, gasostatic treatment, heat-resistance.

The development of the articles of modern and future gas-turbine engines (GTE) and stationary setups is largely determined by the performance characteristics of the blades made of nickel-based heat-resistance alloys.

Special requirements are attached to the working blades of GTE, where the stability of the mechanical properties secures the serviceability of the entire engine. Cast blades of GTE operate under extremely demanding conditions, and casting defects can seriously degrade the fatigue characteristic and long-time strength of parts, which in turn threatens the service life and reliability of the blades.

The mechanical properties of heat-resistant alloys are determined by the chemical composition and technological processes involved in obtaining them.

An effective technological process for increasing the mechanical properties of the blades is gasostatic pressing: HGT — high-temperature gasostatic treatment. The process consists in the following: the cast part is placed into a container (gasostat with inert gas), operating under pressure, and subjected to uniform hydrostatic compression by means of the inert gas at high temperature. The mechanism of compaction includes creep and diffusion. The possibility of using arbitrary ratios of the temperature and pressure makes it possible to obtain tight defect-free castings [1 – 3].

Argon or helium containing nitrogen, oxygen, and hydrogen as impurities are used as the working medium.

At high temperatures the gasostat medium interacts with the surface of the treated parts. Oxides formed on the surface of nickel alloys weaken the grain boundaries and act similarly to cracks.

To prevent the treated parts from interacting with the gasostat medium it is expedient to use protective technological coatings.

The use of protective technological coatings is one of the progressive directions in the technology of heat-treatment of metal that make possible nonoxidative heating and reduce wastes and metal losses [4 – 6].

An advantage of such coatings is that they are formed on the surface of a metal during the heating process. These coatings are products of the reactions occurring at high temperature in the coating material and as a result of its being in contact with the components of the metal and the surrounding gas medium.

The protective capacity of technological silicate coatings is due to the presence in them of glass-forming oxides which are capable of forming on the surface of the alloy a viscous layer that is impermeable to gas and prevents the products of the corrosive medium from diffusing to the surface of the alloy [7 – 10].

The coatings intended for protecting heat-resistant alloys of the type ZhS, which are subjected to gasostatic treatment at temperatures 1230 – 1270°C, must meet the following technical requirements:

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– wide interval of softening of the coating with deformation onset temperature below the oxidation onset temperature of the protected alloy ZhS26;

– increase in the inertness of the coating to the metal substrate at high temperatures;

– easy removal of the coating after gasostating.

The aim of the present work is to investigate the possibility of creating a coating for protecting the surface of parts made from heat-resistant alloys of the type ZhS26 and ZhS6F during the interaction with the gasostat atmosphere at temperatures 1230 – 1270°C.

The following investigations were formulated on the basis of published data and previous scientific-research work on the protection of heat-resistance alloys during thermomechanical treatment:

– choice of metals for the investigation and evaluation of the primary properties of the coatings;

– determination of the temperature–time regimes of gasostating of the alloys ZhS26 and ZhS6F, promoting healing of the interior pores and defects, investigation of the cast structure for the presence of pores and microdefects;

– synthesis of compositions based on frits in the system $BaO–Al_2O_3–SiO_2$ and refractory fillers;

– investigation of the interaction of the alloy with glass ceramic melt at heat-treatment temperatures and the effect of the composition and structure of the oxidized surface of the alloy on the protective properties of the coating.

The method for investigating and evaluating the primary properties of the coatings was chosen. The investigations were conducted on the alloys ZhS26 and ZhS6F.

The alloys ZhS26 and ZhS6F are used for the cast turbine blades of the GTE.

The distribution of the alloying elements in the surface layer of the alloys was studied with a KAMEKA x-ray microanalyzer. This method gives an accurate determination of the depth of the depleted layer and the distribution of the alloying elements. Chemical analysis of the surface of the alloys was done by the spectral method.

The coating was deposited on the surface of the samples by spraying from a paint sprayer. The formation of the coating was matched with the gasostatic-treatment temperature. A preliminary evaluation of the protection capacity of the coating was made visually as well as with the aid of metallographic studies. The properties of the frits and the synthesized compositions were determined by the standard procedure adopted for glass.

The wetting ability of the coatings, the viscosity, and the fusibility are among the properties that determine the serviceability and protective efficacy of the coatings. The viscosity and wetting ability determine the capability of the coating to form continuous gas-impermeable protective layers. The fusibility of the coatings determines the softening interval and the behavior of the coatings in the formation process.

A high vanadium content in the alloy ZhS26 gives rise to aggressive corrosion of the metal as a result of the formation of vanadium oxide with low melting temperature (680°C). Vanadium oxide in the melted state dissolves the oxide film and thereby increases the rate of oxygen diffusion to the surface of the alloy.

Correspondingly, the interaction in complex heterogeneous systems includes the following main stages: transport of the components of the reaction to the phase-separation boundaries; reaction in the contact zone; and, accumulation and transport of the products of the reaction from the phase-contact zone.

The main problem during the synthesis of the compositions of the protective coatings is the maximum reduction of the diffusion rates of the elements of the medium and the components of the reactions to the alloy surface.

Compositions based on frits of the system $BaO–Al_2O_3–SiO_2$ and refractory glasses were synthesized.

The experiments showed that the mechanism of oxidation of the ZhS26 type alloys is determined by the diffusion of not only of metal ions to the boundary of the alloy but also the elements of the coating inside the alloy. The initial state of oxidation to temperature 900°C is associated with the oxidation of nickel in accordance with the law of mass action. High-temperature oxidation is controlled mainly by the diffusion of chromium ions to the surface of the alloy. The presence of cobalt and vanadium in the alloy increases the diffusion flux of chromium, gives rise to loosening of scale, and sharply intensifies oxidation at temperatures above 1200°C.

Since the main requirement of protective technological coatings is protecting the alloy surface from its interaction with the gasostat medium, the composition of the coating was picked by trial and error so that a continuous film would form on the metal at the early stages of heating, i.e., below the temperature of intense depletion of heat-resistance alloys of the type ZhS.

Since NiO forms in the temperature interval 850 – 950°C, the deformation onset temperature of the protective coating should not exceed 800 – 850°C.

The components of the coating must be thermodynamically more stable and have a stronger bond with oxygen than the components of the alloy.

The chemical composition of the coating determines not only its capacity to transition from the solid into the viscous and liquid states at elevated temperatures but also the rate of fusing with formation of the protective layer.

To obtain such a fused layer the possibility of developing coatings based on glass enamel with softening onset temperature 760°C and refractory filler was investigated. With this combination, as the coating is formed, the glass-enamel melt forms a liquid matrix phase in which the solid phase is distributed. When the enamel interacts with the filler the character of the filler distribution in the matrix and the degree of their interaction are very important. Coating frit from the system $BaO–Al_2O_3–SiO_2$ was used as the glass enamel and high-silica glasses as the filler. The physical-chemical properties of the frits and glasses are presented in Table 1.

TABLE 1. Physical-Chemical Properties of Frits and Glasses

Material	Density, g/cm^3	CLTE, 10^{-6} K^{-1}	Deformation onset temperature, °C
Frit ÉV-55	3.5	7.5	760
Glass V-70	2.2	1.1	> 950
Glass V-90	2.2	1.1	975

In connection with the fact that high-silica glass powders possess high dispersity and are similar in nature to glass enamels, on heating they dissolve well in the frit with a continuous (homogeneous) layer impermeable to gas being formed. A coating with such a composition forms a continuous layer at comparatively low temperatures even without the segregation of any liquations.

The investigations were performed on coatings with compositions containing different ratios of the glass enamel and high-silica glass. The coating compositions and some properties are presented in Table 2.

The chemical reactions and physical transformations in the case of multicomponent systems were investigated by means of thermal analysis in connection with the facts that the transformations and chemical reactions in systems are accompanied with heat release or absorption as well as mass change, which is determined to a high degree of accuracy by the thermogravimetric method.

On the basis of the data from differential-thermal analysis it can be supposed that upon the introduction of high-silica glass and upon increasing its content in the coating the exo-effects of ÉV-55 frit shift to higher temperatures. In the case of the No. 3 coating, as the content of high-silica glass increases, the endothermal effect becomes weaker; this can be explained by the fact that as the SiO_2 content of the coating increases more stable compounds are formed at high temperatures.

The interaction of the alloy with the enamel melt at the heat-treatment temperatures and the effect of the composition on the protective properties of the coating were investigated.

A preliminary evaluation of the effectiveness of the coatings was obtained visually according to the appearance. The data on the state of the coatings after heat treatment in a gasostat in the regime $t = 1270$°C, $p = 1700$ atm, and $\tau = 1$ h are presented in Table 3.

It is evident from the data obtained by visual examination that the coating No. 3 showed better results: the bright metal on sections of cleaving attests to high protective capacity of the coating in the course of gasostating and indicates cleaving of the coating occurred after the samples cooled down. The Nos. 1 and 2 coatings showed poor surface protection; this is indicated by burnouts and the presence of layers of corrosion at burnout sites. The coating No. 3 was graded as ÉVTZ.

TABLE 2. Compositions and Physical-Chemical Properties of Coatings

Coating No.	Composition, wt.%			Properties		
	Frit ÉV-55	Glass V-70	Glass V-90	Spreading angle ω, deg	Deformation temperature, °C	
					onset	completion
1	90	10	–	Complete dissolution	760	1150
2	80	15	5	43	800	1180
3	70	30	–	53	800	1200

TABLE 3. Quality of the Coatings after Gasostatic Pressing (GIP)

Coating no.	Surface state after GIP
1	Coating fused, glossy, dark-gray color, pitting corrosion at burnout sites
2	Coating fused, glossy, dark-gray color, 10% cleaving, burnouts observed on separate sections
3	Coating fused, glossy, dark-gray color, 10% cleaving, bright metal beneath cleaving, no pitting or burnouts present

Upon gasostatic treatment of metal articles coated with technological glass ceramic coating ÉVTZ no defective layer or traces of interaction of the coating with the metal are observed; the surface is smooth, has no micropores or porousness, and the grain boundaries come close to the edge. The protective properties of the coatings were confirmed by x-ray spectral microanalysis. No changes in terms of alloying components were observed when using the ÉVTZ coating. In the surface layer of the alloy the elements of the coating, such as Si, Ba, Ca, and Mo, are either no observed or they are present in quantities permitted in the alloy (see Fig. 1).

The investigations showed that ZhS type alloys can be protected from oxidation during gasostatic treatment in the regime $t = 1270$°C, $p = 1700$ atm, and $\tau = 1 - 2$ h.

After treatment in a gasostat the coating was fused and glossy and had a dark-gray color. When the samples are cooled the coating separates from their surface; the metal is bright at the separation site. The separation of the technological coating from the protected parts is a positive effect, since it decreases the work required to remove the coating by 40 – 60%.

The experimental investigations showed that it is possible to develop a technological coating for protecting the surface of ZhS-type alloys interacting with the atmosphere in a gasostat at temperatures 1240 – 1270°C. The coating ÉVTZ protects the surface of the alloy from oxidation and depletion of the alloying elements during high-temperature treatment in a gasostat. The formation temperature of the coating is

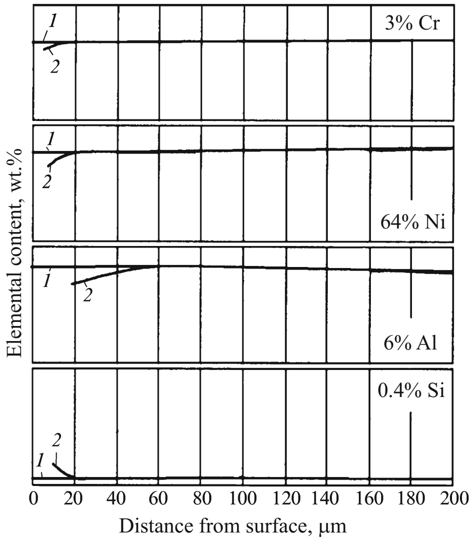

Fig. 1. Distribution of alloying elements and Si in the surface layer of the alloy ZhS26 with coatings after gasostatic pressing (GIP): *1*) content of alloying elements in the alloy ZhS26; *2*) distribution of alloying elements in the alloy ZhS26 with coatings after GIP.

matched with the treatment temperature of parts in a gasostat.

The basic physical-chemical properties and preparation and deposition parameters of the protective technological coating were determined.

The application of the synthesized ÉVTZ coating makes it possible to obtain high-quality GTE blades with stable mechanical properties.

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