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# COATINGS

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## REACTION-CURED COMPOSITE COATINGS AND GLASSES

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The development of reaction-cured coatings is a promising direction in the field of the protection of metallic and nonmetallic structural materials (in operation) in aeronautical engineering. The main feature of these coatings is the possibility of forming (firing) them at close to operating temperatures and increasing their temperature stability at the same time.

***Key words:*** high-temperature coatings, glass, silicon tetraboride, slurry.

Temperature-stable materials and coatings form the foundation guaranteeing the serviceability of the parts used in aerospace engineering [1, 2]. Conventionally, the temperature stability and heat-resistance of aviation materials were increased by searching for and using components with relatively high melting temperatures. However, the potential of this avenue for improving materials and coatings has now been exhausted and they do not even support the level required of next-generation technology. The materials-science problems arising in the development of the reusable orbiter Buran can serve as an example [3].

The atypical materials, specifically, temperature-stable materials and coatings based on inorganic glasses, glass formers, oxygen-free ceramic, and other non-metallic compounds are at the forefront.

The development of thermal protection for reusable spacecraft such as Buran and Space Shuttle has spurred the development of an entire series of new materials and technologies [4]. In reference to the developed materials and technologies, a new terminology identifying the physicochemical properties and technological particularities of the production of the new materials for reusable thermal protection has appeared. Specifically, these terms include 'reaction-cured glass' and reaction-cured coatings'.

The term 'reaction-cured glass' (RCG) was first used by the American specialists James S. Fletcher, Howard E. Goldstein, and Daniel B. Leiser (HACA) in US Patent No. 4093771, according to which reaction-cured glass was specially developed as a foundation for erosion-resistant 'black' moisture-protective coatings for high-porosity, fiber, reusable, thermal protection tiles for Space Shuttle and high-temperature chemical reactors.

However, a closer examination of the terminological particularities of the indicated materials and technologies revealed that the authors of the work use a mixture of glasses with different makeup and components of the type silicon tetraboride and hexaboride, silicon borides, boron, and their mixtures in order to obtain composites used as thin glass coatings for protecting low-density, fiber, high-porosity materials at temperatures from –100 to +1500°C.

Reaction-cured glass and erosion-resistant coatings based on it for operation at temperature 1260°C were developed for reusable, thermal protection tiles for the space shuttle and have entered the scientific technical literature and design documentation under that name [5]. The terms 'reaction-cured glass' and 'reaction-cured coating' are valid because they reflect the technological and physicochemical particularities of obtaining the basic properties of the indicated glass and composite coatings based on them.

The conventional ideas about glass as a material that has no melting temperature point and upon heating to high temperature is capable of gradual viscosity reduction and transitioning from the solid-state into a visco-fluid and liquid state and upon cooling from high to normal temperatures reversibly increasing viscosity and solidifying cannot be applied to reaction-cured glasses and coatings. Upon heating

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reaction-cured glasses and coatings gradually soften and their components interact with one another, and upon reaching high temperatures these materials acquire a structure that is uncharacteristic for silicate glasses and quite high viscosity or they solidify.

At least three high-priority directions of research on reaction-cured composite coatings and glasses can now be singled out:

1) for protection of porous, non-metallic, heat-shielding, and heat-insulating materials;

2) for protection of complexly-alloyed, high-temperature, nickel alloys and high-temperature corrosion-resistant steels and alloys;

3) for protection of carbon-ceramic composite materials based on ceramic-forming polymers, carbon-carbon, and other composites [6].

## MATERIALS AND METHODS OF INVESTIGATION

The following materials are studied in this work:

– 'black', corrosion-resistant, reaction-cured coating for the heat-shielding tiles of the Buran orbiter;

– reaction-cured coatings based on the glass system $BaO–Al_2O_3–SiO_2$ and silicon tetraboride for protecting parts made from high-temperature nickel alloys;

– high-temperature reaction-cured coatings for protecting carbon-ceramic composite materials based on ceramic-forming polymers.

The main feature of these materials is that refractory glass and silicon tetraboride are used in their makeup, which makes it possible to obtain in the process of high-temperature firing and subsequent use structures that are uncharacteristic for silicate enamels.

## RESULTS AND DISCUSSION

### Protection of High-Porosity, Fiber, Nonmetallic Materials

Erosion-resistant reaction-cured coatings whose formation entails a number of physicochemical and phase transformations resulting in the formation of a continuous protective layer at temperatures equal to or even lower than the operating temperature of the coating were developed to protect high-porosity materials.

In contrast to silicate enamels, whose formation is based on reversible transitions of the enamel frit into a viscous-flow state upon heating to the firing temperature and solidification during subsequent cooling, reaction-cured coatings cannot undergo after firing the irreversible processes characteristic for glasses. Therefore, the name of these coatings quite accurately conveys their basic qualitative feature.

There are two known methods of obtaining reaction-cured glasses and coatings based on them for reusable, tile, thermal protection. The American technology includes synthesis of reaction-cured glass by preparation of a mixture of high-silica porous glass and a water solution of boron anhydride [7]. Heat-treatment of such a mixture at temperatures from 75 to 500°C concludes with the formation of solid glass enriched with boron anhydride.

Depending on the composition of the initial mixture and the heat-treatment regime solid glasses with different makeups are obtained as a result of reactions of boron anhydride with high-silica porous glass. Search glasses make it possible to form moisture protective coatings in a wide temperature-time range without shrinkage of the high-porosity tiles. Reaction-cured composite coatings with emissivity at least 0.86 and, in contrast to well-known heat-resistant silicate enamels at very high-temperatures (reaching 1400°C) but no higher than the working temperatures of the coating can be obtained, after grinding, from the indicated glasses with the addition of silicon tetraboride.

The Russian technology of reaction-cured glasses and coatings based on them has fundamental differences from the American technology.

These differences include:

– use of monolithic (non-porous) high-silica glasses, obtained by the skull method, with boron anhydride content 4 – 8% by weight;

– production of bilayer coatings;

– production of a priming coat possessing high emissivity;

– production of reaction-cured composite coatings based on monolithic, borosilicate, high-silica glasses and silicon tetraboride.

In the course of the development of erosion-resistant coatings for tile thermal-protection of the Buran orbiter a technology was developed for obtaining silicon tetraboride $SiB_4$ and hexaboride $SiB_6$ with low free-silicon (< 1%) content, and experimental lots of these materials were fabricated.

The use of these compounds in 'black' coatings of the type EVCh-4M1 (Table 1) provided not only a very high emissivity (> 0.9) and low catalytic properties of the surface of the reusable spacecraft, but also, because of oxythermal reactions of silicon borides with the high-silica matrix glass, very high heat-resistance and thermal stability as well as moisture protection, erosion resistance, very little shrinkage, and the formation of a fire-polished surface of tiles with high aerodynamic quality [8, 9].

### Protection of Nickel Alloys and Steels

Ni–Co–Cr-based high-temperature, weldable, nickel alloys strengthened by different types of chemical-heat treatment have been developed for next-generation engines. A thermally stable structure and high mechanical properties are obtained as a result of the special chemical composition and fabrication technology of these alloys [10].

Heat-resistant glass-enamel coatings are conventionally used to protect high-temperature nickel alloy parts from

**TABLE 1.** Primary Operating Characteristics of EVCh-4M1 Coatings [9]

| Characteristics | Index |
|---|---|
| External appearance | Black coating |
| Coating thickness, mm | 0.3 ± 0.1 |
| Density, $g/m^3$ | 1.8 – 2.0 |
| Added weight due to the coating, $g/m^2$, at thickness 0.3 mm | 640 – 710 |
| Stability in vacuum (2.66 – 10.64) × $10^{-8}$ Pa | Stable, no visible changes in the coating or its mass after tests |
| CLTE, $10^{-6}$ $K^{-1}$ (at 20 – 900°C) | 0.7 ± 0.2 |
| Thermal conductivity, kJ/(kg · K) (in the interval from –150 to +1250°C) | 1.3 – 10 (handbook) |
| Specific heat capacity, kJ/(kg · K) (in the interval from –150 to +1250°C) | 0.45 – 1.29 (handbook) |
| Emissivity (at 1000 – 1250°C) | 0.88 – 0.91 |
| Erosion resistance: | |
| under the flow conditions in a liquid jet engine (LJE) (at 1250°C, 15 min) | Stable, no loss of mass, no cracks |
| under the flow conditions of a magnetohydrodynamic (MHD) generator | |
| Resistance to the cyclic action of temperatures, cycles: | |
| high (20 ↔ 1250°C) | 105 (stable, no cracks) |
| low (20 ↔ 130°C) | 105 (stable, no cracks) |
| Shrinkage of coating material, mm (1250°C, τ = 36 h) | 0.1 |
| Water absorption and water resistance: | |
| water absorption over 96 h, % | ≤ 0.1 |
| change of external appearance of a coating after immersion in water for 96 h | No visible change in the coating |

high-temperature gaseous corrosion during operation. The production of coatings is realized because of the physicochemical particularities of the glassy state, for which softening and solidification processes occur gradually in a certain temperature interval. In this interval, during flow of viscous alloys the mobility of the structural elements of the glass is intensified by means of covalent bonds of the type Si–O and B–O instead of the rupture of bonds. Due to the existence of this temperature interval there is a wide range of working temperatures of heat-resistant enamels based on glass-forming compositions and modifying additives.

The formation temperature (high temperature firing) of the coatings depends first and foremost on the chemical composition of the coatings and the protected substrate. The firing is conducted at temperatures 150 – 300°C higher than the working temperature. The use of EVK type coatings at working temperatures 1200 – 1250°C is problematic because firing would have to be conducted at 1350 – 1500°C, which is close to the melting temperature of the protected alloys and inevitably leads to warping of thin-wall parts, softening, and loss of mechanical properties of the alloys.

A significant volume of test and research results in the development of coatings for high-porosity tiles made of quartz fiber has become the scientific foundation for the development of reaction-cured coatings for modern high-temperature weldable nickel alloys.

It was established that the introduction of silicon tetraboride lowers by 30 – 50°C the formation temperature of coatings based on glasses in the system $BaO–Al_2O_3–SiO_2$. These coatings are serviceable at high temperatures, close or equal to the firing temperature. The onset temperatures of softening and deformation, which are determined by the dilatometric method, correlate with certain experimentally determined firing temperatures of coatings: the temperatures decrease parabolically with increasing $SiB_4$ content.

Flowability tests (GOST R 50045–92 (ISO 4534–80)) attest that an increase of the content of the modifying glass with stoichiometric composition $BaO–Al_2O_3–2SiO_2$ in the makeup of the coatings reduces flowability, which is associated with an increase of coating refractoriness. An increase of the silicon tetraboride content leads to flowability improvement owing to the oxidation of silicon tetraboride and the formation of a borosilicate glass phase that melts more easily than barium-aluminum-silicate glasses.

The parabolic character of the change in the flowability index attests physicochemical transformations occurring in the structure of the studied coatings during firing, giving rise to differences of the reaction-cured coatings from the conventional heat-resistant enamels. However, it is impossible to identify the dominating factor solely on the basis of flowability studies, in which connection it is also necessary to perform dilatometric and fusibility studies of the coatings.

It has been observed that when plates are loaded without preliminary soaking into a furnace for inclined flow the samples partially retain their shape; there is virtually no flow. The shape retention of the samples manifests most clearly with increasing silicon tetraboride content.

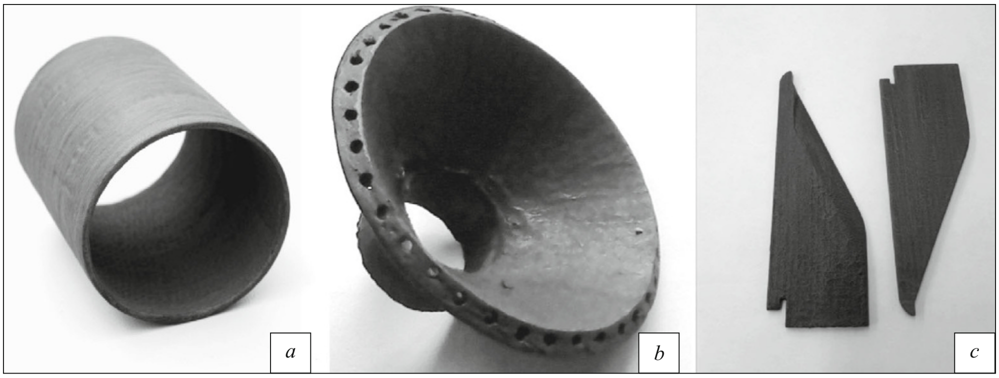


**Fig. 1.** Parts made from crack-resistant ceramic composite material VMK-12P with a reaction-cured coating: *a*) cylindrical blank; *b* ) divider; *c*) blades.

The results of the heat-resistance tests on the developed reaction-cured coatings attest that the coatings promote oxidizability reduction of the VZh171 alloy at the test temperature 1250°C in 100 h (mass gain 1.5 g/(m$^2$ · h) for the uncoated VZh171 alloy and 0.09 g/(m$^2$ · h) for the coated sample).

## Protection of Ceramic Composite Materials Based on Ceramic-Forming Polymers

A crack-resistant, carbon, ceramic, composite material (CM) with the brand name VKM-12P was developed using precursors based on ceramic-forming polymers of the type polycarbosilane and polysilazane [11 – 13]. This CM does not possess adequate temperature stability because of the low relative stability of carbon fibers reinforcing the ceramic matrix. The latter does not give reliable protection to the CM because of inadequate wettability of carbon fibers and filling of the pores between the carbon fibers.

A hybrid reaction-cured coating was developed to protect composite materials. This is a bilayer coating for providing the best protection and minimizing access of oxygen to the protected material. The first layer is a reaction-cured coating based on a glass matrix of the barium aluminum silicate system, modified by the high-temperature, oxygen-free, compounds $MoSi_2$ and $SiB_4$.

A distinguishing feature of this coating is the occurrence of the chemical reactions of oxidation and glass formation in the process of formation and operation of nanostructured ceramic CM [14, 15]. The firing temperature of the coating is 250 – 350°C lower than the working temperature of the CM. The second layer of the coating based on ash and modifying additives $MoSi_2$ and $SiB_4$ solidifies at normal temperature and as a result of the physicochemical transformations that occur it is already completely formed in the course of operation. Thus, the second layer of the nanostructured coating is unfired and is fabricated by the sol-gel technology.

Tests were performed at temperatures 1200 – 1250°C for 8 h on the thermally stable CM with and without a coating. Analysis of the obtained data attests that the mass loss of a sample is equal to 40% and 0.5% without and with a coating, respectively.

The composite material VKM-12P with the use of a hybrid reaction-cured coating possesses the following properties: density 1.8 – 2.0 g/cm$^3$, ultimate strength in bending 200 – 300 MPa, working temperature 1000 – 1300°C, thermal stability 50 cycles in the regime 20 ↔ 1350°C (without failure), and emissivity ≥ 0.8. A heat-pipe, rings, cylinders, cowlings, and paddles were fabricated, jointly with CIAM, from crack-resistant ceramic composite material VMK-12P with a reaction-cured coating. The fabricated parts are shown in Fig. 1.

## CONCLUSIONS

Reaction-curing is the most promising method of obtaining new coatings with improved technological and operational properties. The urgency of development is due to the creation of new durable and reliable materials as well as to the existing scientific foundation, laid in the course of the development of an erosion-resistant coating for the Buran orbiter, for producing such coatings.

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## REFERENCES

1. E. N. Kablov and S. S. Solntsev, “Oxythermosynthesis — a new step towards materials for advanced aerospace engineering,” in: *Aviation Materials, Selected Works of VIAM, 1932 – 2002* [in Russian], VIAM, Moscow (2002), pp. 131 – 137.
2. E. N. Kablov, S. S. Solntsev, V. A. Rozenenkova, and N. A. Mironova, “Modern polyfunctional high-temperature coatings for nickel alloys, metal seal materials, and beryllium alloys,” *Nov. Materialoved., Nauka Tekh.*, No. 1, Art. 5 (2013). URL: http://www.materialsnews.ru (access date Feb. 3, 2019).
3. E. N. Kablov, “Materials for the Buran parts — innovative solutions for the formation of the sixth technological paradigm,” *Aviats. Mater. Tekhnol.*, No. S1, 3 – 10 (2013).

4. N. V. Goldstein, D. B. Leiser, and V. Katvala, “Reaction for cured borosilicate glass coating for low-density fibrous insulation,” in: *Borate Glasses. Structure, Properties, Application*, Plenum Press, New York (1978), pp. 623 – 634.
5. He Meng Wang, Xiaolei Li, Dong Su, et al., “$MoSi_2$–BaO–$Al_2O_3$–$SiO_2$ coating for porous fibrous insulations,” *J. Alloys Comp.*, **657**, 684 – 690 (2016).
6. D. V. Grashchenkov, “Strategy of developing non-metallic materials, metal composite materials, and thermal protection,” *Aviats. Mater. Tekhnol.*, No. S, 264 – 271 (2017); DOI: 10.18577/2071-9140-2017-0-S-264-271.
7. S. S. Solntsev, V. S. Denisova, and V. A. Rozenenkova, “Reaction curing — new trend in the technology of high-temperature composite coatings and materials,” *Aviats. Mater. Tekhnol.*, No. S, 329 – 343 (2017); DOI: 10.18577/2071-9140-2017-0-S-329-343.
8. S. S. Solntsev, “Some features of coatings for the tiles of reusable thermal protection of orbital spaceships,” *Tr. VIAM: Elektron. Nauch.-Tekh. Zh.*, No. 2, Art. 01 (2014); URL: http://www.viam-works.ru (access date September 2, 2019); DOI: 10.18577/2307-6046-2014-0-2-1-1.
9. S. S. Solntsev, “Erosion-resistant moisture-proof thermal control coatings of reusable thermal protection of the Buran orbiter,” *Aviats. Mater. Tekhnol.*, No. S1, 94 – 124 (2013).
10. S. V. Ovsepyan, E. A. Lukina, E. V. Filonova, and I. S. Mazalov, “Formation of the hardening phase in high-temperature nitriding of a heat-resistant deformable Ni–Co–Cr-based alloy,” *Aviats. Mater. Tekhnol.*, No. 1. 3–8 (2013).
11. A. M. Shestakov, N. I. Shvets, V. A. Rozenenkova, and M. A. Khaskov, “Carbon-forming compositions based on polycarbosilane and modified polyorganosilazanes,” *Zh. Prikl. Khim*., **90**(8), 1066 – 1073 (2017).
12. T. D. Karimbaev, M. A. Mezentsev, and A. Yu. Ezhov, “Development and experimental studies of non-metallic parts and components of the hot part of a promising gas-turbine engine,” *Vest. Samar. Univer.*, *Aerokosm. Tekhnika, Tekhnol. Mashinostr.,* **14**(3-1), 128 – 138 (2015).
13. A. M. Shestakov, M. A. Khaskov, and O. Yu. Sorokin, “Inorganic fibers based on organosilicon polymer precursors for high-heat-resistant composite materials (review),” *Tr. VIAM*, No. 1 (73), 74 – 91 (2019); URL: http://www.viam-works.ru (access date February 2, 2019); DOI: 10.18577/2307-6046-2019-0-1-74-91.
14. S. A. Dembovskii and E. A. Chechetkina, *Glass Formation* [in Russian], Nauka, Moscow (1990).
15. N. A. Toropov, V. K. Barakovskii, V. V. Lapini, et al., *Handbook of Phase Diagrams of Silicate Systems*, No. 3, *Ternary Silicate Systems* [in Russian], Nauka, Leningrad (1972).