The change in the compositions of thermal barrier and antioxidant coatings for C/SiC composite materials was examined. Data are reported on the compositions and properties of bi-, tri-, and multilayer coatings. The mechanism of the barrier effect of several compositions is elucidated. The prospects for use of the new compositions of barrier coatings for increasing the temperature of use of the composite materials are demonstrated.

Aviation and space engineering, transport systems, the chemical industry, and thermal and atomic energetics cannot evolve without creating new construction materials suitable for working in extreme conditions — in exposure to high temperatures and pressures, ionizing radiation, dynamic loads, different aggressive media, high gas and liquid flow rates, etc. Such materials are usually created at the same time that methods for protecting them from negative factors are developed.

Intensive research has been conducted in the past ten years on developing composite materials based on nonoxide compounds — carbon, silicon carbide and nitride, etc., in which these compounds can be both matrix and reinforcing filler in the form of continuous or separate fibers, whiskers, and plates (C/C, C/SiC, SiC/SiC composites). These materials are distinguished by high strength characteristics, heat resistance, and low weight, which allows using them in aviation and space engineering as high-temperature construction materials, for fabrication of gas turbine, diesel engine, and heat-exchanger parts, and in triboengineering [1, 2].

In reducing conditions, C/SiC composite materials retain high mechanical property indexes up to a temperature of 2000°C, but in oxidizing conditions, their use is limited by the possibility of oxidation of the carbon at temperatures above 400°C. The SiC/SiC composites were more resistant to high-temperature oxidation due to formation of a barrier layer of SiO$_2$ on the surface of the composite material. However, in the presence of water vapors, oxidation and volatilization of gaseous products of the reaction are intensified according to the reaction:

$$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si(OH)}_4.$$  

For this reason, the use of SiC/SiC composites in humid air is limited by temperatures of 1200 – 1300°C [3, 4].

One possible method for solving this problem is to develop functional barrier ceramic coatings. As a function of the composition of the composite materials, the conditions of their use, and correspondingly the requirements imposed, the coatings can fulfill different functions:

- improve the mechanical properties of the support in a temperature gradient;
- limit chemical processes of oxidation and corrosion of the composites;
- regulate heat transfer at high temperatures of use of the article by changing the thermal conductivity of the material [5].

The analytical review by BCC Research reports the results of marketing studies in the North American market for high-efficient ceramic coating technologies in 2004 – 2009. It was noted that the total production volume of this kind had $1.1 billion in 2004, and the share of high-strength items was 14%, cutting and processing tools was 17%, and approximately 64% of the market was for coatings for engine components. In 2009, the market volume is projected to increase to $1.6 billion, with annual average growth of 7.6%, while coatings for engine components will constitute 68%. The re-
Barrier Coatings for Type C/SiC Ceramic-Matrix Composites

367

sults of estimating the production volume dynamics obtained by different methods, in particular, thermal spraying, physical and chemical deposition from the gas phase (PVD and CVD), etc. (dipping, sol-gel, microoxidation, using laser technologies). As the data in Fig. 1 show, thermal spraying is the basic method of obtaining ceramic coatings. The annual increase in the volume of these articles is 8.5%, primarily due to the fast development of aviation and space engineering. For goods manufactured by PVD and CVD methods, lower five-year growth rates are projected: 5.8 and 5.0%, respectively.

The compositions of the functional coatings must satisfy certain requirements; the fundamental ones are a high melting point, resistance to oxidizing atmospheres and water vapors, low thermal conductivity, and the main one, CLTE values close to the CLTE of silicon carbide. Materials with dominant crystalline phases containing silicates and aluminosilicates — mullite, cordierite, strontium and barium aluminosilicates, and rare-earth element silicates — satisfy these requirements to the greatest degree [2, 6 – 8].

Mullite, 3Al_{2}O_{3} · 2SiO_{2}, is of the greatest interest as a barrier coating for silicon carbide (nitride) due to the low CLTE and high chemical stability. Beginning in the 1980s, coatings made from mullite and/or binary systems of Al_{2}O_{3} and high-melting oxides (ZrO_{2}, Y_{2}O_{3}, etc.) were used for thermal barrier composite materials (thermal barrier coatings — TBC). These coatings significantly increased the crack resistance of the articles [9, 10].

Later, in the 90s, second-generation compositions were developed for barrier coatings for composites — bilayer chemically stable barrier coatings (environmental barrier coating — EBC). A number of conditions must be taken into account in selecting compounds that can fulfill the function of a barrier layer:

- The compounds must be thermodynamically stable and chemically stable in the entire temperature range in the conditions of use of the articles;
- the barrier layer must have compatible physicochemical properties with the support and the coating;
- the barrier layer must decrease the rate of chemical and diffusion processes in the transition layer between support and coating.

A barrier coating was developed (US Patent Nos. 5869146 and 6129954) for silicon-containing ceramics consisting of layers of mullite and zirconium oxide stabilized with 8% Y_{2}O_{3} (YSZ). Mullite has a CLTE intermediate between the CLTE of SiC and YSZ, so that the binder layer of mullite ensures good adhesion with the support. However, the comparatively high activity of the silicon oxide in the mullite caused rapid decomposition of the coating by water vapor. The YSZ composition as the top coating layer provided protection at high temperatures in conditions of high humidity. This composition was selected for the top coating, since it had already been successfully used at the time for thermal barrier coatings on metals and alloys in gas turbine engines. The bilayer coatings protected the ceramics from water vapors at a temperature of approximately 1300°C during hundreds of hours of use, but on long exposure, the water vapors penetrated the barrier layer through cracks, acting on the silicon-containing support, which led to peeling of the coating [10]. US Patent No. 5985470 proposed using compositions based on barium and strontium aluminosilicates (BSAS) of the general type (1 – x)BaO · xSrO · Al_{2}O_{3} · 2SiO_{2} (0 ≤ x ≤ 1) as the binder layer, and zirconium oxide totally or partially stabilized with yttrium oxide and silicates as the coating layer.

The third generation of barrier coatings was developed jointly as a result of research programs at Glenn Research Center (NASA), General Electric Co., and Pratt and Whitney in the US (US Patent No. 6410148) [11]. This type of coating consists of three layers, each with its own functional application. The lower (ground) layer of silicon ensures good adhesion with the support; the middle layer is mullite or mullite + BSAS composite; the top layer is BSAS, which has thermal barrier properties due to the low thermal conductivity. All of the layers are applied by a modified plasma spraying method. This type of coating was introduced by Solar Turbine Co. (USA) for the internal lining of the combustion chambers in gas-turbine engines.

The results of prolonged industrial tests of SiC/SiC composite construction elements in 1997 – 2004 showed an increase in the lifetime at a temperature of 1250°C to 14 – 17,000 h. In addition, the increase in the working temperatures decreased the volumes of nitrogen oxide and CO emissions by 2 and 5 times — to < 15 and < 10 ppm, respectively [12].

Another type of compositions was proposed in US Patent No. 6296942. Silicon-containing ceramics (C/SiC, SiC/SiC, SiC/Si_{3}N_{4}) or metal alloys (Mo, Nb, Fe, Fe – Ni) with silicon can be used as supports. The binder (ground) layer between the substrate and middle layers can be SiO_{2} or metal silicides on which the middle layer, containing mullite,