CHEMICAL STABILITY OF A COMPOSITE MATERIAL BASED ON SILICON AND BORON NITRIDES


Results of a study of the chemical resistance of a composite Si₃N₄ - BN material to the action of acids and alkalis are presented. Independently of the content of BN and the porosity the material resists the action of HCl, HNO₃, H₂SO₄, and KOH. Hydrofluoric acid has a strong effect on the composite material with over 30% BN even after only 10 days of contact. It is shown that the decomposition of the material obeys the rule "glass phase → Si₃N₄" and is selective; BN is more chemically stable than Si₃N₄.

The mechanical and thermophysical properties of ceramic materials in the Si₃N₄ - BN system have been studied quite well by native [1, 2] and foreign [3] researchers. The optimum combination of these properties provides a high wear resistance (at 10 - 20 wt.% BN) and heat resistance (at 20 - 60% BN) of such composite materials and makes them applicable for bearing cages, rotor seals, friction units operating in chemically active media such as mineral acids and alkalis, fuel combustion products, natural gas bearing hydrogen sulfide and nitrogen oxides, melts of marine salt, etc. Under these conditions ceramic materials, specifically, their surfaces, fail as a result of corrosion, and the operating capacity of the parts is mainly determined by their corrosion resistance, data on which cannot be found in preexisting publications. It should be noted that corrosion of a composite material in an aggressive medium is a very complicated process because the composite is a multiphase system.

The aim of the present study consisted of determining the chemical resistance of a composite Si₃N₄ - BN material to mineral acids and alkalis and the effect of various technological factors on the corrosion process.

The material OTM-918 based on Si₃N₄ - BN has a variable composition where the content of BN ranges from 0 to 60% [1]. The mechanical and thermophysical properties of the material vary respectively approaching the properties of pure BN. At the same time, the dense fine-grained Si₃N₄ matrix is substituted by a looser BN matrix (Fig. 1). In hot pressing this is accompanied by a considerable increase in the porosity (from 0 to 0.9%) and a decrease in the density (from 3.3 to 2.1 g/cm³) of the ceramics. The chemical inertness of pure Si₃N₄ and BN, the absence of chemical interaction between them, the presence of such refractory com-

![Fig. 1. Microstructure of Si₃N₄ - BN composite materials containing (a) 10% BN and (b) 60% BN, × 6000.](image-url)
pounds as $\text{Y}_2\text{O}_3 \cdot \text{Si}_3\text{N}_4$ and $10\text{Y}_2\text{O}_3 \cdot 9\text{SiO}_2 \cdot \text{Si}_3\text{N}_4$ together with yttrium silicates in the intergrain phase, the diminishing of their content with growth of the amount of BN, and the higher density of hot-pressed ceramics in the whole range of compositions as compared to materials fabricated by other methods, foreign counterparts included, allow us to expect a high chemical stability of the composite. These very internal factors are responsible for the rate and the nature of the corrosion process, and their variation from composition to composition makes it possible to estimate the importance of each parameter. The external factors that determine the corrosion resistance of the material were the same in each series of experiments.

In most cases liquid corrosion of ceramic materials has the form of chemical interaction that reduces to a reaction between the medium and the ceramic material with the formation of new compounds, solid solutions, etc. A characteristic feature of chemical corrosion is the formation of interaction products directly in the zone of contact between the material and the aggressive medium. Chemical corrosion obeys the main laws of chemical kinetics of heterogeneous reactions and is observed under the action of most aggressive media on ceramic materials. In accordance with the classification of corrosion processes by the type of fracture, corrosion in ceramic materials can have uniform, nonuniform, selective, surface, and intercrystalline forms [4].

Corrosion of $\text{Si}_3\text{N}_4$ and BN in liquid media has been studied for powders; in recent years dense materials began to be studied. The corrosion resistance of powders depends on the purity and the particle size, while that of compact specimens depends on the method of their fabrication, which determines their density and purity [5]. The selective nature of corrosion with respect to various reagents indicates that in all cases the determining factor is the chemical reaction with the medium.

By the data of [5, 6] $\text{Si}_3\text{N}_4$ powder is stable in solutions of sulfuric, hydrochloric, nitric, meta-, ortho-, and pyrophosphoric acids of any concentration, as well as in aqua regia. In heating, hydrofluoric acid decomposes the powder only partially. The reaction occurs with the formation of ammonium silicofluoride and emission of gaseous silicon fluoride, i.e.,

$$\text{Si}_3\text{N}_4 + 16\text{HF} = \text{SiF}_4 \uparrow + 2(\text{NH}_4)_2\text{SiF}_6.$$  

(1)

Many data on the chemical properties of silicon nitride are given in [7] and are ambiguous where the resistance to HF is concerned. Crystalline $\text{Si}_3\text{N}_4$ is an exclusively inert substance; at room temperature and at 70°C it does not react with HF even at a concentration of 48%. At the same time, $\text{Si}_3\text{N}_4$ decomposes rather easily in highly concentrated HF with the formation of $(\text{NH}_4)_2\text{SiF}_6$. In accordance with the data of Morgan Matroc Ltd. (Great Britain), hot-pressed $\text{Si}_3\text{N}_4$ decomposes fully in boiling concentrated HF in 200 h; a more porous reaction-bonded $\text{Si}_3\text{N}_4$ begins to react with 48% HF heated to 70°C after 3 h [8, 9]. It has been established that OTM-914 containing no BN possesses a high resistance to 48% HF [10]. Under normal conditions its acid resistance attains 97.5% after 30 days of contact, and its strength halves. After 3-h boiling the acid resistance of the same material attains 99.7%, and the strength diminishes by only 10%.

Hot pressed materials based on $\text{Si}_3\text{N}_4$ are quite stable even in solutions of alkalis. The mass of NKKKM-80 2 ceramics diminishes in a 20% NaOH solution by 0.24% in 1000 h [5]. By the same data the stability of $\text{Si}_3\text{N}_4$ increases with decrease in the concentration of the alkali, and it virtually stops to decompose in 50% alkali solutions.

The data on the chemical stability of BN are also contradictory [11]. BN is not affected by mineral acids (except for HF) and is extremely inert to any type of chemical interaction. The authors of [5] assume that the stability of BN powders in mineral acids and alkalis depends substantially on the purity of BN and the ordering of the crystal structure. With decrease in the density of the material its stability diminishes. The resistance of BN to diluted acids is higher than to concentrated ones and diminishes in the order $\text{HNO}_3 \rightarrow \text{HCl} \rightarrow \text{H}_2\text{SO}_4$. A full dissolution of BN is observed in the interaction with a concentrated 94% solution of HF, i.e.,

$$\text{BN} + 4\text{HF} = \text{NH}_4\text{BF}_4.$$  

(2)

This reaction is used as a simple analytical method for quantitative determination of BN [11]. In alkali solutions the stability of powders in compact BN specimens is quite high and virtually does not depend on the concentration.

We determined the acid resistance ($K$, %) of OTM-918 in the whole range of compositions in correspondence with GOST 473.181–81. The aggressive media were HF, HCl, $\text{HNO}_3$, $\text{H}_2\text{SO}_4$, and KOH. The total loss of mass was determined for specimens $7 \times 7 \times 30$ mm in size after the tests, as well as the specific loss of mass $\Delta m/s$ (per unit surface), the changes in the phase composition, the residual ultimate bending strength $\sigma_{\text{res}}$, and the microstructure before and after the treatment by acids and alkalis for 10–60 days. The duration of the contact was chosen in correspondence with the service requirements of the articles.

When estimating the chemical stability of a material some other changes should be taken into account in addition to the loss of mass, namely, the possible selective and intercrystalline corrosion and the corrosion cracking [4]. The conducted study has shown that the material possesses a high chemical resistance (> 96%) to the action of HCl, $\text{HNO}_3$, $\text{H}_2\text{SO}_4$, and KOH in the whole range of studied compositions (Table 1) and meets the requirements for acid-resistant ceramics [4].

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2 Reaction-sintered ceramics in the $\text{Si}_3\text{N}_4$ – BN system containing 30–40% SiC and an additive of MgO.