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The High-temperature Corrosion of Constructional Ceramic Materials Based on Silicon Nitride

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The kinetics and mechanism of the processes taking place during the corrosion of ceramic materials based on silicon nitride in an atmosphere of oxygen, air, or fuel combustion products and under the influence of sodium salts have been examined. The influence of the composition and structure of the materials on their stability to oxidation has been demonstrated. The influence of corrosion on the physicomechanical properties of silicon nitride materials has also been examined. Methods of protection from corrosion, and the principles of the production of materials with a high heat resistance, have been described. The bibliography contains 138 references.

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I. INTRODUCTION

One of the most urgent problems in present-day technology concerns the production of ceramic materials suitable for manufacturing parts for gas turbine engines (GTE), heat exchangers, and other high-temperature equipment.[1-6] The use of ceramic GTE makes it possible to increase the temperature of the gas at the outlet from the combustion chamber to 1400°, increase the efficiency, and decrease the fuel consumption.[4] The replacement of heat-resistant alloys by inexpensive ceramic in engine construction also leads to a sharp decrease in the consumption of scarce materials,

such as tungsten, cobalt, and nickel, and to a decrease in the mass and cost of the engine.

In the solution of the problems of producing ceramic materials for engines, an important role is played not only by technologists, materials scientists, and strength specialists, but also by chemists. This is due to the fact that the constructional ceramic must have a high corrosion resistance in gaseous oxidising media. During use, the engine parts may be subjected to the action of atmospheric oxygen, fuel combustion products, and marine salts at temperatures up to 1500°.[7] The corrosion of the materials leads to a significant change in their physicomechanical properties, and may lead to breakdown of the entire ceramic construction, as took place, for example, during the testing of Ford's ceramic stator.[8]

The most promising constructional ceramic materials at present are those based on silicon nitride;[9-12] they are obtained by the following methods:

1) hot pressing in graphite or boron nitride press moulds at temperatures of 1700–1850° and pressures of 10–50 MPa;

2) isostatic hot pressing in static gas chambers under nitrogen pressures exceeding 100 MPa at temperatures up to 2000°;

3) activated sintering in furnaces at normal or slightly increased pressures; activation of the sintering usually requires the introduction of more than 10% of oxide additives into the materials;

4) reaction sintering of blanks of silicon or its mixtures with Si_3N_4, based on the reaction $Si + 2N_2 \rightarrow Si_3N_4$ at temperatures close to 1400°;

5) deposition from the gas phase, based on the reactions of silicon halides (SiF_4, $SiCl_4$, etc.) or silane SiH_4 with ammonia on heating.

Compact non-porous materials can be obtained by ordinary and isostatic hot pressing[9] and by deposition from the gas phase. The porosity of the specimens is usually 5–10% for activated sintering, and 15–30% for reaction sintering.[10]

Although thousands of papers and a number of fundamental monographs[13-17] have been devoted to the study of the high-temperature corrosion of metals, practically no attention was paid to the high-temperature corrosion of silicon nitride ceramics until 10–15 years ago. Although the first paper on the oxidation of Si_3N_4 appeared in 1959,[18] no significant progress was made in this field until the mid-seventies. Only an approach to this problem which was not directed towards the partial question of "the corrosion of Si_3N_4", but towards the complex problem of studying the corrosion of a whole class of materials, with allowance for the individual characteristic features of each material (method of preparation, concentration of impurities and additives, structure, etc.), made it possible to understand the mechanisms of the reactions taking place and to find ways of producing materials with a high corrosion resistance, capable of retaining sufficiently good mechanical properties at the temperatures at which they are used.

Extensive studies in the last ten years have examined the kinetics and mechanism of the corrosion of the ceramics at high temperatures in different media and the influence of corrosion on the crack resistance and other mechanical properties of ceramic materials, and ways of protecting them from active corrosion during use have been found. At the same time, there is little information on this topic in reference books and monographs giving data on the physicochemical properties of nitride ceramic materials.[19-27]

In the present work, an attempt has been made to summarise the progress made in the study of the corrosion of silicon nitride constructional ceramics and the production of materials with a high corrosion resistance at high temperatures.

II. THE THERMODYNAMICS, KINETICS, AND MECHANISM OF THE OXIDATION OF SILICON NITRIDE MATERIALS

Published data on the chemical reactions taking place during the oxidation of silicon nitride are contradictory. It has been suggested[18] that when it is heated in air to 1200°, silicon dioxide and nitrogen are formed by the reaction:

$$Si_3N_4 + 3O_2 \rightarrow 3SiO_2 + 2N_2 \quad (1)$$

Other workers[28,29] detected silicon oxide nitride in the reaction products. This is believed to be formed by the reactions[28]

$$Si_3N_4 + O_2 \rightarrow Si_2N_2O + SiO(gas) + N_2$$
$$4Si_3N_4 + 3O_2 \rightarrow 6Si_2N_2O + 2N_2$$

In Ref.24, another reaction giving Si_2N_2O was proposed:

$$2Si_3N_4 + 3O_2 \rightarrow 2SiO_2 + 2Si_2N_2O + 2N_2$$

The oxide nitride in turn may be oxidised to SiO_2:[29]

$$2Si_2N_2O + 3O_2 \rightarrow 4SiO_2 + 2N_2 \quad (2)$$

A study of the oxidation of powdered Si_3N_4 under non-isothermal conditions[30] established that the oxide nitride is formed in the first stage of the process at temperatures up to 1100°. In the second stage (at temperatures of 1200° and above), Si_3N_4 and Si_2N_2O are oxidised to SiO_2 by reactions (1) and (2). At low partial pressures of oxygen, reactions giving gaseous silicon monoxide take place:[31,32]

$$Si_3N_4 + 3SiO_2 \rightarrow 6SiO(gas) + 2N_2 \quad (3)$$
$$2Si_3N_4 + 3O_2 \rightarrow 6SiO(gas) + 4N_2. \quad (4)$$

A thermodynamic calculation of the equilibria in the Si_3N_4–O_2 system (Fig.1) showed that, in addition to reactions (1)–(4), a whole series of other reactions giving solid (SiO_2, SiO) and gaseous (N_2, N_2O, NO, NO_2, SiO) products may take place:[24]

$$Si_3N_4 + 4O_2 \rightarrow 3SiO_2 + 2N_2O \quad (5)$$
$$Si_3N_4 + 5O_2 \rightarrow 3SiO_2 + 4NO \quad (6)$$
$$Si_3N_4 + 7O_2 \rightarrow 3SiO_2 + 4NO_2 \quad (7)$$
$$2Si_3N_4 + 3O_2 \rightarrow 6SiO(solid) + 4N_2 \quad (8)$$
$$2Si_3N_4 + 7O_2 \rightarrow 6SiO(solid) + 8NO \quad (9)$$
$$2Si_3N_4 + 11O_2 \rightarrow 6SiO(solid) + 8NO_2 \quad (10)$$
$$2Si_3N_4 + 5O_2 \rightarrow 6SiO(gas) + 4N_2O \quad (11)$$
$$2Si_3N_4 + 7O_2 \rightarrow 6SiO(gas) + 8NO \quad (12)$$
$$2Si_3N_4 + 11O_2 \rightarrow 6SiO(gas) + 8NO_2 \quad (13)$$
$$Si_3N_4 + O_2 \rightarrow SiO_2 + 2SiN(gas) + N_2 \quad (14)$$
$$2Si_3N_4 + O_2 \rightarrow 2SiO(solid) + 4SiN(gas) + 2N_2 \quad (15)$$
$$2Si_3N_4 + O_2 \rightarrow 2SiO(gas) + 4SiN(gas) + 2N_2 \quad (16)$$
$$2Si_3N_4 + O_2 \rightarrow 6Si + 2N_2O + 2N_2 \quad (17)$$
$$Si_3N_4 + 2O_2 \rightarrow 3Si + 4NO \quad (18)$$
$$Si_3N_4 + 4O_2 \rightarrow 3Si + 4NO_2 \quad (19)$$

Fig.1 shows that the highest absolute values of the change in the Gibbs free energy correspond to the reactions giving silica. At both low and normal pressures, however, their thermodynamic probability decreases with increase in temperature.

To determine which of the possible reactions of Si_3N_4 oxidation is the main reaction, the gaseous products of the oxidation of Si_3N_4 were studied[33] by mass spectrometry. The species O_2^+, N_2^+, NO^+, N_2^{2+}, and O_2^{2+} were detected; SiO^+ ions could not be detected. It was concluded that the main reaction in the oxidation of Si_3N_4 in an atmosphere of air or oxygen (22.7 kPa) is reaction (6), and that the next stage of the process involves the high-temperature dissociation of NO:

$$2NO \rightarrow N_2 + O_2$$

Infrared spectroscopy at an oxygen pressure of 10^5 Pa [34,35] detected nitrogen dioxide among the oxidation products.

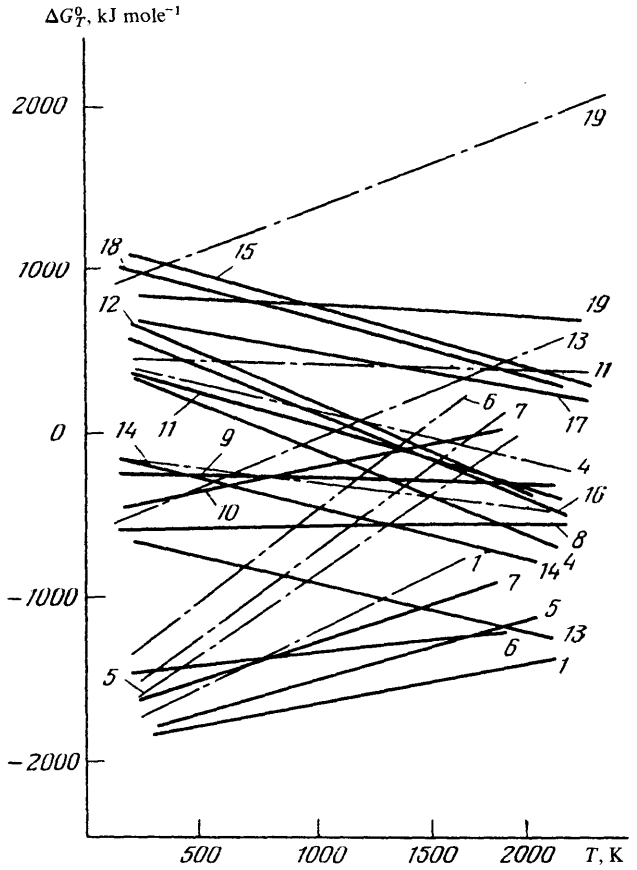


Figure 1. Dependence of the change in the Gibbs free energy ΔG_T^0 on the temperature of the reaction of silicon nitride with oxygen at oxygen pressures of 10^5 Pa (continuous line) and 1.3×10^{-3} Pa (broken line) (the numbering corresponds to that of the equations for the reactions).[24]

In Ref. 36 it was reported that reaction (3) can take place above 1500°. This suggestion was based on the fact that during the oxidation of the materials at high temperatures, the smooth surface of the specimens becomes blistered as a result of active gas liberation through the oxide film. It is also necessary to take account of the fact that at temperatures above 1420°, Si_3N_4 begins to dissociate to the elements, and the silicon formed reacts with SiO_2 to give gaseous silicon monoxide. It has been reported that the additives introduced into the material may have a catalytic influence on the processes taking place during the oxidation. Thus for example the addition of 5% NaF leads to the formation of silicon oxide nitride instead of SiO_2,[37] whereas the presence of magnesium facilitates the oxidation of Si_3N_4 to SiO_2.[38] The most desirable reactions are those giving silicon dioxide, since this facilitates the formation on the surface of the specimen of a protective layer which prevents further oxidation of the material.

At low partial pressures of oxygen, when only gaseous oxidation products are formed,[31,32] or under conditions in which the solid oxide layer formed on the surface does not show protective properties,[39,40] the rate of oxidation is independent of the time from the start of the process. In this case the following linear relationship is observed:

$$dx/d\tau = K_{lin} \text{ or } x = K_{lin}\tau + C_{lin}$$

where K_{lin} is the linear reaction rate constant, C_{lin} the constant of integration, τ the oxidation time, and x the relative change in mass on unit surface area of the specimen ($\Delta m/S$). The fact that the rate of oxidation remains constant with time indicates that the limiting stage of the process is the reaction at the phase interface.[13]

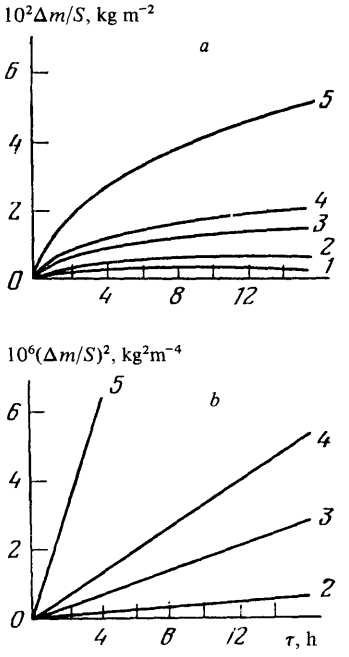


Figure 2. Kinetic curves for the oxidation of Norton's hot-pressed material HS-130 in oxygen, constructed on coordinates $\Delta m/S - \tau$ (*a*) and $(\Delta m/S)^2 - \tau$ (*b*),[31] for different temperatures (°C): *1*) 1090, *2*) 1205, *3*) 1260, *4*) 1315, *5*) 1370.

In those cases where the surface of the specimen is covered by a compact oxide layer during oxidation, a parabolic time dependence is observed (Fig. 2):

$$dx/d\tau = K'_{par}/x \text{ or } x^2 = K_{par}\tau + C_{par}$$

where K'_{par} and K_{par} are the parabolic reaction rate constants, and C_{par} the constant of integration. The fact that the parabolic oxidation law is observed indicates that the rate of the process is limited by diffusion through the oxide layer.[13] This process can be described by the theory of high-temperature oxidation proposed by Wagner,[41] according to which the rate of the overall reaction is determined by the bulk diffusion of the reacting ions or the corresponding point defects, or by electron transfer through the oxide layer. The driving force of the reaction is the change in the Gibbs free energy, associated with the formation of the

oxide from the element and oxygen, as a result of which concentration gradients are produced in the oxidised layer. In this interpretation, the rate of growth of the oxide film is determined by the concentration gradients and the rates of diffusion of the components.

Wagner's theory is applicable to the oxidation of materials based on silicon nitride,[31] but the process is complicated by the fact that, in addition to solid products, gaseous oxidation products are formed; this makes a quantitative estimation and interpretation of the results difficult. The application of Wagner's theory with certain assumptions[42] made it possible to predict that oxidation leading to the formation of silicon monoxide by reactions (3) and (4) can take place, for example at 1300°, only if the oxygen pressure is less than 80 Pa.[31] The ranges corresponding to the "active" oxidation of Si_3N_4, when only gaseous products are formed, and to the "passive" oxidation, when solid products are formed, are shown in Fig.3 [43] (the first lies below the straight line, and the second above it). There is lack of agreement on which is the limiting stage in the oxidation when solid products are formed: diffusion of oxygen to the Si_3N_4/SiO_2 interface,[44] diffusion of nitrogen to the SiO_2/medium interface,[45] or diffusion of additives and impurities from inner layers towards the surface of the specimen.[46]

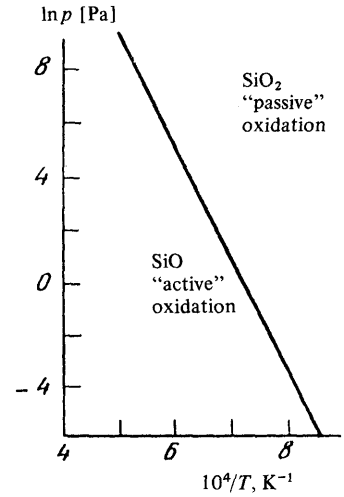


Figure 3. Dependence of the partial pressures of oxygen at which the change from "active" to "passive" oxidation takes place on the temperature of the process.[43]

Table 1 shows that the apparent activation energy of the oxidation of most forms of powdered and compact materials based on Si_3N_4 is close to 300 kJ mole^{-1}, that is it is close to the activation energy of the diffusion of oxygen in silicon dioxide. This indicates that the main contribution to the activation energy is made by the diffusion of oxygen through the oxide layer, and that this is the limiting stage of the process. The activation energy of the oxidation of silicon carbide is also close to 300 kJ mole^{-1} (see Table 1), since in this case also the rate of the process is limited by the diffusion of oxygen through the SiO_2 layer. At the same time, for some materials, the values of E show considerable deviations, towards both higher and lower values. In these cases the mechanism of the oxidation is apparently influenced considerably by other factors such as the diffusion of additives and impurities, transformations in the oxide layer, etc.

Table 1. Apparent activation energies (E) of the oxidation of various materials, and the activation energy of the diffusion of oxygen in silicon dioxide.

Material	Medium	t, °C	E, kJ mole^{-1}	Refs.
β-Si_3N_4 powder	air	1000—1100	280	[30]
β-Si_3N_4 powder	air	1200—1500	390	[30]
Si_3N_4 powder	dry air	1065—1340	285	[47]
Si_3N_4 powder	dry oxygen	1065—1340	255	[47]
α-Si_3N_4 powder	air	1150—1230	294	[48]
Reaction-sintered Si_3N_4	air	1100—1200	130	[49]
Reaction-sintered Si_3N_4	air	<1100	320	[49]
Hot-pressed Si_3N_4 + 1% MgO	dry oxygen	1000—1400	255	[31]
Hot-pressed Si_3N_4 + 1% MgO	moist oxygen	1200—1400	375	[50]
Hot-pressed Si_3N_4 + CeO_2 + SiO_2	air	1100—1370	350	[51]
Hot-pressed Si_3N_4 + 8% Y_2O_3 + 1% MgO	air	<1150	120	[46]
Hot-pressed Si_3N_4 + 8% Y_2O_3 + 1% MgO	air	1150—1350	580	[46]
Hot-pressed Si_3N_4 + 8% Y_2O_3 + 1% MgO	air	>1350	960	[46]
Hot-pressed $Si_{2.9}Be_{0.1}N_{3.8}O_{0.2}$	air	1400—1500	700	[52]
Pyrolytic Si_3N_4 (crystalline)	dry oxygen	1550—1650	390	[53]
Pyrolytic Si_3N_4 (amorphous)	dry oxygen	1550—1650	460	[53]
SiC powder	dry oxygen	1200—1500	277	[54]
Diffusion of oxygen in fused SiO_2	–	925—1225	298	[55]

In all cases except Ref.30, the apparent activation energy E was determined using the Arrhenius equation from the parabolic kinetic curves for the oxidation, obtained under isothermal conditions:

$$K_{par}=A\cdot e^{-E/RT}$$

where A is the pre-exponential factor, R the universal gas constant, and T the temperature. In Ref.30, E was found from the results of experiments under non-isothermal conditions at different heating rates using the equation

$$E=2{,}19R\frac{d(\lg\beta)}{d(1/T_p)}$$

where β is the heating rate, and T_p the temperature of the peak on the corresponding differential thermal analysis curve.

In those cases where the oxidation is accompanied by a continuous change in the area of the reaction surface as a result of the filling of the pores by the oxide phase formed, the change in the mass of the specimens with time may also be given by the logarithmic law:[56]

$$x=K_{\log}\lg\tau+C_{\log}$$

where $K_{\log}$ is the logarithmic rate constant, and $C_{\log}$ a constant. In the opinion of the authors of Ref.57, the kinetics of the oxidation of porous reactive silicon nitride can be described by Evans' equation for the case of self-blocking pores:

$$x=x_\infty(1-e^{-K\tau})$$

where x_∞ is the final increase in mass, corresponding to the

horizontal section on the kinetic curve, and K a constant whose value depends on the time taken to reach this section. The use of various other familiar equations was also proposed. Analysis shows, however, that the kinetic curves for the isothermal oxidation of porous materials (Fig.4) cannot be accurately described by any of these equations throughout the range of temperatures (800–1500°) and times of treatment studied. This is due to the change in the mechanism of the process and the nature of the filling of the pores with increase in the temperature and time of oxidation.

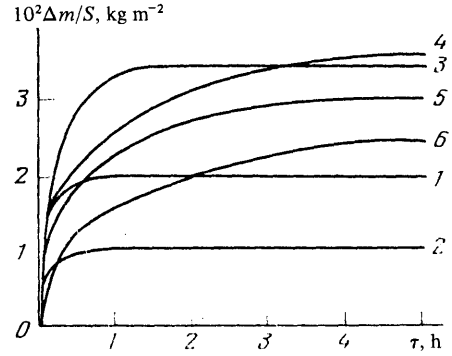


Figure 4. Kinetic curves for the oxidation of the reaction-sintered material NKKKM-80 in air[56] at different temperatures (°C): *1*) 1450, *2*) 1350, *3*) 1100, *4*) 1000, *5*) 900, *6*) 800.

Thus the mechanism of the oxidation may change with change in the conditions of the process (temperature, pressure, and other factors) and in the additives introduced into the ceramic, leading to changes in the composition of the oxidation products and the nature of the kinetic curves.

III. COMPOSITION AND STRUCTURE OF THE OXIDE LAYER

As shown in the previous section, the oxidation of silicon nitride materials in oxygen-containing media at a relatively high partial pressure of oxygen (see Fig.3) begins at temperatures above 700° and leads to the formation of a layer of silicon dioxide on the surface of the specimens.

At temperatures up to 1065°, the silicon dioxide formed is amorphous. At higher temperatures, in the opinion of many workers,[58,59] cristobalite is also formed. In Ref.56, both cristobalite and amorphous SiO_2 were detected throughout the temperature range from 800° to 1450°, but their quantitative ratio in the oxide layer was different for different oxidation temperatures. The appearance of cristobalite has also been observed in the oxidation of silicon oxide nitride.[60] In the oxidation of various materials, the formation of tridymite at temperatures above 1125° [47] and of quartz above 1385° [46] has been observed. There are no published data on the detection of other forms of SiO_2.

The phase transformations in silicon dioxide depend markedly on the temperature, rate of cooling, and presence of impurities.[61] These factors apparently determine whether the silicon dioxide formed in the oxidation is present in the amorphous state or as one of its crystalline forms. In addition to silicon dioxide, the surface layer of specimens oxidised in a charge of Si_3N_4 and other powders which actively absorb oxygen may also contain the oxide nitride.[62] The formation of Si_2N_2O was also detected in the oxidation of reaction-sintered silicon nitride at 1500° in a closed vessel made of a ceramic based on silicon nitride.[56] In a tubular furnace with free access of air, the formation of the oxide nitride could not be detected. It is therefore formed only when there is an oxygen deficit. In an excess of oxygen, the formation of SiO_2 is usually observed.

It has been reported[24] that at temperatures up to 900° in air, solid silicon monoxide may also be formed on the surface of the specimen as a brown phase with inclusions of bright-red crystals. This was not confirmed by other workers, however.[35,40,56] There are no reliable reports of the formation, between the SiO_2 and Si_3N_4 layers, of intermediate layers consisting of lower oxides or the oxide nitride, as observed in the oxidation of many metals[13] and metal-like refractory compounds.[24]

The surface oxide layer always contains impurities with a high affinity for oxygen, in quantities much greater than their average concentration in the bulk of the material. Thus according to Ref.31, after the oxidation of a specimen with the composition Si_3N_4 + 1% MgO at 1400° in dry oxygen, the protective film consists chiefly of enstatite $MgSiO_3$. The presence in the surface layer of up to 40% calcium at a calcium concentration of less than 1% in the starting material has been reported.[58] The migration of calcium, magnesium, and other impurity elements to the surface of the specimen leads to the formation of a silicate phase with a softening temperature in the range 1100–1300°.[38,63] The formation of a low-melting silicate phase, on the one hand, is beneficial, since it leads to the healing of cracks, pores, and other defects[64] and to a more uniform distribution of the oxidation products on the surface of the specimen. On the other hand, diffusion through the liquid layer takes place more readily, leading to an increase in the rate of oxidation. When a liquid phase is formed at the grain boundaries, the strength of the material decreases sharply.[65]

The dissolution of Si_3N_4 in the liquid oxide phase leads to an increase in its viscosity and to the formation of a vitreous coating on the surface of the specimens.[38] The addition of lanthanide oxides, and the presence of water vapour in the reaction atmosphere, on the other hand, favour crystallisation of the oxide layer.[50]

IV. INFLUENCE OF THE COMPOSITION AND STRUCTURE OF THE MATERIALS ON THEIR STABILITY TO OXIDATION

1. Influence of the Phase Composition

Silicon nitride exists in two polymorphic forms with similar structures, differing only in the sequence of tetrahedral elements in the direction of the c axis.[22] The nitriding of silicon usually gives both forms: α-Si_3N_4 is formed preferentially in the temperature range 1200–1400°, and β-Si_3N_4 above 1450°. On heating to 1450–1500°, slow irreversible conversion of the α-phase into the β-phase takes place.[21] Practically all industrial specimens of powdered silicon nitride consist of a mixture of the α- and β-forms.[66,67] At the same time, hot-pressed and sintered materials obtained at ~1700° and above usually do not contain α-Si_3N_4. Its presence is possible only in reaction-sintered materials.

The study of powders with different concentrations of α- and β-Si_3N_4 [24] has shown that, other conditions being equal, the tendency to undergo oxidation is greater for those consisting chiefly of α-Si_3N_4. The initial rate of the process increases with increase in the oxygen pressure, indicating the possible adsorption of molecular oxygen. At certain

temperatures and partial pressures of oxygen, a solid solution of O_2 in α-Si_3N_4 is formed.[24] With increase in the oxidation temperature, the concentration of α-Si_3N_4 in specimens of reaction-sintered Si_3N_4 also decreases.[28] This apparently takes place as a result of the preferential oxidation of the α-phase. The lower stability of α-Si_3N_4 to oxidation may be due to its instability at high temperatures. The rearrangement of the crystal lattice of α-Si_3N_4 facilitates the addition of oxygen atoms and oxidation of the material.

Deposition from the gas phase may give not only crystalline but also amorphous silicon nitride,[12,53] which has a higher stability to oxidation than the crystalline forms.[53]

2. Influence of Porosity

The oxidation of specimens of hot-pressed Si_3N_4, having a density close to the theoretical, takes place chiefly on the surface. The resulting surface oxide layer, depending on the oxidation temperature, the chemical composition of the material, and the oxidising medium, may be porous or compact, crystalline or amorphous.[31,68-71] Typical kinetic curves for the oxidation of compact hot-pressed Si_3N_4,[31] obeying a parabolic time dependence, are given in Fig.2.

The oxidation of specimens of reaction-sintered silicon nitride, having the usual porosity of 15–30%,[72-75] take place throughout the entire volume (the corresponding kinetic curves are given in Fig.4). The rate of oxidation of porous specimens is much higher than that of the compact materials. The difference is particularly marked at relatively low temperatures (compare Figs.2 and 4). As a result of the oxidation of reaction-sintered Si_3N_4 with a porosity of 2270 kg m^{-3} at 1040° for 200 h, 28% SiO_2 accumulated in the specimen, whereas its concentration in the original material (as an impurity at the grain boundaries) did not exceed 4%.[72]

According to Ref.76, the dependence of the rate of oxidation on the porosity is linear and is given by the equation

$$\Delta m = kS_0 + 3kf(1-\rho)/\bar{R}$$

where Δm is the increase in mass, S_0 the geometric surface area of the specimen, f the fraction of open pores (relative to the total porosity), $\bar{R}$ the average radius of the pores, ρ the relative density of the material, and k a coefficient. This equation shows that an important role is played not only by the total fraction of open pores, but also by the radius of the pores (see also Fig.5). In Ref.77 it was suggested that the main influence on the stability to oxidation is in fact shown not by the radius of the pores but by the radius of the channels connecting them. The filling of these channels by an oxide phase having a greater volume than the original Si_3N_4 leads to a decrease in the rate of internal oxidation of the material. Thus for materials with a smaller average radius of the pores (or of the channels connecting the large pores), the formation of a protective layer on the surface of the specimens takes place more rapidly at a lower degree of oxidation (Fig.5).

Active oxidation of the specimen throughout its volume takes place under conditions in which a solid oxide layer exists on its surface. This corresponds to curves *4–6* in Fig.4. When the oxide phase melts (see section III), a viscous protective film, covering all the open pores, is formed after a certain time interval on the surface of the specimens, leading to a change in the nature of the kinetic curves with increase in the oxidation temperature (curves *1–3* in Fig.4).

In the oxidation of the porous material, its density increases,[78] and the porosity decreases, whereas in the oxidation of hot-pressed Si_3N_4 there is a slight decrease in the density. This last feature is due to the fact that the silicon dixode formed is less dense than Si_3N_4. In the oxidation of the compact material, the SiO_2 layer is formed only on the surface, whereas in the oxidation of a porous specimen, only ~25% of the silicon dioxide formed corresponds to the surface layer,[59] and the slight change in the volume of the specimen is accompanied by a fairly large change in its mass.

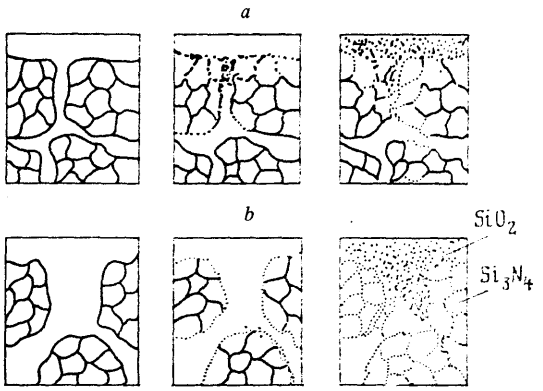


Figure 5. Model of the oxidation of reaction-sintered silicon nitride with fine (*a*) and coarse (*b*) pores under the conditions of formation of a solid oxide layer.

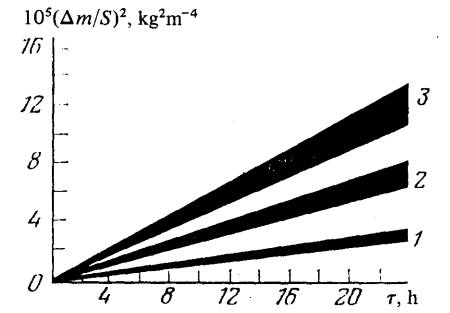


Figure 6. Kinetics of the oxidation of the material HS-130 at 1400° in different media:[81] *1*) CO/CO_2, $p_{total} = 2 \times 10^4$ Pa, $p_{O_2} = 10^{-4}-10^{-1}$ Pa; *2*) O_2, $p_{total} = p_{O_2} = 8 \times 10^2-8 \times 10^4$ Pa; *3*) O_2/N_2, O_2/Ar, $p_{total} = 8 \times 10^4$ Pa, $p_{O_2} = 8 \times 10^2-8 \times 10^4$ Pa.

Even at temperatures below 1000°, oxidation leads to gradual covering of the pores (Fig.6), and, after some time, to the formation of a protective film of silica on the surface of the specimen, which stops practically completely the penetration of oxygen into the inner layers of the material. Under these conditions, the diffusion of oxygen through the layer of oxide becomes the limiting stage of the process. Subsequently, the reaction takes place in the same way as in the oxidation of the non-porous hot-pressed material.

The density and behaviour during oxidation of sintered materials having a porosity of ~10%[79] are intermediate between those of the hot-pressed and reaction-sintered

materials. The materials obtained by deposition from the gas phase have a high density. Their properties are closer to those of the hot-pressed materials,[53] and their mechanical properties and stability to oxidation are often even greater than those of these materials.

3. Influence of Additives and Impurities

Practically all materials based on silicon nitride contain additives to activate sintering: MgO,[80,81] Al_2O_3,[82] Y_2O_3,[83] BeO,[52] CeO_2,[51] ZrO_2,[58] etc. The most frequently used additive is magnesium oxide. The best compaction is achieved when a secondary phase with the composition $MgSiN_2$–Mg_2SiO_4 is formed between the granules.[80] After the oxidation of these materials, the surface layer contains enstatite $MgSiO_3$ and forsterite Mg_2SiO_4,[79] formed by the reactions:

$$2MgO+SiO_2 \rightarrow Mg_2SiO_4$$
$$Mg_2SiO_4+SiO_2 \rightarrow 2MgSiO_3$$

The rate of oxidation increases with increase in the quantity of MgO added. This is due to the fact that the vitreous magnesium silicate phase formed at the grain boundaries softens at temperatures above 1100°, and its viscosity and melting point decrease with increase in the concentration of magnesium in it.[84]

The stability of materials of this type towards oxidation can be increased by adding zirconium dioxide in addition to magnesium oxide.[58] The hot-pressed material containing 1% MgO and 2% ZrO_2 has a much higher stability towards high-temperature oxidation than the same material without zirconium dioxide. It is considered[58] that the addition of ZrO_2 decreases the rate of the diffusion of oxygen through the oxide film and the transfer of magnesium ions to the surface of the specimen. Materials containing added ZrO_2 or ZrC have a high stability at temperatures up to 1500°.

The addition of yttrium oxide makes it possible to obtain a crystalline phase at the grain boundaries, and not the vitreous phase obtained when MgO is used, and also increases the high-temperature strength of the materials.[83] The silicon yttrium oxide nitrides formed by the reaction of Y_2O_3 with Si_3N_4 and SiO_2, which is always present on the surface of the silicon nitride granules, have been studied in detail.[85] It is recommended that the technological conditions be selected in such a way that the secondary phase consists of $Y_4Si_2O_7N_2$. This is facilitated by adding aluminium and magnesium oxides. This material has the greatest stability to oxidation. According to other data,[39] material from the Si_3N_4–$Y_2Si_2O_7$–Si_2ON_2 system has a very high resistance to oxidation.

Cerium oxide has approximately the same influence as yttrium oxide on the properties of the materials.[51] Materials containing added CeO_2 and Y_2O_3 have a high resistance to oxidation at 1300–1400°.[86] In the temperature range 900 to 1200°, the crystalline oxide film formed on the surface of the specimens does not show protective properties, so that intensive oxidation of the materials with a deterioration in their mechanical properties takes place.[40] It has been suggested[39,40] that the temperature separating these two ranges be called the critical temperature (T_c). Above T_c, the oxide layer is compact and shows good protective properties; the kinetics of the oxidation obey a parabolic law, and the rate of oxidation decreases with decrease in the concentration of the additive. Below T_c, the surface layer contains connected pores, and therefore has poor protective properties; the kinetics of the oxidation are close to linear. For the materials of the Si_3N_4–Y_2O_3 system studied in Ref.40, T_c = 1200–1250°. At a temperature below T_c, the maximum rate of oxidation is reached at 1000°.

The formation of a non-porous oxide layer requires that the material contain compounds which lower the liquidus temperature of the phase between the granules. One such compound is Al_2O_3. The addition of 2% aluminium oxide decreases the rate of crystallisation of the phase between the granules, facilitating glass formation, and lowers T_c by 200 K.[40] This material retains an acceptable strength only up to 1200°, but unlike materials to which only Y_2O_3 has been added, it shows good resistance to oxidation at 1000°, since this temperature is only slightly below its T_c value. A hot-pressed material consisting of 93% Si_3N_4, 5% Y_2O_3, and 2% Al_2O_3 showed good resistance in tests involving prolonged oxidation (up to 30 d) at 1200°.[69] The production of a hot-pressed material containing 8% Y_2O_3, whose properties did not deteriorate at 1000–1200°, has been reported.[68] The addition of aluminium oxide to silicon nitride gives so-called sialons,[87,88] which consist of a solid solution with the β-Si_3N_4 lattice, in which some of the silicon atoms are replaced by aluminium atoms, and some of the nitrogen atoms by oxygen atoms. Similar solid solutions are formed when the oxides of beryllium and various other elements are added.

Materials containing added beryllium oxide[52,89] also have a high resistance to oxidation. It has been reported[52] that a hot-pressed material with the composition $Si_{2.9}Be_{0.1}N_{3.8}O_{0.2}$ has a much greater heat resistance than industrial materials being produced. The activation energy of the oxidation of this material is almost twice that for most other silicon nitride specimens (see Table 1).

When the original powders are ground, they usually contain iron or tungsten carbide as impurities, depending on the material used to prepare the grinding bodies and the mill lining. Iron oxides in quantities up to 2.5% are sometimes added deliberately to reaction-sintered materials to facilitate the nitriding process.[90] After pressing or reaction sintering, these impurities are present in the prepared material at the grain boundaries either in the original state or as melts of the silicides or a mixed carbide of iron and tungsten.[38,90] At a high oxygen concentration, they are oxidised and dissolve in the intergranular phase, lowering its melting point. This leads to the formation of a liquid phase in the surface phase at high temperatures and to a deterioration in the high-temperature strength.[91,92]

In addition to the above elements, the technical raw material used to prepare most materials also contains traces of calcium, magnesium, aluminium, strontium, nickel, cobalt, manganese, copper, titanium, and other elements in quantities of 1.00 to 0.01%.[65,98] The presence of these elements in the material leads to a decrease in the viscosity of the silicate glass. The decrease in the viscosity is greater, the greater the ionic radius of the element and the higher the rate of oxidation. The oxidation resistance of the material HS-130, produced by the American firm Norton (Fig.2), is 10 times that of the similar material HS-110 in which the concentration of impurities is 10 times higher.[94] After oxidation, the impurities are present in the vitreous phase or separate as different crystalline phases.[95]

Thus additives and impurities which lower the melting point of the oxide phase may play a beneficial role, facilitating the formation of a compact protective layer even at temperatures of ~1000°. At the same time, at higher temperatures, they lead to a sharp increase in the rate of oxidation of the material. To produce heat-resistant materials, it is apparently necessary to remove the original impurities from the

raw material, and then to introduce a strictly limited quantity of certain additives which give the material the required properties.

V. CORROSION UNDER THE INFLUENCE OF SALTS

During use, the ceramic parts of engines may be subjected to the action of various salts,[7,96] leading to breakdown of the protective oxide layer[97] and to more active corrosion of the material.

The presence of sodium salts in the surface layer leads to a decrease in the viscosity of the oxide phase and to an increase in the rate of oxidation of the specimens.[49] The oxide layer formed on the surface of specimens impregnated before oxidation with solutions of different sodium salts contain many pores and cracks.[98] The cracking of the surface layer is due to the difference in the coefficients of thermal expansion of the material and the sodium silicate glass formed, and the large number of pores is due to the low viscosity of the latter.

It has been reported that materials based on silicon nitride have a high stability to the action of molten NaCl,[98,99] marine salt,[98,100] and LiCl–KCl and LiF–LiCl–KCl mixtures,[101] but that they have a poor corrosion resistance in melts with strong oxidising properties, such as Na_2SO_4 [98] and the eutectics Na_2SO_4–NaCl [99] and Na_2SO_4–V_2O_5.[102] The reaction of silicon nitride with sodium sulphate gives the silicates Na_2SiO_3 and $Na_2Si_2O_5$. The processes taking place during corrosion in an Na_2SO_4 melt can be described as follows. In the temperature range 800–900°, the surface layer of the material is oxidised by atmospheric oxygen according to Eqn.(1). When the salt melts (at 890°), it begins to react with the silicon dioxide formed

$$2SiO_2+2Na_2SO_4\rightarrow 2Na_2SiO_3+2SO_2+O_2$$

leading to its dissolution. After the SiO_2 layer has dissolved, the salt reacts with Si_3N_4:

$$6Na_2SO_4+2Si_3N_4+3O_2\rightarrow 6Na_2SiO_3+4N_2+6SO_2$$

Silicon nitride materials have a higher resistance to the action of molten Na_2SO_4 than silicon carbide materials.[99]

VI. CORROSION IN DIFFERENT GASEOUS MEDIA

According to Ref.18, the rate of oxidation of silicon nitride in moist air is twice that in dry air. The reaction of Si_3N_4 with water vapour gives ammonia:

$$Si_3N_4+6H_2O\rightarrow 3SiO_2+4NH_3$$

At the same time, in other studies,[50] even mass spectrometry did not detect ammonia in the products of the reaction of Si_3N_4 with moist air (the partial pressure of water vapour was 3.3×10^3 Pa). The activation energy of the oxidation of hot-pressed silicon nitride in moist oxygen is greater than that in dry oxygen (see Table 1). This is attributed to the change in the viscosity of the oxide film as a result of the dissolution and diffusion of OH^- ions in it.[50]

At high temperatures, silicon nitride materials have a greater resistance in CO–CO_2 mixtures containing oxygen at a partial pressure of 10^{-4}–10^{-1} Pa, compared with an atomosphere of oxygen or air.[81] The shaded areas in Fig.6 give the ranges corresponding to the kinetic curves for the oxidation of hot-pressed silicon nitride in oxygen, CO–CO_2, and mixtures of oxygen with argon and nitrogen. At an oxygen pressure of 1.33 Pa in the CO–CO_2 mixture, a mass loss is even observed, due to the formation of gaseous silicon monoxide. The rate of oxidation of Si_3N_4 is independent of the partial pressure of nitrogen in the gas mixture.[31] Hydrogen also has no significant influence on silicon nitride.[18] Heating powdered Si_3N_4 in a stream of chlorine for 1 h at 1200° leads to an increase in mass of 1%.[18]

Silicon nitride ceramic has a high resistance to corrosion under the influence of the products of the combustion of high-quality fuel.[102] If however these products contain sodium and vanadium, even at concentrations of 0.005%, very strong corrosion of the material is observed. After 225 h at a temperature of 900–1100°, an oxide layer with a thickness of ~1 mm, containing up to 75% SiO_2, 7% V_2O_5, and 8% Na_2O, is formed on the surface of specimens of reaction-sintered silicon nitride.[102]

In spite of the limited amount of available data, it may be concluded that silicon nitride materials can be used successfully in atmospheres of dry nitrogen, hydrogen, chlorine, oxides of carbon, and also fuel combustion products at temperatures above 1000°. The working atmosphere, however, should not contain moisture or elements such as sodium, vanadium, etc. which lead to modification of the protective oxide layer on the surface of the material and to an increase in the rate of corrosion.

VII. THE INFLUENCE OF OXIDATION ON THE PROPERTIES OF THE MATERIALS

Oxidation has a marked influence on most physicomechanical properties of a material. A particularly important role is played by the internal oxidation of porous materials, but at high degrees of oxidation there is a marked change in the properties of even compact hot-pressed materials. Thus when reaction-sintered and hot-pressed silicon nitride is used in an oxidising medium at high temperatures, the influence of oxidation cannot be neglected, and must be taken into account when predicting the properties of the materials.

The increase in the concentration of SiO_2 in the material on oxidation leads to an increase in the coefficient of thermal expansion.[57] As a result of the increase in volume when Si_3N_4 is converted into SiO_2 and the difference in the coefficients of thermal expansion of the material and the oxide phase, compression stresses are produced in the surface layers of the specimens, leading to an increase in the strength of the material. When the stresses are too high, however, cracking of the surface layer takes place, with deterioration in the properties of the material.[103] Compression stresses are produced in the surface layer during the oxidation of the hot-pressed material containing added ZrO_2 even at temperatures of 600–800°.[104] This is due to the fact that it contains a secondary phase with the composition $ZrO_{2-2x}N_{4x/3}$ ($0.25\leq x\leq 0.43$), which at temperatures above 500° is oxidised to give monoclinic ZrO_2, with an increase in volume by 45%. At the temperatures at which the process takes place, neither Si_3N_4 nor Si_2N_2O are oxidised. Since the material is compact, the oxidation of the secondary phase takes place only on the surface. The compression stresses produced increase the strength, preventing the production of cracks in the surface layer.

Published data on the influence of oxidation on the strength of the materials are contradictory. According to some authors,[72,105] oxidation leads to a decrease in the bending strength, the strength decreasing to a greater extent with increase in the time of treatment. According to other data,[106,107] oxidation leads to an increase in the strength of the specimens as a result of the healing of surface defects. It is reported[107] that although oxidation increases the strength of the material in the initial period, increase in the

time of treatment at 1200° to 100 h leads to a decrease in the strength of hot-pressed Si_3N_4 as a result of etching of the grain boundaries and the formation, along the boundaries, of grooves which act as stress concentrators and which may develop into cracks when a load is applied. At the same time it has been reported[108,109] that increase in the treatment time from 5 to 100 h does not lead to a change in the strength of reaction-bonded silicon nitride, irrespective of the temperature of testing (Fig.7). Treatment of specimens of reaction-bonded Si_3N_4 in air for 24 h at 1400° leads to an increase in its high-temperature strength.[26]

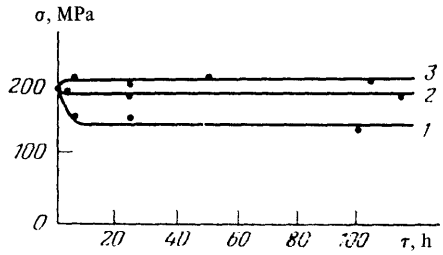


Figure 7. Dependence of the tensile strength of reaction-sintered silicon nitride at 20° on the time of treatment in air[108] at different temperatures (°C): *1*) 1400, *2*) 1200, *3*) 1000.

The bending strength of reaction-bonded and hot-pressed specimens of silicon nitride after oxidation at 1370° with and without an applied load was studied in Ref.105. During oxidation without the load, the strength of the reaction-sintered material increased, but that of the hot-pressed material decreased as a result of the growth of the nitride granules.

All the above data related to the strength determined in bending tests. In Ref.110 it was shown that the changes in the surface of the specimens produced by oxidation, as a result of the non-uniform distribution of the stresses, have a greater influence on bending than on elongation.

According to data obtained by the AiResearch Manufacturing Co., treatment for 50 h in air at 980° leads to an increase in the strength of hot-pressed silicon nitride. Turbine rotor blades produced by the firm were subjected to this treatment. The reaction-sintered materials were subjected to treatment for 2 h at 1400° or for 1 h at 1460°, followed by slow cooling in the furnace to room temperature.

Internal oxidation leads to a sharp deterioration in the creep resistance of the material.[77] Materials based on Si_3N_4 show good creep resistance at high temperatures in protective and reducing media. On heating in air or in oxygen, however, a silicate phase is formed as a result of oxidation of the material along the grain boundaries, leading to an increase in creep.

The influence of various changes taking place in the structure of materials during oxidation on their mechanical properties at room temperature and high temperatures has been analysed.[111-115] Some of the processes taking place during oxidation lead to an increase in the strength, crack resistance, and creep resistance (healing of defects, removal of impurities from the inner layers of the material, etc.), whereas others lead to a deterioration in the mechanical properties (cracking of the oxide layer, etching of the grain boundaries, etc.).[113] By selecting definite oxidation conditions depending on the structure and composition of the material, it is possible to achieve an increase in its strength and other mechanical characteristics. Extensive oxidation of a material leads to a deterioration in the mechanical characteristics; this is usually observed in the oxidation of porous specimens or during oxidation under conditions in which the oxide layer formed does not exhibit protective properties. It is therefore necessary to protect materials from active oxidation.

VIII. THE EFFECT OF SALTS ON THE STRENGTH AND CRACK RESISTANCE OF THE CERAMIC

Oxidation in the presence of sodium salts leads to a decrease in the strength and the critical stress intensity factors (Table 2), both at room temperature and at 1200°.[98] The decrease in strength at high temperatures is due to the formation of a liquid silicate phase in the surface layers of the material, and the decrease at room temperature is due to cracking of the oxide layer (see section V). The higher the oxidation temperature, the lower the strength of the specimens at room temperature.

Table 2. The influence of salts on the strength and crack resistance of the reaction-sintered material NKKKM-81.[98]

Form of treatment	T = 20°		T = 1200°	
	σ_b, MPa	K_{I_c}, MN m$^{-3/2}$	σ_b, MPa	K_{I_c}, MN m$^{-3/2}$
Without treatment	207	3,21	177	3.19
Corrosion in an NaCl melt at 950° (1 h)	195	3.14	128	2.83
Oxidation at 1200° (15 min) in the presence of NaCl	163	—	131	2,71
Oxidation at 1200° (15 min) in the presence of marine salt	157	—	110	2.57
Oxidation at 1200° (15 min) in the presence of Na_2SO_4	177	—	93	2.38

Notation: T is the temperature at which the tests were carried out, σ_b the bending strength, and K_{I_c} the critical stress intensity factor.

Table 2 shows that corrosion in melts of marine salt, sodium chloride, and the $NaCl-Na_2SO_4$ eutectic leads to a deterioration in all the mechanical characteristics of the materials at all temperatures of testing.[98,116,117] Increase in the time of treatment in molten NaCl from 1 h to 5 h, however, does not lead to a further decrease in strength.[98] Molten salts which have a stronger corrosive action on the material lead to a marked decrease in strength. This is due to the formation of defects in the surface layer of the specimens as a result of the corrosion breakdown of the grain boundaries and individual phase components of the material.[98,116]

In spite of the fact that corrosion under the influence of salts leads to considerable deterioration in the properties of silicon nitride materials, there is very little published information on methods of protection from "salt" corrosion.

IX. CORROSION UNDER STRESS

It is well known that the simultaneous action of a corrosive medium and mechanical loading on metals,[118] glass,[119] molecular crystals,[120] plastics,[121] and other materials leads to so-called corrosion under stress or to corrosion cracking. Since only the first steps are now being taken in the use of ceramics as constructional materials, the corrosion of silicon nitride ceramic under stress has been little studied.

The authors of Ref.122 consider that materials based on Si_3N_4 do not undergo corrosion under stress. This conclusion was based on the following factors: 1) the energy of thermal activation of the process is much higher than the typical energy for a chemical reaction; 2) attempts to stimulate the growth of a crack at the temperature of the surrounding medium in the presence of corrosive agents were unsuccessful; and 3) in the study of corrosion under stress at high temperatures, cracks produced artificially showed a tendency to close. At the same time, it has been reported[123,124] that reaction-sintered and hot-pressed silicon nitride specimens are sensitive to corrosion under the influence of stresses in moist air, water vapour, and aqueous media at temperatures up to 300°. The lower the pH of the medium, the lower the strength of the specimens. The authors of Ref.123 consider that the corrosion of silicon nitride materials under stress is due to ion exchange between the medium and a vitreous phase between the granules. Since practically all materials based on Si_3N_4 contain a secondary vitreous phase, they should be sensitive to corrosion under stress to the extent that the glasses and their breakdown can be described by the theory developed for glasses by Charles and Hillig.[125]

The influence of the external medium may also be due to the dependence of the time to breakdown on the magnitude of the applied load, observed in static fatigue tests on silicon nitride materials.[126,127] When a reaction-sintered ceramic based on silicon nitride was tested in air at temperatures close to 800°, a marked deterioration in the strength properties, which depended on the time of treatment under load, was detected. In this case, not only did the chemical reaction with the medium influence the mechanical properties, but the mechanical stresses also influenced the oxidation process. The quantity of cristobalite in the specimens after testing increased with increase in the applied load.[128] The information available at present, however, does not make it possible to determine reliably the mechanism of the breakdown of silicon nitride ceramic under the influence of mechanical stresses in a corrosive medium.

X. THE PROTECTION OF THE MATERIALS FROM OXIDATION

Various methods of protection from oxidation have been described. The chief method for protecting the ceramic is by depositing coatings of nitrides, carbides, or oxides on its surface.[129-131] Silicon nitride and carbide obtained by deposition from the gas phase have a very high resistance to oxidation. Oxide coatings can also provide reliable protection for the materials. The optimum work capacity of articles with coatings is achieved by depositing silicon nitride, since this ensures good adhesion to the support and a decrease in the possibility of separation or cracking of the coating when heated as a result of a difference in the temperature coefficients of linear expansion of the support and the coating.[25] The principal methods used to apply coatings are by deposition from the gas phase[129,130] and by plasma spraying.[131,132]

The reactions of silicon halides or silane with ammonia are widely used to obtain protective coatings of silicon nitride. The method of pyrolytic deposition with controlled nucleus formation[133] makes it possible to obtain fine-granular coatings consisting of equiaxial crystals. The deposition of a fine-granular coating with a thickness of 0.05 mm and granule dimensions of 1–10 μm on the surface of specimens of reaction-sintered silicon nitride increases the resistance of the material to oxidation during cyclic heating to 1200° by a factor of 100.[133] To give the ceramic other special properties in addition to corrosion resistance (erosion resistance, hardness, etc.), it is also possible to deposit composite coatings with a matrix of amorphous Si_3N_4 and inclusions of TiN, BN, and other compounds.[134]

Coatings of silicon carbide are obtained by the gas-phase synthesis of SiC from volatile silicon halides and hydrocarbons.[135] The deposition of a coating of pyrolytic silicon carbide on the surface of the material by the decomposition of trichloromethylsilane in a tubular furnace at 920° has been proposed.[75,136] The material with a porosity of 25%, covered with a layer of SiC, had an absolute creep resistance at 1200°, indicating the absence of internal oxidation. Coatings of titanium and zirconium diborides and aluminium nitride can also be applied.[133]

Good results were obtained when specimens with a porosity of 28% were impregnated with liquid silicon in a nitrogen atmosphere.[137] After this treatment, a compact protective layer with a thickness of 40–100 μm was formed on the surface of the specimens. An interesting feature is that this layer consisted entirely of β-Si_3N_4, which is known to be extremely stable to oxidation, whereas its concentration in the specimen did not exceed 4%. The increase in the mass of specimens with a coating thickness of 45 μm during their oxidation in the temperature range 800–1400° was one tenth of that for the non-protected specimens. For specimens with a film thickness of 100 μm, practically no increase in mass was observed up to 1400°. The specimens showed a high resistance to oxidation in moist air at 1400°, whereas under similar conditions the non-protected specimens were oxidised to the extent of 30%. In practice, however, the use of this method of protection encounters considerable difficulties, associated with the need for thorough removal of oxygen-containing silicon compounds from the surface, since Si_3N_4 containing SiO_2 or Si_2N_2O on its surface is not wetted by liquid silicon.

According to data given by Norton, reaction-sintered materials can be protected from oxidation by treating with solutions of $Al(NO_3)_3$, $ZrOCl_2$, organometallic compounds of zirconium, or a mixture of $ZrOCl_2$ and $Y(NO_3)_3$. After repeated impregnation, the specimens are heated in a nitrogen atmosphere; the decomposition products collect and fill the pores on the surface of the specimens. The strength of the materials remains unchanged after this treatment, but if materials to which zirconium compounds have been added are heated for 50 h in air at 1230°, their bending strength increases considerably.

Impregnating porous reaction-sintered materials with organosilicon compounds followed by their thermal decomposition makes it possible to increase the resistance of the materials not only to oxidation but also to corrosion under the influence of salts.[138]

The processes described above are not always easy to carry out from the technological viewpoint. A much simpler method of protection is by preliminary oxidation of the specimens under appropriate conditions. As already noted, to obtain useful materials it is necessary to create conditions favouring the formation on the surface of the articles (during use in an oxidising medium at high temperatures) of a compact protective oxide layer. In a certain temperature range (for most materials at temperatures close to 1000°), however, the rate of oxidation is already fairly high, but a protective layer has not yet been formed. This is particularly dangerous for porous materials, since it may lead to their extensive internal oxidation. To eliminate undesirable phenomena, it has been proposed that a compact oxide layer be produced artificially on the surface of reaction-sintered materials by placing them for a short time in a furnace heated to 1300 to 1350°.[56] Thermal treatment in this way is used by the AiResearch Manufacturing Co. to protect materials from further oxidation during use, with a simultaneous increase in their strength.

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Thus oxidation during use represents a serious danger for silicon nitride materials, since it may lead to a marked deterioration in their mechanical characteristics. This applies particularly to porous reaction-sintered ceramic. At the same time, a knowledge of the regular features of the process makes it possible, by using definite oxidation conditions, to achieve an increase in the strength of the materials and to protect them from active oxidation during subsequent use. Here it is necessary to take account of the fact that the materials described in the present review differ considerably in their behaviour in oxidising media at high temperatures, depending on their composition and structure.

Although much of the published material on the oxidation of silicon nitride ceramic is contradictory, the principal regular features of this process have now been established. At the same time, however, corrosion under the influence of salts and in an atmosphere of fuel combustion products has still been insufficiently studied. In addition, the conditions under which a ceramic based on silicon nitride undergoes corrosion under the influence of stresses have not yet been established. To ensure that the materials can function at high temperatures in media containing salts of sodium and other metals, a more detailed study of the corrosion processes using modern methods of physicochemical analysis is necessary.

Although silicon nitride materials may undergo considerable corrosion in the media described above at temperatures higher than 1000°, with a deterioration in their mechanical properties, they nevertheless retain under these conditions a higher strength than other heat-resistant and corrosion-resistant metallic alloys.

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