SOME FEATURES OF THE STRENGTH PROPERTIES
OF SILICON NITRIDE CERAMICS AT HIGH TEMPERATURES

Yu. G. Gogotsi, V. P. Zavada,
and V. V. Traskovskii

Materials based on silicon nitride are used extensively for preparing thermally stressed components of various high-temperature devices. In view of this, in developing these materials the main attention is devoted to providing the required level of mechanical properties under operating temperature conditions. Since initially the main direction for using silicon nitride materials in structures is gas turbine engine components [1] intended for operation at temperatures above 1000°C, in the majority of cases strength has been determined in this temperature range [2, and others].

The study of material mechanical properties at temperatures above 1000°C is also connected with the widespread opinion that the strength of ceramics based on Si_3N_4 is mainly governed by the condition of the intergranular phase which softens at 1100-1400°C depending on the type and amount of activated sintering additives introduced. In view of this the strength of the majority of silicon nitride materials decreases at temperatures above 1100°C [3].

As a result of summarizing the data of numerous studies for dense uniform ceramic materials it has been established [4] that the temperature dependence for ultimate strength includes three temperature zones. In the initial temperature zone the ultimate strength remains constant or changes a little. In the next temperature zone it decreases at first and then it increases, which is connected with development of plasticity. In the third temperature zone there is marked ceramic loss of strength due to development of creep. A similar temperature dependence for ultimate strength is observed with testing silicon nitride ceramics in a vacuum [5] as a result of a viscoelastic transition in the intergranular phase. However, since materials intended for operation in oxidizing atmospheres are normally tested in air, oxidation occurring during testing may markedly affect the nature of the temperature dependence for ultimate strength and other ceramic properties [6]. Reasons for the change in ultimate strength for materials based on Si_3N_4 as a result of oxidation have previously been analyzed [7]. However, in these studies, as in many others, the effect of oxidation was only studied at temperatures above 1000°C.

Data are given in the present work for the mechanical properties of reaction-sintered silicon nitride ceramics (similar to those considered in [7]) at temperatures up to 1400°C with a more detailed study of the temperature range 600-900°C. Ultimate strength in air and in a neutral atmosphere under three-point bending conditions (distance between the supports 20 mm) was determined in specimens 3.5 × 5 × 25 mm in size, and precritical crack development in air was studied in double-torsion specimens 2 × 25 × 75 mm in size. All of the specimens were cut from blanks 7 × 50 × 150 mm in size.

For the ceramics studied there is a reduction in strength typical for silicon nitride materials at temperatures above 1000°C, developing both in air and in a neutral atmosphere (Fig. 1). In addition, with testing in air in the temperature range 700-800°C there is some reduction in ultimate strength which is almost undeveloped in a neutral atmosphere. Since this phenomenon more than likely may be connected with material oxidation, in order to strengthen the effect and to estimate the degree of its development with prolonged loading some of the specimens were exposed previously at high temperature under load σ_{pr} (lower than the failure load in short-term tests) for half an hour, and then their residual strength σ_{res} was found by increasing the load (at the same temperature) to failure. In the case of testing in a neutral atmosphere prior exposure under load even for 20 h did not markedly alter the strength (Fig. 2). In contrast to this with testing in air at 800°C in spite of the short time of exposure there was a drop in specimen strength, and this was more intense, the greater the amount of prior loading (with prior loading to 177 MPa specimens failed during exposure under load). At the same time, at 1100°C prior loading did not affect test results. It is noted that simple oxidation (without loading) for half an
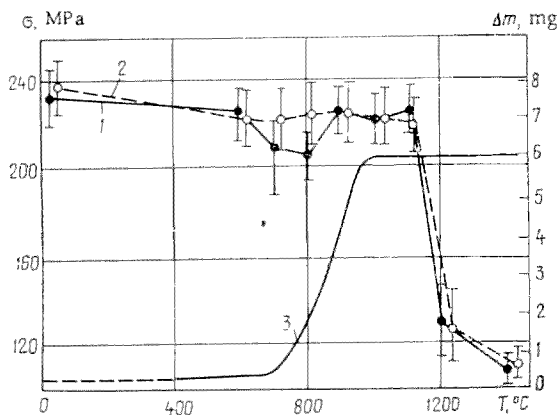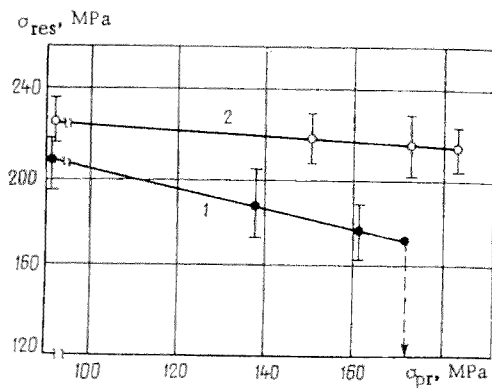
Fig. 1. Dependence of ultimate strength for specimens tested in air (1), in a neutral atmosphere (2), and weight increase (3) on temperature.

Fig. 2. Dependence of residual strength for specimens on the amount of prior stressing with testing in air (1) and in a neutral atmosphere (2) at 800°C.
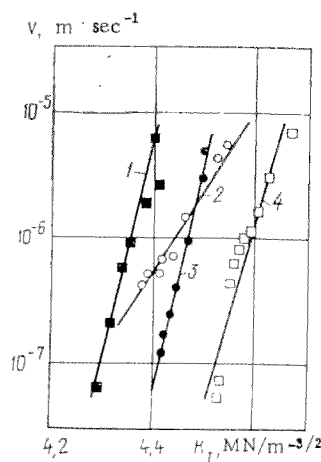

Fig. 3. Typical $K_I - V$-diagrams at different temperatures: 1) $n = 166$, $T = 900°C$; 2) $n = 62$, $T = 800°C$; 3) $n = 163$, $T = 600°C$; 4) $n = 146$, $T = 20°C$.
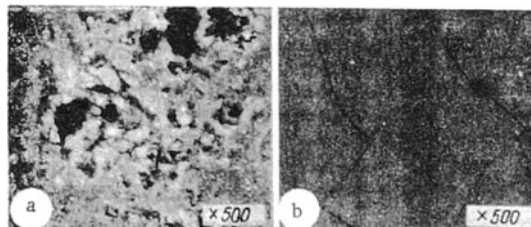
Fig. 4. Surface of specimens oxidized at 800°C (a) and 1200°C (b).

hour at 800°C did not alter the strength (Figs. 1 and 2). Thus, for the ceramics in question the region for a strength reduction is found in the temperature range 600-900°C.

Analysis of data in the literature [8, 9, and others] showed that at 600-1000°C there is a reduction in strength for both porous reaction-sintered materials [8] and for dense hot-pressed materials [9]. This indicates that a reduction in strength is quite common for silicon nitride ceramics. However, since detailed studies have not been carried out previously for the strength properties of silicon nitride ceramics in this range (there is only information about individual random points falling in this temperature range), it is difficult to talk about temperature limits for different materials.

Apart from a reduction in strength, some reduction in the crack resistance has been established [10] for hot-pressed Si_3N_4 with additions of MgO and $Y_2O_3 + Al_2O_3$ at 1000°C (the K_{Ic} value was not determined at lower temperatures). A similar reduction in K_{Ic} has been recorded previously by us in studying ceramic NKKKM-81, which is close in composition and preparation technology to that being studied. No marked changes in K_{Ic} were observed in the present work in determining the $K_I - V$-diagram for ceramic NKKKM-84. In addition, it was found that at 800°C there is a sharp reduction in exponent n (Fig. 3) in the equation describing crack growth rate:

Fig. 5

Fig. 6

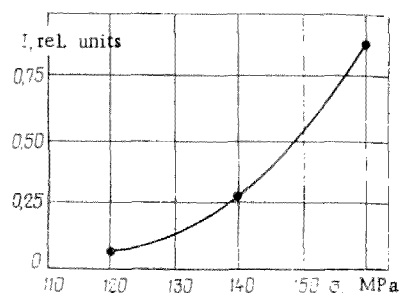Fig. 5. Fracture surface of a specimen previously exposed at a stress of 177 MPa for 20 min at 800°C.

Fig. 6. Dependence of relative intensity of crystobalite peaks in the compression region due to loading after testing at 800°C.

$$V = \alpha \cdot K_I^n .$$

This points to activation of precritical crack growth in this temperature range. At both higher and lower temperatures ceramic NKKKM-84 resists slow failure much better. Activation of precritical crack growth at 800°C agrees with the fact that a reduction in residual strength after exposure under constant load is more clearly defined than for the short-term strength (Figs. 1 and 2).

Thus, with tests in air in the temperature range being studied there is a marked reduction in almost all of the main mechanical properties of the ceramic. The mechanism for loss of strength requires explaining. Since no reduction in short-term and residual strength (Fig. 2) was noted with testing in an inert atmosphere (argon), it is possible to assume that it is connected with the effect of test atmosphere, and in fact with material oxidation. In fact, with programmed heating (at a rate of 15 deg/min by means of an OD-103 derivatograph) oxidation of the test ceramic occurs more rapidly at 700-1000°C (Fig. 1). An active increase in weight Δm for specimens is observed in the thermogravimetric curve as a result of occurrence of the reaction

$$Si_3N_4 + 3O_2 = 3SiO_2 + 2N_2,$$

accompanying formation of a hard porous oxide layer (Fig. 4a) exhibiting low protective properties [11]. At temperatures above 1000°C the oxidation process slows down rapidly since as a result of diffusion of additions and impurities towards the specimen surface an easily melting silicate layer forms at it [7] healing open pores (Fig. 4b*).

Oxidation at a temperature up to 1000°C leads to formation of a layer of silicon dioxide consisting mainly of α-crystobalite and also certain amounts of trydimite and amorphous phase, so that the oxide layer is in the solid state and it does not exhibit any marked plasticity [11]. Oxidation observed at these temperatures for porous reaction-sintered ceramic causes densification of the surface layer as a result of an increase in volume with transformation of Si_3N_4 into SiO_2, and development of internal stresses in it. At temperatures above 1000°C, when plasticity effects develop in the oxide layer and in the intergranular secondary phase, these stresses are easily relaxed, but in the temperature range in question brittle failure of oxidized surface layer fragments is possible.

*Cracking of the surface layer occurred after specimen cooling as a result of the presence of thermal stresses caused by the difference in linear thermal expansion coefficients for Si_3N_4 and SiO_2 [12] due to $\alpha \rightarrow \beta$-transformation in crystobalite.

Electron microscope studies of specimens tested at 800°C in air showed a considerable number of cracks in the subsurface layer to a depth of 30-40 μm (Fig. 5). To a greater depth the specimen is weakly oxidized and it retains quite high porosity, and elongated crystals of $\beta-Si_3N_4$ are readily seen in the fracture.

However, cracks could arise not only during exposure at 800°C, but also as a result of specimen cooling. Supporting this last suggestion is, in fact, crack formation at the edges of SiO_2 fragments. By exhibiting a greater linear thermal expansion coefficient, areas of SiO_2 during cooling are compressed more strongly than Si_3N_4, as a result of which they break and cracks form at their edges. In addition, although the cracks observed (Fig. 5) are apparently not the direct reason for loss of strength for the ceramic in question at 800°C, formation of low-strength, brittle oxide phase may promote propagation of a failure crack, and at the mouth of a crack, which is accompanied by a considerable increase in volume (by more than 70%), an unwedging effect develops.

An alternative mechanism for the reduction in strength properties at ~ 800°C in air may be the process of material corrosion cracking, i.e., loss of strength as a result of the simultaneous effect of a mechanical stress and a chemically active medium with which in accordance with the Fuller and Thomson crack growth model [13] the chemical reaction at the crack tip promotes breaking of the bond between material atoms. This mechanism is in good agreement with development of the reduction in mechanical characteristics only with testing in air, and not in an argon atmosphere, with the data provided for the effect of the amount of prior loading on the degree of loss of strength, with absence of a marked reduction in the strength of specimens not subjected to loading during oxidation. In addition, by means of x-ray phase analysis it has been established that the relative* intensity of peaks I for the main oxidation product, i.e., crystobalite on specimens tested at 800°C, increases with an increase in prior loading (Fig. 6).

Consequently, the mechanical properties of the material are affected by its chemical reaction with the atmosphere. However, in turn mechanical stresses affect the oxidation process. At higher temperatures, development of this mechanism is maintained by formation of a solid oxide layer preventing access of oxygen, and also possibly existence of the Ioffe effect (rounding of the tip of a crack with which there is a sharp increase in K_{Ic} [6] as a result of the development of plasticity).

Thus, the strength properties of ceramic at ~ 800°C in air are reduced, which, judging from data in the literature, is inherent for other silicon nitride materials. This phenomenon has not been considered previously, since on the one hand strength properties are only markedly reduced with prolonged loading for which experimental data is limited, and on the other hand in this temperature range (up to the temperature corresponding to glassy phase softening) the mechanical properties are traditionally assumed to be unchanged.

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*The most intense peak for crystobalite (101) and the silicon nitride peak (110) closest to it have been compared.

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EXPERIMENTAL STUDY OF THE EFFECT OF CYCLE

ASYMMETRY ON THE LIFE OF CORRUGATED EXPANSION

JOINTS

A. I. Kartsev, V. Yu. Dedusenko,   UDC 621.165:539.43:31
and V. V. Kudrenko

Previous theoretical–experimental studies [1–3] of corrugated expansion joints showed the need to allow for the pulsating character of loading of these structural elements, which are in very common use in construction of power plants. These elements work beyond the elastic limit. An integral method has been proposed for evaluating their service life, and the method has opened up the possibility of significantly increasing the strength of normalized expansion joints.

The basis of the proposed method is the notion that the relative deflection of the lens $\bar{\Delta}$, being an integral characteristic of the loading of the structure, can serve as a parameter of service life in pulsating loading. An empirical relation was obtained to connect this quantity with the number of cycles to failure N:

$$\bar{\Delta} N^k = M, \tag{1}$$

where $\bar{\Delta} = \frac{\Delta}{\Delta_t}$ (Δ is the range of the displacement experienced by the lens; Δ_t is the limiting elastic deflection of the lens), i.e., the axial displacement of the inside contour of the lens at which plastic strains occur inside the lens; k and M are constants for the given class of structures.

This method was later substantiated statistically for axial expansion joints [4].

However, since about 80% of all expansion joints in pipelines work as hinged inserts, i.e., experience angular displacements, it is important to evaluate the strength of expansion joints under antisymmetric loading. The studies [5, 6] were devoted to theoretical determination of characteristics of the stress–strain state (SSS) of expansion joints, including the angular displacements.

This study reports results of an experimental investigation of the low-cycle fatigue of full-scale specimens of corrugated (lens-shaped) expansion joints OST 34-235-73 under different types of loading. We chose expansion joints Du250 and Du700 for testing.

The tests were conducted on an automatic unit especially designed and built by the Institute of Problems of Machine Design of the Ukrainian Academy of Sciences and the "Turboatom" Industrial Association. The unit was designed to study the operating characteristics of expansion joints under pulsating loading. It permits both axisymmetric and antisymmetric cyclic deformation of specimens.

In safe-life tests conducted to determine characteristics of low-cycle fatigue, the manipulated variable is the displacement (range) $\Delta = 2\Delta_a$ (in axial loading) or the angle of rotation of the lens axis $\gamma = 2\gamma_a$ (in antisymmetric loading).

Figure 1 shows the scheme of deformation of the specimens for these types of loading.

The form of the loading cycle with respect to the displacements was assumed to be symmetrical: $\Delta_a = \pm \frac{\Delta}{2}$ and $\gamma_a = \pm \gamma/2$.