

# OXIDATION-INDUCED CHANGES IN MECHANICAL PROPERTIES OF SILICON NITRIDE CERAMICS

J. Gubicza, P. Arató and F. Wéber

Research Institute for Technical Physics and Materials Science, H-1525 Budapest P.O.Box 49, Hungary

The effect of oxidation on the room-temperature mechanical properties of four different silicon nitride ceramics is investigated. The strength and the elastic modulus of the whole material and the hardness, the fracture toughness and the elastic modulus of the internal region (without surface oxide layer) are determined for the materials oxidized at temperatures up to 1400°C. It is found that the fracture toughness decreases during oxidation at 1000°C. Reduction of the elastic modulus of the materials oxidized at 1400°C is also observed. A part of the changes in the mechanical properties is interpreted by the changes in the phase composition.

## 1. INTRODUCTION

Silicon nitride ceramics are generally used in high temperature oxidizing environments. During oxidation of these ceramics a strongly oxidized layer is formed on the surface<sup>1,2</sup>. This layer has a great influence on the oxidation resistance and the room-temperature mechanical properties of silicon nitride. It was established by numerous authors that the strength decreased during oxidation because of the large defects in the surface oxide layer<sup>3,4</sup>. Although this scale protects the internal region of the material from the strong oxidation, the chemical and the phase compositions of the internal part change during the oxidation heat-treatment<sup>1,5</sup>. These changes in the compositions may induce changes in the mechanical properties of the internal part.

In this paper the oxidation-induced changes in the room-temperature mechanical properties of the whole sample (strength, elastic modulus) and those of the internal part (hardness, fracture toughness and elastic modulus) are investigated for different silicon nitride materials oxidized at temperatures up to 1400°C.

## 2. EXPERIMENTAL PROCEDURES

Mixtures of  $\text{Si}_3\text{N}_4$ ,  $\text{AlN}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  powders were milled in ethanol in a planetary type alumina ball mill. The compositions of the four starting powder mixtures are given in Table 1. The samples were compacted by dry pressing at 220 MPa. The materials were sintered in high purity nitrogen by a two-step sinter-HIP method using BN embedding powder. The dimensions of as-sintered specimens were approximately 3.5 mm x 5 mm x 50 mm. The samples were ground before oxidation. Oxidation took place in static air at 800°C, 1000°C, 1150°C, 1300°C and 1400°C for up to 48h. The oxidation resistance of the samples was characterized by the weight-gain and the density-loss data. The apparent density of the as-sintered and the oxidized materials was measured by the Archimedes method.

TABLE 1  
The compositions of the starting powder mixtures of the materials investigated.

Material	Composition (wt%)			
	$\text{Si}_3\text{N}_4$	$\text{AlN}$	$\text{Al}_2\text{O}_3$	$\text{Y}_2\text{O}_3$
X	90.9	0	3	6.1
A	90	0	4	6
B	87	4	4	5
F	69	15	12	4

The Young's modulus and the strength of the samples were determined before and after the oxidation by a room temperature four point bending test with spans of 40 and 20mm. The hardness and the indentation fracture toughness of the internal region were determined before and after oxidation by a Vickers diamond indenter using a load of 100 N. Before the indentation measurement a wide surface region of the sample was removed by grinding and the new surface was carefully polished. The fracture toughness was calculated by the formula of Niihara et al.<sup>6</sup> because Palmqvist cracks were observed at the corners of the Vickers pattern for all the materials investigated. The elastic modulus of the internal part is significantly different from that of the whole sample oxidized at 1300°C and 1400°C because at these temperatures the porous surface oxide layer is relatively thick as compared with those formed at lower temperatures. The Young's modulus of the internal region of these materials was measured by depth sensing indentation (DSI) method. The loading rate and the maximum load were 14.4 mN/s and 500 mN, respectively. For

the explanation of the oxidation induced changes in the mechanical properties, the crystalline phases formed in the materials were identified by X-ray diffraction (XRD).

### 3. RESULTS AND DISCUSSION

The oxidation behaviour of our materials was characterized by the weight-gain and the density-loss data. The values of these quantities were different from zero only after oxidation at 1300°C and 1400°C (Table 2). The decrease of the apparent density during oxidation is a consequence of the increasing porosity in the material. Significant difference in the oxidation resistance of the materials investigated can be observed after oxidation at 1400°C. As can be seen in Table 2, material F is the most oxidation resistant material among the four ceramics. The oxidation rate of material X is higher than that of material F. Materials A and B are the least oxidation resistant materials and the oxidation rate of B is a bit higher than that of A.

TABLE 2

The weight-gain ( $\Delta m/A$ ) and the density-loss ( $\Delta \rho$ ) data for the materials oxidized at 1300°C and 1400°C.

Material	1300°C		1400°C	
	$\Delta m/A$ (mg/cm <sup>2</sup> )	$\Delta \rho$ (%)	$\Delta m/A$ (mg/cm <sup>2</sup> )	$\Delta \rho$ (%)
X	0.49	1.6	1.34	4.7
A	0.47	1.6	4.04	8.0
B	0.59	1.1	4.68	9.3
F	0.47	0.3	0.69	1.3

The Vickers hardness (HV) numbers of the internal regions of the as-sintered and the oxidized materials can be seen in Figure 1. The standard deviations of the hardness values are less than 0.3 GPa. The hardness of the materials investigated does not change significantly during oxidation, except for material B oxidized at 1300°C, the hardness of which is higher than that in the as-sintered state. This increase of hardness can be attributed to the change in the phase composition during oxidation as follows. The XRD analysis showed that  $\beta$ -SiAlON ( $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ ) was the major phase in each as-sintered material. It was observed that the  $z$  value of  $\beta$ -SiAlON increased with the increase of aluminium and oxygen contents of the starting powder mixture ( $z=0$  for materials X and A,  $z=0.5$  for material B and  $z=1.0$  for material F). The  $z$  value changed during

oxidation only in material B at 1300°C where a large amount of  $\beta$ -SiAlON phase with high z value ( $z=0.8$ ) was formed beside the major  $\beta$ -SiAlON ( $z=0.5$ ). This phase formation may cause the increase of hardness of material B. This idea is supported by the observation that material F, in which the major  $\beta$ -SiAlON phase has also high z value ( $z=1.0$ ), has the highest hardness among the four as-sintered materials.

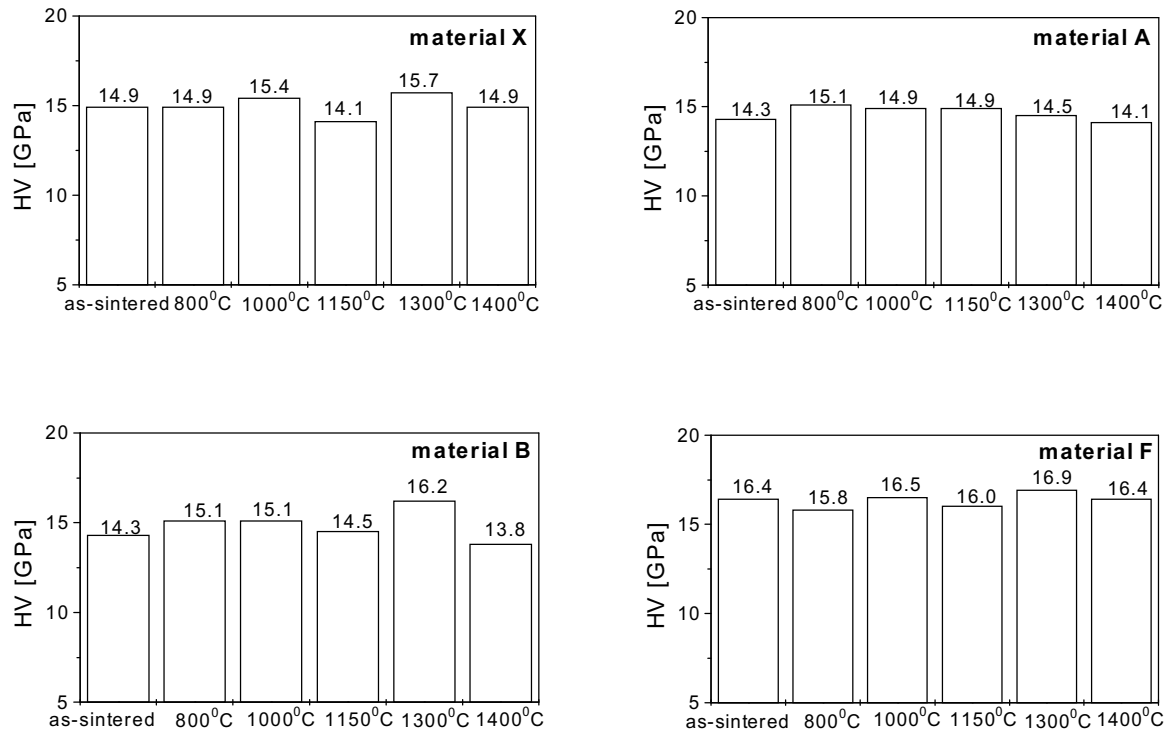


FIGURE 1

The Vickers hardness of the internal region of the as-sintered materials and those oxidized at different temperatures.

The indentation fracture toughness data of the internal part of the as-sintered materials and those of the materials oxidized at different temperatures are shown in Figure 2. The standard deviations of the toughness values are less than  $0.2 \text{ MPam}^{1/2}$ . The most significant change in  $K_{IC}$  is its decrease after oxidation at 1000°C for all the materials investigated. This reduction of toughness can be explained by the crystallization of the intergranular phase. Crystalline minor phases were not detected in the as-sintered state as well as after oxidation at 800°C. At 1000°C  $\text{Y}_2\text{SiAlO}_5\text{N}$  (B-phase) in materials B and F,  $\beta\text{-Y}_2\text{Si}_2\text{O}_7$  and  $\text{Y}_2\text{SiAlO}_5\text{N}$  in material X and  $\beta$ -

$Y_2Si_2O_7$  in material A were formed as crystalline intergranular phases. As a consequence of this crystallization the density of the intergranular phase increases and the volume of it decreases<sup>4,5,7</sup>. The latter can cause development of tensile stresses at the grain boundaries<sup>4</sup>. These stresses may result in easy crack propagation at the grain boundaries and lower fracture toughness of the materials oxidized at 1000°C. Although crystalline intergranular phases were also observed after oxidation at temperatures higher than 1000°C, such a significant decrease of the toughness was not detected probably because of annealing of the stresses developed due to crystallization<sup>4</sup>.

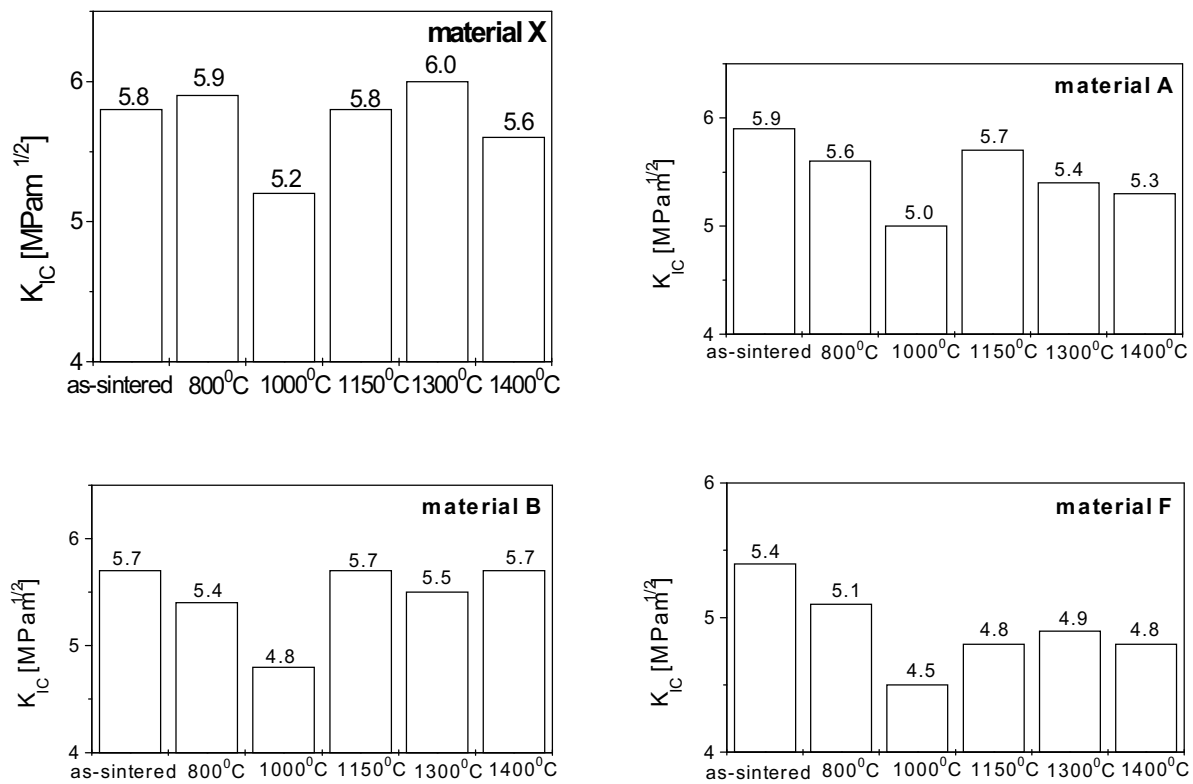


FIGURE 2

The fracture toughness of the internal part of the materials in the as-sintered state and after oxidation at different temperatures.

The effect of oxidation at different temperatures on the four point bending strength is illustrated in Figure 3. The standard deviation of the strength values is 11%. The strength decreases with the increase of the oxidizing temperature for all the compositions. At the temperatures below 1000°C the strength degradation can be explained by the decrease of the fracture toughness. At higher temperatures the large defects (e.g. cavities, cracks) in the strongly oxidized surface scale

can cause the reduction of the strength<sup>3,4</sup>. As the thicker oxide layer probably contains larger defects, the higher strength degradation occurs in the material having thicker surface oxide scale. It has been found that the thicker oxide layer is linked to the higher density-loss after oxidation<sup>8</sup>. Consequently, the higher the reduction of the strength is, the higher the density-loss is after oxidation at 1400°C (see Figure 3 and Table 2).

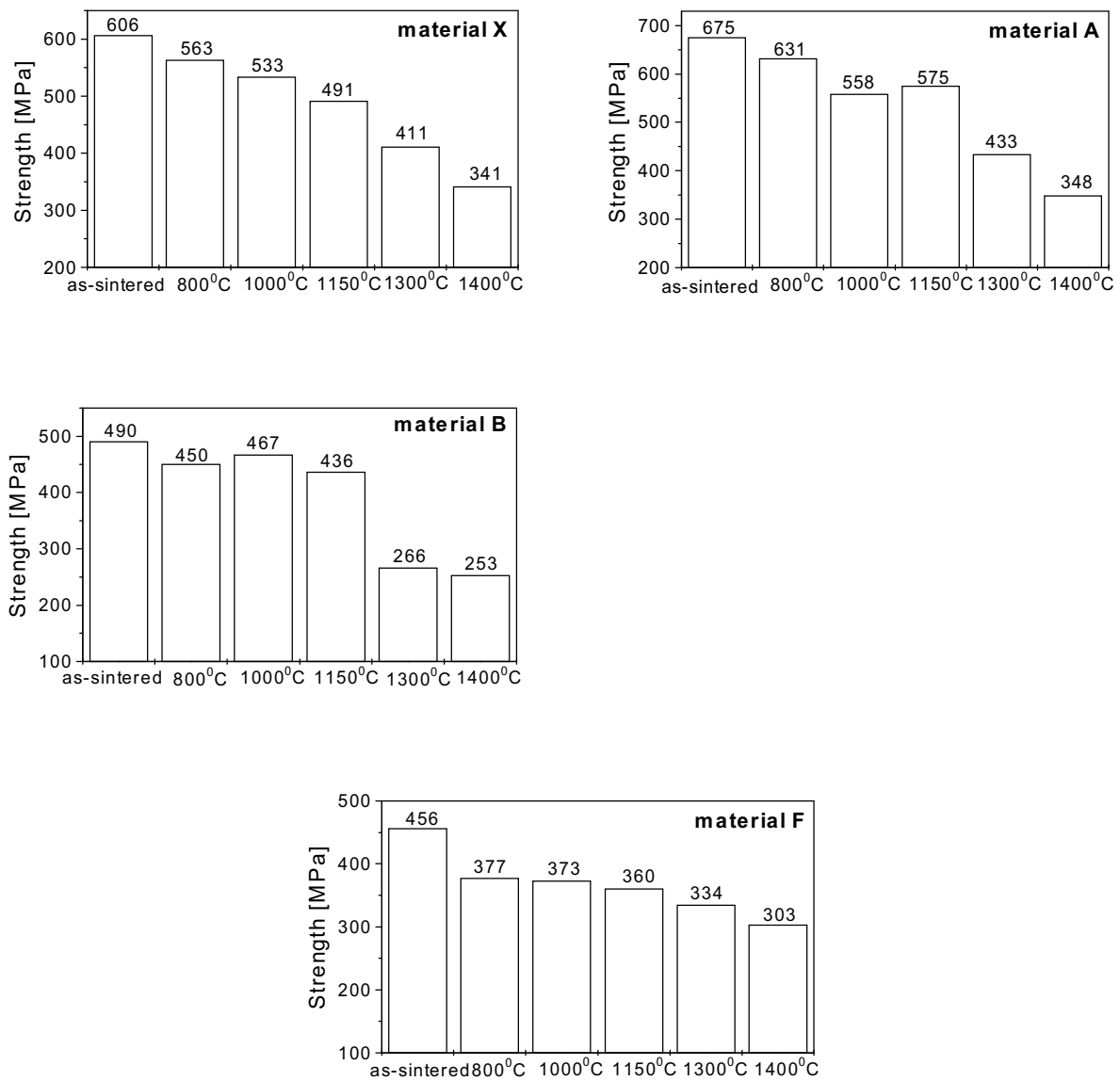


FIGURE 3

The four point bending strength of the as-sintered and the oxidized materials.

The effect of the oxidation on the Young's modulus of the whole material and that of the internal part is shown in Figure 4. The standard deviations of the elastic moduli are less than 10 GPa. The elastic modulus of the whole sample decreases significantly during oxidation at 1400°C for all materials. The role of the low modulus of the porous oxide layer in this reduction of elastic modulus has been discussed elsewhere<sup>9</sup>. The oxidation at 1400°C results in significant internal modulus reduction too for all the materials investigated. The reason for this decrease of modulus can not be the increase of the internal porosity because the hardness as well as the modulus ought to have decreased significantly with increasing porosity<sup>10,11</sup>. This internal modulus reduction may be caused by the change in the chemical composition of the intergranular phase during oxidation.

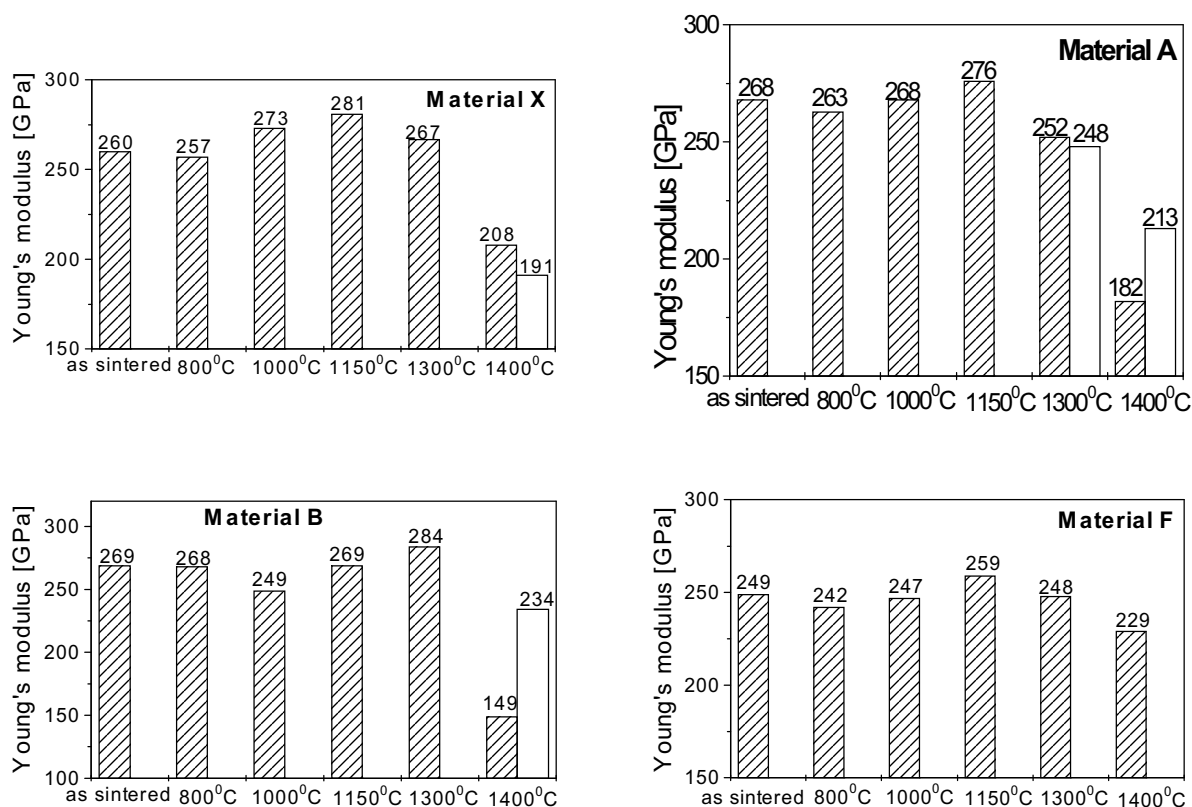


FIGURE 4

The influence of oxidation on Young's modulus of materials investigated. The shaded and the open columns represent the moduli of the whole sample and the internal part, respectively.

#### 4. SUMMARY

The oxidation-induced changes in the mechanical properties of the whole sample and the internal region of silicon nitride ceramics with four different compositions were studied.

The hardness changed significantly only during oxidation of material B at 1300°C. The increase of the hardness was probably due to the increase of the amount of the major  $\beta$ -SiAlON phase with high aluminium and oxygen contents ( $z=0.8$ ). This idea was supported by the observation that material F, in which the major  $\beta$ -SiAlON phase had also high  $z$  value ( $z=1.0$ ), had the highest hardness among the four as-sintered materials.

The  $K_{IC}$  of each material was significantly lower after oxidation at 1000°C than it had been before. This reduction of toughness was probably due to the internal tensile stresses developed at the grain boundaries because of the crystallization of the intergranular phase. At higher temperatures these stresses are assumed to be annealed because the deterioration of the toughness was not observed.

The strength decreased with increase of the oxidizing temperature for all the compositions. At the temperatures below 1000°C the strength degradation may be mainly due to the decrease of the fracture toughness. Above 1000°C the reduction of the strength is thought to be a consequence of the increase of the defect size in the surface oxide layer.

A significant reduction of the internal Young's modulus was observed for all the materials after oxidation at 1400°C. This was caused by the low modulus of the porous surface scale and the decrease of the modulus of the internal region. The latter might have been caused by the change in the composition of the intergranular phase.

#### ACKNOWLEDGEMENT

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