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HIGH TEMPERATURE OXIDATION OF SILICON NITRIDE

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ABSTRACT

The influence of high pressures on silicon nitride structure and its resistance to scaling were studied for the first time. For this end the method of continuous TG and DTA-DTG-TG complex thermal analysis were used.

It is found that the silicon nitride synthesized under high static pressure possesses a higher resistance to oxidation in air and the process is described by a log dependence. It is shown that the thermal stability improvement is related with the nature of silicon dioxide (fibrous silica) formed on the surfaces of oxidized samples.

A number of valuable physical and chemical properties inherent in nonmetal nitrides explain the constant interest to the silicon nitride as a refractory, structural and tool material. The effect of high pressures on the resistance to scaling in Si_3N_4 was studied in /1/.

The silicon nitride powder with the specific surface area of 1.5 mg/g, the grain size of $1\text{-}280\cdot10^{-6}$ m and the molar contents (%) of Si_{tot} = 59 and N_{bind} = 36.1 was chosen. Spectral analysis allowed to discover Fe, Al and Ca impurities as well as traces of Cu, Pb, SN, Zr, Cr, Ni and Mn. X-ray phase analysis showed the presence of α-Si_3N_4 and β-Si_3N_4 and silicon oxynitride (Si_2OH) in all starting powders. The silicon nitride oxydation was studied on powders, hot-pressed samples and on samples synthesized at high static pressures of 3000, 5000 and 7000 MPa. To study the influence of high pressures on structure and scale-forming mechanism a number of current physical techniques was used. Thus, the oxidation kinetics was studied by the continuous TG technique in the temperature range of 773-1573 K in air. DTA on the Q1500D-type system was also applied. Metallographic and X-ray diffraction studies were carried out on the reflection-type microscope "Neophot-2" and on the УРС-2.0 X-ray apparatus.

It is found that the density of samples after high pressure impact, $\rho' = 3.501\cdot10^{-3}$ kG/m^3, increases considerably compared with the hot-pressed samples, $\rho = 3.100\cdot10^{-3}$ kG/m^3.

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X-ray diffraction analysis of the samples to be tested showed the lattice distortion and the increase of β-Si_3N_4-phase in samples prepared under high pressures. Only several lines on the X-ray pattern showed the presence of a small amount of α-Si_3N_4 as well. The microscopic studies of the samples showed the segregation of free silicon at the grain boundaries. Authors of /2/ also observed the precipitation of free silicon in the form of rounded particles. The microhardness of samples to be tested that were prepared at p=70 MPa was equal to 43.14 GPa under $5 \cdot 10^{-2}$ kG load, compared with hot-pressed samples (H_μ = 32.75 GPa).

Derivatographic studies of the Si_3N_4 powders showed that in the atmosphere of air oxygen the insignificant polymorphic transformations occurred in silica formed from free silicon at 473-523 K, and adsorption-desorption processes, rather insignificant though, also occurred. The low adsorption activity of the powders under study can be explained by the singularities of the fine crystalline structure of silicon nitride. It is evident from /3,4/ that the presence of silicon atoms can be explained by the fact that each of the fourth hybride sp^3-orbit of Si atom is overlapped by a hybride sp^2-orbit of N atom.

It can be seen from Fig.1 that the group of oxidation isotherm for the samples obtained at high pressure is located much lower than the oxidation curves for the hot-pressed samples. The higher stability of samples of the first group is also evident from the microscopic observation data. It is quite clear that all the samples manifest high resistance to oxidation in air, and those synthesized at 7000 MPa do not suffer any oxidation with temperature rise up to 1473 K. On the basis of kinetic studies it was found that the oxidation process for the hot-pressed samples is described by a parabolic dependence which shows the diffusion nature of the oxidation (Table 1). The effect of high pressure on the scale-forming mechanism is considerable. Thus, the variation of the oxidation is time log dependent but its dependence, in fact, is more complicated due to the nature of the silica film formed. The graphic analysis and the construction of corresponding $\frac{1/\Delta p}{S\tau} - \tau$ dependences at 1373 and 1473 K showed that after 1 1/2 hour of oxidation the curves revealed an inflection. The latter confirms the assumption about the alteration in the nature of the oxide phases formed which is also evident from the microscopic observation data. In fact, the initial oxidation is accompanied by

β-quartz and α-cristobalite formation. The tridymite is not formed due to the presence of microinclusions in silicon nitride under high pressure which are not conductive to its formation. The both silica modifications transform further into a special form - fibrous silica. Notwithstanding the X-ray amorphicity the fibrous silica shows a characteristic loop with d = $3.58 \cdot 10^{-10}$ m on Debye powder pattern. The results are in a good agreement with those in /5/.

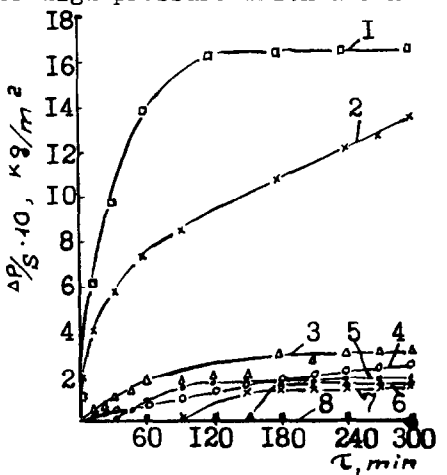

Fig. 1 Oxidation isotherms for hot-pressed and high-pressure treated Si_3N_4 samples
1 - hot-pressed ($T_{oxid.}$ = 1473 K)
2 - same ($T_{oxid.}$ = 1373 K)
3 - p = 3000 MPa, 1573 K ($T_{oxid.}$ = 1373 K)
4 - p = 7000 MPa ($T_{oxid.}$ = 1373 K)
5 - p = 5000 MPa ($T_{oxid.}$ = 1373 K)
6 - p = 3000 MPa ($T_{oxid.}$ = 1473 K)
7 - p = 5000 MPa ($T_{oxid.}$ = 1473 K)
8 - p = 7000 MPa ($T_{oxid.}$ = 1473 K)

The DTA results additionally confirmed that the silicon nitride after high pressure action is inert to the atmosphere up to 1773 K. On the typical oxidation thermogram gor Si_3N_4 (Fig.2) the DTG-TG curves are represented with straight lines. The appearance of a small exothermal peak can be detected on the DTA curve in the 813 - 1103 K range which is related with the formation of the extremely thin β-quartz and α - cristobalite films. The behaviour of the DTA curves shows the absence of mutual transformation of both the first and the second order in silica up to 1593 K and then at 1593-1710 K it shows an endothermal peak which is related with the formation of the fibrous silica confirmed by microscopy and X-ray analysis.

The above studies allow to conclude that high static pressures exercise a considerable influence on the silicon nitride oxidation mechanism. The pecularities observe, however, do not provide exhaustive information on the variation in the fine crystalline silicon nitride structure caused by a high pressure and more in-depth study is necessary here.

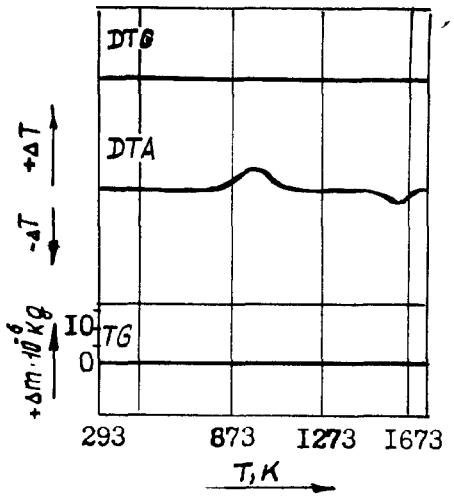

Fig. 2 Oxidation thermogram for Si_3N_4 prepared at 1573 K and 7000 MPa

Table 1 Constants of the parabolic ($kg^2/m^4 \cdot s$) and the logarithmic ($kg/m^2 \cdot s$) rates of oxidation for Si_3N_4

Temperature K	Sample			
	Hot-pressed	3000 MPa	5000 MPa	7000 MPa
	$K_{parabol.}$	K_{log}		
1173	$8.26 \cdot 10^{-11}$	-	-	-
1273	$1.17 \cdot 10^{-9}$	-	-	-
1373	$4.44 \cdot 10^{-9}$	$6.96 \cdot 10^{-4}$	$1.50 \cdot 10^{-4}$	do not oxidize
1473	$3.24 \cdot 10^{-8}$	$1.40 \cdot 10^{-4}$	$1.68 \cdot 10^{-4}$	do not oxidize

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