INITIAL MICROSTRUCTURAL DEVELOPMENT OF SURFACE OXIDIZED LAYER DURING SILICON NITRIDE OXIDATION

Daniel S. Morais and Ana Helena A. Bressiani
Instituto de Pesquisas Energéticas e Nucleares
mmc CP 11049 , Pinheiros , CEP 05422-970 , S. Paulo - SP - Brazil

Silicon nitride-based ceramics have been used in many high temperature applications in oxygen atmosphere [1]. Under these conditions the oxidation kinetic is very fast in the early stages, decreasing as a function of time. Metal oxides, such as Al_2O_3, Y_2O_3 or rare earth oxides, improve densification but turn the silicon nitride-based ceramics less resistent to oxidation than the ones sinterized without additives [2].

This study shows the changes on surface microstructure of a silicon nitride-based ceramic containing alumina and a rare earth concentrate as sintering additives, during oxidation for 16 hours at 1200 °C. XRD (X-ray diffraction), SEM (scanning electron microscopy) and EDS (energy dispersion spectroscopy) were performed in order to identify both phase formation and morphological changes.

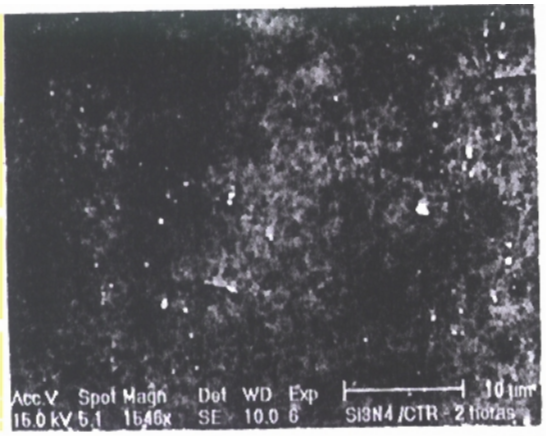
Just two hours after starting the experiment, a SiO_2 layer was grown on the sample surface. Because this layer is very thin Si_3N_4 grains can be seen as dark regions in the background (figure 1). Four hours latter the Si_3N_4 grains remain visible. The cation migration from grain boundary to surface leads to $Y_2Si_2O_7$ precipitation and a small amount of silica cristalizes as α-cristobalite (figure 2). The same cristalized phases are identified after eight hours, in larger amount, as shown in figure 3. The oxide layer is now too thick to see the silicon nitride grains.

$Y_2Si_2O_7$ phase was not identified after 16 hours (figure 4). According to data reported in the literature this phase was dissolved in the glassy matrix to be reprecipited later on another form [3,4]. On the other hand, there is extensive SiO_2 cristalization. An interesting observation is that α-cristobalite does not cristalize near the silica fibers.

The amount of nitrogen bubbles on surface is very small, but the bubble in figure 4 got special attention because it gives some important informations. Firstly, the matrix EDS analisys on bubble surface gives a more precise chemical composition of the oxided layer, because the nitrogen gas debonds and keeps off the oxide scale from silicon nitride substrate. Bubbles seem to be formed before silica cristalization, because there are no cristals on their surfaces. The grain phase near the pore is Al_2O_3, precipitated from the alumino silicate glass matrix, perhaps due to the perturbation during the pore formation. Finally, in silicon nitride ceramics with sintering additives the diffusion barrier model cannot be applyed to kinetics analisys [5], because silica cristalization is not so extense, and large areas remain as glassy phase.

References

[1] N.S. Jacobson ; J. Am. Ceram. Soc. 76 [1] (1993) 3-28
[2] M.H. Lewis, P. Barnard ; J. Mat. Sci. 15 (1980) 443-448
[3] F. Castro, J. Echeberria, M. Fuentes; J. Mat. Sci. Lett. 11 (1992) 101-105
[4] M.J. Pomeroy, R. Ramesh, S. Hampshire; Key Engineering Materials vol 89-91 (1994) 283-288
[5] M. Backhaus-Ricoult, Y.G. Gogotsi; J. Mater. Res. 10 [9] (1995) 2306-2321



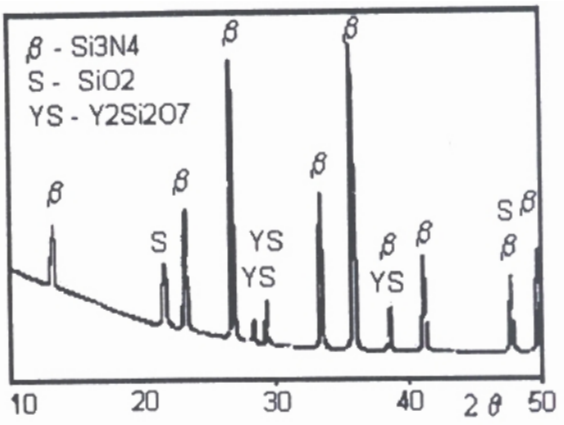
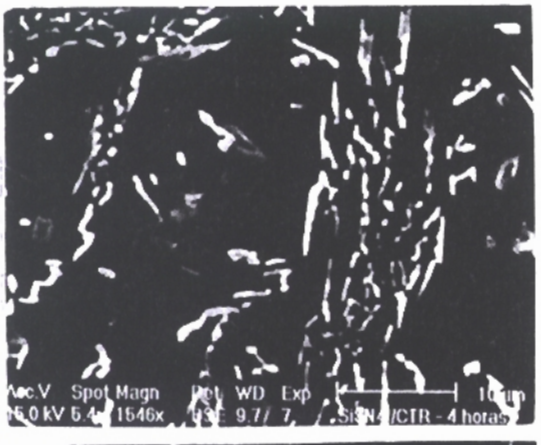


Figure 1



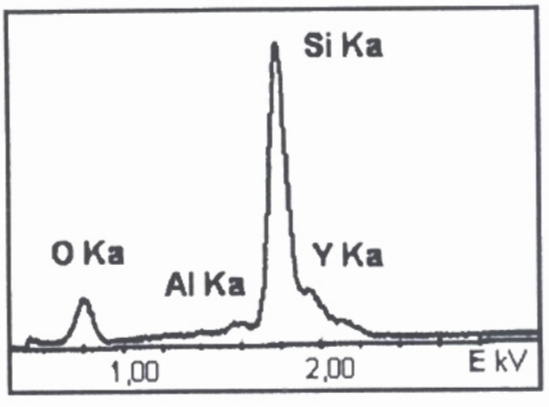


Figure 2

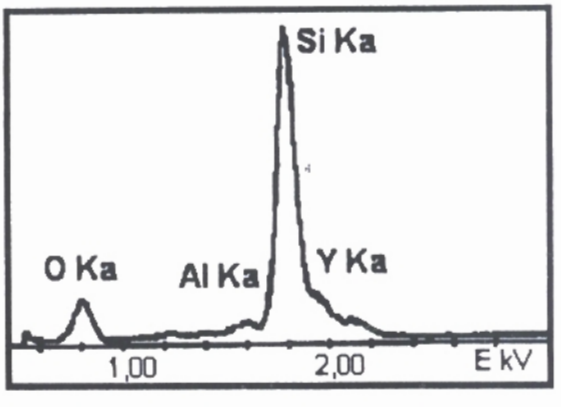
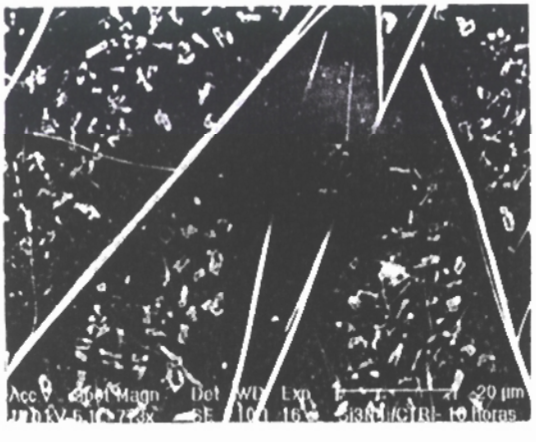


Figure 3



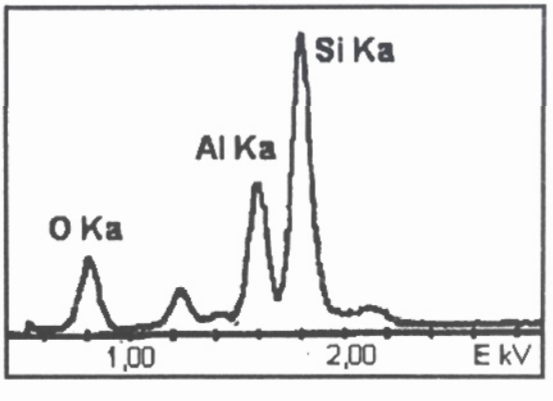


Figure 4.