JOURNAL OF MATERIALS SCIENCE 26 (1991) 3249–3252

Surface oxidation kinetics of Si_3N_4-4%Y_2O_3 powders studied by Bremsstrahlung-excited Auger spectroscopy

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Samples of silicon nitride powder containing 4.0% Y_2O_3 in weight were heated in air at temperatures between 900 and 1000 °C. The average SiO_2 layer thickness on the Si_3N_4 powder particles, as a function of time at a particular temperature, was measured by Bremsstrahlung-excited Auger electron spectroscopy. Oxidation was found to follow a linear rate law with an activation energy of 56 ± 1.5 kcal mol^{-1}. The yttrium level measured by X-ray photoelectron spectroscopy was also found to decrease as a function of the oxide layer thickness. This suggests that there is a reaction between the Si_3N_4 and Y_2O_3 particles which results in the formation of an yttrium-rich phase at the interface between the surface SiO_2 layer and the underlying Si_3N_4 particle.

1. Introduction

Silicon nitride (Si_3N_4) ceramics have found a myriad of applications due to their favourable combination of properties, such as high mechanical strength at high temperature, high fracture toughness, good thermal shock and chemical resistivity, and high wear resistance. However, one significant disadvantage of the Si_3N_4 ceramics is the difficulty in producing fully dense parts from pure powders by a normal sintering process. To obtain fully dense ceramics, Y_2O_3, MgO, Al_2O_3, etc. are used as sintering aids. These additives form a liquid phase at high temperatures and thus promote densification by liquid phase sintering.

In the densification of Si_3N_4 powders containing sintering additives, silicate-related eutectic liquids are formed by using part of the SiO_2 from the surface of the starting powders [1]. It is now recognized that these sintering liquids have M–Si–O–N composition in the sintered silicon nitride ceramic. The selection of metallic ion M, which is added mainly as an oxide, is restricted by its stability in oxynitride liquids via the redox reaction:

$$1/3\,Si_3N_4 + O_2 \rightarrow SiO_2 + 2/3\,N_2$$
$$(\Delta G = -153 \text{ kcal at } 1500\,^{\circ}C)$$

Y_2O_3 is one of the most widely used sintering additives for Si_3N_4 ceramics intended for high temperature applications, mainly due to the high eutectic temperature (~ 1650 °C) of the mixed-oxide liquid (Y_2O_3–SiO_2). In addition, the high valency of Y_2O_3 offers a good compromise between the increasing difficulty of sinterability with higher-valence ions and increased softening temperature of glass (Y_2O_3–SiO_2) in the Si_3N_4 ceramics. Both the quantity and the viscosity of the oxynitride liquid have an influence on the crystallization process and therefore on the resulting microstructure. The microstructure of a Si_3N_4 ceramic has a strong influence on its fracture toughness because of its dependence on morphological anisotropy within the fine-grained polycrystalline structure.

The above discussion clearly shows that composition of the liquid phase formed by the reaction of SiO_2 at the Si_3N_4 surface and Y_2O_3 as a sintering additive has a significant influence on the microstructure and the resulting mechanical properties of the sintered Si_3N_4 ceramics. Reactions and mechanisms leading to the glass formation in the Si_3N_4 ceramics at high temperatures have not received much attention. In particular, kinetic processes leading to the formation of glass phases by the reaction of bulk (Y_2O_3 and Si_3N_4) and surface phases (SiO_2) have not been studied in detail. Therefore, oxidation characteristics of silicon nitride powders, containing Y_2O_3 as sintering additive, provide important information in the design of microstructures for specific applications [2]. Cubicciotti and Lau [3] have examined the oxidation characteristics of hot-pressed Si_3N_4 ceramics. Their data show that there may be a different oxidation mechanism occurring at temperatures below ~ 1400 °C than that at temperatures above 1400 °C [3–5]. At temperatures above ~ 1400 °C, parabolic oxidation has been observed.

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In a recent study, the initial surface oxidation kinetics for SiC whiskers heated in air at temperatures between 600 and 800 °C were studied by X-ray photoelectron spectroscopy (XPS) [6]. The SiO_2 layer thicknesses on these whiskers were determined from the SiC to SiO_2 2*p* intensity ratios. At these low temperatures, the oxidation rate was observed to be linear for the first 10 nm of oxide growth.

In the present study, Bremsstrahlung-excited Auger electron spectroscopy (AES) has been used to investigate the initial oxidation of yttria-containing silicon nitride powders. Samples were heated in air at 900, 950 or 1000 °C. During the initial growth of the oxide, it is expected that the surface chemical reaction will be the dominant rate determining step, and so a linear rate law should apply.

2. Experimental procedure

Silicon nitride powder containing 4 wt % Y_2O_3 was obtained from Norton (Northboro, Massachusetts). Samples were placed in alumina crucibles and heated in air for 0.5, 1.0, 2.0 or 4.0 h at 900, 950 or 1000 °C. A Leco Model 542-27 furnace was used. The temperature accuracy was ± 2 °C. The photoelectron spectrometer was a modified AEI ES-100. The details of the furnace and the spectroscopic analysis are described in a previous study [6].

3. Results and discussion

Fig. 1 shows the overall XPS survey scan of a Si_3N_4–4% Y_2O_3 powder sample heated for 2 h at 1000 °C. The scan ranges from kinetic energy ~ 500 eV to ~ 1700 eV. The photoelectron peaks and X-ray induced Auger electron peaks are labelled. In a previous study of SiC whisker surface oxidation [6], the Si 2*p* XPS signal was used to probe the surface oxide film growth. In the case of Si_3N_4, the binding energy separation between the oxide and nitride silicon 2*p* peaks is less than 1.5 eV [7] and hence in the XPS studies using non-monochromatic Mg X-rays, these peaks will be unresolved. Such spectra are reproduced in Fig. 2 for a sample before and after heating at 1000 °C for 4 h. A shift of only 0.7 eV in the peak binding energy was observed. The silicon KLL Auger peaks from Si_3N_4 and SiO_2, however, have an energy separation of ~ 3.4 eV and are clearly resolved. The silicon KLL Auger transition, being at ~ 1610 eV, will not be excited by the characteristic Magnesium X-rays. Previous studies have shown that higher energy Bremsstrahlung radiation associated with the characteristic radiation can be used to excite Auger transitions that would be otherwise inaccessible [8, 9].

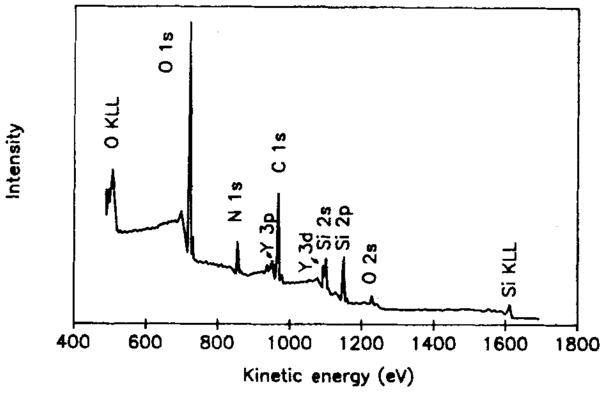

Figure 1 An overall X-ray photoelectron (XPS) spectrum of a Si_3N_4 powder sample containing 4% Y_2O_3.

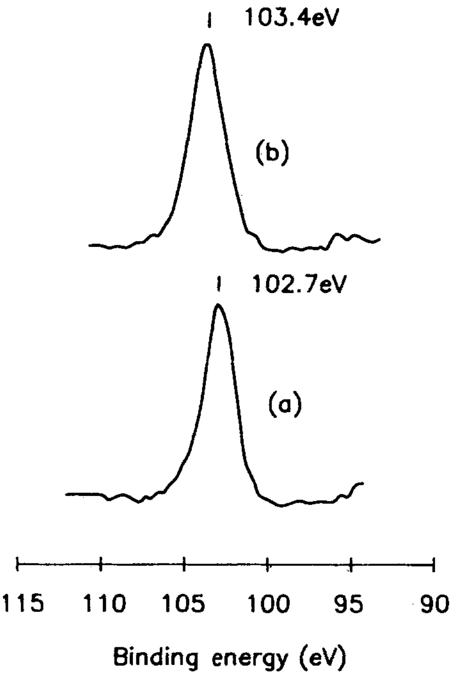

Figure 2 Silicon 2*p* XPS spectra of Si_3N_4–4% Y_2O_3 sample (a) before heating and (b) heated 4 h at 1000 °C.

Fig. 3 shows the silicon KLL Auger spectra for samples of the Si_3N_4–Y_2O_3 powder heated at 1000 °C for 0.5, 1.0, 2.0 and 4.0 h. The spectrum of the unheated powder is also shown. The peak from SiO_2 is at 1608.5 ± 0.3 eV kinetic energy while the peak from Si_3N_4 is at 1611.5 ± 0.2 eV. If R is the silicon KLL ratio of the Si_3N_4 and SiO_2 peaks, then the average oxide layer thickness, t, on the Si_3N_4 particles can be written as:

$$t = -\lambda \ln[R/(R + R^*)] \qquad (1)$$

where λ is the mean free path of the silicon KLL Auger electron and R^* is the ratio of the silicon KLL intensity from a pure (unoxidized) Si_3N_4 sample to that from a completely oxidized sample. Following the method developed in the previous study [6], the value of R^* can be obtained from the ratio of the y- and x-intercepts in a plot of Si_3N_4 against SiO_2 intensities. Fig. 4 shows such a plot for the samples analysed in this study. The intensities given in this plot are the integrated areas (in counts per second) under the SiO_2 and Si_3N_4 component peaks. Data from two of the twelve heated samples were considered as outliers and are not included on this plot. The best least-squares fit to these data gives:

$$I_n = -(1.22 \pm 0.11)I_o + (281.4 \pm 9.8) \qquad (2)$$

where I_n and I_o are the silicon KLL intensities from Si_3N_4 and SiO_2, respectively. From Equation 2, the value of R^* was calculated to be 1.22 ± 0.19. From the work of Powell [10], a value of 3.8 nm was determined for λ. Table I gives the values for the average oxide

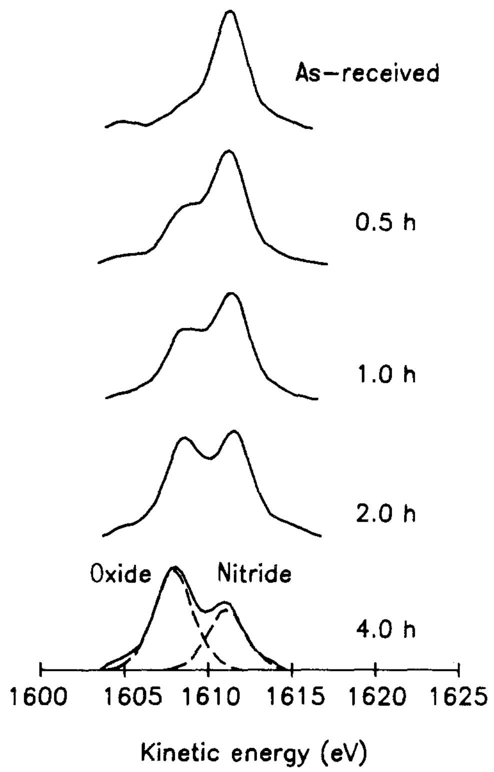

Figure 3 Bremsstrahlung-excited silicon KLL Auger electron spectra of Si_3N_4–4% Y_2O_3 powder samples heated in air for 0, 0.5; 1.0, 2.0, and 4.0 h at 1000 °C.

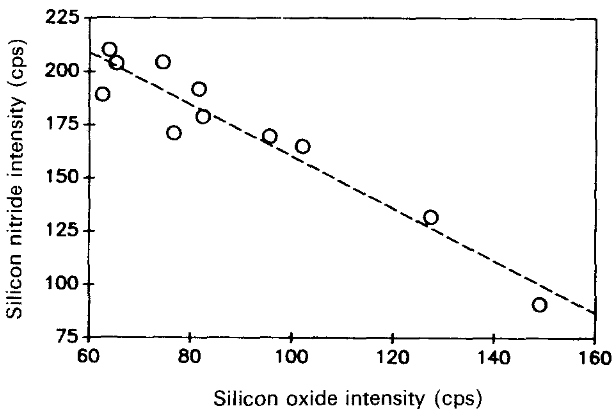

Figure 4 Nitride against oxide silicon KLL Auger intensities for the Si_3N_4–4% Y_2O_3 powders heated at 900 to 1000 °C.

thicknesses, t, on the silicon nitride particles as well as the errors in these thickness measurements, δt, calculated using the method described previously [6]. The average oxide thicknesses are plotted in Fig. 5 as a function of heating time for the three different temperatures. The equations for the lines shown in Fig. 5 are:

$$900\,^{\circ}\mathrm{C}\text{: } t = (0.106 \pm 0.027)h + (1.228 \pm 0.062) \quad (3)$$

$$950\,^{\circ}\mathrm{C}\text{: } t = (0.219 \pm 0.018)h + (1.128 \pm 0.041) \quad (4)$$

$$1000\,^{\circ}\mathrm{C}\text{: } t = (0.707 \pm 0.045)h + (1.401 \pm 0.103) \quad (5)$$

where h is the heating time in hours. The slopes of these lines are the linear rate constants. These are plotted in an Arrhenius plot in Fig. 6. The activation energy determined from this plot is $56 \pm 1.5\,\mathrm{kcal\,mol^{-1}}$.

It was also found that the measured yttrium level decreased as the average silicon surface oxide thickness on the Si_3N_4 particles increased as shown in Fig. 7. In this figure, the two Y 3d peaks at 160.5 and 158.4 eV are due to the spin-orbital splitting of 3/2 and 5/2, respectively. Fig. 8 shows the logarithm of the yttrium-to-silicon ratio plotted as a function of oxide thickness. Linear regression analysis yielded a correlation coefficient of 0.93 if all 13 data points were used and 0.96 if one point rejected. The fact that the logarithm of the normalized yttrium intensity appears to be a linear function of the oxide thickness suggests that there may be an yttrium-containing layer formed at the interface between the surface SiO_2 layer and the underlying Si_3N_4. Electron microprobe analysis has shown that an yttrium-rich layer does form at the SiO_2/Si_3N_4 interface on hot-pressed yttria-doped silicon nitride oxidized at 1460 °C in 150 torr O_2 [3]. At this temperature, the oxide layer formed was quite thick, ~ 15 µm. The yttrium-rich layer was believed to be due to crystals of $Y_2Si_2O_7$. Therefore, it appears that the reaction between surface SiO_2 and bulk phase yttria initiates at a much lower temperature than the normal hot pressing temperature of 1700 to 1850 °C. Availability of abundant oxygen for the glass formation reaction to proceed at low temperatures (900 to 1000 °C in this study) could be one of the factors for the formation of an yttrium-containing layer on the powder.

TABLE I Bremsstrahlung-excited silicon KLL Auger results for Si_3N_4–4% Y_2O_3 powders heated in air

Time (hours)	Temperature (°C)	SiO_2 KLL intensity (cps)	Si_3N_4 KLL intensity (cps)	t(nm)	δt(nm)
0.0	As-received	36.6	179.8	0.84	0.16
0.5	900	65.3	203.4	1.26	0.23
1.0	900	62.7	188.4	1.30	0.22
2.0	900	65.9	162.4	1.53	0.27
4.0	900	90.0	207.2	1.62	0.28
0.6	950	63.9	209.7	1.20	0.22
1.0	950	74.4	203.9	1.40	0.25
2.0	950	81.5	191.7	1.59	0.28
4.0	950	95.5	169.4	1.99	0.32
0.5	1000	76.7	170.7	1.66	0.26
1.0	1000	101.7	164.6	2.13	0.34
2.0	1000	127.7	132.0	2.95	0.38
4.0	1000	148.9	91.0	4.17	0.42

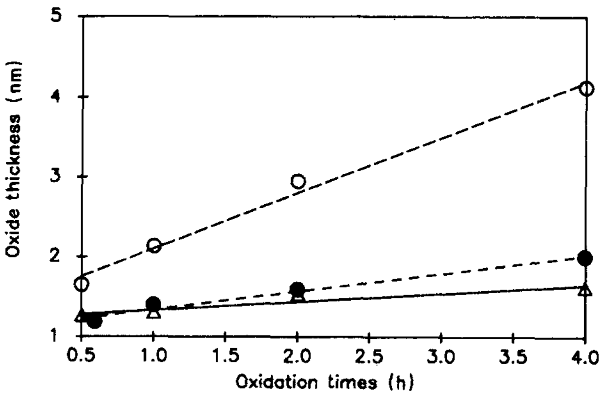

Figure 5 Surface oxide film growth on Si_3N_4–4% Y_2O_3 powders during heating at △, 900; ●, 950 and ○, 1000 °C.

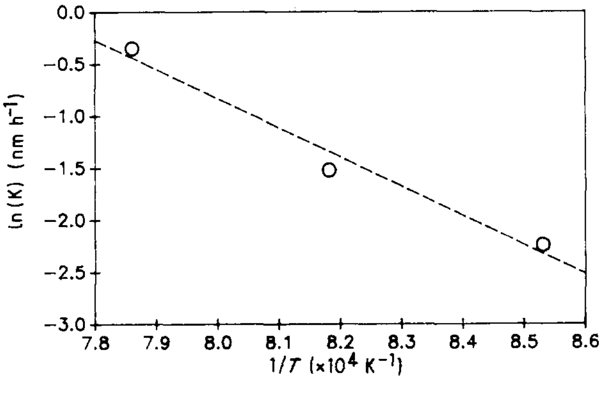

Figure 6 Surface oxidation rate constants against $1/T$ for Si_3N_4–4% Y_2O_3 powders heated in air at 900 to 1000 °C.

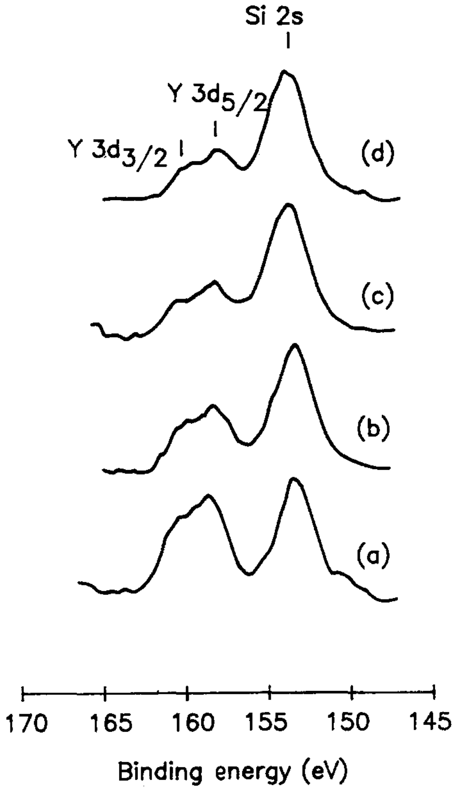

Figure 7 Yttrium 3d and silicon 2s XPS spectra from Si_3N_4–4% Y_2O_3 powder samples (a) unheated, and heated at 1000 °C for (b) 0.5 h, (c) 2 h, (d) 4 h.

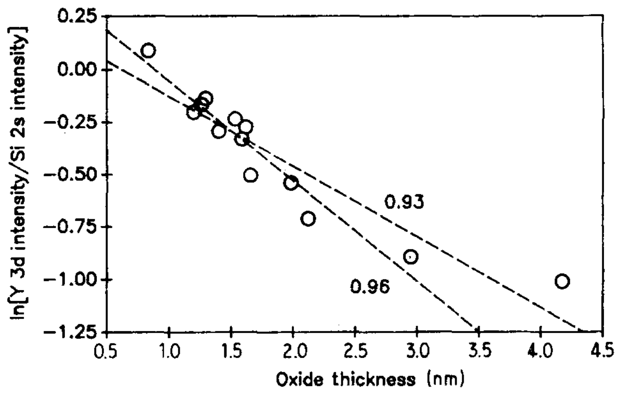

Figure 8 Logarithm of normalized yttrium intensity, ln[I(Y 3d)/I(Si 2s)], against oxide film thickness for Si_3N_4–4% Y_2O_3 powders.

4. Conclusions

Bremsstrahlung-excited Auger electron spectroscopy has been used to measure the average SiO_2 layer thickness on the Si_3N_4 powder containing 4.0 wt % Y_2O_3 heated in air at temperatures between 900 and 1000 °C. Silicon KLL spectra were used to determine the relative amounts of SiO_2 and Si_3N_4 in the near-surface region. The average SiO_2 layer thicknesses were determined from the silicon KLL data using equations derived in a previous study [6]. The oxidation was found to follow a linear rate law at 900, 950 and 1000 °C. An activation energy of 56 ± 1.5 kcal mol^{-1} was measured for this temperature range.

The logarithm of the yttrium intensity in the near-surface region on these powders was found to decrease as a linear function of the oxide thickness. This result suggests that there is a reaction between the Y_2O_3 and Si_3N_4 particles which results in an yttrium-rich layer at the interface between the SiO_2 surface layer and the underlying Si_3N_4 particle.

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Received 30 April
and accepted 14 August 1990