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Effect of grinding on the texture and reactivity of Si_3N_4

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It has been concluded that the preliminary dry grinding of α-Si_3N_4 and β-Si_3N_4 in a planetary ball mill dramatically increases their reactivity towards the corrosion by oxygen and water at high temperature (1480°C). It has been shown that the reactivity of both phases with water vapour is considerably higher than that with oxygen. Moreover, α-Si_3N_4 has a corrosion resistance considerably higher than β-Si_3N_4 in spite of the fact that α-Si_3N_4 ground samples have a smaller crystal size and a higher concentration of microstrains than the ground β-Si_3N_4 samples. The different corrosion resistance of both silicon nitrides has been attributed to the difference in their crystalline structures, what would lead to different oxidation mechanisms. Amorphous silica is the product obtained from the oxidation of α-Si_3N_4 by oxygen or water, while α-cristobalite is the oxidation product obtained from the corrosion of β-Si_3N_4. © *2004 Kluwer Academic Publishers*

1. Introduction

Si_3N_4 is an important material used in many industrial applications because of its high resistance to chemical corrosion, its favorable mechanical strength at high temperatures and its excellent thermal shock resistance [1–3]. However, the potential applications of Si_3N_4 as structural material are limited by the difficulty of get pure and dense materials with high reliability. The sintering of silicon nitride is performed by the rearrangement and solution-reprecipitation processes, both of which are brought about through a liquid phase. The final structure depends on the initial phase of Si_3N_4; the α-Si_3N_4 leads to the formation of whiskers during the sintering, while the β-Si_3N_4 phase produces grain morphology [4, 5]. The difficulty in sintering pure Si_3N_4 originates from the fact that Si_3N_4 contains strong covalent Si—N bonds, which hinder diffusibility. To achieve sufficient densification, the use of additives like Al_2O_3 and Y_2O_3, are required [6–8], but these additives tend to reduce both its mechanical strength and the corrosion resistance of silicon nitride.

The properties of dense Si_3N_4 depend to a large extent on the preparation and processing of the starting powders. Microstructures constituted by whiskers enhance the mechanical properties of this material. The extended use of this material at high temperature into corrosive ambient explains the number of papers devoted to the study of the oxidation behavior of silicon nitride ceramics [9–13]. It has been concluded from these studies that silicon nitride has two types of high temperature oxidation behavior. The first one is a passive oxidation that takes place at high oxygen potentials and is associated with a weight gain because of the formation of a protective layer on the surface that protects the inner silicon nitride from later oxidation and helps to maintain the mechanical properties of the starting material. The second one is an active oxidation resulting in a significant mass loss at low oxygen potentials, which often leads to the degradation of the mechanical properties of silicon nitride. On the other hand, there are not many studies about high-temperature oxidation behavior of silicon nitride powders, and the correlation between the texture of Si_3N_4 powders and their chemical stability is not well established. The sintering can be promoted by increasing the surface and strain energy stored by starting powder. Thus, the reduction of the powder size is an important step in Si_3N_4 preparation and processing. Grinding is very often used for both decreasing particle size and mixing additives in order to promote the densification of silicon nitride [14–20]. The scope of the present work is to analyze the influence of dry grinding on both the texture and the high-temperature reactivity of silicon nitride powders towards the corrosion by oxygen and water.

2. Experimental

Two samples of Si_3N_4, phases α and β, supplied by Aldrich were used. The samples were ground in a planetary ball-mill, Fritsch Pulverisette 7, with a speed of 750 rpm. The mill was equipped with a WC jar (capacity 45 cm^3), containing 2 balls (15 mm in diameter) of the same material. An amount of 3 g of the sample

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TABLE I Textural properties and reactivity of α-Si_3N_4 and β-Si_3N_4 towards the oxygen and water as a function of the grinding time

Sample	Grinding time (h)	D (nm)	$\langle \varepsilon^2 \rangle^{1/2} \cdot 10^{-3}$	S_{BET} (m^2/g)	Oxidation percentage (O_2)	Oxidation percentage (water vapour)
α-Si_3N_4	0	18.3	1.72	11.7	3.8	7
	0.5	20.5	1.67	12.1	7.6	10
	2	14.7	2.01	10.5	11.4	12
	5	12.5	2.18	10.5	11.4	12
β-Si_3N_4	0	296.8	0.42	2.6	9	15.5
	0.5	61.9	1.19	4.1	13.2	18.3
	2	29.1	1.69	4.1	11.4	21.2

was dry-milled (for 0–5 h) under helium atmosphere in order to avoid oxidation.

The powder X-ray diffraction patterns of the samples were obtained with a Philips PW 1710 instrument equipped with a scintillation counter, using Cu K_α radiation and a graphite monochromator. The crystallite size (coherently diffracting domain size) and the microstrains level were simultaneously derived from the analysis of the (201) peak of α-Si_3N_4 and of the (101) peak of β-Si_3N_4, respectively, by means of the variance method [21]. The calculations were carried out with a computer program described by Edwards and Toman [22] and modified by the same authors [23]. This program automatically adjusts the background and corrects the effect of the so-called "satellite group" lines on the low angle of the $K_{\alpha 1}$ line.

TEM examinations were performed using a Hitachi H800 microscope. The samples were first ultrasonically

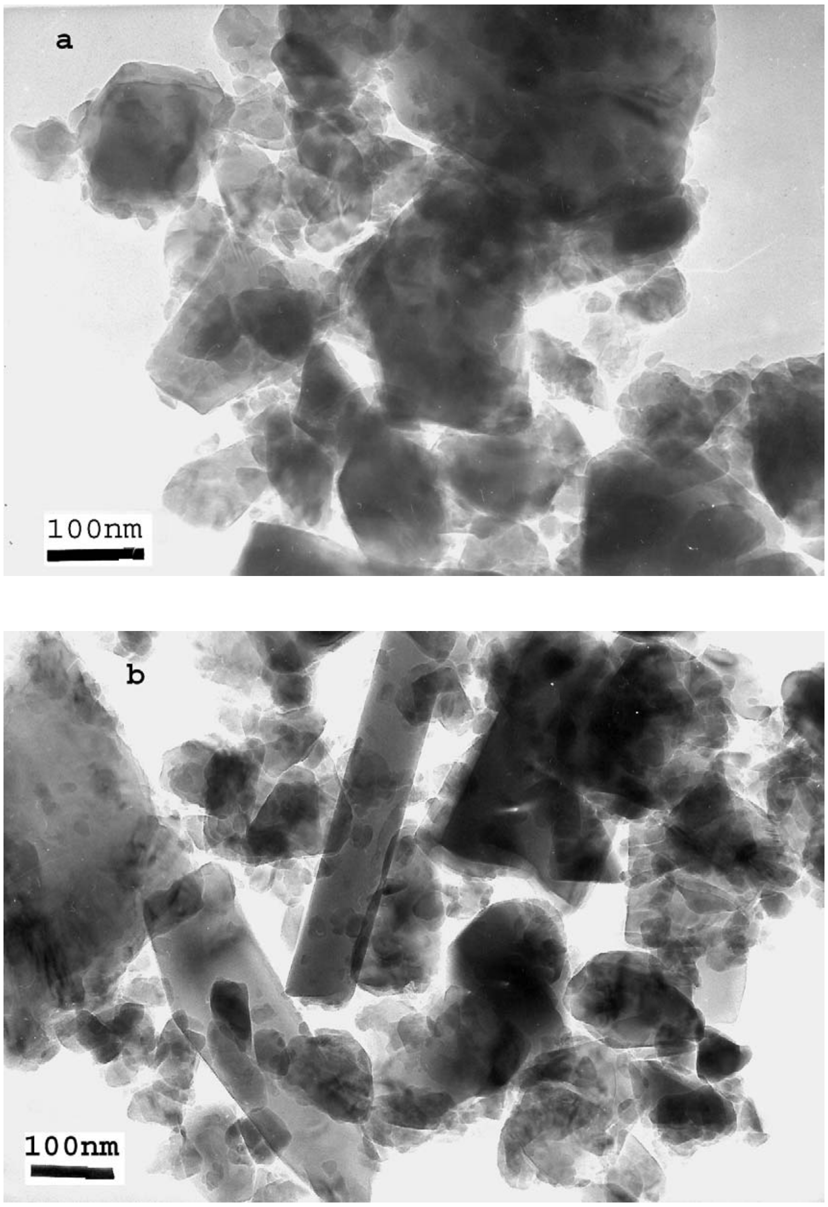

Figure 1 TEM micrographs of silicon nitride powders: α-phase as received (a) and after milling for 30 min (b) and 120 min (c); β-phase as received (d) and after milling for 30 min (e). (*Continued*)

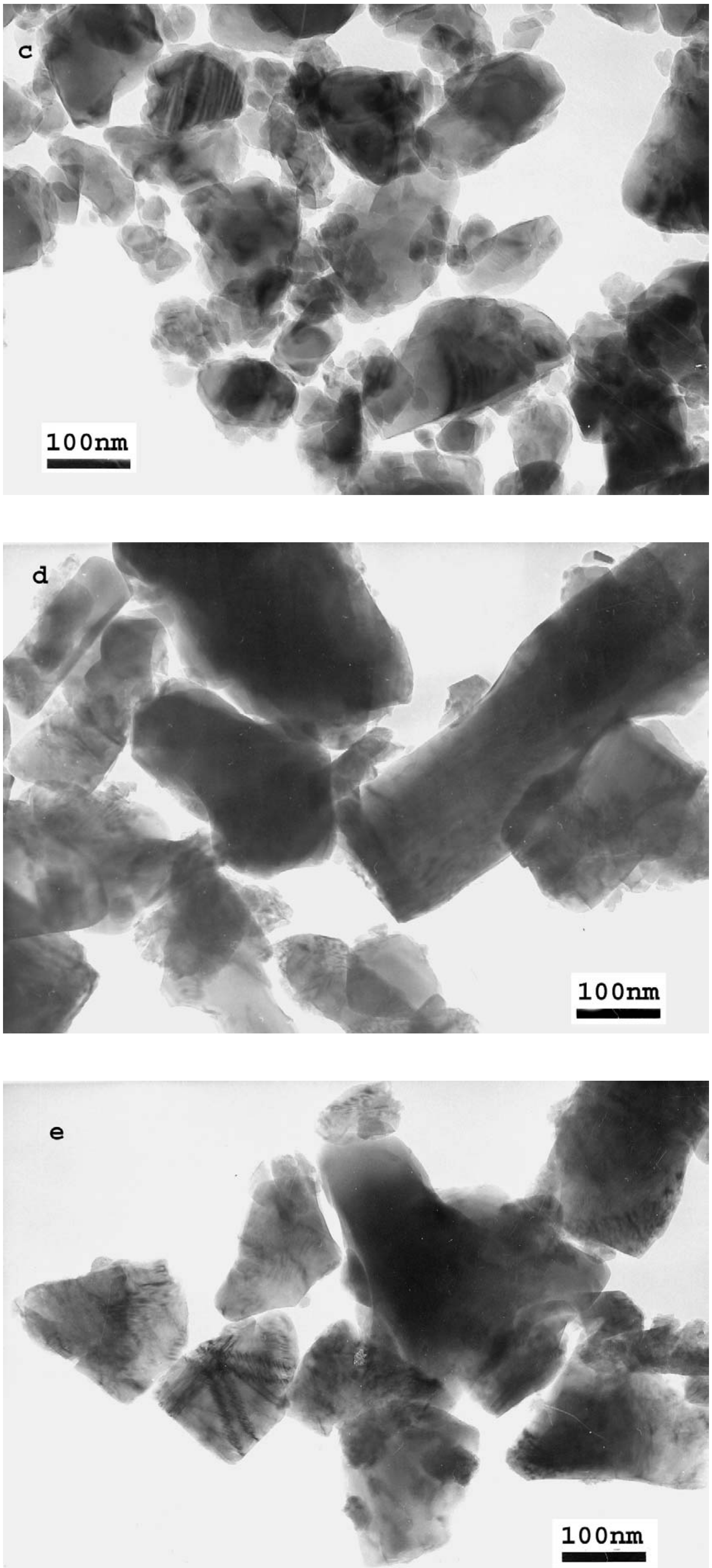

Figure 1 (*Continued.*)

dispersed in ethanol, and a drop of this dispersion was deposited on a thin carbon film supported by copper grid.

Surface area determinations of the samples were carried out using a single point BET method with an Adsorptmeter Micromeritic, model 2200.

X-ray photoelectron spectra were recorded with a Leybold-Heraeus LHS-10 spectrometer working in the $\Delta E =$ cte mode with a pass energy of 50 eV using the Mg K_α radiation.

3. Results and discussion

Two samples of Si_3N_4, α and β phases, were ground for different times in a planetary mill using jar and balls made of WC. Table I shows the values of coherently diffraction domains, D, and the level of the microstrains, $\{\varepsilon^2\}^{1/2}$ for α and β Si_3N_4. It can be seen that the crystallite size of both phases decreases while the level of the microstrains increases upon increasing the milling time. A similar relationship has been previously found for many other ceramic materials [24], and it could be understood by assuming that the particles of the powder samples are formed by small crystallites welded in a mosaic structure and that the corresponding grain boundaries constitute the main contribution to the microstrains. Therefore, the higher the number of grain boundaries in a particle, the lower the size of the crystallites. The data of specific surface area of samples given in Table I suggest that this parameter does not undergo significant changes during grinding. This behaviour would be explained by assuming that the increase of the surface area (expected from the breaking of the particles during grinding) is compensated by the cold-welding promoted by the microstrains generated during the mechanical treatment. It is well known [25] that both small particle sizes and microstrains help the contact between the particles favouring their cold-welding. The results obtained are in a good agreement with those reported by Lönnberg [14] for the grinding of Si_3N_4 in ethanol.

The micrographs of the as received and ground samples (Fig. 1) suggest that the particle size distribution of α-Si_3N_4 and β-Si_3N_4 becomes more homogeneous and that the particle size decreases with increasing the grinding time.

In order to study the effect of grinding on the reactivity of both silicon nitride phases towards the oxidation, two sets of thermal experiments were carried out by heating the samples up to 1480°C at a heating rate of 5 K/min under a flow rate of 30 cm^3/min: the first set was conducted under a flow of a dry mixture of gases with a composition of 21% O_2 and 79% He, and the second one under a flow of helium saturated with water vapour at room temperature. The weight-gains of heated samples under these conditions are shown in Table I. These results show that the reactivity of silicon nitride with oxygen and water vapour increases with increasing the grinding time. It is also clear that α-Si_3N_4 is more resistant to corrosion than β-Si_3N_4. Moreover, these results show that the rate of corrosion by oxygen according to the reaction:

$$Si_3N_4 + 7O_2 \rightarrow 3SiO_2 + 4NO_2$$

is noticeably lower than that by water according to:

$$Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4NH_3.$$

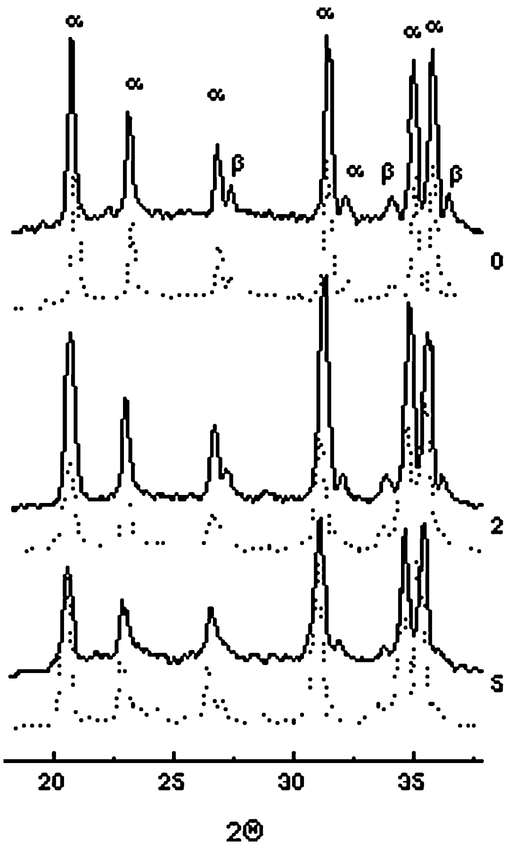

Figure 2 XRD patterns of as received and milled samples of α-silicon nitride after thermal treatment under a flow of He (30 cm^3/min) with 21% O_2 (solid line) and He saturated with water vapour (dotted line).

This behaviour is in a good agreement with data previously reported [10–12]. This shows that the activation energy for the corrosion of silicon nitride by oxygen is higher than that for the corrosion by steam.

Figs 2 and 3 show the XRD patterns of the samples corresponding to the two set of thermal treatments at 1480°C under dry and wet atmosphere. These results point out that the oxidation of β-Si_3N_4 either by oxygen or steam leads to the formation of α-cristobalite while in the case of α-Si_3N_4 no crystalline phase of silicon dioxide was detected by XRD. The results obtained from the X-ray photoelectron spectrum of an

TABLE II Analysis of the XPS spectral data obtained for the α-Si_3N_4 sample ground for 120 min

Sample	Si 2p (eV)	O 1s (eV)	N 1s (eV)
α-Si_3N_4 120 min	102.8	532.4	397.6
α-Si_3N_4 [Refs. 27, 28]	101.9	–	397.7
Si_2N_2O [Ref. 26]	102.1	532.4	298.2
SiO_2 [Ref. 26]:			
Cristobalite	103.1	532.3	
Silica-gel	103.4	532.7	

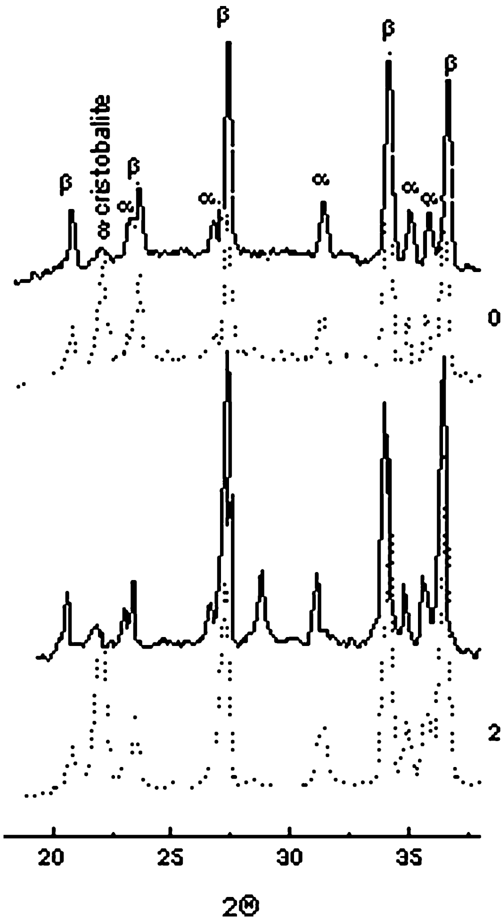

Figure 3 XRD patterns of as received and milled samples of β-silicon nitride after thermal treatment under a flow of He (30 cm^3/min) with 21% O_2 (solid line) and He saturated with water vapour (dotted line).

α-Si_3N_4 sample, ground for 2 h and heated at 1480°C under dry 21% oxygen +79% helium atmosphere, are shown in Table II. The oxygen-silicon energy bonds reported for α-Si_3N_4, SiO_2 and Si_2N_2O [26–28] are also included in Table II for a comparison. It can be deduced from these data that the oxygen bonded at the surface of the α-Si_3N_4 sample can be ascribed to amorphous silica since any other crystalline silica phase has been detected by XRD. These results suggest that the oxidation of α-Si_3N_4 and β-Si_3N_4 takes place through different mechanisms. The different reactivity for as received and ground samples can not be explained by changes in surface area because this parameter remains practically unchanged during the mechanical treatment. Thus, the decrease of the resistance to corrosion by grinding of silicon nitride would be ascribed to the microstrains generated during the mechanical treatment. It is noteworthy to point out that the reactivity of β-Si_3N_4 towards the oxidation is higher than the corresponding reactivity of α-Si_3N_4, in spite that α-Si_3N_4 samples present lower crystal sizes and higher level of microstrains than β-Si_3N_4. This finding suggests that the differences in reactivity between the two phases of silicon nitride must be associated with the different storage capacity for lattice defects of both crystalline structures.

The results obtained allow to conclude that it is more convenient to prepare compacted bodies of α-Si_3N_4 rather than of β-Si_3N_4 for using this material as structural ceramic at high temperature in corrosive surrounding because of the higher reactivity of β-Si_3N_4. It can be concluded that for any technological application of silicon nitride is very important to take into account its textural modification induced by grinding.

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