

Effect of Iron and Silicon Addition on the Densification, Microstructure and Mechanical Properties of Silicon Nitride

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In the present work, the attention was concentrated on the microstructure optimization of normal sintering silicon nitride by the interference with the $\alpha \rightarrow \beta$ Si_3N_4 transformation and grain size distribution of β grains. It was observed that iron has a significant influence on the $\alpha \rightarrow \beta$ Si_3N_4 transformation, allowing the formation of a great number of b-phase nuclei. Under appropriate conditions of temperature and time, more homogeneous microstructure results, in which the grains present a high aspect ratio and a low degree of abnormal grain growth, achieving an *in situ* reinforcement. The refinement of the microstructure was accompanied by an increase of fracture toughness values (K_{IC}) for samples sintered under the best densification conditions.

1. INTRODUCTION

Since there are limitation regarding the reduction of the amount and the use of more refractory sintering aids

in the normal sintering of silicon nitride based ceramics, the present work has a main focus the *morphology and spatial distribution of β Si_3N_4 grains* aiming for the mechanical properties improvement of these nonoxide based ceramics. They could be used up to temperatures around 1150°C, as products like cutting tools and mechanical seals. Examining the literature concerning the direct nitridation of silicon compacts, some authors have suggested that the iron, besides acting as a catalyser of the reaction by the increasing the diffusion rate of silicon, promotes the growth of β -phase by the formation of silicon rich low melting point eutectic - SiFe_x [1-3]. It has been also observed that if high purity silicon is used for the nitridation reaction, there is tendency to form almost exclusively the α -phase [4]. So, the effect of iron and silicon addition on the $\alpha \rightarrow \beta$ Si_3N_4 transformation, morphology and grain size distribution of b phase, as

Table 1
Relative density (% of theoretical density) and fracture toughness K_{IC} (Mpa.m^{1/2})

Si ₃ N ₄ 5% Y ₂ O ₃ -5% Al ₂ O ₃		Without Addition	Iron Silicon				Silicon		
			0.25%	0.5%	1.0%	2.0%	0.25%	0.5%	1.0%
d_t (g/cm ³)		3.270	3.268	3.267	3.263	3.257	3.267	3.263	3.257
1700°C	K_{IC}	4.8	4.7	4.1	4.4	4.1	4.9	4.9	5.1
15 min	% d_t	97.8	97.8	97.3	98.0	97.4	97.5	98.1	98.0
1700°C	K_{IC}	4.8	5.1	4.4	4.7	4.9	4.5	4.7	4.3
30 min	% d_t	97.2	97.0	97.8	98.0	97.9	98.2	98.1	97.6
1700°C	K_{IC}	4.6	5.2	5.3	6.1	5.7	4.6	5.1	5.0
60 min	% d_t	97.2	97.8	97.8	98.4	99.2	97.5	98.0	98.0
1700°C	K_{IC}	4.7	5.2	5.3	5.6	5.5	5.0	5.1	5.0
90 min	% d_t	97.2	98.0	98.8	98.4	99.2	98.8	99.0	98.2

well as on the densification and mechanical properties of normal sintering silicon nitride were investigated.

2. EXPERIMENTAL PROCEDURE

Different amounts of iron, varying from 500 to 4000 ppm, in the form of iron silicon, and high purity silicon varying from 500 to 10000 ppm, were added to silicon nitride powder containing 5 wt% Al₂O₃ and 5 wt% Y₂O₃ (Ube Kousan Co., Grade SN-COA, Fe < 100 ppm, Ca < 50 ppm and α - β Si₃N₄ > 95 wt%). Because of the low degree of sinterability of the as received powder, all the mixtures were milled in attrition mill during 6 h using ethyl alcohol P.A. as a fluid, according to the recommended conditions for suitable increase of surface area and minimal impurities pick [5]. After drying, the mixtures were sieved through 65 mesh screen to eliminate large agglomerates and uniaxially pressed at 60 MPa followed by cold isostatic pressing at 200 MPa. The samples were sintered at 1675°C and 1700°C, with a soaking time varying from 15 to 90 minutes, under 0.2 MPa nitrogen pressure and using a powder bed of 50% BN and 50% as received silicon nitride powder. For each sintering condition, all the compositions tested were evaluated regarding the degree of sinterability, microstructure and fracture toughness (indentation method). The bending strength and Weibull distribution of selected compositions sintered at 1700°C/90 minutes, were also determined.

3. RESULTS AND DISCUSSION

For all compositions heat treated at the different sintering conditions tested, the values of densities range from 97.7% to 99.2% of the theoretical density. These relatively high densities are ascribed to the high surface area of the powder mixtures and the sintering conditions used. As presented in Table 1, the highest values of density were observed for the mixture with 2% of iron silicon sintered at 1700°C/60 and 90 minutes.

Regarding the fracture toughness- K_{IC} , we can notice that: a) at 1700°C/60 and 90 minutes, as showed in table

1 and at 1675°C/90 minutes, all the compositions containing iron silicon present K_{IC} values higher than that verified for the composition without iron silicon, with a more pronounced increase for the mixtures with 1% and 2% SiFe_x. In addition, a maximum in K_{IC} values at 1% SiFe_x was observed; b) the values of K_{IC} for all compositions containing only silicon are close to that observed for the basic composition; and c) at 1700°C/15 minutes, as shown in Table 1, and at 1675°C/30 minutes, all the values of K_{IC} for the compositions containing SiFe_x are smaller than the value of K_{IC} observed for the basic composition, with a tendency to decrease as the amount of iron silicon increases.

Analysing the SEM micrographies of all the mixtures tested at different sintering conditions, it was observed that the average aspect ratio of β -grains increases with the amount of iron silicon added, resulting in a more refined microstructure. Also a high number of grains showing abnormal growth was observed in the composition without SiFe_x and in the mixtures containing only silicon. Figure 1 shows, as an example, the characteristic effects of iron silicon and silicon additions, observed at different degrees in the other samples sintered at different conditions.

The refinement of microstructure observed with the addition of iron silicon may be due to the fact that iron silicon either accelerates the growth of pre-existing β -particles or acts as sites for the heterogeneous nucleation of β -grains. However, it seems most probable that, with the increase of the densities of such nuclei, a greater number of β -grains grow at the same time, leading to a more uniform microstructure, as it can be observed in Figure 1. With the addition of iron silicon the X-ray diffraction analysis at 1500°C/10 minutes showed a relative increase in β -Si₃N₄ diffraction peaks intensities.

The maximum values of K_{IC} observed in Table 1, are due to the occurrence of a steric hindrance caused by a simultaneous growth of a great number of β -grains which were nucleated by the influence of iron silicon [6]. Although more refined microstructures are obtained, the

decreasing of the β -grains average length caused by steric hinderance, decrease the effect of *in situ* reinforcement directed related to the β crystals morphology. On the other hand, the decrease in K_{IC} values observed for the samples sintered at 1700°C/90 minutes may be due to the abnormal growth of β -grains. In spite of the refinement of the microstructure observed for the mixtures sintering at 1675°C/30 minutes and at 1700°C/15 minutes the decrease in K_{IC} values with the addition of iron silicon is due to the fact that, in such conditions, the temperature and time were not sufficient for suitable grain growth in order to allow an *in situ* reinforcement.

The higher values of Weibull parameter m observed in the compositions with 1% and 2% SiFe_x, showed in Table 2, can be ascribed to the better homogeneity of the microstructure caused by the addition of iron silicon.

4. CONCLUSIONS

In normal sintering of silicon nitride, containing yttrium and aluminum oxides as sintering aids, the addition of iron silicon seems to promote a refinement in the microstructure, influencing the $\alpha \rightarrow \beta$ transformation and controlling the growth rate of β -grains. It was observed that iron has a significant influence on the $\alpha \rightarrow \beta$ -Si₃N₄ transformation, allowing the formation of a great number of β -phase nuclei. Under appropriate conditions of temperature and time it results in a more homogeneous microstructure, in which the grains present a high aspect ratio and a low degree of abnormal grain growth, achieving an *in situ*

reinforcement. The refinement of the microstructure was accompanied by an improvement in the mechanical properties, specially, the fracture toughness- K_{IC} — with an increase of more than 30% when compared with no iron containing samples — and the Weibull parameter “ m ”. The experimental results have shown that the formation of an iron silicon rich low melting point eutectic-SiFe_x, where occurs the solution of particles followed by the reprecipitation under β form, is the most probable mechanism to explain the effect of iron on the $\alpha \rightarrow \beta$ transformation.

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Table 2
Bending strength ($\sigma_{0.5}$) and Weibull distribution parameters

Si ₃ N ₄ 5% Y ₂ O ₃ + 5% Al ₂ O ₃	Without Addition	Iron Silicon		Silicon	
		1.0%	2.0%	0.5%	1.0%
No. of samples	27	24	26	22	22
$\sigma_{0.5}$ (MPa)	714	674	768	629	610
m	4.5	8.5	7.8	5.5	6.7
R	0.97	0.99	0.99	0.97	0.94

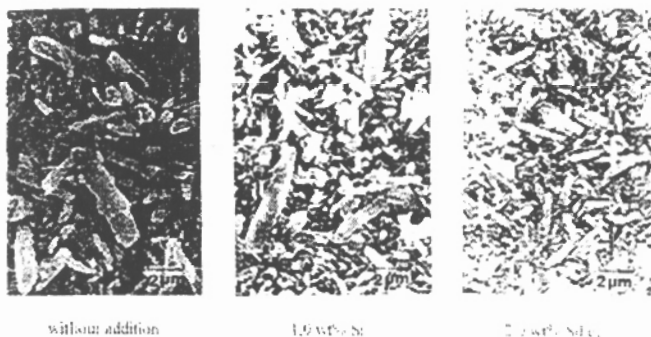


Figure 1. Microstructure of samples sintered at 1700°C/60 minutes.