

Effect of iron and silicon addition on the densification, microstructure and mechanical properties of silicon nitride

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Abstract

In this work, attention was concentrated on the microstructure optimization of normal sintering of silicon nitride by interference on the $\alpha \rightarrow \beta$ -Si₃N₄ transformation and the morphology and spatial distribution of β -Si₃N₄ grains, aiming for improvement of the mechanical properties in these non-oxide based ceramics. 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, a more homogeneous microstructure results, in which the grains have a high aspect ratio and exhibit 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.

Keywords: Iron addition; Silicon addition; Mechanical properties; Silicon nitride

1. Introduction

Since there are limitations regarding the reduction in amount and use of more refractory sintering aids in the normal sintering of silicon nitride based ceramics, recrystallization of the vitreous phase by heat treatment [1,2] and the “design” of microstructure, particularly by controlling grain growth of the β -Si₃N₄ phase, thus achieving an “in situ reinforcement”, have been important issues of research.

Recent works [3–5] report the obtainment of “in situ” composites either by growing β -Si₃N₄ within a matrix composed of equiaxed grains of α -sialons during normal sintering or by the use of gas pressure sintering process. Most recently, it has been shown that it is possible to achieve “in situ reinforcement” by adding β -particles in powders with small amounts of β -grains, until a certain limit, because powders with higher initial β -nuclei densities exhibit coarser microstructures with additional β -particles [6]. Also, the growth rate of β -grains should be controlled to avoid steric hindrance [6].

Some authors have suggested that iron, besides acting as a catalyser of the direct nitridation of silicon compacts by increasing the diffusion rate of silicon, promotes the growth of β -phase by the formation of silicon rich low melting point eutectic -SiFe_x [7–9]. It has also been observed that if high purity silicon is used for the nitridation reaction, there is a tendency to form almost exclusively the α -phase [10]. So, the effect of iron and silicon addition on the $\alpha \rightarrow \beta$ -Si₃N₄ transformation, morphology and grain size distribution of β -phase, as well as on the densification and mechanical properties of normal sintering silicon nitride, were investigated in this work. To ensure that the composition with iron silicon could be used up to temperatures around 1150 °C on products like cutting tools and mechanical seals, dilatometric tests and oxidation curves at 1200 °C were also performed.

2. Experimental procedure

Different amounts of iron, varying from 500 to 4000 ppm, in the form of iron silicon, and high purity silicon,

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%
dt(g cm ⁻³)		3.270	3.268	3.267	3.263	3.257	3.267	3.263	3.257
1675 °C	K_{IC}	4.7	4.6	4.6	4.2	4.3	4.4	4.9	4.9
30 min	% d_t	97.8	97.9	98.3	97.5	98.3	97.0	98.4	97.7
1675 °C	K_{IC}	4.8	4.7	4.8	4.6	5.2	4.8	4.6	4.7
60 min	% d_t	97.8	97.9	97.5	98.1	98.7	97.1	97.9	98.4
1675 °C	K_{IC}	4.7	4.8	5.0	5.7	4.9	4.2	4.8	4.9
90 min	% d_t	98.1	97.8	97.8	97.3	98.2	98.2	97.5	98.4
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

varying from 500 to 10 000 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 -Si₃N₄ > 95 wt.%). Because of the low degree of sinterability of the as-received powder, all mixtures were milled in an attrition mill for 6 h using ethyl alcohol P.A. as a fluid, according to the recommended conditions for a suitable increase of surface area and minimal impurities pickup [11]. After drying, the mixtures were sieved through a 65 mesh screen to eliminate large agglomerates and, then, uniaxially pressed at 60 MPa, followed by cold isostatic pressing at 200 MPa. Samples were heated using a constant heat rate of 25 °C min⁻¹ and sintered at 1675 and 1700 °C, in a graphite element furnace under 0.2 MPa nitrogen pressure and using a powder bed of 50% BN and 50% as-received silicon nitride powder. The soaking time was varied from 15 to 90 min.

For each sintering condition, all compositions were evaluated for the degree of sintering by Archimedes method. Vickers indentations were made at 98 N load on the polished surfaces. Fracture toughness values were calculated from the results of seven crack length measurements using the Anstis, Chantikul, Lawn and Marshall equation [12], corrected with respect to porosity. The polished surfaces were overetched in molten NaOH for microstructural observation in the scanning electron microscope. Additionally, different series of samples were heat treated in the range 1500 to 1650 °C, then, the evolution of the $\alpha \rightarrow \beta$ transition was determined by X-ray diffraction analysis. The bending strength and Weibull distribution at room temperature and the oxidation behavior at 1200 °C of selected compositions sintered at 1700 °C 90 min⁻¹, were also determined.

3. Results and discussion

For all compositions heat treated at the different sintering conditions, the values of densities range from 97.0% 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% iron silicon sintered at 1700 °C for 60 and 90 min.

Regarding the values of fracture toughness K_{IC} presented in Table 1, we can notice: (a) at 1700 °C, 60 and 90 min and at 1675 °C, 90 min, all compositions containing iron silicon gave 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 was observed at 1% SiFe_x; (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 min and at 1675 °C 30 min, 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 images of all mixtures tested at different conditions, it was observed that the average aspect 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. Fig. 1 shows, as an example, the characteristic effects of iron silicon and silicon additions, observed at different degrees in other samples sintered at different conditions [13]. The refinement of microstructure observed with

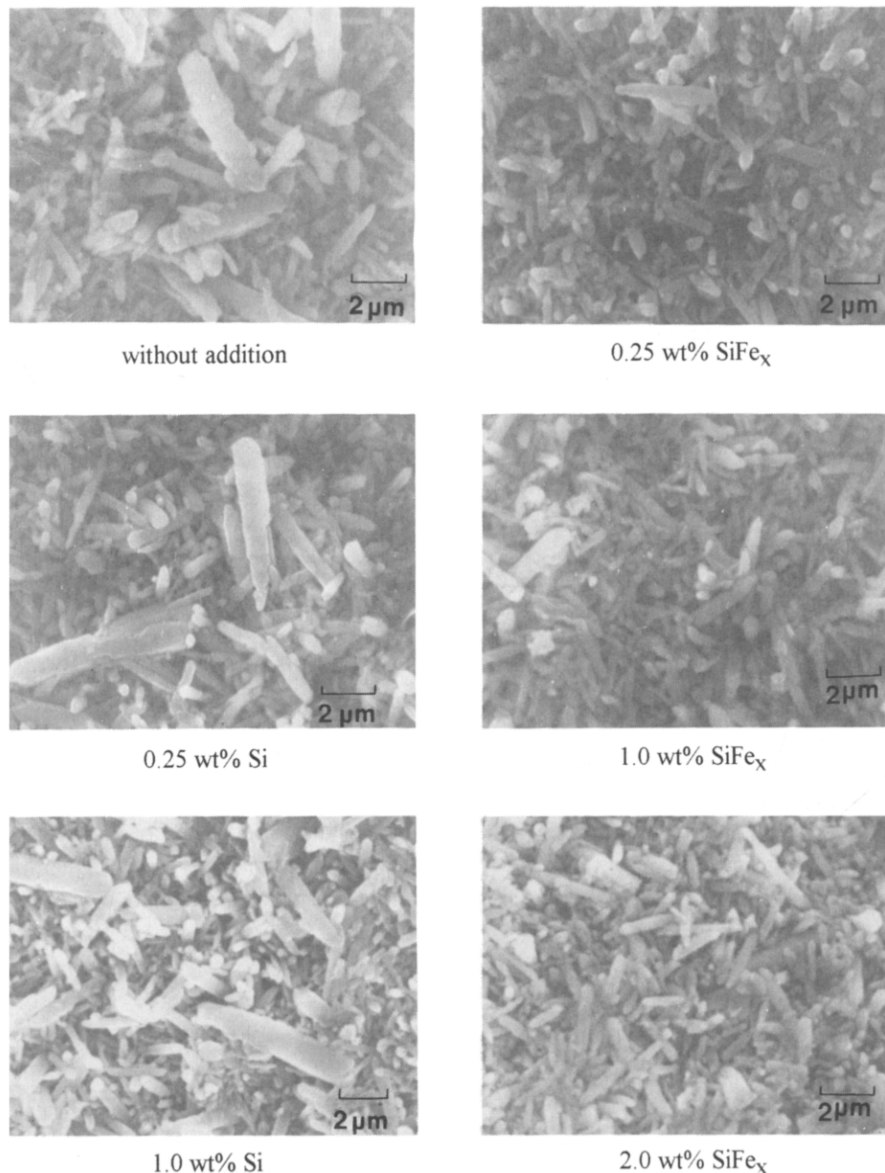


Fig. 1. Microstructure of samples sintered at 1700 °C 60 min⁻¹.

the addition of iron silicon may be owing to the fact that it accelerates the growth of pre-existing β -particles and acts as sites for heterogeneous nucleation of β -grains. However, it seems most probable that, with increase of such nuclei densities, a greater number of β -grains grow at the same time, leading to a more uniform microstructure, as observed in Fig. 1. Also, a relative increase in β - Si_3N_4 X-ray diffraction peaks intensities was observed with the addition of iron silicon in samples heat treated at 1500 °C 10 min [13].

The gradual increase in density of β -grains with increase of iron silicon amount, and the X-ray diffraction results [13], show that iron silicon has a significant effect on the $\alpha \rightarrow \beta$ -transformation, leading to the occurrence of heterogeneous nucleation of the β -phase. According to Petzow and Hoffman [6], neither a homogeneous nor a heterogeneous nucleation of β - Si_3N_4 has a significant influence on microstructural development;

only pre-existing β -particles of the starting powder seem to grow. In our opinion, the different grain densities observed in samples with iron silicon as compared to those without it, indicates that heterogeneous nucleation of the β -phase caused by SiFe_x plays, also, an important role in microstructural development.

Comparing data from Table 1 with the microstructures of the respective compositions, a direct correlation is observed between fracture toughness values and the size and morphology of β -grains. In fact, at 1675 °C 90 min, and at 1700 °C 60 and 90 min—conditions that favour high densities— K_{IC} increases as the microstructure becomes more refined and uniform with an increase of SiFe_x content. In such conditions, the combination of sintering time and temperature was appropriate for the necessary grain growth to improve K_{IC} values.

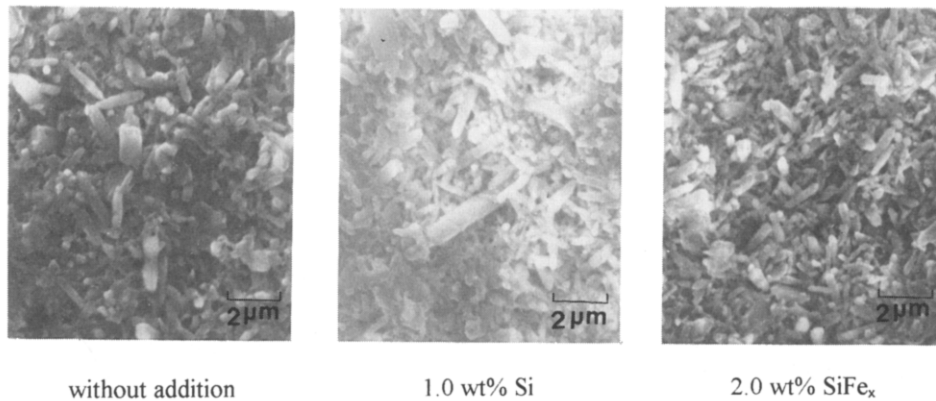


Fig. 2. Microstructure of samples sintered at 1700 °C 15 min⁻¹.

The maximum values of K_{IC} observed in Table 1 are owing to the occurrence of a steric hindrance effect caused by simultaneous growth of a great number of β -grains that were nucleated by the influence of the iron silicon addition [13]. Although more refined microstructures are obtained, a decrease in average length of the β -grains caused by steric hindrance decreases the effect of in situ reinforcement in a manner directly related to the β crystal morphology.

In spite of the refinement of microstructure observed for the mixtures sintered at 1675 °C 30 min⁻¹ and 1700 °C 15 min⁻¹, the decrease in K_{IC} values with the addition of iron silicon is owing 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. An example can be seen in Fig. 2.

For the same amount of SiFe_x addition, an increase in sintering time causes a gradual increase in K_{IC} values, which is associated with the progressive growth of β -grains. However, the decrease in K_{IC} values observed for the samples sintered at 1700 °C 90 min⁻¹, may be owing to the abnormal growth of β -grains.

As shown in Table 1, all compositions sintered at 1675 °C min⁻¹ and 1700 °C 15 min⁻¹ have densities greater than 97% of the theoretical density, presenting microstructures with small grain sizes, as shown in Fig. 2. This fact is in accordance with results presented by Herrmann et al. [14], where it was verified that grain growth occurs at the final stage of liquid phase sintering, just after conclusion of the $\alpha \rightarrow \beta$ transformation.

The values of three points bending strength ($\sigma_{0.5}$), the Weibull parameter m and the correlation coefficient R of Weibull distribution of samples sintered at 1700 °C 90 min⁻¹ are given in Table 2. The bending strength values for all compositions tested are in the expected range for normal sintering silicon nitride. 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 better homogeneity of the microstructure caused by the addition of iron silicon.

The weight gain of the basic composition and the mixtures containing 0.5% silicon and 1.0% and 2.0% iron silicon sintered at 1700 °C 90 min⁻¹ [13], during oxidation treatment at 1200 °C for 500 h, gave parabolic kinetics, which is a typical behavior of high density silicon nitride based ceramics. It should be pointed out that the composition containing 1.0% SiFe_x gave a weight gain of only 0.275 g cm⁻² after 400 h at 1200 °C. This result can be considered highly satisfactory when compared with curves observed for β -Sialon ceramics (Si_{6-x}Al_xO_xN_{8-x}, $x = 0.4$ and 1.5) + YAG-(3Y₂O₃ + 5Al₂O₃) [15,16], which are known to have good oxidation resistance at 1200 °C.

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, a 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.

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	
		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

The reinforcement of 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 iron-free samples, and the Weibull's parameter m . The experimental results have shown that the formation of an iron silicon rich low melting point eutectic-SiFe_x, giving solution of α particles and reprecipitation of β , is the most probable mechanism to explain the effect of iron on the $\alpha \rightarrow \beta$ transformation.

The addition of iron silicon has been shown to be a simple way to affect the "microstructural design" of silicon nitride based ceramics, where the morphology of β -grains is responsible for the mechanical properties, in particular, for the relatively high fracture toughness of these ceramics. Nevertheless, for each basic composition and sintering process, optimization of the iron silicon amount to be added, as well as the appropriate sintering conditions, have to be determined.

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