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EFFECT OF IRON SILICON ADDITION IN THE SINTERING BEHAVIOR OF SILICON NITRIDE

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ABSTRACT

Different percentages of iron silicon were added to silicon nitride powder containing a fixed amount of sintering aids. The mixtures were pressed at 60MPa and sintered at 1675°C and 1700°C in a graphite furnace under 0.2MPa nitrogen pressure. For each sintering condition, all the compositions tested were evaluated with respect to the degree of sinterability, microstructure and fracture toughness. It was observed that, as the amount of iron silicon increases, the average lenght and thickness of β-grains seem to decrease. All samples with iron silicon also presented a greater value of fracture toughness (K_{IC}) when compared with no iron silicon containing samples.

I. INTRODUCTION

Considerable research efforts have been made during the last years to improve the properties of silicon nitride based ceramics, which are among the most promising materials for structural applications [1-3]. Some ways have been studied to improve the reability and mechanical properties of these materials, particulary, the fracture toughness. In general, these searches aim at the optimization of the ceramic processing steps, with emphasis on the use of powders with controlled purity and granulometry and the reduction of sintering aids combined with the use of high pressures during sintering [4,5]. The recrystalization of vitreous phase by heat treatment, the reinforcement by fibers and wiskers [6,7] and, finally, the "design" of microstructure, particulary by controlling the grain growth of β-Si_3N_4 phase achieving an "in situ reinforcement", have been also important issues of research.

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Recent works [8-10] report the obtention of "in situ" composites during normal sintering either by growing the β-Si_3N_4 in a matrix composed by equiaxial grains of α-sialons or using the gas pressure sintering process. More recently it has been shown that it is possible to achieve an "in situ reinforcement" by adding additional 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 [11]. Also, the growth rate of β-grains should be controlled to avoid steric hindrance [11]. By the other side, 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 increase of the diffusion rate of silicon, promotes the growth of β-phase by the formation of silicon rich low melting point euthetic -$SiFe_x$ [5,12-14]. It has been also observed that if high purity silicon are used for the nitridation reaction, there is a tendency to form almost exclusively the α-phase [15].

Considering that the determinant factors to achieve in situ reinforcement are ascribed to the obtention of β-grains with high aspect ratio and low degree of abnormal grain growth and, taking into account that in the sintering of silicon nitride based materials the iron silicon liquid phase formed at low temperature could influence the course densification and the α-β transformation, compositions containing iron silicon were tested in this study. The amount of iron silicon added was varied in order to have different concentration of sites of heterogeneous nucleation of β-phase.

II. EXPERIMENTAL PROCEDURE

High purity silicon nitride powder already containing 5 wt% Al_2O_3 and 5 wt% Y_2O_3 (Ube Kousan Co., Grade SN-COA, Fe < 100 ppm, Ca < 50 ppm and α-Si_3N_4 > 95 wt%) and iron silicon (CSN- 20 wt% of Fe) were used. Five compositions were prepared : 0; 0.25; 0.50; 1.00 and 2.00 wt% of iron silicon. 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 pickup [16]. The mixtures were dried and hand mixed with agata mortar and pestle. The powders were then sieved through 65 mesh screen to eliminate large agglomerates.

The powder compositions were compacted at 60 MPa into 15 cm by 15 cm pastilles using a two-way action hard steel die. The densities of the compacts were about 1.60 g/cm^3. The samples were placed in a BN coated graphite crucible with a powder bed of 50% BN and 50% as-received silicon nitride powder. Sintering were done in a graphite element furnace using a constant heat rate of 25°C/min. A flowing high purity nitrogen gas was used. Over 1300°C, the furnace chamber was pressurized with 2.0 atm of N_2 to decrease dissociation of Si_3N_4. Sintering conditions were the following: I - 1675°C, 60 min; II - 1700 °C, 30 min; III - 1700°C, 60 min. Temperature was contolled by a C-C/B thermocouple.

The samples density were determined by the Archimedes method. After cutting with a diamond disc of 0.3 mm, the specimens were polished down from 15 to 2.5 µm using diamond pastes. Vickers identation were done on the polished surfaces under98 N. The fracture toughness values were calculated from the results of seven crack lenght measurements using the Lawn, Evans and Marshall equation [17] - corrected with respect to the porosity [18]. The polished surfaces were overetched in molten NaOH for microstructural observation in scanning electron microscope. Additionaly, different series of samples were heat treated in the range 1500^{o}C to 1650^{o}C for determination the α and β transition by X-ray diffraction analysis.

III. RESULTS AND DISCUSSION

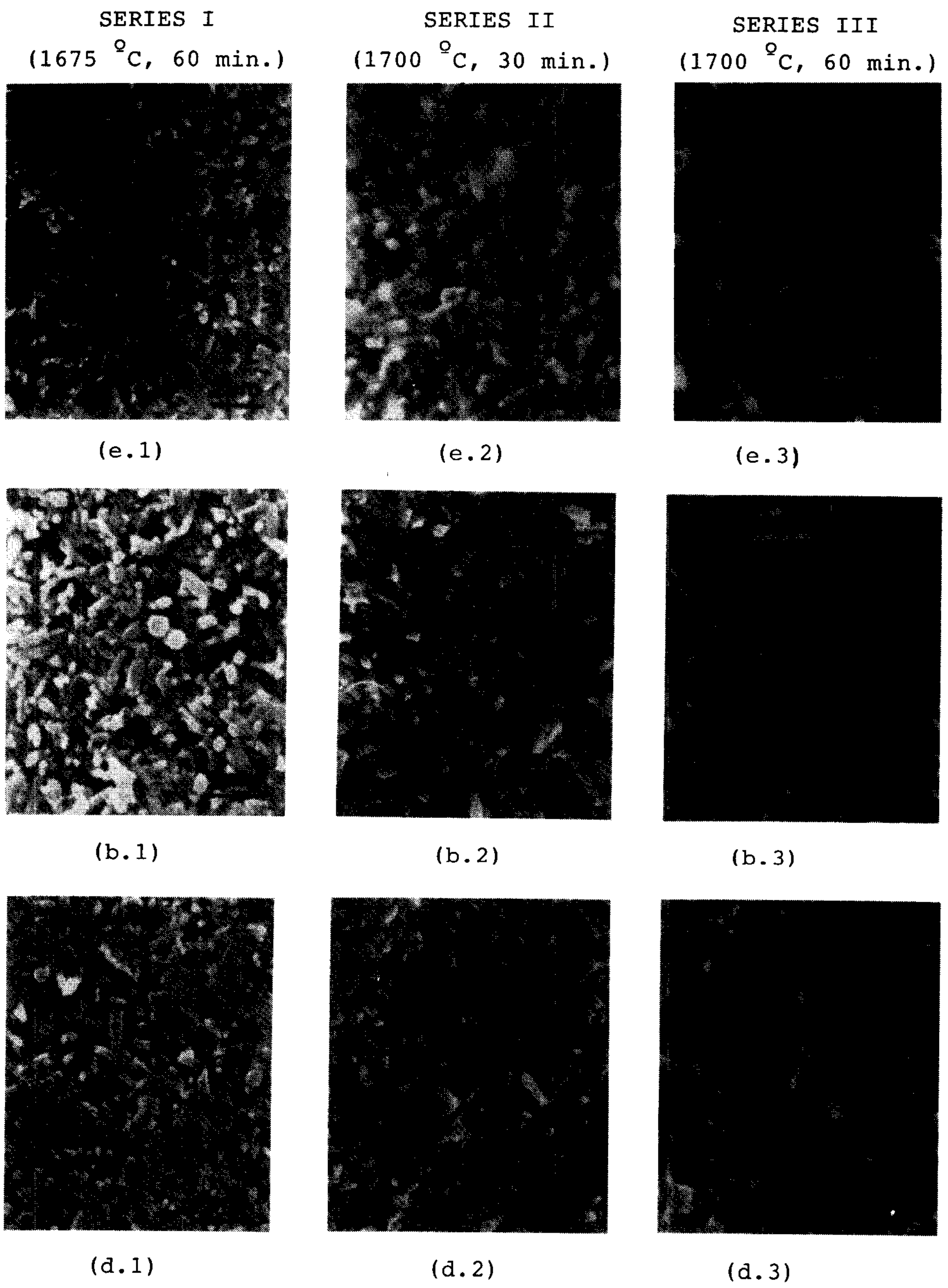
For all compositions heat treated at the different sintering conditions tested (I - 1675^{o}C, 60 min; II - 1700^{o}C, 30 min; and III - 1700^{o}C, 60 min.), the values of densities range between 99,4 % to 99.8% theoretical density . This relatively high densities are ascribed to the high surface area of the powder mixtures and the sintering conditions used. The X-ray diffraction analysis at 1500^{o}C - 10min showed a relative increase in the intersities of β- Si_3N_4 diffraction peaks, with the addition of iron silicon.

The effect of iron silicon additions on the microstructural evolution for the sintering conditions tested, is showed in the Figure 1. In each series, as the amount of iron silicon increases, the average lenght and thickness of β-grains seem to decrease. Also, it can be observed in the three series, a greater number of grains showing abnormal growth in the samples without iron silicon. On the hand of SEM observations, it also sems that the average aspect ratio of β- grains increases with the increasing in the amount of iron silicon added. The Table 1 shows an increase in the values of fracture toughness in all samples containing iron silicon additions, when compared to those without addition.

Table 1. Fracture Toughness (K_{IC}) of Materials with Different Amount of Iron Silicon.

	Fracture Toughness (MPa.m$^{1/2}$)				
SiFe (wt%)	0 (E)	0.25 (A)	0.50 (B)	1.00 (C)	2.00 (D)
I-1675^{o}C 60min	5.2	5.7	7.2	6.1	6.8
II-1700^{o}C 30min	5.7	5.9	5.9	6.2	7.2
III-1700^{o}C 60min	5.8	5.9	6.4	6.7	6.6

Comparing the data of Table 1 and the microstructures shown in the Figure 1, it can be observed that there is a tendency of increase the K_{IC} values with the refinement of the microstructure caused by the addition of iron silicon. It may be due to the fact that iron silicon either accelerates the growth o preexisting β-particles or acts as sites of heterogeneous nucleation of β-grains. However, it seems to be most probably that, with the increase of the densities of such nuclei, a greater number of β-grains growth at the same time given a more uniform microstructure, as it can be observed from the Figure 1.



SERIES I (1675 °C, 60 min.)

SERIES II (1700 °C, 30 min.)

SERIES III (1700 °C, 60 min.)

(e.1) (e.2) (e.3)

(b.1) (b.2) (b.3)

(d.1) (d.2) (d.3)

Figure 1. Overetched Surfaces of materials (Si_3N_4+5 wt% Y_2O_3+5wt Al_2O_3) :
(e.1), (e.2) and (e.3)-without addition of iron silicon;
(b.1), (b.2) and (b.3)-with addition of 0.5 wt% of iron silicon;
(d.1), (d.2) and (d.3)-with addition of 2.0 wt% of iron silicon.

IV. CONCLUSIONS

In normal sintering of silicon nitride containing ytrium and alumina oxides as sintering aids, the addition of iron silicon seems to promote a refinement in the microstructure, exercing an influence in the α - β transformation and controlling the growth rate of β-grains. It was also observed an increase in fracture toughness with the addition of iron silicon.. Further studies, including statistical image analysis of the size of β-grains , must be done to clarify the mechanisms involved.

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