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Research Article

Effect of SiC on the Properties of Pressureless and Spark Plasma Sintered Si_3N_4 Composites

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Abstract

Si_3N_4-SiC composites were prepared by adding SiC particles to the matrix in different weight ratios.The samples were sintered with two different methods. The samples were produced by pressureless sintering and spark plasma sintering method. In the first method, cold isostatic pressing method was used to press the composites. The samples were pressureless sintered at 1850 ^{0}C for 1 hour under the nitrogen atmosphere. In the second method, the samples were spark plasma sintered at 1650 ^{0}C under nitrogen atmosphere under 40 MPa for 5 minutes. AlN and Y_2O_3 were also added to Si_3N_4-SiC composite mixture to aid sintering. Addition of SiC particles to the Si_3N_4 matrix play critical role in controlling of densificication and microstructure properties of the sintered samples. The effect of composition and microstructure on properties of sintered samples was analyzed.

Keywords: Silicon nitride, silicon carbide, composite, microstructure

Basınçsız ve Spark Plazma Sinterlenmiş Si_3N_4 Kompozitlerin Özelliklerine SiC'ün Etkisi

Öz

SiC partikülleri matriks içine farklı ağırlık oranlarında katılarak Si_3N_4-SiC kompozit hazırlanmıştır. Numuneler iki farklı yöntem ile sinterlenmiştir. Numunelere basınçsıs sinterleme ve spark plazma sinterleme yöntemleri uygulanmıştır. Birinci yöntemde, kompozitleri preslemede soğuk izostatik metodu kullanılmıştır. Numuneler 1850 ^{0}C'de azot atmosferi altında 1 saat basınçsız olarak sinterlenmiştir. İkinci yöntemde, numuneler azot atmosferi altında 1650 ^{0}C'de 5 dakika spark plazma ile sinterlenmiştir. AlN and Y_2O_3 sinterlemeye yardımcı olması için katılmıştır. SiC partiküllerinin Si_3N_4 matrisine eklenmesi, sinterlenmiş numunelerin yoğunluk ve mikroyapı özelliklerinin kontrol edilmesinde kritik rol oynar. Bileşim ve mikroyapının, sinterlenmiş numunelerin özelliklerine etkisi analiz edilmiştir.

Anahtar Kelimeler: Silisyum Nitrür, silisyum karbür, kompozit, mikroyapı

1. Introduction

Composite ceramics have better mechanical properties than monolithic ceramics. Si_3N_4/SiC ceramics could be used in applications up to 1500 ^{0}C temperature, such as turbine and automobile engine component, also in energy applications because of its

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many good properties such as low thermal conductivity, thermal shock resistance, chemical stability and oxidation resistance (Ting et al.,2012; Jun et al.,2013; Jyothi et al.,2014; Hededusova et al.,2009; Yusen et al.,2018; Ravindra et al., 2015; Baloj et al.,2007; Jianfeng et al.,2007).

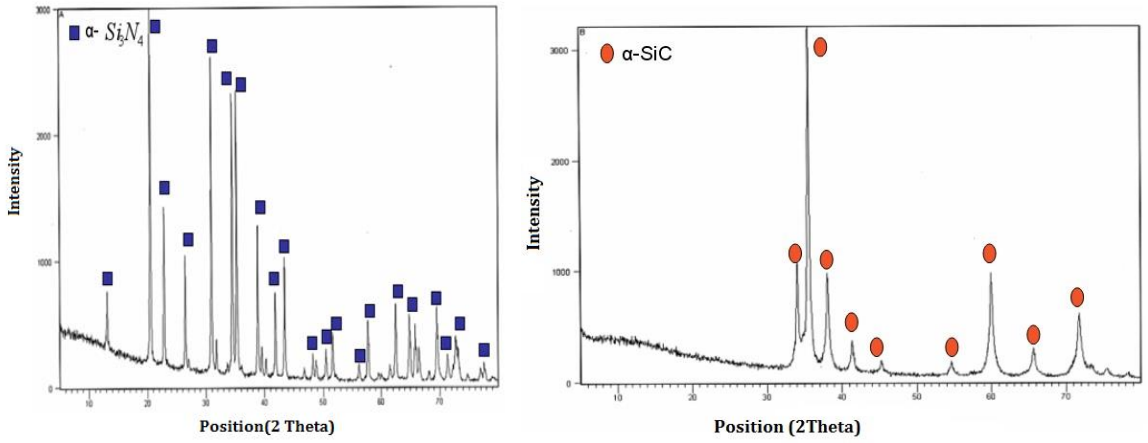
SiC particles disperse as a second phase in the matrix of Si_3N_4 particles and / or in the grain boundary. However, in the production of composites, hot pressing process and pressureless sintering of Si_3N_4 and SiC powder of fine particles can have sometimes problems and often does not produce the expected results (Lojanova et al.,2010). Different types of sintering additives are used in nonoxides ceramics, such as MgO, Al_2O_3, Y_2O_3, etc. Due to the high surface energy which causes the agglomeration of the SiC particles in the Si_3N_4 matrix, gives rise to difficulties to obtain a homogeneous dispersion (Asit et al.,2006; Tatarko et al.,2013).

Generally, it is difficult to obtain highly dense Si_3N_4 ceramics. In addition, high sintering temperature and the application of external pressure are beneficial to their full densification. To date, pressure-assisted sintering method has been introduced to achieve silicon nitride ceramics with high density (Yao et al.,2018).

The aim of the present work is to prepare SiC reinforced silicon-nitride composites by pressureless and spark plasma sintering, and to study the sintering, density and microstructure of the resultant composites.

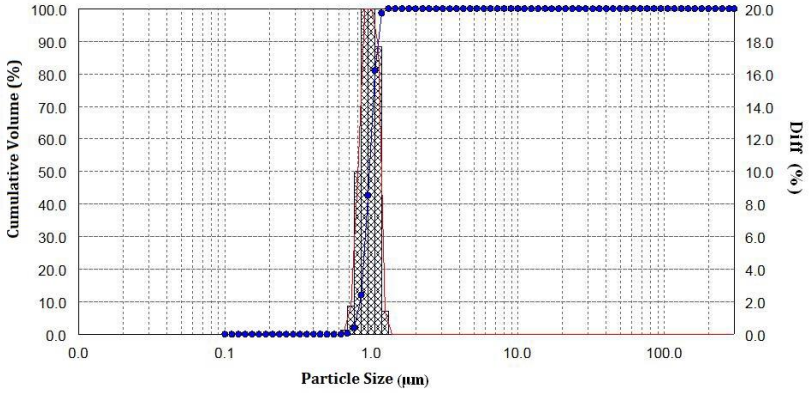
2. Material and Methods

The starting mixtures of Si_3N_4-SiC composites consisted of the following powders: Commercial α-Si_3N_4 powder (UBE Industries, SN-E10), SiC powder (H.C Starck Grade UF-25) were used as powder precursors. Figure 1 shows XRD patterns of the starting powders. High purity AlN (H.C. Starck Grade C, Germany) and Y_2O_3 (H.C. Starck Grade C, Germany) were used as additives for liquid-phase sintering to promote densifications given in the previous study (Taslicukur et al.,2012). Particle size distribution of Si_3N_4 and SiC was given in Figure 2.

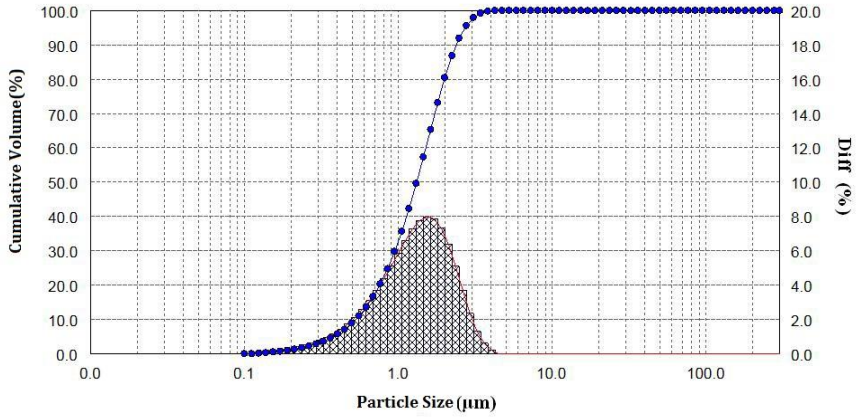


(a) (b)

Figure 1. XRD spectrum of (a) α- Si_3N_4 powder (b) SiC powder



(a)



(b)

Figure 2. Particle size distribution of **(a)** Si_3N_4 **(b)** SiC

Composition of composite powder mixtures was given in Table 1. Si_3N_4, SiC, AlN and Y_2O_3 were mixed with ethanol for 5 h. 1 wt % binder polyvinyl alcohol (PVA) was added to ensure the strength before sintering process. The slurries were dried at 150 ^{0}C for 12 h, and then sieved to a particle size < 150 µm. In the pressureless sintered method, the mixture was cold pressed under 1,5 tons and then cold isostatic pressed under 150 MPa for 4 min. The compacts were sintered at 1850 ^{0}C for 1 h under nitrogen atmosphere. In the spark plasma sintering method, the samples were spark plasma sintered at 1650 ^{0}C under nitrogen atmosphere under 40 MPa for 5 minutes.

Table 1. Composition of starting mixtures

Sample (wt%)	Si_3N_4 (wt%)	SiC (wt%)	AlN (wt%)	Y_2O_3 (wt%)
SiC10	80	10	5	5
SiC20	70	20	5	5
SiC30	60	30	5	5

Archimedes' immersion method was used to measure the densities of the samples. The crystal structure of the samples were investigated by X-ray diffractometry (XRD) analysis, X'Pert Pro MRD Panalytical diffractometer. Scanning electron microscopy(SEM) (JEOL JSM-7000 F) was used to characterize the microstructure of the samples. Hardness of the samples was tested on a micro Vicker(Struers Duramin A-300) with an applied load of 2 kg.

3. Research Findings

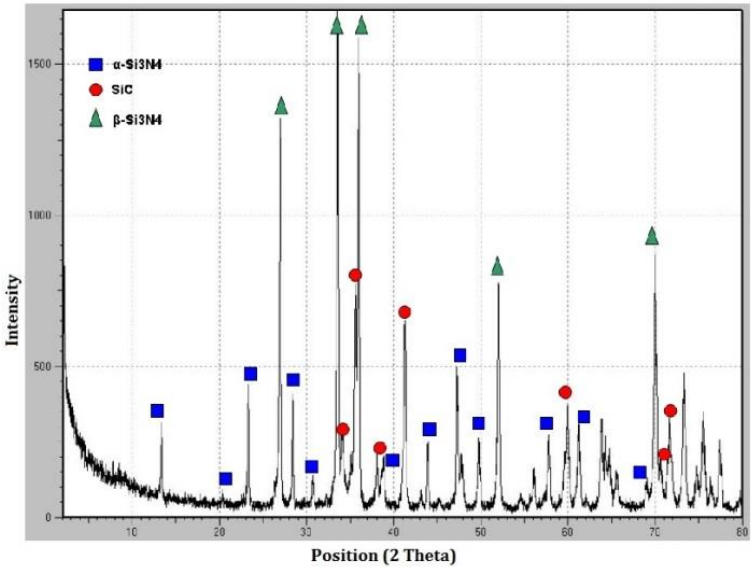
Relative density decreases due to the increase of SiC (by weight %) content in the composite as seen in Table 2. The composite which was reinforced with 10(wt%) SiC has the highest relative density 84.16% and the relative density of the sintered sample having 30 % by weight SiC decreases to % 79.31 in the pressureless sintered composite. It is difficult to sinter SiC because of its strong covalent bond structure with pressureless sintering. This behaviour could be attributed to the presence of SiC particles, which tend to inhibit shrinkage and densification during firing. As the Si_3N_4 matrix shrinks, a rigid SiC particle generates a shear stress in the matrix and a tensile hoop stress at the particle-matrix interface. Until this shear stress can be relaxed by shear flow in the matrix or by viscous flow of the liquid phase, the hoop stress will act to inhibit sintering and to reduce densification, this effect being dependent on the volume of the SiC inclusions(Gunay et al.,1995). The composite which was reinforced with 10(wt%) SiC has the highest relative density 99.60 % and the relative density of the sintered sample having 30 % by weight SiC decreases to % 99.30 in the spark plasma sintered composite. Nearly the full density was achieved using spark plasma sintering technique.

Table 2. Relative density of samples pressureless sintered at 1850 ^{0}C for 1 hour and spark plasma sintered at 1650 ^{0}C for 5 minutes

Sample (wt%)	Relative Density (%) (pressureless-1850 ^{0}C)	Relative Density (%) (spark plasma sintered-1650 ^{0}C)
SiC10	84.16	99.60
SiC20	84.12	98.70
SiC30	79.31	99.30

Si_3N_4 presents two different morphologies in Si_3N_4-SiC materials. It was found that α-β transformation of the Si_3N_4/SiC composite occured during sintering. Taslicukur et al, sintered Si_3N_4-C composites to synthesize Si_3N_4-SiC composites by in-situ carbothermal reduction process at 1700 ^{0}C and 1850 ^{0}C in the previous study, indicated that the relative density of the samples increased due to the increase of the sintering temperature. The sintering temperature, 1850 ^{0}C, was determined according to the previous study(Taslicukur et al.,2012). Figure 3 also illustrated that β-Si_3N_4 was the major phase in

all of the samples. α-Si_3N_4 and SiC peaks were also determined. When SiC (wt amount %) increases in the Si_3N_4 matrix, the intensity of β-Si_3N_4 phase decreases. X-rays results indicated that α-β transformation is not fully completed because of the short sintering time and / or the low sintering temperature. Taslicukur et al, spark plasma sintered Si_3N_4/SiC composite at 1650 ^{0}C under nitrogen atmosphere under 40 MPa for 5 minutes. Higher hardness values of the composites were determined due to the addition of harder SiC into the Si_3N_4 matrix(Taslicukur et al.,2012). The composite with 10 wt% has the hardness of 21.4 GPa, while the composite with 30 wt% has the hardness of 22.5 GPa.



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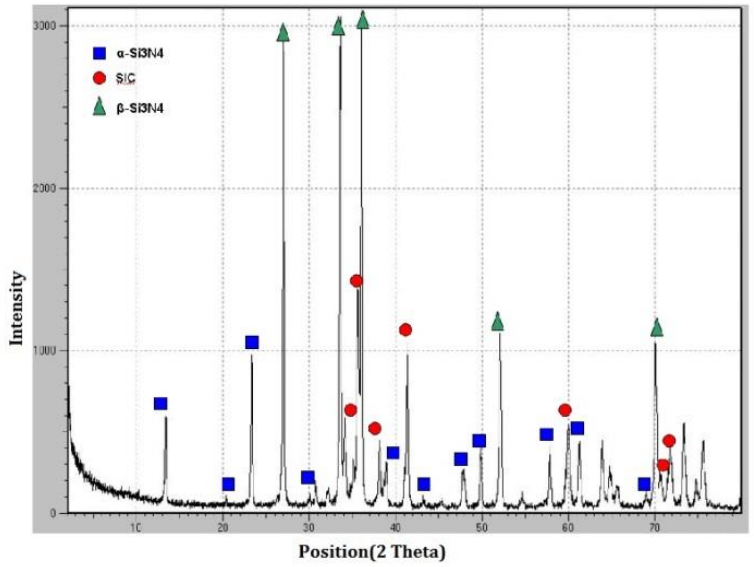
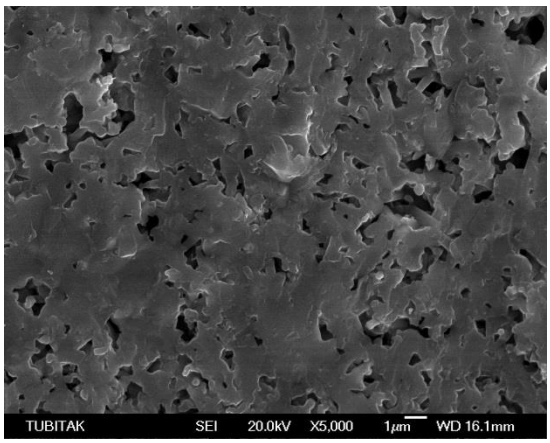


(b)

Figure 3. XRD patterns of composite samples sintered at 1850 ^{0}C for 1 hour under nitrogen atmosphere **(a)** Si_3N_4-20 wt% SiC and **(b)** Si_3N_4-30 wt% SiC.

Figure 4 illustrates the SEM images of Si_3N_4/SiC ceramics composites sintered at 1850 ^{0}C for 1 h under nitrogen atmosphere. It is noticed that due to the increase of SiC in the Si_3N_4 matrix, equiaxed grains formed instead of elongated grains. The SiC particles located around the β-Si_3N_4 grains and prevented the densification of the Si_3N_4 matrix(Rice,1998). SiC particles hindered the grain growth of silicon nitride by grain boundary pinning (Lojanova et al., 2010). As can be seen from Figure 4(c), it was found that the β-grains in the structure decreased and an equaxial structure was formed.



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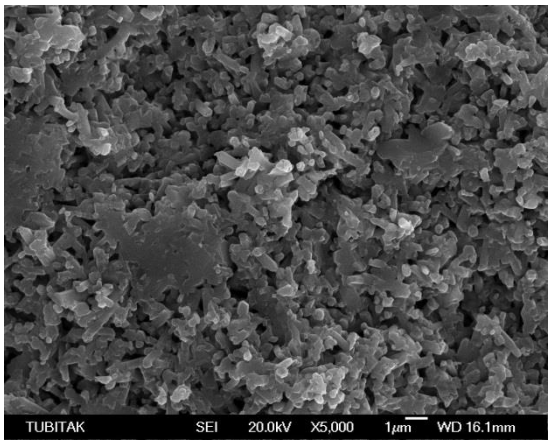

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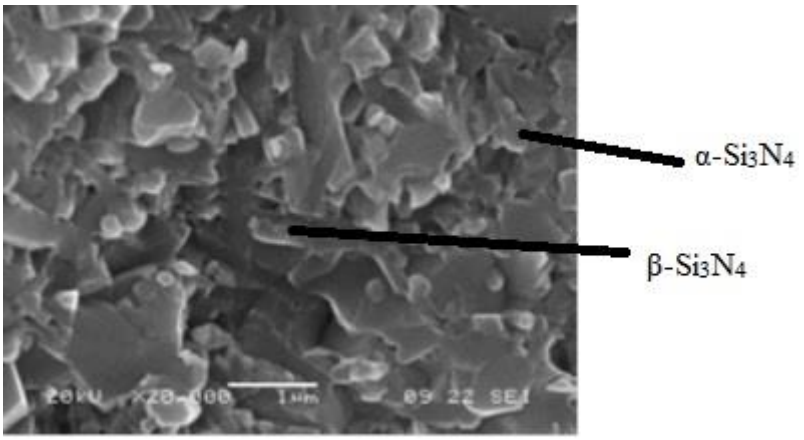

(c)

Figure 4. SEM micrographs of the Si_3N_4-SiC composites sintered at 1850 ^{0}C for 1 h under nitrogen atmosphere **(a)** Si_3N_4-20 wt% SiC and **(b)** Si_3N_4-30 wt% SiC **(c)** spark plasma sintered at 1650 ^{0}C under 40 MPa for 5 min- Si_3N_4-10 wt% SiC

4. Results

Preparation of Si_3N_4/SiC composites with pressureless sintering and spark plasma sintering have been performed using AlN and Y_2O_3 as sintering additives. The influence of SiC particle amount on the density and microstructure of Si_3N_4/SiC composites was investigated. According to XRD results, main phases are α-Si_3N_4, β-Si_3N_4 and SiC. SiC prevents the transformation of α-Si_3N_4 to β-Si_3N_4 and it also inhibits the growth of β-Si_3N_4 grains in the Si_3N_4 matrix. Relative density decreased from %84.16 to %79.31, when the content of SiC(%wt) increased from %10 to

%30. Si_3N_4/SiC composites were prepared via spark plasma sintering at 1650 ^{0}C under 40 MPa under nitrogen atmosphere in a very short time, 5 min, with nearly full density. The results indicate that the presence of SiC as a second phase lowered the densification. Higher hardness values of the composites were achieved due to the addition of SiC into the Si_3N_4 matrix.

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