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Fabrication and characterizations of high density Si_3N_4 - ZrO_2 ceramics

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Abstract

Silicon nitride and zirconia were mixed with SiO_2, MgO, Y_2O_3 as sintering additives and pressureless sintered at 1650°C in N_2 atmosphere for 2 h. The XRD results showed α-Si_3N_4 was partially transformed to β-Si_3N_4 with 3:3:5 weight ratio of SiO_2 : MgO : Y_2O_3. However, at 5 wt% of ZrO_2 addition promoted phase transformation of α-Si_3N_4 to β-Si_3N_4 while 35 wt% of ZrO_2 completely transformed to β-Si_3N_4 phase. Si_3N_4 has a lower density than ZrO_2, bulk density of samples increases in correlation with the amount of ZrO_2. Because there was no difference in hardness and flexural strength between sintered Si_3N_4 samples with hardness of 13.41 GPa and 648.13 MPa along with increasing ZrO_2 variation up to 55 wt%. Furthermore, with 75 wt% ZrO_2, the hardness was reduced to 10.57 GPa and the flexural strength decreased to 208.16 MPa. SEM images of Si_3N_4 samples demonstrated the dense microstructure and 5 wt% ZrO_2 showed homogeneous ZrO_2 distributed among the Si_3N_4 grains. As a result, the hexagonal rod-like form of β-Si_3N_4 is clearly visible in 75 wt% ZrO_2. Therefore, Si_3N_4 with ZrO_2 can be sintered with the homogeneous microstructure of the α-Si_3N_4 to β-Si_3N_4 transformation and tolerable mechanical properties vary with ZrO_2 content.

1. Introduction

Silicon nitride (Si_3N_4) and zirconia (ZrO_2) ceramics have been highly accepted for use in structural applications due to their high fracture toughness, hardness, strength, chemical inertness, high temperature stability, wear resistance, low coefficient of friction, and biocompatibility. Currently, Si_3N_4 ceramics are one of the most used groups of high thermal application and processing, especially nozzles, valves, cutting tools, turbochargers, heater sheaths, abrasive material, and metallurgical casting and machining in general [1,2]. However, sintered silicon nitride by conventional sintering had failed due to primarily problem of the low interatomic diffusion ability and the high temperature dissociation of Si_3N_4, which resulted in microstructural coarsening [3]. Nowadays, it is well known that Si_3N_4 was manufactured using the nitridation mechanism from packed of silicon powder or sintered with various additives in high nitrogen pressure. Accordingly, several sintering aids such as yttria, magnesia, and alumina must be added to reduce the sintering temperature via the liquid-phase mechanism. During sintering, the smaller powders of alpha phase begin to dissolve with the liquid phase and recrystallize into a beta phase with a hexagonal needle shape and grain growth with traces. Due to the fact that the process of transformation from α-Si_3N_4 to β-Si_3N_4 is irreversible mechanism. Then, there have been no reports on sintered material mechanical properties testing between alpha phase and beta phase for comparative purposes. A glassy phase exists between the grain boundaries, resulting in a higher density [4]. Moreover, the high nitrogen pressure atmosphere is required to prevent the mass loss of Si_3N_4. Mitomo *et al.*, in 1977, discovered the Si_3N_4 with 90% density was obtained by using packing powder with 1 MPa of nitrogen pressure. Subsequently, Giachello *et al.* demonstrated that high nitrogen pressure could be avoided by using compacted Si_3N_4 powder containing MgO as a sintering additive embedded in Si_3N_4 powder [5]. In 2006, Wasanapiarnpong *et al*. found that the Si_3N_4 ceramics powder with SiO_2-MgO-Y_2O_3 as sintering additive were successfully sintered with high degree of alpha to beta phase transformation at 1600°C to 1750°C in 1 atm of N_2 atmosphere without packing powder [6].

For the zirconia (ZrO_2) has been utilized in various commercial products in the field such as seal, pump and milling media [7]. In the past, pure ZrO_2 is difficult to sintering because restriction of phase transformation from tetragonal to monoclinic at 950°C on cooling resulting in 4% of volume expansion. This change in shape of volume transformation can result in catastrophic fracture and structural inconsistency [8]. Presently, stabilized zirconia with many oxides such as Y_2O_3, MgO, CeO_2 etc. could be eliminated effect from phase transformation especially when yttria was added into zirconia has two important effects. It broadens the range of the tetragonal phase field and lowers the temperature at which the tetragonal-monoclinic transformation occurs. From the excellent property about stress induce

transformation toughening mechanism of zirconia is widely accept that led zirconia used as reinforcing in ceramic composite. The most dominant are alumina-zirconia composites, which outperform conventional alumina in terms of strength, toughness, and wear resistance. Recently, zirconia-based nanocomposites for biomedical applications as dental implants, hip joint have been developed with linking several toughening mechanisms such as tetragonal-monoclinic transformation, microcracking, and crack deviation due to the secondary phases. During the past decade Si_3N_4 and ZrO_2 have been studied in the different sintering atmosphere. However, a recent study was attempted to develop Si_3N_4 composite materials utilizing ZrO_2 as a reinforcement phase. Although the use of tetragonal zirconia as a reinforcement phase can effectively improve the fracture toughness of Si_3N_4 ceramics, the well-known high-temperature interaction between the ZrO_2 component and the Si_3N_4 matrix has been frequently observed during sintering at temperatures above 1600°C, resulting in the formation of deleterious ZrN or ZrON phases [9].

Therefore, this study purposed on extensive various composition between Si_3N_4-ZrO_2 materials with sintering additives in unique sintering atmospheres and without packing powder by investigated on phase, density, hardness, flexural strength and microstructure after nitrogen gas pressureless sintering.

2. Materials and experimental

The raw materials used were various compositions of high purity α-Si_3N_4 powders (SN E-10 grade, Ube Industries Ltd., Tokyo, Japan) and 3 mol% Y_2O_3 stabilized ZrO_2 powders (Inframat, Advanced Materials) at 5, 35, 55 and 75 wt% with SiO_2 (KE-P30, Nippon Shokubai Co. Ltd., Osaka, Japan), MgO (MJ-30, Iwatani Corp., Tokyo, Japan), and Y_2O_3 (RU, Shin-Etsu Chemical Co. Ltd., Tokyo, Japan) as sintering additives by weight ratio of SiO_2 : MgO : Y_2O_3 at 3:3:5 was shown in Table 1. Then the starting material powders were mixed by ball milling in a high-density polyethylene bottle (HDPE) with Si_3N_4 ball in 99.9% ethanol for 24 h. The slurry was dried to powder in a rotary evaporator at 60°C through a 100-mesh screening sieve. The powders were uniaxially pressed at 25 MPa and cold isostatic press at 250 MPa for 5 min. The pellets were sintered at 1650°C for 2 h in a nitrogen atmosphere of 0.1 MPa. All sintered samples were measured for bulk densities using the Archimedes method. Phase compositions were determined by X-ray diffraction (D8-Advance, Bruker Corp., Billerica, MA, USA) with Cu-Kα radiation. The hardness values of the sintered materials were prepared by grinding and polishing, then measured using Vickers hardness indentation at 10 kN for 15 s. Finally, polished surface of samples was chemically etched with HF for 15 s for the microstructure observation using a scanning electron microscope (JSM 6480LV, JEOL Ltd., Tokyo, Japan).

3. Results and discussion

3.1 Phases composition

Figure 1 indicates the XRD patterns of the SN, 5Zr, 35Zr, 55Zr, 75Zr, and Zr samples. It shows that the Si_3N_4 (SN) sample contains both β-Si_3N_4 and α-Si_3N_4 as the main phases has already occurred at 1650°C with SiO_2, MgO, and Y_2O_3 as sintering additives. The SiO_2-MgO-Y_2O_3 system has an eutectic temperature about 1400°C that liquid phase sintering can be performed to achieve high densification at 1650°C for 0.1 MPa in N_2 without packing powder [6,10].

Considering the peak height of the first three peaks compared between beta and alpha silicon nitride phases to estimate the proportions of the two phases, it was found that in the SN sample, the beta phase was about 70% and the alpha was about 30%. While the 5Zr sample was found to contain 83% beta, 12% alpha. It can be seen that the addition of 5 wt% of ZrO_2 promotes the α to β phase transformation, which is consistent with the research of H. Hyuga *et al.* [11]. While adding 35 wt% of ZrO_2, only β-Si_3N_4 and tetragonal zirconia (t-ZrO_2) phases were found. No α-Si_3N_4 phase was found indicating that the addition of 35 wt% of ZrO_2 completes the phase transformation. For the Zr sample, the sample contained single-phase tetragonal zirconia that confirmed the absence of the effect of sintering in the nitrogen atmosphere.

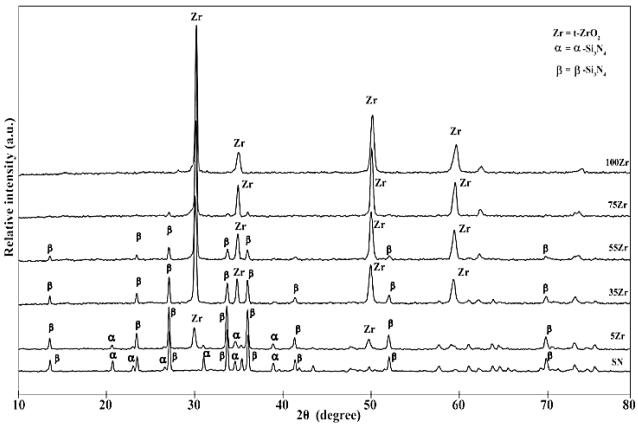

Figure 1. XRD patterns of Si_3N_4 (SN), 5 wt% ZrO_2 (5Zr), 35 wt% ZrO_2 (35Zr), 55 wt% ZrO_2 (55Zr), 75 wt% ZrO_2 (75Zr), ZrO_2 (Zr) samples sintering at 1650°C for 2 h.

Table 1. Starting materials with various composition.

Composition	SN	5Zr	35Zr	55Zr	75Zr	Zr
Si_3N_4	89	84	54	34	14	-
SiO_2	3	3	3	3	3	-
MgO	3	3	3	3	3	-
Y_2O_3	5	5	5	5	5	-
ZrO_2		5	35	55	75	100
Total	100	100	100	100	100	100

3.2 Density and water absorption

For the bulk density and relative density in Table 2. shows the changes in the bulk density, and relative density of the Si_3N_4-ZrO_2 composite ceramic samples SN, 5Zr, 35Zr, 55Zr, 75Zr, and Zr, respectively. With an increase in the ZrO_2 content of the raw material, it can be seen that the bulk density of the samples increased relatively. The Si_3N_4 (SN) samples have a density of about 3.18 g·cm^{-3} and the 5Zr samples have 3.28 g·cm^{-3} where the bulk density increases related to the amount of ZrO_2 due to the density of ZrO_2 being higher than that of the Si_3N_4 materials. Furthermore, Zr samples have a density of 6.05 g·cm^{-3} close to normal sintered ZrO_2 that shows no effect of the ambient pressure N_2 for ZrO_2 and the XRD results demonstrated t-ZrO_2 without any ZrN formation. The bulk density of sintered samples was contrasted with relative density since the bulk density shows an increasing trend with amount of ZrO_2 while the relative density reveals the effect of sintering additives. For SN, 5Zr, 35Zr, 55Zr, 75Zr and Zr samples have 98.70, 99.30, 99.15, 98.50, 97.20, and 99.18% relative density, respectively, with the relative density higher than 95% relative density shows that the SiO_2-MgO-Y_2O_3 additive suitable plays the role in the approval of the sinterability of the samples.

3.3 Mechanical properties

Figure 2 Show the mechanical properties between Vickers hardness and flexural strength of all sintered samples as a role of ZrO_2 content. The hardness decreased with increasing amount of ZrO_2. The inappreciably decrease in porosity of the samples may be related to the slightly dropped in hardness. A similar pattern emerged in the results of the flexural strength test. The SN samples exhibited higher hardness value when compared with a higher ZrO_2 content. It can be seen that the hardness value of samples with 5 wt% to 75 wt% of ZrO_2 decreases from 13.34 GPa to 10.57 GPa with increasing of the zirconia. It is widely known that the intrinsic property of the material has a significant impact on the hardness of dense multiphase ceramics because the hardness of Si_3N_4 is mostly higher than the hardness of ZrO_2. According to reports, the hardness values of ceramics made of TZP, α-Si_3N_4, and β-Si_3N_4 are respectively between 11 GPa and 13 GPa, 23 GPa, and 20 GPa [12,13].

Additionally, we should be considered how α-Si_3N_4 transform to β-Si_3N_4 during sintering because the significant partial portion of alpha phase dissolve by SiO_2-MgO-Y_2O_3 liquid phase system and change to the beta phase was mainly referred by the phase transformation for the sample containing higher amounts of stablized ZrO_2. As a result,

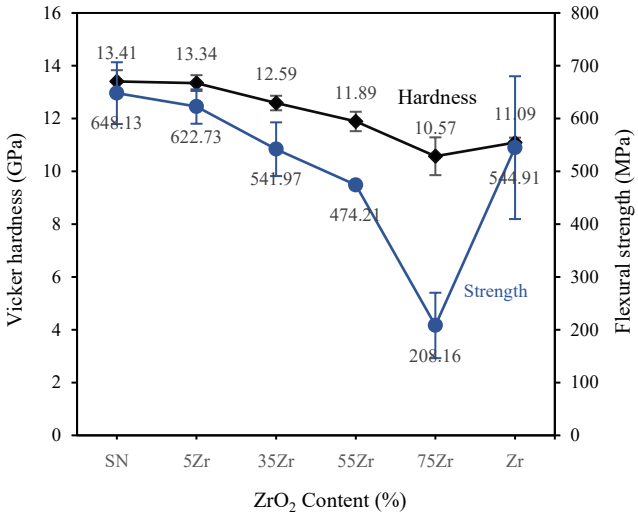

Figure 2. Vickers hardness and flexural strength of sintered Si_3N_4-ZrO_2 ceramics

the accelerated modification of alpha to beta may also subsidize to the recognized hardness decreasing in Si_3N_4-ZrO_2 ceramics [14]. The coincidental trend of the flexural strengths with hardness has shown a high value of 648.13 MPa for the SN sample particularly results from the achievement of a 98.43% relative density and a slightly decrease to 622.73 MPa for 5Zr by increasing the amount of ZrO_2. With regard, the increment of porosity results in the low flexural strength falling from 541.97 MPa for 35Zr, 474.21 for 55Zr, and 208.16 MPa for 75Zr respectively. Although the porosity of the Zr sample is not different from that of another sample but high strength because its exhibits a monolithic ZrO_2.

3.4 Microstructure

Figure 3 shows the SEM micrographs of the sintered samples with polished surface. SN sample with SiO_2, MgO and Y_2O_3 as sintering additive and Zr sample, the microstructure becomes homogeneous, dense, and low porosity correlate with high relative density and good mechanical properties.

However, in Figure 3(b), the microstructure of the 5Zr sample is remain uniform with light area of the ZrO_2 grain in their microstructure. According to the results, the grain growth mechanism of the elongated β-Si_3N_4 grains is derived from the phase transformation mechanism and the added ZrO_2 can promote α to β phase transformation [15]. Also, by ZrO_2 addition, complete phase transformation of α to β through liquid phase sintering leads to β-Si_3N_4 hexagonal rod-like grains formation clearly in the 75Zr sample in agreement with XRD results.

Table 2. Bulk density, relative density, apparent porosity, and water absorption of sintered sample at 1650°C for 2 h under 0.1 MPa N_2.

Samples	SN	5Zr	35Zr	55Zr	75Zr	Zr
Bulk density (g·cm^{-3})	3.18	3.28	3.84	4.31	4.89	6.05
Theoretical density (g·cm^{-3})	3.22	3.30	3.87	4.38	5.03	6.10
Relative density (%)	98.70	99.30	99.15	98.50	97.20	99.18
Apparent density (g·cm^{-3})	3.18	3.28	3.85	4.32	4.90	6.06
Apparent porosity (%)	0.13	0.11	0.26	0.15	0.30	0.18
Water absorption (%)	0.04	0.03	0.07	0.04	0.06	0.03

*3 samples/test

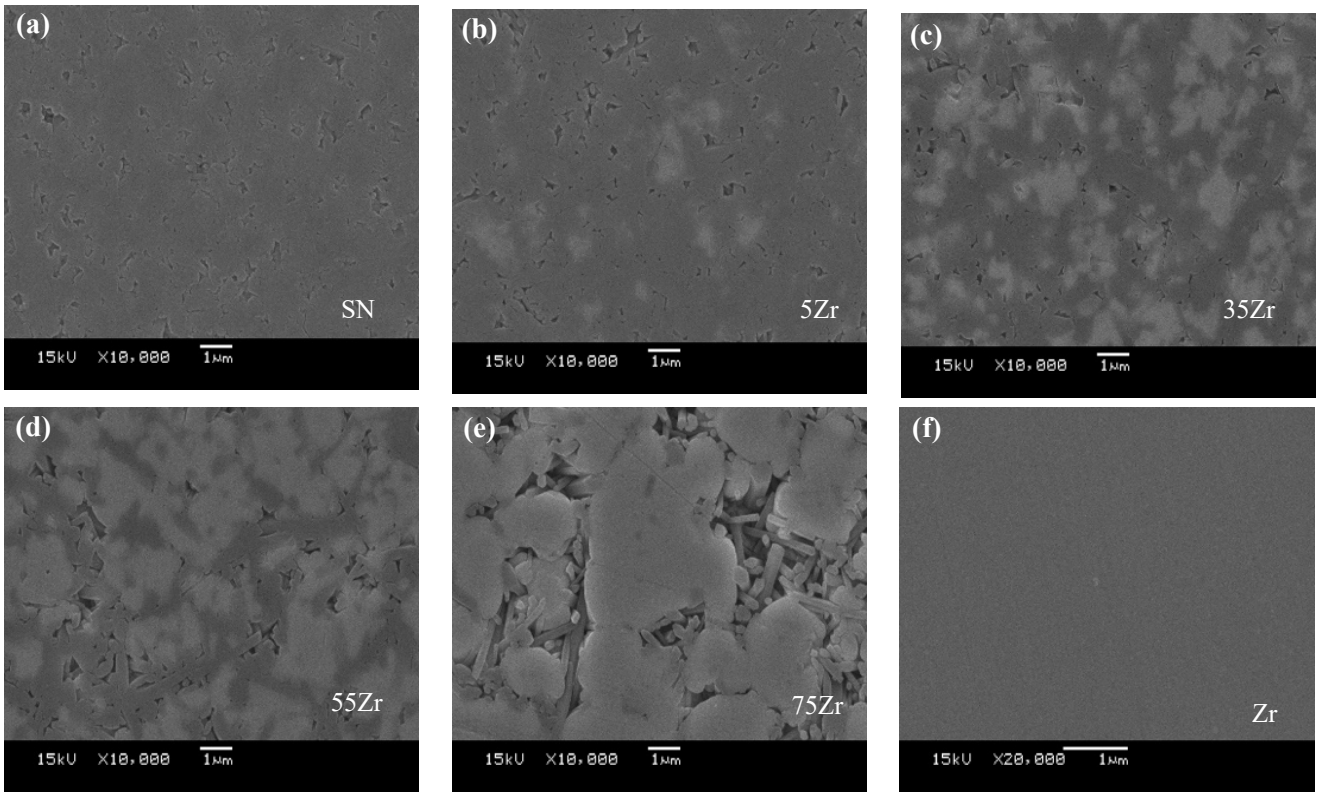

Figure 3. SEM micrographs of (a) Si_3N_4 (SN), (b) 5 wt% ZrO_2 (5Zr), (c) 35 wt% ZrO_2 (35Zr), (d) 55 wt% ZrO_2 (55Zr), (e) 75 wt% ZrO_2 (75Zr), (f) ZrO_2 (Zr) samples sintered at 1650°C for 2 h.

4. Conclusions

Silicon nitride and zirconia were mixed with SiO_2, MgO, Y_2O_3 and then pressureless sintering. According to the XRD results, the starting powders of α-Si_3N_4 were partially transformed to β-Si_3N_4 with 3:3:5 weight ratio of SiO_2 : MgO : Y_2O_3, respectively. At 5 wt% of ZrO_2 was performed phase transformation of α-Si_3N_4 to β-Si_3N_4 while 35 wt% of ZrO_2 effectively transformed to β-Si_3N_4 phase. The bulk density of the samples increases directly with the amount of ZrO_2. The hardness and flexural strength between sintered samples with high hardness of 13.41 GPa and 648.13 MPa along with increasing ZrO_2 variation up to 55 wt%. But 75 wt% ZrO_2, the hardness decreased to 10.57 GPa and the flexural strength reduced to 208.16 MPa. SEM microstructures were presented, which showed a dense and homogeneous ZrO_2 dispersion between Si_3N_4 grains of 5 wt% of ZrO_2 corresponding with the hexagonal rod-like of β-Si_3N_4 is evidently at 75 wt% ZrO_2. From a distinctively sintering atmosphere, Si_3N_4 and ZrO_2 could be sintered together with uniform microstructure and mechanical properties acceptable.

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