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Fabrication of pressureless sintered dense β-SiAlON via a reaction-bonding route with ZrO_2 addition

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Abstract

A reaction-bonding and post-sintering process was applied to fabricate pressureless sintered β-$Si_{6-Z}Al_ZO_ZN_{8-Z}$ ($Z = 1$–3) ceramics with monoclinic ZrO_2 added to the starting powder. Samples with ZrO_2 showed enhanced nitridation and achieved near theoretical density following post-sintering, although this could not be achieved in the samples produced without ZrO_2. Thus the ZrO_2 is effective in both enhancing the nitridation of Si and as a sintering additive for densification of β-SiAlON. Part of the added monoclinic ZrO_2 was transformed to tetragonal ZrO_2, and the ZrN phase was also formed due to reaction with nitrogen during the reaction-bonding process. After the post-sintering process, the ZrN phase remained only in the $Z = 3$ composition. In the other compositions the ZrN reacted with SiO_2 to form both tetragonal and monoclinic ZrO_2 phases. These differences are explained in terms of the increasing densification and grain growth for Al_2O_3 rich compositions and the ZrN being trapped inside such grains in the case of the $Z = 3$ sample.

Keywords: D. Sialon; Silicon nitride; Reaction bonding; Zirconia

1. Introduction

SiAlON ceramics are promising materials for high-temperature, high corrosive environments and high mechanical stress applications because they offer high thermal shock resistance and high strength retention at elevated temperature as well as good erosion resistance and low creep properties [1–4]. Amongst the different fabrication procedures for silicon nitride-based ceramics, reaction-bonded processing has some advantages, such as low sintering shrinkage and low raw material cost [5–7]. However, the application of these RBSN ceramics is limited due to the low fracture strength, high porosity and long processing time. The long processing time is a serious issue which is difficult to solve due to the intrinsic process of the nitridation of silicon. Generally, for obtaining RBSN ceramics, the nitridation of silicon is carried out near its melting temperature despite the fact that the reaction between silicon and nitrogen is exothermic. This means that rapid nitridation of silicon can easily lead to melting of the silicon due to the self-heating reaction prior to the completion of nitridation. To overcome this problem, many researchers have reported the catalytic nitridation of silicon for fabricating raw silicon nitride powder and RBSN ceramics [8–11]. Iron is the most famous and well-known catalyst for promoting the nitridation of silicon, and is generally contained as an impurity in the raw material of low cost grade silicon powders. However, when dense silicon nitride ceramics are required to be fabricated using reaction bonding and a post-sintering process, iron acts as a type of defect for reducing mechanical properties such as fracture strength and Weibull modulus [12]. The catalytic effect of other metals and oxides such as chromium, calcium, copper and silver on the nitridation of silicon has also been reported [9].

Reaction bonding combined with a post-sintering process can also be used to fabricate SiAlON ceramics. Kaga et al. reported the fabrication and mechanical properties of elongated

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α-SiAlON ceramics via a reaction-bonding route [13]. Brown et al. reported the fabrication of pressureless sintered β-SiAlON ceramics with Y_2O_3 as a sintering additive via a reaction-bonding route [14]. In that work, the Y_2O_3 performed a nitridation enhancing role in the early stages of nitridation due to reaction with SiO_2 on the surface of the silicon powder. However, reports on the fabrication of β-SiAlON ceramics via a reaction-bonding process in the absence of conventional rare earth oxide additives is very limited.

The authors have reported an effective enhanced effect of ZrO_2 on silicon nitridation [15] and densification with $MgAl_2O_4$ additive during post-sintering process [16]. This process should also be effective for the fabrication of SiAlON ceramics. In this study, dense β-SiAlON ceramics via a reaction-bonding route with monoclinic ZrO_2 addition were fabricated, and the nitridation, densification behavior and the microstructure were investigated.

2. Experimental procedure

ZrO_2 containing β-SiAlON with compositions of $Z = 1$–3 in the chemical formula $Si_{6-Z}Al_ZO_ZN_{8-Z}$ were chosen for this study. Hereafter, the ZrO_2 containing β-SiAlON with the composition of $Z = 1$, 2, and 3 are referred to as ZZ1, ZZ2 and ZZ3, respectively. Powders of Si (Hi-Si #600, Yamaishi Kinzoku, Tokyo, Japan), AlN (F grade, Tokuyama, Tokyo, Japan), Al_2O_3 (AKP-50, Sumitomo Chemical Co. Ltd., Tokyo, Japan) and ZrO_2 (TZ-0 grade, monoclinic phase, Toso. Co. Ltd., Tokyo, Japan) were used as a raw powders. The compositions of the starting powder used in this study are shown in Table 1. The starting powder compositions were chosen such that the final sintered bodies would contain 5 mass% of ZrO_2 assuming that the silicon starting powder is fully converted to SiAlON during the nitridation process. For comparison, SiAlON materials with the same Z value but without ZrO_2 additions, and powders of Si and ZrO_2 mixed powders only ($Z = 0$; corresponding to the silicon nitride composition with ZrO_2) were also prepared.

The powders were homogeneously mixed by planetary ball milling for 1 h in ethanol using a silicon nitride pot and silicon nitride balls and then dried using a vacuum evaporator. The oxygen content of the silicon powder following ball milling was 1.43 wt% as determined by a combustion type oxygen analyzer (Nitrogen Oxygen Determinator TC436, LECO, MI, USA). The mixed powders were uni-axially pressed in a 15-mm-diameter stainless steel die then cold isostatically pressed at 200 MPa. The obtained green compacts had about 5 mm thickness. Precise weights and dimensions of the green compacts were measured to clarify the degree of nitridation and dimensional change during heating. The green compacts were placed on a carbon plate, which was coated with BN spray and surrounded by an outer graphite crucible.

The nitridation of silicon compacts was conducted in a carbon heater furnace (Hi-multi 10000, Fuji Denpa Co. Ltd., Tokyo, Japan) at 1200–1450 °C for 0–4 h with 2 L/min high-purity nitrogen flow. The dimensions and weights of the nitridation samples were measured for comparison of the dimensional change and nitridation behavior. Phase identification was performed by powder XRD analysis (Rint2500, Rigaku Corp., Tokyo, Japan).

Following nitridation of the samples, they were post-sintered at 1800 °C for 8 h under nitrogen atmosphere at a pressure of 0.9 MPa. Phase composition and lattice parameter of the fabricated samples were measured by powder XRD analysis. The lattice parameters of the fabricated β-sialon were measured and calculated from the peaks corresponding to β-Si_3N_4 (0 0 2), (0 4 1), (1 4 0), (2 3 1), (0 5 0), (1 4 1) and (3 3 0) using Si powder as an internal standard. Densities of the samples were measured using the Archimedes' method in distilled water. Polished and fractured surfaces were observed using scanning electron microscopy (SEM, JSM-6330F, JEOL, Ltd., Tokyo, Japan) equipped with an X-ray energy-dispersive spectroscope (EDS, JED-2300F, JEOL, Ltd., Tokyo, Japan).

3. Results and discussion

Fig. 1 shows nitridation behavior of the samples with and without ZrO_2 corresponding to a SiAlON composition of $Z = 1$.

Table 1
Composition of starting powder mixture (mass%).

Specimen ID[a]	Si	Al_2O_3	AlN	ZrO_2 [b]
β-SiAlON				
Z1	74.84	17.95	7.22	0
Z2	53.84	32.92	13.23	0
Z3	37.01	44.93	18.06	0
ZrO_2 added β-SiAlON				
ZZ1	69.35	16.63	6.69	7.32
ZZ2	50.24	30.72	12.35	6.68
ZZ3	34.73	42.16	16.95	6.16

[a] Corresponding Z value ($Si_{6-Z}Al_ZO_ZN_{8-Z}$) when starting powder is fully reacted to SiAlON.

[b] Corresponding 5 mass% of ZrO_2 when silicon powder of starting is fully nitrided.

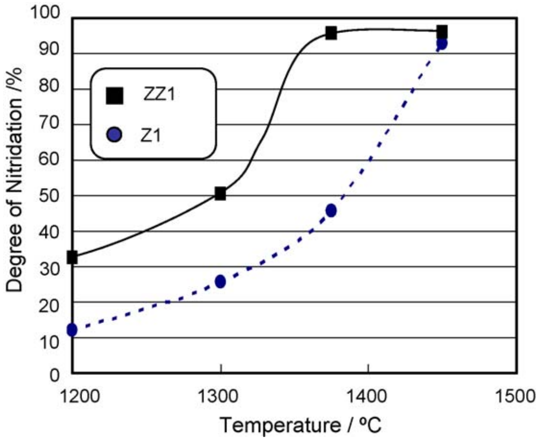

Fig. 1. Degree of nitridation of the reaction bonded SiAlON (Z1; $Z = 1$) and ZrO_2 doped SiAlON (ZZ1; $Z = 1$) specimens as a function of temperature. The ratio was calculated from Si content in the samples at the starting composition considering surface oxide of Si powder.

The degree of nitridation is based on calculation of the weight gain associated with the nitridation of silicon according to

$$3\text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4$$

According to this reaction, the increase in mass of a silicon compact when fully nitrided is 1.665 times the original mass of silicon. For nitridation temperatures below 1300 °C, neither of the samples were fully nitrided. However, even at this nitridation condition, the sample with added ZrO_2 indicated almost twice the degree of nitridation when compared to sample without ZrO_2. For nitridation temperatures over 1375 °C, the degree of nitridation was around 95% for samples containing ZrO_2. The degree of nitridation of the sample without ZrO_2 was significantly lower at about 45.5% indicating that the nitridation of silicon without ZrO_2 was not completely finished at this temperature.

Fig. 2 shows X-ray diffraction spectra of the ZrO_2 added samples nitrided at 1450 °C for 4 h. No residual silicon was identified in any of the samples, indicating the complete nitridation of Si powder during this process condition. The main silicon nitride related phases of the samples were α- and β-Si_3N_4, and the amount of β-Si_3N_4 phase increased with increasing the Z value. α-Al_2O_3, one of the starting powders, was also detected, whereas the originally added monoclinic ZrO_2 was observed as tetragonal ZrO_2 and ZrN phases. The, β-SiAlON phase was not observed at this stage of the heating process.

These results indicate that the addition of ZrO_2 to silicon powder significantly promotes the conversion of silicon to silicon nitride at lower temperatures when compared to the silicon only sample. This behavior is the same trend as that observed for the case of reaction bonded Si_3N_4 ceramics with ZrO_2 additions. The authors have reported the nitridation enhancement behavior of ZrO_2 on silicon powders [15] and silicon nitridation behavior with ZrO_2 by thermo-gravometric analysis in addition to the fabrication of reaction bonded Silicon nitride samples [17]. In those works, ZrO_2 additions to silicon powder decreased the starting temperature of the main reaction step in the nitridation of silicon. In the present study, the fabrication of SiAlON via a reaction-bonding route indicates the same behavior. Following nitridation, the fact that the nitrided silicon derived phase was not SiAlON but silicon nitride indicates that the presence of Al_2O_3 does not affect the nitridation enhancing effect of ZrO_2 on silicon powder.

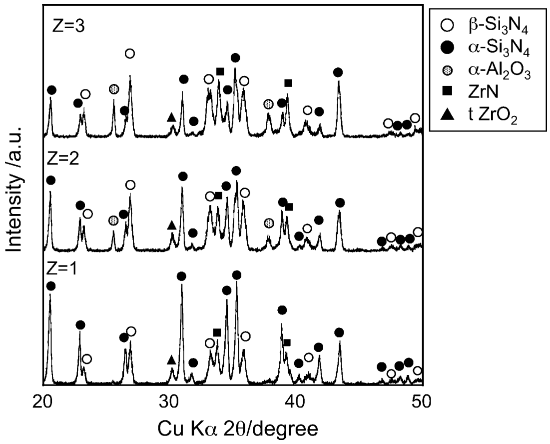

Fig. 2. X-ray diffraction spectra of inside the samples after reaction bonded ZrO_2 doped SiAlON (Z = 1–3). Reaction bonded condition was 1450 °C for 4 h.

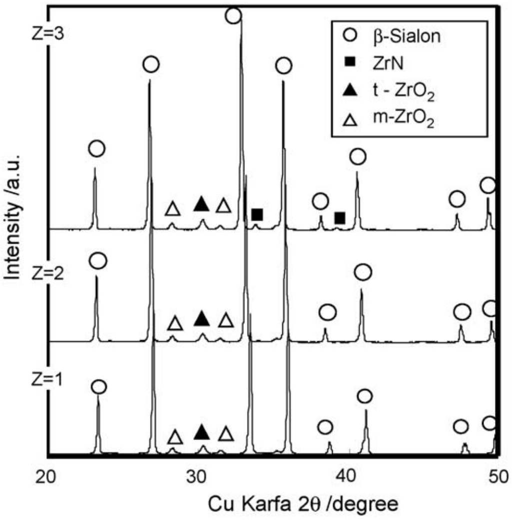

Fig. 3. X-ray diffraction spectra of inside the samples after post-sintered ZrO_2 doped SiAlON (Z = 1–3). Reaction bonded condition was 1450 °C for 4 h. Post-sintered was 1850 °C for 8 h.

Fig. 3 shows X-ray diffraction spectra of the samples post-sintered at 1800 °C for 8 h following nitridation. In all samples the only SiAlON phase observed was the β-phase, and other Si_3N_4 and α-SiAlON phases were not identified. The peaks associated with the (1 0 1) and (2 1 0) planes of SiAlON were shifted to lower diffraction angles with increasing Z value as would be expected due to an increasing lattice parameter with increasing degree of substitution of Al and O into the silicon nitride structure. Monoclinic and tetragonal ZrO_2 phases were identified for every composition. The ZrN phase which was identified following the reaction-bonding process was identified only in the ZZ3 sample following post-sintering, and could not be identified in ZZ1 and ZZ2 samples.

Fig. 4 shows the measured lattice parameter of the ZrO_2 added samples as a function of Z value. Calculated theoretical lattice parameters determined from the powder diffraction file database (JCPDS 48-1615, 48-1616, 36-1333, 48-1617), are also shown in Fig. 5 (dashed line). The lattice parameters of all samples show good agreement with theoretical values. This result indicates that the ZrO_2 added for the fabrication of the SiAlON ceramics did not form any solid solution with silicon nitride. This is consistent with other reports on the fabrication of Si_3N_4-based composites (including SiAlON) with ZrO_2 additions [18–20].

Fig. 5 shows the bulk density and open porosity of the fabricated samples. The SiAlON samples without ZrO_2 addition could not be densified in this sintering condition. On the other hand, ZrO_2 added SiAlON had no open porosity and obtained very close to theoretical density despite not having a conventional rare earth oxide as sintering additive. This result indicates that the ZrO_2 acts not only to enhance the

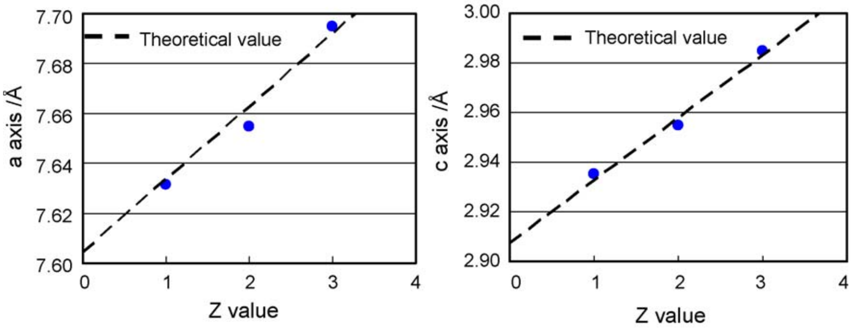

Fig. 4. Lattice parameters of the fabricated ZrO_2 doped SiAlON.

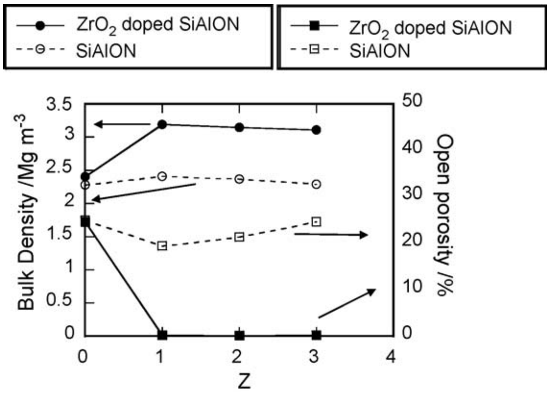

Fig. 5. The bulk density and open porosity of the fabricated ZrO_2 doped SiAlON.

nitridation effect but also serves as a sintering additive for densification of β-SiAlON ceramics.

At these processing conditions, the $Z = 0$ sample with (silicon nitride) was not fully densified for samples both with and without ZrO_2, indicating that the presence of ZrO_2 alone is not sufficient for densification. It has been reported that the presence of Al_2O_3 is effective for the sintering of ZrO_2 added Si_3N_4 ceramics [21–23]. In the normal SiAlON fabrication process Al_2O_3 is contained in the starting powders, and in the case of the reaction-bonding process the fact that the SiAlON phase was not formed following the nitridation stage implies the remaining presence of Al_2O_3. It is considered that this residual Al_2O_3 reacts with ZrO_2 and forms a eutectic liquid phase during the higher temperature post-sintering step and this aids the densification of SiAlON.

Fig. 6 shows SEM images of the polished surfaces of the ZrO_2 added SiAlON samples. No large pores were observed in any of the samples. In the case of the $Z = 1$ sample, the white area seen in the figure was identified at the grain boundary as found in conventional silicon nitride ceramics. EDS analysis showed that these areas were rich in zirconium and oxygen, but aluminum and silicon was not identified (Fig. 7). This zirconium rich area became more finely dispersed with increasing Z value.

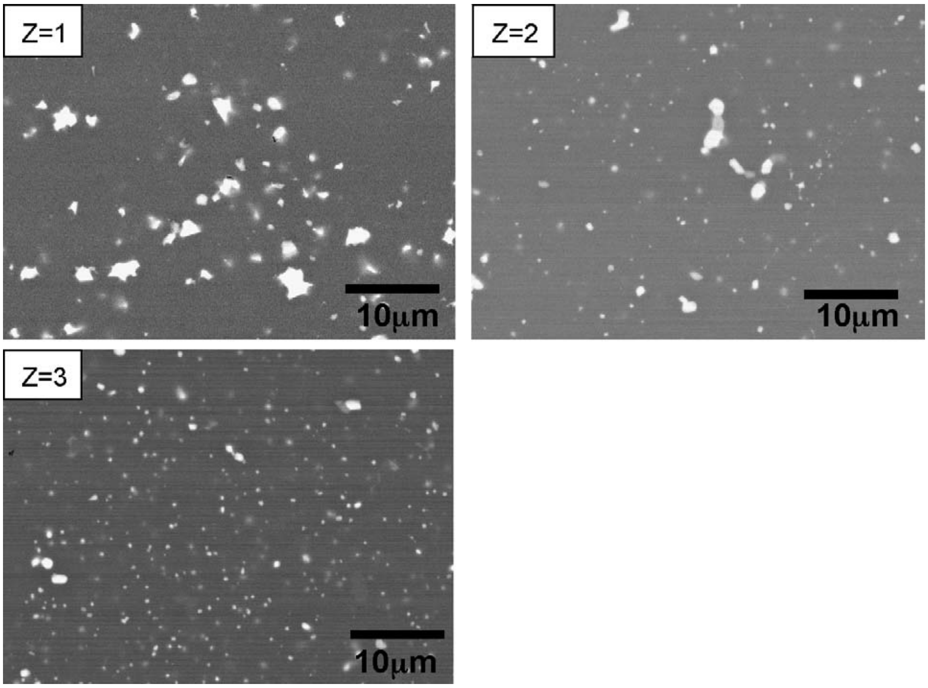

Fig. 6. Backscattered images of the fabricated ZrO_2 doped SiAlON.

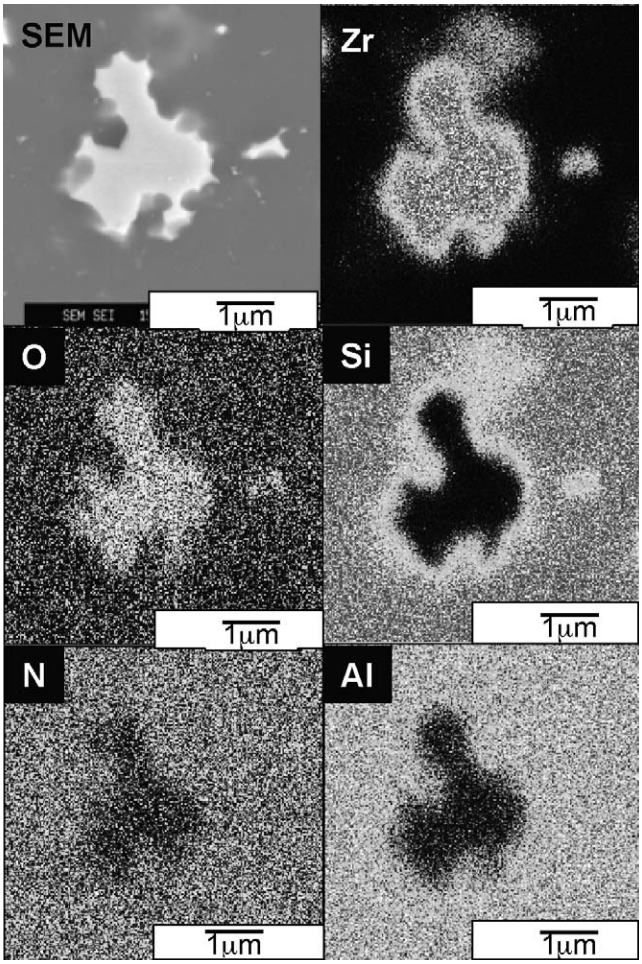

Fig. 7. EDS analysis result of the dispersed ZrO_2 compound in SiAlON ceramics.

Fig. 8 shows the fractured surfaces of the ZrO_2 added SiAlON ceramics. In the $Z = 1$ sample, elongated rod like grains were observed and the fracture morphology indicated intergranular fracture. According to an increase in the Z value, coarse grains were observed instead of the rod like grains and the fracture morphology changed from intergranular to intragranular fracture. The grain size was increased with increasing Z value. In addition, fine particles, which appear white in the SEM images, were present inside the SiAlON grains. The XRD analysis showed that after the reaction-bonding step ZrN phase was present in all samples. However, following the post-sintering process, this phase was not identified for the ZZ1 and ZZ2 samples. In a previous report, Si_3N_4 ceramics fabricated with ZrO_2 via a reaction-bonding route and post-sintering also showed the absence of the ZrN phase in the sintered bodies and the Zr related phases were present at the grain boundary like the formation of a grain boundary phase. It was shown that the ZrN phase reacted with SiO_2, and formed ZrO_2 phases with the evolution of N_2 and SiO_2 gases above 1673 K. In the present work, the ZrN phase was very fine and located inside the grains indicating that ZrN phase was incorporated in the SiAlON grains before being able to react with oxygen which was present in the grain boundary phase. The SEM results showed that grain size increased with increasing the Z values. This behavior is due to the fact that the Al_2O_3 rich SiAlON composition is easy to densify, and the growth of SiAlON grains is rapid. For the ZZ3 composition, the densification and grain growth is considered to occur rapidly such that the ZrN is trapped within the grains and cannot react with SiO_2. As result, in this sample the fine size ZrN particles were maintained and located inside the SiAlON grains.

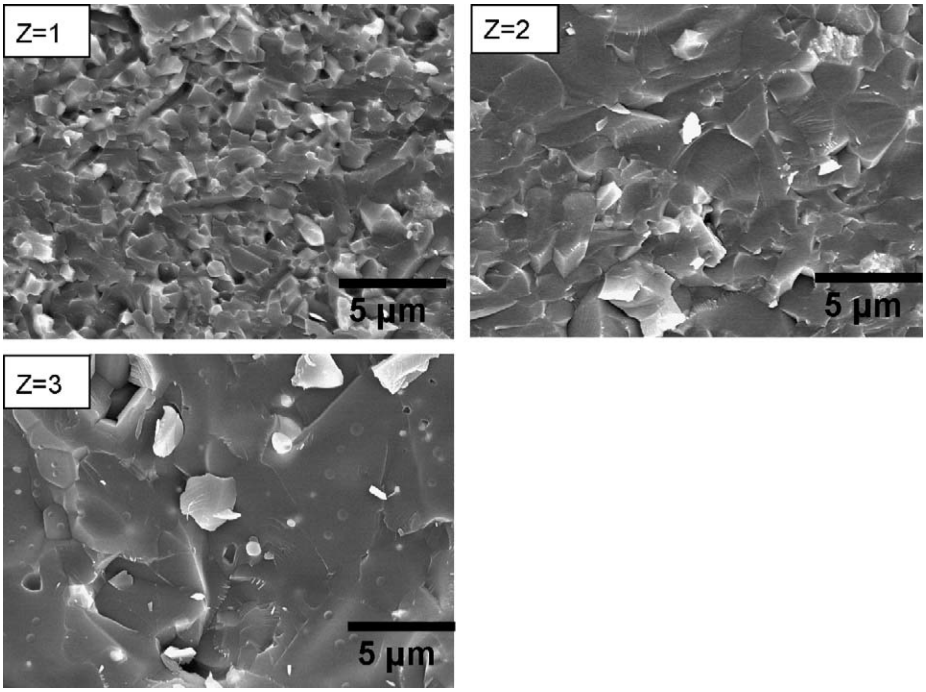

Fig. 8. Fractured surfaces of the fabricated ZrO_2 doped SiAlON ceramics.

4. Conclusion

A reaction-bonding and post-sintering process was applied to fabricate pressureless sintered (-$Si_{6-Z}Al_ZO_ZN_{8-Z}$ ($Z = 1$–3) ceramics with monoclinic ZrO_2 added to the starting powder. The ZrO_2 acts to both enhance the nitridation of Si, the same as the case of the fabrication of reaction bonded silicon nitride, and as a sintering additive for the densification of β-SiAlON without any other sintering additives.

The ZrO_2 was partially transformed to tetragonal ZrO_2 and ZrN during the nitridation stage. In the case of the low Z value SiAlONs the ZrN resorted back to ZrO_2 following the post-sintering process due to reaction with SiO_2. Grain growth increased with Z value and for the $Z = 3$ SiAlON composition, the ZrN formed during sintering was trapped inside the rapidly growing grains. This work has shown that the formation of dense, pressureless sintered β-SiAlON ceramics is possible using low cost powder and without the conventional rare earth sintering additives.

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