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Sintering of β-Sialon with 5 mol% Y_2O_3–ZrO_2 additives

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The sintering behaviour of β-Sialon composition powders with 5 mol% Y_2O_3–ZrO_2 additives at 1750° C for 1.5 h in nitrogen or argon atmospheres was studied. β-Sialon composition powders could be pressureless-sintered to about 93% theoretical density by the addition of 5 wt% 5 mol% Y_2O_3–ZrO_2. By HIPing the pressureless-sintered bodies the density was increased to higher than 98% theoretical density, and uniform submicrometre ZrO_2 particles were homogeneously dispersed in the β-Sialon matrix, resulting in an increase of fracture toughness, K_{1c}, from 5.1 to about 5.7 $MN\,m^{-1.5}$. Increasing the amount of tetragonal ZrO_2 transformable to monoclinic phase in the β-Sialon matrix increased K_{1c}.

1. Introduction

The composites of Si_3N_4 with ZrO_2 incorporated in the matrix are considered to be very promising materials with good mechanical properties and oxidation resistance. Several investigators [1–9] have reported that zirconia can be used as a sintering aid for Si_3N_4. However, addition of ZrO_2 alone is not effective in the sintering of Si_3N_4 due to the decomposition of Si_3N_4 with the easy formation of ZrN and/or Zr–O–N compounds and an insufficient amount of zirconium oxynitride liquid. When ZrO_2 is added to Si_3N_4 together with the other components, namely Al_2O_3 and Y_2O_3 as second additives, Si_3N_4 can be sintered or hot-pressed to high density. Dutta and Buzek [5] reported that Si_3N_4 with 10 wt% zyttrite (yttria-stabilized zirconia) as a sintering aid could be hot-pressed to full density and the room-temperature strength, creep and oxidation resistance of hot-pressed bodies were significantly higher than those of commercial materials. However, fracture toughness of the hot-pressed material which consisted of β-Si_3N_4 and a cubic ZrO_2 phase was not reported. It is well known that a suitable dispersion of t-ZrO_2 particles in composite materials improves fracture toughness. Claussen and Jahn [6] reported that the fracture toughness of Si_3N_4 sintered or hot-pressed with ZrO_2 and Al_2O_3 introduced through wear of alumina milling media increased with the increase of ZrO_2 volume up to a maximum, and has suggested that unstabilized ZrO_2 dispersions represent potential means for the development of thermal-shock resistant ceramics. Also, Lange [7] reported that the zirconium oxynitride phase, $ZrO_{2-2x}N_{4x/3}$ $(0.25 < x < 0.43)$, which was readily oxidized at 500° C to monoclinic ZrO_2, existed as a secondary phase in Si_3N_4 hot-pressed with 5 to 30 mol% ZrO_2. Therefore, a catastrophic surface compressive stress induced by the oxidation of the zirconium oxynitride phase would be developed in the matrix. Tjrnlund *et al.* [8] reported that the formation of ZrN could be suppressed or eliminated under controlled sintering conditions.

More recently, Sanders and Mieskowski [9] reported that Si_3N_4 could be sintered to 99% theoretical density with Y_2O_3–stabilized ZrO_2 additive by using a nitrogen pressure of 2.5 MPa and a temperature of 2140° C. Sintered bodies exhibited excellent high-temperature flexural strength, equal to hot-pressed Si_3N_4/ZrO_2 composite material. We have reported [10] that β-Sialon powders with 5 wt% additive of 3 mol% Y_2O_3–ZrO_2 could be sintered to dense bodies and the fracture toughness increased with an increase in the amount of tetragonal ZrO_2 transformable to monoclinic phase at the grain boundaries. The purpose of the present work was to investigate the effect of the amounts of sintering aid and sintering atmospheres on the pressureless sinterability of β-Sialon powders 5 mol% Y_2O_3–ZrO_2 and to evaluate the effect of HIPing treatment on density and mechanical properties.

2. Experimental details

Powder mixtures of the desired composition Si_3N_4, AlN, Al_2O_3 ZrO_2 and Y_2O_3 were ball-milled for 4 h in a plastic bottle with alumina balls in isopropanol. The composition of $z = 1$ in β-Sialon, $Si_{6-z}Al_zO_zN_{8-z}$, was selected on the basis of the results of preliminary work. 5 mol% Y_2O_3–ZrO_2 powder was prepared from $Y(NO_3)_3$ and ZrO_2. After drying at 140° C, the powders were uniaxially pressed into discs of 13 mm diameter, and then isostatically pressed under 300 MPa. The compacts were pressureless-sintered at 1750° C for times up to 3 h under nitrogen or argon atmospheres in a BN crucible. A protective powder bed, which consisted of mixtures of BN powder and powder of identical compositions with the compacts, was used to suppress the decomposition of Si_3N_4 at elevated temperatures. Some sintered bodies were further hot-isostatically pressed at 1750° C for 1.5 h under an argon gas pressure of 200 MPa. Density was

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TABLE I Effects of amount of additives and sintering atmosphere on sinterability* of β-Sialon and properties of sintered bodies

5 mol % Y_2O_3–ZrO_2 (wt %)	Atmosphere	Density (%)	Wt loss (%)	ZrN†	H_v (GPa)	K_{Ic} ($MN\,m^{-1.5}$)
0	N_2	~68	3.97		–	–
5	Ar	92.1	1.88	○	11.3	4.7
	N_2	92.7	9.20	×	11.7	5.1
10	Ar	90.6	0.80	○	11.2	–
	N_2	90.9	2.29	×	11.0	–

*at 1750° C for 1.5 h

†○, formation: ×, little or no formation.

measured by the Archimedes method. The phases of as-sintered and polished surfaces were identified by X-ray diffraction. Vickers hardness, H_v, and fracture toughness, K_{Ic}, were measured using the indentation technique by applying 20 kgf for 15 sec [11]. The microstructure was characterized by SEM and electron probe microanalysis (EPMA).

3. Results and discussion

3.1. Effect of 5 mol % Y_2O_3–ZrO_2 additives on the sinterability of β-Sialon

The effect of 5 mol % ZrO_2–Y_2O_3 additives on the sinterability of β-Sialon composition powder and the properties of pressureless sintered bodies is shown in Table I. β-Sialon, $Si_{6-z}Al_zO_zN_{8-z}$, with the composition of $z = 1$, showed relatively high sinterability, compared with other z values in the β-Sialon series. A specimen with the composition of $z < 1$ showed poor sinterability because of an insufficient amount of liquid phase, while one with the composition of $z > 1$ showed greater weight loss, resulting in decrease in the density. Therefore, the composition of $z = 1$ in β-Sialon was selected as suitable for pressureless-sintering. Without any additive, β-Sialon composition powders could not be densified. β-Sialon with 5 mol % ZrO_2–Y_2O_3 additives can be sintered to higher than 90% theoretical density. Sintered bodies with 5 wt % additive showed a higher density than those with 10 wt % additive. The weight loss during the sintering depended strongly on sintering atmospheres; that is, weight loss tends to increase on sintering in a nitrogen atmosphere instead of an argon atmosphere. The formation of ZrN film was observed on the surfaces of the specimens sintered in an argon atmosphere, but not in a nitrogen atmosphere. Higher sintering temperatures or longer sintering times caused a greater weight loss and the formation of larger amounts of ZrN. The formation of ZrN was considered to take place by the following reaction

$$\tfrac{1}{3}Si_3N_4 + \tfrac{1}{2}ZrO_2 \rightarrow SiO(g) + \tfrac{5}{12}N_2 + \tfrac{1}{2}ZrN \quad (1)$$

The equilibrium partial pressure of the gas phases in this reaction is related to the free energy change, $-\Delta G$, by

$$-\Delta G = RT \ln (P_{SiO} P^{5/12}) \qquad (2)$$

Thus, the reaction rate would be dependent on the partial pressures of SiO gas and nitrogen gas. It turns out that ZrN formed more easily in argon than in a nitrogen atmosphere. This ZrN film was assumed to prevent further decomposition of β-Sialon by suppressing the vaporization of SiO gas and nitrogen gas from the interior of the sintered bodies. In these sintered β-Sialon bodies with ZrO_2–Y_2O_3 additive, the formation of the zirconium oxynitride phase, $ZrO_{2-2x}N_{4x/3}$ as reported by Lange [7], was not detected. This phase was also reported by Vasilos *et al.* [12] in hot-pressed Si_3N_4 materials with 10 and 20 wt % additions of commercial cubic ZrO_2. Whether the zirconium oxynitride phase forms or not may be related to sintering temperature and also Y_2O_3 content. Furthermore, a HIPing treatment was carried out to examine the effect on density and to evaluate the microstructure of the matrix. The results were shown in Table II.

By HIPing the sintered bodies with 5 wt % additive, the density increased to higher than 98% theoretical density. On the other hand, in 10 wt % addition the density is almost the same as that of pre-HIPed bodies and 10 wt % addition seems to facilitate the decomposition rather than the densification. The phases of as-sintered and polished specimens were examined by XRD analysis. In the sintered β-Sialon bodies, tetragonal and monoclinic ZrO_2 were identified. The ratio of tetragonal phase to monoclinic phase was found to decrease by coarse grinding, which means

TABLE II Effect of HIPing treatment of sintered bodies on density and mechanical properties

5 mol % Y_2O_3–ZrO_2 (wt %)	PreHIPing atmosphere	HIPed at 1750° C for 1.5 h at 200 MPa under Ar						
		Density (%)	Wt loss (%)	XRD*			H_v (GPa)	K_{Ic} ($MN\,m^{-1.5}$)
				β	t	m		
5	Ar	98.2	0.4	83	8	tr.	15.4	4.0
	N_2	98.5	0.2	58	5	3	15.7	5.7
10	Ar	91.8	0.7	53	9	4	12.2	–
	N_2	90.0	0.5	49	11	5	10.0	–

*Peak height of XRD profiles taken from polished surfaces of HIPed β-Sialon bodies, t = tetragonal, m = monoclinic, tr = trace.

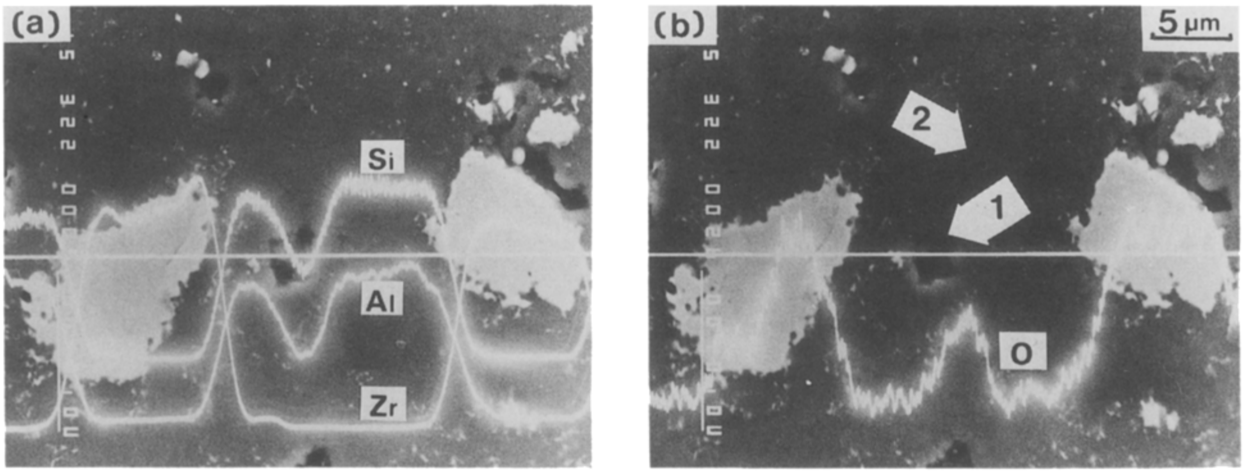

Figure 1 EPMA micrographs of polished surfaces of pressureless-sintered β-Sialon bodies with 5 wt % additive.

that the tetragonal ZrO_2 in the matrix can be transformed to monoclinic phase.

3.2. Microstructure

Fig. 1 shows EPMA micrographs of the polished surface of pressureless-sintered bodies with 5 wt % additive. Large ZrO_2 particles, larger than 10 μm, as well as submicrometre ZrO_2 particles were observed in sintered bodies, along with pores and the segregation of ZrO_2 particles. Also, the dark area shown by arrow 1 in Fig. 1b contained impurities such as iron, calcium, potassium, sodium etc. and seems to be a glassy phase. On the other hand, these impurities were not detected in the matrix region shown by arrow 2. Fig. 2 shows scanning electron micrographs of HIPed β-Sialon with 5 mol % Y_2O_3–ZrO_2 additive. In the case of 5 wt % addition, the segregation of large ZrO_2 particles disappeared after the HIPing process and submicrometre ZrO_2 particles were uniformly dispersed in the matrix. This result suggests that the further dissolution–reprecipitation of ZrO_2 took place during HIPing at 1750° C, although the HIPing could retard the dissolution–reprecipitation process by increasing the viscosity of oxynitride liquid. In the case of 10 wt % addition, pores and segregation were still observed. This may be due to the decomposition of excess liquid phase existing during HIPing.

The compositions of sintered β-Sialon bodies

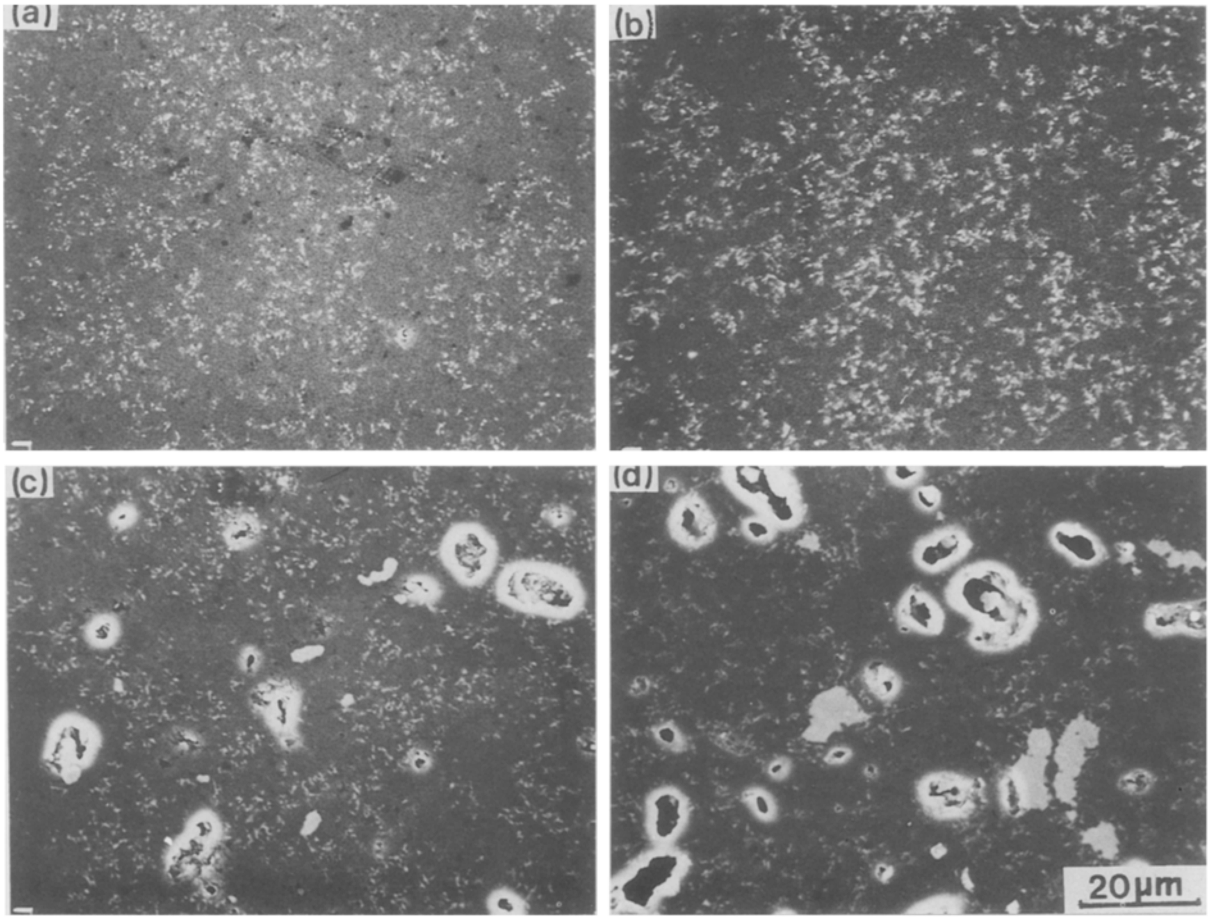

Figure 2 Scanning electron micrographs of polished surfaces of HIPed β-Sialon bodies. (a) 5 wt %, argon; (b) 5 wt %, nitrogen; (c) 10 wt %, argon; (d) 10 wt %, nitrogen.

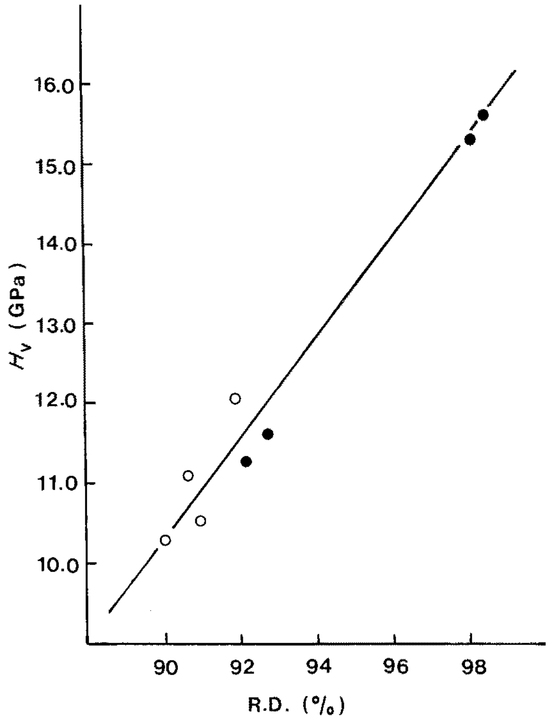

Figure 3 Vickers hardness of β-Sialon bodies as a function of relative density. (●) 5 wt %, (○) 10 wt %.

depended on the pressureless-sintering atmosphere. By EPMA technique, the composition of β-Sialon tered in an argon atmosphere was confirmed to be almost the same as that of original starting powder mixture ($z = 1$). However, the composition of β-Sialon sintered in a nitrogen atmosphere changed from the original composition, that is, the atomic ratio of Si to Al is 5.8 : 1, which showed the value of $z < 1$.

3.3. Mechanical properties

The pressureless-sintered bodies with 5 wt % additive exhibited H_v higher than 11 GPa and K_{Ic} higher than 4 MN m$^{-1.5}$, while those with 10 wt % additive showed

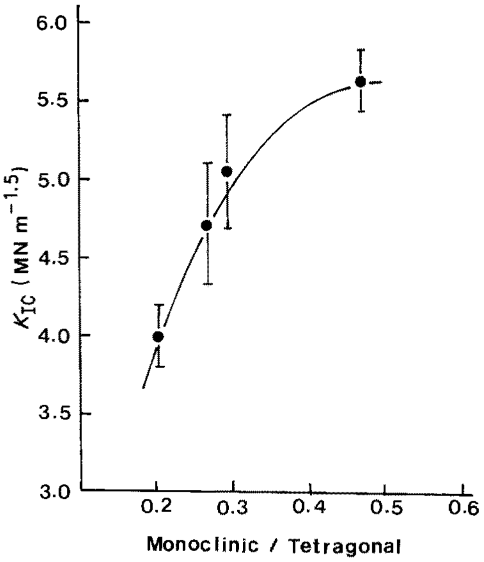

Figure 4 Fracture toughness of β-Sialon bodies as a function of the ratio of monoclinic to tetragonal ZrO_2 calculated from XRD profiles on the polished surfaces of sintered bodies.

somewhat lower H_v and higher K_{Ic}, as shown in Table I. Furthermore, by HIPing the pressureless-sintered bodies with 5 wt % additive, the values of H_v and K_{Ic} increased significantly from 11.7 GPa and 5.1 MN m$^{-1.5}$ to 15.7 GPa and 5.7 MN m$^{-1.5}$, respectively. On the other hand, in 10 wt % addition the values of H_v and K_{Ic} did not change significantly, as shown in Table II. The hardness, H_v, of sintered bodies depended strongly on the density, as shown in Fig. 3 and increased proportionally with the increasing density. However, the fracture toughness, K_{Ic} did not depend on the density, and was appreciably influenced by the distribution state of ZrO_2 particles. The tetragonal ZrO_2 in the sintered body can be transformed to monoclinic phase on fracturing or polishing the sintered body. In this study, X-ray diffraction

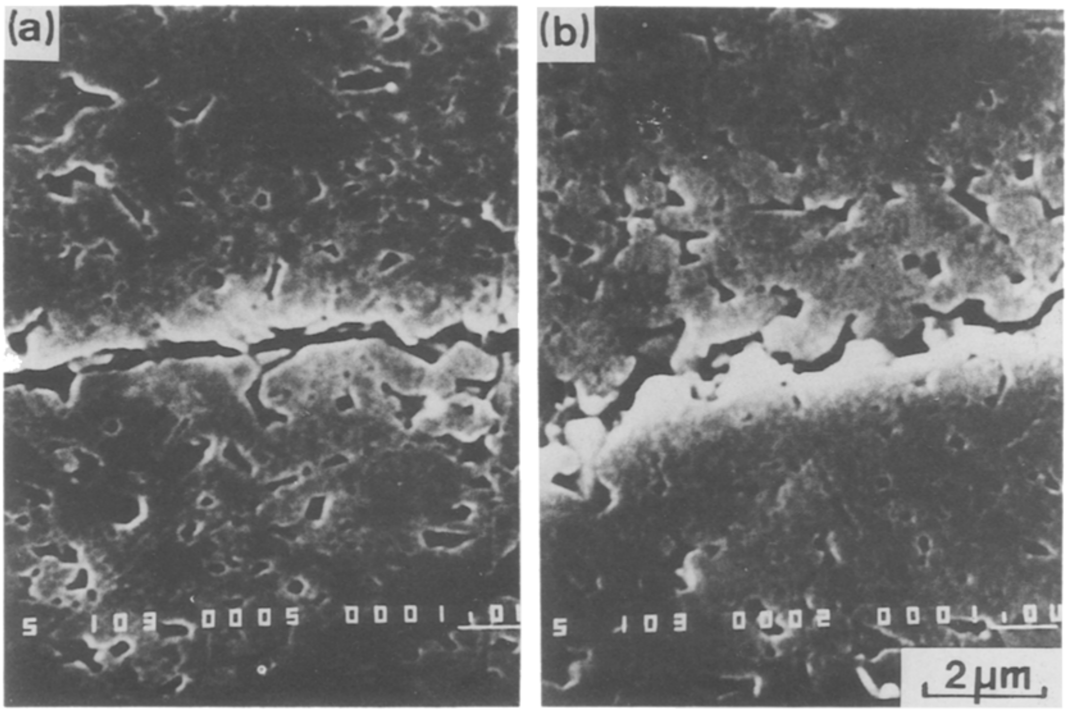

Figure 5 Scanning electron micrographs of cracks propagated by Vicker's indentation. (a) $K_{Ic} = 2.8$ MN m$^{-1.5}$, (b) $K_{Ic} = 5.7$ MN m$^{-1.5}$.

(XRD) analysis was done on polished surfaces to elucidate the transformation of ZrO_2, which might act as a toughening aid of β-Sialon. Fig. 4 shows the values of K_{Ic} plotted against the ratio of monoclinic to tetragonal phase calculated from the peak height ratio of XRD profiles taken from the polished surface of sintered bodies. K_{Ic} increased with an increase of the ratio of monoclinic to tetragonal phase, which corresponds to the ease of transformation of ZrO_2 in the original sintered body with the stress induced by polishing. By polishing the specimen, the decrease in the tetragonal ZrO_2 peak and the corresponding increase in the monoclinic ZrO_2 reflection took place, indicating that transformation toughening can indeed be operative in this material. The increase of this ratio, that is, the increased amount of tetragonal ZrO_2 particles with effective particle size which can be readily transformed into the monoclinic phase by polishing, can be found to lead to the increase of K_{Ic}. In this case, the compressive stress due to the volume change also might be helpful in increasing of K_{Ic}.

Fig. 5 shows scanning electron micrographs of the cracks propagated by Vicker's indentation. The specimen with higher K_{Ic} exhibited a greatly deflected crack which indicated the energy release for crack propagation, compared with the specimen with low K_{Ic} value.

4. Conclusions

Sintering of β-Sialon composition powders with 5 mol % Y_2O_3–ZrO_2 additives was studied and the following results were obtained.

1. Y_2O_3-doped ZrO_2 is a very effective sintering aid for β-Sialon. β-Sialon powder can be pressureless-sintered to about 93% theoretical density by using 5 mol % Y_2O_3–ZrO_2 additive.

2. By subsequent HIPing, the density of sintered bodies with 5 wt % additive could be increased to higher than 98% theoretical density, and submicrometre ZrO_2 particles were homogeneously dispersed in the β-Sialon matrix, resulting in an increase of fracture toughness, K_{IC}, from 5.1 to about 5.7 MN m$^{-1.5}$.

3. The higher amount of tetragonal ZrO_2 transformable to monoclinic ZrO_2 with the stress induced by polishing can be found to lead a higher K_{Ic} of sintered β-Sialon.

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