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Influence of additive content on the anisotropy in hot-pressed Si_3N_4 ceramics using grain orientation measurements

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Abstract

The influence of additive content on the microstructure and its mechanical properties in planes parallel and normal to the hot-pressing axis of Si_3N_4 ceramics has been investigated by direct measurement of the grain orientation from SEM micrographs and orientated Vicker's indentations. It is shown that an increasing additive content leads to a microstructure with grains of higher aspect ratios, resulting in an increase of the fracture toughness. Furthermore, the difference in mechanical anisotropy between the planes parallel and normal to the hot-pressing directions is gradually reduced with increasing additive content, due to the smaller degree of orientation of the elongated β-Si_3N_4 grains in the plane parallel to the hot-pressing direction.

Keywords: A. Hot pressing; D. Si_3N_4; Anisotropy; Characterization; Fracture toughness

1. Introduction

One key issue of high quality and reliable structural Si_3N_4-based ceramics is a high fracture toughness which can be achieved by the combination of several factors such as: use of high quality starting powders, optimization of the processing parameters thus reducing the frequency and the size of defects, the production of grains with high aspects ratios and control of the interfacial bonding strength between the β-Si_3N_4 grains and the intergranular phase [1–3]. Improvement of the aforementioned parameters led to Si_3N_4 ceramics which routinely exhibit fracture toughness values higher than 6 MPa $m^{1/2}$. More recently, Becher et al. [4] and Kanzaki et al. [5] achieved even higher fracture toughness by adding small quantities of β-Si_3N_4 to the starting powder mixtures, acting as seeds, to facilitate the α- to β-Si_3N_4 phase transformation and resulting in large β-Si_3N_4 grains of high aspect ratio embedded in a matrix of smaller β-Si_3N_4 grains, that produced high fracture toughness, around 9–10 MPa $m^{1/2}$.

The high fracture toughness of Si_3N_4-based ceramics is the result of their microstructure, consisting of high aspect ratio β-Si_3N_4 grains, difficulting the crack-propagation principally by the crack bridging and crack deflection mechanisms [6–11]. According to these studies, fracture toughness increases with increasing aspect ratio and volume content of these grains.

One of the principal aspects affecting Si_3N_4 ceramics produced by hot-pressing is the microstructural anisotropy of these materials [12–14]. These microstructural variations lead to anisotropic mechanical properties, due to the preferential orientation of the elongated β-Si_3N_4 grains perpendicular to the hot-pressing direction [12,13], which in some cases results in a variation of up to 50% in the fracture toughness in the directions longitudinal and transversal to the hot-pressing axis [15].

In the present work, fracture toughness has been determined by the crack length of Vicker's indentations [16]. The variation of the fracture toughness due to the anisotropy of the hot-pressed Si_3N_4 ceramics has been investigated in planes parallel and normal to the hot-pressing direction, using different indentation angles. The results are presented in relation to the additive content. Furthermore, this work emphasizes the determination of the anisotropy by simple, direct and reliable observation technique of the grains orienta-

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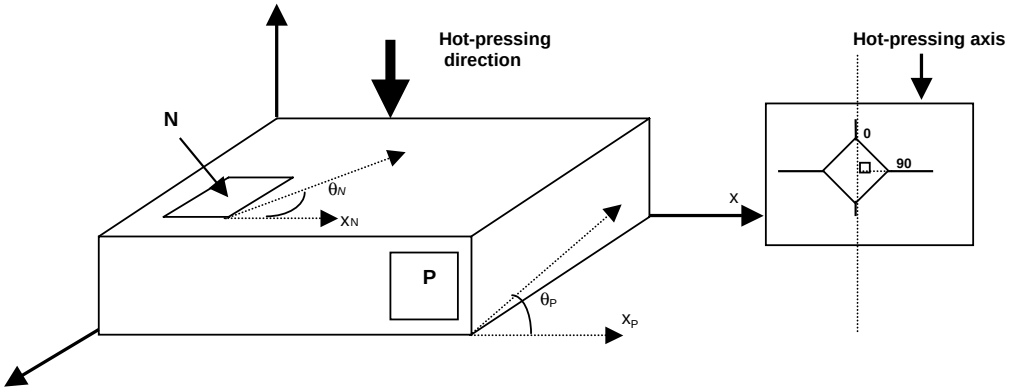

Fig. 1. Schematic figure of toughness anisotropy measurements by oriented Vicker's indentations in an uniaxially hot-pressed specimen. Two different planes were analyzed in the experiments: (i) crack plane normal to the hot-pressing direction (N) and (ii) parallel to the hot-pressing direction (P). θ_N, grain orientation angle related to the N plane; θ_P, grain orientation angle related to the P plane. (Based on refs. [10] and [16].)

tion in planes parallel and perpendicular to the hot-pressing axis, evaluating also grain size and grain morphology, correlating these results with mechanical properties.

2. Experimental procedure

Commercial α-Si_3N_4 (H.C. Starck, LC-12), Al_2O_3 (Baikalox, CR-6), and a mixed concentrate of yttrium and rare earth oxides, CRE_2O_3, produced at DEMAR-FAENQUIL, were used as starting powders. Previous works [17–19] have shown that the yttrium–rare earth oxide mixture, CRE_2O_3, is a solid solution consisting mainly of Y_2O_3 (44%), Yb_2O_3 (17%), Er_2O_3 (14%) and Dy_2O_3 (10%), and is an effective and cheap substitute for pure Y_2O_3 as sintering additive for Si_3N_4 ceramics, presenting similar sinterability and mechanical properties at room temperature. The total additive content was varied between 5 and 20 vol.%, maintaining a relationship of 60 mol% of Al_2O_3 and 40 mol% CRE_2O_3.

Powder batches were produced by ball milling for 2 h using ethanol as milling media. After mixing, the powder batches were dried first in a rotary evaporator and subsequently in an oven at 120 °C for 12 h. Prior to hot-pressing the powder mixtures were sieved through a 60 mesh screen. Hot-pressing was done at 1750 °C for 30 min under a pressure of 20 MPa in nitrogen atmosphere, obtaining sintered specimen of approximately 20 mm diameter and 7 mm height.

The theoretical density of the samples was calculated according to the rule of mixtures and the final density after hot-pressing was measured by the immersion method in distilled water, using Archimedes' principle. The phase composition of the hot-pressed samples has been determined by X-ray diffraction, and the amount of phase transformation of α- to β-Si_3N_4 was evaluated by the method proposed by Gazarra et al. [20]. For microstructural analysis by scanning electron microscopy (SEM) the hot-pressed specimens were cut and polished, and the surface was etched by a molten mixture of NaOH and KOH in the proportion 1:1 at 500 °C during 1 to 3 min depending on the intergranular phase content.

The grain size distributions and aspect ratios were determined using the method proposed by Wötting et al. [2], based on the grains width and length measurements from SEM micrographs of polished sections perpendicular (normal—N) to the hot-pressing direction at 10,000× magnification. This method depends on the statistic consideration that about 10% of the grains are cut parallel to their crystallographic *c*-axis and therefore show the realistic length and width of the elongated, rod-like β-Si_3N_4 grains. The average grain size is the mean value of 10% of the highest grain lengths observed, and by the length–width ratio of these grains the average aspect ratio has been determined.

Between 1000 and 1200 grains were measured using the software by LEICA Qwin-Image Processing and Analysis System for analysis, in order to obtain the average width, length and orientation of the grains. This orientation of the grains was evaluated by determining the angle θ between the *c*-axis of the β-Si_3N_4 grains and the *x*-axis of the planes normal and parallel to the hot-pressing direction, see Fig. 1.

The hardness and fracture toughness were determined by Vicker's indentations [13–16], under an indentation load of 2 kg, for 30 s, in planes parallel (P) and normal (N) to the hot-pressing direction, as illustrated in Fig. 1. In plane P the toughness anisotropy was measured by aligning the two axes of the Vicker's indenter at angles of 0 and 90° in regard to the hot-pressing direction [12]. Twenty-one indentation measurements have been made for each value measured. Like this, the mean values and the standard deviation of the means are determined.

3. Results and discussion

3.1. Phase analysis and final density

The phase analysis of the hot-pressed specimen by X-ray diffraction (XRD) revealed only the presence of β-Si_3N_4 for

Table 1
Microstructural characteristics of hot-pressed specimen (plane N)

Composition	Final relative density (%)	Average grain size (μm)	Planar grain density (no. of grains per μm^2)	Aspect ratio
Si_3N_4 + 5 vol.% Al_2O_3/CRE_2O_3	98.2 ± 0.3	2.5 ± 0.8	1.28	6.5 ± 1.1
Si_3N_4 + 10 vol.% Al_2O_3/CRE_2O_3	98.5 ± 0.2	2.9 ± 0.9	1.20	9.5 ± 1.4
Si_3N_4 + 15 vol.% Al_2O_3/CRE_2O_3	98.6 ± 0.1	3.6 ± 1.0	1.01	10.1 ± 1.4
Si_3N_4 + 20 vol.% Al_2O_3/CRE_2O_3	98.0 ± 0.2	4.1 ± 1.0	0.87	11.2 ± 1.5

all compositions studied, indicating that the α- to β-Si_3N_4 transition has been completed and, furthermore, that the additives formed an amorphous intergranular phase.

The relative densities of the samples after hot-pressing presented values higher than 98% for all compositions.

3.2. Microstructure

During liquid-phase sintering of Si_3N_4 ceramics, the α-Si_3N_4 grains dissolve in the liquid phase and precipitate in the form of elongated, hexagonal β-Si_3N_4 grains. The morphology (aspect ratio) depends to a large degree on the additives used and their quantity, under otherwise identical conditions (time, temperature, etc.). The results of the microstructural analysis of the hot-pressed samples of plane N, normal to the hot-pressing direction, are summarized in Table 1; listing the average grain sizes, the planar grain density, defined as number of grains per area, and the aspect ratio of the β-Si_3N_4 grains.

Besides the mean grain size listed in Table 1, Fig. 2 shows the cumulative grain size distributions of the β-Si_3N_4 grains for the four compositions studied with 5, 10, 15 and 20 vol.% of additives.

It is well known that the anisostropic growth of β-Si_3N_4 grains is related to the different growth rate on the basal plane and the lateral planes of the hexagonal β-Si_3N_4 prism. This behavior results in the atomic roughness difference between basal and lateral plane of the β-Si_3N_4 grains. In these grains, the *c*-direction are not faceted, present higher roughness that prismatic planes (faceted). Like this, the growth rate in the *c*-axis is higher that in the *a*-axis, which leads to the anisotropic growth of these grains [22–24]. During hot-pressing, this effect of preferential grain growth is further enhanced by the applied pressure [25], resulting in grains of even higher aspect ratios, as shown in Table 1.

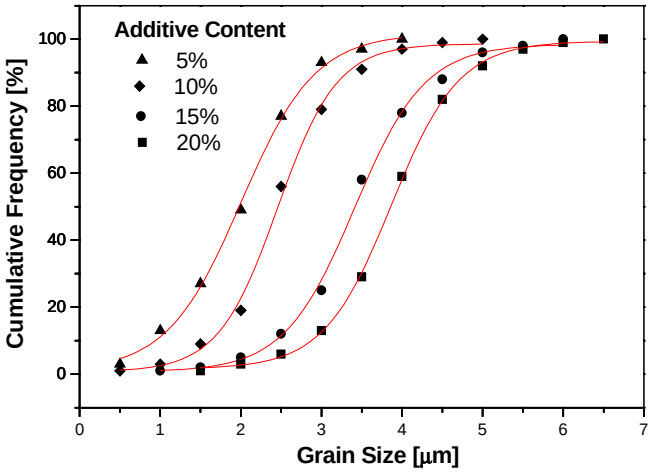

Fig. 2. Cumulative grain size distributions as function of the additive content.

Furthermore, it can be observed that with increasing additive content larger grains are produced, due to the smaller degree of steric hinderance. In consequence, the planar grain density decreases with increasing additive content, as confirmed by the results listed in Table 1 and illustrated in Fig. 3. Furthermore, it can be observed that the aspect ratios of the β-Si_3N_4 grains increase with increasing additive content, from 6.5 to 11.2 for 5 and 20 vol.% additives, respectively, see Fig. 4. This result is explained by the higher grain growth velocity of the β-Si_3N_4 grains along their *c*-axis, when compared to the *a*- and *b*-axis, consistent with the work of Lee and Bowman [12].

In order to evaluate the anisotropy of the microstructure of these hot-pressed samples, the angles between the *c*-axis of the β-Si_3N_4 grains and the planes normal (θ_N) and parallel (θ_P) to the hot-pressing direction have been determined, as illustrated in Fig. 1. For a random orientation of the grains, the average angle should be 45° and the theoretical standard deviation 25.98°. The experimental results are summarized in Table 2, and shown graphically in Fig. 5. As can be observed, the grains in the plane normal to the hot-pressing direction are distributed randomly in respect to their orientation, resulting in angles θ_N near 45° for all compositions studied, independently of the additive content.

On the other hand, in the plane parallel to the hot-pressing direction an alignment of the grains is observed, reflected by the angle θ_P, inferior to 45° as expected for a random orientation. The angles θ_P rise gradually with increasing additive

Table 2
Orientation of grains in planes normal and perpendicular to the hot-pressing direction

Composition	Grains angle (θ)	
	$\theta_{(N)}$ (N plane) (°)	$\theta_{(P)}$ (P plane) (°)
Si_3N_4 + 5 vol.% Al_2O_3/CRE_2O_3	43.3 ± 24.1	12.9 ± 14.0
Si_3N_4 + 10 vol.% Al_2O_3/CRE_2O_3	46.4 ± 23.5	25.9 ± 19.6
Si_3N_4 + 15 vol.% Al_2O_3/CRE_2O_3	44.9 ± 23.4	29.5 ± 21.2
Si_3N_4 + 20 vol.% Al_2O_3/CRE_2O_3	44.5 ± 20.8	35.1 ± 23.5

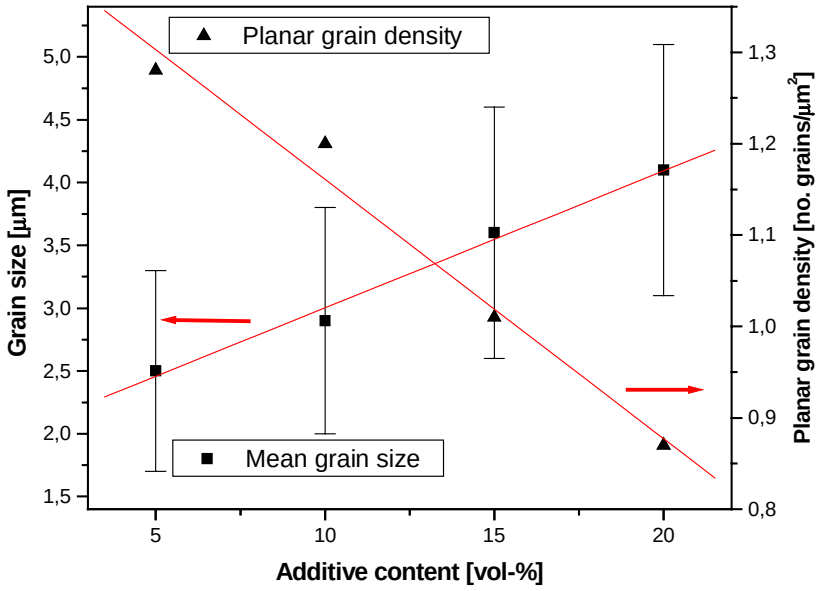

Fig. 3. Mean grain size and planar grain density as function of the additive content.

content, see Fig. 5, from 12.9 to 35.1° for an additive content of 5 and 20 vol.%, respectively, indicating a decreasing degree of orientation. This observation is further sustained by the increasing values of the standard deviation of the angle θ_P. The alignment is less pronounced for higher additive contents, as can be clearly seen from Fig. 5, with a tendency towards random orientation, i.e. isotropic microstructure, for higher amounts of intergranular phase.

The alignment of the β-Si_3N_4 grains during hot-pressing is known to the result of pressure gradients in planes parallel and perpendicular to the hot-pressing axis [12–26]. Therefore, the grains with *c*-planes perpendicular to the hot-pressing direction grow preferably. An X-ray diffraction technique comonly used to determine the anisotropy in planes parallel and perpendicular to the hot-pressing direction is based on the ratio of the peak areas between the (1 0 1) and (2 1 0) planes of the β-Si_3N_4 grains [12,26]. This technique has been shown to be very useful when analyzing the grain orientation of Si_3N_4 ceramics with similar morphological characteristics, i.e. same aspect ratio and same average grain size. However, Si_3N_4 ceramics sintered with different additive contents exhibit distinct morphological characteristics, turning this method unsuitable for a comparative analysis of the anisotropy of these materials. Therefore, we chose the direct determination of the grain orientation from SEM micrographs to evaluate quantitatively the microstructural anisotropy.

The results shown in Fig. 5 indicate that higher additive contents result in a decreasing difference between the average angles of the orientation in planes perpendicular (θ_N)

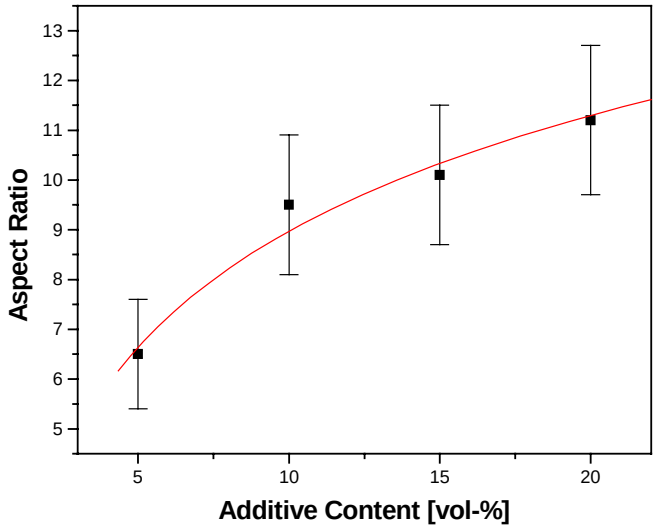

Fig. 4. Aspect ratio as function of the additive content.

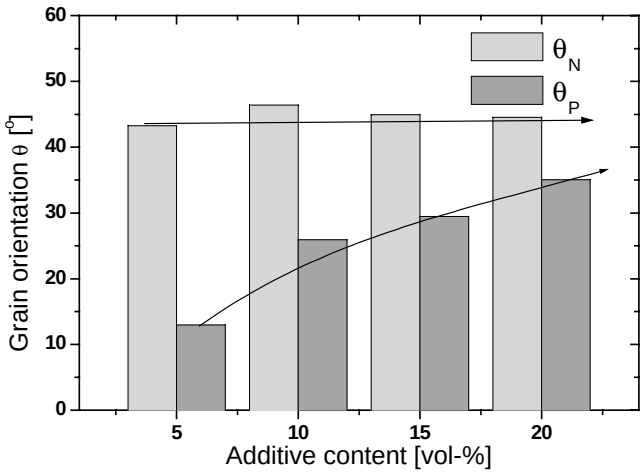

Fig. 5. Grain orientation as function of the additive content. θ_N, average grain angle in the N plane; θ_P, average grain angle in the P plane.

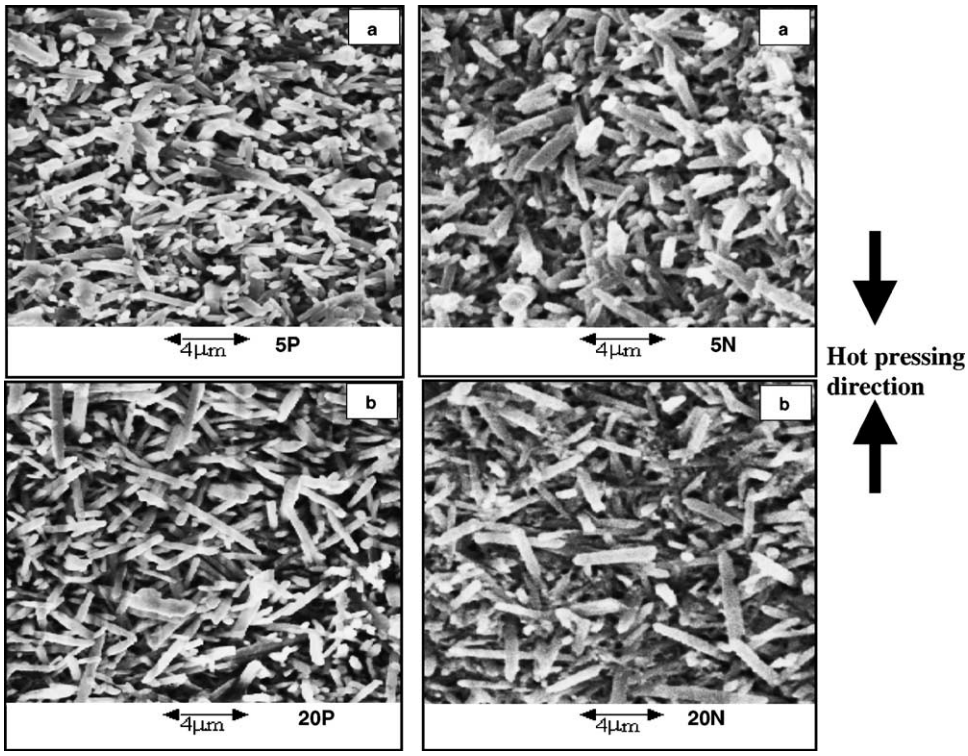

Fig. 6. Scanning electron micrographs of surfaces parallel (P) and normal (N) to the hot-pressing axis for (a) 5 vol.% and (b) 20 vol.% additives.

and parallel (θ_P) to the hot-pressing direction, as schematically shown in Fig. 1. This observation is in aggreement with a possible grain rotation during hot-pressing as proposed by Yoon et al. [26] and steric hinderance effects. Higher additive contents result in enhanced growth velocities and at the same time in a lesser degree of steric hinderance. Furthermore, we suggest that with increasing additive contents rotation of grains at contact can take place more easily, and, consequently result in a smaller degree of anisotropy. These findings are document by the micrographs shown in Fig. 6 and illustrated in Fig. 7 for samples containing 5 and 20 vol.% additives.

3.3. Mechanical properties

The results of the Vicker's hardness, fracture toughness and its standard deviations, determined on the plane N, normal to the hot-pressing direction are summarized in Table 3.

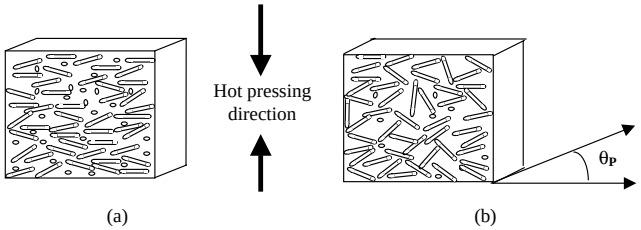

Fig. 7. Schematic orientation of β-Si_3N_4 grain growth in Si_3N_4 hot pressed, in plane parallel to the hot-pressing axis: (a) 5 vol.%; (b) 20 vol.%.

As can be seen, the hardness decreases gradually with increasing additive content, because of the inferior hardness of the amorphous intergranular phase. This affirmation is supported by fact that, in all compositions (5–20 vol.% of Al_2O_3/CRE_2O_3), no solid solution Si_3N_4 (SiAlON) are formed and the intergranular phase composition is not considerably altered. Like this, the increase of the additive content leads to the increase of the intergranular phase content and, consequently, to the decrease of the β-Si_3N_4 fraction in the mixture.

The fracture toughness increases with increasing additive content, consistent with the observation that increasing additive contents result in larger grains with higher aspect ratios, see Table 1, causing a higher degree of crack deflection and therefore higher toughness. No dependency of the fracture toughness on the orientation of the indentation mark has been found, signifying that plane N is isotropic in regard to the propagation of cracks, consistent with the random orientation of grains in this plane as shown in Table 2 and Fig. 5.

The results of the hardness measurements, fracture toughness and standard deviation, obtained by Vicker's

Table 3
Hardness and fracture toughness (plane N)

Composition	Hardness (GPa)	K_{IC} (MPa m$^{1/2}$)
Si_3N_4 + 5 vol.% Al_2O_3/CRE_2O_3	16.28 ± 0.32	5.9 ± 0.2
Si_3N_4 + 10 vol.% Al_2O_3/CRE_2O_3	15.83 ± 0.29	6.0 ± 0.2
Si_3N_4 + 15 vol.% Al_2O_3/CRE_2O_3	15.12 ± 0.24	6.3 ± 0.3
Si_3N_4 + 20 vol.% Al_2O_3/CRE_2O_3	14.96 ± 0.35	6.5 ± 0.3

Table 4
Planar grain density, hardness and fracture toughness (plane P)

Composition	Planar grain density (no. of grains/μm^2)	Hardness (GPa)	Fracture toughness K_{IC} (MPa $m^{1/2}$)			
			0°	90°	Average	K_{IC} difference 0–90° (%)
Si_3N_4 + 5 vol.% Al_2O_3/CRE_2O_3	1.85	15.86 ± 0.28	6.6 ± 0.5	5.2 ± 0.2	5.9	26.9
Si_3N_4 + 10 vol.% Al_2O_3/CRE_2O_3	1.63	15.55 ± 0.15	6.5 ± 0.4	5.6 ± 0.4	6.1	16.1
Si_3N_4 + 15 vol.% Al_2O_3/CRE_2O_3	1.23	14.68 ± 0.24	6.4 ± 0.4	5.8 ± 0.4	6.1	10.3
Si_3N_4 + 20 vol.% Al_2O_3/CRE_2O_3	1.12	14.15 ± 0.24	6.2 ± 0.4	5.9 ± 0.3	6.1	5.1

indentation in plane P, separated into orientations of 0 and 90° in relation to the hot-pressing direction are listed in Table 4. As observed for plane N, the hardness also decreases with increasing additive content in plane P, because of the intergranular phase increase and consequently, reduction of the β-Si_3N_4 fraction in the matrix. On the other hand a strong dependency of the fracture toughness on the direction in the plane P has been observed. For the direction parallel to the hot-pressing direction (0°), crack growth is effectively inhibited because of the preferential orientation of the elongated β-Si_3N_4 grains at approximately 90°. For the other direction of 90°, substantially lower fracture toughness values have been measured. The fracture toughness determined for the two directions differs up to 27% for the composition with the lowest additive content of 5 vol.% and gradually diminishes with increasing additive content to approximately 5% for samples with 20 vol.% additives as shown in Fig. 8, because of the decreasing degree of grains orientation in this plane. Two examples of the dependency of crack length on orientation are shown in Fig. 9 for specimen with 5 and 20 vol.% of additives.

The hardness and average fracture toughness values of plane P are inferior to those determined for plane N, probably because of the smaller planar grain density of plane P in relation to plane N.

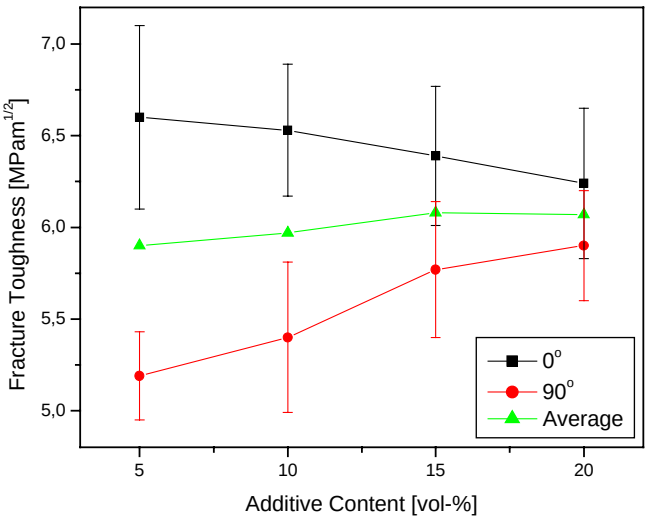

Fig. 8. Anisotropy of fracture toughness (plane P) in relation of additive content.

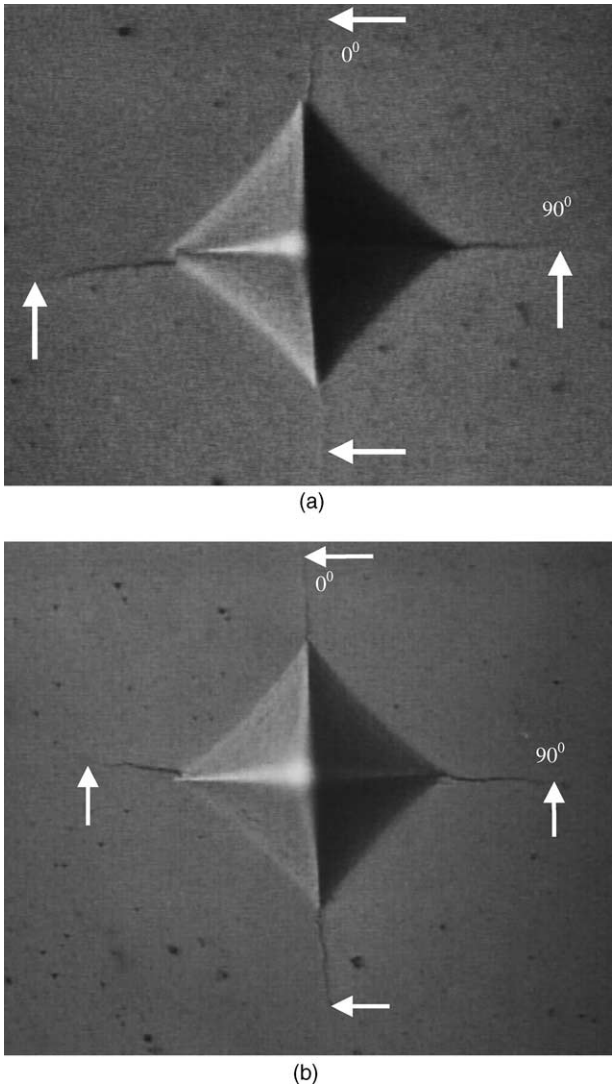

Fig. 9. Vicker's indentation marks orientated at 0 and 90° to the hot-pressing direction in plane P. (a) 5 vol.% additives and (b) 20 vol.% additives.

4. Conclusions

It has been shown that the direct determination of the orientation of the β-Si_3N_4 grains by analysis of SEM micrographs is a simple and reliable technique to determine the anisotropy of hot-pressed Si_3N_4 ceramics, permitting a

comparison of microstructures composed of grains with different sizes and aspect ratios, as well as changing amounts of intergranular secondary phases. In planes normal to the hot-pressing direction no preferential orientation of the grains has been found, independent of the additive content. In planes parallel to the hot-pressing direction, a preferential orientation of the grains has been verified, depending strongly on the additive content. With increasing additive content a tendency for a random orientation of the grains is observed.

The preferential orientation of the grains reflects also in the variation of the mechanical properties, especially fracture toughness. Fracture toughness values varied up to 27% for Si_3N_4 with an additive content of 5 vol.% in planes normal and perpendicular in regard to the hot-pressing direction. This difference is gradually reduced with increasing additive content to only 5% for an additive content of 20 vol.%, due to a lesser degree of steric hinderance and grain rotation. Crack propagation is effectively hindered in directions perpendicular to the grain orientation, causing higher fracture toughness in these directions.

Acknowledgements

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