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Effect of AlN-content on the microstructure and fracture toughness of hot-pressed and heat-treated LPS–SiC ceramics

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Abstract

The influence of additive content on the microstructural development of hot-pressed and heat-treated LPS–SiC has been investigated using $AlN–Y_2O_3$ mixtures at a molar ratio of 80:20, varying the total amount from 5, 10, 15 to 20 wt.%. Specimen were hot-pressed at 1900 °C for 1 h in nitrogen atmosphere under an applied pressure of 25 MPa and subsequently heat-treated at 2000 °C for 1, 2, 4 and 8 h.

It has been found that the transformation rate of β- into α-SiC is retarded by higher AlN-contents and the formation of the 6H α-SiC polytype is favored. Furthermore, grain growth during annealing is also effectively inhibited. While hardness remained almost unchanged, fracture toughness varied with additive content and/or duration of the heat-treatment. Fracture toughness increased during the first 1 or 2 h of annealing,depending on the AlN-content, and diminishing for more prolonged treatments. The maximum fracture toughness has been determined for samples containing 10 wt.% of additives, hot-pressed and annealed during 1 h.

Keywords: SiC; Liquid phase sintering; Microstructure-final; Phase analysis; Fracture toughness

1. Introduction

Silicon carbide is a compound of relatively low density, high hardness, elevated thermal stability and good thermal conductivity, resulting in good thermal shock resistance. Because of these properties, SiC materials are widely used as abrasives and refractories.

However, it has not been possible to sinter SiC to theoretical density without additives or external applied pressure, because of its covalent bonding character. The conventional densification route of SiC via solid-state sintering using small quantities of B or Al and C or compounds thereof[1–3] is widely applied today to produce components on a commercial base. The driving forces for densification are volume and surface diffusion which are enhanced by the addition of boron and aluminium. In order to increase the diffusion coefficient, sintering temperatures in the range of 2050–2200 °C are applied.

An innovative approach to solid-state sintering of SiC has been initiated in the 1980s by Omori and Takei,[4] who sintered SiC to high densities via liquid-phase sintering using Al_2O_3 and Y_2O_3 as additives. Since then a growing interest for liquid-phase sintered SiC ceramics is noted, because this type of material offers the opportunity of increasing fracture toughness by controlling the microstructure.[5–10] In general, the microstructural control is achieved making use of the β- to α-SiC phase transition. The formation of platelet shaped α-SiC grains is thereby influenced by the α/β-SiC ratio of the starting powders, the additive system beside the sinter parameters temperature, time and atmosphere. Fracture toughness values of 6–7 MPa $\sqrt{m}$ have been reported, signifying an almost 100% increase when compared to solid-state sintered SiC ceramics.

Rixecker et al.[11–13] investigated the pressureless sintering with oxynitride additives, starting from $AlN–Y_2O_3$ powder mixtures. They report that using AlN as additive and a nitrogen sintering atmosphere the weight loss during sintering can be effectively minimized, because the decomposition of AlN is avoided by the nitrogen atmosphere. On the other hand, it is known that a nitrogen atmosphere re-

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duces the sintering rates and also hinders the β- to α-SiC transformation.[14–16]

This work investigates the influence of the A1N–Y_2O_3 additive content on the β to α-SiC phase transition in hot-pressed and heat treated LPS–SiC ceramics, on the microstructure and its influence on fracture toughness and hardness.

2. Experimental procedure

Powder batches were produced using β-SiC powder (Grade B10, H.C. Starck), with an average particle size of 0.79 μm and a specific surface area of 13 m^2/g. The additives were AlN (Grade C, H.C. Starck) and Y_2O_3 (Grade Fine, H.C. Starck) with average particle sizes of 1.05 and 1.07 μm and specific surface areas of 7 and 15 m^2/g, respectively. Furthermore, α-SiC powder (FCP-15, Norton, AS) was used. Four powder batches were prepared, each containing 1 wt.% of α-SiC to act as seeds. The additive content varied from 5, 10, 15 to 20 wt.% of the total mixture, maintaining a constant molar ratio of AlN:Y_2O_3 of 80:20. The compositions prepared are listed in Table 1.

Mixing was performed by attrition milling using Si_3N_4 balls as grinding media and isopropylic alcohol as vehicle. After mixing, the powder batches were dried in a rotary evaporator, crushed and screened through a 325 mesh sieve. After attrition milling, the powders had almost identical particle size distributions (see Fig. 1), with average particle sizes of 0.66 μm.

Samples were hot-pressed at 1900 °C for 1 h under an applied pressure of 25 MPa in nitrogen atmosphere. The heating rate was 10 °C/min and the cooling rate about 20 °C/min, until the inertia of the furnace prevailed. The final shape of the hot-pressed samples were discs of approximately 25 mm diameter and 7 mm height. Samples were cut from the discs and further heat-treated at 2000 °C under 0.2 MPa flowing nitrogen atmosphere during 1, 2, 4 and 8 h. Bulk densities were measured by the Archimedes' method. Observation of the microstructural development has been performed by scanning electron microscopy on fracture surfaces and polished and plasma etched surfaces. The phase composition of the hot-pressed and heat-treated samples was determined by X-ray diffraction of crushed specimen using Cu-K_α radiation, a step width of 0.01° with an exposure time of 5 s per position. Quantitative phase analysis of the SiC polytypes was conducted using a programme based on the work of Ruska and Gauckler.[17] For computation the intensities of the peaks at 2θ 33.7, 34.2, 34.9, 35.7, 38.2 and 41.5° were determined.

Table 1
Designation and composition of powder mixtures

Sample designation	β-SiC (wt.%)	α-SiC (wt.%)	AlN (wt.%)	Y_2O_3 (wt.%)
A80-5	94	1	2,103	2,897
A80-10	89	1	42,065	57,934
A80-15	84	1	63,099	86,901
A80-20	79	1	84,130	115,868

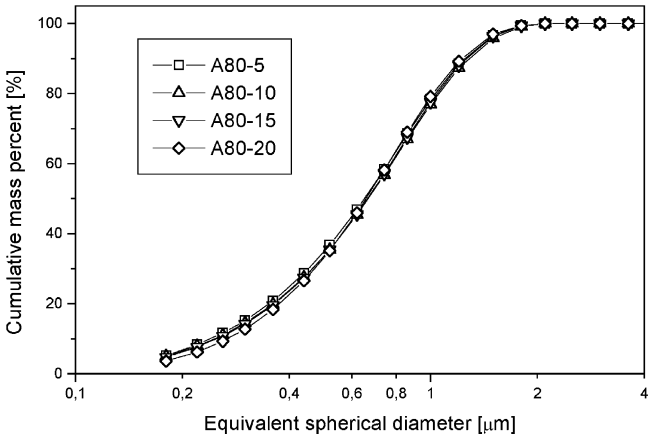


Fig. 1. Particle-size distributions of attrition milled powder batches.

Hardness was determined by Vickers indentation under a load of 9.81 N. The fracture toughness was calculated by the length of the cracks originating from the edges of the indentation marks, using the equation described by Niihara et al.[18]:

$$K_{I_c} = 0.018 HV\sqrt{a}\left(\frac{E}{HV}\right)^{0.4} \times \left(\frac{c}{a} - 1\right)^{-0.5} \quad (1)$$

where K_{I_c} is the fracture toughness of the material, HV the Vickers hardness, E the Young's modulus (for LPS–SiC a value of 400 GPa was assumed), c the crack length and a the half indentation diameter.

3. Results and discussion

All samples reached final relative densities higher than 98.5% t.d. after hot-pressing. A slight decrease of the relative densities of the further heat-treated samples was observed with increasing duration of the treatment, but limited to less than 0.5% for all compositions studied.

Fig. 2 shows fracture surfaces of the hot-pressed samples. While the overall grain sizes remained very fine for all compositions investigated, it can be noted that the grain sizes decrease with increasing additive content. Furthermore, the grain shape remained globular, only sample A80-5 exhibits some hexagonal, platelet like shaped grains, indicating that under the hot-pressing conditions, 1900 °C during 1h under nitrogen atmosphere, the β- to α-SiC phase transformation did not occur and that high AlN-contents retard the phase transition, in agreement with observations published by Nader et al.[9]

With increasing duration of the heat-treatment, grain growth occurs, as demonstrated in Fig. 3, using specimen of composition A80-10 as example. Furthermore, the

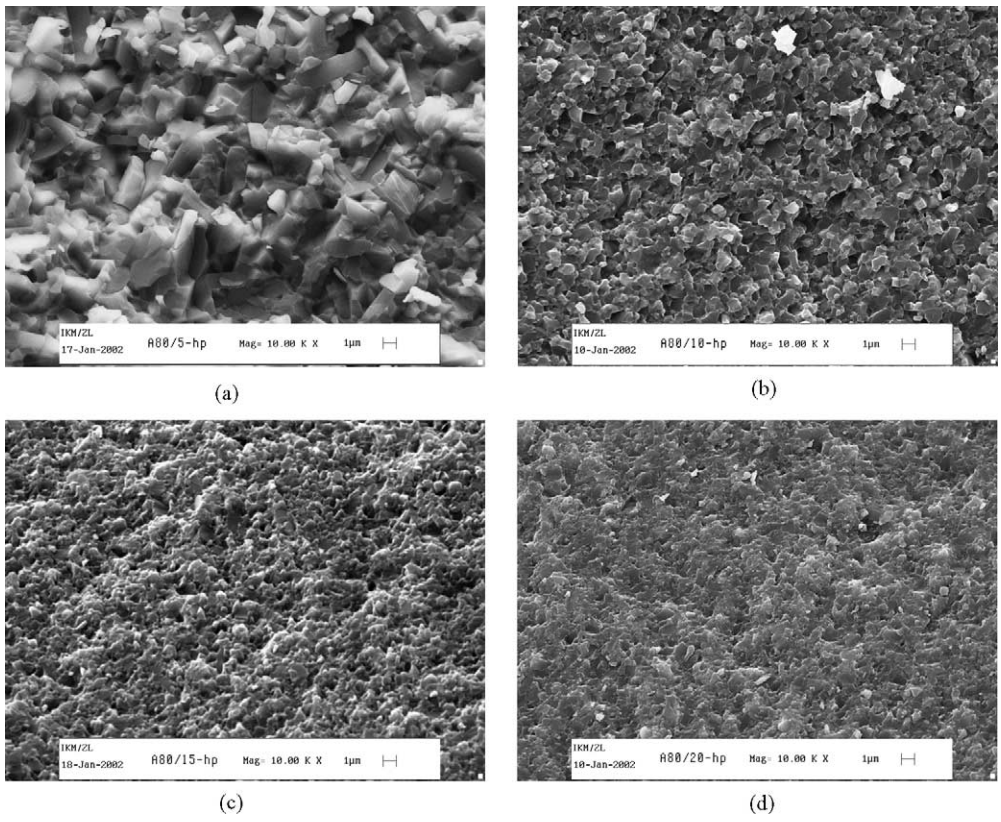


Fig. 2. Fracture surfaces of samples after hot-pressing: (a) A80-5, (b) A80-10, (c) A80-15 and (d) A80-20.

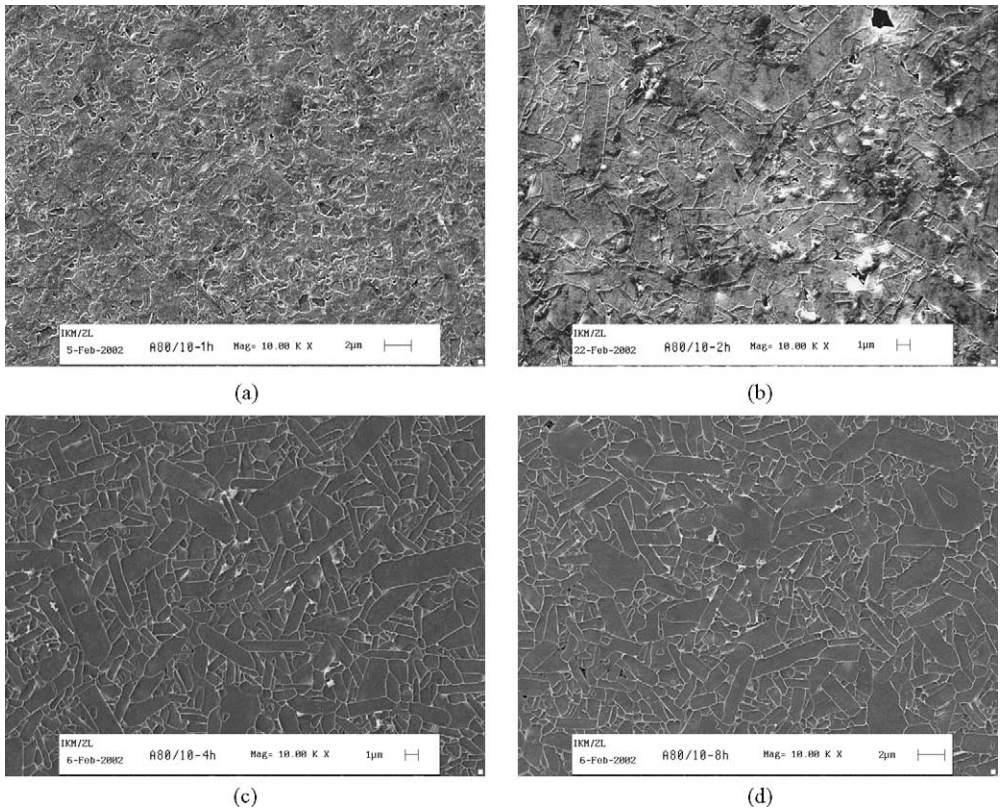
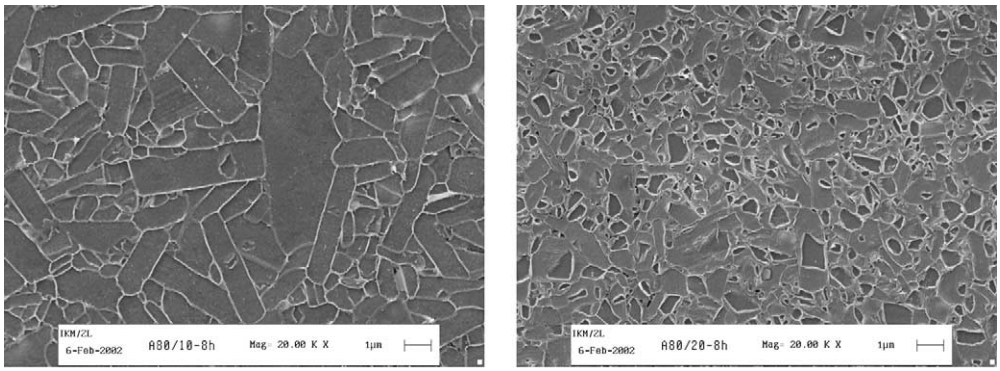


Fig. 3. Microstructures of samples A80-10 after hot-pressing and annealing during (a) 1 h, (b) 2 h, (c) 4 h and (d) 8 h.



(a) (b)

Fig. 4. Microstructures of samples: (a) A80-10 and (b) A80-20 after hot-pressing and annealing during 8 h.

grain morphology is no longer equiaxed, but changes into a platelet like form, indicating that the β- to α-SiC phase transition has taken place. The grain growth—due to the heat treatments at 2000 °C—is substantially less for higher AlN-contents, as evident from Fig. 4, where the microstructures of specimen with 10 and 20 wt.% additive, treated during 8 h are compared.

The results of the X-ray diffraction analysis revealed only the presence of β- and α-SiC; no further crystalline phases have been detected, indicating that the additives formed an amorphous intergranular phase. In Fig. 5 the X-ray patterns of the samples with 10 wt.% additives, hot-pressed and subsequently heat-treated, are compared. From these patterns an increase of the amount of the α-SiC polytypes 6H and 4H with increasing duration of the heat-treatment can be noted. The same is true for the other compositions studied. Fig. 6 shows the results of the quantitative SiC polytype analysis of the X-ray patterns of all samples. While for the samples containing only 5 wt.% additives, A80-5, only minor changes in the overall phase composition during heat-treatment of the hot-pressed samples are observed, a clear dependency of the further β- to α-SiC phase transformation with time and additive content is noted for the other compositions studied. These findings can be better interpreted by the calculation of the β/α-SiC ratios, shown graphically in Fig. 7. As can be seen, the β/α ratios decrease for all compositions studied with increasing duration of the heat treatment, indicating increasing amounts of β-SiC transformed into α-SiC. Furthermore, a clear dependency of the transformation rates with the additive content is noted, i.e. higher AlN-contents reduce the transformation, as can be observed by the higher β/α-SiC ratios for samples with higher additive content, under otherwise identical conditions.

While for a sample containing 5 wt.% additives, A80-5, the polytypes found were predominantly the 4H and 6H polytypes, for the other sample compositions the principal SiC modification found has been the polytype 6H and

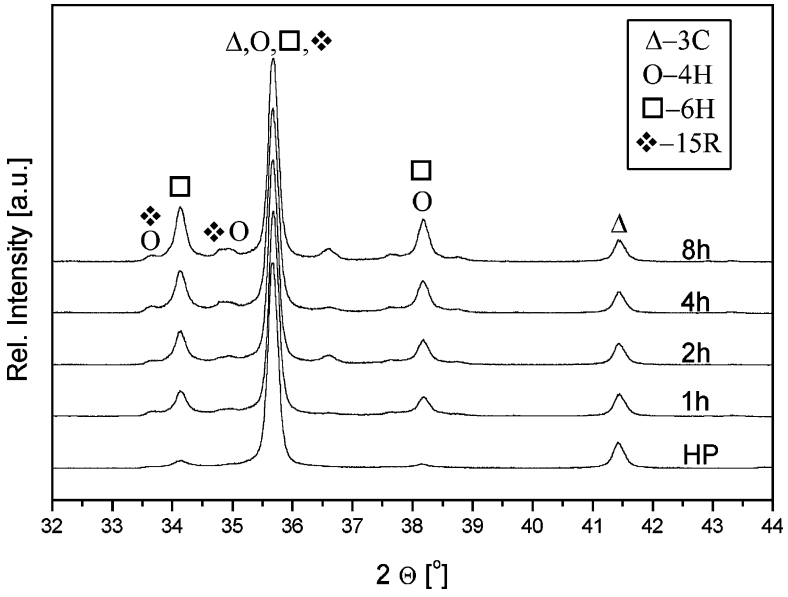


Fig. 5. X-ray diffraction patterns of sample A80-10, hot-pressed and annealed at 2000 °C during 1, 2, 4 and 8 h.

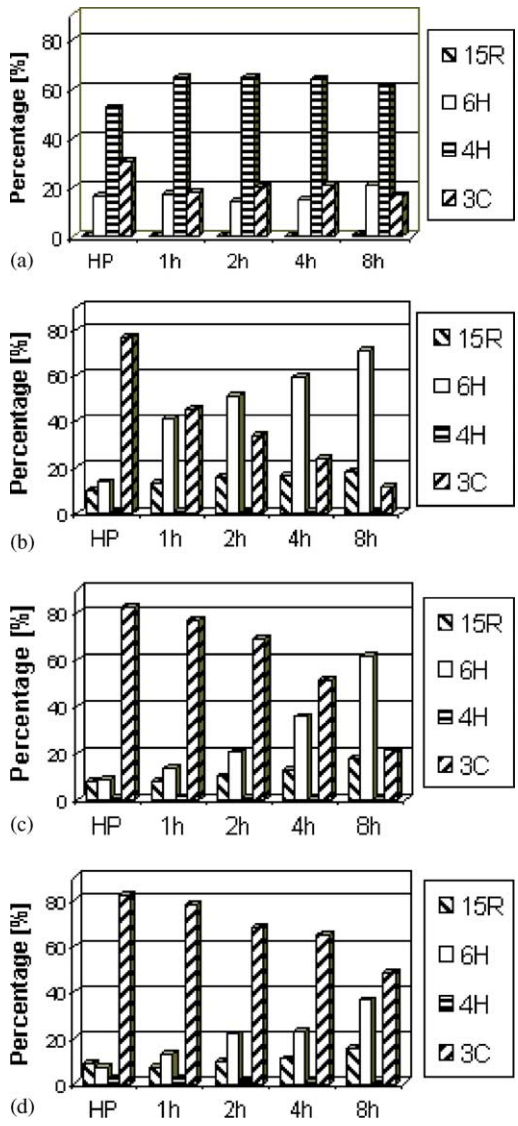


Fig. 6. Quantitative polytype analysis of samples: (a) A80-5, (b) A80-10, (c) A80-15 and (d) A80-20 after hot-pressing and annealing.

to a minor extend 15R. While the relative amounts of the α-SiC polytypes remained almost unchanged in the case of sample composition A80-5, increasing 6H/15R ratios with increasing duration of the heat-treatment have been found for the other sample compositions. Furthermore, it has been found that the 6H/15R ratio decreases with increasing additive content, indicating that a higher AlN-content shifts the relative amounts of the 6H and 15R polytypes to the 15R polytype. These findings are illustrated in Fig. 8, where the 6H/15R ratios of samples containing 10, 15 and 20 wt.% additives are plotted in relation to the time of heat treatment.

The results of the hardness and fracture toughness measurements are resumed in Table 2. No significant changes of hardness with the additive content or time of the heat-treatment could be observed. In the case of the fracture toughness however, see also Fig. 9, it can be affirmed

Table 2
Vickers hardness HV1 and fracture toughness of the hot-pressed and annealed specimens

Specimen	Conditions	HV1	K_{I_c} (MPa $\sqrt{m}$)
A80-5	hp	2428 ± 116	4.04 ± 0.18
	hp + 1 h annealing	2390 ± 95	4.41 ± 0.29
	hp + 2 h annealing	2495 ± 82	4.13 ± 0.12
	hp + 4 h annealing	2534 ± 132	4.00 ± 0.18
	hp + 8 h annealing	2341 ± 92	3.97 ± 0.11
A80-10	hp	2401 ± 137	4.16 ± 0.15
	hp + 1 h annealing	2123 ± 106	4.62 ± 0.22
	hp + 2 h annealing	2284 ± 95	4.41 ± 0.20
	hp + 4 h annealing	2315 ± 77	4.27 ± 0.17
	hp + 8 h annealing	2154 ± 51	4.03 ± 0.16
A80-15	hp	2368 ± 63	3.93 ± 0.10
	hp + 1 h annealing	2457 ± 62	4.02 ± 0.09
	hp + 2 h annealing	2439 ± 99	3.98 ± 0.15
	hp + 4 h annealing	2385 ± 68	3.86 ± 0.14
	hp + 8 h annealing	2271 ± 103	–
A80-20	hp	2341 ± 126	3.81 ± 0.12
	hp + 1 h annealing	2342 ± 61	3.91 ± 0.11
	hp + 2 h annealing	2350 ± 94	3.98 ± 0.15
	hp + 4 h annealing	2463 ± 76	3.80 ± 0.14
	hp + 8 h annealing	2270 ± 96	3.89 ± 0.08

that fracture toughness of all samples increased during the heat-treatment when compared to the only hot-pressed samples. Maximum values are obtained after 1 h of annealing at 2000 °C for samples containing 5, 10 or 15 wt.% additives, while for the sample containing 20 wt.% additives the maximum value was reached after 2 h. The initial increase in fracture toughness is caused by the formation of hexagonal, platelet-shaped α-SiC grains of high aspect ratio. Further heat-treatment results in grain coarsening, i.e. slightly larger grains, but with lower aspect ratios, and therefore decreased fracture toughness.

Furthermore, a significant variation of the fracture toughness with the additive content has been verified. The highest fracture toughness have been obtained for the sample containing 10 wt.% additives, A80-10, under all conditions studied. A clear relationship between additive content, transformation kinetics and microstructural development could be established, which is reflected in the determined fracture toughness. While under a low AlN-content as in sample A80-5 a more equiaxed microstructure with medium toughness results, too high AlN-contents, as in samples A80-15 and A80-20, effectively hinder the phase transformation and the grain growth, also resulting in low fracture toughness. The best results in terms of the fracture toughness were achieved with samples containing 10 wt.% of additives, i.e. composition A80-10, hot-pressed at 1900 °C and annealed at 2000 °C during 1 h. In this case, an elongated, platelet-like microstructure has been formed, resulting in the highest fracture toughness of all compositions studied.

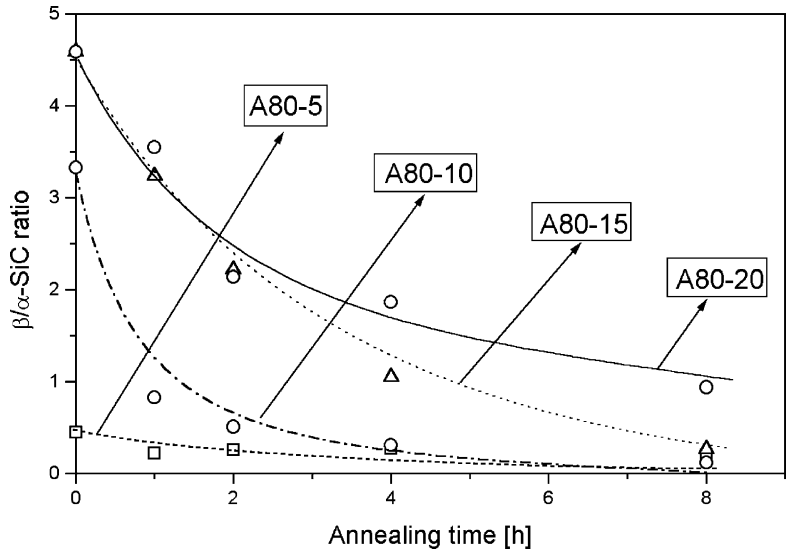


Fig. 7. β/α-SiC polytype ratios of the samples after hot-pressing and heat-treatment.

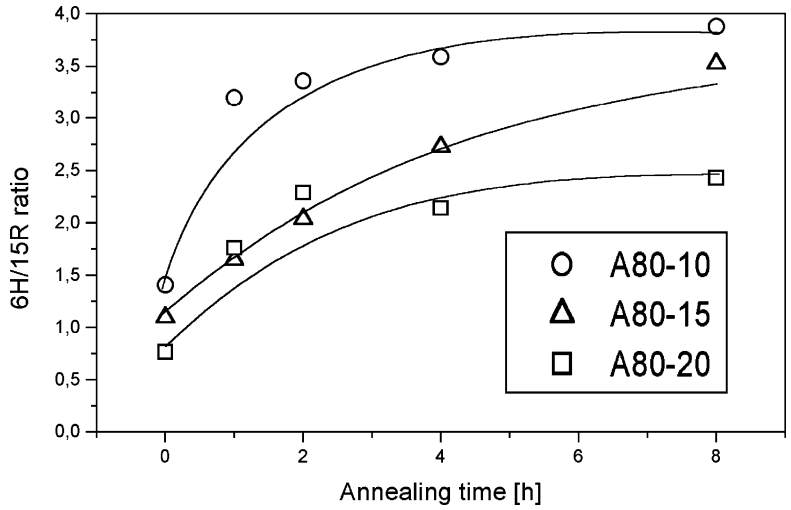


Fig. 8. 6H/15R polytype ratio of samples A80/10, A80/15 and A80/20, after hot-pressing and annealing.

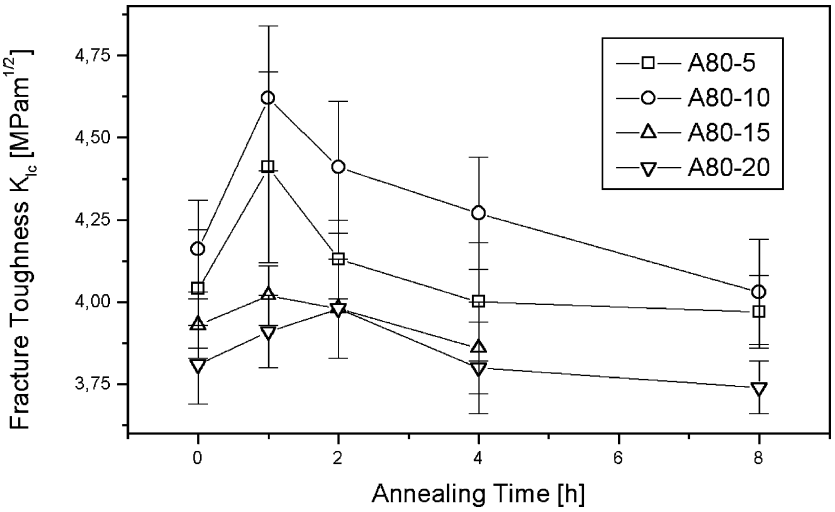


Fig. 9. Fracture toughness of the hot-pressed and annealed samples.

4. Conclusions

Hot-pressing of SiC with AlN–Y_2O_3 additives at 1900 °C resulted in dense materials, with a fine, equiaxed microstructure. X-ray diffraction analysis revealed that this temperature is insufficient to promote the β- to α-SiC phase transition.

The phase transition and growth of platelet shaped α-SiC grains was achieved during a subsequent heat-treatment at 2000 °C. The transformation rate and grain growth is strongly affected by the AlN-content of the samples. Higher AlN-contents effectively reduce the transformation rates and favor the formation of the 6H α-SiC polytype. Furthermore, high AlN-contents hinder grain growth, affecting fracture toughness. While at low additive content the overall amount of liquid phase is insufficient to permit extensive grain growth, at too high contents the transformation and grain growth are inhibited. Therefore, an optimum amount of additives exists, permitting phase transformation and grain growth. The highest fracture toughness was obtained for the sample with 10 wt.% additives, hot-pressed and heat-treated during 1 h.

Acknowledgements

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