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Phase composition and fracture toughness of Si_3N_4–ZrO_2 with CeO_2 additions

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Abstract

Zirconia toughened Si_3N_4 was prepared with addition of CeO_2 by applying hot pressing technique. Phase composition, densification, fracture toughness and hardness were investigated as a function of hot pressing temperature and CeO_2 content. The absence of nitrogen containing zirconia phase was discussed. Fracture toughness of Si_3N_4–ZrO_2(+CeO_2) with 12 mol% of CeO_2 in ZrO_2 reached 15 MPa m$^{1/2}$. Dominating toughening mechanism according to our data seems to be stress induced microcracking. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1. Introduction

Transformation toughening of Si_3N_4 with ZrO_2 dispersoids was first reported by Claussen [1]. Later on, a great deal of publications appeared which confirmed the toughening effect of a Si_3N_4 matrix by ZrO_2 with different stabilizing oxides [2–6]. The valency of cations in stabilizing oxides and their concentration determine the concentration of oxygen vacancies in substitutional ZrO_2–Me_xO_y solid solutions. Oxygen vacancies in the dispersoid phase enable the incorporation of nitrogen on oxygen sites, giving rise to ZrN or ZrON formation which is not desirable [7,8]. In the Si_3N_4–ZrO_2 system without stabilizers, N-containing zirconia phases were not found [9], i.e. the total ZrO_2 was monoclinic. In the case of Ca^{2+} as stabilizing oxide, N-containing ZrO_2 phases were not detected, independent of whether prereacted CaO–ZrO_2 solid solution or CaO + ZrO_2 mixture of the same composition was added to Si_3N_4 [3]. However, with Y^{3+} as stabilizing oxide, ZrON was detected both with addition of presynthesized YPSZ or with a corresponding mixture of Y_2O_3 + ZrO_2 in the Si_3N_4 matrix [9], which suggested that presynthesizing of ZrO_2 solid solution to form an additive might not be effective in preventing N-containing zirconia formation.

The reason for ZrN formation in Y_2O_3–ZrO_2–Si_3N_4 system may be searched for in the liquid phase composition, melting temperature and properties. Surrounded by the liquid in which α-Si_3N_4 is getting dissolved, YPSZ can take up nitrogen which occupies oxygen sites. In the case of CaO, however, the melting temperature is considerably lower, and fast densification inhibits vapour reaction in which ZrN can be formed [3,5].

With CeO_2 as stabilizing oxide Ce^{4+} ions should produce substitutional solid solutions of the $Zr_{1-x}Ce_xO_2$ type, without additional point defects (oxygen vacancies). Therefore, no N incorporation in ZrO_2 may be expected during the processing. On the other hand, ceria is less expensive and more stable in water vapour in comparison with yttria. This work presents the influence of temperature and CeO_2 concentration on the phase composition, densification and the fracture toughness of Si_3N_4. It was found that high fracture toughness is strongly related to chemical composition of the starting mixture and for constant chemical composition is strongly dependent on the hot pressing conditions.

2. Experimental work

Starting powder, α–Si_3N_4–LC12 (H. C. Starck), was homogenized with ZrO_2 (Magnesium Electron) and CeO_2 (Merck) in a vibratory mill made of tungsten carbide, for 2 h in isopropanol. Composition of starting mixtures with varying CeO_2 content are given in Table 1. Oxygen content in the Si_3N_4 powder was 1.8 mass%. Hot pressing temperatures ranged from 1600°C–1780°C

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Table 1
Starting compositions (mass%)

Mixture	Si_3N_4	ZrO_2	CeO_2	mol% CeO_2 in ZrO_2
A	70	27.60	2.74	6.7
B	70	25.20	4.80	12.0
C	70	22.24	7.76	20.0
D	99	—	1	—
F	97	—	3	—

with heating and cooling rates of 45 and 15°C min^{-1}, respectively. Isothermal hot pressing time was 1 h (in argon atmosphere). Density, fracture toughness and hardness were measured. Indentation fracture toughness was measured by making 10 indents under the load of 100 N for 10 s X-ray diffraction analysis was performed (using Siemens D-500 instrument) to identify the phases, present as well as to determine t + c modifications of ZrO_2. SEM analysis was performed using a JEOL-35 microscope, and elemental analysis using ISIS Link 300 to determine the composition of ZrO_2 grains (~5 µm in diameter was analysed), quantitatively.

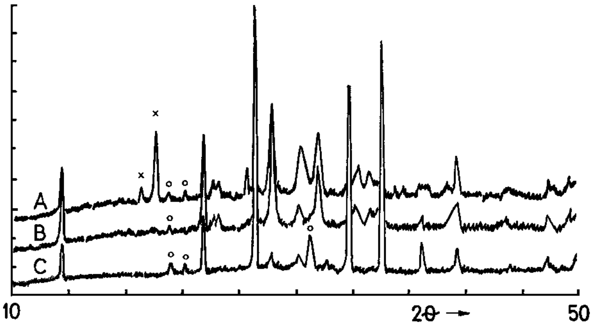


Fig. 1. X-ray pattern of samples A, B and C, at 1700°C, 1 h. ×, Si_2N_2O; o, N-apatite.

3. Results and discussion

3.1. Phase composition change with CeO_2 addition

Phase composition change of the starting mixtures (Table 1) as a function of temperature is followed by X-ray analysis. The obtained results are summarised in Table 2 and Fig. 2. The intensities of characteristic peaks of Si_2N_2O (Fig. 1) decrease while the ones of Ce-N-apatite ($5Ce_2O_3.Si_2N_2O.4SiO_2$) increase with increasing CeO_2 content. It should be outlined that with samples B only traces of Ce–N–apatite were found by X-ray, may be due to its small amount or small particle size. The existence of Si_2N_2O in samples A indicate that a reaction of CeO_2 with Si_3N_4 according to

$$2Si_3N_4 + 6CeO_2 \rightarrow 3Si_2N_2O + 3Ce_2O_3 + N_2 \qquad (1)$$

is dominant. On the other hand, the fact that Si_2N_2O was not detected in samples C means that it had already reacted with SiO_2 and Ce_2O_3 to form Ce–N–apatite (Table 2). This is possible if additional SiO_2 is formed according to the reaction

$$Si_3N_4 + 12CeO_2 \rightarrow 3SiO_2 + 6Ce_2O_3 + 2N_2 \qquad (2)$$

The samples C containe a larger amount of CeO_2 as compared to samples A. Therefore, it can be assumed that in addition to reaction (1), reaction (2) could take place, as well, in the mentioned composition C. To

Table 2
Intensities of characteristics peaks (%) of phases detected in Si_3N_4–CeO_2 and Si_3N_4–ZrO_2–CeO_2 samples as a function of hot pressing temperature and CeO_2 content

Sample	T (°C)	Si_3N_4, t[a]	ZrO_2, t	Si_2N_2O	$5Ce_2O_3.Si_2N_2O.4SiO_2$	CeO_2 (mass%)
A	1500	39	41	20	—	2.7
	1650	42	44	14	tr[b]	
	1700	42	45	13	tr	
	1780	44	46	10	10	
B	1500	40	40	20	—	4.8
	1600	41	36	18	6	
	1650	33	36	25	8	
	1700	52	48	—	tr	
	1780	52	48	—	tr	
C	1500	50	13	—	37	7.8
	1600	58	20	—	2	
	1700	59	24	—	17	
D	1650	78	—	14	8	1.0
	1700	79	—	14	14	7
F	1650	83		10	7	3.0
	1700	85	—	8	7	

[a] t, total.
[b] tr, traces.

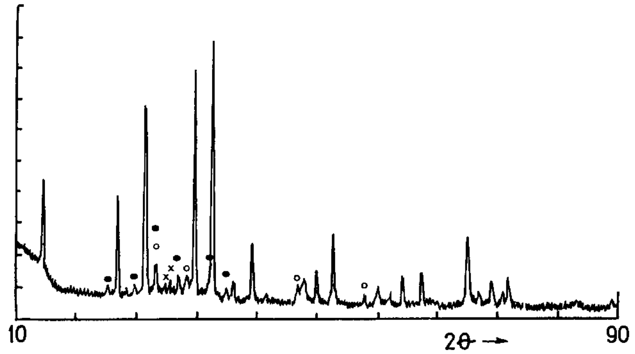


Fig. 2. X-ray patttern of Si_3N_4+10 mass% CeO_2, 1780°C, 1 h. o, CeO_2, ×, Ce_2O_3, •, crystobalite.

support this assumption a separate sample containing 10 mass% CeO_2 in Si_3N_4 was sintered at 1700 and 1780°C in Ar. In this composition peaks of β-Si_3N_4, CeO_2, traces of Ce_2O_3 were detected at 1780°C (Fig. 2) and in addition the peaks of SiO_2. This proved that with even higher CeO_2 content reaction (2) was dominant in the Si_3N_4–ZrO_2–CeO_2 system.

The reaction (1) and (2) cannot take place without reduction of Ce^{4+} to Ce^{3+}. Literature data [10] pointed out that this process takes place in Ar, in excess of 1700°C, as was found in the sintering experiment described above. However, the presence of Ce–N–apatite in our hot pressed samples at 1500°C indicate that under the given hot pressing conditions the mentioned reduction does take place (samples C, Table 2).

According to microanalysis data (Table 3) nitrogen was not detected within the zirconia grains. Nitrogen containing zirconia phases were detected in none of the compositions studied. The reason may be the low temperature at which liquid phase forms in this system which suppressed gas forming reactions [5]. Literature data [11] showed that in the Si_3N_4–CeO_2 system, liquid phase is formed at about 1450°C and its amount progressively increases with increasing CeO_2 content. Our data (Table 2, Fig. 1) proved that the intensities of ZrO_2 peaks decrease with increasing CeO_2 in Si_3N_4–ZrO_2–CeO_2 system. With highest CeO_2 concentration diffraction line intensities of ZrO_2 are very low. In addition, from SEM micrographs (Fig. 3) a larger amount of glassy phase is evident in samples C (Fig. 3(c)) which suggests that ZrO_2 got dissolved in the liquid phase. Moreover, by hot pressing of samples C, highest densities were obtained at temperatures as low as 1500°C, indicating that liquid phase in the studied system appeared below 1500°C.

Table 3
Composition of ZrO_2 grains in sample B, 1700°C

Element	O	Zr	Si	Ce	Hf
at%	61.32	32.50	5.55	0.01	0.63

According to the results in Table 3, a much higher concentration of Si (7.5 mass% SiO_2) than Ce (0.04 mass% CeO_2) is present within zirconia grains. On the other hand, the interplanar spacings "d" in ZrO_2m measured from $(11\bar{1})$ and (111) peaks decreased with increasing temperature from 0.3160 (starting value) to 0.3148 nm and from 0.2837 (starting value) to 0.2833 nm, respectively, which also points to the dissolution of Si^{4+} in ZrO_2m (ionic radii of Si^{4+} and Zr^{4+} are 0.42 and 0.84 Å, respectively). The mentioned results indicate that anion vacancies are not created in ZrO_2, because a great majority of Zr^{4+} is substituted by Si^{4+} and only a small number of Zr^{4+} is exchanged most probably for Ce^{4+} ions (which are smaller than Ce^{3+}). The possibility of the existence of Ce^{4+} ions under similar experimental conditions was mentioned in the case of α-SiAlON sintered in the presence of $Y_2O_3+CeO_2$ additive [12]. Besides, Ce^{4+} is shown [13] to enter the ZrO_2 lattice in the solid state which, applied to our case, means during the heating up period. This was proved on the basis of the X-ray data obtained for ZrO_2+10 mass% CeO_2 sample. The sample was hot pressed up to 1400°C and immediately cooled down, whereby the heating rate and the atmosphere were kept identical as in the hot pressing experiments with the Si_3N_4–ZrO_2–CeO_2 system. On the basis of X-ray data it appears that Ce ions are in the fourvalent state, which is proved by the appearance of the $Zr_{0.4}Ce_{0.6}O_2$ solid solution diffraction line ($d=0.3062$ nm). This means that zirconia grains are in fact $Zr^{4+}_{1-x-y}Si^{4+}_xCe^{4+}_y$ solid solutions, with $x>>y$. As far as the valent state of the Ce ions in the liquid phase is concerned, as suggested by our data, they are most probably in the threevalent state. This could be proved on the basis of the presence of Ce–N–apatite which was formed by crystallization from that liquid.

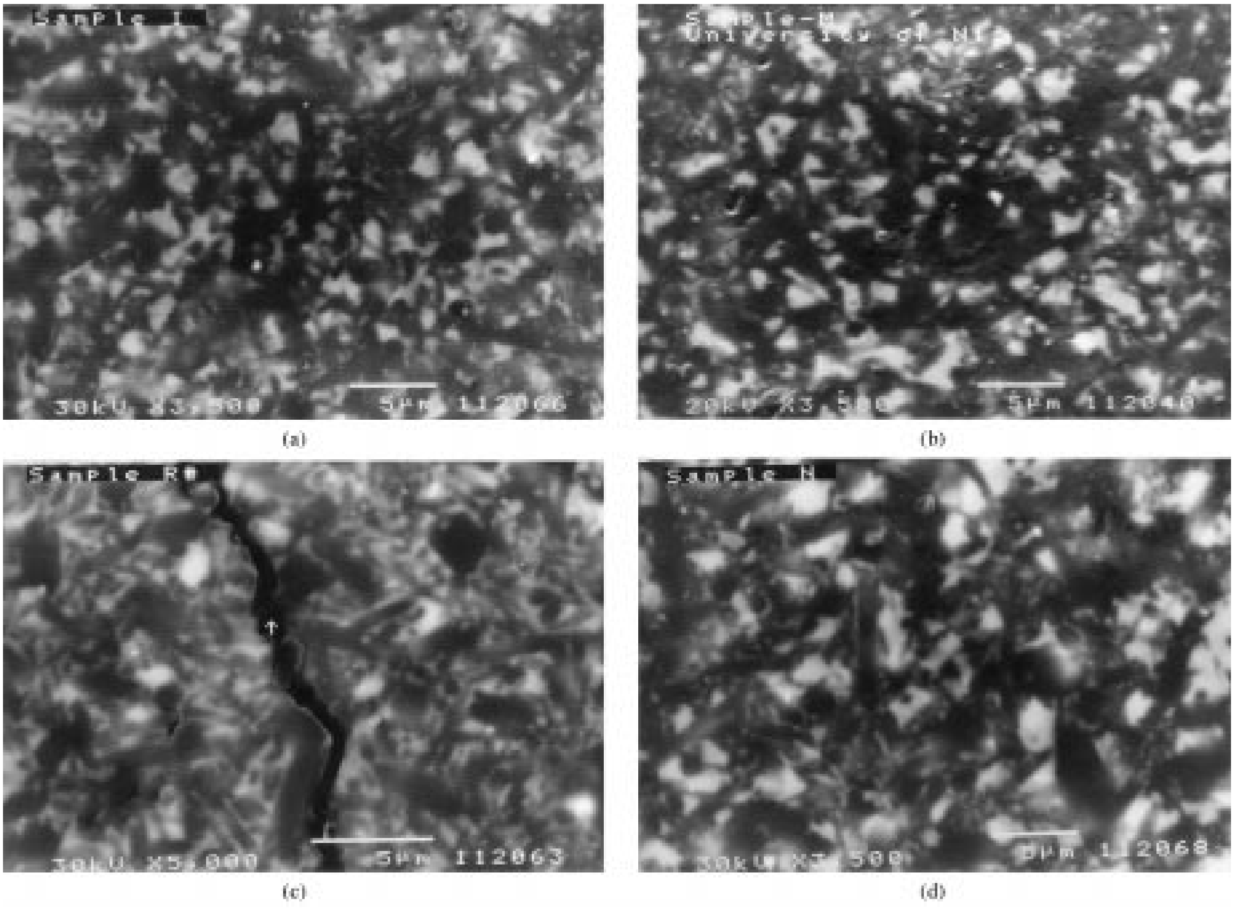
3.2. Densification

Densification of Si_3N_4–ZrO_2–CeO_2 (compositions A, B and C, Table 1) was followed as a function of temperature and CeO_2 amount. The results in Fig. 4 show that samples which do not contain ZrO_2 (D,F) achieved full density at 1700°C. Densification of ZrO_2 containing samples depended on CeO_2 content and temperature which is more obvious from Fig. 5 Typical densification curves for liquid phase sintered samples as a function of the additive content at constant temperature are obtained [14]. Optimum CeO_2 concentration according to the given data is found in composition B (3.81 mol% CeO_2) at 1700°C. With lower and higher CeO_2 amount lower and higher densities were achieved respectively, due to insufficient (samples A) or too high (samples C) liquid phase amount. With samples C highest density was obtained at 1600°C (Fig. 4) which is in agreement with the above discussion on liquid phase amount. The amount of liquid in C is too high and as it keeps increasing with increasing temperature the sintered density decreases [14]. It can also be noticed that the amount of CeO_2 is almost the same in samples A and F (Table 1) but the densification degree is much higher in the system without ZrO_2 (Fig. 4). The reason is the fact that the amount of the liquid phase in samples F is higher due to higher SiO_2 content introduced via the Si_3N_4 (Table 4).

Not only the amount of the liquid phase affects densification. The viscosity of the liquid is a very important parameter in densification as well. In Table 4 calculated amounts of the liquid forming oxides in the Si_3N_4–ZrO_2–CeO_2 compositions investigated are given taking into account the oxygen content in the starting silicon nitride powder. These mixtures are not the eutectic mixtures. In the compositions investigated they represent relative fractions of oxides among which liquid phase will be formed during heating. The concentration of CeO_2 increases (with SiO_2 being constant) from A to C which may result in lowering the liquid phase viscosity during densification. Taking this into account and bearing in mind the highest amount of the liquid in samples C it may be understandable why this composition would have the highest density at temperatures below 1600°C. Indeed, this was proved by additional hot pressing of composition C at 1550°C whereby the densification degree of 99.5 % TD was attained.

3.3. Fracture toughness

The dependence of fracture toughness and hardness on the amount of CeO_2 are given in Fig. 6. It is obvious that the hardness of the composition without ZrO_2 (sample F) is much higher as compared to composites containing zirconia. The indents in sample B at 1650 and 1700°C (Fig. 7) are large, metal like and correspond to the low hardness values. Fracture toughness passes through a maximum at 3.81 mol% CeO_2. With further increase of CeO_2 the fracture toughness at constant temperature decreases sharply in sample C. It should be recalled that the amount of liquid phase increased with the increase in CeO_2 content (Fig. 3(b) and (c)). Besides, the composition of the intergranular phase changed, as mentioned before. If samples B and C are compared at 1700°C (which are highly dense at 1700°C contrary to sample A) the total amount of crystalline zirconia (Fig. 1)



(a) (b) (c) (d)

Fig. 3. SEM micrographs of (a) sample A, (b) sample B and (c) sample C hot pressed at 1700°C, and (d) sample B hot pressed at 1780°C, 1 h.

is lower in C, due to the dissolution of ZrO_2 in the liquid. Bearing also in mind that the content of Ce–N–apatite in C is high, it could be accepted that the composition of the glassy phase is richer in ZrO_2 and poorer in CeO_2 and SiO_2. It is also suggested by our results in Table 2, that the intergranular phase composition in sample B is different comparing to C. According to the data in Tables 2 and 4, glassy phase in B is rich in CeO_2 and SiO_2 with lower ZrO_2 content.

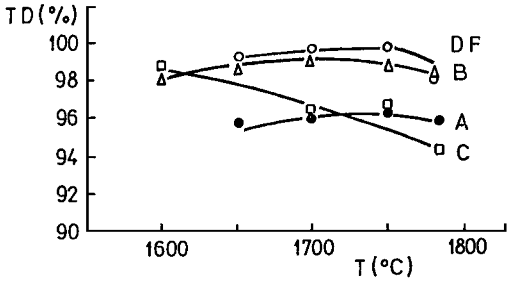


Fig. 4. Densification degree as a function of temperature: (A) 2.74 mass% CeO_2, (B) 4.80 mass% CeO_2, (C) 7.76 mass% CeO_2, (D) 1 mass% CeO_2, (F) 3 mass% CeO_2.

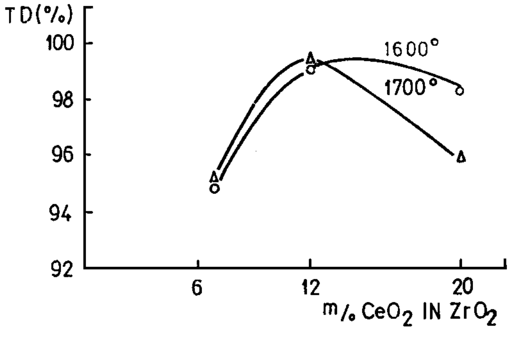


Fig. 5. Densification degree vs CeO_2 content.

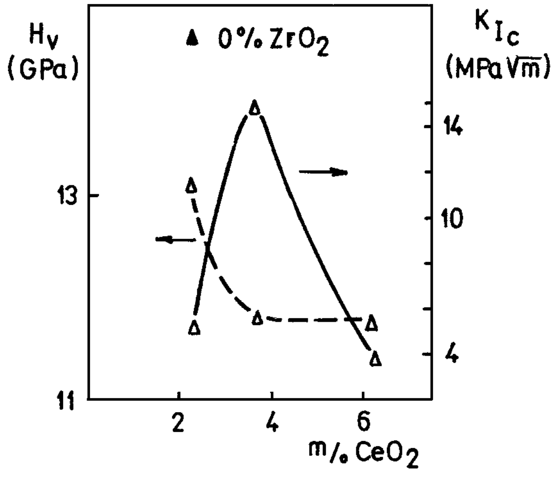


Fig. 6. Fracture toughness at 1700°C vs CeO_2 content (mol%) in the composite (D, hardness of sample F).

The amount of c + t ZrO_2 in composition C (Table 5) is higher whereas the total content of crystalline zirconia is considerably lower, (Fig. 1). Being not–transformable it does not affect the fracture toughness in a positive sense. It was found that with composition C, K_{Ic} and H_v were independent of temperature in the range 1650–1780°C. This indicates that the toughening concept with zirconia is no longer valid in this composition. It is due to the large amount of liquid (Fig. 3(c)) in which zirconia is dissolved and on the other hand due to the low total crystalline zirconia content which is obviously too low to be effective in the toughening process.

Table 4
Liquid forming oxides (mass%)

Mixture	SiO_2	ZrO_2	CeO_2
A	7.35	84.19	8.46
B	7.35	77.83	14.82
C	7.35	68.68	23.97
D	77.06	0	22.94
F	52.38	0	47.62

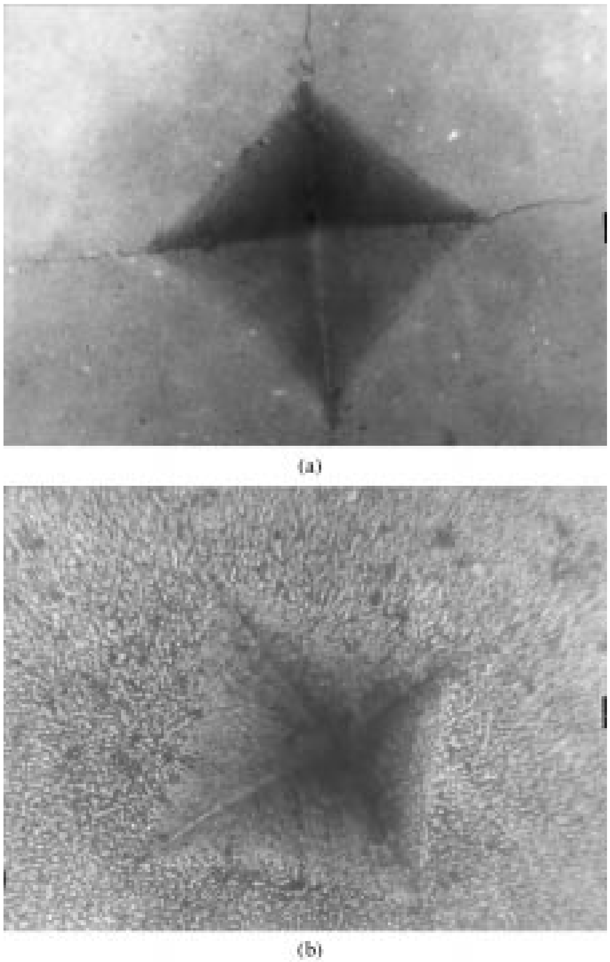


Fig. 7. Vickers indents: (a) 1650°C and (b) 1700°C, sample B (×560).

Table 5
ZrO_2(c + t) calculated from XRD lines intensities (%)

Sample	1600°C	1650°C	1700°C	1750°C	1780°C
A	—	28	32	29	17
B	20	13	15	11	6
C	—	25	35	33	36

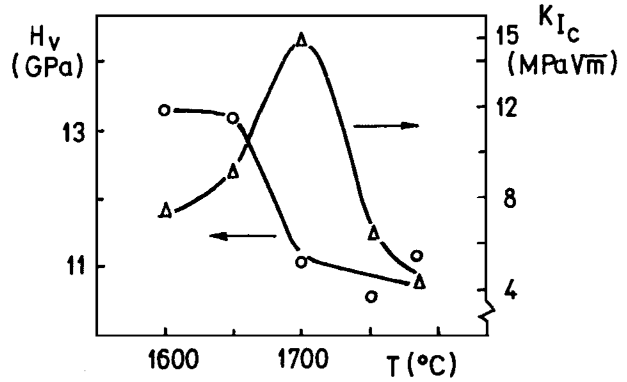


Fig. 8. Fracture toughness of composition B vs hot pressing temperature.

Fracture toughness of composition B, being most interesting, was studied as a function of hot pressing temperature (Fig. 8). The same type of curve as in Fig. 6 with a maximum at 1700°C, is obtained. With increasing hot pressing temperature the fracture toughness decreased. Vickers hardness sharply drops at 1700°C, and continues to decrease with further temperature increase.

According to the data in Table 2 it can be accepted that the composition of the liquid phase in B samples, conincides with an invariant poit of the Si_3N_4–ZrO_2–CeO_2–SiO_2 system, the temperature of which is ~1700°C.

According to the data in Table 2 and in Figs. 1 and 7b, Ce–N–apatite is dispersed in the glassy phase in the form of fine particles.

It may be worth mentioning that composition B from Table 4 was hot pressed at 1700°C. The sample contained large amount of the liquid phase, but it is important to outline that the sample was very "soft", indicating that the nature of the intergranular phase in the composite might be of great importance both for hardness and for fracture toughness.

Sample B contains a very high percentage of the monoclinic phase (Table 5). This proves that the majority of ZrO_2 remained unstabilized at room temperature which was also found for the hot pressed SiAlON/ZrO_2 composites containing 12 mol% CeO_2 [5]. According to our data Si ions in the ZrO_2 grains obviously do not act as c + t stabilizers. Some tetragonal content (Table 5), may be due to a low concentration of Ce^{4+} dissolved in zirconia (also found in Ref. 15). The majority of ZrO_2 t, however, is due to very fine zirconia particles which remained untransformed during cooling. High fraction of tetragonal zirconia, as mentioned, did transform during cooling from 1700°C, into monoclinic, creating high residual stresses which do not exceed critical tensile stress in the intergranular phase. Results in Fig. 6, showing the decrease of hardness and fracture toughness with increasing temperature above 1700°C, indirectly point to the fact that in sample B at 1700°C, stress induced microcracking is the dominant toughening mechanism. With further increase in temperature the amount of liquid phase increased (Fig. 3(b),(d)), its composition changed, and ZrO_2 grains got larger. During cooling tetragonal zirconia transformed into monoclinic thus creating high concentration of microcracks in the intergranular layer which are responsible for lower fracture toughness and the observed low hardness.

It was shown [16,17] that the composition of the intergranular phase plays an important role in fracture toughness. The same conclusion can be drawn from our results. Composition of the intergranular phase (rich in Ce ions) corresponding to an invariant point, is unique in creating conditions under which the stress induced microcracking is most efficient in toughening of composition B hot pressed at 1700°C.

4. Conclusion

With increasing CeO_2 content density passes through a maximum. The optimum additive amount is found to be 3.81 mol% CeO_2, at 1700°C. Nitrogen containing zirconia phases were not observed in the compositions studied, primarily because of the low liquid forming temperature (<1500°C). Within zirconia grains high concentration of Si and low concentration of Ce ions were found. Most of ZrO_2 is present in the form of the monoclinic phase. Fracture toughness is strongly influenced by both CeO_2 content and the hot pressing conditions. The intergranular phase in sample with 3.81 mol% CeO_2 is rich in ceria, at 1700°C. Its composition correspond to an invariant point in the Si_3N_4–ZrO_2–CeO_2–SiO_2 system. Stress induced microcracking is found to be the dominating toughening mechanism in samples having 3.81 mol% CeO_2 hot pressed at 1700°C in which K_Ic was cca 15 MPa $m^{1/2}$.

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