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Sintering, Hardness and Indentation Fracture Toughness (K_{IC}) of Mullite and its Composite with 15 wt% X-Phase Sialon

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Abstract

A commercially pure mullite was sintered to 99·7% of its theoretical density by pressureless sintering at 1740°C. An addition of 15 wt% pre-produced X-phase sialon improved the sinterability of the composite. The composite is about 5% and 9% better than mullite (of about the same degree of densification) in terms of hardness and indentation fracture toughness respectively.

Optical and scanning electron microscopes were used to obtain micrographs. From the microstructural evidence it is suggested that these improvements are as a result of changes in the distribution and size of grains, brought about by the addition of X phase. However, the grain size of the starting powders and the method of addition of X phase were found to be factors which could affect the degree and mode of improvement.

Ein kommerziell reiner Mullit wurde mit einer Dichte von 99·7% der theoretischen Dichte durch druckloses Sintern bei 1740°C hergestellt. Die Zugabe von 15 Gew.% vorproduziertem X-Phasen-Sialon verbesserte die Sinterfähigkeit des Verbunds. Der Verbund ist um etwa 5 bzw. 9% bezüglich der Härte und der Eindrucksbruchfestigkeit besser als Mullit (bei der selben Dichte).

Die Proben wurden mit Hilfe des Lichtmikroskops und des Rasterelektronenmikroskops untersucht. Aus diesen Untersuchungen läßt sich schließen, daß die Verbesserungen auf eine Veränderung in der Korngrößenverteilung, verursacht durch die Zugabe von X-Phase, zurückzuführen ist. Es hat sich jedoch gezeigt, daß die Korngröße des Ausgangspulvers und die Art wie die X-Phase zugegeben wird, den Grad der Verbesserung beeinflussen können.

On a préparé de la mullite pure de qualité commerciale, présentant une densité égale à 99·7% de la densité théorique, par frittage naturel à 1740°C. La frittabilité de ce composite peut être améliorée par une addition de 15% de sialon (phase X) fabriqué au préalable. La dureté de ce composite ainsi que sa résistance à la fracture évaluée par indentation sont respectivement de 5% et 9% supérieures à celles d'une mullite ayant le même niveau de densification.

On a examiné le matériau aux microscopes optique et à balayage. Les observations microstructurales suggèrent que ces améliorations proviennent d'un changement dans la distribution et la taille des grains, provoqué par l'ajout de phase X. On a néanmoins constaté que la taille de grains des poudres de départ et la manière dont la phase X est ajoutée peuvent affecter le degré et les caractéristiques de ces améliorations.

1 Introduction

Over the past two decades the numerous reported works on mullite ($3Al_2O_3 \cdot 2SiO_2$) are an indication of how its recognition as a material for high-temperature structural applications has been growing. Several works[1–6] attribute this recognition to the material's high covalency, which has led to superior properties, such as high melting temperature, good thermal shock (fracture) resistance, relatively low density, good chemical stability and low thermal expansion. However, it has been shown[7] that to maximize these properties a close compositional and microstructural control of mullite is necessary.

The sintering of stoichiometric pure mullite is very difficult, often necessitating hot pressing to achieve close to a full densification. In a bid to improve the sinterability of mullite and hence maximize its good mechanical properties, Si_3N_4[5] and whiskers of SiC[8] have been added to mullite matrix composites. Yamagishi *et al.*[9,10] reported an improvement

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(relative to mullite of a density of about 96% of its theoretical value) in flexural strength by the addition of X phase. The latter was produced *in situ* by the reaction sintering of mullite/β′ sialon ($z = 2$), but the authors[9,10] reported a negligible improvement in the room temperature fracture toughness.

The work on additions of Si_3N_4[7] and SiC[8] was by hot pressing and with ultrafine starting powders of 80 nm, while that of Yamagishi *et al.*[9,10] was by pressureless sintering, with grain sizes between 1 and 15 μm. In the present work, a means of achieving close to full densification by pressureless sintering of the two materials under study is investigated. A comparative study of the materials is also undertaken, with a view to understanding how the X phase addition and the method of adding it improve sinterability, hardness and indentation fracture toughness.

Relative to SiC and Si_3N_4 additions, X phase additions could prove to be more cost effective. This is because the X phase of the present work is relatively inexpensively produced by the carbothermal reduction and nitriding of mullite, obtained *in situ* from kaolinitic clays. Another cost related attraction of the method under investigation is that if the pressureless sintering technique is tailored to achieve the same microstructural control usually offered by the hot pressing technique, the former would be preferable.

2 Experimental Procedure and Materials

X phase sialon was produced by simultaneous carbothermal reduction and nitriding of kaolinitic clays. The experimental details of the production schedule can be found in previous work[11,12] by the authors. The commercially pure mullite (CPM) was supplied by the Baikalox company, France. Its characteristics are given in Table 1.

To achieve a true comparison of the two materials—CPM and 15 wt% X phase/85 wt% CPM—both were sintered under the same conditions. Prior to sintering, the powders were both comminuted for 70 h by ball milling (using alumina balls) in a wet (propan-2-ol) medium and then dried.

Table 1. Characteristics of the Baikalox commercially pure mullite (SA 193 CR)

Characteristics	*Values*	*Remarks*
Conversion rate	99%	Minimum
Chemical purity	99.2%	Minimum
Specific surface area	3.5 ± 1.5 m^2/g	BET
Apparent density	0.60 g/cm^3	—
Green density	1.35 g/cm^3	13.8 MPa pressure
Mean agglomerate size	2 μm	

Subsequent X-ray analysis of the dried powders indicated that they were not contaminated by the alumina balls. The dried powders were then uniaxially compacted with a pressure of about 14 MPa and isostatically cold pressed into pellets of 14 mm diameter at a pressure of 345 MPa. Sintering was carried out in a nitrogen atmosphere at 1660°C, 1700°C and 1720°C (for different durations) for the milled composite, and at 1720°C and 1740°C for the CPM for 2 h. The unmilled composite, a mixture of (5 min) vibratory milled X phase and as received CPM powders, was also sintered at 1660°C for 6 h and at 1700°C for 2 h with a view to quantifying the effect of the milling operation on the sinterability of the composite. A mixture (by weight) of 38.5% SiO_2–38.5% Si_3N_4–23% BN was used as the sintering bedding powder. The densities of sintered bodies were determined using the Archimedes method.

Sintered samples were analysed by X-ray diffraction (XRD) for any transformations during sintering. None occurred, but the composite sintered at 1720°C revealed no X phase. This led to the determination of the nitrogen content of unsintered mullite and X phase, as well as of sintered mullite and the composite (both sintered at 1720°C). The aim was to ascertain what happened to the X phase addition. A Leco inert gas fusion machine was used for this purpose.

Hydrofluoric (HF) acid (40%) was used for the etching of the samples. A satisfactory etching was obtained after 100 min. Optical micrographs were made with Nikon (Epiphot) microscope and the microstructure of the samples was also studied using the scanning electron microscope (SEM), Philips 500. With the aid of the macrostage of an image analyser, Olympus, Q2M, the SEM micrographs were used to determine the grain sizes of the samples.

The hardness values of milled samples that sintered to above 98% of their theoretical densities, and the unmilled composite sample that sintered to 95% of its theoretical density were determined using Vickers indentation tester, with a load of 10 kg. For each sample five indentations were made.

2.1 Remarks on the method for the calculation of the fracture toughness K_{Ic}

The indentation method was adopted for its simplicity, rapidity and the size of the samples. The simplicity and rapidity of the indentation method have made it very widely studied and used for the determination of K_{Ic}.[13]

Generally, the view that the indentation method gives a relatively overestimated value of K_{Ic} has always been held. However, finding that the indentation method, irrespective of the equation used, consistently gave a lower value than that obtained from single edge notched bend (SENB) tests. Glandus *et al*[13] proposed an equation that takes into account Poisson's ratio by means of an empirical function. In the present study, apart from the density, no other physical property of the materials was determined. Hence the equation proposed by Shetty *et al*[14] was used

$$K_{Ic} = 0.0889(HP/4l)^{1/2} \qquad (1)$$

where H is hardness (in Pa) given as

$$H = 0.4636P/a^2 \qquad (2)$$

where P is the applied load on the indenter in N, l (in m) is the crack length from the corner where the crack joins the indent to its entire extension and a (in m) is half the diagonal length of the indent (Fig. 1).

However, eqn (1) is for Palmqvist type of cracks (Fig. 1), which may be shown experimentally as those cracks which, on the indented sample being polished, their traces separate from the indent. Another criterion for a crack to be of the Palmqvist type is that the dependence of l and c ($c = l + a$) on indentation load should be linear. Therefore, before using eqn (1) in this study, these two criteria were shown to be verified. Figure 2 is the indent before and after polishing an indented mullite sample. The samples of the composite material showed similar appearance. Many materials can show both Palmqvist and median (Fig. 1; on polishing the indented sample the traces of crack remain attached to the indent) types of crack: the Palmqvist cracks that appear when low loads are used could evolve into median cracks at higher loads. At both low and high loads of the present study, the crack system was consistently of the Palmqvist type. In Fig. 3 the linear relationship of l and c of a mullite sample with the applied load is demonstrated. The composite

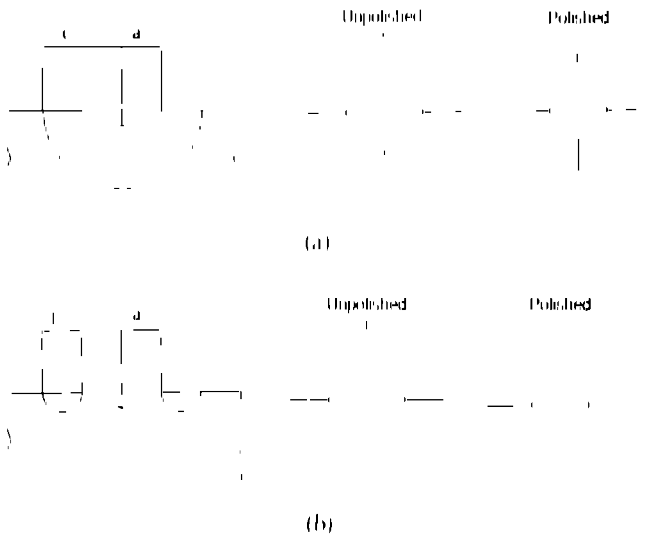
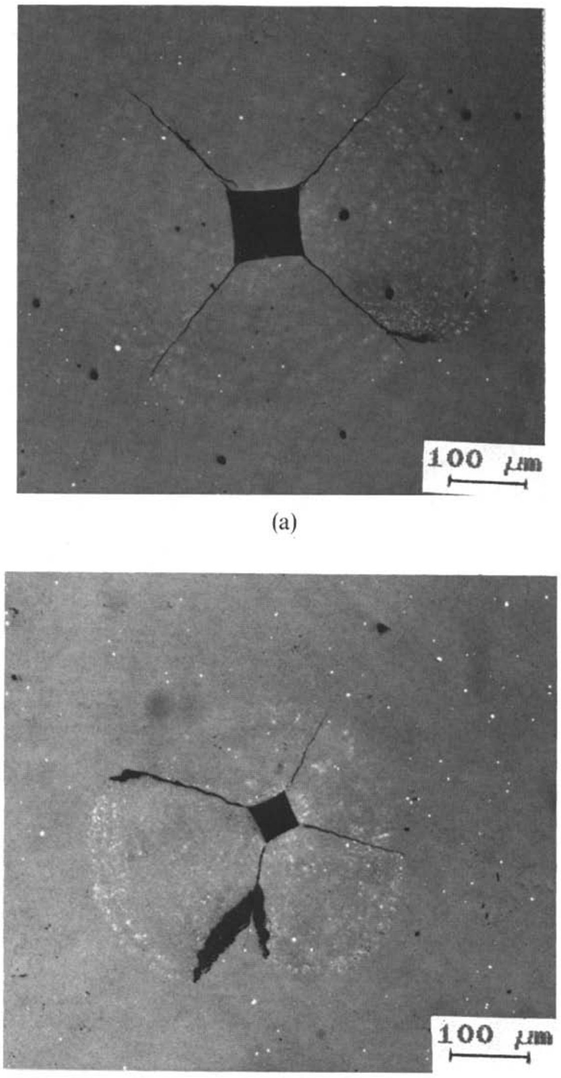


Fig. 1. (a) Median and (b) Palmqvist crack systems induced by Vickers indentation.



(a)

(b)

Fig. 2. Micrographs of an indented sample of commercially pure mullite (CPM) showing a Palmqvist crack system: (a) unpolished and (b) polished.

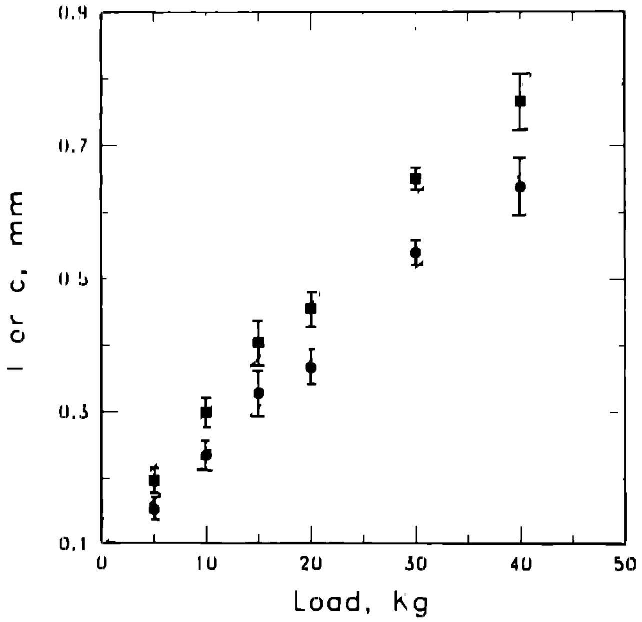


Fig. 3. Linear relationship of (●) l and (■) c of the CPM sample on indentation load.

showed similar relationships. The regression equations are

$$l = 0{\cdot}047 + 0{\cdot}014P \quad (3)$$

(regression coefficient, $r = 0{\cdot}995$)

and

$$c = 0{\cdot}085 + 0{\cdot}016P \; (r = 0{\cdot}995) \quad (4)$$

3 Results and Discussions

3.1 Sintering process

Table 2 is the summary of the results on the sintering of the materials. It indicates that the milling operation improved the density of the composite sintered at 1700°C for 2 h by about 8%. Despite the longer duration (6 h) of sintering of the unmilled composite at 1660°C, the milled sample, sintered at the same temperature for 4 h, showed an improvement in density of 1·6%.

From Table 2 it emerges that higher sintering temperatures (limited by the achievement of the highest percentage of theoretical density) are preferable to long dwelling periods at relatively lower temperatures. Thus, after 4 h at 1660°C only 96·6% of the theoretical density of the milled composite was achieved, as compared to 99·4% achieved for the same material at 1700°C sintered for just 2 h. This is the result of an accelerated shrinkage rate. This is because, as has been demonstrated,[15] higher temperatures bring about increased shrinkage rate, while shrinkage rate decreases with time. A similar effect was observed on sintering mullite X phase composites by the present authors,[16] consequent upon which better bulk densities and reduced shrinkage rate were respectively obtained at higher temperatures and longer sintering periods. High temperatures therefore make short dwell periods possible. Hence the bedding powder remained effective throughout the duration of the sintering process of the present study.

The theoretical density of mullite was approximately 99·7%, achieved at 1740°C. This is in contrast to the work by Yamagishi *et al.*[10] where, using the same pressureless sintering technique, about 95·9% of the theoretical density of mullite was obtained at 1650°C, and at 1700°C the degree of densification reduced to about 95%. The difference between the present work and that of Yamagishi *et al.*[10] in the optimal sintering temperature of mullite may lie in the bedding powder used, because in the latter either mullite alone or no bedding powder was used. Further support to this suggestion could be found in the work by the present authors,[16] whereby use of non optimal bedding powder led to a deterioration of the densification process by between 3 to 5%.

3.2 Hardness and fracture toughness, K_{Ic}

The results of the study on hardness, indentation fracture toughness and grain sizes of the two materials, in the milled form and sintered at 1740°C, 1720°C and 1700°C are summarized in Table 3. In Table 3 is also included the result obtained from the unmilled composite sintered at 1660°C for 6 h.

It can be seen that the mullite sample with the density of 99·7% of its theoretical value (obtained by sintering for 2 h at 1740°C) had marginally lower values of hardness and K_{Ic}, in comparison with the same mullite sintered at 1720°C for 2 h. The composite sintered at 1720°C had the same K_{Ic} value, but a hardness value higher than that of mullite sintered at 1720°C. The highest values of both properties (11831 MPa and 3·7 MPa m$^{1/2}$ respectively for hardness and K_{Ic} values) were obtained for the composite sintered at 1700°C for 2 h, which had a density of 99·4% of its theoretical value. In comparison with the mullite sample of about the same degree of densification of the present work, this represents an improvement in hardness and K_{Ic} values of about 4·9% and 8·8% respectively. However, relative to the unmilled composite sintered at 1660°C for 6 h, with 95% of its theoretical density (hardness and K_{Ic} values of 8652 MPa and 3·2 MPa m$^{1/2}$ respectively), the values of these two properties for the milled composite represent an improvement in hardness and toughness properties

Table 2 Sintering conditions and densities of materials

No	*Material*	*Condition*	*Sintering* *Temp* °*C*	*Time, h*	*Bulk density* $g\,cm^{-3}$	% *Th*[a]
1	CPM[b]	Milled, 70 hrs	1740	2	3·15	99·7
2	CPM	Milled, 70 hrs	1720	2	3·11	98·4
3	15 X[c] 85 CPM	Unmilled	1700	2	2·87	91·5
4	15 X 85 CPM	Unmilled	1660	6	2·98	95
5	15 X 85 CPM	Milled, 70 hrs	1660	4	3·03	96·6
6	15 X 85 CPM	Milled, 70 hrs	1720	2	3·10	98·8
7	15 X 85 CPM	Milled, 70 hrs	1700	2	3·12	99·4

[a] = Theoretical

[b] = Commercially pure mullite

[c] = X phase sialon 15, 85 = respective percentages of materials in the composite

Table 3. Hardness, indentation fracture toughness, K_{Ic} and grain sizes of samples sintered under different conditions

Material	*Condition sintered* (°C/hrs)	*Density* (g cm^{-3})	*Density* (% Th)	*Grain size* (μm)	*Hardness* (MPa^{b})	[illegible] $\times 10^{-3}$	K_{Ic} (MPa m$^{1/2}$)
Milled CPM^{a}	1740/2	3.15	99.7	2.6 ± 1	11279 ± 176	0.185 ± 0.023	3.4 ± 0.1
Milled CPM	1720/2	3.11	98.4	2 ± 1	11643 ± 184	0.183 ± 0.027	3.5 ± 0.2
Milled 15% X 85% CPM	1720/2	3.10	98.8	1.7 ± 1	11831 ± 188	0.185 ± 0.021	3.5 ± 0.1
Milled 15% X 85% CPM	1700/2	3.12	99.4	1.4 ± 1	11831 ± 188	0.171 ± 0.033	3.7 ± 0.2
Unmilled 15% X 85% CPM	1660/6	2.98	95	nd^{c}	8652 ± 347	0.166 ± 0.018	3.2 ± 0.1

^{a} – commercially pure mullite
^{b} – to convert MPa to kg mm^{-2} (VHN) divide by 9.80665
^{c} – not determined

of 36.7% and 15.6% respectively. The importance of milling in obtaining the correct particle size distribution before sintering is therefore clearly established. It is proposed that the milling operation, which leads to a reduction of the powder grain sizes and optimization of size distribution provides an improvement of the properties of mullite and of the composite. It follows therefore that when comparing the effects of additions of composite materials to mullite on its mechanical properties (which depend on the grain size of the material), as far as possible similar grain sizes should be used. For instance if the results obtained on mullite samples (with 10 vol.% Si_3N_4) of 80 nm grain size[9] are to be compared with those obtained on 15 wt% X phase 85 wt% mullite samples of 1 to 15 μm grain size,[10] an ambiguous interpretation may be reached because it will be difficult to ascertain the true relative effect of different additions. For the samples with 80 nm grain size,[9] room temperature flexural strength and K_{Ic} values of about 610 MPa and 3.5 MPa m$^{1/2}$ respectively were observed. Flexural strength was not determined in the present work, but as regards the room temperature K_{Ic} value although values may vary according to the method used by authors, the present results are an improvement on the values of between 1 and 3.5 MPa m$^{1/2}$ reported[2,5,9] in the literature for monolithic mullite or its composites. The final development of properties depends on sintering and extent of densification and grain growth which are discussed in the next section.

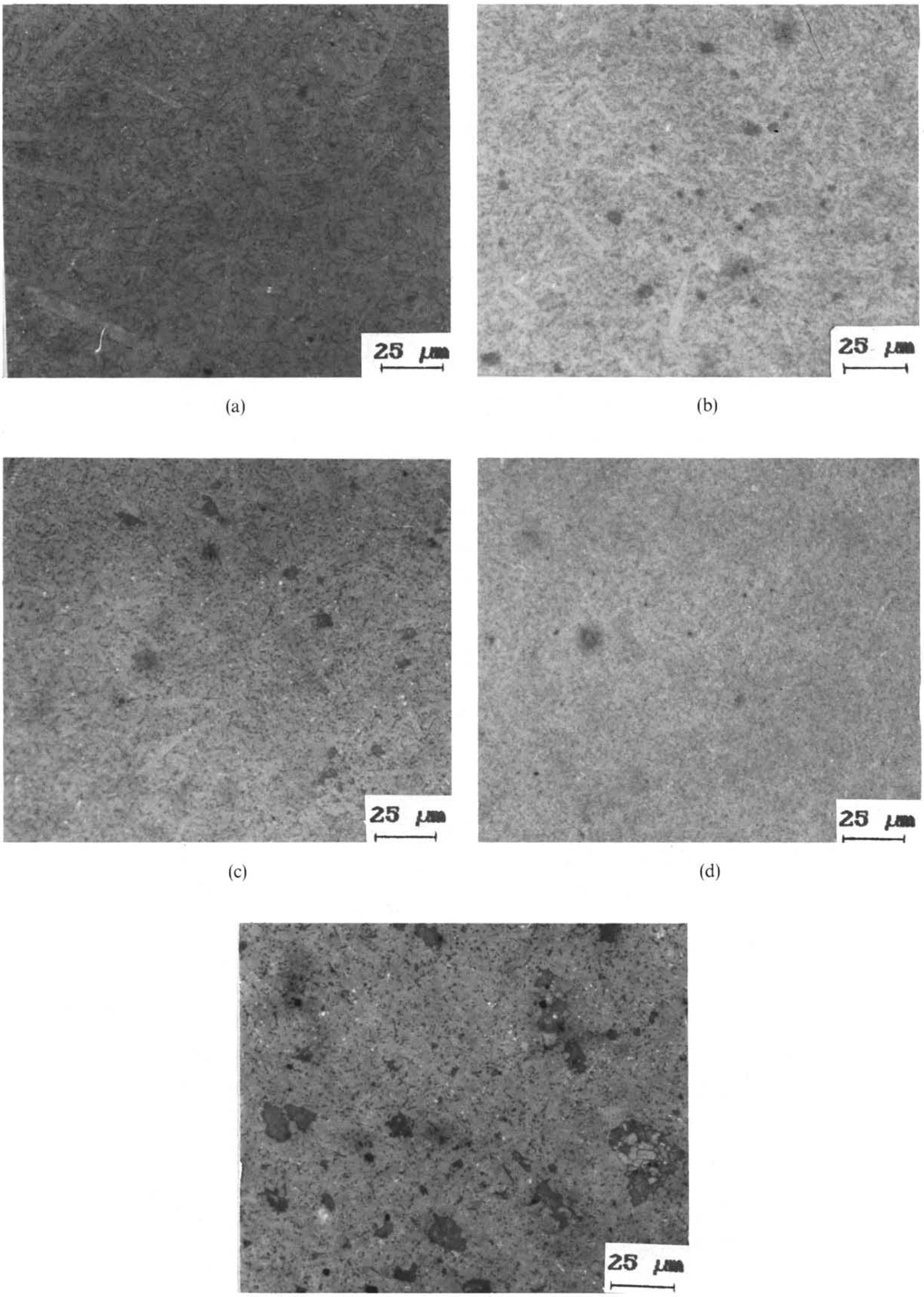
3.3 Microstructural features

The improved hardness and K_{Ic} values of the composite relative to those of pure mullite, can be explained through the microstructural evolution of the sintering process.

In Fig. 4 are the optical micrographs of the samples revealing the degree of porosity in them. More information on their grain sizes however was obtained from SEM. The SEM micrographs are shown in Fig. 5. Although the highest density of 3.15 g cm^{-3} (99.7% of mullite's theoretical density) was achieved for the CPM at 1740°C this high temperature inevitably led to a large grain size (relative to those of the other samples) of 3 ± 1 μm with an aspect ratio of 4.5 ± 0.5, Fig. 5(a). The reduced sintering temperature of 1720°C resulted in an average grain size of 2 ± 1 μm for the CPM, Fig. 5(b), and a slight improvement in properties, relative to those of the sample shown in Fig. 5(a).

The effect of X phase on the microstructure can be observed on comparing Fig. 5(b) with Fig. 5(c) (CPM and composite samples, respectively sintered at 1720°C). The microstructure in Fig. 5(c) is of a more uniform grain size distribution and it has a smaller average grain size of 1.7 ± 1 μm.

The XRD analysis of the composite sample (Fig. 5(c)) sintered at 1720°C, however, revealed no X phase. Yamagishi *et al.*[10] limited the sintering temperature of a similar composite to 1700°C for the reason that X phase decomposes at 1720°C — its congruent melting temperature. The X phase addition was obtained by in situ reaction (pressureless) sintering of mullite mixed with 5 vol.% β' sialon ($z = 2$). However, in the present work, though the sample sintered at 1720°C revealed no X phase in the XRD analysis, a density of 98.8% of its theoretical value was obtained. An indication of what may have happened to the X phase constituent is evident in Fig. 5(c) whereby it presented the largest area of black features, in relation to the rest of the micrographs (the black features being referred to should not be confused with the pores of Fig. 5(e)). These black features are the glassy constituent of the sample. Hence this sample (Fig. 5(c)) has the highest content of glass (silica rich phase). The high content of glass was brought about by the inability of X

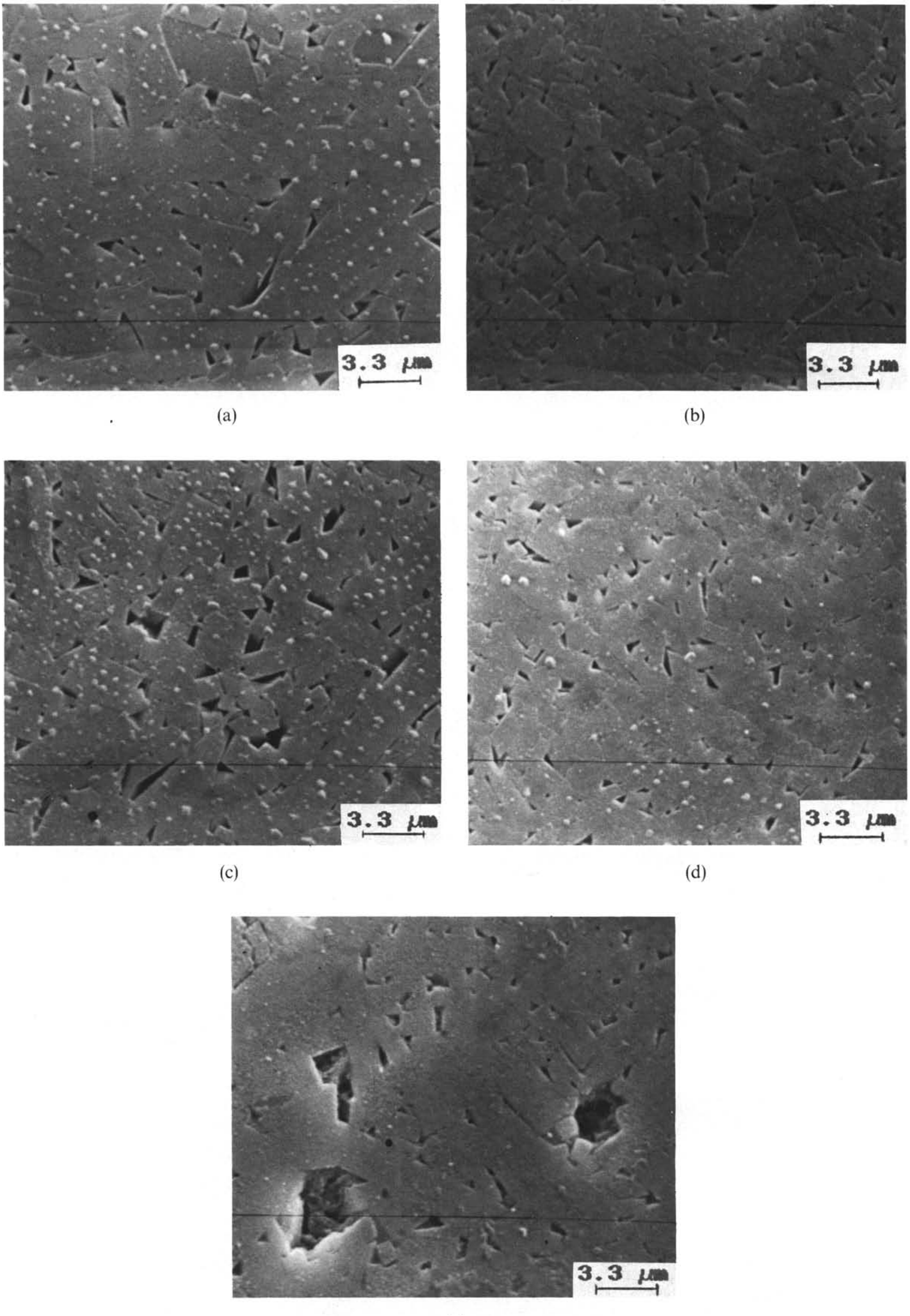


(a) (b)

(c) (d)

(e)

Fig. 4. Optical micrograph of samples sintered to the indicated percentage of theoretical density at the given temperatures and durations in N_2 atmosphere (a) CPM, 99.7%, 1740°C, 2 h, (b) CPM, 98.4%, 1720°C, 2 h, (c) 15 wt% X phase 85 wt% CPM, 98.8%, 1720°C, 2 h, (d) 15 wt% X phase 85 wt% CPM, 99.4%, 1700°C, 2 h, (e) 15 wt% X phase 85 wt% CPM, 95%, 1660°C, 6 h.



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

Fig. 5. Scanning electron micrographs of samples sintered to the indicated percentage of the theoretical density at the given temperatures and durations in N_2 atmosphere. (a) CPM, 99.7%, 1740°C, 2 h. (b) CPM, 98.4%, 1720°C, 2 h. (c) 15 wt% X phase 85 wt% CPM, 98.8%, 1720°C, 2 h. From the X-ray analysis this sample showed no X phase, but note the highest incidence of black features (glassy constituent). (d) 15 wt% X phase 85 wt% CPM, 99.4%, 1700°C, 2 h. (e) 15 wt% X phase 85 wt% CPM, 95%, 1660°C, 6 h.

phase that melted at 1720°C to recrystallize during the rapid cooling cycle. Thus it remained as an additional amorphous constituent of the sample, thereby leading to the availability of more area for attack by HF during the etching operation.

Further evidence to confirm that X phase was still present in the composite sintered at 1720°C was obtained by analysing unsintered X phase and mullite, as well as mullite and composite sintered at 1720°C, for their nitrogen content. The unsintered sample of mullite had a nitrogen content of about 150 parts per million (ppm). The sintered mullite had about 1200 ppm. This implies that during the sintering process in nitrogen gas, some nitrogen dissolved into the sintering liquid phase. The composite had a nitrogen content of about 7800 ppm. Thus the nitrogen content of the composite attributable to the presence of X phase was about 6600 ppm. Unsintered X phase contained 45120 ppm of nitrogen. 15% of the nitrogen content of unsintered X phase satisfactorily accounts for the nitrogen content observed in the sintered composite brought about by the presence of the phase. Therefore the entire amount of X phase of the composite was present as an amorphous constituent. Although the partial composition of nitrogen in X phase does not have a direct bearing on the foregoing rationalization, it should be mentioned that 4.5 wt% N observed by this method is lower than the partial nitrogen contents indicated by the different formulae so far proposed in the literature for the phase. This may be related to the particle size of the powder used, because higher counts were obtained with finer powders, the solid forms giving the lowest count.

Figure 5(d) shows the microstructure of a sample of the milled composite sintered at 1700°C for 2 h. The micrograph shows relatively reduced and even distribution of grain sizes, which led to the sample's better mechanical properties. The average grain size in Fig. 5(d) was found to be 1.4 ± 1 μm. Hence the presence of crystalline X phase (confirmed by XRD) improves the sinterability of mullite at lower temperatures, and leads to a microstructure of relatively even distribution and reduced grain sizes. This effect can be considered synonymous with that of additions on grain stabilization. It has been suggested[11] that in cases where the grains of an additive phase discretely occupy the pores, a limiting grain size (GS) can be achieved through the obstruction of otherwise easy migration of grain boundaries, and that the GS for given volume fraction (V_1) of the additive phase (which is X-phase in this case) and average pore size, d, is obtained according to equation

$$GS = d/V_1 \tag{5}$$

Thus the pore size, d, is effectively reduced by the discrete occupation of the given volume fraction of X phase. Another method[17] through which an additive phase could reduce the grain size of sintered composites is by the former being available at impurity concentration and forming solid solution with the matrix. The solid solution impurity may segregate at grain boundaries, where it can also impede grain boundary migration. The amount of X phase sialon in the present work is so large that its consideration as not being an impurity is justified.

Hot pressing, usually carried out at temperatures lower than those for pressureless sintering, is employed when there is a need to achieve a full densification with reduced grain sizes of sintered samples. Additions of X phase sialon in mullite may therefore limit the use of hot pressing of this composite to only cases of advanced microstructural control; that is, in the presence of X phase sialon, temperatures lower than those currently in use for hot pressing would be required. For pressureless sintering, the maximum advantage of the improving effect of X phase addition is taken if the starting powders are of fine grain sizes, and at temperatures greater than 1660°C. These conditions are evident from Table 2, where even after 4 h at 1660°C only a density of 96.6% (compared to 99.4% at 1700°C for 2 h) of the theoretical density of the milled composite was obtained, while at 1700°C for 2 h, a density of 91.5% of its theoretical value was achieved for the unmilled composite. In Fig. 5(e) is the micrograph of a sample of the unmilled composite sintered at 1660°C for 6 h, in which 95% of its theoretical density was obtained. The unmilled composite sintered at 1700°C for 2 h presented a similar microstructure.

4 Discussion

The method through which X phase/mullite composite is made may also affect the value and variation of its physical and mechanical properties. Using the same sintering technique, but with an in situ method of producing the X phase sialon, Yamagishi *et al.*[9,10] obtained a density of 97.5% of the theoretical value of a composite similar to that under the present study. They also observed, relative to monolithic mullite, a 10% improvement in the room-temperature flexural strength, but only 5% improvement in the room temperature K_{IC}. This is despite the fact that the mullite sample of their work was only about 96% of its theoretical density, and thus must have relatively inferior mechanical properties to mullite samples with greater than 98% of theoretical density, obtained by the same pressureless sintering route.

However in the present work, where pre-produced X phase is mixed with mullite and their grain sizes further reduced, a density of 99·4% of the composite's theoretical value was achieved. The improvement in toughness (9%) is more significant than that in hardness (5%). In comparison with the values and variation of the properties of the composite in the study by Yamagishi *et al.*[9,10] it seems the uncontrolled nature of microstructural evolution during the transformations associated with reaction sintering is unfavourable to the toughness property.

This suggestion stems from the results of an unpublished work by the present authors in which it was observed that the uncontrolled nature leads to a 'chaotic' structure, Fig. 6(a), and a heterogeneous distribution of grain sizes, Fig. 6(b). In this unpublished work, 40 wt% X phase 60 wt% mullite powder was obtained by simultaneously reducing (carbothermally) and nitriding kaolinitic clays. During subsequent sintering of the powder, further transformation of mullite to X phase occurred, leading to a 50 wt% X phase 50 wt% mullite composition. In the same work, a similar composition obtained after sintering a mixture of 50 wt% pre-produced X phase with 50 wt% CPM, in which no transformation took place, resulted in the microstructure shown in Fig. 6(c) (compare with Fig. 6(a) and (b)). Hence using pre-produced X phase instead of that produced *in situ* not only removes the limitations imposed by the uncontrolled nature of transformations but also offers the opportunity of reducing the grain sizes of the constituents further. This would invariably lead to the improvement of strength and more so, the toughness of the composites.

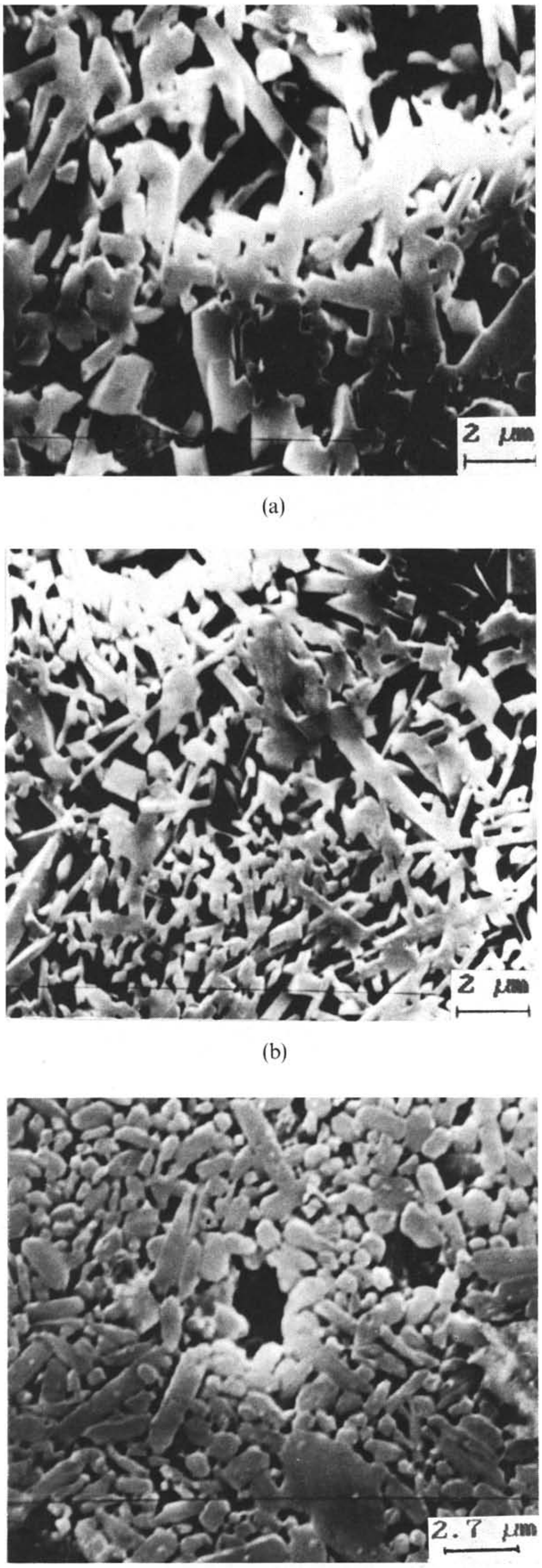


Fig. 6. Scanning electron micrographs of sintered 50 wt% X phase 50 wt% mullite typifying the microstructural evolution of the process with reactions showing (a) a 'chaotic' arrangement of grains, and (b) a heterogeneity of grain size distribution in the same sample as (a). (c) the microstructural evolution of the same composition, but with pre-produced X phase in a commercially pure mullite. No transformation occurred. Note the orderliness and relatively even distribution of grain sizes.

5 Conclusions

Densities in excess of 99·3% of their theoretical values were obtained for commercially pure mullite, CPM, and 15 wt% X phase sialon 85 wt% CPM composite sintered at 1740°C and 1700°C respectively for 2 h by pressureless sintering. In comparison with the work of other authors, this has been possible due to the positive effect of the bedding powder used in the present work.

The presence of X phase sialon in CPM was found to improve the sinterability of the composite at relatively low temperatures (which led to finer grain sizes), and to promote a relative uniformity in the distribution of grain sizes. It is proposed that the effect is achieved through the discrete occupation of pores in the composite by X phase sialon. The improvement effect is present even when the sialon is in an amorphous (glassy) state at 1720°C.

Consequent upon the improved microstructure realized by an addition of 15 wt% X phase sialon in CPM, better hardness and room temperature K_{Ic} values, relative to those of samples of CPM, were obtained The improvement is more noticeable if the starting powders are of reduced grain sizes

Using additions of pre produced X phase sialon is shown to be a more effective method than that based on in situ produced X phase, for producing X phase sialon/mullite composites of improved strength and toughness values.

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