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Crack Evolution and Estimation of Fracture Toughness of HfO_2/SiCN(O) Polymer Derived Ceramic Nanocomposites**

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In this study the crack evolution and fracture toughness of HfO_2/SiCN(O) ceramic nanocomposites were studied. These ceramics crack radially under indentation in contrast to Hertzian crack in SiOC ceramics. This difference was attributed to the variance in Poisson's ratio and elastic modulus to hardness ratio. Fracture toughness by crack opening displacement and radial crack length measurement was 0.8–1.2 MPa.m$^{1/2}$ and 2.5–3 MPa.m$^{1/2}$, respectively. The open network forming structure resulted in the over estimation of fracture toughness value by RCL.

In recent years studies on the synthesis and properties of transition metal oxide modified polymer derived ceramic (PDC) nanocomposites have been extensively carried out.[1–5] Due to their exciting properties these materials have been envisaged for various structural and functional applications. However, due to the inherent brittle nature, the applications of PDC materials as structural materials are limited. This could be overcome by suitable microstructural design using reinforcing elements and removal of any stress raising flaws.[6–8] Nevertheless, an understanding on the fracture toughness behavior of these PDCs is important. Hence, the fracture toughness values can be estimated by the accurate determination of the critical stress intensity factor under mode I loading (K_{IC}).

Several methods have been used in the literature for the determination of the fracture toughness. For instance, single edge notched beam test (SENB) was used for the deter of fracture toughness in SiC,[9] SiOC[10], and SiCN[11] PDCs. Another common method is to use the Vickers indentation, wherein from the measurement of radial crack length (RCL) effective determination of fracture toughness is possible. Nishimura *et al.* have determined the fracture toughness value of SiCN PDC using RCL method.[12] Another simple and reliable technique to determine the fracture toughness is the measurement of the crack opening displacement (COD) at the crack tip of the indentation crack produced by Vickers indentation.[13,14] Bauer *et al*.[15] and Janakiraman *et al*.[16] have used the COD method for the accurate determination of fracture toughness in SiCN PDCs.

Despite the aforementioned studies, the fracture toughness evaluation of the PDC nanocomposites is lacking in the literature. Moreover, in most of the above mentioned studies cold pressing and thermolysis route have been adopted, thereby resulting in a less dense structure. Hence, to overcome this limitation a pulsed electric current sintering (PECS) technique was used to produce fully dense PDCs. This is possible since sintering is carried out after the thermolysis and hence, the mass loss is insignificant. In the current study, crack evolution behavior of HfO_2/SiCN(O) PDC nanocomposite was studied. This was compared to the crack evolution observed in SiOC PDCs. Moreover, the fracture toughness values of HfO_2/SiCN(O) PDC nanocomposite was estimated using both the RCL and COD method and the values obtained from both the methods were compared.

1. Experimental Methods

HfO_2/SiCN(O) PDC nanocomposites were produced by the solid state thermolysis (SST) of hafnium alkoxide modified polysilazane. The details of the synthesis procedure were discussed elsewhere.[2] The as-thermolysed ceramics were sintered using pulsed electric current sintering (Sumitomo Coal Mining Co. Ltd, Japan) to produce pellets of diameter 20 mm.[3] Sintering was carried out at in vacuum at 1500 °C and will be referred to as SiHfCNO1500. The pressure,

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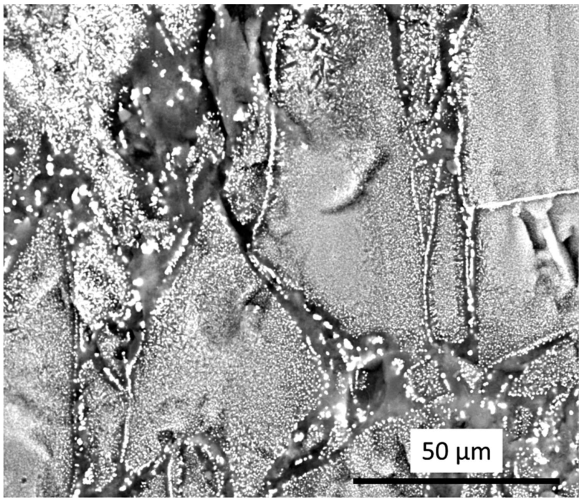

Fig. 1. Back scattered electron micrograph of HfO_2/SiCN(O). Bright regions indicate enriched regions of HfO_2.

holding time and heating rate were 30 MPa, 30 min, and 50 °C min^{-1}, respectively. For comparison of the deformation behavior, experiments were also carried out on SiOC ceramics obtained by the solid state thermolysis of polyhydridomethyl siloxane.[17] Similar sintering procedure as in the case of SiHfCNO1500 was adopted for the pulsed electric current sintering of SiOC and the sintered ceramic will be hereafter referred to as SiOC1500.

An ultrasonic resonant frequency testing method was used to determine the Poisson's ratio of these material systems. To determine the fracture toughness using RCL method, Vickers indentation was carried out at an indentation load of 9.81 N for a holding time of 10 s so as to ensure that the radial cracks generated around the Vickers indent are present within an individual particle. The obtained cracks were imaged using field emission scanning electron microscope (Quanta 400, USA). Images of the cracks were taken from the crack tip to the crack origin for the effective determination of crack opening displacement. For the radial crack length measurements, crack lengths were measured from the center of the indent to the tip of the crack. The elastic modulus (E) of 313 GPa and hardness (H) value of 18.2 GPa, required for the determination of the fracture toughness was taken from the nanoindentation studies reported earlier.[3] The microstructure of SiHfCNO1500 ceramic was taken using FEI Quanta 200 (USA) scanning electron microscope in the back scattered electron (BSE) mode.

2. Results and Discussion

Figure 1 shows the BSE image of SiHfCNO1500 ceramic. The bright regions in the micrograph indicates the presence of HfO_2 nanoparticles. In brittle materials, deformation upon indentation can occur either by densification (anomalous) or by shear flow (normal). In those materials where densification is favored, radial crack formation is difficult to occur. Even if radial cracks are observed its length will be significantly shorter. The optical micrograph obtained in-situ indicating the evolution of radial cracks upon indentation for SiHfCNO1500 at a maximum load of 9.81 N is shown in Figure 2**(a)**. Cracks were observed to evolve radially inferring the "normal like" behavior of these ceramics. For comparison crack evolution observed in SiOC PDC was studied and is shown in Figure 2(b). In SiOC PDC, at comparable load, only Hertzian cone cracks were observed. There was no indication of any radial cracking. Hence, the evolution of the cracks in SiOC PDCs can be considered analogous to the anomalous glasses such as fused quartz with no formation of radial cracks. This suggests that the crack evolution observed in HfO_2/SiCN(O) ceramics is different from that observed in SiOC PDCs even though both the material systems tend to undergo densification under the indenter.

One of the reasons for the difference in the crack evolution between HfO_2/SiCN(O) and SiOC PDC could possibly because of the differences in the chemical structure and the type of chemical bonding. For instance, SiOC PDCs were reported to develop Hertzian cone cracks,[18] whereas, in SiCN ceramics radial cracks were observed.[15,16] Since the structure of HfO_2/SiCN(O)PDC nanocomposite is similar to

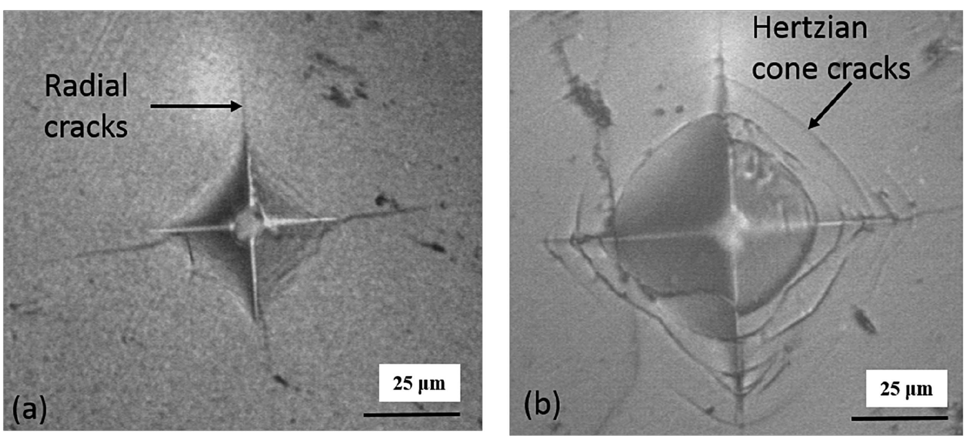

Fig. 2. Crack evolution in (a) HfO_2/SiCN(O) and (b) SiOC PDCs.

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Table 1. Poisson's ratio and modulus to hardness ratio of fused quartz, SiOC1500, and SiHfCNO1500.

Material system	υ	E/H
Fused quartz	0.17	8.22
SiOC1500	0.22	8.64
SiHfCNO1500	0.25	17.20

that of SiCN, consisting of Si–C and Si–N bonds, it could be considered that these ceramics also undergo deformation by radial crack formation. However, in SiOC PDC the presence of large fraction of glass forming element such as Si-O might have resulted in the significant resistance to microcracking.

Recently, studies were conducted wherein the effect of Poisson's ratio on the indentation deformation behavior is discussed.[19–22] It was observed that Poisson's ratio plays a detrimental role in deciding the ability of the material to accommodate the contact loading.[19] Moreover, it was observed that glasses with large υ value ($\upsilon > 0.25$) tend to deform normally by forming radial cracks while for those with small υ value ($\upsilon < 0.20$) anomalous behavior was observed.[22] In the present study, υ of HfO_2/SiCN(O)PDC nanocomposite was higher than that of SiOC and fused quartz ceramics (Table 1). This suggests that the large υ value of HfO_2/SiCN(O) PDC nanocomposite might have resulted in the formation of radial cracks. Another key factor is the E/H ratio, and this ratio is much higher for SiHfCNO1500 in contrast to SiOC1500 and fused quartz ceramics. It was observed that for materials with large E/H ratio (for example: sapphire (E/H ≈ 16) and MgO (E/H ≈ 25) radial cracks tend to occur easily, for comparable υ values[22]. Hence, it could be suggested that the higher υ and E/H value of Si-Hf-C-N(O) ceramics could have contributed to its "normal like" behavior.

From the radial crack length observed in HfO_2/SiCN(O) PDC nanocomposite, the fracture toughness was determined (Eq. 1).

$$K_{1C} = \frac{\chi P}{c^{3/2}} \quad (1)$$

where P is the load, c is the crack length and χ is the coefficient which is defined as

$$\chi = \xi \left(\frac{E}{H}\right)^{1/2} \quad (2)$$

where $\xi = 0.016$ is the geometry constant. The coefficient χ determines the radial crack length in the Vickers indentation.[23] Accordingly, K_{1C} values of 2.5–3 $MPam^{1/2}$ were obtained. This was comparable to the K_{1C} value (2.1 $MPam^{1/2}$) reported for the amorphous SiCN ceramic by RCL method.[12] It should be noted that the quantity, $\xi = 0.016$ used in Equation 2 is obtained by calibration against normal materials which deform by shear flow.[24] However, these PDC nanocomposites are open network forming structured materials capable of undergoing densification under an indenter. Hence, the radial crack lengths observed will be reduced in length, thereby resulting in the overestimation of K_{1C} value.

To overcome this limitation, COD method was adopted wherein from the crack profile the K_{1C} value was estimated. This method for the evaluation of K_{1C} value in PDCs was reported earlier.[15,16] Figure 3 shows the crack profile used for the

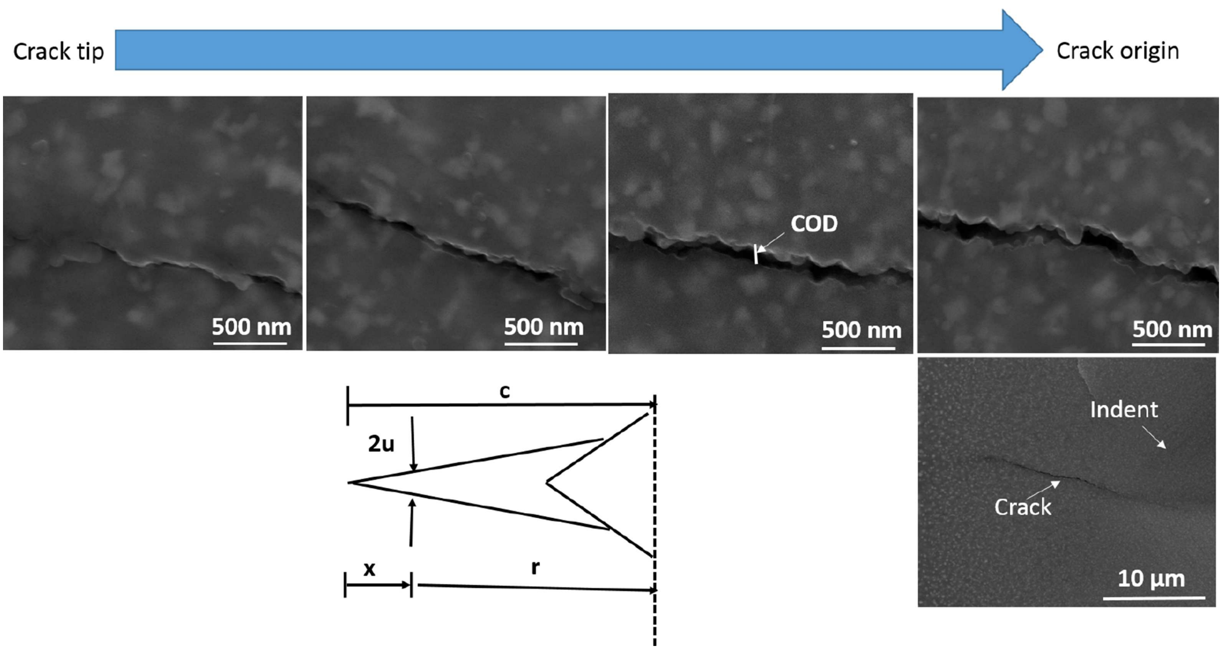

Fig. 3. Crack profile after indentation of HfO_2/SiCN(O) PDC nanocomposite, showing the COD from the crack tip to the crack origin.

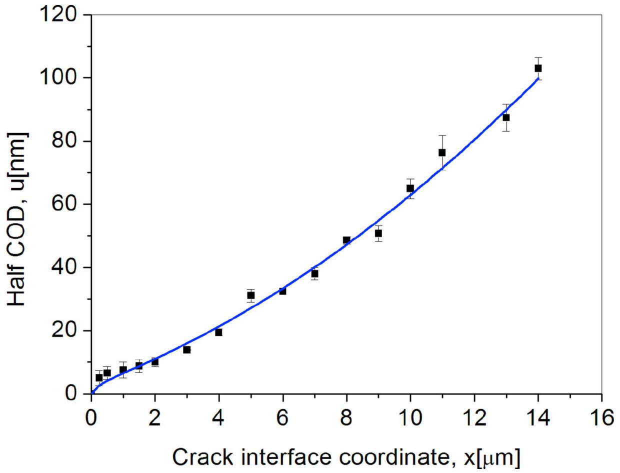

Fig. 4. Half of the crack opening displacement is plotted as a function of crack interface coordinate measured from the crack tip. Solid line shows the fitted line as per Equation 4.

determination of K_{IC} value in HfO_2/SiCN PDC nanocomposite. The following parabolic function is used to describe the half of the crack opening displacement (u) at the crack tip (Eq. 3).

$$u(x) = \left(\frac{K_{tip}}{E'}\right)\left(\frac{8x}{\pi}\right)^{1/2} \quad (3)$$

where, K_{tip} is the stress intensity factor at the crack tip which is equal to K_{IC} under equilibrium conditions, E' is the elastic modulus for plane strain and x is the distance from the crack tip. However, because of the increase in residual stress an increase in distortion of the crack profile away from the crack tip occurs.[15] Hence, a better approximation is obtained by modifying the Equation 3 accounting for the distortion due to residual stress (Eq. 4).

$$u(x) = \left(\frac{K_{tip}}{E'}\right)\left(\frac{8x}{\pi}\right)^{1/2} + Bx^{3/2} + Cx^{5/2} + \ldots \quad (4)$$

Accordingly, the fracture toughness is determined by fitting the crack profile (Figure 3) using Equation 4. The solid curve shown in Figure 4 corresponds to the fitted data. A correlation coefficient of 0.98 was obtained. For the estimation of fracture toughness, the slope (K_{tip}/E') obtained from Figure 4 is multiplied against E'.

Hence, the fracture toughness value was determined and the value obtained was 0.8–1.2 $MPam^{1/2}$. It is to be noted that the value obtained by COD method is lower than the value determined by RCL method. This suggests that the K_{IC} value determined by RCL method is over estimated. Bauer *et al* have also reported a similar difference in the fracture toughness value measured using ICL and COD methods in SiCN PDCs.[15] The values reported were 2.5 $MPam^{1/2}$ (ICL) and 0.7 $MPam^{1/2}$ (COD) respectively.[15] Moreover, in another study by Janakiraman *et al*. Si–C–N ceramics K_{1C} value measured using COD method was ~ 1 $MPam^{1/2}$.[16] These values were comparable to the K_{IC} values reported for oxide glasses.[25] The difference in the fracture toughness values measured using radial crack length measurement and COD could be accounted to the open structure these ceramics possess. For instance, in a study carried out on the fracture toughness measurement of soda lime and borosilicate glasses, the authors have reported a difference in values between the two methods in borosilicate glass in contrast to soda lime glass.[26] The reason for this was accounted to the open network forming structure of certain kind of glasses wherein the fracture toughness measurement by radial crack length measurement leads to abnormally high values. This is because for the materials with high open structure the plastic component of contact deformation is compression driven thereby radial crack formation is limited. This results in the overestimation of the fracture toughness values determined by radial crack length measurements. To correct this error the authors have suggested a new geometry factor (ξ) value of 0.006 in place of 0.016 in the Equation 2.[26] Henceforth, after making this correction in ξ value, the fracture toughness value measured by RCL measurement is 0.96 ± 0.15 $MPam^{1/2}$ which is in close agreement with the value obtained by COD.

3. Conclusions

The crack evolution in HfO_2/SiCN(O) PDC nanocomposite was different from the crack pattern observed in SiOC PDCs. This difference in the crack patterns was attributed to the higher Poisson's ratio and large E/H value of the HfO_2/SiCN(O) PDC nanocomposite. The fracture toughness was measured by two methods and the value obtained from the ICL method was higher than the value obtained by COD method. This was correlated to the reduced radial crack lengths because of the open network forming characteristics of these PDCs. Henceforth, the value obtained by COD of 0.8–1.2 $MPam^{1/2}$ was considered as the actual fracture toughness value of HfO_2/SiCN(O) PDC nanocomposites.

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