

Toward Better Personal Ballistic Protection

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Abstract. A Canadian ceramic armour team composed of scientists from several government research organizations in Canada was formed to explore the potential of composite ceramic materials for personal armour applications. Methods to impregnate and integrate single walled carbon nanotubes additives into ceramic matrix of Al₂O₃ were explored. Various volume of single wall carbon nanotubes as well as different processing approaches were used to prepare samples in an attempt to optimize mechanical properties. The processing approaches investigated were pressureless sintering, hot pressing and hot isostatic pressing. Other Al₂O₃ ceramic composites were also fabricated and evaluated. These included Al₂O₃ composites reinforced with Al₂O₃ fiber fabric and Al₂O₃ fiber fabric with multi wall carbon nanotubes grown onto the fiber surface. Those composites ceramic sample were tested, and the results were compared with some of the commercial single component armour ceramic. Boron nitride nanotubes, being thermally more stable than carbon nanotubes, were also investigated as an alternative to the single wall carbon nanotubes. In this paper, parameters influencing mechanical properties of composite ceramic armour are discussed. Results from mechanical properties are shown.

Keywords: armour materials, composite ceramic materials, carbon nanotubes, Boron nitride nanotubes

1. INTRODUCTION

Ceramics materials show physical properties and performances that make them suitable for armour applications. In fact, the high compressive strength and hardness of ceramic materials contribute to high resistance to the loading produced by a penetrator at impact. However, despite their relatively low areal density, ceramic armour plates contribute to a large portion of the personal armour weight. Also, their inherent brittleness and low fracture toughness severely limit the multi-hit capabilities. Considering materials properties, armour performance has not been successfully correlated to a specific material characteristic or a static material property. Therefore, what the characteristics of an ideal ceramic should be is not clearly known. The key material properties taken in our study as guide to the development of new ceramics for light armours are density, hardness, and fracture toughness. The density defines the weight of the armour. The hardness influences the capability of destroying the projectile tip. The toughness is the resistance to fracture and defines the amount of energy per volume that material can absorb before rupturing. As a rule-of-thumb, hardness higher than that of the projectile is desirable for armour ceramics. High fracture toughness is also desirable to minimize the shattering of the ceramic on impact which may improve the ability of the material to resist multiple hits. Unfortunately, hardness and toughness tend to follow an inverse relationship in most materials, which means that an increase in hardness is generally accompanied by a decrease in fracture toughness.

Reinforcing the ceramics with carbon nanotubes (CNTs) has a great potential to improve or maintain the ballistic properties while reducing the weight of the armor, because the one dimensional CNTs are expected to reside within the boundaries of the ceramic grains, and as a result, limit the crack

propagation and strengthen the ceramic. It has been reported [1, 2, 3] that low loadings of CNTs can have a significant enhancement of hardness and fracture toughness. In this work, efforts were focused on using single walled carbon nanotubes (SWCNTs) as fillers for monolithic Al₂O₃ matrix to maximize the mechanical performance of the ceramic composite and minimize the mass loading of CNTs.

Other reinforcement approaches were tried, such as alumina fiber fabric reinforcement and alumina fiber fabric covered with CNTs (3D structure), mostly to investigate what would best benefit the ceramic in term of mechanical properties and improve the failure resistance.

2. POTENTIAL MATERIALS PROCESSES WHEN USING SINGLE WALL CARBON NANOTUBES (SWCNTs)

The materials processes investigated were hot pressing (HP), hot isostatic pressing (HIP), cold isostatic pressing (CIP) and pressureless sintering (PS). Test samples were made with high purity commercially available ceramic powder (over 99.5% for Al₂O₃). For each manufacturing process, different conditions (pressure, temperature profile, sintering time, etc.) were applied on monolithic samples. Details of processing are available in Ref [4, 5]. Comparing mechanical properties with the results obtained for commercial ceramics allowed to establish the best material processing conditions that were subsequently used to fabricate ceramic composite samples reinforced with SWCNTs.

Results showed that hot pressing (HP) is the preferred process to maintain or ameliorate mechanical properties of Al₂O₃ ceramics reinforced with SWCNTs. This paper analyses HP results for different SWCNTs preparation techniques and variable wt% load when mixed with Al₂O₃ ceramic matrix.

3. OPTIMISATION OF AL₂O₃ REINFORCED WITH SWCNTs

Many parameters can affect the efficiency of the carbon nanotubes to improve ceramic armour failure resistance. At first, intensive work was done to insure good compatibility of the CNTs with the Al₂O₃ ceramic matrix [4, 5]. Considering compatibility is under control, other parameters such as variation in CNTs wt% content, CNTs dispersion, pressure used during sintering can all affect the quality of the ceramic composite and their relative influence must be evaluated. Observations from scanning electron microscope and relative density after sintering were used to control the quality of the ceramic. Table 1 summarized results for different parameters when using hot pressing fabrication method with a sintering temperature of 1500 °C is maintained for a period 30 min. The full sintering cycle takes 10 hours including the heating and cooling temperature periods. The densities shown in Table 1 were estimated using the theoretical Al₂O₃ density of 3.95 g/cm³.

Table 1. Summary for Al₂O₃ reinforce with SWCNTs, hot pressed, Temp. = 1500 °C, time = 30 min.

Sample ID	Functionalization process	Mixing Process	Sample Diameter cm	Pressure (MPa)	SWCNTs wt%	Density (%)
1	OH	BM	7.0	27.85	1	99.19
2	OH	SP	7.0	27.85	1	95.48
3	OH	SP	3.2	35.99	1	98.67
4	PVA	SP	3.2	35.99	1	98.65
5	OH	SP	5.1	26.34	5	87.00
6	OH	SP	7.0	27.85	5	89.07
7	OH	SP	7.0	34.82	5	89.71
8	PVA	SP	7.0	51.08	5	88.33
9	PVA	SP	5.1	68.95	5	90.55
10	OH	SP	7.0	51.08	10	90.67
11	OH	SP	5.1	68.95	10	90.98

SWCNTs = Single Wall Carbon Nanotubes

BM = Ball Milling

SP = Solution Processing

OH = covalently functionalized with HydrOxyl groups via ozonolysis

PVA = non-covalent functionalized with polyvinyl alcohol as a surfactant

The results presented in Table 1 are thoroughly discussed in the following sections.

3.1 Dispersion and density control

Intuitively, it is expected that a proper dispersion of CNTs would contribute to restrain the failure propagation. Therefore, it is important to find ways to control the dispersion and to verify what dispersion pattern would best work to restrain failure propagation. During the synthesis of the SWCNTs/ Al_2O_3 composite, functionalization (covalent or non-covalent) of the CNTs surface and powder mixing (ball milling or solution processing) used before the sintering process could both influence the dispersion. Fig. 1 summarized the functionalization approaches used in this research.

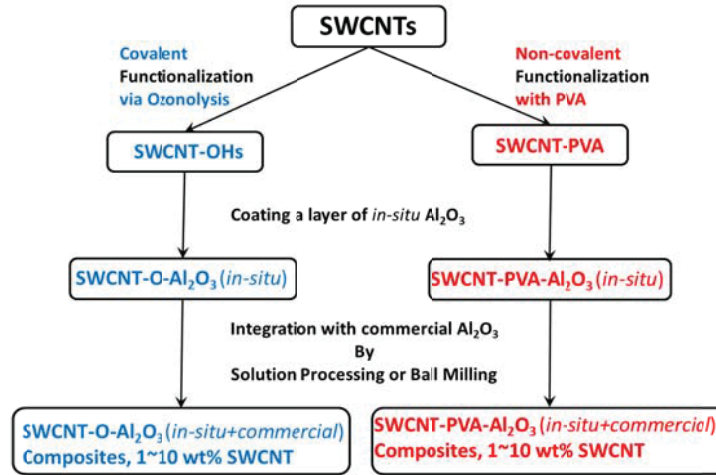


Figure 1. Schematic illustration of the synthesis of SWCNT/ Al_2O_3 composite

CNTs can be covalently or non-covalently functionalized. The covalent functionalization (identified as OH in Table 1) form stronger chemical bonds between the functional group and the CNTs, but tend to cause defects on the CNTs sidewalls. The non-covalent functionalization (identified as PVA in Table 1) has weaker chemical bonds, but preserves the integrity of the CNTs [5]. As seen in Figure 2 for a mixture of Al_2O_3 with 5 wt% SWCNT, both functionalization methods result in relatively uniform CNTs dispersion.

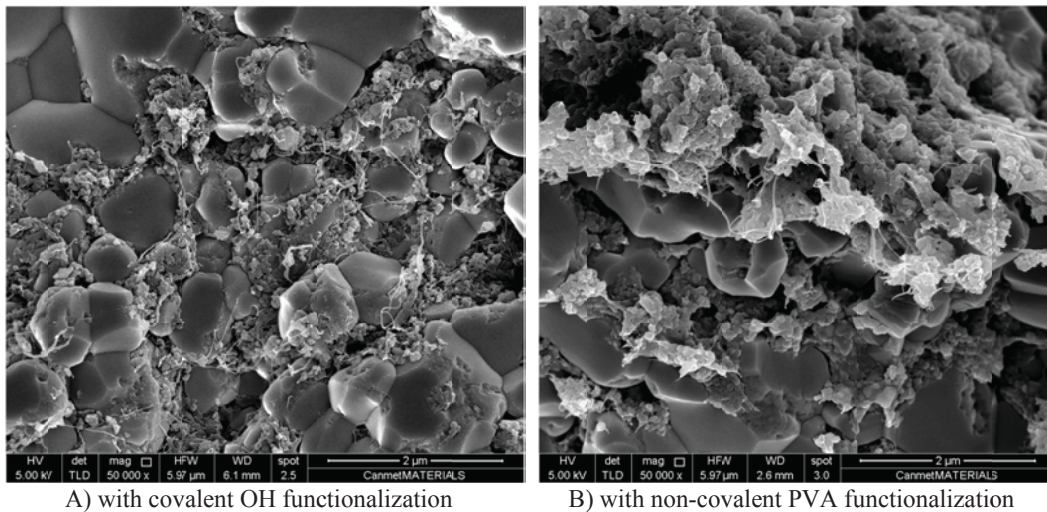


Figure 2. Microstructure of Al_2O_3 + 5 wt% SWCNT sintered at 1500°C for 30 min; magnification 50k

Also, as evidenced from Table 1, samples # 3 and #4 were prepared with the same CNTs wt% content, at the same pressure and with the same mixing process. Results show that both functionalization approaches have no influence in the final ceramic composite density.

After CNTs are functionalized and surface coated with layers of Al_2O_3 , they are ready to be mixed with the ceramic matrix powder. Two mixing processes have been used: ball milling (BM) process and solution processing (SP). The ball milling process consists of placing in a container the ceramic powder with the surface coated CNTs. While the container rotates, the stainless steel balls move mixing the ceramic powder with the surface coated CNTs till it becomes homogeneous. The solution processing starts with the ceramic powder and the surface coated CNTs suspended in distilled water. The mixture is sonically stirred until a homogeneous dispersion is obtained, and then dried. After hot pressing, the microstructure (see Figure 3) of the ceramic composite powders mixed using ball milling process shows that CNTs tend to cluster, while the ceramic composite powder mixed using solution processing results in a more uniform distribution. Also, the grain sizes for ball milling are bigger than the one observed for solution processing.

Table 1 lists all the different combinations of processes/factors affecting the density. The highest density was produced for the ball milling process. However, increasing pressure using the solution process has improved the density, in particular for the 1 wt% CNTs, bringing it closed to the values obtained for the BM process.

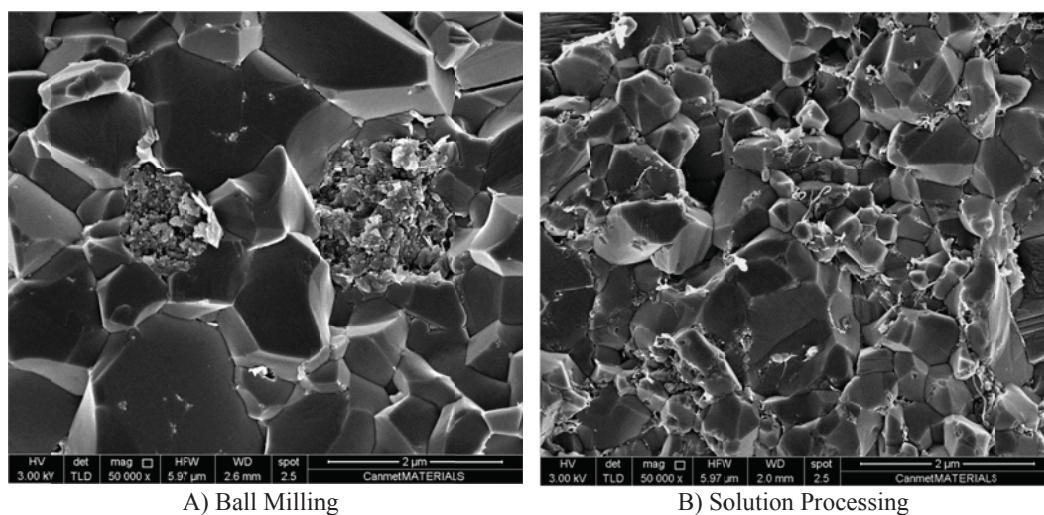


Figure 3. Microstructure of $\text{Al}_2\text{O}_3 + 1 \text{ wt}\%$ SWCNT sintered at $1500 \text{ }^\circ\text{C}$ for 30 min; magnification 25k

To improve the failure resistance of ceramic, it is expected that a higher wt% of CNTs would improve the resistance failure to crack propagation. But first, it has to be verified how the wt% of CNTs may affect the composite ceramic densification. As such, we have varied CNTs content in the ceramic from 1 to 10 wt%. Surprisingly, the ceramic having high wt% of CNTs showed considerable reduction of density. In fact, after increasing the CNTs content from 1 to 5 wt% (Table 1, sample #2 vs #6), the density has drastically decreased. Even increasing the pressure applied during the sintering (Table 1, sample #6 vs #7) had not influenced the density meaningfully. The same can be said for the composites with 10 wt% CNTs.

From the cases summarized in Table 1, only the 1 wt% CNTs has shown interesting results and all further investigation has used this wt% CNTs content only.

4. MULTIWALL BORON NITRIDE NANOTUBES REINFORCEMENT (MW-BNNTs)

BNNTs are non-oxide ceramic. They are structurally similar to CNTs, namely long cylinders with diameter of several to hundred nanometers and length of many micrometers, and they both possess exceptional elastic properties (Young's modulus in the range of 0.5 to 1 TPa). However, BNNTs are more thermally and chemically stable than CNTs. They have a much higher resistance to oxidation (up to $1100 \text{ }^\circ\text{C}$ compare to $500 \text{ }^\circ\text{C}$ for CNTs) [6, 7]. With their one-dimensional structure and high Young's modulus, MW-BNNTs are ideal reinforcement components for ceramic composite materials.

The MW-BNNTs used in this study were not functionalized and mixed with commercial alumina by solution processing. They were hot pressed using the same sintering condition as previous ($T = 1500 \text{ }^\circ\text{C}$, maintain 30 min). The nanotubes content was limited to 1 wt% MW-BNNTs.

5. CERAMIC FIBER REINFORCEMENT

Another approach that can contribute to improve failure resistance is by reinforcing ceramic with ceramic fiber fabric. In this case, the fabric layers should act as a crack arresting barriers, resulting in improved fracture resistance. This approach is not expected to affect other material properties such as the hardness or the density of the ceramic composite.

When producing ceramic/ceramic fiber composite, materials were manually layered until pre-determined ratios were achieved inside a graphite die. Care was taken to ensure even volumes of powder were incorporated between each layer of fabric. Hot pressing fabrication method was used with the same sintering condition as previous ($T = 1500\text{ }^{\circ}\text{C}$, maintain 30 min). Two Al_2O_3 composites with fiber additions were tried: one received 8% fiber by volume and the other 18% fiber by volume. Only results from 18% by volume are shown in this paper, having produced better performance. See Figure 4 for sample cross-section (fiber layering).

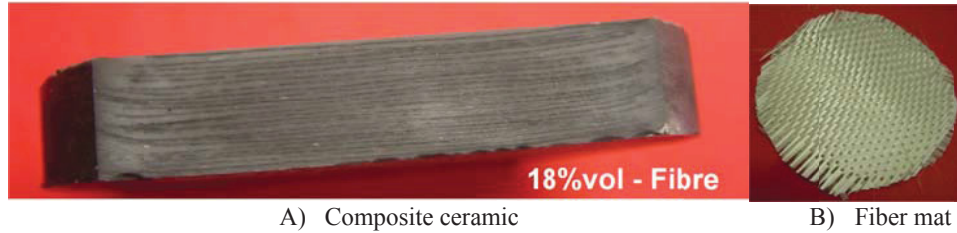


Figure 4. Cross-section of Al_2O_3 ceramic composite with 18% volume Al_2O_3 fiber mat

6. CERAMIC 3D STRUCTURE REINFORCEMENT (Al_2O_3 FIBER COVERED BY MWCNTs)

Compared to monolithic ceramic, the 3D structure is expected to improve many mechanical properties (interlaminar fracture toughness, hardness, delamination resistance, etc.) [8].

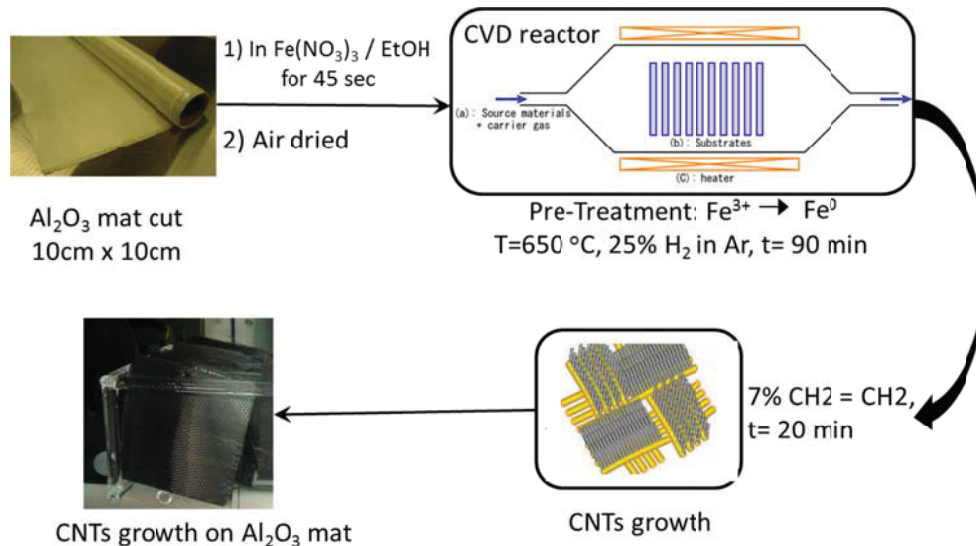


Figure 5. Schematic of CNTs growth on Al_2O_3 fiber mat

The CNTs Al_2O_3 fiber mat composites were prepared by a modified catalytic chemical vapour deposition (CVD) method [9, 10]. The aluminum oxide fiber mats were cut into 10 cm squares. The coating is done through soaking the mat into a catalyst solution (100 g / L iron nitrate ($\text{Fe}(\text{NO}_3)_3$ in ethanol (EtOH)) for 45s, and air dried. The catalyst stained mats were loaded into the CVD reactor in 16 mat batches after vertically hanging them with high temperature nickel wire on a custom fabricated quartz fixture. The catalyst stained mats were heated to $650\text{ }^{\circ}\text{C}$ under a purge of 25% hydrogen in argon (H_2 in Ar) and held for 90 minutes prior to CNTs growth. CNTs growth was initiated by introducing 7% ethylene ($\text{CH}_2=\text{CH}_2$) into the gas flow for 20 minutes. The CNTs covered mats were cooled and removed from the reactor (Fig. 5).

The SEM pictures (Fig. 6) show a nice coverage of the CNTs on the alumina yarns/fiber. Unlike the free standing CNTs which tend to agglomerate, the CNTs grown on the mat are fixed, thus the problem of agglomeration is avoided. The 3D mat was manually layered with ceramic powder incorporated between layers and hot pressed. At this stage, the CNTs on the coated mats were not covered with alumina. Although no adhesion tests have been made, substantial property improvements are expected.

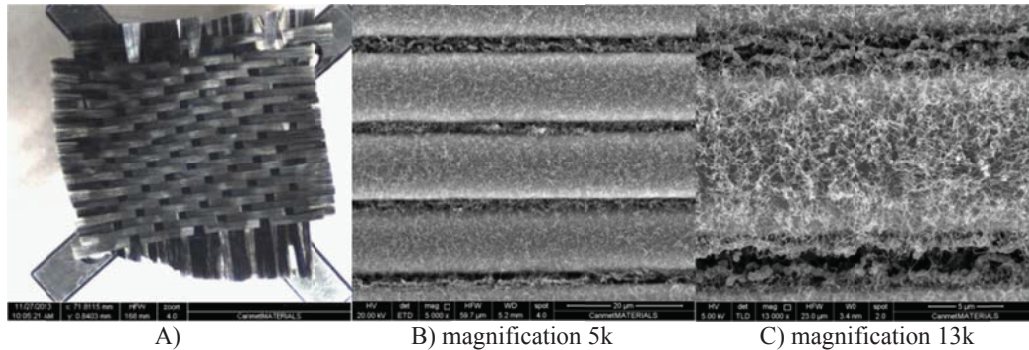


Figure 6. Macroscopic and microscopic views of alumina fabric coated with MWCNTs

Preliminary bending tests were done after the composite ceramic was hot pressed and the fracture surface confirms the presence of the MWCNTs after the processing. Also, it was found that cracks propagated preferably along the Al_2O_3 matrix (interlayer). Occasionally, cracks were found to have propagated through the alumina fiber of the fabric (intralayer) and between the alumina fiber/ alumina matrix interface (intralayer).

7. RESULTS AND DISCUSSION

Ceramic powder was obtained from two suppliers (Accumet and Saint-Gobain) which provide materials with two different particulate grain sizes. The monolithic ceramic were done using the two particulate grain sizes, but the ceramic composite were all done using the material from Saint-Gobain, having the biggest grain sizes.

7.1 Hardness

Woodward et al. [11] noted that if the ceramic is of a sufficient hardness to blunt or otherwise destroy the projectile tip, the ballistic performance of the armour is improved. Therefore, the ceramics hardness should be high enough to initiate the fracture of the projectile tip and the tile thickness big enough to fracture the entire projectile core.

Fig. 7 shows hardness results obtained following the ASTM C1327 for Vickers hardness, using an indentation pressure of 1 Kgf. The red line shows the maximum and minimum value obtained from samples. From these results, the highest hardness measured was for the monolithic alumina ceramic with the smaller grain sizes, which is consistent with literature data [12].

Since the ceramic composite were made using the larger particulates sizes, the comparison of the influence of the CNTs should be made with the monolithic ceramic made with the same material. Results showed that the addition of CNTs improved the hardness. If we compare the results from the composite matrix reinforced with the CNTs with the one reinforced with the BNNTs, the last one shows higher hardness. In the case of fiber reinforced composites, the hardness is not affected since the fiber layers reside inside the ceramic while the hardness is measured only on the surface. This is confirmed by the results. However, the case of the CNTs/alumina fiber (3D structure) shows a significant increase in the hardness, possibly indicating the presence of the CNTs forest near the surface from the last layer of the alumina fiber mat.

From the hardness results, the smaller the ceramic particulate grain sizes, the better it is. Also, adding layer of ceramic fiber covered by nanotubes greatly increase the hardness. Finally, we can imagine that the best combination would be a composite ceramic made of the finest particulates and reinforced with BNNTs grown on ceramic fibers. However, knowing the difficulties to grow BNNTs on fiber, the best case scenario at this point is a composite ceramic made of the finest particulates and reinforced with CNTs grown on ceramic fibers.

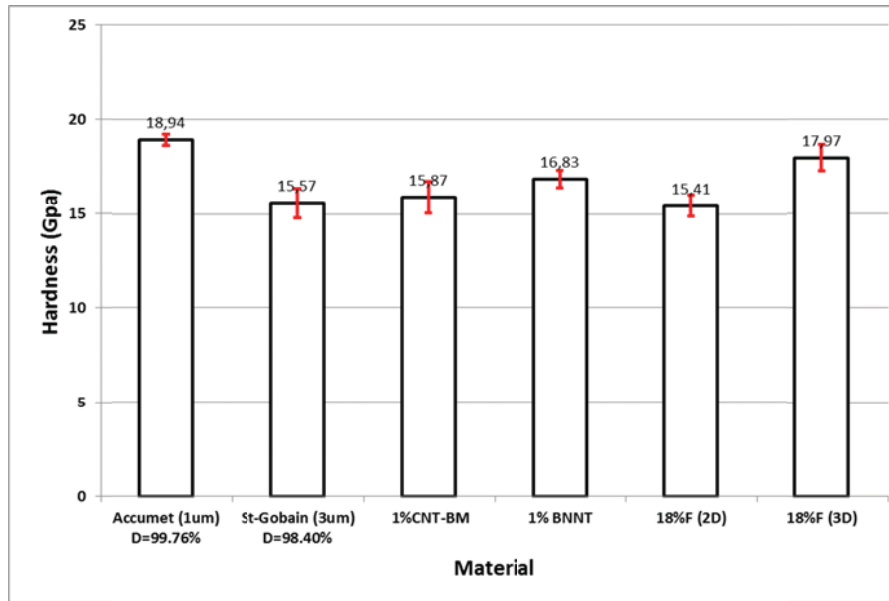


Figure 7. Summary of Vickers hardness tests for alumina and alumina composite ceramics

7.2 Toughness

Fracture toughness measure material ability to resist fracture in the presence of a crack. As such, toughness can guide the selection of conditions for making large sample required in ballistic tests.

Fig. 8 shows toughness results obtained following the ASTM C1421 for chevron notch method. The red line shows the maximum and minimum value obtained from samples. At the moment this paper was prepared, the evaluation of the toughness for the 3D structure was not completed. Therefore, it is not possible to confirm how this combination compares with the other options.

Results from Fig. 8 show that the grain size has not affected much the toughness. The addition of CNTs or BNNTs has improved the toughness by about 4%. The addition of the ceramic fiber mat has greatly improved the toughness (by about 27%), much more than the nanotubes.

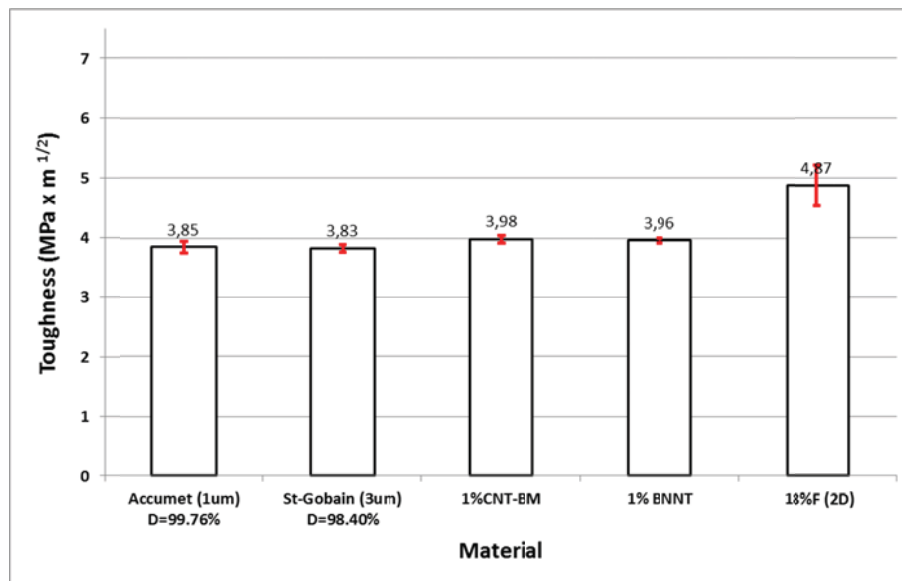


Figure 8. Chevron notch toughness (K_{Ic}) results for alumina and alumina composite ceramics

8. CONCLUSION

In an attempt to improve the failure resistance of ceramic, series of conditions were applied in composite ceramic with various reinforcements. Reinforcements considered were single wall carbon nanotubes, multiwall boron nitride nanotubes, ceramic fiber fabric and ceramic fiber fabric covered by multi wall carbon nanotubes (3D structure).

To control the dispersion of SWCNTs integrated in Al_2O_3 composite matrix, covalent or non-covalent functionalization were evaluated as well as ball milling and solution processing mixing method. Both functionalization methods shown ceramic composites with relatively uniform SWCNTs dispersion. However, while the solution processing creates relatively uniform SWCNTs dispersion, the SWCNTs tend to cluster when using ball milling. Also, the composite ceramic produced following the ball milling process shows larger grain sizes with the highest density of all sample tested.

In an attempt to investigate how the wt% of SWCNTs would affect the mechanical performances, the composite ceramics were tested with a variation of 1 to 10 wt% of SWCNTs. Only the 1 wt% SWCNTs has shown interesting results and all further investigation were limited to the 1 wt% SWCNTs content.

From all the reinforcements investigated, the most interesting conditions were obtained by the composite ceramic made of the finest matrix particulates and reinforced with CNTs growth on ceramic fibers in a 3D structure.

Boron nitride nanotubes show great potential, however, there is no technology available to grow BNNTs on fiber.

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