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4 **Improvement of Vickers hardness measurement on SWNT/Al<sub>2</sub>O<sub>3</sub> composites**  
5 **consolidated by spark plasma sintering**  
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26 **Abstract**  
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30 Dense alumina composites with different **carbon** nanotube content were prepared by  
31 colloidal processing and consolidated by Spark Plasma Sintering (SPS). Single-wall  
32 carbon nanotubes (SWNTs) were distributed at grain boundaries and also into  
33 agglomerates homogeneously dispersed. Carrying out Vickers hardness tests on the  
34 cross-section surfaces instead of top (or bottom) surfaces has shown a noticeable  
35 increase in the reliability of the hardness measurements. This improvement has been  
36 mainly attributed to the different morphology of carbon nanotube agglomerates, which  
37 however does not seem to affect the Vickers hardness value. Composites with lower  
38 SWNT content maintain the Vickers hardness of monolithic alumina, whereas it  
39 significantly decreases for the rest of compositions. The decreasing trend with  
40 increasing SWNT content has been explained by the presence of higher SWNT  
41 quantities at grain boundaries. Based on the results obtained, a method for optimizing  
42 Vickers hardness tests performance on SWNT/Al<sub>2</sub>O<sub>3</sub> composites sintered by SPS is  
43 proposed.  
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55 **Keywords:** Carbon nanotubes; Alumina; Nanocomposites; Spark plasma sintering;  
56 Vickers hardness  
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## 1. Introduction

Based on the exceptional combination of axial strength and resilience of high-aspect-ratio carbon nanotubes (CNTs) [1–4], either single-wall or multi-wall (MWNTs), the development of composites has been significantly promoted in the last decade. Much of the work has been focused on CNT/Al<sub>2</sub>O<sub>3</sub> composites, specially using MWNTs despite their “sword and sheath” failure type make them less structurally stable than SWNTs. A great variety of conflicting results are reported in literature. In some works no reinforcement is observed [5–7] while in others fracture toughness ( $K_{IC}$ ) increases [8–16], but no clear trend is found when changing the amount of CNTs.

The effect of CNT addition on composite hardness is not well established either. While several studies found the composite hardness worsens noticeably incorporating carbon nanotubes compared to the hardness value of monolithic alumina [7,8,10,13–15], other authors reported enhanced hardness for composites with CNTs [11,12,16,17]. For instance, Yi et al [10] found a decreasing trend in Vickers hardness of SWNT/Al<sub>2</sub>O<sub>3</sub> composites prepared by combustion reaction and quick pressing. By adding 0.5, 1 and 2 wt. % SWNT, hardness values dropped 21%, 26% and 58% respectively as compared with alumina. Bakhsh et al [14] also found decreasing hardness values for 1, 2 and 3 wt. % MWNT/Al<sub>2</sub>O<sub>3</sub> composites prepared by conventional sintering in flowing argon atmosphere. On the contrary, Mo et al [11] found that MWNT addition of 1.5 and 3 vol. % slightly enhanced the hardness of CNT/alumina composites with an increase of 5% and 7% respectively as compared with monolithic alumina.

Regarding top views of Vickers indentation sites published elsewhere [6,10], it should be noted that the diagonals of indenter imprint are not observed in the composite with carbon nanotubes. Recently, Thomson et al. [7] have questioned the validity of the Vickers method to quantify the hardness in 10 vol. % SWNT/Al<sub>2</sub>O<sub>3</sub> composites fabricated by Wang et al. [6] because the surface finishing was not acceptable, arguing that the presence of large pores impedes indents measuring. However, no considerations about the absence of impression of the pyramid’s edges after Vickers indentation were discussed.

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4 Heterogeneous dispersion and distribution of CNTs in the ceramic matrix, poor  
5 chemical compatibility between CNTs and alumina hindering effective transfer load and  
6 the large differences in the scales of the matrix microstructure and the carbon nanotubes  
7 have been stated as main obstacles to transfer the desirable CNT mechanical properties  
8 to the brittle ceramic matrix [5,7,11,14,15]. Adequate dispersion of CNTs is very  
9 difficult owing to their tendency to form bundles in order to minimize their surface area.  
10 Although aqueous colloidal processing has been assessed as an efficient technique  
11 producing adequate dispersion of CNTs throughout ceramic matrix grain boundaries  
12 after sintering [18–20], the presence of agglomerates seems to be unavoidable.  
13 Recently, Poorteman et al [21] fabricated MWNT/alumina composites with low MWNT  
14 content (0.6 and 1.4 vol. %) by a colloidal processing route to optimize electrostatic  
15 repulsion. The suspension was rapidly frozen with liquid nitrogen followed by freeze-  
16 drying to preserve the homogeneity of the mixture. Even those hot-pressed composites  
17 showed extended CNT agglomerated zones (~ 50 µm size) despite all the precautions  
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31 The presence of agglomerated CNTs, usually related to high CNT concentration, has  
32 been pointed out as responsible for both the decrease of the fracture toughness  
33 [11,14,15] and for the same decreasing trend followed by the hardness values with  
34 increasing CNT content [14]. Moreover, sintering of CNT/alumina composites usually  
35 results in reduced density with increasing amount of CNTs in the matrix [14,16]. This  
36 reduction in density has been attributed to the presence of agglomerates and leads to a  
37 reduction in mechanical properties. Recently, Sarkar and Das [16] incorporated  
38 MWNTs into Al<sub>2</sub>O<sub>3</sub> from a low level (i.e. 0.15 vol. %) to minimize the effect of severe  
39 agglomeration. These authors found a trend of decreasing sinterability with increasing  
40 CNT content above 0.6 vol. % MWNT and pointed out that with only 1.2 vol. %  
41 MWNT, the aggregates acted as pores of similar dimensions playing a negative role in  
42 densification. It is assumed that agglomeration becomes relevant for high CNT content  
43 due to dispersion difficulties during processing [18], however no systematic studies  
44 have been carried out to quantify this assumption. Unfortunately, this lack of  
45 publications providing quantitative information to characterize the agglomeration of  
46 CNTs impedes to precisely compare the goodness among different processing methods  
47 and dispersion routines.  
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4 Besides the CNT tendency to gather and the difficulty above mentioned for comparison,  
5 the mechanical properties of brittle ceramic matrix composites present an inherent  
6 substantial scatter. Large scatter of mechanical data-set should be analyzed according to  
7 statistical methods for component designing with these materials. Promising results in  
8 this direction have been recently published [22]. This study revealed that MWNTs  
9 enhance mechanical properties of MWNT/Al<sub>2</sub>O<sub>3</sub> compared to pure alumina and the data  
10 treatment performed with statistical tools suggested better structural reliability of the  
11 former [22]. Unfortunately, reliability studies of mechanical properties of CNT/ceramic  
12 composites are extremely limited, which keeps away the actual real-life application of  
13 these composites.  
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23 In this paper, aqueous colloidal processing of SWNTs and alumina powder has been  
24 performed to minimize the heterogeneity in the CNT dispersion and composite powders  
25 were subsequently consolidated by SPS to avoid damage the carbon nanotubes and  
26 excessive grain growth of the matrix. The SWNT agglomerates distribution has been  
27 characterized for the different SWNT content and the Vickers hardness has been  
28 evaluated for these SWNT/Al<sub>2</sub>O<sub>3</sub> composites. Additionally, the effect of agglomerate  
29 distribution on the Vickers imprint formation has been addressed for the first time.  
30 Weibull statistical analysis of Vickers hardness data has also been performed to assess  
31 the reliability of SWNT/Al<sub>2</sub>O<sub>3</sub> composites for structural applications and to establish the  
32 actual effect of the agglomerates on mechanical properties of CNT/alumina composites.  
33 In view of the results obtained, a method for improving hardness measurements in such  
34 composites has been proposed.  
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## 44 **2. Experimental procedure**

### 45 **2.1 Raw materials and processing**

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48 Monolithic polycrystalline alumina and SWNT/alumina composites with different  
49 carbon nanotube content (1, 3, 5 and 10 vol. % SWNT) were prepared from  $\alpha$ -alumina  
50 powder (99% purity and 30–40 nm particle size) supplied by Nanostructured and  
51 Amorphous Materials Inc. (Houston, TX) and HiP-co SWNTs provided by Carbon  
52 Solutions Inc. (Riverside, CA). Details about colloidal processing of composite powder  
53 with acid treated SWNTs have been reported elsewhere [19]. This procedure was  
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4 specifically developed to achieve a highly homogeneous distribution of SWNTs at  
5 ceramic grain boundaries [19].  
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9 The materials were consolidated by SPS (Syntex Inc. Model 515S, Dr Sinter Inc.,  
10 Kanagawa, Japan) using the following sintering conditions: sintering temperature of  
11 1300°C for 5 minutes, applied uniaxial pressure of 75 MPa, and heating and cooling  
12 ramps of 300 and 50 °C/min, respectively. These conditions were selected based on a  
13 previous study of the authors [23] devoted to optimize the sintering conditions for  
14 monolithic alumina in order to achieve maximum density values with minimum grain  
15 coarsening. Prepared samples were 15 mm diameter and 3 mm thickness,  
16 approximately.  
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## 23 24 **2.2 Density and microstructural characterization** 25

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27 Bulk densities were measured by the Archimedes method using distilled water as  
28 immersion medium. Theoretical density values for the composites were calculated by  
29 the rule of mixtures assuming density values of 3.97 g cm<sup>-3</sup> for Al<sub>2</sub>O<sub>3</sub> and 1.80 g cm<sup>-3</sup>  
30 for SWNTs.  
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36 The structural integrity of SWNTs in the composites after SPS sintering was assessed  
37 by Raman spectroscopy performed on fracture surfaces using a dispersive microscope  
38 (Horiba Jobin Yvon LabRam HR800, Kyoto, Japan) equipped with a 20-mW He-Ne  
39 green laser (532.14 nm).  
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45 Microstructural studies of composite fracture surfaces have been performed by high-  
46 resolution scanning electron microscopy HRSEM (HITACHI S5200) to analyze the  
47 distribution of SWNTs in the alumina matrix, and to characterize the ceramic grains  
48 morphology. Distribution and morphology of SWNT agglomerates present in the  
49 composites were characterized by low magnification conventional SEM (JEOL  
50 6460LV). Cross-section (c.s.) and in-plane (i.p.) slices, i.e. surfaces parallel and  
51 perpendicular to the SPS pressing direction were polished with diamond paste up to 1  
52 μm for morphological studies. Additionally, polished surfaces devoted to characterize  
53 the alumina grains were thermally etched at 1200 °C for 20 minutes in air to reveal grain  
54 boundaries. The morphology characterization was made measuring about 200 grains or  
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4 agglomerates respectively to obtain the equivalent planar diameter as size parameter,  $d$   
5 (or  $D$ ) =  $2(\text{area}/\pi)^{1/2}$ , and the shape factor,  $f$  (or  $F$ ) =  $(4\pi \cdot \text{area})/(\text{perimeter})^2$ . Hereafter,  
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7 lowercase letters will refer to alumina parameters and uppercase letters to agglomerates.  
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9 Surface density of agglomerates was evaluated from the area fraction covered by them  
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11 in low magnification SEM micrographs.  
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### 13 14 **2.3 Mechanical testing**

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17 Vickers hardness measurements were carried out on samples polished up to 1  $\mu\text{m}$   
18 diamond paste. 19.6 N load was applied for 10 seconds using a diamond Vickers  
19 indenter (Duramin Struers, Germany). Vickers hardness tests were performed on both  
20 c.s. and i.p. surfaces. 30 indents were made on each surface avoiding boundary effects  
21 (*i.e.* keeping the appropriate distance from sample edges and between indentation  
22 marks), in well-separated and randomly selected regions to verify data consistency.  
23 Only 15 indents were performed on each orientation in monolithic alumina for  
24 comparison. The hardness value  $H_V$  (in GPa) was calculated from the indentation load  $P$   
25 and the diagonal of the Vickers imprint  $a$ :  $H_V = 1.854 (P/a^2)$ .  
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35 For samples exhibiting more than 9 suitable tests, the  $H_V$  data-set was statistically  
36 analyzed using a 2-parameter *Weibull* distribution to quantify its scatter. According to  
37 *Weibull* statistics, the cumulative probability ( $p$ ) of a parameter,  $H_V$  in our case, can be  
38 expressed as:  $p = 1 - \exp[-(H_V/H_{V0})^m]$  where  $H_{V0}$  is the *Weibull scale* parameter,  
39 *i.e.* the characteristic value of hardness having 63.2% probability, and  $m$  is the *Weibull*  
40 *modulus* that describes the extent of scatter in a given data-set. The cumulative  
41 probability can be obtained from empirical data using the approach:  $p_i = (i - 0.5)/n$   
42 where  $i$  is the rank of the  $i$ th observation corresponding to data-set arranged in  
43 ascending order and  $n$  is the total number of observations.  
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52  $H_{V0}$  parameter is a measure of the nominal hardness of the material and usually  
53 increasing  $H_{V0}$  values will be found with increasing values of average hardness.  
54 Parameter  $m$  is related to the reliability of a distribution, so higher  $m$  values indicate a  
55 lower scatter (narrower data distribution) and, hence, higher reliability. Thus a  $1/(1-p)$   
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4 plot on a natural log(log) scale versus  $H_V/H_{V_0}$  on a natural log scale should give a  
5 straight line of slope  $m$  and from its intercept can be evaluated  $H_{V_0}$  value.  
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### 8 9 **3. Results and discussion**

#### 10 11 12 **3.1 Microstructural characterization**

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16 Table 1 shows the density values of monolithic alumina and SWNT/Al<sub>2</sub>O<sub>3</sub> composites  
17 after consolidation by SPS. The nomenclature used to refer to the composites is also  
18 included. The increase in relative density of SWNT/Al<sub>2</sub>O<sub>3</sub> composites with rising  
19 carbon nanotubes content implies that SWNTs promote densification in these materials.  
20 Present results differ from most of the published results on CNT/Al<sub>2</sub>O<sub>3</sub> composites  
21 [9,10,12,14,16] where CNTs inhibit densification of Al<sub>2</sub>O<sub>3</sub>. Only few works report  
22 relative densities ~100% [8] or densification enhancement with CNT incorporation  
23 [11,17]. In our case, this favorable sinterability suggests the presence of an effective  
24 diffusion layer bonding the SWNTs and the alumina grains. According to the sintering  
25 temperature used, the formation of an aluminum oxy-carbide phase (Al–O–C interphase  
26 among SWNTs and Al<sub>2</sub>O<sub>3</sub> grains) is possible [22,24].  
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37 Figure 1 presents the characteristic fracture surfaces exhibited by the composites which  
38 illustrate the adequate dispersion of SWNT bundles surrounding alumina grains.  
39 Transgranular fracture zones are appreciated in composite C1, while the other  
40 composites mostly exhibit intergranular fracture. CNTs remain attached to the grains  
41 taking their shape and no pull-out is observed after intergranular fracture. SWNTs  
42 located mainly parallel to the fracture surface, implying few pull-outs, have also been  
43 observed in SWNT reinforced zirconia toughened alumina (ZTA) composites [25].  
44 Whereas the alumina grains surrounded by SWNTs are scarce in C1, it appears that  
45 SWNTs cover most of the grain boundaries in the composites with higher CNT content.  
46 The series of high-magnification micrographs show that SWNTs look like a black  
47 covering that coats an increasing portion of alumina grain surfaces with increasing  
48 SWNT content. The higher the amount of carbon nanotubes, the larger the grain surface  
49 coated by them. Dark regions are composed by SWNTs as confirmed by Raman  
50 spectroscopy (not shown). Similar microstructure has been previously observed in other  
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4 SWNT/Al<sub>2</sub>O<sub>3</sub> composites [6,19,20]. In MWNT/Al<sub>2</sub>O<sub>3</sub> nanocomposites only Huang et al.  
5 [26] observed this particular microstructure also in their fracture surface. These authors  
6 relate the observation of printed CNTs like stamps on the alumina grains with carbon  
7 diffusion into alumina lattice [26]. This idea suggests that the appearance of CNTs like  
8 a blanket coating the grains observed in these composites could be indicative of the  
9 presence of Al–C–O interphase between CNTs and alumina grains referred by [22,24].  
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16 Table 1 displays global results of morphological parameters of alumina grains. No  
17 differences were observed on results from i.p. and c.s. surfaces, so the mean grain size,  
18 its standard deviation and the shape factor values presented in table 1 are the average  
19 parameters from both orientations. HRSEM observations of polished and thermally  
20 etched surfaces evidenced the existence of anomalous alumina grain growth together  
21 with an elongated aspect of the matrix grains regardless the composition and orientation  
22 (not shown). Similar mean grain size (below 1 μm) and shape factor (about 0.7) were  
23 measured in composites with lower SWNT content (C1 and C3) and no significant  
24 differences were observed compared to monolithic alumina grains [23] except for  
25 narrower size distributions (smaller  $\sigma_d$ ). Conversely, finer grain size with narrower  
26 distributions were found in composites with high carbon nanotube content (C5 and  
27 C10), but differences in relation to the grain shape were not appreciated.  
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38 Low-magnification SEM micrographs (figure 2) illustrate the arrangement and  
39 morphology of SWNT agglomerates in the i.p. and the c.s. surfaces. Although many  
40 processing efforts were devoted to obtain a homogeneous distribution of SWNTs, it is  
41 obvious that the presence of agglomerates in the composites has not been avoided. It is  
42 interesting to note that the existence of agglomerates has not entailed detrimental effect  
43 on density values (table 1). The rough finish observed is due to pull-out of the alumina  
44 grains, which takes place during the polishing process of the composites. This is in  
45 agreement with the observations of Echeberria et al. [25] on rougher finishing in  
46 surfaces with small alumina grains and CNTs compared to flat finishing in areas  
47 consisting of large-grains without CNTs. These latter zones are inexistent in our  
48 composites due to the adequate dispersion of SWNTs achieved.  
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59 While the agglomerates (dark phase) are randomly oriented on the i.p. surface (fig. 2a),  
60 a strong alignment is clearly observed from micrographs on the c.s. plane (fig. 2b), with  
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4 their major axis disposed perpendicular to the direction of applied pressure during  
5 sintering. Only Thomson et al. [7] have also referred anisotropic orientation of CNT  
6 agglomerates in alumina. Similar agglomerate size, about 6 – 8  $\mu\text{m}$  (table 2), was found  
7 regardless the SWNT content on the i.p. sections. Smaller sizes were measured on the  
8 c.s. surfaces for each composite. Furthermore, agglomerate shapes were also very  
9 sensitive to orientation. Whereas more rounded shape is found on the i.p. surfaces ( $F =$   
10 0.6), a marked elongation was observed in the c.s. agglomerates ( $F = 0.4 - 0.5$ ). These  
11 morphological characteristics suggest that the agglomerates are flattened structures.  
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19 Regarding the surface density of agglomerates  $\rho_s$ , no remarkable differences have been  
20 found in relation to surface orientation. A considerable increase in the surface density of  
21 agglomerates with increasing SWNT content up to 5 vol. % was observed, changing  
22 from 0.6 % in C1 to 2.4 % in C5 (table 3). However, similar agglomerate surface  
23 density was found for C5 and C10 composites. These results highlight the need to  
24 characterize agglomerate densities for each prepared composite with different SWNT  
25 content.  
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33 Assuming that the area fraction covered by agglomerates in SEM micrographs is equal  
34 to its volume fraction in composites (Delesse's principle of stereology), the percentage  
35 of the CNT content that are agglomerated was estimated from the bulk density of  
36 agglomerates and the SWNT content for each composition ( $A\% = 100\rho_V /$   
37  $SWNT\ vol.\%$ ). The SWNT vol. % contained in the agglomerates can be directly  
38 inferred from agglomerate bulk density. The SWNT vol. % dispersed at the grain  
39 boundaries is directly the difference between the total SWNT content and the SWNT  
40 content within the agglomerates. Hereinafter, A-SWNTs and GB-SWNTs will refer to  
41 SWNTs arranged in agglomerates and at grain boundaries respectively. From these  
42 calculations, similar percentages of the SWNT content ( $\sim 40 - 60\%$ ) were agglomerated  
43 in composites up to 5 vol. % SWNT, leading to both higher A- and GB-SWNT net  
44 contents in composites with higher SWNT content (table 3). This percentage is even  
45 smaller in the case of C10 ( $\sim 20\%$ ) than for the former compositions, which results in a  
46 net A-SWNT content similar to that of composite C5 and a larger amount of SWNTs  
47 distributed at the grain boundaries. Although it has generally been assumed by other  
48 authors that agglomeration increases in case of high CNT content due to dispersion  
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4 difficulties, the results presented here point otherwise. These calculations are in  
5 agreement with increasing amounts of SWNT bundles embedded among ceramic grain  
6 boundaries observed by HRSEM (fig. 1). Besides, the matrix refinement found in high  
7 SWNT content composites (C5 and C10, table 1) also supports that the predominant  
8 volume fraction of SWNTs is placed in networks surrounding the ceramic grains.  
9 Despite the presence of agglomerates, the GB–SWNT fraction has effectively inhibited  
10 the matrix grain growth since the presence of SWNTs at ceramic grain boundaries  
11 disfavor both grain boundary sliding and diffusion during densification [27,28].  
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### 19 **3.2 Evaluation of Vickers hardness in SWNT/Al<sub>2</sub>O<sub>3</sub> composites**

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22 Since microstructural characterization revealed anisotropy in agglomerate morphology,  
23 hardness both on i.p. and c.s. surfaces was evaluated. Regarding the formation of the  
24 indentation marks, most of the i.p. imprints were not well defined for all composites, i.e.  
25 the diagonals of the Vickers imprint were not visible (fig. 3a), while a higher number of  
26 proper well formed indentations were obtained on c.s. surfaces (fig. 3b). Up to our  
27 knowledge, no similar findings have been published in literature. Since Vickers  
28 hardness is calculated from diagonals of indenter imprints, the topography of each  
29 imprint was examined to discard those without the characteristic Vickers indenter  
30 regular shape. These optical images of typical indenter marks also show that polished  
31 surfaces have a rough finish due to grain pull–out during polishing. Vickers sites also  
32 exhibit typical lack of classical radial cracks in the indentation impression [6,25].  
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43 A trend of decreasing on the number of Vickers marks showing visible diagonals with  
44 increasing SWNT content can be clearly appreciated for all compositions in the bar  
45 chart graph of figure 4. Furthermore, these results also point out that the use of cross–  
46 section surface allows an accurate measurement of Vickers hardness in these  
47 composites more efficiently. As an example of the inefficiency of the procedure on i.p.  
48 surface, after 30 indentations performed in C3, only one proper measure was  
49 accomplished (fig. 4). In contrast, 24 proper imprints were obtained on c.s. surface for  
50 the same number of performed indentations. For composites with higher SWNT  
51 content, no suitable imprints were found on their respective i.p. surfaces (therefore, bars  
52 of C5 and C10 are not shown for these cases in fig. 4).  
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4 Since the ceramic grain morphology resulted very similar in both i.p. and c.s. surfaces,  
5 any discrepancies found in the definition of the imprint between both surfaces may be  
6 due to a different cause, most likely related to the different arrangement and shape of  
7 the CNT agglomerates. Taking into account that the agglomerates dispersed in the  
8 alumina matrix are SWNT entangled networks, they are bent during loading acquiring  
9 the shape of the indenter. Once the load is removed they are expected to elastically  
10 spring back to their original conformation.  
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17 Therefore, SWNT aggregates can be visualized as elastic networks which prevent  
18 plastic deformation by indentation. Recently, Sarkar and Das [22] referred MWNTs  
19 stayed intact in their positions in indented regions of pressure-less sintered  
20 MWNT/alumina composites, while alumina matrix exhibited permanent deformation.  
21 The finding of unaffected carbon nanotubes by the indenter tip-CNT direct interaction  
22 during the indentation load cycle [22] supports that the contact between the indenter tip  
23 and elastic SWNT agglomerates prevents the formation of imprints properly. The  
24 probability of finding agglomerates is proportional to the agglomerate surface density.  
25 When the indenter is pushed in the direction of the sintering applied pressure, the  
26 rounded shape and larger size of the agglomerates favors greater contact surface with  
27 the indenter. However, in the cross-section areas the agglomerates exhibit smaller size  
28 with a much higher aspect ratio, very thin and elongated in the direction perpendicular  
29 to the applied pressure, leaving larger agglomerate-free areas in contact with the  
30 indenter, which allows permanent deformation of the matrix during indenter  
31 penetration. This idea could also explain the decrease in the number of suitable imprints  
32 with increasing SWNT content, which would be due to the increase of agglomerate  
33 density. This also suggests a control technique to compare SWNT dispersion in these  
34 composites consisting of making a fixed number of Vickers indentations so that the  
35 number of unsuitable marks can roughly provide direct information on the level of  
36 SWNT agglomeration. The decreasing tendency in the number of proper marks  
37 observed between C5 and C10 for indentations performed on their cross-section  
38 surfaces (figure 4) suggests that the extent of SWNT layer covering the alumina grains  
39 could also affects the imprint formation. These CNTs are randomly dispersed in the  
40 alumina matrix and acquire the tortuous shape of alumina grain boundaries. Our results  
41 suggest that the higher the surface contact among indenter and SWNTs (both in  
42 agglomerates as at grain boundaries), the greater the number of unsuitable indentations.  
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4 Vickers hardness values were evaluated only from indentations showing well defined  
5 marks. Values determined for each material resulted very similar both for the different  
6 orientations examined and for the different scanned zones on each surface (table 4).  
7 Therefore, although applied pressure during SPS leads to preferential alignment of  
8 SWNT agglomerates perpendicular to the pressing direction, directly observed on  
9 agglomerates distribution (fig. 2b), anisotropic effects have not been observed in the  
10 values of Vickers hardness for these SWNT/Al<sub>2</sub>O<sub>3</sub> composites. Except for the  
11 composite C1 whose hardness is similar to that of monolithic alumina, H<sub>V</sub> values of the  
12 composites with higher SWNT content are lower. This can be explained by the fact that  
13 SWNTs are a softer component [17]. Despite the drop observed in composite hardness  
14 with respect to alumina, it is interesting to note the high hardness value measured for C5  
15 on c.s. surface (15.4 GPa), a value 40 % higher than that found for a similar composite  
16 also indented on its c.s. surface [7].  
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28 The greater number of proper imprints found in c.s. surfaces allows a higher accuracy  
29 on the hardness measurements performed on these surfaces in comparison to those  
30 carried out on i.p. surfaces. This is supported by the reduction of the standard deviation  
31 of the data measured on c.s. surfaces due to the greater number of appropriate  
32 measurements (table 4). Therefore, the indentation of the cross-section surface is  
33 proposed for these composites in order to achieve superior preciseness in hardness  
34 measurement.  
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41 *Weibull* plots (figure 5) of H<sub>V</sub> data obtained from indentations performed on c.s.  
42 surfaces of the composites show satisfactory linear fits consistent with the Weibull  
43 distribution proposal. Results of Weibull statistics are tabulated in table 4.  
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48 A decreasing trend of the *Weibull* moduli (i.e. slope of the linear regression lines) with  
49 increasing SWNT content is observed. Hence, the H<sub>V</sub> data present a higher scatter in  
50 composites with higher SWNT content because the lower *m* means the greater the  
51 variability of hardness. Compared to monolithic alumina ( $m_{Al_2O_3} = 40.2$ ), the addition of  
52 SWNTs leads to a poorer structural reliability (i.e. low *m* values). Notwithstanding the  
53 above, the decrease is not very pronounced in the case of low carbon nanotube content  
54 ( $m_{C1} = 31.2$ ). Nearly invariable reliability was found for C3 ( $m_{C3} = 15.0$ ) and C5 ( $m_{C5} =$   
55 14.8) composites. Such large variability would lead to uncertainties in obtaining a  
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4 precise  $H_V$  value for composites with high SWNT content. Since the agglomerate  
5 density for all these composites is different, this similarity in *Weibull moduli* found for  
6 C3 and C5 rules out that the increased scatter of  $H_V$  data with increasing SWNT content  
7 from 1 to 3 vol. % is due to a greater presence of agglomerates. The fact that interfacial  
8 bonding between alumina grains degrades with SWNT addition, in agreement with  
9 increasing tendency to intergranular fracture exhibited by the composites (fig. 1),  
10 suggests that GB–SWNTs could be the weakest flaw controlling the  $H_V$  scatter. The  
11 decreasing trend of *Weibull moduli* with increasing SWNT content up to 3 vol. % could  
12 be related to higher possibility of indentation zones with alumina grains surrounded by  
13 GB–SWNTs. HRSEM inspections support that the alumina grains surrounded by  
14 SWNTs were scarce in C1 and an increasing fraction of alumina grains was coated by  
15 carbon nanotubes with increasing SWNT content (fig. 1). Once the GB–SWNTs cover  
16 most of the grain boundaries in the composites, this effect saturates leading to a  
17 stabilization of  $m$  value in composites with higher CNT content (C3 and C5). Thus, the  
18 continuity degree in the GB–SWNT distribution could be the key point controlling the  
19 variability of hardness.  
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33 The characteristic values of Weibull distributions  $H_{V0}$  exhibit the similar decreasing  
34 trend than transversal  $H_V$  data with increasing SWNT content (i.e., leftward shift  
35 observed in Weibull plots for composites), changing from 19.3 to 15.9 GPa for  
36 composites with 1 and 5 vol. % SWNT, respectively. The C1 composite shows a slight  
37 increase in  $H_{V0}$  compared with the value of 19.0 GPa found for monolithic alumina in  
38 agreement to mean  $H_V$  values also reported in table 4. The composites C1 and C3  
39 exhibited similar matrix microstructures whereas C5 even showed refined grain size  
40 (table 1). Therefore, the  $H_{V0}$  decreasing trend with increasing SWNT content observed  
41 in figure 5 is not expected from matrix microstructure differences. Moreover, the  
42 increasing agglomerate surface densities found in these composites lead to similar  
43 percentages of SWNT content arranged into agglomerates in all them with increasing  
44 both A– and GB–SWNT vol. % as SWNT content increases (table 3). The hardness  
45 decrease could be explained arguing that CNT incorporation involves the addition of a  
46 softer phase and interfacial bonding between alumina grains worsens with SWNT  
47 addition. Therefore, more quantity of SWNTs at grain boundaries must be the  
48 responsible of the  $H_{V0}$  decrease.  
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4 Performing similar statistical analysis, an improvement of  $H_V$  in pressure-less sintered  
5 MWNT/alumina composites has been reported by Sarkar and Das [22]. These authors  
6 propose that the adequate grain boundary cohesion achieved by flexible multi-walled  
7 carbon nanotubes entangling alumina grains could be responsible of the superior  $H_V$   
8 reliability of the composites over pure alumina despite the presence of CNT  
9 agglomerates. Our results point in the opposite direction to that suggested by the  
10 previous authors. SWNT addition reduces the reliability of hardness values in alumina-  
11 based composites. It affects negatively the grain boundary cohesion in SWNT/alumina  
12 composites and SWNTs distributed at grain boundaries are pointed as the critical flaw.  
13 It is suggested that the fraction of alumina grains surrounded by SWNTs controls the  
14 variability of hardness values, whereas the increasing amount of GB-SWNTs is  
15 responsible of the decrease in characteristic hardness values with increasing SWNT  
16 content. The presence of agglomerates does not play a fundamental role on the  $H_V$   
17 distribution in these composites.  
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#### 29 **4. Conclusions**

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33 SWNT/ $Al_2O_3$  composites with carbon nanotube content from 1 to 10 vol. % were  
34 prepared by colloidal processing and SPS. An increasing trend in their relative density  
35 with increasing SWNT content has been observed. Dense composites with submicron  
36 alumina matrix were obtained with SWNTs distributed at grain boundaries and into  
37 agglomerates homogeneously dispersed. The agglomerate size and shape resulted very  
38 sensitive to orientation, exhibiting a much higher elongation in the direction  
39 perpendicular to the applied pressure in cross-section areas than on in-plane surfaces  
40 where agglomerates were more rounded without exhibiting preferred orientation. The  
41 characterization of SWNT agglomerates performed in this work indicates that  
42 increasing SWNT content (from 1 to 5 vol. %) involves similar percentage of the  
43 SWNT content placed in agglomerates (~ 50%).  
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54 A decreasing trend of the number of Vickers marks showing visible diagonals with  
55 increasing SWNT content was clearly appreciated for all compositions. In order to  
56 optimize the performance of Vickers hardness tests, indentation on the cross-section  
57 surfaces is proposed. Superior hardness measurement reliability when testing on cross-  
58 section surfaces over in-plane ones is mainly attributed to the different agglomerate  
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4 morphology observed between these orientations. A control technique to compare  
5 SWNT level of agglomeration in these composites is proposed consisting of evaluating  
6 the number of imprints without pyramidal diagonal marks after making a fixed number  
7 of Vickers indentations. This number provides rough information on the level of SWNT  
8 agglomeration.  
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14 Although applied pressure during SPS leads to preferential alignment of SWNT  
15 agglomerates perpendicular to the pressing direction, anisotropic effects have not been  
16 observed in the values of Vickers hardness. The decreasing trend in  $H_V$  with increasing  
17 SWNT content observed for these SWNT/ $Al_2O_3$  composites has been explained by the  
18 presence of higher SWNT quantities at grain boundaries. The presence of agglomerates  
19 does not play a fundamental role on the  $H_V$  distribution in these composites.  
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## 25 26 **Acknowledgements**

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**Figure captions**

**Figure 1.** HRSEM micrographs of fracture surfaces: (a) C1, (c) C3, (e) C5 and (g) C10. Details corresponding to higher-magnification micrographs are shown in (b), (d), (f) and (h). The dark regions are SWNT bundles (arrows) surrounding alumina grains (light regions).

**Figure 2.** SEM micrographs showing the SWNT agglomerate distribution on (a) in-plane and (b) cross-section surfaces of composite C10. Compression axis during SPS is indicated in (b) by arrows.

**Figure 3.** Optical images illustrating the different appearance of the imprints in C1 composite after indenting on (a) i.p. and (b) c.s. surfaces.

**Figure 4.** Statistical bar chart with percentages of proper indentations carried out on the different composites in both the in-plane (solid bars) and cross-section (hollow bars) surfaces.

**Figure 5.** Weibull plots of  $H_V$  data of C1, C3 and C5 obtained on transversal surface orientation (solid regression lines). Data of monolithic  $Al_2O_3$  are represented for comparison (dashed regression line).

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**Table 1.** Theoretical and relative density and morphological parameters of alumina grains.

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Material	SWNT content (vol. %)	$\rho_{th}$ (g cm <sup>-3</sup> )	$\rho_r$ (%)	$\langle d \rangle$ ( $\mu\text{m}$ )	$\sigma_{\langle d \rangle}$ ( $\mu\text{m}$ )	f
Al <sub>2</sub> O <sub>3</sub> *	0	3.97	97.7	0.7	0.6	0.67 ± 0.14
C1	1	3.95	98.5	0.6	0.3	0.68 ± 0.10
C3	3	3.90	99.7	0.7	0.4	0.67 ± 0.12
C5	5	3.87	99.8	0.5	0.4	0.71 ± 0.12
C10	10	3.75	100	0.5	0.3	0.67 ± 0.12

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\* Data from reference [23].

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**Table 2.** Morphological parameters of SWNT agglomerates measured on i.p. and c.s. surfaces for each composite.

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Material	i.p.			c.s.		
	$\langle D \rangle$ ( $\mu\text{m}$ )	$\sigma_{\langle D \rangle}$ ( $\mu\text{m}$ )	F ( $\pm 0.20$ )	$\langle D \rangle$ ( $\mu\text{m}$ )	$\sigma_{\langle D \rangle}$ ( $\mu\text{m}$ )	F ( $\pm 0.20$ )
C1	7.9	6.3	0.63	2.7	1.9	0.50
C3	6.4	3.8	0.61	5.5	3.9	0.53
C5	8.5	7.0	0.60	5.3	3.9	0.41
C10	7.6	5.7	0.56	6.0	6.0	0.43

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**Table 3.** Surface density of SWNT agglomerates, percentage of carbon nanotube content in agglomerates and A- and GB-SWNT vol. % calculated for each composite.

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Material	$\rho_s$ (%)	A%	A-SWNT (vol. %)	GB-SWNT (vol. %)
C1	0.6	60	0.6	0.4
C3	1.3	43	1.3	1.7
C5	2.4	48	2.4	2.6
C10	2.1	21	2.1	7.9

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**Table 4.** Vickers hardness values of monolithic alumina and SWNT/Al<sub>2</sub>O<sub>3</sub> composites. The number of suitable measurements is indicated in parenthesis. Results of Weibull statistics for c.s. H<sub>V</sub> data are also tabulated.

Material	H <sub>V</sub> (GPa)			Weibull parameters	
	i.p.	c.s.	global	<i>m</i>	H <sub>V0</sub> (GPa)
Al <sub>2</sub> O <sub>3</sub>	18.3 ± 0.4 (15)	18.7 ± 0.5 (15)	18.5 ± 0.5 (30)	40.2 ± 1.7	19.0
C1	18.7 ± 1.5 (8)	18.9 ± 0.7 (27)	18.9 ± 1.0 (35)	31.2 ± 1.5	19.3
C3	17.1 (1)	16.8 ± 1.3 (24)	16.8 ± 1.0 (25)	15.0 ± 0.4	17.3
C5	n/a	15.4 ± 1.5 (9)	15.4 ± 1.5 (9)	14.8 ± 1.0	15.9
C10	n/a	14.0 ± 0.7 (5)	14.0 ± 0.7 (5)	n/a	n/a

Figure  
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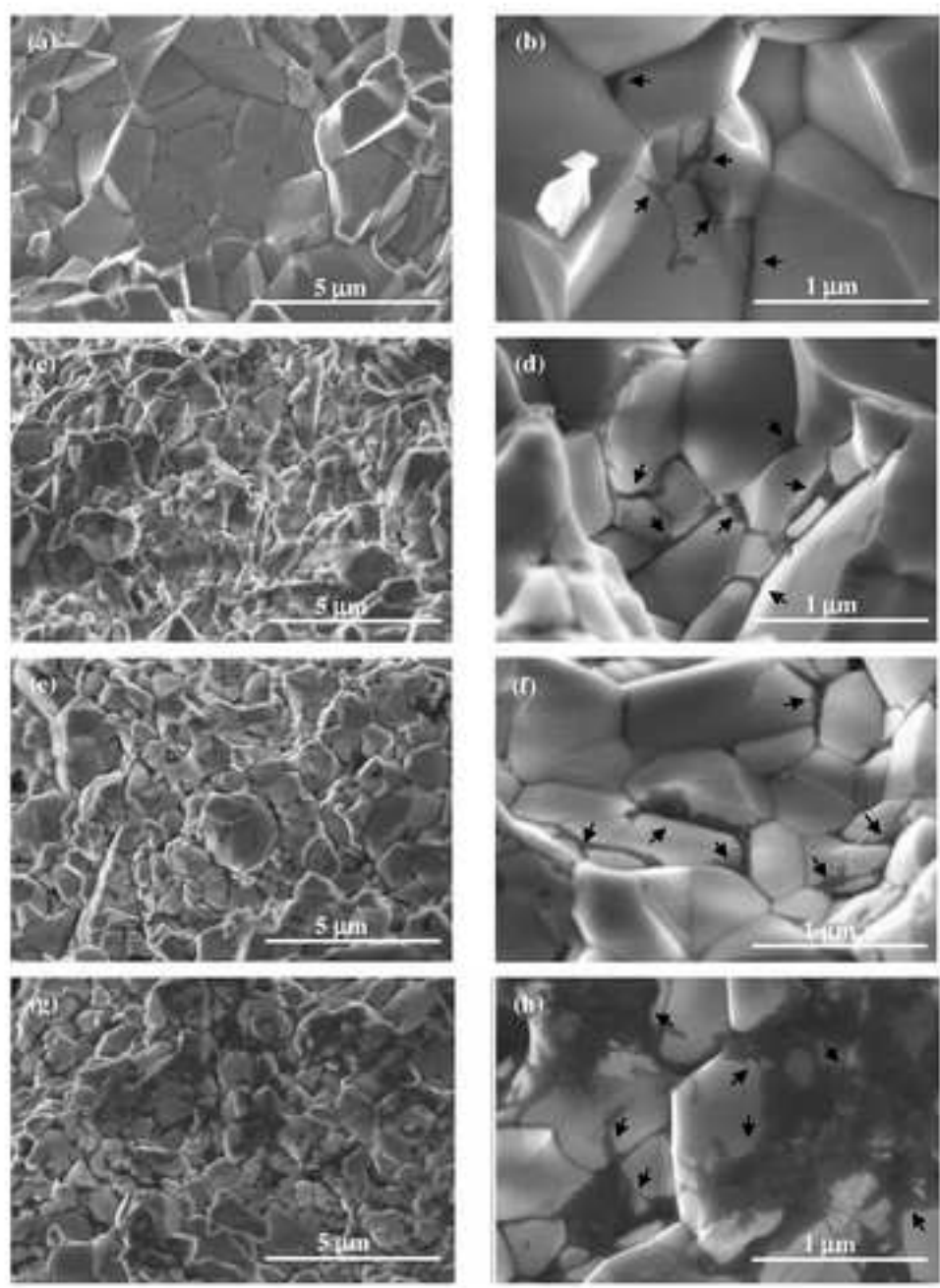
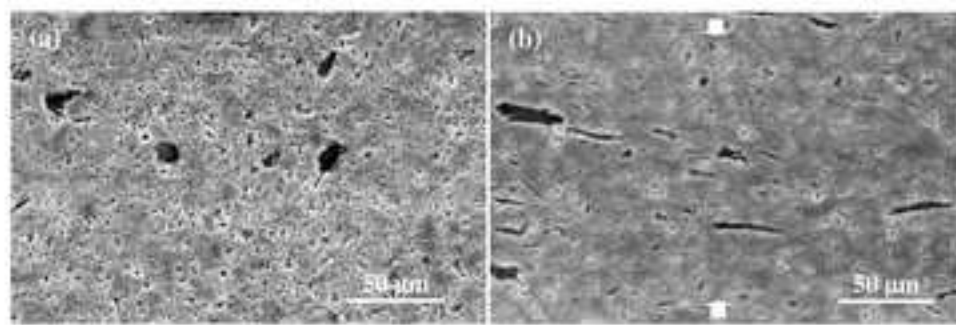


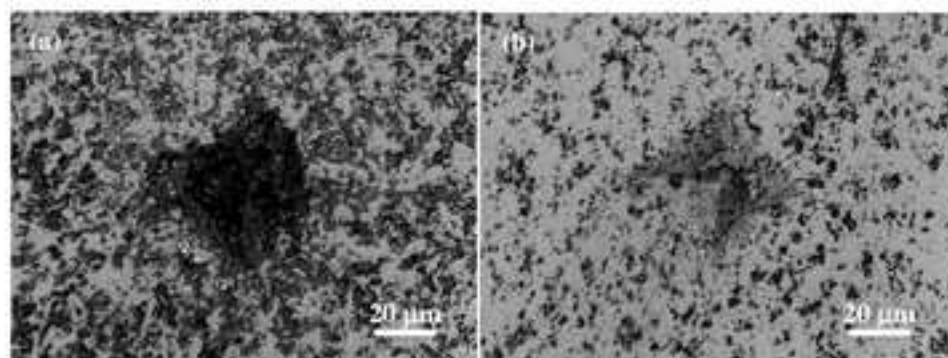


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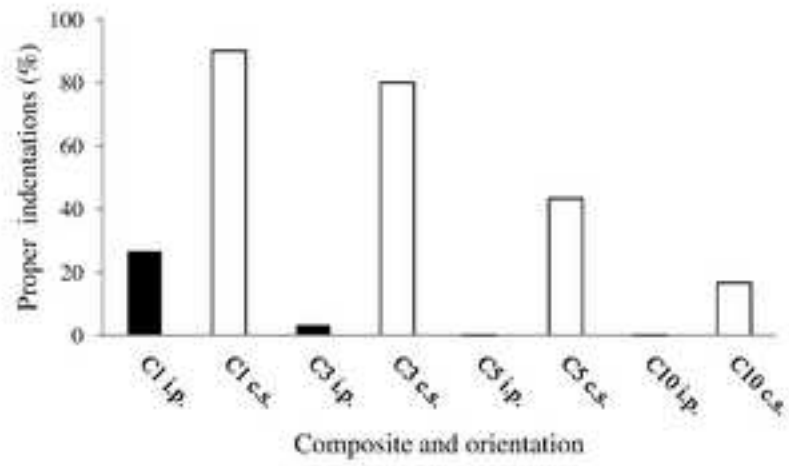
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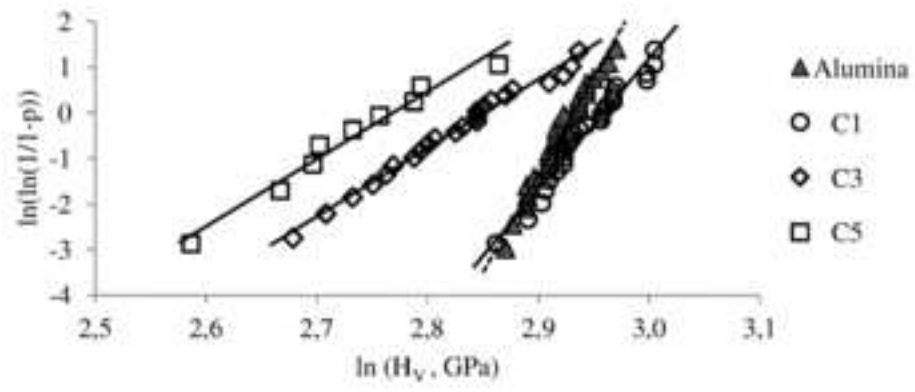
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**Figure captions**

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3  
4 **Figure 1.** HRSEM micrographs of fracture surfaces: (a) C1, (c) C3, (e) C5 and (g) C10.  
5 Details corresponding to higher-magnification micrographs are shown in (b), (d), (f) and  
6 (h). The dark regions are SWNT bundles (arrows) surrounding alumina grains (light  
7 regions).

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12 **Figure 2.** SEM micrographs showing the SWNT agglomerate distribution on (a) in-  
13 plane and (b) cross-section surfaces of composite C10. Compression axis during SPS is  
14 indicated in (b) by arrows.

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20 **Figure 3.** Optical images illustrating the different appearance of the imprints in C1  
21 composite after indenting on (a) i.p. and (b) c.s. surfaces.

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25 **Figure 4.** Statistical bar chart with percentages of proper indentations carried out on the  
26 different composites in both the in-plane (solid bars) and cross-section (hollow bars)  
27 surfaces.

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32 **Figure 5.** Weibull plots of  $H_V$  data of C1, C3 and C5 obtained on transversal surface  
33 orientation (solid regression lines). Data of monolithic  $Al_2O_3$  are represented for  
34 comparison (dashed regression line).