Nitrogen-doped-CNTs/Si₃N₄ nanocomposites with high electrical conductivity

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Abstract

Novel highly electrically conducting nanocomposites consisting of a silicon nitride (Si_3N_4) ceramic matrix containing up to 13.6 vol.% of nitrogen-doped multi-walled carbon nanotubes (CNx) were fabricated. As-synthesized CNx were treated with hydrogen peroxide in order to efficiently detach/isolate the nanotubes from bundles, then they were mixed with the ceramic powders and, fully densified using the spark plasma sintering (SPS) technique. Composites containing 13.6 vol.% CNx reached an electrical conductivity of $2174 \text{ S}\cdot\text{m}^{-1}$ that is the highest value reported hitherto for carbon nanotubes/ Si_3N_4 nanocomposites. The nitrogen doping also favoured a strong mechanical interlocking between the nanotubes and the Si_3N_4 matrix; when compared to the undoped carbon nanotubes. These novel nanocomposites could be used in devices associated to power generation or telecommunications.

Keywords: Carbon nanotubes; Silicon nitride; Ceramics; Nanocomposites; Electrical conductivity

1. Introduction

Silicon nitride (Si_3N_4), a remarkable high temperature structural ceramic, is commonly employed in engineering parts due to their excellent mechanical and tribological properties.^{1,2} However, alternative functionalities such as electrical conductivity would enhance the performance of Si_3N_4 in current applications, e.g. reducing the static electricity of the Si_3N_4 bearings under working conditions. In other cases, the miniaturization of Si_3N_4 devices is essential, such as the strategic power generation industry (e.g. micro-turbines and micro-rotors) or the telecommunications

1 area (e.g. micro-electro-mechanical systems, MEMS). An inherent problem associated
2 with Si_3N_4 lies in the difficulty of machining it in geometrically complex morphologies.
3
4 In fact, hard Si_3N_4 micro-components are extremely difficult to form using conventional
5 processes, and electrical discharge machining (EDM) is one of the most efficient
6 techniques to overcome these difficulties.³ The main problem for using EDM for
7 ceramics is that the machined material must exhibit a minimal value of electrical
8 conductivity, and therefore changing Si_3N_4 from insulating to conducting material is
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Unfortunately, very few works⁴⁻⁷ have reported extraordinary increases in the
 Si_3N_4 electrical conductivity by adding low amounts of carbon nanotubes (CNTs), a
highly electrically conducting 1-dimensional carbon allotrope.⁸ In particular, a
maximum electrical conductivity of $130 \text{ S}\cdot\text{m}^{-1}$ was reported for nanocomposites
containing 5 wt.% of multi-walled CNTs (MWCNTs).⁵ This change in electrical
response of alike composites was further exploited by Malek et al.⁹ who produced a
micro-gear of a MWCNTs/ Si_3N_4 material by EDM. Despite the attained success, higher
electrical response of Si_3N_4 materials would be desirable to gain efficiency in EDM
operation, and also looking for the fabrication of novel MEMS acting not only as a pure
mechanical support but as an electrical device as well.¹⁰

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1 fully dense CNx/Si₃N₄ nanocomposites containing up to 13.6 vol.% of nitrogen-doped
2 nanotubes exhibiting high electrical conductivity, while maintaining an acceptable
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4 mechanical performance.
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10 11 **2. Materials and methods**

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13 CNx were synthesized by floating catalyst chemical vapour deposition (CVD) at
14 800 °C in flowing argon at 2.5 l·min⁻¹. In particular, an aerosol solution containing 6
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16 wt.% of ferrocene (FeCp₂) and 94 wt.% of benzylamine (C₇H₉N) was used as source of
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18 carbon and nitrogen, respectively.¹⁷ In order to disperse the nanotubes, as-synthesized
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20 CNx bundles were sonicated for 30 h in hydrogen peroxide (H₂O₂).
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27 Si₃N₄ nanocomposites containing 3 wt.% and 8 wt.% of H₂O₂-treated CNx (5.3
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29 and 13.6 vol.%, respectively) were prepared following a similar procedure as that
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31 reported for MWCNTs/Si₃N₄.¹⁸ In particular, both constituents, CNx and ceramic
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33 powders mixture were separately dispersed in ethanol. While CNx were sonicated in an
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35 ultrasonic bath for 1 h, the ceramic powders mixture consisted of Si₃N₄ (SN-E10, UBE
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37 Industries, Japan) and sintering additives - 2 wt.% of Al₂O₃ (SM8, Baikowski Chimie,
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39 France) and 5 wt.% of Y₂O₃ (Grade C, H.C. Starck GmbH & Co., Germany) - was
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41 previously attrition milled for 2 h employing Si₃N₄ balls. Subsequently, both (CNx and
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43 ceramic powders) ethanol suspensions were blended at adequate proportions in the
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45 ultrasonic bath under continuous stirring for an additional 1h. The resulting
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47 CNx/powder slurry was dried in a rotary evaporator, oven dried at 120 °C for 24 h, and
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Two additional nanocomposites, one containing 5.3 vol.% of pristine
commercial MWCNTs (Nanolab Inc., USA) and another one containing oxidized

MWCNTs (MWCNTs-OX) were also fabricated for comparative purposes. In order to achieve oxidation, nanotubes were treated with HNO₃ plus H₂SO₄ at volumetric ratio of 3:1 for 4 h at 80 °C following same procedure described elsewhere.¹⁹

Disc specimens of 20 mm x 3 mm were spark plasma sintered (SPS, Dr. Sinter, SPS-510CE, Japan) at temperatures of 1585-1600 °C for 5 min, applying a uniaxial pressure of 50 MPa during the heating cycle, and using a vacuum atmosphere of ~ 4 Pa.

Apparent density (ρ) was measured by the water immersion method, and the relative density was estimated assuming a theoretical density (ρ_{th}) of 3.23 and 1.80 g·cm⁻³ for Si₃N₄ and nanotubes, respectively. The $\alpha \rightarrow \beta$ -Si₃N₄ transformation degree in the specimens was determined by X-ray diffraction (XRD, Bruker D5000, Siemens, Germany).²⁰ Micro-Raman spectra of the as-synthesized and H₂O₂-treated CN_x, as well as the nanocomposites, were recorded using a confocal Raman-AFM equipment (Alpha300 WITec GmbH, Germany), and the 532 nm laser excitation wavelength. X-ray photoelectron spectroscopy (XPS, Axis-Ultra Kratos, UK) was employed to determine the nitrogen doping in the CN_x before and after the treatment with H₂O₂, as well as within the sintered nanocomposites. Areas of 220 μm^2 were scanned for the different samples using a binding energy range from 1250 to 10 eV. The quantification of the atomic percentage of each detected element was done using the CasaXPS Version 2.3.16 software that considers the area under each peak element and the ionization cross sections of each element.

Pristine and as-treated CN_x, as well as the microstructure of the sintered specimens, were analyzed by field emission scanning electron microscopy (FESEM, S-4700, Hitachi, Japan). Median grain diameter (d_{50}) and aspect ratio (AR_{50}) of the matrix were quantified by imaging analysis methods on FESEM micrographs considering at least 700 features. DC electrical resistivity data were determined in the composites

specimens from room temperature to 2 K using a Physical Properties Measurement System (PPMS, Quantum Design, USA). For the mechanical characterization, elastic modulus (E), Vickers hardness (H_V) and fracture toughness (K_{IC}) were measured using an instrumented microindenter (Zhu 2.5, Zwick/Roell, Germany) that simultaneously records load and specimen displacement. H_V and E were determined with Vickers pyramidal indenters at a peak load of 49 N, E being assessed by the equipment software using the unload part of the load/penetration curve in the elastic regime and H estimated from the optical measurement of the impression left after indenting. A maximum indentation load of 196 N was applied in order to determine K_{IC} values using the Miranzo et al.'s expression.²¹ At least five well-defined indentations were performed per specimen and load condition.

3. Results and Discussion

Figure 1 corresponds to the Raman spectrum of the as-synthesized CNx. The three characteristics Raman bands of CNTs (D, G and G') are clearly distinguished, with an intensity ratio I_D/I_G of 1.80 (Table 1). This ratio is commonly used as a tool to estimate the crystallinity of CNTs and, in the present case, the high I_D/I_G value would indicates a large number of defects in the nanostructures, which should be associated to both amorphous carbon species and nitrogen and oxygen atoms within carbon nanotubes that break the symmetry of crystalline graphite.

XPS analyses confirmed the nitrogen doping within CNx (Fig. 2), which was estimated to be *ca.* 1.6 wt.% (Table 1). The carbon C1s core level peak (Fig. 2a) exhibited the presence of sp^2 - and sp^3 -hybridized carbon (284.3 and 285.1 eV, respectively).²² Interestingly, the H_2O_2 treatment of as-synthesized CNx lead to an

1 increase on the sp^2 bonding content (from 73.5 to 84%), which infers an amorphous
2 carbon removal that is also in agreement with the results obtained by Raman
3 spectroscopy where the I_D/I_G ratio decreased up to 1.24 (Table 1). The H_2O_2 treatment
4 also contributed to eliminate the iron carbide particles present within CN_x and increased
5 the concentration of carbonyl and carboxyl groups (Fig. 2b), thus suggesting the surface
6 functionalization of carbon nanotubes. In addition, the NO_x band (Figs. 2c,d) showed
7 an increase, from 18.9 to 27.3, corresponding to a slight oxidation of the nitrogen atoms
8 present within the structure, and decreasing the substitutional nitrogen atoms from
9 66.6% (pristine CN_x) to 35.9% (H_2O_2 -treated CN_x). Despite this reduction, the nitrogen
10 doping content was still *ca.* 1.0 wt.% (Table 1).
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25 As synthesized CN_x consisted of large and numerous bundle-like aggregates
26 (Figs. 3a-c), which are hardly dispersed using sonication methods and common
27 dispersing agents for plain CNTs. In addition, FESEM observations confirmed the
28 presence within the CN_x batch of other undesired nanoparticles (Fig. 3c) that could
29 correspond to amorphous carbon and metal impurities. The CN_x solution in H_2O_2
30 sonicated for 30 h allowed the complete dispersion of the bundles or ropes (Fig. 3d-f),
31 showing nicely dispersed individual nanotubes, typically of 1-5 μm length and 50-100
32 nm diameter, and absence of impurity particles. In fact, as mentioned above, the I_D/I_G
33 ratio decreased to 1.24, indicating a larger degree of crystallinity within the nanotubes.
34 Accordingly, the H_2O_2 treatment produces both excellent CN_x dispersions and cleaning
35 of the nanotube surface, while preserving most of the N-doping as substitutional
36 nitrogen within the graphitic network.
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55 The route employed for processing CN_x/Si_3N_4 nanocomposites produced fully
56 dense materials ($> 99\%$ of the theoretical value, Table 2) with a good dispersion of the
57 CN_x within the ceramic matrix (Fig. 4), even for the material with the highest CN_x
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content (13.6 vol.%). In addition, the fast heating rates ($133\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) of SPS technique avoided the nanotubes degradation at the sintering temperatures, as confirmed by Raman spectroscopy. In particular, the I_D/I_G for the nanocomposites decreased from 1.24 (H_2O_2 treated CN_x) to 0.88 and 0.62 for the materials with 5.3 and 13.6 vol.% of CN_x , respectively. This decrease on I_D/I_G could be due to two possible reasons that could simultaneously occur: i) a higher degree of crystallinity of nanotubes after sintering caused by the removal of some amorphous carbon residues and, ii) the relaxation of the lattice distortion in the nanotube structure produced by the nitrogen atoms²³ that would take place due to the high SPS temperatures. XPS analysis of the CN_x nanocomposites confirmed that nitrogen doping remained after the SPS process (Fig. 5). While monolithic Si_3N_4 material exhibited two peaks in the N 1s spectrum located at 397.5 and 399.6 eV (Fig. 5a), ascribed to Si-N bonds, both CN_x nanocomposites showed an additional peak located at ~ 401 eV (Fig. 5b,c) which corresponds to highly coordinated N atoms replacing C atoms in the nanotubes.²⁴ However, the precise quantification of this nitrogen doping in the nanocomposites is not an easy task because of the overlapping between the C-N and Si-N peaks, the latter linked to the ceramic matrix.

Interestingly, the sintering kinetics of the SPSed $\text{CN}_x/\text{Si}_3\text{N}_4$ nanocomposites revealed some differences when compared with Si_3N_4 composites containing undoped MWCNTs. In particular, the down shifting of the temperature of the maximum shrinkage rate associated to particle rearrangement, from $1234\text{ }^{\circ}\text{C}$ to $1083\text{ }^{\circ}\text{C}$, in composites with 5.3 vol.% of nanotubes (Fig. 6). As it has been previously reported by some of the present authors,^{25,26} the electrowetting mechanism, responsible for the enhanced densification of Si_3N_4 materials during the initial stage of the liquid phase sintering process in the SPS, becomes more efficient when an electrical conductor, such

as CNTs, is incorporated into the Si_3N_4 insulating matrix. This fact experimentally manifests by a decrease on the temperature of the maximum particle rearrangement. Therefore, at first glance, the observed temperature decrease for CNx nanocomposites would indicate that these nanotubes are better electrical conductors than MWCNTs. Accordingly, the shrinkage rate-temperature curve of SPS could be used as a tool to predict in a comparative way the electrical properties of different carbon nanostructures/ Si_3N_4 composites.

It should be pointed out that the eutectic temperature of the current oxide additives system ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$, $\sim 1380^\circ\text{C}$) is higher than the estimated value for the maximum particle rearrangement rate of the CNx nanocomposites, and therefore, it wouldn't affect electrowetting. At this respect, some considerations can be made. First, the presence of iron impurities from the catalyst could reduce the temperature for the first liquid formation. Second, during the SPS process of electrical conductors, as in CNx nanocomposites, high temperature spots may locally occur within the powder compact producing local melting. Last but not least, it should be noticed that SPS is an extremely dynamic process and the temperature is overall measured at the surface of the graphite die so precise sample temperature is not known. Therefore, local liquid formation can occur at lower than expected nominal temperatures. Although a precise value for the maximum particle rearrangement rate temperature cannot be given, it is clear that the sintering process is significantly accelerated when using N-doped nanotubes.

When the CNx content increased to 13.6 vol.%, the particle rearrangement temperature rose up to 1197°C , showing a trend similar to undoped (or pure carbon) MWCNTs nanocomposites. The delay in the densification rate for this nanotube content

is attributable to the development of the tensile stresses in the matrix produced by non-sinterable particles of high aspect ratio (e.g. nanotubes).²⁵

One of the main issues that must be considered in order to improve the mechanical properties of CNTs/ceramics nanocomposites is the nanotube/matrix interface, which must be strong enough to promote the load transfer between the filler and the matrix but sufficiently weak for the occurrence of toughening mechanics such as bridging, debonding and pull-out. As it can be seen in Table 2, the monolithic material exhibits a better mechanical response than the carbon nanotubes containing nanocomposites, which is mainly due to the inter-tube sliding and the matrix grain refinement in the nanocomposites that would considerably reduce K_{IC} , with d_{50} and AR_{50} that are $\sim 25\%$ and 13% respectively, lower than for the monolithic Si_3N_4 . However, the 5.3 vol.% CNx nanocomposite exhibits an enhanced mechanical performance compared to the material containing a similar amount of undoped MWCNTs (Table 2), revealing E and H_V values ca. 30% higher, and 8% K_{IC} increase, as well. It is important to emphasize that both nanocomposites present similar density, matrix grain diameter and aspect ratio ($d_{50} \sim 240$ nm and $AR_{50} \sim 1.5$, Table 2), thus allowing a direct comparison between their properties, except the slightly higher amount of α - Si_3N_4 content in the CNx nanocomposite (63 versus 40%, Table 2) that could partially explain its larger H_V value. These results would imply that CNx are more strongly attached to the Si_3N_4 matrix than undoped MWCNTs, in a similar manner as it happens in Si_3N_4 composites with functionalized CNTs.¹⁹ In fact, the mechanical properties of CNx nanocomposite are quite similar to those of Si_3N_4 with oxidized MWCNTs (Table 2), where the oxidation of the nanotube outer walls by anchoring hydroxyl and carboxyl groups resulted in a better mechanical interlocking with the Si_3N_4 grains. In the present work, the long treatment with H_2O_2 used to disentangle (or

disperse) the CNx bundles, seems to produce an identical effect. When the CNx content in the composites increased to 13.6 vol.%, the mechanical parameters (E , H_V , K_{IC}) substantially decreased, probably due to an increase of the nanotube-nanotube interconnections. FESEM observations (Fig. 7) confirm the efficient anchoring of CNx , showing numerous examples of nanotube bridging and pull-out.

Resistivity measurements from room temperature to 2 K carried out for the CNx and MWCNTs nanocomposites show a semiconductor-like behaviour (Fig. 7a), with resistivity values at room temperature of 0.211, 0.269, 0.134, and 0.046 $\Omega \cdot \text{cm}$ for undoped MWCNTs, oxidized MWCNTs, 5.3 vol.% CNx and 13.6 vol.% CNx nanocomposites, respectively. These values corresponded to electrical conductivities (σ_e) of 474, 372, 746, and 2174 $\text{S} \cdot \text{m}^{-1}$ (Table 2). Although it has been already reported that the insulating behaviour of Si_3N_4 changes to semiconductor with the addition of low amounts of CNTs (below 0.9 vol.%),⁷ superior values are obtained in the present work. The nanocomposite containing 5.3 vol.% of undoped MWCNTs reached a σ_e value of 474 $\text{S} \cdot \text{m}^{-1}$ that is 3.5-5.0 times higher than values reported previously (maximum of 130 $\text{S} \cdot \text{m}^{-1}$ for 5 wt.% MWCNTs⁵ and of 92 $\text{S} \cdot \text{m}^{-1}$ for 6 vol.% SWCNTs⁶). Even more appealing is the 57% increase in the electrical conductivity of CNx nanocomposite ($\sigma_e = 746 \text{ S} \cdot \text{m}^{-1}$) for the same amount of nanotubes, i.e. 5.3 vol.%, and the 360% raise ($\sigma_e = 2174 \text{ S} \cdot \text{m}^{-1}$) for the 13.6 vol.% CNx content, which to the best of our knowledge, is the highest value reported so far for CNTs/ Si_3N_4 nanocomposites. Therefore, as it was expected,¹⁴ the introduction of nitrogen atoms into CNTs raises the electrical conductance above the undoped ones.²⁷ Previous research carried out by some of the present authors has pointed out that the electrical conductivity of CNx increased from 195 $\text{S} \cdot \text{m}^{-1}$, for the as-synthesized CNx, to 935 $\text{S} \cdot \text{m}^{-1}$, for the H_2O_2 treated CNx.

This phenomenon could be explained in terms of a p-type doping created by

1 physisorbed oxygenated molecules on the surface of CNx nanotubes. However, strong
2 oxidative processes carried out with nitric acid, or mixtures with sulphuric acid, could
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4 indeed modify the charge carriers', thus leading to a hopping transport regime and to an
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6 increase in the electrical resistivity.¹⁶ In this way, Talla et al.¹⁶ found a reduction of the
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8 electrical conductivity of 4.5 times for strong acid-treated CNx/polycarbonate
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10 nanocomposite when compared to the same material containing pristine CNx. This
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12 effect could also explain the decrease in σ_e (~ 22%) observed for (pure carbon)
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14 MWCNTs-OX/Si₃N₄ nanocomposite compared to MWCNTs/Si₃N₄ one (Table 2).
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20 We applied to the resistivity data, the variable range hopping theory for
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22 Coulomb gap (d=1) (Fig. 8c), two-dimensions (2D-VRH) (Fig. 8b), and three
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24 dimensions (3D-VRH) (Fig. 8d), where the resistivity exhibited $T^{-1/2}$, $T^{-1/3}$, and $T^{-1/4}$
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26 dependencies,²⁸ respectively. All the nanocomposites exhibited a better fitting for the
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28 3D-VRH (Fig. 8d), getting the highest matching at temperatures below 60 K for both
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30 MWCNTs nanocomposites, and below 9 K and 6 K for 5.3 vol.% CNx and 13.6 vol.%
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32 CNx nanocomposites, respectively. The 3D-VRH behaviour indicates that the electrons
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34 travel well through the entire sample in all directions due to a good ohmic contact at the
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36 interface between the nanotubes and the Si₃N₄ grains. This performance has also been
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38 observed for p-doped SWCNTs with boron atoms;²⁹ whereas pristine CNx followed the
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40 2D-VRH model²² in good agreement with the presence of disordered CNTs.³⁰
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51 4. Conclusions

52 In summary, homogenous and fully dense CNx/Si₃N₄ nanocomposites
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54 containing up to 13.6 vol.% of nitrogen-doped nanotubes were fabricated. These
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56 nanocomposites exhibited a three-dimensional variable range hopping conduction with
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1 electrical conductivity values of $2174 \text{ S}\cdot\text{m}^{-1}$, which appears to be the highest value ever
2 reported for CNTs/Si₃N₄ nanocomposites hitherto. This enhanced electrical
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4 performance is also inferred from the sintering behaviour, since the presence of CN_x
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6 enhances the electrowetting mechanism shifting the Si₃N₄ particle rearrangement
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8 temperature to a lower value than in the case of nanocomposites containing pure carbon
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10 MWCNTs. The mild oxidizing treatment with H₂O₂ efficiently disperses the CN_x tubes
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12 from bundles and, at the same time, promotes a stronger anchoring between the
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14 nanotubes and the matrix, thus leading to an improved mechanical performance, *i.e.*,
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16 *30% higher E and H_V values, and 8% increase on K_{IC}, when compared to the undoped*
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18 *CNT material. However, these values are lower than those obtained for the monolithic*
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20 *material mainly due to the inter-tube sliding and matrix refinement in the*
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22 *nanocomposites.*
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32 **Acknowledgements**

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35 This work was supported by the Spanish Government under the projects MAT2012-
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37 32944, and by the CSIC project I-LINK0119. M. Terrones thanks JST-Japan for
38
39 funding the Research Center for Exotic NanoCarbons, under the Japanese Regional
40
41 Innovation Strategy Program by the Excellence, and the Penn State Center for
42
43 Nanoscale Science for a seed grant on layered systems. M. Terrones acknowledges the
44
45 Air Force Office of Scientific Research for the Project MURI: Synthesis and
46
47 Characterization of 3D Carbon Nanotube Solid Networks Award No.: FA9550-12-1-
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Captions

Figure 1. Micro-Raman spectrum for as-synthesized CNx showing the characteristic G-, D- and G'-bands, corresponding to graphitic materials.

Figure 2. XPS spectra of (a,b) C1s and (c,d) N1s core levels for as-synthesized CNx (a,c) and H₂O₂-treated CNx (b,d).

Figure 3. FESEM micrographs of as-synthesized (a-c) and H₂O₂-treated (d-f) CNx showing numerous bundle-like aggregates and nice dispersed individual nanotubes, respectively.

Figure 4. FESEM micrographs of the fracture surfaces corresponding to 5.3 vol.% CNx (a,b) and 13.6 vol.% CNx (c,d) nanocomposites, where a good dispersion of the CNx within the ceramic matrix is observed.

Figure 5. XPS spectra of N1s core levels for monolithic (a) and nanocomposites containing 5.3 vol.% CNx (b) and 13.6 vol.% CNx (c).

Figure 6. Temperature of the particle rearrangement stage of the nanocomposites as a function of the nanotubes content, both undoped CNTs²⁵ and CNx.

Figure 7. FESEM micrographs of the fracture surface corresponding to 13.6 vol.% CNx nanocomposite showing examples of toughening mechanisms such as CNx bridges (a-c) and pull-out (c-d).

Figure 8. (a) Resistivity (ρ) versus temperature, and variable range hopping fitting for (b) Coulomb gap ($d=1$), (c) two-dimensions (2D-VRH), and (d) three dimensions (3D-VRH) for 5.3 vol.% MWCNTs, 5.3 vol.% MWCNTs-OX, 5.3 vol.% CNx and 13.6

vol.% CNx nanocomposites. Points correspond to experimental data and the fittings are represented by lines.

Table legends

Table 1. Raman intensity ratio between D and G bands (I_D/I_G), and elemental atomic percentage for oxygen, carbon and nitrogen assessed from XPS spectrum for pristine and treated CNx.

Table 2. Apparent (ρ) and relative densities (ρ_{th}), α -phase content, median grain diameter (d_{50}) and aspect ratio (AR_{50}), Elastic modulus (E), Vickers hardness (H_V), fracture toughness (K_{IC}), and dc electrical conductivity (σ_e) for the different nanocomposites as a function of the nanotubes type (MWCNTs, oxidized MWCNTs, and CNx) and content.

Table 1. Raman intensity ratio between D and G bands (I_D/I_G), and elemental atomic percentage for oxygen, carbon and nitrogen assessed from XPS spectrum for pristine and treated CNx.

Material	I_D/I_G	O (%)	C (%)	N (%)
Pristine CNx	1.80	3.07	95.33	1.60
Treated CNx	1.24	2.09	96.90	1.01

Table 2

Table 2. Apparent (ρ) and relative densities (ρ_{th}), α -phase content, median grain diameter (d_{50}) and aspect ratio (AR_{50}), Elastic modulus (E), Vickers hardness (H_V), fracture toughness (K_{IC}), and dc electrical conductivity (σ_e) for the different nanocomposites as a function of the nanotubes type (MWCNTs, oxidized MWCNTs, and CNx) and content.

Material	ρ (g·cm ³)	ρ_{th} (%)	α -phase (%)	d_{50} (nm)	AR_{50}	E (GPa)	H_V (GPa)	K_{IC} (MPa·m ^{1/2})	σ_e (S·m ⁻¹)
Si ₃ N ₄	3.23	99.9	40	297	1.8	359 ± 22	18.9 ± 0.1	6.7 ± 0.1	10 ⁻¹³
5.3 vol% MWCNTs/Si ₃ N ₄	3.15	99.4	40	237	1.5	238 ± 6	12.3 ± 0.2	4.8 ± 0.1	474
5.3 vol% MWCNTs-OX/Si ₃ N ₄	3.16	99.5	56	220	1.5	305 ± 9	17.9 ± 0.1	5.4 ± 0.1	372
5.3 vol% CNx/Si ₃ N ₄	3.15	99.4	63	238	1.6	308 ± 15	16.1 ± 0.7	5.2 ± 0.5	746
13.6 vol% CNx/Si ₃ N ₄	3.03	99.3	40	231	1.6	233 ± 9	12.4 ± 0.6	4.5 ± 0.2	2174

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 5

Figure 6

Figure 7

Figure 8