Borrell Tomás, MA.; Rocha, VG.; Torrecillas, R.; Fernandez, A. (2011). Improvement of Carbon Nanofibers/ZrO2 Composites Properties with a Zirconia Nanocoating on Carbon Nanofibers by Sol–Gel Method. Journal of the American Ceramic Society. 94(7):2048-2052. doi:10.1111/j.1551-2916.2010.04354.x.

Improvement of CNFs/ZrO_2 composites properties with a zirconia nanocoating on carbon nanofibers by sol-gel method

A. Borrell[1*], V.G. Rocha[2], R. Torrecillas[1], A. Fernández[2]

[1]*Centro de Investigación en Nanomateriales y Nanotecnología (CINN) (Consejo Superior de Investigaciones Científicas - Universidad de Oviedo - Principado de Asturias), Parque Tecnológico de Asturias, 33428 Llanera (Asturias), Spain*

[2]*Fundación ITMA, Parque Tecnológico de Asturias, 33428 Llanera (Asturias), Spain*

*a.borrell@cinn.es

ABSTRACT

The development of new carbon nanofibers-ceramic nanocomposite materials with excellent mechanical, thermal and electrical properties is interesting for a wide range of industrial applications. Among the ceramic materials, zirconia stands out for their excellent mechanical properties. The main limitations in the preparation of this kind of nanocomposites are related with the difficulty in obtaining materials with homogeneous distribution of both phases and the different chemical nature of CNFs and ZrO_2 which causes poor interaction between them. CNFs-reinforced zirconia nanocomposites ZrO_2/xCNFs (x=1-20 vol.%) were prepared by powder mixture and sintered by spark plasma sintering (SPS). ZrO_2-reinforced carbon nanofibers nanocomposites CNFs/xZrO_2 (x=20 vol.%) were prepared by powder mixture and a surface coating of CNFs by wet chemical route with zirconia precursor is proposed as a very effective way to improve the interaction between CNFs and ZrO_2. After SPS sintering an improvement of 50% in fracture strength was found for similar

nanocomposite compositions when the surface coating was used. The improved mechanical properties of these nanocomposites are caused by stronger interaction between the CNFs and ZrO_2.

Keywords: Sol-gel method, carbon nanofibers, spark plasma sintering, mechanical properties, nanozirconia.

1. INTRODUCTION

The discovery of carbon nanotubes (CNTs) has generated considerable interest owing to their small size, high aspect ratio, low mass and excellent mechanical, electrical and thermal properties [1,2] but the low rate production of this kind of structures limit their applications. Carbon nanofibers appear as an alternative to CNTs showing similar properties, although with slightly different sizes [3]. Carbon nanofibers (CNFs) have cylindrical or conical structures that have diameters varying from a few to hundreds of nanometers and lengths ranging from less than a micron to tens of microns. The internal structure of carbon nanofibers is comprised of different arrangements of modified graphene sheets, and the main distinguishing characteristic of nanofibers from nanotubes is the stacking of graphene sheets of varying shape [4].

Concerning the design of composites with ceramics, research has been mainly focused on alumina-based composites, and only limited work has been done on other systems, e.g. silicon nitride or zirconia [5-7]. Furthermore, the carbon reinforcing element has generally been CNTs and only a few studies have involved CNFs. Therefore, the potential advantages of CNFs vs. CNTs (price, production rate) as reinforcing elements are still largely unexplored. Zirconia (3Y-TZB) is a material

extensively used for many structural applications due to its excellent mechanical properties. Zirconia and/or zirconia-based composites are interesting multifunctional materials that have been used for many applications, such as solid-oxide fuel cells, oxygen sensors and ceramic membranes, due to their good high-temperature stability, high breakdown electrical field or large energy bandgap [8].

Some publications have recently appeared illustrating the advantages of CNFs as reinforcing elements in alumina, silicon carbide and hydroxyapatite-based composites [9-11] and only a limited number of publications dealing with the mechanical properties of CNTs/ZrO_2 [12,13] and CNFs/ZrO_2 [14,15] composites. Sun et al. [12] studied the mechanical and fracture behavior of MWCNTs/3Y-TZP composites containing 0.1-1.0 wt.% MWCNTs and SWCNTs prepared by spark plasma sintering (SPS). They found that the addition of CNTs had a negative influence on the hardness of the composites and no influence or a negative influence on the fracture toughness. The CNTs often agglomerate at the ZrO_2 boundaries, and the weak bonding between the CNTs and zirconia are the reasons why the reinforcing effect of the CNTs is limited. Additionally, according to the results of Dusza et al. [15], the presence of the CNFs makes densification more difficult. Consequently, the ZrO_2+1.07wt.% CNFs nanocomposite prepared by Hot-press (HP), even if it shows significantly higher electrical conductivity compared with monolithic zirconia it exhibits lower mechanical properties. Regarding the densification of the CNTs/ZrO_2 or CNFs/ZrO_2 composites, authors have mainly used HP or SPS that has been already reported as a feasible technique for ceramic-CNTs composites densification [16,17]. The SPS, also known as field assisted sintering technique (FAST), is a sintering technique which can consolidate powder compacts by applying an on-off dc electric pulse under uniaxial pressure [18]. This technique can work at heating rates of the order of hundreds of degrees per minute, reaching high

temperatures in very short time, leading to dense materials after cycles of heating/cooling of the order of a few minutes [19]. These features allow achieving microstructures unattainable by other sintering techniques. Zirconia particles in the nano-size range have been synthesized using various routes such as sol-gel [20,21], co-precipitation [22,23], ball milling [24], hydrothermal process [25,26], gas phase synthesis and microemulsion methods [27-29]. Among the various synthesis methods, sol-gel method is the most promising and thus has been widely investigated because it produces solid particles of high purity and high specific surface area.

The aim of the present contribution is to investigate the preparation of two types of nanocomposites based on zirconia-carbon nanofibers system: zirconia matrix reinforced with carbon nanofibers and carbon matrix reinforced with zirconia nanoparticles. In the second case, two synthesis routes are compared: mixture of commercial powders and sol-gel method using a zirconia precursor. Sol-gel process is used to disperse zirconia nanoparticles homogeneously in CNFs matrix by entrapping the dispersed CNFs in the gel network formed by ZrO_2 precursor. The powders obtained by the two different routes have been sintered by SPS and the composites obtained were compared in terms of mechanical and electrical properties.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of composite powders

2.1.1. Mixed powders

The materials used in this study were commercial carbon nanofibers (CNFs) having average outer diameter of 20-80 nm and lengths >30 microns, supplied by Group Antolin Engineering (Spain), and ZrO_2 (TZ-3YB) nanopowders (Tosoh Corp., Japan)

with average particle size of 180 nm. The CNFs are generated via the vapor growth method (VGCNFs) [30] using a floating catalyst of nickel in solution (6-8%). Powders mixtures of ZrO_2/CNFs = 99/1 - 93/7 - 80/20 vol.% and CNFs/ZrO_2 = 80/20 vol.%, were dispersed in ethanol (Panreac Quimica) in a high energy attrition milling (Union Process, EE.UU) using zirconia media of 2 mm in diameter at 400 rpm and milling time of 1 hour. After milling, the resultant homogeneous mixture (ZrO_2/CNFs or CNFs/ZrO_2) slurry was dried at 60 ºC and the dried powder was sieved under 60 microns.

2.1.2. Surface coating of CNFs

The surface coating of CNFs was carried out employing sol-gel processing route. Zirconium oxychloride octahydrate $ZrOCl_2$ $8H_2O$ (Merck, p.a. grade) was used as zirconia precursor. Under magnetic stirring the appropriate amount of zirconium oxychloride was firstly dissolved in 400 mL of distilled and deionized water in order to obtain 20 vol.% of ZrO_2 on the final composite powder (CNFs+20vol.% ZrO_2). Subsequently, the CNFs were added to the zirconium precursor solution under stirring. Finally, the pH was adjusted to 10.5 with a buffer NH_4OH solution (28 wt.%). The mixture was heated up to 60-70 ºC in order to evaporate the solvent leading to the gel formation. The gel was dried in air at 120 ºC for 24 h and the dried powder was sieved under 60 microns to achieve a uniform distribution of particle sizes. Thermogravimetric analysis of the modified powder (TGA Star System, Mettler Toledo) was carried out up to 1000 ºC at 5 ºC min^{-1} heating rate under argon atmosphere in order to determine the temperature for chlorides removal. The powder was then pirolized under inert atmosphere at the selected temperature. In order to obtain tetragonal stabilized zirconia in the final composite powder an additional composition was prepared by sol-gel

method. The composition of this composite powder was CNFs+20vol.% (3Y-ZrO_2) that will be designed as CNFs+20vol.% YSZ. The procedure was similar to the previously described, in which the appropriate amount of yttrium chloride YCl_3 $6H_2O$ was used as yttria precursor to achieve a 3mol.% Y_2O_3 in the zirconia particles.

2.2. SPS and characterization of sintered bodies

The powder samples were placed into a graphite die with an inner diameter of 20 mm and cold uniaxially pressed at 30 MPa. Then, they were introduced in a spark plasma sintering apparatus HP D 25/1 (FCT Systeme) under low vacuum (10^{-1} mbar) and sintered at different temperatures for 1 min under an applied pressure of 80 MPa and a heating rate of 100 ºC min^{-1}. The samples are regular disks and bulk density of the sintered bodies was measured by the geometric method. The fracture strength was measured using biaxial testing employing the equations of Kirstein and Woolley [31], Vitman and Pukh [32], and the standard specification ASTM F394-78 [33]. All tests were carried out at room temperature using the universal machine Instron (Model 8562) with a cross-head displacement speed of 0.002 mm s^{-1}. X-ray diffraction (XRD) analysis was performed on a Siemens X-ray diffractometer (Model D 5000), which has a geometry type "Bragg-Brentano" with Cu-k_α radiation (λ = 0.15418 nm, 40 kV, 30 mA). The measurements were done in the 15-80º range and the step size and time of reading were 0.02º and 0.3 s, respectively. The electrical resistivity of monolithic and composite materials studied in this work was determined according to ASTM C611. The specimens were placed between two sheets of copper connected to a power supply which allowed working at different current intensities. The measures were carried out by fixing the intensity of the current at 0.5 A using a multimeter of fixed pegs (9.55 mm separation), determining the voltage drop.

3. RESULTS AND DISCUSSIONS

3.1. Composites obtained from mixing powders

Table 1 summarizes the density and fracture strength of the monolithic zirconia, CNFs and the ZrO_2/CNFs composites sintered by Spark Plasma Sintering at 1200 and 1500 ºC. It is worth to note that monolithic zirconia sintered by SPS either at 1200 or 1500 ºC show almost the same fracture strength value and close to the theoretical value for zirconia (1200 MPa). In the literature it can be found that optimum sintering temperature by SPS for this type of materials is around 1200 ºC [34]. However, higher temperatures allow obtaining slightly higher properties when (3Y-TZP) is used and operation conditions adjusted. As it can be seen in the micrograph of Figure 1 where the fracture surface of zirconia material sintered at 1500 ºC is shown, the grain growth in comparison with starting powder (180 nm) even after treatment at 1500 ºC is negligible. The microstructure is maintained in the nanoscale and thus the mechanical properties are similar or even better.

Nevertheless, the density and therefore the fracture strength of ZrO_2/CNFs composites sintered at 1500 ºC are higher than corresponding to those sintered at 1200 ºC. As it can be seen in Table 1 the fracture strength of 100% CNFs material is considerably higher at 1500 ºC. This fact has been shown in previous work [35], thus the ZrO_2/CNFs properties show the strong influence of the sintering temperature due to the presence of CNFs. The addition of this soft phase results in lower density and fracture strength in the composites. Other authors have demonstrated that CNFs hinder grain growth in the composite during sintering giving rise to higher mechanical

properties [14,36]. As it has been previously shown, zirconia grain growth is negligible even in the monolithic material and we have not observed further hindering of grain growth due to CNFs addition. Then, the mechanical properties decrease proportionally to the soft carbon phase (CNFs) content. Other reason for this lack of reinforcement of zirconia materials with CNFs could be the difficulty in dispersing both phases homogeneously [14]. Additionally, it can be expected a poor cohesion between CNFs and zirconia because of their very different chemical nature. These problems become more marked in carbon matrix composite (ZrO_2+80vol.% CNFs) which is not possibly to densify.

Fracture surfaces of the composites sintered at 1500 ºC were examined by scanning electron microscopy as shown in Figure 2. SEM micrographs (a) and (b) show the microstructure of the composites with lower contents of CNFs. The grain size is very close to the raw ZrO_2 powder and there is no porosity. As other authors observed, it can be appreciated in the SEM micrographs (c) and (d) that the zirconia grain size is smaller in composites with high CNFs percentages due to the big dispersion of the ceramic particles into the carbon nanofibers. The sintered monolithic zirconia was fully dense and the composites with low CNFs contents show high density (99%) but the (ZrO_2+80vol.% CNFs) composite shows porosity, as it can be seen in Figure 1(d). This porosity is associated with clustering of the CNFs. The process of carbon matrix composites (CNFs/ZrO_2) fabrication should be improved.

The electrical resistivity of the composites was measured at room temperature and no significant changes have been found on the values of sintered composites at 1200 or 1500 ºC as its electrical resistivity only depends on the material composition.

The electrical resistivity values of the composites with 1, 7, 20 and 80 vol.% of CNFs were $>10^{10}$, 10^{2}, 10^{-1} and 10^{-2} Ω cm, respectively. Ceramic matrix composites with very low electrical resistivity have been produced thus ZrO_2+7vol.% CNFs shows an electrical resistivity only one order of magnitude higher than the CNFs raw material and nine order lower than the zirconia. Therefore, a promising composite for electrical discharge machining (EDM) has been designed as it was possible to obtain a nanocomposite with ~600 MPa fracture strength and very low electrical resistivity. The EDM is a potential and attractive technology for the machining of ceramics if these materials are provided with sufficiently high electrical conductivity [37].

3.2. Wet chemical route (sol-gel) composites

Figure 3 shows the thermogravimetric analysis of the CNFs+20vol.% ZrO_2 and CNFs+20% YSZ powders synthesized by sol-gel process. Both curves are very similar the small amount of yttria precursor added is not reflected in the weight loss.

Four main weight losses can be easily observed in the DTG analysis. In the first step T_{max} takes place at 85 ºC and the weight loss is less than 5% which may be attributed to the water used as solvent in the mixture process. In the second step the main weight loss occurs between 200-350 ºC and is due to the removal of chlorides residuals of the zirconia precursor. The weight loss is around 20%. Third step has a small weight loss between 450-550 ºC which corresponds to the elimination of ammonium chloride formed between the buffer solution and the precursor. Finally the very small weight loss at 650 ºC was previously observed in TG analysis of CNFs dried from water slurry. Then this small weight loss is related with water adsorbed in carbon nanofibers not with the precursors used in this research. Considering these results, the powder was

thermally treated at 800 ºC for 2 h in argon atmosphere, in order to remove residuals, without CNFs combustion.

The sol-gel powders were sintered up to 1500 ºC by SPS in order to compare with mixture powders composites of the same composition. The XRD analysis in Figure 4 shows that zirconia was formed during the sintering process at 1500 ºC, in the CNFs+20vol.% ZrO_2 composite fabricated by sol-gel method. As it can be expected an important amount of monoclinic zirconia is formed after cooling due to the stabilizing absence. In nanocomposites prepared by mixing powder and sol-gel (yttria-stabilized) methods it appears virtually pure zirconia tetragonal phase.

Table 2 shows the density and fracture strength of the materials sintered at 1500 ºC. As reference the characteristics of CNFs+20vol.% ZrO_2 composite obtained by mixing powders are included in this table.

The relative density of CNFs+20vol.% ZrO_2 nanocomposite prepared by sol-gel is slightly higher than the density of CNFs+20vol.% ZrO_2 material prepared by mixing powders. Nevertheless, the surface coating of CNFs with a zirconia precursor leads to considerably higher fracture strength materials. From a chemical point of view, sol-gel process allows the formation of a three dimensional network which perfectly interconnect the particles in the hole volume. Consequently, as carbon nanofibers have been well dispersed in the sol, they were homogeneously coated by the gel layer. Heat treatment will lead to the formation of zirconia nanoparticles very well dispersed in the composite powder. Although, the non-stabilized sol-gel powder lead to monoclinic zirconia phase after sintering in the composite, it shows similar fracture strength to the

yttria-stabilized (CNFs+20% YSZ) composite and almost 50% higher than the mixed powders composite. This increase in the mechanical properties is not accompanied by a decrease in the porosity of the material (only 1% difference in relative densities). Additionally, the similar properties of both nanocomposites prepared by sol-gel method points out that no significant reinforcement by phase transformation of zirconia nanoparticles is needed for getting this improvement. Then, the strength improvement is related with a stronger interaction between components.

The value of the electrical resistivity of the composites obtained by sol-gel method is 10^{-2} Ω cm, being this value the same as corresponding to the material obtained by powder mixing. The electrical resistivity was measured in both directions, parallel and perpendicular to the direction of the applied pressure during sintering, and in both directions were achieved similar results. This is indicative of a homogenous dispersion of CNFs and zirconia. Then, zirconia-reinforced CNFs nanocomposite with improved mechanical properties and maintaining very low electrical resistivity have been obtained by combining chemical synthesis routes and new sintering techniques. These results show that in some cases conventional ceramic processes such as traditional powder mixing are relieved by chemical synthesis methods that allow reactions control, and the nucleation and growth of nanocrystals at the molecular level.

4. CONCLUSIONS

Dense ZrO_2/carbon nanofibers composites which exhibit high mechanical properties and significantly higher electrical conductivity compared with monolithic zirconia have been developed. ZrO_2+7vol.% CNFs composite showed ~600 MPa fracture strength and high electrical conductivity which allow machining the composite by EDM. In spite of

the high ceramic phase content the electrical conductivity of the new composites is similar to the carbon material. In order to achieve a good densification of the composites, the sintering temperature must be 1500 ºC. The surface coating of carbon nanofibers using a zirconia precursor is a very interesting method to obtain carbon matrix CNFs/ZrO_2 composites with enhanced interaction between ceramic and carbon phases. By sol-gel process CNFs+20vol.% ZrO_2 nanocomposite has been prepared with close to 50% higher fracture strength than that prepared by conventional mixing powders. Phase agglomeration and weak cohesion bonding with zirconia grains have been avoided with this method.

ACKNOWLEDGEMENTS

This work has been carried out with financial support of National Plan Projects MAT2006-01783 and MAT2007-30989-E and the Regional Project FICYT PC07-021. A. Borrell, acknowledges the Spanish Ministry of Science and Innovation for her research grant BES2007-15033.

REFERENCES

1. S. Iijima, “Helical microtubules of graphitic carbon”, Nature, 354 56-58 (1991).

2. A. Merkoci, “Carbon nanotubes in analytical sciences”, Microchim. Acta, 152 [3-4] 157-174 (2006).

3. T. Uchida, P. D. Anderson, M. L. Minus, and S. J. Kumar, “Morphology and modulus of vapor grown carbon nano fibers”, J. Mater. Sci., 41 [18] 5851-5856 (2006).

4. A. V. Melechko, V. I. Merkulov, T. E. McKnight, M. A. Guillorn, K. L. Klein, D. H. Lowndes, and M. L. Simpson, “Vertically aligned carbon nanofibers and related

structures: Controlled synthesis and directed assembly", J. Appl. Phys., 97 [4] 041301 (2005).

5. P. Hvizdoš, V. Puchý, A. Duszová, and Ján Dusza, "Tribological behavior of carbon nanofiber-zirconia composite", Scrip. Mater., 63 [2] 254-257 (2010).

6. Cs. Balazsi, Z. Kónya, F. Wéber, L.P Biró, and P. Arató, "Preparation and characterization of carbon nanotube reinforced silicon nitride composites", Mater. Sci. Eng. C, 23 [6-8] 1133-1137 (2003).

7. J. Tatami, T. Katashima, K. Komeya, T. Meguro, and T. Wakihara, "Electrically conductive CNT-dispersed silicon nitride ceramics", J. Am. Ceram. Soc., 88 [10] 2889-2893 (2005).

8. S. Y. Lee, H. Kim, P. C. McIntyre, K. C. Saraswat, and J. S. Byun, "Atomic layer deposition of ZrO_2 on W for metal-insulator-metal capacitor application", Appl. Phys. Lett., 82 [17] 2874-2876 (2003).

9. S. Maensiri, P. Laokul, J. Klinkaewnarong, and V. Amornkitbamrung, "Carbon nanofiber-reinforced alumina nanocomposites: Fabrication and mechanical properties", Mater. Sci. Eng. A, 447 [1-2] 44-50 (2007).

10. K. Hirota, H. Hara, and M. Kato, "Mechanical properties of simultaneously synthesized and consolidated carbon nanofiber (CNF)-dispersed SiC composites by pulsed electric-current pressure sintering", Mater. Sci. Eng. A, 458 [1-2] 216-225 (2007).

11. S. Kobayashi, and W. Kawai, "Development of carbon nanofiber reinforced hydroxyapatite with enhanced mechanical properties", Composites: Part A, 38 [1] 114-123 (2007).

12. J. Sun, L. Gao, M. Iwasa, T. Nakayama, and K. Niihara, "Failure investigation of carbon nanotube/3Y-TZP nanocomposites", Ceram. Int., 31 [8] 1131-1134 (2005).

13. T. Ukai, T. Sekino, A. Hirvonen, N. Tanaka, T. Kusunose, T. Nakayama, and K. Niihara, “Preparation and electrical properties of carbon nanotubes dispersed zirconia nanocomposites”, Key Eng. Mat., 317-318 661-664 (2006).

14. A. Duszová, J. Dusza, K. Tomášěk, J. Morgiel, G. Blugand, and J. Kuebler, “Zirconia/carbon nanofiber composite”, Scrip. Mater., 58 [6] 520-523 (2008).

15. J. Dusza, G. Blugan, J. Morgiel, J. Kuebler, F. Inam, T. Peijs, M. J. Reece, and V. Puchy, “Hot pressed and spark plasma sintered zirconia/carbon nanofiber composites”, J. Eur. Ceram. Soc., 29 [15] 3177-3184 (2009).

16. X. Wang, N. P. Padture, and H. Tanaka, “Contact-damage-resistant ceramic/single-wall carbon nanotubes and ceramic/graphite composites”, Nature Mater., 3 539-544 (2004).

17. G. D. Zhan, J. D. Kuntz, J. E. Garay, and A. K. Mukherjee, “Electrical properties of nanoceramics reinforced with ropes of single-walled carbon nanotubes”, Appl. Phys. Lett., 83 [6] 1228-1230 (2003).

18. R. G. Joanna, and Z. Antonios, “Sintering activation by external electrical field”, Mater. Sci. Eng. A, 287 [2] 171-177 (2000).

19. W. Yucheng, and F. Zhengyi, “Study of temperature field in spark plasma sintering”, Mater. Sci. Eng. B, 90 [1-2] 34-37 (2002).

20. S. Shukla, and S. Seal, “Mechanisms of room temperature metastabel tetragonal phase stabilization in zirconia”, Inter. Mater. Rev., 50 [1] 1-20 (2005).

21. H. Kumazawa, T. Inoue, and E. Sada, “Synthesis of fine spherical zirconium particles by controlled hydrolysis of zirconium alkoxide in high temperature range above 50 ºC”, Chem. Eng. J, 55 93-96 (1991).

22. F. Haase, and F. Sauer, “The surface of sulfated zirconia-periodic ab initio study of sulfuric acid adsorbed on ZrO_2(101) and ZrO_2(001)”, J. Am. Chem. Soc., 120 [51] 13503-135012 (1998).

23. K. Matsui, H. Suzuki, and M. Ohagi, “Raman spectroscopic studies on the formation mechanism of hydrous-zirconia fine particles”, J. Am. Ceram. Soc., 78 [1] 146 (1995).

24. M. Gateshki, V. Petkov, G. Williams, S. K. Pradhan, and Y. Ren, “Atomic-scale structure of nanocrystalline ZrO_2 prepared by high-energy ball milling”, Phys. Rev. B, 71 [22] 224107-224116 (2005).

25. W. Pyda, K. Haberko, and M. M. Bucko, “Hydrothermal crystallization of zirconia and zirconia solid solutions”, J. Am. Ceram. Soc., 74 [10] 2622-2629 (1991).

26. G. Dell’Agli, and G. Mascolo, “Hydrothermal synthesis of ZrO_2-Y_2O_3 solid solutions at low temperature”, J. Eur. Ceram. Soc., 20 [2] 139-145 (2000).

27. C. Y. Tai, B. Y. Hsiao, and H. Y. Chiu, “Preparation of silazane grafted yttria-stabilized zirconia nanocrystals via water/CTAB/hexanol reverse microemulsion”, Mater. Lett., 61 [3] 834-836 (2007).

28. C. Y. Tai, M. H. Lee, and Y. C. Wu, “Control of zirconia particle size by using two-emulsion precipitation technique”, Chem. Eng. Sci., 56 [7] 2389-2398 (2001).

29. C. Y. Tai, and B. Y. Hsiao, “Characterization of zirconia powder synthesized via reverse microemulsion precipitation”, Chem. Eng. Commun., 192 [10-12] 1525-1540 (2005).

30. L. Ci, J. Wei, B. Wei, J. Liang, C. Xu, and D. Wu, “Carbon nanofibers and single-walled carbon nanotubes prepared by the floating catalyst method”, Carbon, 39 [3] 329-335 (2001).

31. A. F. Kirstein, and R. M. Woolley, “Symmetrical bending of thin circular elastic plates on equally spaced point supports”, J. Res. Natl. Bur. Stand. C, 71 1-10 (1967).

32. F. F. Vitman, and V. P. Pukh, “A method for determining the strength of sheet glass”, Zavod. Lab, 29 863-867 (1963).

33. ASTM Standard F394-78, STM Annual Book of Standards, Vol. 15.02, Section 16. American Society for Testing and Materials, Philadelphia, PA, 466-490 (1996).

34. W. Li, and L. Gao, “Rapid sintering of nanocrystalline ZrO_2(3Y) by spark plasma sintering”, J. Eur. Ceram. Soc., 20 [14-15] 2441-2445 (2000).

35. A. Borrell, A. Fernandez, C. Merino, and R. Torrecillas, “High density carbon materials obtained at relatively low temperature by spark plasma sintering of carbon nanofibers”, Int. J. Mater. Res., 101 [1] 112-118 (2010).

36. J. Dusza, J. Morgiel, P. Tatarko, and V. Puchy, “Characterization of interfaces in ZrO_2-carbon nanofiber composite”, Scrip. Mater., 61 [3] 253-256 (2009).

37. B. Lauwer, J. P. Kruth, W. Liu, W. Eeraerts, B. Schacht, and P. Bleys, “Investigation of material removal mechanisms in EDM of composite ceramic materials”, J. Mater. Proces. Technol., 149 347-352 (2004).

Captions:

Fig. 1. Fracture surface of monolithic zirconia sintered by SPS at 1500 ºC/80 MPa/1 min.

Fig. 2. Fracture surface of composites sintered at 1500 ºC: (a) 1, (b) 7, (c) 20 and (d) 80 vol.% of CNFs.

Fig. 3. TG and DTG analysis of the powders synthesized by sol-gel method solid line; non-stabilized powder and dot line; yttria-stabilized powder.

Fig. 4. XRD diffractograms of the powders prepared by mixing powders and sol-gel methods, sintered by SPS at 1500 ºC.

Table I. Characteristics of ZrO_2/CNFs composites materials obtained from powders mixing sintered by SPS at 1200 ºC and 1500 ºC and 80 MPa for 1 min under vacuum.

Samples	Relative density (%TD)		Fracture strength (MPa)	
	1200 ºC	1500 ºC	1200 ºC	1500 ºC
ZrO_2	99.9	99.9	998 ± 10.9	1082 ± 11.2
ZrO_2+1vol.% CNFs	98.4	99.9	663.3 ± 4.1	900.8 ± 6.3
ZrO_2+7vol.% CNFs	95.7	99.7	588.4 ± 3.8	591.8 ± 5.2
ZrO_2+20vol.% CNFs	92.7	98.8	284.7 ± 2.5	335.0 ± 2.1
ZrO_2+80vol.% CNFs	83.4	92.3	40.8 ± 1.8	57.2 ± 2.4
CNFs	82.1	89.4	38.0 ± 2.1	60.8 ± 2.7

Table II. Characteristics of the different CNFs+20vol.% ZrO_2 composites sintered by SPS at 1500 ºC and 80 MPa for 1 min.

Samples	Relative density (%TD)	Fracture strength (MPa)
CNFs+20vol.% ZrO_2 (**powders mixing**)	92.3	57.2 ± 2.4
CNFs+20% YSZ (**sol-gel yttria stabilized**)	93.7	90.2 ± 2.1
CNFs+20vol.% ZrO_2 (**sol-gel without yttria**)	93.9	99.5 ± 2.8