3YTZP-ALUMINA-NANODIAMOND COMPOSITES WITH GEMOLOGICAL PROPERTIES

L.A. Díaz¹*, S. Rivera², T. Rodríguez-Suárez¹, J.F. Bartolomé³, M.A. Montes-Morán⁴, J.S. Moya³, R. Torrecillas¹

¹ Centro de Investigación en Nanomateriales y Nanotecnología (CINN) Consejo Superior de Investigaciones Científicas (CSIC) - Universidad de Oviedo (UO) - Principado de Asturias (PA), Parque Tecnológico de Asturias, 33428 - Llanera, Asturias, Spain, ² Nanoker Research, S.L., Edificio CEEI, Parque Tecnológico de Asturias, 33428 - Llanera, Asturias, Spain, ³ Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), C/ Sor Juana Inés de la Cruz 3, 28049 - Cantoblanco, Madrid, Spain, ⁴ Instituto Nacional del Carbón (INCAR), Consejo Superior de Investigaciones Científicas (CSIC), C/Francisco Pintado Fe 26, 33011 - Oviedo, Asturias, Spain

* Corresponding author (l.a.diaz@cinn.es)

Keywords: composites, 3Y-TZP, alumina, nanodiamonds, gemological properties, PECS.

General Introduction

Tetragonal stabilized zirconia with 3 mol% yttria (3YTZP) is widely used for structural materials due to its superior properties, such as high strength, and toughness (based on the transformation toughening mechanism) [1]. Up today, many studies have been carried out to obtain colored zirconia in order to satisfy individual aesthetic requirements. The basic colour of 3Y-TZP is opaque or translucent, white to ivory and there are several studies and patents aimed to achieve zirconia ceramics with colour variations to be used in several application fields: decoration, dental, machinery, artificial jewellery, etc.

Colored zirconia-based ceramics have been traditionally produced by adding pigments [2], by graphite impregnation methods [3], by doping with various oxides, including aluminium oxide, manganese oxide, cobalt oxide, chromium oxide, nickel oxide, and ferric oxide [4, 5], by reduction heat treatments [6], etc., but the main drawback of this approach is that defects are frequently generated resulting in a drop in physical and mechanical properties, making impossible its use as structural material [7]. An example could be the recent efforts to develop colored zirconia for dental applications, where aesthetics is one of the most important properties [8, 9].

The aim of the present investigation is to produce a wide range of greyscale ceramics with enhanced functionality and reliability. This work reports on the design and characterization of a new family of zirconia – alumina – nanodiamond composites which have been processed following a non conventional route integrating two steps: 1) a colloidal method and 2) the traditional powder mixing homogenization.

In these composites, the introduction of alumina contributes to increasing the hardness and nanodiamond the critical element for generating the different color gradients of the materials. In this paper we have used the so-called ultrafine-dispersed diamonds (UDD) or detonation nanodiamonds (DND) [10]. It has been tested that small additions of nanodiamonds, in the range from 0,5 to 5 vol% can noticeably improve the structural properties of the final composites [11].

Experimental Procedure

The following raw materials were used as starting powders: i) TZ-3Y-E (Tosoh, Japan) with an average grain size of 40-70 nm and a specific surface area of 10.7 m²gr⁻¹, ii) and TM-DAR grade α-Al₂O₃ powder (Taimei Chemicals Co., Japan) with a specific surface area of 14.6 m²gr⁻¹ and an average grain size of 150 nm and iii) Ultrafine-dispersed diamonds (UDD) or detonation nanodiamonds (DND or nD) UDA-S type powders (Secna, Russia) with an average grain size of 10 nm.

In addition, the following chemical precursors were also used: i) aluminum chloride (Sigma-Aldrich, Spain), ii) zirconium IV-propoxide (70% solution in 1-propanol) (Sigma-Aldrich, Spain), and iii) 99.97% absolute ethanol (Panreac, Spain).

The processing route can be divided into four main steps:
1) As a first step, the 3Y-TZP powders were coated with an alumina amorphous layer, by using aluminum chloride as precursor and subsequently by using thermal treatment (900ºC/2h) in order to activate the formation of γ-alumina transition phase (Fig.1).

2) The second step consisted in coating α-alumina powders with zirconia nanoparticles by means of zirconium alcoxide as chemical precursor [12].

3) Finally (Fig.1), both chemically modified raw materials (A+B) were mixed using a ratio of 80/20 in volume, respectively, in a polypropylene container by using zirconia balls for 72 hours, in order to ensure a good homogeneity of the mixture.

4) Once the slurry was dried at 60ºC, this composition (A+B) was finally doped with several amounts of nanodiamonds (0.1, 0.3, 1, 3, and 5 vol. %) by following a mixing procedure with zirconia balls. Previously, the nanodiamonds were dispersed in an ultrasonic bath, Dr. Hielscher GmbH - type UIP1000, 8 A, 50/60 Hz.

The obtained powders were sintered by Pulsed Electrical Current Sintering (PECS) (FCT System GMBH, HPD25, Germany) using a graphite dye under vacuum (10^-2 mbar) at temperatures ranging from 1200 ºC to 1500 ºC. The temperature was measured by using an optical pyrometer focused on the upper part graphite punch, at about 5 mm from the sample, being 100 MPa and 3 min the applied pressure and dwell time, respectively. By this way disks of 20 mm diameter and about 3 mm height were obtained.

Materials density was measured according to the Archimedes method in deionized water. The microstructure was studied by using Field Emission Scanning Electron Microscopy (FESEM) (FEI: Quanta FEG 650). The flexural strength (3-point bending test) and fracture toughness were measured in an Instron 8562 testing machine, and the microhardness (Buehler Micronet 5103 equipment), was also evaluated. The flexural strength and the fracture toughness measurements (KIC) were tested by using six beams with 3 mm x 4 mm x 15 mm dimensions for each temperature. KIC measurements were performed using the single-edge-notched-beam technique (SENB) (a/w=0.4 and notch radius≈ 100 µm) in accordance with the guidelines described in the ASTM C1421 standard [13]. Indentation tests were carried out in Vickers indenter applying a load of 200 g with a dwell of 10 s on polished material surfaces, performing at least 30 indentations per sample.

The color of the discs was also analyzed by using a spectrophotometer apparatus (Konica Minolta CM-700d model), which is based on the CIE standard light source of D65 as a light source, with a measurement area of 8 mm. The surface finish of all samples was polished down to 1 micron with a sample thickness of 3 mm approximately. The final results were an average of four readings on each disc.

Reflectivity measurements were obtained using a MPV2 Combi Leitz microscope in reflected white light using oil immersion lenses (32x), 10x oculars. The reflectance determinations were performed on polished samples and oil immersion (n = 1.518) with monochromatic light of 548 nm, following the procedure described in the ISO standard 7404-5 (2009) for coals [14].

Raman spectroscopy was the technique employed in the study of nanocomposites after undergoing PECS. Raman spectra were obtained for the sintered samples in a LabRAM HR 800 Horiba Jobin Yvon spectrometer equipped with a CCD detector. A green laser (λ = 532 nm) was used as incident beam (2 µm in diameter) that was focused on the sample surface using an optical microscope (BXFM, from Olympus) coupled to the spectrometer. Spectra were collected after 20 s of exposure. A 1800 lines mm^-1 grating was used to split the inelastic radiation into high resolution spectra (0.3 cm^-1).
Results and discussion

Fig. 2 shows the greyscale palette obtained for the set of materials PECSed at different temperatures.

Fig. 2. Greyscale palette obtained for all compositions PECSed at different temperatures.

All sintered materials presented densities higher than > 99% th. The highest density values were obtained at sintering temperatures of 1400 and 1500 °C.

The Raman study shows that spectra obtained corresponding to sp² carbon materials were the dominant spectral in all cases. In Figure 3, the Raman spectrum of the composition of the composite with 5 vol% DND sintered at 1200 and 1500 °C is shown.

Fig. 3. Raman spectra of the composite with 5 vol% DND PECSed at 1200°C and 1500°C. The arrow shows the hump at 1150 cm⁻¹.

These spectra show peaks at wave numbers below 900 cm⁻¹ corresponding to vibrations of the crystalline zirconia-yttria network. The most intense bands occurred between 900 and 1800 cm⁻¹. These features, as well as the second order spectra recorded at-wave numbers higher than 2300 cm⁻¹, are characteristic of sp² carbon materials. The presence of a hump at 1150 cm⁻¹ in the spectrum of the materials PECSed at 1200°C (see arrow in Fig.3) could be assigned to the presence of sp³ structures coming from the starting nanodiamonds. This feature disappears when the processing temperature increases to 1500°C. A small, broad band at 1100 cm⁻¹ (see circle in Fig.3), which could be assigned to the occurrence of the so-called tetrahedral amorphous carbon (ta-C), is nevertheless perceptible in that spectrum, ta-C would be then an intermediate during the conversion of nanodiamonds into sp² carbon under both temperature and pressure.

The obtained values of flexural strength for all sintered compositions range from 400 MPa to 1600 MPa (Fig.4). The lowest values correspond to the composition of the composites without nanodiamond additions that were subsequently thermally treated at 1100°C/1h. It is well known that PECS introduce residual stresses at grain boundaries that inhibit crack growth, resulting in an improvement in the flexural strength [15]. It has been observed a general tendency to decrease the flexural strength values when the amount of nanodiamond is increased above 1% in volume.

The lowest fracture resistance values were obtained for the composite with 5% of nanodiamond, and the maximum values correspond to thermal treatments at 1400 and 1500°C that also corresponds with the highest density values.

Fig. 4. Flexural strength values of all compositions. W.T. (without thermal treatment), T (thermal treatment to 1100°C) of 0 vol% DND.

The fracture toughness values vary from 6.5 to 16 MPa.m¹/² (Fig.5) depending on the sintering temperature. For the composite without DND the maximum toughness corresponds with a sintering temperature of 1400°C and it seems that the fracture toughness it is not very much affect by a subsequent thermal treatment. It has been also observed that the presence of small amounts of nanodiamond (up to 3 vol%) does reduces the fracture toughness of the composites, but it is necessary to adjust the sintering
temperature to maintain the optimum conditions. At higher concentrations than 3 vol% a reduction in the mechanical properties has been observed. The composite without DND sintered at 1400°C is in any case the composition having the best values (17 MPa.m$^{1/2}$) followed by the composite with a 0,3 vol% sintered at 1500°C (15,5 MPa.m$^{1/2}$). In all cases, when the samples are subjected to annealing at 1100°C for 1 hour a decrease in the mechanical properties both toughness and fracture resistance has been observed.

The measured Vickers hardness values are exposed at Figure 6. The maximum values are obtained for the composition with 0,3 vol% DND and are 16,17 GPa and 16,04 GPa corresponding to sintering temperatures of 1400 and 1500 °C respectively. The lower microhardness values correspond to compositions with 5 vol% DND.

Figure 7 shows the maximum reflectance values (7-5%) corresponding to nanocomposites with 0% vol DND and decrease gradually to 1.72% for the case of the composition with 5 vol% nD sintered at 1500 °C.

According to the colorimetric data of the specimens, the white index L* varies from 98 for 0 vol. % DND to 40 for 5 vol.% DND, respectively.

Figure 8 and Figure 9 show the microstructure corresponding to the studied composites with 0,3 vol% DND and 5 vol% DND sintered at 1500°C.

The grain size decreases when the amount of nanodiamond is increased (see Figures 8 and 9). Also it has been noticed than the grain size of the
composites gradually increases with the sintering temperature.

Fig.9. FESEM (electron backscattered) microstructure image corresponding to the composite with 5 vol% DND sintered at 1500°C. (White color: zirconia. Grey: alumina. Black: DND).

Conclusions

3Y-TZP-alumina-nanodiamond composites can be considered as a new family of materials with high toughness and bending strength, presenting a large variety of metalized colors (white index L° 98 to 40), that can be used in the gemology industry, among other applications where coloured ceramics are needed. The introduction of nanodiamond in the preparation of the materials allows to produce composites with continuous and wide variability of gray shades, from light colors to almost black. The mechanical behavior of these nanocomposites is very similar up to a maximum amount of DND of 0.3 vol% decreasing slightly above this content.

Acknowledgements

The authors would like to express their gratitude to Prof. S.Perfilov (Technological Institute for Superhard and Novel Carbon Materials - TISNCM, Troitsk, Moscow reg. 142190, Russia) for supplying the DND used in this work, and I. Suárez- Ruiz and J. R. Montes (Instituto Nacional del Carbón, INCAR-CSIC) for their support with the reflectivity measurements. This work has been supported by the Spanish Ministry of Economy and Competitiveness and the European Development Research Fund (ERDF) under the MAT2012-38645 project.

References
