doi:10.1017/S1431927614014342
Microsc. Microanal. 21 (Suppl 6), 2015

Multiwall Carbon Nanotubes / Porcelain Stoneware Composites: a view under the microscope

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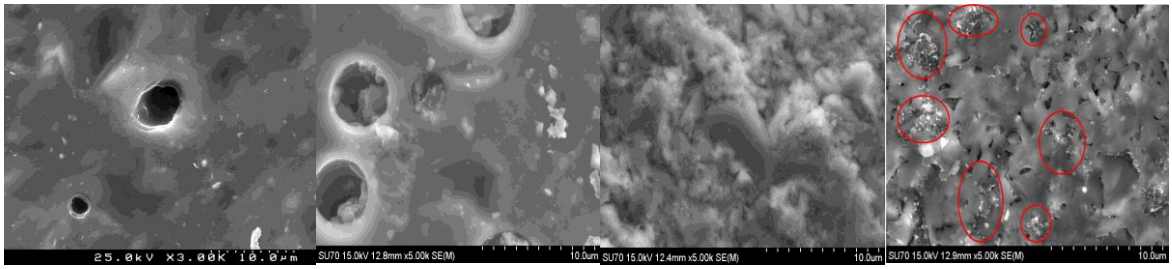
Porcelain tiles also known as porcelain stoneware are light-colored ceramic widely used in floors and walls in both internal and external environments. They are produced from a triaxial composition of clay (rich in kaolinite), quartz and feldspar [1]. Sintered tiles (in a fast fire for 40-60 min, at 1180-1220 ^{o}C) are composed of vitreous and crystalline phases (mainly quartz and mullite). Currently, there is a need to minimize the thickness of porcelain stoneware between 3 to 5.5 mm. However, as the thickness is reduced mechanical properties become a limiting property. Thus additives are usually needed to improve the mechanical strength and fracture toughness of the thinner tiles. Carbon Nanotubes (CNTs) are known to be one of the strongest materials in nature (Young's modulus of 270 – 950 GPa and tensile strength of 11 - 63 GPa), because of that, CNTs have been used in reinforcement applications. Nevertheless the restricted thermal stability of CNTs under air or oxidizing atmospheres may limit their application [2]. Aiming to improve tiles mechanical properties, in this work Multiwall Carbon Nanotubes (MWCNTs) / porcelain stoneware composites are prepared and the microstructure of the obtained materials systematically studied by Scanning Electron Microscopy (SEM –Hitachi SU70). No studies have been reported before on the use of CNTs as additives for porcelain stoneware.

Purified MWCNTs having diameter and length around 10-35 nm and ~10 μm, respectively were used. The MWCNTs tubes (1 wt %) were mixed in the slurry of the porcelain paste by high ultra-sonication to guarantee a uniform dispersion. After drying and pressing, the compacts were sintered in air and nitrogen atmospheres. For comparison purposes samples were prepared with and without CNTs. XRD of composites sinter in air shows the formation of mullite phase, whereas when sintered in nitrogen no mullite phase was observed for samples with and without CNTs. SEM microstructures of the ceramics sintered in air and nitrogen are shown in Fig. 1. The porcelain stoneware sintered in air shows dense microstructure (2.28 g/cm^3) with some residual porosity (Fig. 1 (a)), whereas when sintering in nitrogen the ceramic almost did not densify (1.82 g/cm^3) (Fig. 1 (c)). In the case of the composites (with MWCNTS) after sintering in air (Fig. 1 (b)) dense microstructure (2.11 g/cm^3) where obtained through with a slight increase in the porosity when compared to the previous; this effect might be related to the oxidation of MWCNTs. Differently the composites sintered in nitrogen keep MWCNTs intact and uniformly distributed inside the porcelain (marked in red circle Fig. 1(d)) and show dense microstructures (2.08 g/cm^3). Fig. 2 (a) shows a magnified view of the composite sintered in nitrogen and the EDS mapping shows the distribution of all the elements in the porcelain stoneware (Fig 2 (b)). Fig. 2(c) illustrates, how MWCNTs bridge crack development during mechanical test. It can be concluded from above microscopy study that MWCNTs can be an effective additive for porcelain stoneware, though the need of a reducing atmosphere may be a concern for the industry. This aspect is under further investigation.

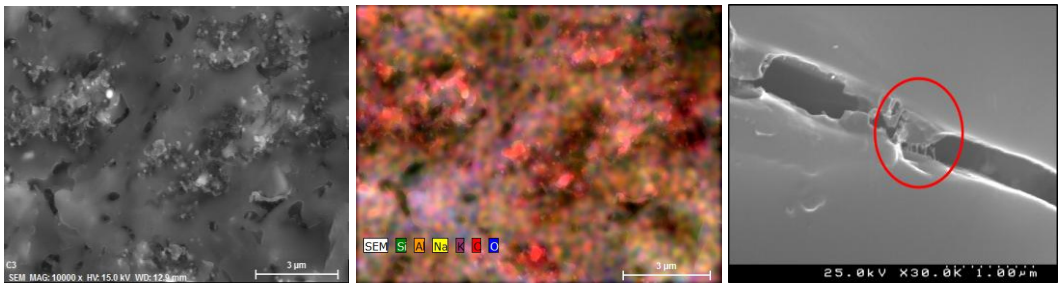
The authors acknowledge FEDER, QREN, COMPETE, CICECO and FCT. Amit Mahajan acknowledges FCT the financial support (SFRH/BD/65415/2009).

[1] Sánchez, E., *et al*., *Ceramics International*, **36**, 831-845, 2010.
[2] Mahajan, A., *et al*., *Materials Letters*, **90**, 165-168, 2013.



(a) (b) (c) (d)

Fig 1.SEM micrographs of porcelain stoneware (a) and MWCNTs/porcelain stoneware composites (b) sintered in air and porcelain stoneware (c) and MWCNTs/porcelain stoneware composites (d) sintered in nitrogen at 1200 ^{0}C, where the red circles indicates the presence of MWCNTs in the matrix.



(a) (b) (c)

Fig. 2 (a) SEM micrographs and correspondent (b) EDS mapping of MWCNTs/porcelain stoneware composites. The EDS map shows a uniform chemical distribution of all the elements in the sample, sintered in nitrogen at 1200 ^{0}C. (c) MWCNTs bridging the crack occurred in MWCNTs/porcelain stoneware composite during mechanical characterization, marked by red circle.

https://doi.org/10.1017/S1431927614014342 Published online by Cambridge University Press