



Nano-oxides to improve the surface properties of ceramic tiles

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The aim of the present work is to realise ceramic tiles with superior surface mechanical characteristics and chemical resistance, by the addition of nano-oxides, such as zirconia and alumina, since such advanced ceramics oxides are well known for their excellent mechanical properties and good resistance to chemical etching. In order to avoid any dangerousness, the nanoparticles were used in form of aqueous suspension and they were sprayed, by airbrush, directly onto the dried ceramic support, before firing.

To observe the distribution of the nanoparticles and to optimise the surface treatment, SEM-EDS analyses were carried out on the fired samples. XRD analysis was conducted to assess the phases evolution of the different materials during the firing step. The surface mechanical characteristics of the samples have been evaluated by Vickers' hardness and scratch test. In addition, also chemical resistance tests were performed.

Microstructural observations allowed to understand how alumina and zirconia nanoparticles acted to improve the surface performances of the modified ceramic tiles.

Keywords: ceramic tiles, nanoparticle oxides, microstructure, mechanical properties.

Nanoóxidos para mejorar las propiedades superficiales de revestimientos cerámicos

La finalidad de este trabajo es la de realizar baldosas con mejores características mecánicas superficiales, al incorporar óxidos de partículas nanométricas, como la circonia y la alúmina, ya que se sabe que estos óxidos confieren unas propiedades mecánicas excelentes además de una buena resistencia al ataque químico. Para evitar cualquier peligro, las partículas nanométricas se usaron en forma de suspensión acuosa y se pulverizaron, por medio de un aerógrafo, directamente sobre el soporte cerámico seco, antes de la cocción.

Para observar la distribución de las partículas nanométricas y para optimizar el tratamiento de la superficie, se realizó un análisis por MEB-EDS sobre las muestras cocidas. Se llevó a cabo un análisis de difracción de rayos X (DRX) para evaluar la evolución de las fases de los distintos materiales durante la fase de cocción. Las características mecánicas de la superficie de las muestras han sido evaluadas por el ensayo de resistencia al rayado y de dureza Vickers. Además, también se llevaron a cabo ensayos de resistencia química.

Las observaciones microestructurales han permitido entender cómo actuaron las partículas nanométricas de alúmina y circonia para mejorar las prestaciones superficiales de las baldosas cerámicas modificadas.

Palabras clave: partículas nanométricas de óxidos, microestructura, propiedades mecánicas

1. INTRODUCTION

Nowadays, nanopowders are of extreme interest in many fields of application for their peculiar physical and chemical properties, essentially given by their dimensions [1,2,3]. In material science, nanostructured functionalised coatings are generally obtained by using quite complex and expensive methodologies, such as sol-gel, physical or chemical vapour depositions. In addition, the risk for the human health, mainly related to the inhalation and skin contact with the nanoparticles, can not be neglected, being object of a still open debate [4,5].

The peculiar characteristics of nano-sized materials, in particular enhanced chemical reactivity, might be exploited to develop silicatic based ceramics with new working surface, characterised by superior properties. Even if many works have been published regarding the improvement of the mechanical-physical properties of porcelain stoneware material, which

represent till now the best product among all the typologies of ceramic tiles [6,7,8], there is an increasing interest in the development of porcelain stoneware tiles with functionalised surfaces. The use of nanotechnology could results rather interesting and able to solve these requirements. In example, titania nanoparticles has been used to develop functionalised ceramic tiles with self-cleaning and photocatalytic surfaces [9,10]. The presence of nanomaterials, by improving their surface properties, should be able to give to ceramic tiles a higher added value, further broadening their application spectrum.

In the present work, porcelain stoneware tile samples, with superior surface mechanical characteristics and chemical resistance, were obtained by the use of nanoparticles oxides of zirconia and alumina. These oxides have been chosen for their excellent chemical and wear resistance and high hardness.

To avoid any dangerousness, the starting nanoparticles were in form of aqueous suspension and they were applied onto the green ceramic body by spraying with an airbrush. The use of the air-brushing system, even if it does not promote a continuous surface coating, should favour the penetration of the nanoparticles through the green material, favouring the interaction with the ceramic body during the firing step.

2. EXPERIMENTAL

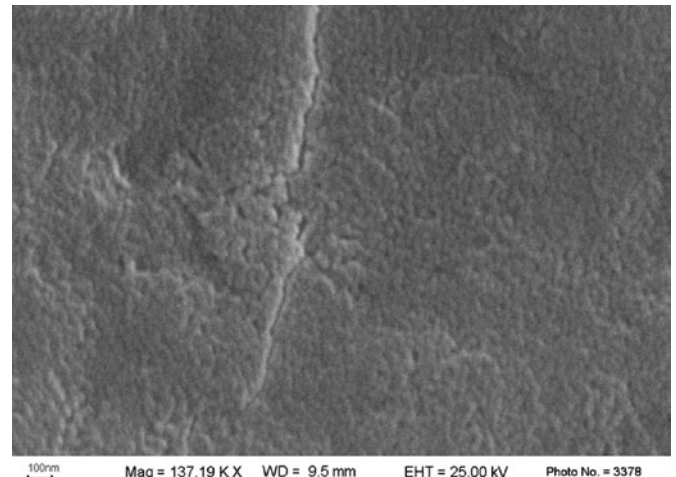
Two nano-suspensions of alumina and zirconia, denoted A and Z (Ce.Ri.Col., Colorobbia, I), respectively, were selected for the present work. In order to identify their mineralogical phases, the suspensions were dried at 110°C and the powder were analysed by a diffractometer (PANalytical, PW3830, NL), in the angular range 10-60 °2θ, with steps of 0.02° and 1 s/step. The characteristics of the nano-suspensions are reported in Table 1.

An industrial porcelain stoneware mix, denoted P, was selected as ceramic support. The chemical and mineralogical composition of the mix, determined by inductively coupled plasma optical emission spectroscopy (ICP-OES Optima 3200 XL, Perkin-Elmer, USA) and X-ray diffraction analyses (PANalytical, PW3830, NL), is reported in Table 2.

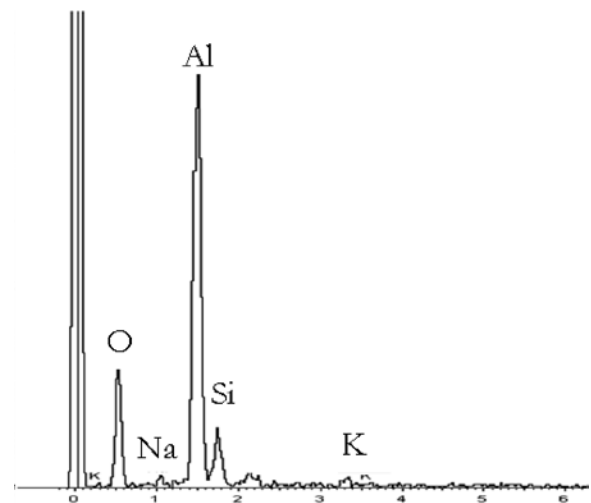
The mixed raw materials were wet milled, with 33 wt% of water and 0.6 wt% of dispersant (Fluicer CF907, Zschimmer & Schwarz Group, D), in porcelain jar with alumina media, for 1h. The particles size distribution of the slurry, determined by using a laser particle size analyser (MASTERSIZER 2000, Malvern, UK), is characterised by values of d_{10} , d_{50} and d_{90} of 1.5, 6.4 and 22.3 μm, respectively. The suspension was dried for 24h at 110°C and the obtained cake was crushed and sieved at 125 μm.

The specimens, in form of disk of about 40 mm in diameter, were prepared by adding to the dried powder, 6 wt% of water and uniaxial pressing at 52 MPa.

The nanosuspensions, A and Z, were sprayed directly on the green ceramic specimens, after drying at 60°C, by airbrush, with a pressure of 0.2 MPa and a distance of about 20 cm from



a)



b)

Figure 1 - SEM micrograph of the surface of AP sample (a) and corresponding EDS spectrum (b).

TABLE 1 – PHYSICAL AND MINERALOGICAL CHARACTERISTICS OF THE NANO-SUSPENSIONS.

Nano-suspension	Oxide	Dispersant	Concentration, wt%	Average dimension, nm	Mineralogical phases
A	Al ₂ O ₃	water	1	70	gibbsite amorphous alumina
Z	ZrO ₂	water	4	80	amorphous zirconia

TABLE 2 - CHEMICAL (OXIDES wt%) AND MINERALOGICAL COMPOSITION OF THE PORCELAIN STONWARE MIX.

SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	L.O.I.	Mineralogical phases
72.36	17.15	0.48	0.49	0.68	0.25	1.85	3.53	3.19	Quartz Albite Sanidine Kaolin Illite

the specimen surface. On the surface of each specimen, of 13 cm² area, about 1 g of nano-suspension was applied, in four steps, by rotating each time the specimen of 90°. The ceramic samples with the nanosuspensions A and Z were denoted AP and ZP, respectively.

The sintering of all the samples was performed in a laboratory electric muffled furnace, at the maximum temperature of 1180°C, with a heating rate of 5°C/min, 5 min of soaking time and natural cooling to room temperature.

The fired samples were characterized on the basis of their linear shrinkage and water absorption, following the Standard EN ISO 10545-3 [11].

The surface microstructure of the samples was studied with a SEM (EVO 40, ZEISS, D) equipped with an EDS system (Inca, Oxford Instruments, UK). In order to qualitatively examine the crystalline phases developed on the ceramic surfaces, with and without the nano-particles, X-ray diffraction analyses were carried out, in the angular range 5-60 °2θ, with steps of 0.02° and 1 s/step.

Micro-hardness tests (Zwick, 3212, D) were performed on the as fired surfaces, at the indentation loads of 0.49 and 1.96 N, at least seven measurements were performed for each indentation load.

A scratch tester (Open Platform, CSM Instruments SA, CH), equipped with a Rockwell diamond indenter, 200 μm in diameter, was used to produce micro-scratches, of 2 mm in length, on the surfaces of the specimens. The tests were performed with a progressively increasing load from 1N till 30 N with a loading rate of 14.5 N/min.

The chemical resistance of the ceramic surfaces was evaluated by using a basic solution, KOH solution (20 g/l). A glass cylinder, 10 mm in diameter and 2 mm high, was made adhering to the sample surface, by using a sealed material, and it was filled with the basic solution. After 7 days the solution was removed. Microstructural observations of the samples before and after the chemical etching were performed with the aid of a scanning electron microscope.

3. RESULTS AND DISCUSSION

The presence of the nano-oxides layer has not changed the linear shrinkage and water absorption values, which were the same, 8.5% and 0.01wt.%, respectively, in all the fired samples, P, AP and ZP.

The morphological analysis carried out on the surfaces of the samples AP, Fig. 1a, and ZP, Fig. 2a, allowed to recognise

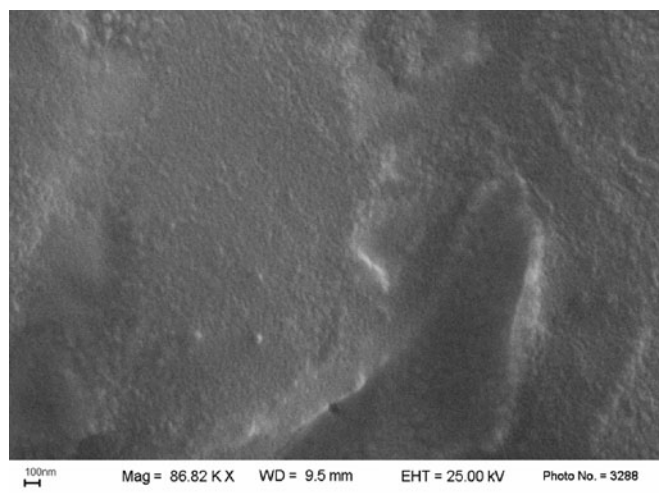
TABLE 3 - SURFACE MINERALOGICAL COMPOSITION OF THE FIRED SAMPLES.

Sample	Mineralogical phases
P	Quartz, Mullite, Plagioclase
AP	Quartz, Mullite, Plagioclase, α-alumina
ZP	Quartz, Mullite, Plagioclase, t-zirconia

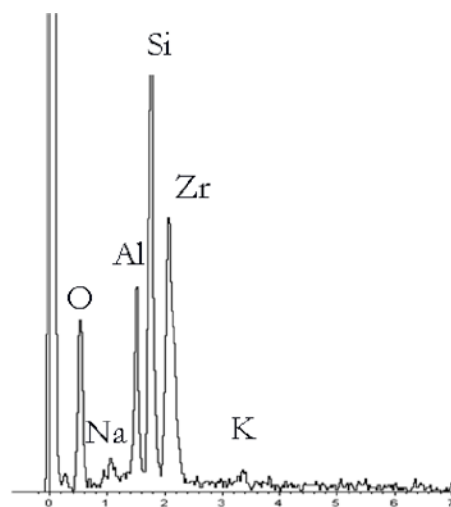
the presence of nano-sized grains of alumina and zirconia, as revealed by the EDS spectrum, Figs. 1b and 2b, respectively, which dimensions are not significantly different from the ones of the nano-particles present in the starting suspensions A and Z. These nanostructures cover, in a rather homogeneous way, all the ceramic surface of the substrate.

The mineralogical composition of the differently treated surfaces is reported in Table 3.

The adopted sintering conditions allowed the complete crystallisation of the starting oxides particles. For the A nano-suspension, gibbsite (Al(OH)₃) and amorphous alumina were transformed in α-alumina, for the Z nano-suspension, amorphous zirconia was crystallised in its tetragonal phase. It is to underline that even if without any stabilizing oxide, only the tetragonal phase, metastable at room temperature, is present. The maximum temperature, reached during the firing step, did not allow a growth of the zirconia grains till the critical dimension for the tetragonal to monoclinic phase transformation [12,13,14]. In this way, the tetragonal retention is maximised and it is positively available to increase the mechanical performances by stress induced phase transformation.



a)



b)

Figure 2 - SEM micrograph of the surface of ZP sample (a) and corresponding EDS spectrum (b).

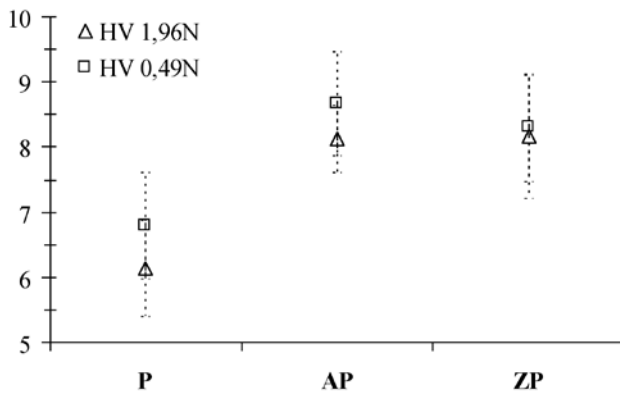


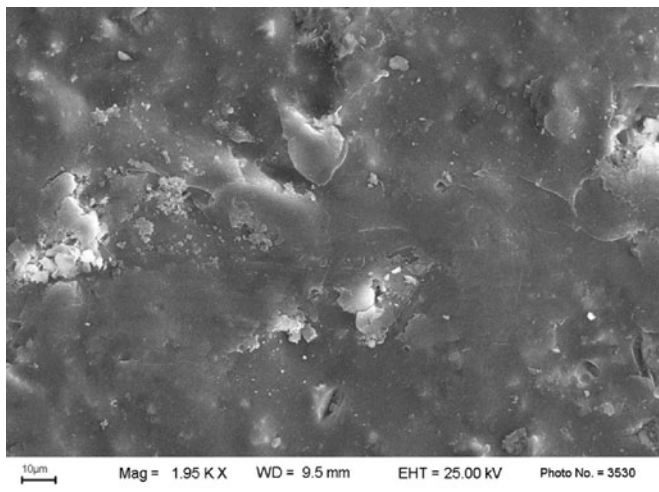
Figure 3 – Vickers' Hardness of the samples.

The results of the mechanical characterisation of the surfaces, in terms of Vickers' hardness, are reported in Fig. 3. Due to the contribution of the alumina and zirconia nano-structured layers, in both the samples, AP and ZP, the micro hardness significantly increases. The increase of the micro hardness values, when the applied load decreases, is due to the "indentation size effect" (ISE) [15].

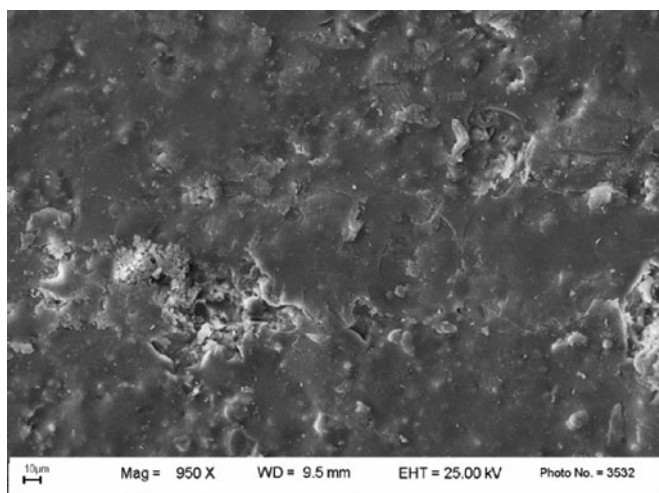
The microstructural observations of the scratches allowed to underline the different behaviour presented by P, AP and ZP samples.

Sample P shows a brittle behaviour typical of ceramic material. Already at the beginning of the scratch run, the surface asperities in contact with the indenter break and the so formed debris are compacted and smeared onto the ceramic surface, Fig. 4a. P is also the only sample for which a critical load [16] was reached, with a L_{Cl} value of 14N. That is revealed by Figure 4b, where the complete hertzian cracks on the scratch scar are clearly visible.

The presence of the nano-structured layers, in AP and ZP, strongly changes the scratch resistance, by increasing it,

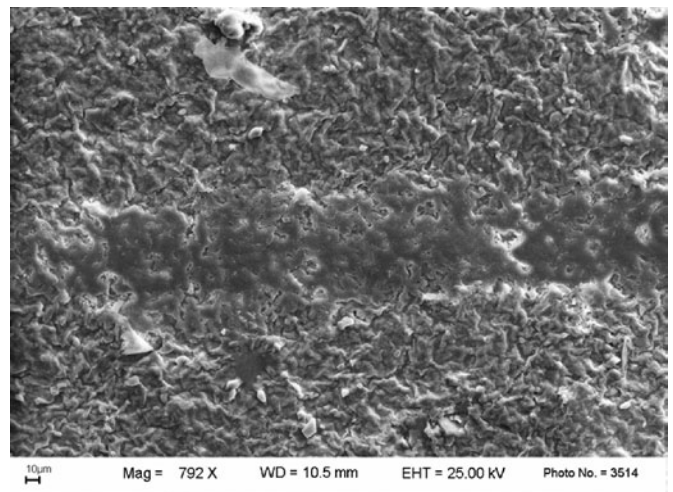


a)

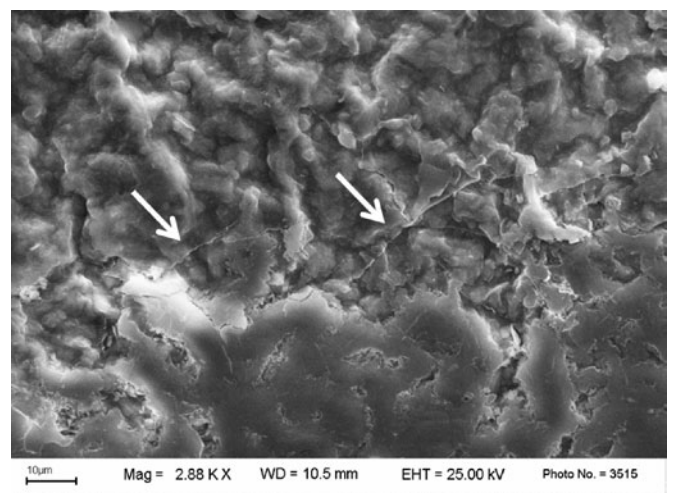


b)

Figure 4 - SEM micrographs of the scratch in P sample: (a) deformed debris at the beginning of the scratch run, and (b) the hertzian cracks at LC1 position.



a)



b)

Figure 5 - AP sample, SEM micrographs of (a) the end of the scratch and (b) a magnification of (a) in which cracks emerging from the scratch scar are arrowed.

and the scar morphology. In both the samples, the scratches present surfaces smoother than the original ones, Figs. 5 and 6. The materials appear to be strongly deformed and, only in their final parts, some cracks, emerging from the external of the scratch scars, are visible (Figs. 5b and 6b). The cracks, in any case, have not enough energy to branch and to cause the formation of herztian cracks. This behaviour is in agreement with the nanometric dimension of the oxides grains, forming the surface layer; it is well known in fact as the reduced grain dimension favours high level of plastic deformation in comparison with the same micrometric material [17].

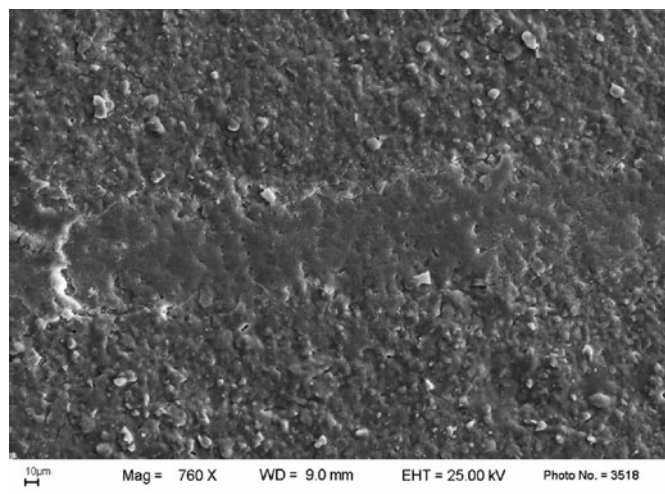
The SEM observation of the surface of the samples after the basic chemical etching showed as, for such kind of silicate based materials, the corrosion begins with the de-polymerisation of the glassy phase. It is known as silicate glasses, that generally resist to water and acid attack, are susceptible to strong alkaline solution, due to the presence of OH⁻ ions able to break the silica-oxygen link, destroying the silicate network [18]. According to this mechanism, the surface of P sample, after the basic etching, presents a large

dissolution of the glassy phase that reveals the presence of the mullite crystals, Fig. 7, much more resistant to alkaline environment [19,20]. The same phenomenon is active for the surface treated samples, but the presence of alumina and zirconia, by covering in a rather homogeneous way the silicate surface, prevents the corrosion of the glassy phase. Only very narrow area, interested by the basic corrosion, were detected, Fig. 8.

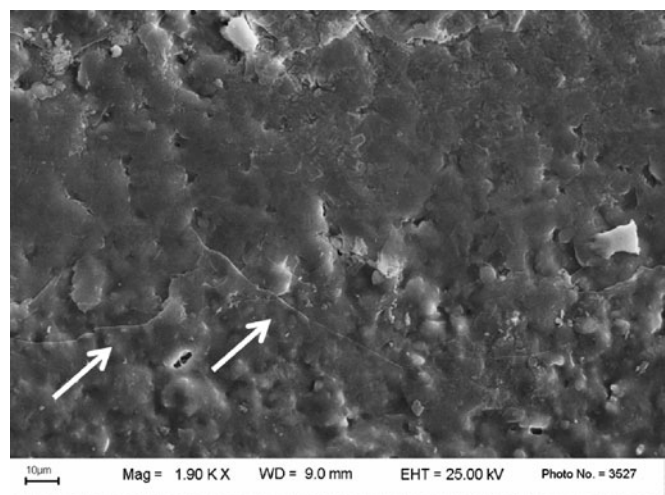
4. CONCLUSION

In the present work, the possibility, to functionalise the surface of porcelain stoneware materials with nano-oxides layers, has been successfully tested. The presence of nano-oxides improves the surface characteristics of porcelain stoneware, in terms of hardness and scratch resistance. Also the chemical resistance in basic environment is improved.

The nano-oxides layer, by covering in a homogeneous way the ceramic surfaces, showed a good interaction with the

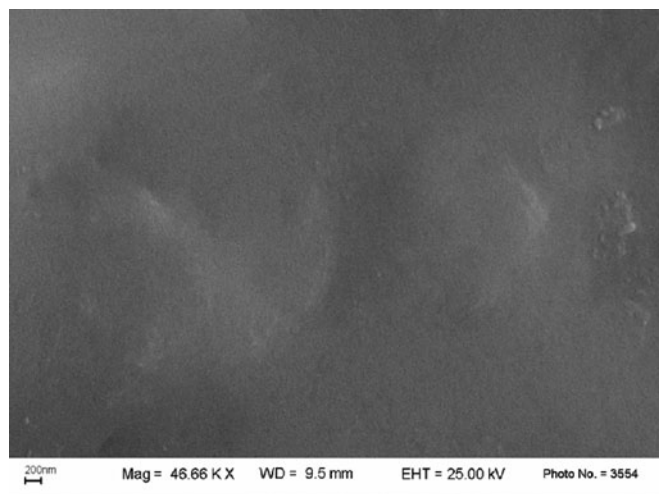


a)

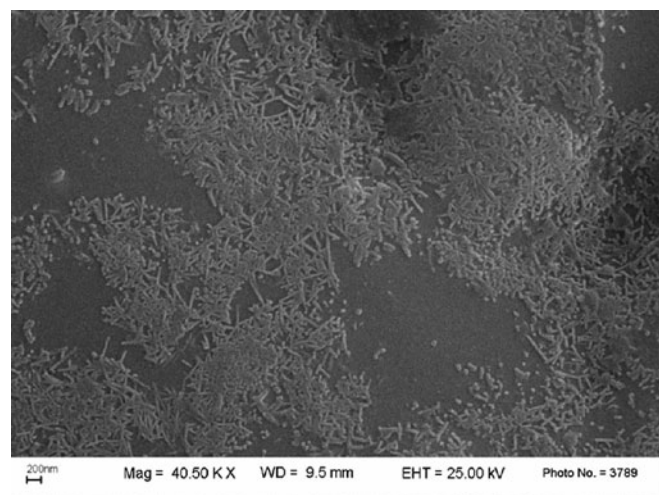


b)

Figure 6 - ZP sample, SEM micrographs of (a) the end of the scratch and (b) a magnification of (a) in which cracks emerging from the scratch scar are arrowed.



a)



b)

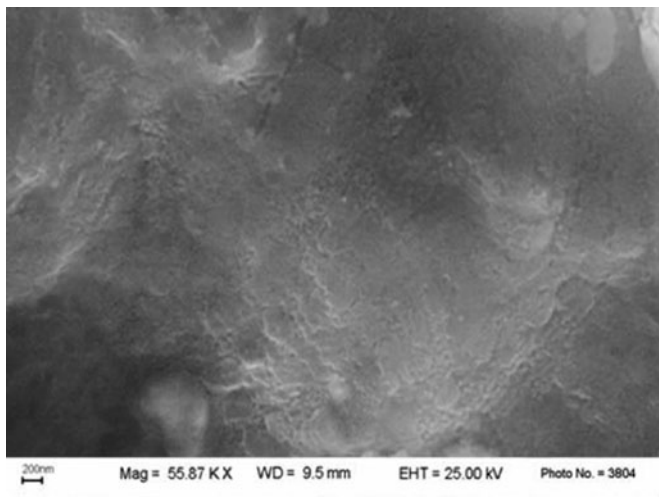
Figure 7 - SEM micrographs of P sample before (a) and after (b) the chemical etching, the elongated crystals are mullite.

substrate that is responsible of the positive obtained results. The combined use of the nano-suspension and air-brushing, to functionalise the ceramic surfaces, resulted to be strictly compatible within the traditional ceramic processes.

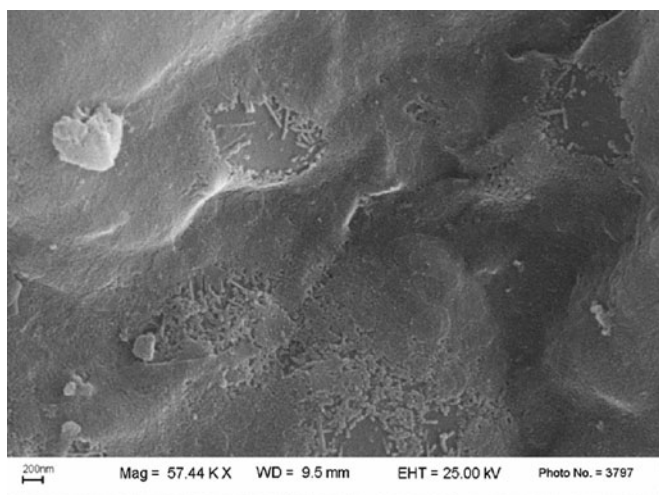
Further works, such as assessment of the penetration level of the oxides, influence of the concentration of the nano-suspension and quantitative evaluation of the chemical etching, are in progress.

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a)



b)

Figure 8 - SEM micrographs of AP sample before (a) and after (b) the chemical etching, the elongated crystals are mullite.

REFERENCES

1. H. Gleiter, Nanostructured materials: state of the art and perspectives, *Nanostructured Materials*, 6, 22-36, 1995.
2. P. Moriarty, Nanostructured materials, *Reports on Progress in Physics*, 65, 287-381, 2001.
3. K.P. Jayadevan, T.Y. Tseng, Oxide Nanoparticles, *Encyclopedia of Nanomaterials*, 8, 333-376, 2004.
4. A. Maynard, D. Rejeski, Too small to overlook, *Nature*, 460, 174, 2009.
5. V. Murashov, J. Howard, Essential features for proactive risk management, *Nature Nanotechnology*, 4, 467-470, 2009.
6. C. Leonelli, F. Bondioli, P. Veronesi, M. Romagnoli, T. Manfredini, G.C. Pellacani, V. Cannillo, Enhancing the mechanical properties of porcelain stoneware tiles: a microstructural approach, *Journal of the European Ceramic Society*, 21, 785-793, 2001.
7. M. Dondi, G. Ercolani, G. Guarini, C. Melandri, M. Raimondo, E. Rocha e Almendra, P.M. Tenorio Cavalcante, The role of surface microstructure on the resistance to stains of porcelain stoneware tiles, *Journal of the European Ceramic Society*, 25, 357-365, 2005.
8. A. Tucci, L. Esposito, L. Malmusi, E. Rambaldi, New body mixes for porcelain stoneware tiles with improved mechanical characteristics, *Journal of the European Ceramic Society*, 27, 1875-1888, 2007.
9. F. Bondioli, R. Taurino, A.M. Ferrari, Functionalisation of ceramic tile surface by sol-gel technique, *Journal of Colloidal Interface Science*, 334, 195-201, 2009.
10. P. São Marcos, J. Marto, T. Trindade, J.A. Labrincha, Screen-printing of TiO₂ photocatalytic layers on glazed ceramic tiles, *Journal of Photochemistry and Photobiology A: Chemistry*, 197, 125-131, 2008.
11. EN ISO 10545-3: Ceramic tiles – Definition, classification, characteristics and marking, 1998.
12. R.C. Garvie, The occurrence of metastable tetragonal zirconia as crystallite size effect, *Journal of Physical Chemistry*, 69, 1238, 1965.
13. R. Srinivasan, L. Rice, B.H. Davis, Critical particle size and phase transformation in zirconia: transmission electron microscopy and X-ray diffraction studies, *Journal of the American Ceramic Society*, 73, 3528-3530, 1990.
14. S. Scholz, S. Kaskel, Surface functionalization of ZrO₂ nanocrystallites for the integration into acrylate nanocomposite films, *Journal of Colloid and Interface Science*, 323, 84-91, 2008.
15. J. Gong, J. Wu, Z. Guan, Examination of the Indentation Size Effect in Low-load Vickers Hardness Testing of Ceramics, *Journal of the European Ceramic Society*, 1999, 19, 2625-2631.
16. ISO 20502, Fine ceramic (advanced ceramics, advanced technical ceramics) – Determination of adhesion of ceramic coatings by scratch testing, 2005.
17. A.J.A. Winnubst, M.M.R. Boutz, Y.J. He, A.J. Burggraaf, H. Verweij, Plasticity of Nanocrystalline Zirconia Ceramics and Composites, *Ceramics International*, 23, 215-221, 1997.
18. R. Eppler, D. Eppler, Glazes and Glass Coatings, *American Ceramic Society, Ohio*, 2000.
19. L. Fröberg, T. Kronberg, S. Törnblom, L. Hupa, Chemical durability of glazed surfaces, *Journal of the European Ceramic Society*, 27, 1811-1816, 2007.
20. V. Cannillo, L. Esposito, E. Rambaldi, A. Sola, A. Tucci, Microstructural and mechanical changes by chemical ageing of glazed ceramic surfaces, *Journal of the European Ceramic Society*, 29, 1561-1569, 2009.

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