EFFECTS OF NANO-OXIDES ON THE SURFACE PROPERTIES OF CERAMIC TILES

E. Rambaldi, A. Tucci, L. Esposito, D. Naldi, G. Timellini

Centro Ceramico Bologna, Italy

ABSTRACT

The aim of the present work is to obtain 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 attack. 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 phase 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, chemical resistance tests were also performed.

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

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, this being the 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 represents till now the best product among all the types 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 nanoparticle 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.

Nano-suspension	Oxide	Dispersant	Concentration, wt%	Average dimension, nm	Mineralogical phases
A	Al_2O_3	water	1	70	gibbsite amorphous alumina
Z	ZrO_2	water	4	80	amorphous zirconia

Table 1. Physical and mineralogical characteristics of the nano-suspensions.

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.

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	ppc	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

Table 2. Chemical (oxides wt%) and mineralogical composition of the porcelain stoneware mix.

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 the specimen surface. On the surface of each specimen, of 13 cm^2 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.

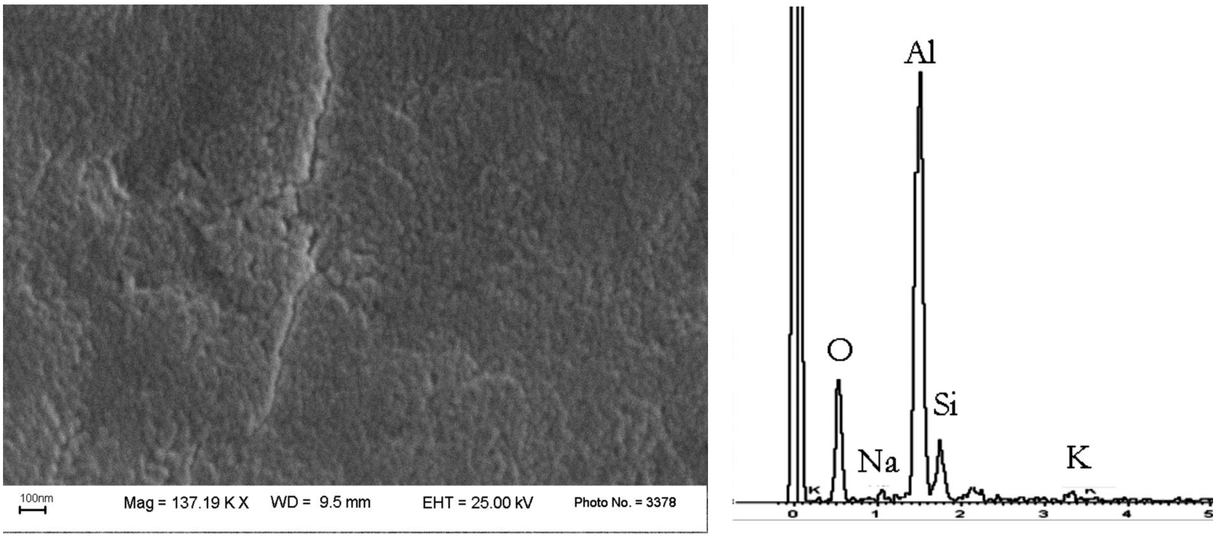
A scratch tester (Open Platform, CSM Instruments SA, CH), equipped with a Rockwell diamond indenter, 200 µm in diameter, was used to produce micro-scratches, of 2 mm in length, on the surfaces of the specimens. The tests were performed with a progressively increasing load from 1N till 30 N with a loading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

3. RESULTS AND DISCUSSION

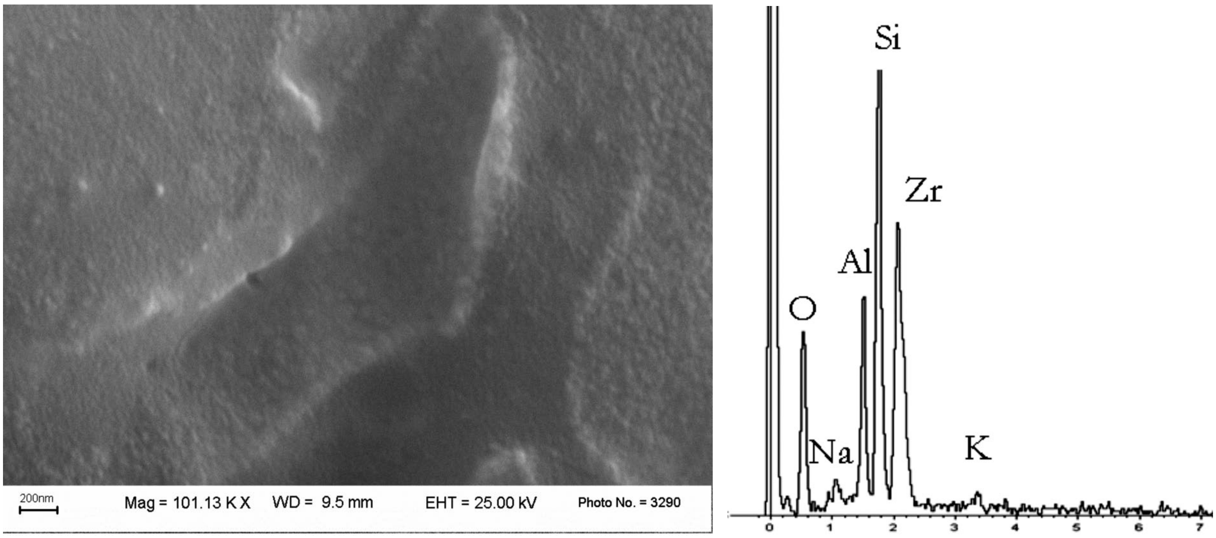
The presence of the nano-oxide layer has not changed the linear shrinkage and water absorption values, which were the same, 8.5% and 0.01 wt%, respectively, in all the fired samples, P, AP and ZP.

The morphological analysis carried out on the surfaces of the samples AP, figure 1a, and ZP, figure 2a, allowed to recognise the presence of nano-sized grains of alumina and zirconia, as revealed by the EDS spectrum, figures 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.



a) b)

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



a) b)

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

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 may be noted that, even 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.

The results of the mechanical characterisation of the surfaces, in terms of Vickers' hardness, are reported in figure 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].

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

Table 3. Surface mineralogical composition of the fired samples.

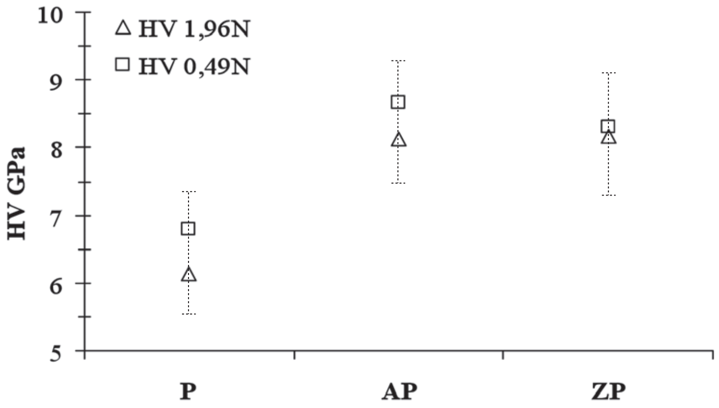
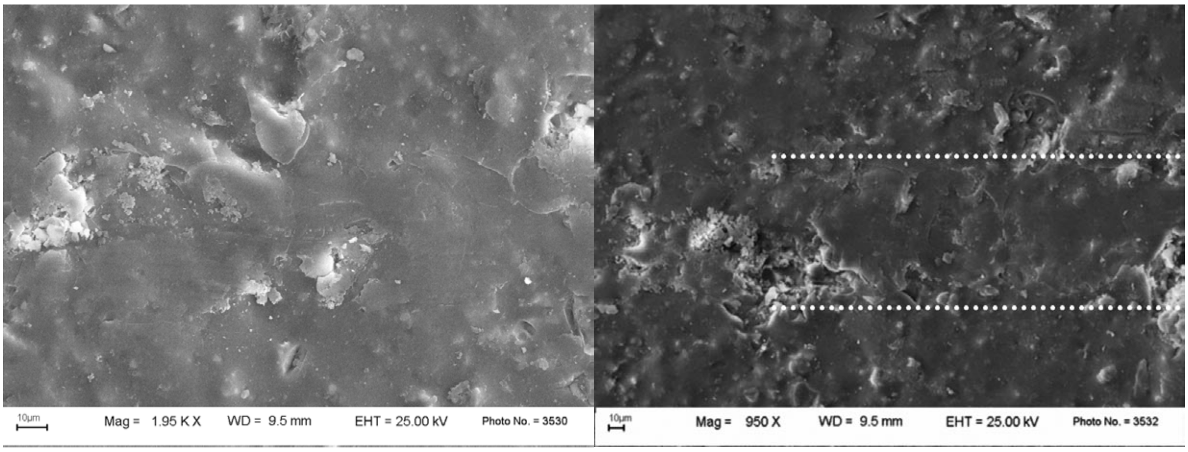


Figure 3. Vickers' hardness of the samples.

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

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, figure 4a. P is also the only sample for which a critical load [16] was reached, with a L_{C1} 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, and the scar morphology. In both the samples, the scratches present surfaces smoother than the original ones, figures 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 (figures 5b and 6b). The cracks, in any case, have not enough energy to branch and to cause the formation of Hertzian cracks. This behaviour is in agreement with the nanometric dimension of the oxide grains, forming the surface layer; it is well known in fact that the reduced grain dimension favours a high level of plastic deformation in comparison with the same micrometric material [17].



a) b)

Figure 4. SEM micrographs of the scratch in sample P: (a) deformed debris at the beginning of the scratch run, and (b) the Hertzian cracks at L_{C1} *position.*

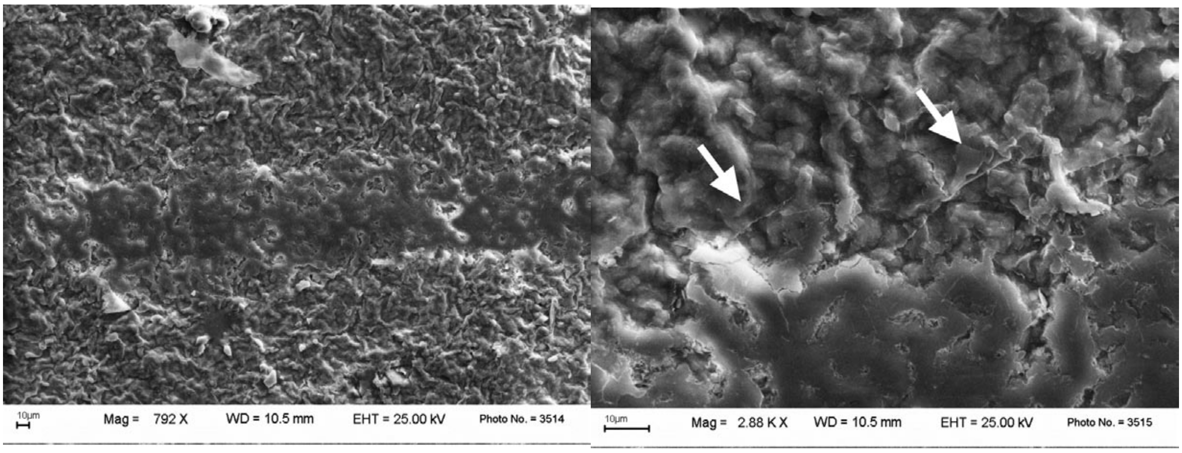
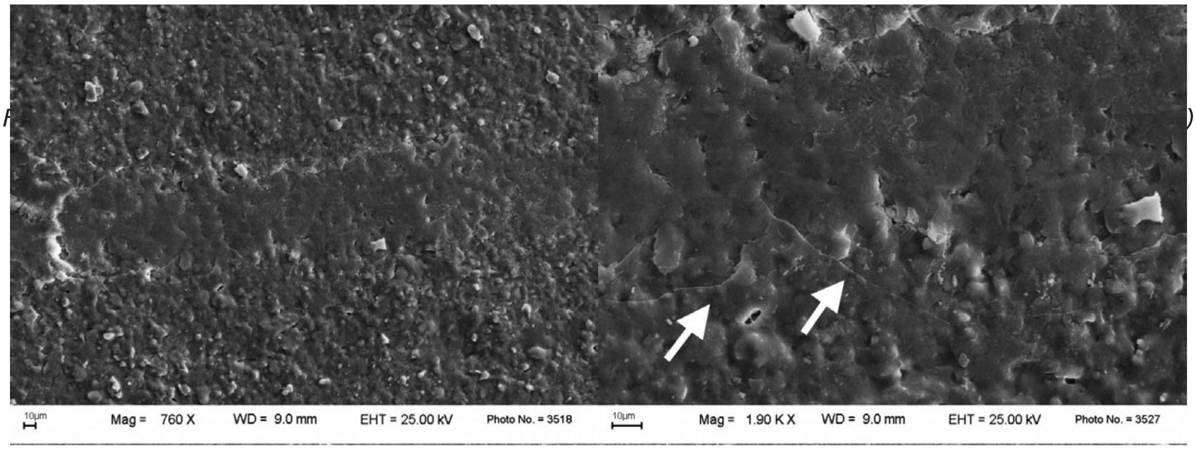


Figure 5. AP sample, SEM micrographs of (a) the end of the scratch and (b) a magnification of (a) in which cracks emerging from the scratch scar are arrowed.



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.

The SEM observation of the surface of the samples after the basic chemical attack showed that, for such types of silicate-based materials, corrosion begins with the de-polymerisation of the glassy phase. It is known that 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 attack, presents a large dissolution of the glassy phase that reveals the presence of the mullite crystals, figure 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 areas, affected by the basic corrosion, were detected, figure 8.

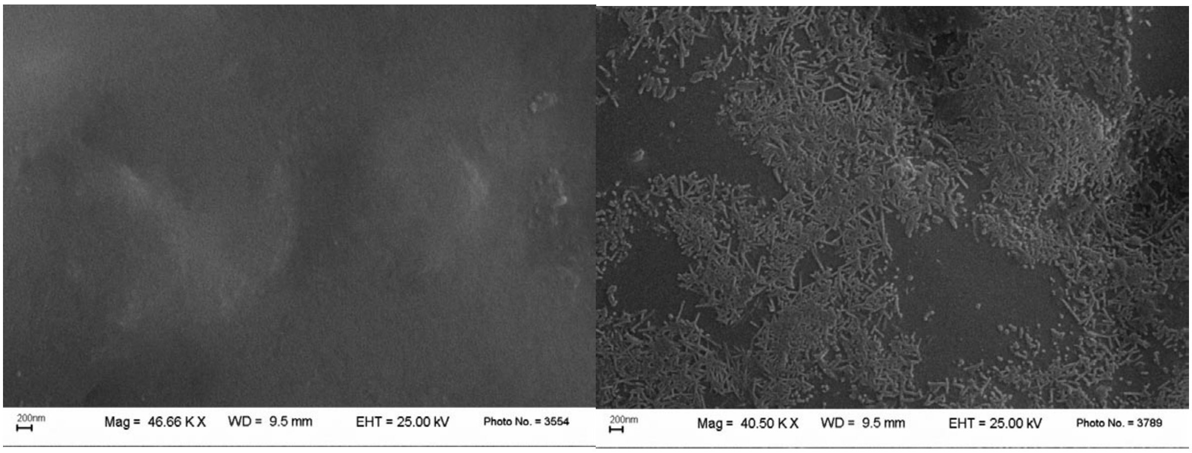


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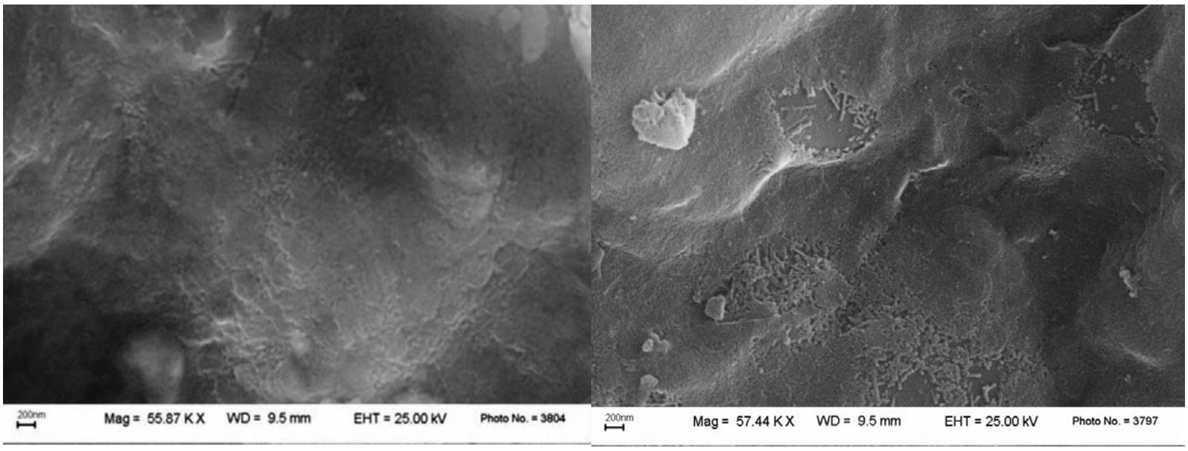
Figure 7. SEM micrographs of sample P before (a) and after (b) the chemical attack, the elongated crystals are mullite.



a) b)

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

4. CONCLUSION

In the present work, the possibility, to functionalise the surface of porcelain stoneware materials with nano-oxide 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-oxide layer, by covering in a homogeneous way the ceramic surfaces, showed a good interaction with the 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 attacks, are in progress.

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