PHOTOCATALYTIC CERAMIC TILES: KEY FACTORS IN INDUSTRIAL SCALE-UP (AND THE OPEN QUESTION OF PERFORMANCE)

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ABSTRACT

Photocatalytic and highly hydrophilic ceramic surfaces were realized by deposition of nanostructured TiO_2 coatings on porcelain stoneware large slabs, produced by *Lamina* technology. Different techniques (silicon roller and ink-jet printing) were used to apply nanotitania coatings on industrially-sintered products in a set of experimental conditions (titania load, surface coverage) and surface finishing (glazed/unglazed) by additional annealing steps. A complete physical and functional characterization of coated surfaces allowed feasibility to be assessed through the industrial scale-up from a pilot line (tile size 40x40 cm) to the production plant (slab size 300x100 cm) by the adoption of suitable, fast and environmentally friendly technological solutions. Key factors affecting the photocatalytic activity are discussed by addressing the open question of actual performance attainable on ceramic tiles.

1. INTRODUCTION

In the field of ceramic tiles, the realization of even larger dimensions and reduced thicknesses is a topical industrial phenomenon involving innovative technical solutions able to produce ceramic slabs with dimensions up to 3.6 x 1.2 square metres and a thickness of 3-4 mm [1-3].

Large-sized porcelain stoneware slabs are suitable for both outdoor and indoor applications, as building and construction elements [1-3] - i.e. floorings, wall coverings, roofings, ventilated façades, insulating panelling, tunnel coverings - especially combined with the functionalization of their surface, providing de-soiling and de-polluting performances [4-7]. Photocatalytic surfaces – obtained by deposition of a titanium dioxide layer – are able to reduce air pollution, to prevent materials from becoming sooty and dark, improving the environmental safety and quality of life [8-10]. In addition, the high hydrophilicity, induced by TiO_2 coatings, promotes *antifogging* and *self-cleaning* performances [11-12].

However, large scale applications are up today still limited because of technological hindrances concerning the industrial scale-up of functionalised materials. The main constraints are represented by the need of:

(i) immobilizing the photocatalyst on an inert support, like the ceramic surface, by suitable deposition and sintering techniques [7,13];

(ii) modifying the production cycles (*e.g.* including additional annealing steps) in order to avoid the anatase-to-rutile phase transformation [14-15];

(iii) getting materials with lasting performances able to preserve over time their additional functionalities in different working conditions [16].

In recent years, many papers have reported the photoinduced catalytic activity and wettability of TiO_2-coated surfaces [6,9,10], highlighting the role played by process and product variables [12,18-20]. In the building sector, however, some additional parameters - *i.e.* wide surfaces to be processed, availability of deposition techniques, output rate to be kept as high as usual, cost of the final product - represent critical points to be overcome, requiring adequate technical solutions. In addition, the latest standards for the assessment of photoactivity in terms of degradation of NO_x (UNI 11247), organic dyes (UNI 11238-2) or wetting behaviour (ISO 27448) imply setting up reliable methods and procedures. The reason why some coatings are superhydrophilic, but not active in the decomposition of organic dyes, NO_x or BTEX is still poorly understood.

In this work, nanostructured TiO_2 coatings were realized on porcelain stoneware large-sized slabs by using industrial deposition technologies, such as ink jet printing and roller printing, already available in many manufacturing plants for decorative purposes. In this context, the possibility of obtaining, in one single step, the deposition of the active semiconductor and the direct microstructuring of tile surfaces was investigated. The objectives are:

(i) evaluating the effect of processing variables - deposition methodology, photocatalyst amount and thermal treatments - on the coating structure;

(ii) assessing both the wetting behaviour and photoactivity of functionalised surfaces processed in different ways;

(iii) outlining technical advantages or hindrances connected with the industrial scale-up of photoactive construction materials in the framework of the open discussion on effective performance of ceramic tiles.

2. MATERIALS AND METHODS

Different porcelain stoneware (PS) surfaces were selected from an industrial manufacturer (Table 1): glazed (G) and unglazed (U) tiles were sampled as semi-finished (unfired, G* and U* series) and finished products (fired, GF and UF series). All products were fully characterized, as reported in a previous work [1].

A commercial 100% nano-anatase suspension (Colorobbia Italia) was printed on ceramic surfaces; the suspension has an average particle size of 10 nm (Dynamic Light Scattering, Zetasizer Nanoseries Malvern Instr.), a surface tension of about 40 $mN \times m^{-1}$ (OCA 15 Tensiometer, Data Physics Instr.) and viscosity values of 32 and 6 $mPa \times s$, respectively, at room temperature and 80°C (Bohlin C-VOR 120 rotational rheometer).

Nano-TiO_2 layers were deposited by means of a) roller printing (System Rotocolor® equipment, by using in-line available cylinders at pilot scale) and b) ink jet printing (Spectra Galaxy JA 256/80 AAA apparatus; drop size: 80 pL, drop velocity 8 $m \times s^{-1}$, drop frequency 20 kHz). Very different amounts of anatase were used: from 0.4 to 4.6 $g \times m^{-2}$ on both uncoated glazed and unglazed porcelain stoneware surfaces (Table 1).

	Glazed	Unglazed	TiO_2 amount by Rotocolor® (g/m^2)	TiO_2 amount by ink jet (g/m^2)	Thermal treatment conditions
Reference	**G**	**U**			
Unfired	G1*	U1*	1.4	-	Electric roller kiln Industrial cycle 1210°C, 50 min
	G2*	U2*	2.0	-	
	G3*	U3*	3.4	-	
	G4*	U4*	3.7	-	
	G5*	U5*	4.6	-	
	G6*	U6*	-	0.4	
	G7*	U7*	-	0.6	
Finished	GF1	UF1	1.4	-	Electric chamber kiln Annealing from 400°C to 1000°C, 60 min
	GF2	UF2	2.0	-	
	GF3	UF3	3.4	-	
	GF4	UF4	3.7	-	
	GF5	UF5	4.6	-	
	GF6	UF6	-	0.4	
	GF7	UF7	-	0.6	

Table 1. Sampling of PS surfaces, amounts of printed TiO_2 and thermal treatment conditions

Semi-finished G* and U* samples were fired in an industrial roller kiln at a maximum temperature of 1210°C and thermal cycle of 50 minutes, while finished products (GF, UF series) underwent annealing steps in a laboratory chamber kiln at 400, 600, 800 and 1000 °C with a thermal cycle of about 60 minutes (Table 1).

Phase composition and thermal stability of TiO_2 layers were determined by X-Ray Diffraction (XRD, Bruker D8, LynkEye detector, CuKα radiation, 10-80°2θ, 16 s of equivalent time per step) quantifying the anatase/rutile ratio by Rietveld refinement and the anatase crystallite size by means of the Debye-Scherrer equation (LaB_6 reference material, SRM660a) [22]. Surface microstructure was investigated by SEM (Leica Cambridge Stereoscan 360) and confocal microscopic (Leica Cambridge Microsystem Heidelberg GmbH) observations.

Wetting of surfaces was assessed by means of contact angle (CA) with water (OCA 15 Tensiometer, Data Physics Instr.); for each surface, CA in different points were measured, providing average values before and after irradiation for 2 hours with a UV-A lamp (OSRAM Ultra-Vitalux 300 W, light intensity 3 $mW \times cm^{-2}$ in the 300-400 nm range). The photocatalytic activity of selected ceramic slabs was determined as follows:

a) the degradation of a droplet of methylene blue (MB) solution (500 ppm in water) deposited on the surface and allowed to dry, determining a MB degradation index by the change of absorbance (Eye-One, GretagMacbet™) before and after irradiation with the UV-A lamp for 30, 60, 120, 180 and 240 minutes;

b) the oxidation degree of a nitrogen oxides ($NO+NO_2$) mixture in a chamber reactor, equipped with a chemiluminescence detector (NO_x flux: 0.03 l/min; T: 24 ± 1 °C; RH: 44 ± 5 %; UV-A intensity: 5 $mW \times cm^{-2}$).

Durability and lasting performances of coatings, in terms of wettability variations, were checked after brushing abrasion (2500 cycles) with neutral detergent. The water-coating CA of aged surfaces was measured after UV-A irradiation.

3. RESULTS AND DISCUSSION

3.1 Surface phase composition

Due to the current sintering processes in the manufacturing of building materials, it is necessary to select experimental conditions able to preserve the as-deposited anatase as the active phase, by preventing both the crystallite growth and anatase-to-rutile transformation [23-24]. The analysis of surface phase composition allowed the anatase-to-rutile ratio to be quantified, i.e. 100*A/(A+R), as a function of the processing conditions (Fig. 1).

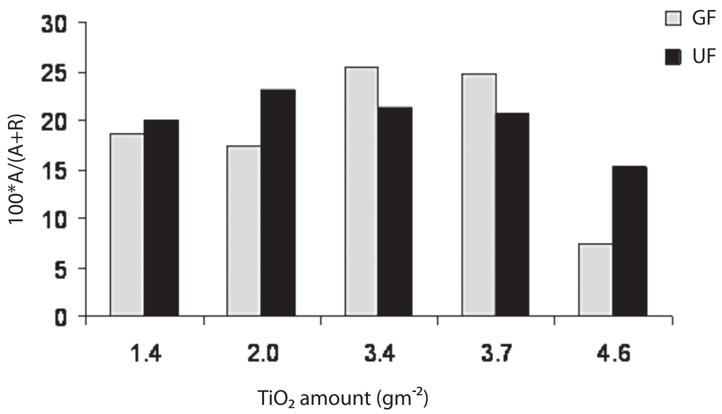

Figure 1. Anatase-to-rutile ratio in GF and UF samples after annealing at 1000°C

The following conclusions can be drawn:

- whatever are the deposition procedure and TiO_2 amount, anatase is the only phase detected on both GF and UF surfaces for thermal annealing up to 600°C;
- anatase-to-rutile transformation occurs at higher temperature, but whereas at 800°C just small traces of rutile are detectable, at 1000°C the anatase on the surface is drastically reduced and the anatase-to-rutile ratio reaches values between 7% and 25% for GF samples and between 15% and 23% for UF ones (Fig. 2);
- overall, glazed surfaces present a wider anatase-to-rutile range and the kinetic of conversion is faster when higher amounts of TiO_2 are deposited by the roller technology;
- a complete conversion of anatase occurs during industrial firing at 1210°C, so rutile is the only phase found.

As far as crystallite size, some general trend can be outlined: up to 600°C, crystal size is in the 15-20 nm range, still comparable with that of the as-deposited anatase; then, crystallites grow quite fast with TiO_2 layers deposited by roller printing presenting particle dimensions between 90 and 150 nm, while ink jet printing gives rise to a crystal size more or less between 60 and 80 nm. The crystallite growth rate (calculated for the UF series as the ratio between the difference of crystallite size at higher and lower temperature and the temperature range, Fig. 2) depends in a more complex way on printing technology and on the amount of active particles on the surface. It is quite evident, however, that in the 800-1000°C range the growth rate is much faster, with the only exception of the UF6 sample.

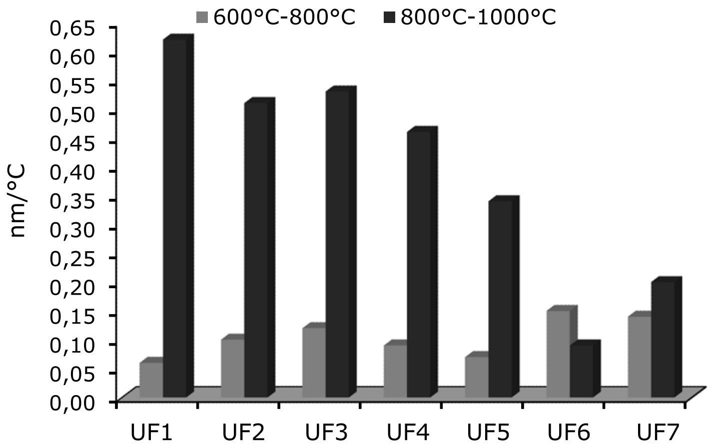

Figure 2. Crystallite growth rate (nm/°C) in the 600-800°C and 800-1000°C range

3.2 Coating microstructure and morphology

SEM and confocal microscopic analyses provided a different appearance of functionalized surfaces obtained by roller (GF1) and ink jet printing (GF6), thermally treated at 800°C and 1000°C (Figures 3 and 4).

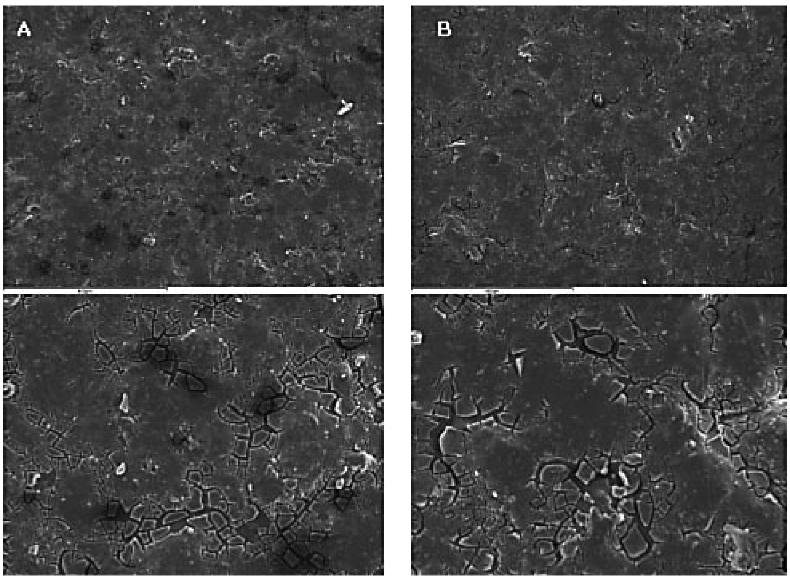

Figure 3. SEM micrographs of GF1 sample after annealing at 800°C (A) and 1000°C (B) at two magnifications: 400 µm and 100 µm.

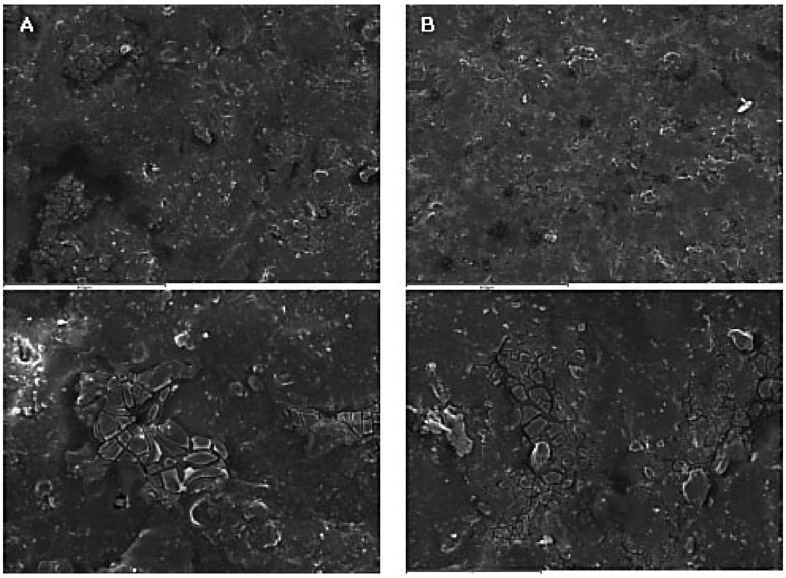

Figure 4. SEM micrographs of GF6 sample after annealing at 800°C (A) and 1000°C (B) at two magnifications: 400 μm and 100 μm.

For both samples, TiO_2 layers are detectable at bigger magnification; however, annealing at 1000°C makes the surfaces smoother if compared with texture obtained at 800°C. TiO_2 particles appear as a flakes assemblage, whose spatial distribution and frequency depend on the deposition technique, being greater when roller printing is used and a higher amount of TiO_2 is deposited (GF1 samples, Fig. 3). These statements seem to be supported by confocal microscopy analyses (Fig. 5) which reveal that coating thickness varies from about 70 μm (ink jet printing) to 100 μm (roller printing) and that, whatever the annealing temperature, ink jet printed surfaces show a more continuous coating when compared with the other ones. However, it can be emphasized that:

i) both techniques are suitable to obtain the direct patterning and coverage of large areas;

ii) TiO_2 amounts as low as 0.5-0.6 $g \times m^{-2}$ are, in any case, enough to produce textured, functional coatings;

iii) the deposition technique is a critical issue to ensure a proper nanotitania texturing on the ceramic surface.

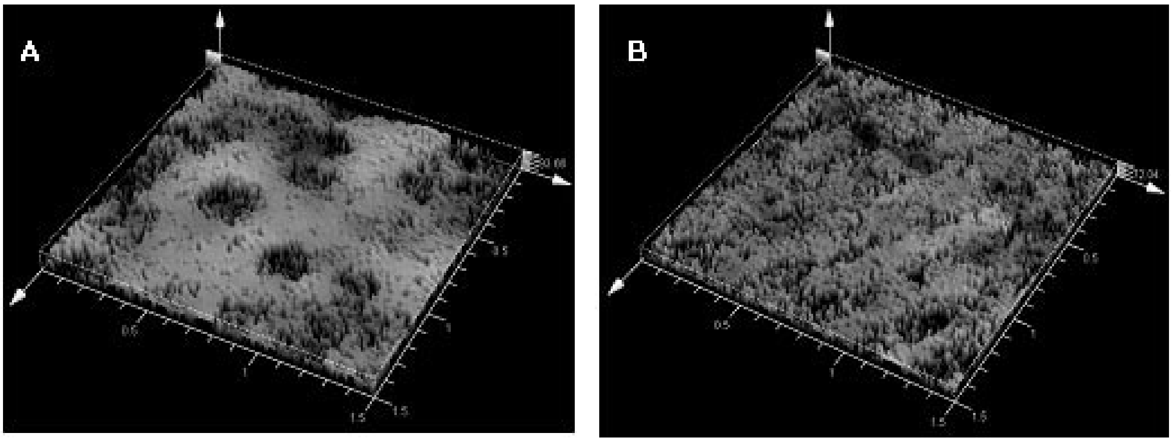

Figure 5. Confocal microscopic images of GF1 (A) and GF6 (B) samples. The x-y plane is 1.5x1.5 mm, the z-axis is 93 µm (A) and 72 µm (B).

3.3 Surface wettability and photoinduced hydrophilicity

Contact angles (CA) with water of TiO_2-coated surfaces, before and after irradiation, were determined, taking the industrially-manufactured uncoated slabs as reference (CA=47° and 56° for glazed and unglazed tiles, respectively). Before irradiation, CA of coated surfaces is quite variable with thermal treatments, confirming the tendency towards a poor hydrophilicity (Table 2); upon exposure to UV-A light, involving band gap excitation of the semiconductor layer, CA of all samples treated up to 800°C - functionalized by both printing techniques - rapidly decreases approaching values below 5°, hence yielding superhydrophilic surfaces where water droplets spread out [8,10-11]. The exceptions are represented by functionalized samples which underwent annealing at 1000°C or industrial firing at 1210°C, whose CA values after a prolonged irradiation are very similar to those of as-coated, not already activated surfaces. This behaviour, as expected, is due to a large extent to the anatase-to-rutile conversion which, simulating the fast cycles of ceramic tile kilns, took place over a wide thermal interval between 600 and 1200°C, even if the maximum rate of phase transition is found around 900-1000°C.

Overall, it can be claimed, on one hand, that ink jet printing is suitable to obtain photoactive, top-layered structured materials with enhanced attitude to link water molecules by managing very low TiO_2 quantities; this involves - as a key issue - a quite limited cost growth of the functionalized products, especially when processing concerns large-sized elements. On the other hand, Rotocolor® equipment itself can find extensive applications, beyond the decorative ones, in the control of surface wettability through nano-suspension deposition, thanks also to both process speed and the easiness of cleaning operations, allowing undemanding management of different suspensions.

Temperature	400°C	600°C	800°C	1000°C	1210°C
GF1	46 (<5)	24 (<5)	34 (<5)	19	20 (G1*)
GF2	43 (<5)	23 (<5)	35 (<5)	15	26 (G2*)
GF3	49 (<5)	27 (<5)	32 (<5)	17	23 (G3*)
GF4	50 (<5)	24 (<5)	40 (<5)	19	25 (G4*)
GF5	52 (<5)	25 (<5)	35 (<5)	22	26 (G5*)
GF6	44 (<5)	31 (<5)	35 (<5)	18	20 (G6*)
GF7	51 (<5)	33 (<5)	40 (<5)	25	36 (G7*)
UF1	51 (<5)	25 (<5)	31 (<5)	23	30 (U1*)
UF2	52 (<5)	21 (<5)	36 (<5)	18	43 (U2*)
UF3	41 (<5)	28 (<5)	19 (<5)	17	23 (U3*)
UF4	46 (<5)	30 (<5)	29 (<5)	13	33 (U4*)
UF5	53 (<5)	25 (<5)	39 (<5)	19	41 (U5*)
UF6	42 (<5)	45 (<5)	31 (<5)	9	23 (U6*)
UF7	47 (<5)	51 (<5)	39 (<5)	18	26 (U7*)

Experimental error 5% relative

Table 2. Wetting behaviour of TiO_2-coated surfaces, before irradiation, as contact angles (°) after annealing steps (GF, UF series) or industrial firing (G, U* series). In brackets CA after irradiation*

3.4 Photocatalytic activity of ceramic surfaces

Methylene blue degradation: among organic dyes, methylene blue (MB) test is widely used for assessing activity of TiO_2 layers, since MB has a strong staining power, thus representing a quite severe test for photo-oxidation ability of semiconductors [25-28].

In this work, two representative TiO_2-coated surfaces – annealed, respectively, at 600 or 800°C – were chosen and their activity in the degradation of a highly concentrate MB solution was assessed (Fig. 6, where the percentage of MB degradation has been plotted against irradiation time). The efficiency of coated samples is very high when compared with the uncoated one, but the process kinetic depends on annealing conditions: the MB degradation by the sample treated at 600°C reaches, after just 30 minutes of irradiation, values close to 90% and, after more or less one hour, is almost complete. On the other hand, the sample treated at 800°C, although is able to promote a complete degradation of dye after more or less one hour, presents a certain inertia to be activated.

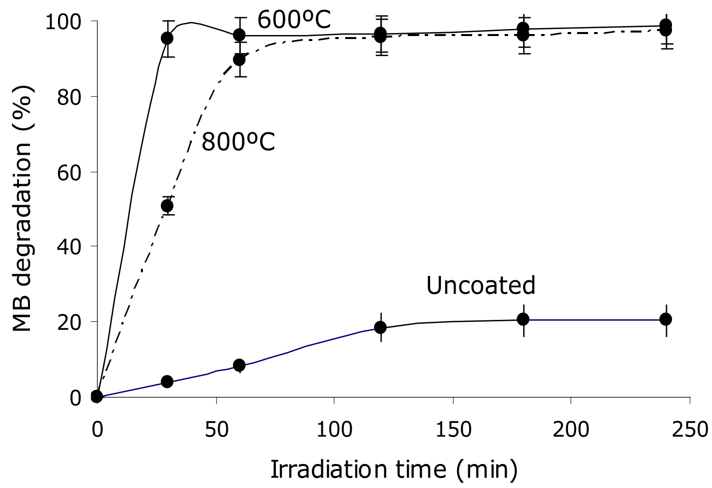

Figure 6. Degradation of MB solution by samples annealed at 600°C and 800°C as a function of irradiation time: comparison with the uncoated one.

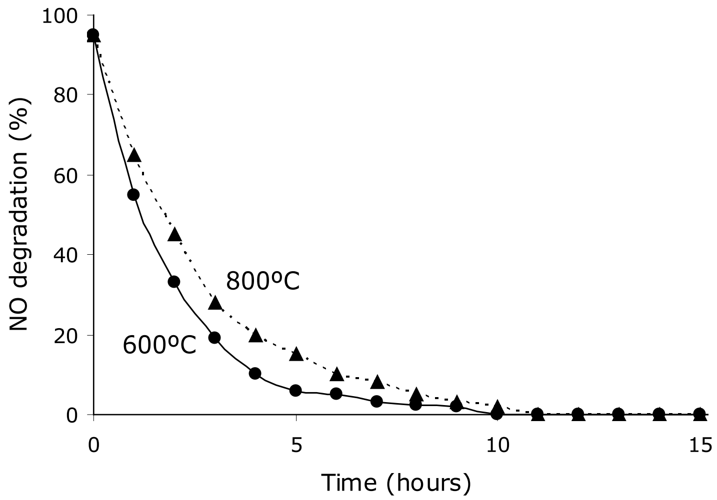

Figure 7. Degradation of nitrogen oxide (NO) performed by samples annealed at 600°C and 800°C vs time.

De-NOx activity: the attitude of the same surfaces towards the oxidation of NO is illustrated in figure 7 (more or less the same trend concerns the degradation of NOx). Both samples exhibit a rather high reactivity in the adopted experimental conditions, determining a degradation up to 95% of NO concentration; however, the following differences can be outlined:

i) overall, the degradation kinetics of nitrogen oxide is faster if compared with that of dioxide;

ii) the sample treated at a lower temperature (UF1, 600°C) was confirmed to be more reactive than that treated at 800°C. In particular, NO degradation was almost complete after 6-8 hours, while for nitrogen dioxide the same level of degradation was achieved after about 28 hours (Fig. 7).

These results, combined with those concerning dye degradation, suggest that the kinetics of photoactivity is correlated to both the anatase/rutile ratio and the anatase crystal growth. These two phenomena take place when the temperature increases: surface activity decreases when rutile is formed and anatase dimensions increase; as a consequence, it is expected to stop working once anatase-to-rutile conversion is complete. It deserves to be noted that functionalised surfaces, as realized in this work, present at the same time a high degradation power against both organic dyes and inorganic oxides, also coupled with a favourable wetting behaviour, which makes them extremely attractive for practical applications.

However, it must be considered that photoactivity determinations are strongly dependent on experimental variables and should be carried out in standardised conditions. The lack of international standards on both the experimental procedures and product classification is giving rise to a spreading of claimed performances of prototypal and industrial ceramic tiles.

3.5 Durability and lasting properties of surfaces

The forecast of lasting performances – i.e. wear resistance, chemical stability and photoactivity maintenance - of coated surfaces in the different working conditions is a quite hard task. Looking at their behaviour after brushing, simulating ageing phenomena at a laboratory scale, it is found that superhydrophilic performances can be preserved to some extent when higher amounts of TiO_2 are deposited and annealing is performed at higher temperatures (Table 3).

This is the case of the UF5 sample, functionalized by roller printing through deposition of 4.5 g$\times$m^{-2} of TiO_2 and thermally treated at 800°C, whose wettability after ageing is still acceptable due to the improved resistance of the coating to mechanical wear. In these processing conditions, notwithstanding the incoming anatase-to-rutile conversion, the coating adhesion is ensured and performances kept to an adequate level. This is clear comparing the wettability of the UG4 surface, whose lower amount in terms of TiO_2 per unit area involves a worse performance after abrasion. A similar behaviour is presented by the sample UF6, obtained by ink jet deposition of 0.6 g$\times$m^{-2} of TiO_2.

Sample	Before	After
UF4 400°C	<5	24
UF4 800°C	<5	22
UF5 400°C	<5	26
UF5 800°C	<5	9
UF6 400°C	<5	34
UF6 800°C	<5	24

Table 3. Contact angles (°) of surfaces under UV irradiation before and after ageing

Finding a compromise between photoactivity (best at lower annealing temperature) and coating adhesion (best at higher annealing temperature) is the main goal of industrial scale-up of photocatalytic ceramic tiles.

4. CONCLUSIONS

The production of large-sized, photoactive building materials is feasible at the industrial scale through suitable technological solutions, in many cases already available for in-line decoration purposes. Nanostructured TiO_2 coatings, in fact, have been deposited by ink-jet or roller printing of nano-anatase suspensions by modifying, in one step, chemical and microstructural parameters of surfaces. Such coatings need to be consolidated through additional thermal steps which, even though implying a significant modification of current production cycles of ceramic tiles, represent the proper solution to both preserve the active phase and keep mechanical and functional performances to an adequate level. At all events, a direct functionalization of unfired ceramics is not practicable, because the high sintering temperature (around 1200°C) is detrimental for the photocatalytic performance.

Both the deposition technologies and thermal conditions influence the nanotitania texturing, in terms of thickness, homogeneity and particle size. Product characteristics and photoactivity indicate that ink jet printing is suitable to obtain photoactive, top-layered, structured materials with enhanced attitude to link water molecules (CA below 5°) by managing TiO_2 quantities as low as 0.4 $g \times m^{-2}$; this latter circumstance involves a limited cost growth of industrial products, especially when large-sized elements are concerned. On the other hand, this work suggests that roller printing can find an extensive application in the control of surface photoactivity, thanks to the die box-holding cylinders ability to apply TiO_2 nanosuspensions in a controlled way. The high speed and flexibility of the deposition process makes this technology an excellent tool for surface functionalization.

In order to achieve a highly active and durable photocatalytic ceramic tile, it is necessary to get proper anatase nanoparticles and their adhesion on the ceramic surface as a textured coating. A compromise must be pursued in the thermal treatment to control anatase size growth and phase transformation (better at low temperature) and homogeneity and strength of adhesion (better at high temperature). Characterization of the photoactivity must be conducted in strictly controlled conditions and results referred to an overall benchmark.

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