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Printing nano TiO_2 on large-sized building materials: Technologies, surface modifications and functional behaviour

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Abstract

The industrial feasibility of large-sized, photocatalytic building materials was assessed by the adoption of suitable, fast and environmental friendly technological solutions. Nanostructured TiO_2 coatings can be realized by ink-jet or roller printing of nano-anatase suspensions by modifying, in one single step, the chemistry and microstructural features of products. Functional coatings must be consolidated through additional thermal steps, which necessarily entail modifications of the current production cycles of ceramic tiles. This is due to the fact that the direct functionalization of unfired ceramics is detrimental to the photocatalytic performance. The microstructure of coatings depends on deposition technologies and processing conditions. However, photoactive materials that also display superhydrophilic behaviour can be obtained by employing much lower amounts of TiO_2 than 1.0 g m^{-2}, and by annealing at temperature as low as 400–500 °C. A limited increase of the cost of products is involved, especially in the case of large-sized elements.

Keywords: A. Sintering; B. Microstructure-final; B. Surfaces; D. TiO_2; E. Functional applications

1. Introduction

In the field of ceramic tiles, the latest market trends encourage the production of tiles having large dimensions and ever decreasing thicknesses. Innovative technological solutions have been devised to produce ceramic slabs having surface dimensions up to 3.6 m × 1.2 m and thickness down to 3–4 mm only [1–3].

The development of porcelain stoneware large slabs, which find applications both as outdoor and indoor building and construction elements (i.e. flooring, wall covering, roofing, ventilated façades, insulating panelling, tunnel lining), has recently received significant attention [1,3], especially in combination with the functionalization of their surface, as such products provide de-soiling and de-polluting capabilities [4–7]. Photocatalytic surfaces – obtained by deposition of a titanium dioxide layer – can be considered as eco-friendly materials, able to reduce air pollution in urban areas and to prevent houses, walls, tunnels, etc. from becoming sooty and dark, thus improving environmental safety and quality of life [3,8–10]. In addition, the high hydrophilicity induced by TiO_2 coatings promotes a favourable wetting behaviour, enhancing both antifogging and self-cleaning performances, since the micro-droplets of condensed water spread out on the surfaces forming a continuous water layer [3,11,12].

However, some technological challenges are still to be met in view of the scaling-up of such innovative construction materials to industrial standards, so that as of today large-scale applications are still limited. 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 an additional annealing step) in order to avoid the anatase-to-rutile phase transformation, which implies a reduction of photoactivity [14–16];
(iii) obtaining materials with lasting performances, able to preserve over time their additional functionalities in different working conditions [17,18].

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In recent years, many papers have reported the photoinduced catalytic activity and improved wettability of TiO_2-coated surfaces [6,9,10]. In this context, several solutions have been evaluated to single out appropriate technologies (e.g. sol–gel processes, chemical and physical vapour deposition, thermal spraying, electron-beam evaporation), each time highlighting the role played by process and product variables in obtaining the coating structure and performance [12,19–21]. In the building sector, however, some additional constraints – i.e. wide surfaces to be processed, availability of in-line deposition techniques, output rate to be kept as high as usual, cost of the final product – represent critical points to be addressed, all of them requiring adequate, prompt, and possibly cheap technical solutions while avoiding waste of material.

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

(i) modelling the effect of processing variables – deposition methodology, photocatalyst amount and thermal treatments – on the coating structure;
(ii) assessing both the wetting behaviour and the photoactivity of functionalized surfaces processed in different ways;
(iii) outlining the technical advantages or drawbacks connected with the industrial scale-up of photoactive construction materials and, particularly of large-sized ones.

2. Materials and methods

Different porcelain stoneware surfaces were selected from the production of 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 to their physical, technological and mechanical properties, as reported in a previous work [1].

A commercial nano-anatase suspension in dietylenglycol from Colorobbia (Italy) was chosen to be printed on ceramic surfaces. Its particle size distribution (Dynamic Light Scattering, Zetasizer Nanoseries Malvern Instruments), surface tension (OCA 15 Tensiometer, Data Physics Instruments) and viscosity (Bohlin C-VOR 120 rotational rheometer, both at room temperature and 80 °C) were determined. Such a TiO_2 suspension is 100% anatase, with average particle size of 10 nm, surface tension of about 40 mN m^{-1} and viscosity values of 32 and 6 mPa s at room temperature and at 80 °C, respectively.

Nanotitania layers were deposited by means of: (a) roller printing (System Rotocolor® equipment) and (b) ink jet printing (Spectra Galaxy JA 256/80 AAA apparatus). Ink-jet printing parameters (drop size: 80 pL, drop velocity 8 m s^{-1}, maximum drop frequency 20 kHz) were chosen to match the rheological properties of the suspension with the instrument's technical specifications. The deposition by Rotocolor® was performed at a pilot scale by using the available in-line die box-holding cylinders. Very different amounts of anatase were used to functionalize the surfaces depending on the technique, i.e. 0.4 and 0.6 g m^{-2} for ink jet printing, and from 1.4 to 4.6 g m^{-2} for roller printing (Table 1). Uncoated glazed and unglazed porcelain stoneware surfaces were taken as reference.

The functionalized surfaces were processed in a different way: G* and U* samples were fired in an industrial roller kiln, at a maximum temperature of 1210 °C with a thermal cycle of 50 min, while finished products (GF and UF series) underwent annealing steps in a laboratory chamber kiln at 400, 600, 800 and 1000 °C, with a thermal cycle of about 60 min (Table 1). In any case, colourless and transparent sintered coatings were obtained (even if a change in the gloss of surfaces appeared for the highest titania loading).

Phase composition and thermal stability of TiO_2 layers were determined by X-Ray Diffraction (XRD, Bruker D8, LynkEye

Table 1
Sampling of porcelain stoneware surfaces, amounts of printed TiO_2 and thermal treatments conditions.

	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	