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Inorganic hydrophobic coatings: Surfaces mimicking the nature

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Abstract

Added value products are being developed in ceramic industry. Different optical effects as bright metallic shine or new functionalities as hydrophobicity or bactericide characteristics are the new properties searched on the tiles. In this study, we prepare glassy coatings for tiles based on copper pigment by a conventional industrial process. The obtained coatings present different aesthetical aspects, including bright metallic aspect which confers a high decorative value to the tile. Furthermore, these metallic coatings present hydrophobic properties with contact angles with water as high as 115° and also bactericide characteristics. Superficial microstructure and nanoparticles were found in the bactericide-hydrophobic samples, resembling the surface of hydrophobic leaf surfaces. This structure was formed by the crystallization of CuO nanoparticles as Tenorite due to the copper saturation of the glassy matrix at the surface of the coatings.

Keywords: B. Microstructure-final; B. Surfaces; D. Glass; E. Functional applications

1. Introduction

Surfaces showing an apparent contact angle larger than 90° with liquids, and most specifically with water, are considered hydrophobic surfaces, while those presenting contact angles higher than 150° are super-hydrophobic [1]. Super-hydrophobic surfaces have attracted significant attention for their potential use in many different applications [2]. In this field, a broadly followed tendency is to mimic the structural design of natural super-hydrophobic leaves [3], particularly those of the Lotus flower (Nelumbo Nucifera). These leaves present contact angle with water droplets over 150°, producing nearly spherical droplets that roll over the leaves instead of sliding. This fact impedes the wetting of the leaves and also removes superficial contaminants that are taken away by the rolling water drops. The superhydrophobic properties of the lotus leaves are based on the hierarchical combination of micro- and nano-structures on their surface, together with the presence of hydrophobic molecules [4]. Different studies reveal that the surface texture pattern is a key factor of the hydrophobic properties of these leaves [5,6], and hence, hierarchically structured surfaces presenting hydrophobic properties are expected to present lotus effect [7]. In particular, in the case of nanostructured surfaces, where composite Cassie-Baxter interfaces appear between the surfaces and water drops [8], it is demonstrated that increasing the nanoroughness (or fraction of intergranular empty spaces on the surface) leads to higher contact angle, i.e., the hydrophobic character of the surface, makes this effect even more evident when a microstructuration of the surface is also present.

In the Lotus leaves, surface structuring arises at different hierarchical levels. At the micro-scale, the epidermal cells create a sculpturing of the surfaces; the surface of each cell presents a further structuration at the nanoscale produced by the presence of nanosized hairs or tubules [9]. In other words, two main surface morphologies are present, one at micrometer size, due to the different cells, and another one at nanometer size, corresponding to the structures present at the surface of each cell.

A number of methods have been reported in the literature to fabricate structures similar to the ones found on

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hydrophobic plants, including plasma [10], laser and chemical etching [11,12], lithographic patterning, electrochemical deposition, sol–gel, coating-by-coating assembly and chemical or vapor deposition [13]. However, these methods present certain limitations for industrial applications and have not been transferred to commercial products because most of them are only applicable on small substrates and require either time consuming processing steps or expensive machinery [14]. Moreover, hydrophobic and super-hydrophobic coatings are usually mechanically instable and do not even resist wiping with a cloth, highly limiting their potential uses. Therefore, a simple, inexpensive and convenient strategy to form patterned structures is highly needed.

In the same way, bactericide surfaces are pursued in combination with auto-clean surfaces. The activity in the field of inorganic bactericides is related to materials supporting silver or copper metal nanoparticles [15,16], nanorough surfaces [17] or photocatalytic nanoparticles [18]. However, the industrial implantation of photocatalytic function is not an easy task. As an example, the coatings must be irradiated with UV light to achieve the desired characteristics, representing a serious limitation.

The ceramic tiles industry is one of the fields where applications of hydrophobic and bactericide surfaces are straightforward. The potential of producing self-cleaning surfaces would mean a paramount advance on this market, both for the public and for the manufacturing companies [19,20]. The main problems that must be solved in order to incorporate new functionalities to ceramic tiles are the high temperatures used in their fabrication (about 1000 °C or higher) and the highly reactive components employed. Moreover, high production rates and low production costs are also common requirements of this market. And finally, these products must present some technical characteristics and more specifically high wear strength, being not affected by common use.

In order to satisfy the necessities of the ceramic sector, nanostructured hydrophobic ceramic glazes were previously developed by adding metallic nanoparticles supported on sepiolite fibers [21]. This method was compatible with the standard fabrication process of tiles but the metallic nanoparticles supported on sepiolite were not commercially available because of the product cost. The new challenge is to develop new nanostructured functional glazes using available materials in the market.

In this work we present new developments on bactericide-hydrophobic surfaces for industrial ceramic tiles by using Fe_2O_3 and Cu microparticles. The sintering procedure was the same fast-firing process commonly employed in the industry for the preparation of ceramic tiles. The bactericide-hydrophobic coating so obtained possesses a hierarchical structure similar to that of the hydrophobic leaf surfaces and it is resistant enough to be used in standard applications.

2. Experimental procedure

Hydrophobic glazes were prepared following a standard procedure in the ceramic tile industry [22]. For the preparation of the glaze, an homogeneous suspension in water of commercial frit, Kaolin, Fe_2O_3 and metallic copper was prepared. The frit corresponds to an industrial standard used in stoneware industry and was supplied by Kerafrit S.A. The composition of this frit is shown in Table 1. Metallic copper particles, with an average particle size of 3 μm and Fe_2O_3 particles with size < 5 μm were purchased from Aldrich. The solid content was 40%wt and the relative mass proportion of each component on the solid was: 78%wt frit, 10%wt Cu, 5%wt Fe_2O_3 and 7%wt kaolin.

The suspension was homogenized by ball milling for a period of 20 min using 0.2%wt of sodium trypolyphosphate as deflocculant and 0.2%wt of carboxymethyl cellulose to improve the adhesion of the glaze to the green tile. The suspension was sprayed on the surface of a stoneware green tile substrate producing coatings with thicknesses ranging from 50 μm to 250 μm. Then, the tiles with the glaze coatings were dried at 90 °C and fast-fired in an air atmosphere using a Pirometrol furnace. The heating rate was ca. 30 °C/min and the maximum temperature was 1200 °C (held for 5 min). This sintering cycle corresponds to a standard industrial fast-firing process of stoneware ceramic tiles. The total firing cycle was 55 min.

The glaze surfaces were characterized by X-ray diffraction analysis, performed with Cu Kα radiation using a Siemens D500 Diffractometer in grazing angle (0.5°) the step time being 2 s with an increase of 0.02°. The crystallite size was studied from XRD using the Debye–Scherrer equation. The roughness of the surface was measured with a Surtronic 3+ roughmeter from Taylor Hobson Precision (England) taking account the Ra value (average of profile variation on the vertical axis). The microstructure was studied by a field emission scanning electron microscope (FE-SEM, Hitachi S-4700) and the nanostructure was studied by atomic force microscope (AFM) in non-contact mode with a WITec 300 microscope and by transmission electronic microscope (JEOL JEM-2100F) at 300 kV. The samples were slimmed for TEM study using a Dimple Grinder and an ion miller from Gatan. Water contact angle was measured with the drop shape analysis system Easy Drop Standard from Krüss using deionized water drops of 4.0 ± 0.1 μL.

The bactericide characteristics of the coatings were measured according to the standard JIS Z 2801. Control and test surfaces are inoculated with 10^5 colony-forming units (CFU) of microorganisms and they are allowed to incubate undisturbed in a humid environment for 24 h. After incubation, microbial concentrations are determined. Reduction of microorganisms relative to initial concentrations and the control surface is calculated according to the parameter R, bactericide effect is consider when $R > 2$.

$$R = \log \frac{CFU_{on\ control\ sample}}{CFU_{on\ test\ sample}} \quad (1)$$