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Robust and easy-repairable superhydrophobic surfaces with multiple length-scale topography constructed by thermal spray route

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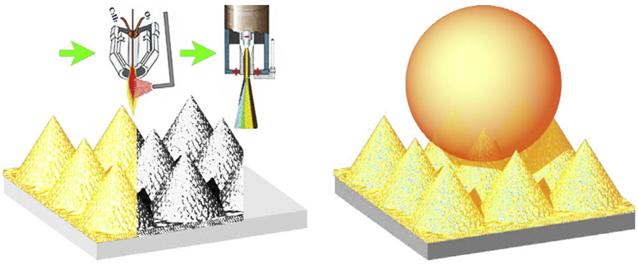
HIGHLIGHTS

- Coating with multiscale structure was made by thermal spray and nano modification.
- Ceramic matrix with cone-like geometry was fabricated by plasma spray deposition.
- The superhydrophobic surfaces are mechanically robust and easy-repairable.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper demonstrates a thermal spray route for making superhydrophobic surfaces with mechanically robust and easy-repairable performances. Cone-like geometry with multi-scale topographical structures was firstly achieved by plasma spray deposition of titania using stainless steel mesh as shielding plate, then polytetrafluoroethylene/nano-copper composites were deposited by suspension flame spray onto the patterned titania coating. The coatings exhibit superhydrophobicity with a water contact angle of ~153° and a sliding angle of ~2°. Unlike the surfaces with normal structure, the coatings with multiple length-scale structure retain the superhydrophobicity even after severe mechanical abrasion. The superhydrophobicity can be further easily restored after it is damaged by abrasion. The thermal spray construction of superhydrophobic surfaces proposed in this research offers the advantages of precisely tailoring the surface textures and surface chemistry cost-efficiently over as large an area as desired, showing bright prospects for versatile applications.

1. Introduction

Superhydrophobic surfaces have drawn extensive interests from both academia and industry during the past decades due to their potential applications in various fields, for example anti-corrosion [1,2], anti-icing [3,4], self-cleaning [5,6], antifouling [7,8], and drag-reducing [9,10]. However, practical applications of the superhydrophobic surfaces are usually restricted by their poor mechanical stability. In nature, plants retain their superhydrophobicity by reconstructing their surfaces with micro-/nano-hybrid structures and releasing wax-like materials after destroyed [11–13]. Yet it is almost impossible for the superhydrophobic surfaces made artificially to follow nature's way when destroyed. Therefore, fabrication of the superhydrophobic surfaces with favorable mechanical stability and easy reparability is to be developed towards accomplishing long-term functional applications.

To enhance their mechanical properties, the superhydrophobic surfaces with micro-/nano- hierarchical structures have been

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attempted. For example, Kondrashov et al. reported a mechanically robust superhydrophobic surface with hierarchical roughness consisting of silicon microcones and silicon nanograss, which was achieved by a cryogenic deep reactive ion etching process [14]. Emelyanenko et al. developed a durable superhydrophobic coating on stainless steel based on nanosecond IR laser micro- and nanotexturing with subsequent chemisorption of fluorooxysilane [15]. Groten et al. fabricated superhydrophobic surfaces with combined micro-/nano-scale structures by silicon etching and subsequent coating with a monolayer of fluoropolymer [16]. The abovementioned techniques offer the superhydrophobic surfaces promising mechanical strength. However, these strategies raise the concerns of cost and processing complexity. Developing cost-efficient methods for large-scale fabrication of superhydrophobic surfaces with favorable mechanical stability and easy reparability is highly desirable. Recently, we have proposed a thermal spray route for constructing novel superhydrophobic coatings [17,18], providing the possibilities of fabricating large-scale superhydrophobic surfaces using a wide variety of engineering materials deposited on various substrates [19,20].

The idea of constructing superhydrophobic surfaces with mechanically robust and easy-repairable performances is inspired from natural hydrophobic surfaces which are able to self-heal both their structures and surface chemistry after damaged. Several recent studies report the surfaces with a roughness at two length scales to ensure that hydrophobicity retains well even after some surface features are worn away [21–23]. In this study, we present a new superhydrophobic surface with multiple length-scale structure for enhanced mechanical strength and ease of healing after destruction. Titania coating with the surfaces in cone geometry was made by plasma spray, followed by suspension flame spray deposition of polytetrafluoroethylene (PTFE)/copper nanoparticles (nano-Cu) as a top layer. The hydrophobicity and mechanical strength of the surfaces were systematically assessed and elucidated.

2. Experimental

Commercial titania powder with the size range of +15–45 μm (Sun-spraying Science and Technology Co., Ltd., China) was used as the starting feedstock for coating fabrication. The coatings were deposited by atmospheric plasma spray (APS–2000 K, Beijing Aeronautical Manufacturing Institute, China) on stainless steel plates (316L). The plasma net energy of 30 kW was used for fabricating the coatings. Micropatterned topographical features of the coatings were achieved using stainless steel mesh as shielding plate. The meshes with the size of 74 μm, 125 μm, and 173 μm were used in turn for constructing cone-like geometry. Argon was used as the primary gas and the powder carrier gas with the flow rate of 42 l/min and 4 l/min, respectively. The auxiliary gas was hydrogen with the flow rate of 11 l/min. The powder feeding rate was 50 g/min and the spray distance was 150 mm. Further fabrication of a PTFE/nano-Cu layer was made on the pre-micropatterned titania coatings. PTFE/nano-Cu suspension was employed for the coating deposition according to an established protocol by suspension flame spray [17]. The FS-4 flame torch (Wuhan Research Institute of Materials Protection, China) was employed for the spraying. For preparing the PTFE/nanoparticles suspension, Cu nanoparticles with the size of ~835 nm in mean diameter (Xinshengfeng Technology Co., China) were added into alcohol. The suspension with Cu concentration of 5.0 wt.% and PTFE (Zhejiang Juhua Co., China) concentration of 5.0 wt.% were prepared.

Microstructure of the coatings was characterized by field emission scanning electron microscopy (FESEM, FEI Quanta FEG250, the Netherlands). Chemical composition of the samples was detected by X-ray diffraction (XRD, Bruker AXS, Germany) using Cu Kα radiation operated at 40 kV and 40 mA. Contact angle and sliding angle measurements were carried out using a video-based optical system (Dataphysics OCA20, Germany). The numerical values were measured at room temperature after water droplet was knocked down onto the surface of the samples. Volume of each distilled water droplet was 5 μl for contact angle measurement and 15 μl for sliding angle measurement. For every contact/sliding angle for each sample, five measurements were made from different surface locations. Sizes of the starting particles were examined using Zetasizer Nano ZS (Malvern Instruments, UK). Mechanical durability of the constructed coatings was assessed by scratch testing method, which has been extensively used for evaluating hydrophobic surfaces [24–29]. 800 # sandpaper was used as the abrasion surface. The hydrophobic surfaces were tested facing the sandpaper with varying sliding distances under an applied pressure of 25 kPa.

3. Results and discussion

To comparatively investigate the influence of topography of the surfaces on their hydrophobicity and mechanical durability, the as-sprayed titania coatings without the assistance of stainless steel mesh were also fabricated. The as-sprayed titania coatings display relatively smooth topographical morphology with typical rough microstructure (Fig. 1a-1) and their thickness is tunable by easily controlling the spray processing (e.g., ~90 μm as shown in Fig. 1a-2). Two length-scaled topographical morphology of the titania coatings was successfully fabricated with the aid of the mesh shielding during the plasma spraying (Fig. 1b and c). The unique micropatterned surfaces show clearly the cone-like structural features with two length scales profile. The mesh size decides crucially the key topographical features of micropatterned titania coatings, namely the height and root diameter of the cones and the distance between two adjacent cones. The unique protrusions exhibit the diameter of ~128 μm (Fig. 1b-1), ~192 μm (Fig. 1b-2), ~342 μm (Fig. 1 b-3) at root and are sharp at top, respectively, depending on the size of the shielding mesh used for the fabrication of the surfaces. Cross-sectional view of the cone geometry shows clearly unique structural feature (Fig. 1c and the enlarged view shown as the inset in Fig. 1c). In addition, almost identical microstructures are seen for all the coatings (insets in Fig. 1a-1 and b-1), which suggest porous nature of the microenvironment on the surfaces of the constructed coating matrix. The micro-porous structures provide ideal platform for settlement of additional nanomaterials. These features should affect performances of the coatings.

Further modification of the as-sprayed titania coatings was done by the suspension flame spray deposition of PTFE/nano-Cu composites. Morphologies and size distribution of the untreated and PTFE treated Cu nanoparticles are shown in Fig. 2. The starting well-dispersed Cu nanoparticles have the size of ~835 nm in mean diameter (Fig. 2a). After the PTFE treatment, Cu particles get notably aggregated, showing the size of ~15.3 μm in mean diameter (Fig. 2b). XRD characterization of the untreated titania coatings suggests presence of anatase and rutile (Fig. 3a), indicating certain transformation of anatase to rutile during the plasma spraying. This is normal since anatase transforms to rutile at elevated temperatures. Indeed the phases do not matter in this case. The additional construction of the PTFE/nano-Cu layer is further evidenced by the XRD detection (Fig. 3b). The results show successful modification of the titania coatings with the PTFE/nano-Cu top layer.

Wettability assessment revealed superhydrophilic nature of the as-plasma sprayed titania coatings with a water contact angle of less than 10°, regardless of additive patterning or not. After the further construction of the PTFE/nano-Cu top layer, all the coatings display superhydrophobicity with water contact angle (CA) of