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Efficient one-step fabrication of ceramic superhydrophobic coatings by solution precursor plasma spray

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ABSTRACT

Superhydrophobic ceramic coatings with high water contact angle and excellent water repellency were fabricated by a one-step solution precursor plasma spray process without using any low-surface-energy polymeric modifiers. The coating composition and microstructure were characterized, and showed a two-length scale micron/nano-sized hierarchical structure. The hydrophobicity of the coatings was tested via water contact angle measurement, water roll-off angle and droplet impact tests. The water contact angle of the coatings reached 163° and the water roll-off angle was about 6.5°. The microstructure and hydrophobicity of the coatings could be varied by tailoring the parameters of the spraying process. The results indicate that solution precursor plasma spray is an efficient method by which to fabricate various hydrophobic ceramic coatings in large scale.

1. Introduction

Superhydrophobic surfaces which exhibit water contact angle (WCA) larger than 150° and roll-off angle smaller than 10° have numerous applications in self-cleaning, anti-corrosion, anti-icing and drag reduction etc [1]. The wettability of the surfaces is generally determined by the surface energy which is controlled by the surface chemical composition, and the surface topography which can enhance both the hydrophobicity and hydrophilicity [2]. In terms of these two factors, numerous approaches have been applied to fabricate superhydrophobic surfaces which mainly include lithography, template, electrospinning, sol-gel and etching etc [3]. These approaches focus on using low-surface-energy polymeric modifiers and constructing appropriate structures on the substrate surfaces. In spite of the excellent hydrophobicity, these artificial surfaces are not durable and deteriorate quickly in harsh working conditions such as high temperature and abrasive wear [2]. In addition, most of these techniques are very complicated, time-consuming and low-efficiency which are not suitable for large-scale fabrication.

Plasma spray, as a highly-industrialized thermal spray technique, is widely used due to its high deposition rate, simple operability and the capability to melt almost all kinds of materials. Solution precursor plasma spray (SPPS) is a newly developed plasma spray process which uses aqueous solution precursors as feedstock. The aqueous solution precursors are injected into the plasma jet, and undergo a series of thermo-physical and thermo-chemical transformations including aerodynamic breakup, solvent evaporation, solute precipitation, pyrolysis, sintering and heating etc [4]. Very fine splats and particles can be formed which makes SPPS process to be capable of fabricating finely-structured coatings. Using the high-efficiency SPPS process to make superhydrophobic coatings in large scale has incomparable advantages over some present synthetic methods, as discussed in reference [5] where a high power (about 170 kW) plasma torch using axial feeding was used.

In this work, solution precursor plasma spray coatings were deposited using a torch of traditional design, with a maximum power of 50 kW, using radial injection. Coatings with a variety of microstructures, surface topographies and wetting behaviors could be fabricated by changing the process parameters of the SPPS process, which include the torch power, torch nozzle size and geometry, plasma gas composition, solution type, spraying distance, etc. Superhydrophobic ceramic coatings were obtained using this high-efficiency, one-step process without using any low-surface-energy polymeric modifiers. The hydrophobicity of the coatings were characterized by the WCA, water roll-off angle and dynamic impact tests.

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2. Experimental

2.1. Materials

Rare earth oxides over the entire lanthanide series have been reported to be intrinsically hydrophobic due to their particular electronic structure [6]. The 99.999% ytterbium nitrate pentahydrate ($Yb(NO_3)_3{\cdot}5H_2O$, Pangea International Limited, Shanghai, China) was used as feedstock. The solution precursor in 1 M/L molar concentration was prepared by dissolving $Yb(NO_3)_3{\cdot}5H_2O$ into the mixture of 50 wt% distilled water and 50 wt% pure ethanol. The substrates used were sandblasted 304 stainless steel (diameter is 25.4 mm, thickness is 3 mm).

2.2. Process parameters

A commercial F4-VB torch (Oerlikon Metco) was used for solution precursor plasma spray deposition of the Yb_2O_3 coatings. For the coatings described in the following, the torch was operated at a current of 700 A with an Ar/H_2 mixture as the plasma forming gas. The gas flow rates were 50 LPM for Ar and 10 LPM for H_2, which led to a total power of about 47 kW. The solution was fed into the plasma jet by a peristaltic pump via a 200 μm inner-diameter orifice with a feed rate of 33–36 g/min. The standoff distance was 30 mm. A turntable sample holder was used to get a high torch transverse speed of 1 m/s. The torch moved vertically in front of the turntable at 6 mm/s to deposit the whole substrate area for 40 passes. The as-sprayed coatings were vacuum treated (1–15 Pa) for about 24 h to remove moisture and loosely-bound oxygen species from the surface. The hydrophobicity of the coatings was characterized by the WCA, water roll-off angle, and dynamic water droplet impact behavior on the coating surface. A high speed camera (Fastcam SA5, Photron, CA, USA) was used to capture the still images showing the WCA, and to record the water roll-off test and dynamic impact of droplets at 1000 fps and 2000 fps respectively. The water roll-off angle was determined by slowly increasing the tilt angle of the substrate until the droplet began to move, then measuring the substrate angle from the corresponding frame. The WCA and roll-off angle were obtained by analyzing the images obtained using ImageJ [7], and were reported as the average of 5 measurements ± one standard deviation.

3. Results and discussion

The XRD pattern of the coatings (Fig. 1a) shows that the coating material matched with the Yb_2O_3 reference pattern at all peaks. This indicated the $Yb(NO_3)_3{\cdot}5H_2O$ solution precursors formed Yb_2O_3 coating after experiencing a series of thermo-physical and thermo-chemical transformations in the plasma jet. The sharp peaks also proved the coating material was crystalline. Using the process parameters described above, a 55 μm thick coating could be deposited over an area of 0.1 m^2 in only about 15 min, which showed SPPS is a highly efficient method for the fabrication of superhydrophobic coatings.

Fig. 1b shows the extremely high WCA of the coating. Water droplets of different volumes placed on the coating surface presented smooth near-spherical shapes. The WCA was measured as 163 ± 1.5° by placing water droplets with a volume 6–7 μl on different coating areas. To exam the stability of the wetting behavior, the WCA was followed for a period of about 3 min, with no measurable change in the WCA.

The cross sectional microstructure (Fig. 1c & d) exhibited obvious cluster structures with gaps between them. The clusters developed after the coating thickness exceeded about 18 μm, and grew to a height of about 56 μm as marked in Fig. 1d. The cluster structures resulted from a shadowing effect, as has been observed previously in suspension and solution precursor spray processes [8]. This effect arises when small particles are entrained in the plasma gas flow as it is diverted parallel to the substrate. The particles then do not impact the substrate along a path normal to the substrate, but rather impinge on surface asperities. Consequently, the cluster

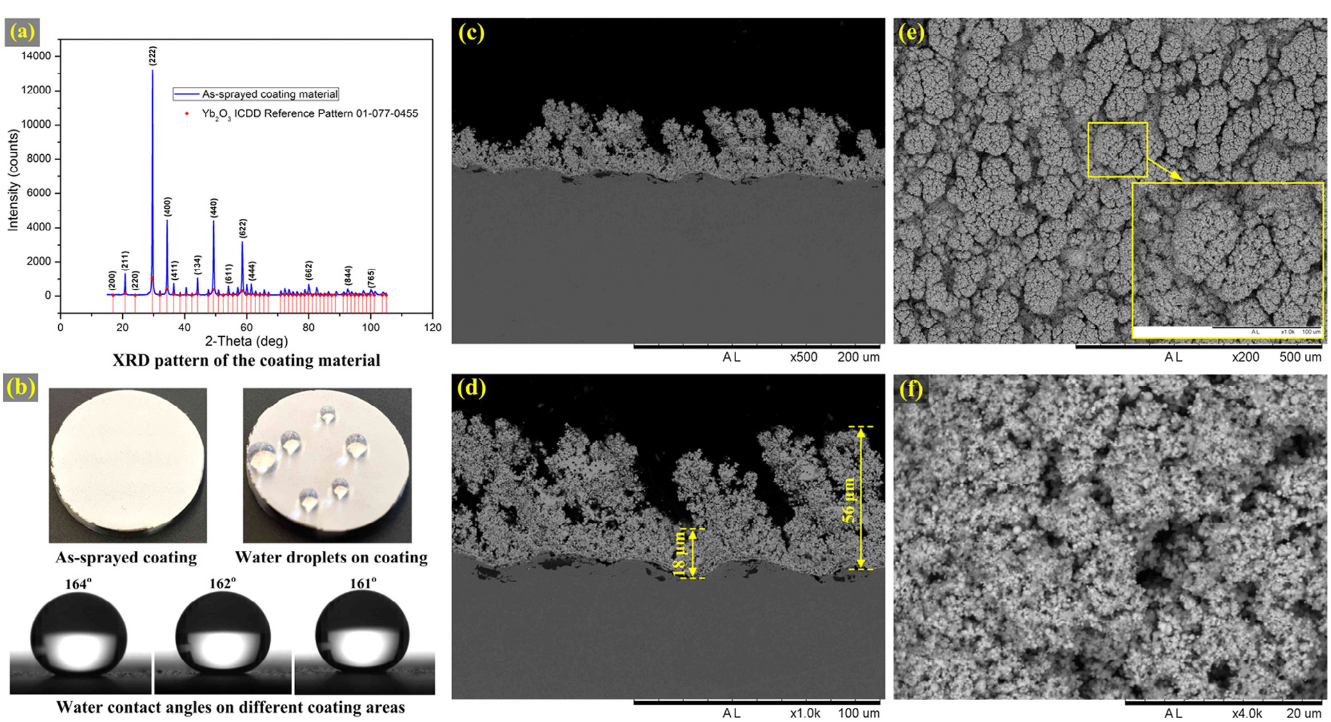

Fig. 1. (a) XRD pattern of the coating material; (b) Water droplets on the coating and WCA measurement; (c, d) Cross sectional microstructure; (e, f) Top surface microstructure.