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A super-hard superhydrophobic Fe-based amorphous alloy coating

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ABSTRACT

Poor durability prominently limits the application of superhydrophobic coatings. In this study, a super-hard superhydrophobic Fe-based amorphous alloy coating was prepared on Q235 steel substrate via plasma spraying and further surface modification with heptadecafluoro-1,1,2,2-tetrahydro-decyl-1-trimethoxysilane (FAS17). The SEM observation showed that the coating surface feature varied with plasma spray power. The coating with a spray power of 30 kW has a triple-level hierarchical surface feature with no-flattening particles in dozens of micron size, adherent splashing particles in several micron size, and wool-like oxides with nano size. The corresponding water contact angle and sliding angle were 154° ± 2° and 4° ± 1°, respectively. The X-ray diffraction results revealed that the coatings have amorphous structure; however, the crystallization and oxidation may occur with increasing spray power. The energy dispersive spectroscopy result confirmed that the nano wool-like oxides comprise multi metal oxides, in which Fe, C, and Mo dominated. The adherent splashing particles were rarely found at 15 kW, whereas the wool-like oxides were not at all observed at 15 and 22.5 kW. Thus, the hydrophobicity decreased when the spray power increased. The X-ray phosphorescence spectroscopy test verified the chemical bonding of FAS17 and coatings. In addition, in virtue of super-high microhardness of 884 ± $61HV_{0.1}$, the superhydrophobic coating at 30 kW spray power displayed excellent anti-wear property under a pressure as high as 10 kPa.

1. Introduction

Superhydrophobic coatings with water contact angle (WCA) > 150° and sliding angle (WSA) lower than 10° have a wide potential application in the fields of self-cleaning, anti-corrosion, anti-icing, water proofing, biomedical instrument, marine antifouling [1,2], etc. There are two key factors to fabricate superhydrophobic coatings: low surface energy and appropriate surface features (to trap the air within Cassie-Baxter state or increase the true contact area within the Wenzel state) [1]. Concerning the first factor, hydrophobic polymers are always preferred by researchers, especially fluorinated polymer [3]. However, the poor mechanical durability prominently limits the application of these polymers. Significant efforts have been focused to improve the mechanical durability with metal oxides to form composite coatings, for example WO_3 [4], TiO_2 [5], SiO_2 [6], ZnO [7], and Cu_2O [8], by the virtue of higher strength, stiffness, and hardness of oxides. Nevertheless, polymer/oxides composite coatings have relatively low adhesion strength if used on metal surfaces.

Therefore, metallic superhydrophobic coatings have attracted extensive attention owing to the better coordination of strength, toughness, and adhesion. Cu [9], Ni [10], Co [11], Fe [12], and their alloys [13,14] coatings were fabricated via electro brushing [15,16], electrodeposition [11], electroless plating [17], thermal spraying [18], and further chemical modification methods. Among these methods, thermal spraying is notable for its good adherent strength, high efficiency, and wide application for various substrate and coating materials.

Fe-based amorphous alloy coatings are attractive for the ultra-hardness, anti-corrosion, and anti-wear properties [19]. However, Fe-based amorphous alloy coatings fabricated by the high velocity oxy-fuel (HVOF) spray and further modified with dodecanethiol displayed a WSA as high as 16° [19], because of the lack of hierarchical surface features like lotus leaves.

Herein, we report a new Fe-based amorphous alloy superhydrophobic coating with hierarchical surface features. This coating was prepared via plasma spray with various powers and further immersion in alcoholic FAS17 solution. The hierarchical surface microstructure was controlled by the plasma spray powers, exhibiting one-level, two-level, and three-level features. Thus, the hydrophobicity differed for the coatings with different surface features. In addition, the three-level hierarchical surface presents superhydrophobicity. This newly constructed superhydrophobic coating has ultrahigh microhardness and durability against strong abrasion, showing long-term superhydrophobicity. This study also provides an effective and easy

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Table 1
Element wt% obtained by the combination of LA-ICP-MS (#) and XRF (*) analyses.

Element	Fe#	Cr#	Mo#	C*	Si*	Co#	Al*	Y#
wt%	67.19	21.00	8.84	2.56	0.22	0.15	0.02	0.01

method for controlling the hierarchical surface feature of superhydrophobic metal coatings via moderate oxidation.

2. Experimental

2.1. Fabrication of coating

A commercial spherical ferrous-based amorphous alloy powder with D10 of 12 μm, D50 of 29 μm, and D90 of 56 μm purchased from Guanzhou Wandun Amorphous Metals Trading Limited was used as the feedstock. The chemical composition obtained by the combined analysis of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS, ESI NWR 213-7900) and X-Ray Fluorescence Spectroscopy (XRF, Bruker S8 TIGER) is listed in Table 1. Because large roughness was testified against hydrophobicity, the as-received powder was screened by 500-mesh before spray in order to decrease the surface roughness of the sprayed coatings. Then, the coating was fabricated via air plasma spraying (APS) process. ATSM A283 steel plates with $10 \times 5 \times 2\ \mathrm{mm}^3$ were employed as the substrates. The Runs 1, 2 and 3 correspond to the spray powers of 15, 22.5, and 30 kW, respectively. The arc currents were kept at 300, 450, and 600 A, corresponding to the Runs 1, 2, and 3, respectively. The other spray parameters such as the arc voltage of 50 V, argon flow rate of 3000 L/h, hydrogen flow rate of 80 L/h, spray distance of 100 mm, and gun pass speed of 350 mm/min were kept constant.

2.2. Surface modification by FAS17

The as-sprayed coating was further modified by heptadecafluoro-1,1,2,2-tetrahydro-decyl-1-trimethoxysilane (FAS17) (97%) to reduce the surface energy. For the condensation reaction of the functional group $-OCH_3$ of FAS17 and –OH of the coating [20], the samples were immersed in a 0.1 mol/L FAS17 alcoholic solution at 60 °C for 2 h and then air-dried in an oven at 120 °C for 1 h. The samples were ultrasonically cleaned with ethyl alcohol (analytical reagent grade) before and after immersing in FAS17 solution.

2.3. Characterization

Surface morphology was observed by scanning electron microscopy (SEM, SU3000, Hitachi), field-emission scanning electron microscopy (FESEM, Sigma500, Zeiss) with secondary electron mode and LSCM (LSM700, Carl Zeiss). Phase analysis was determined by X-ray diffraction (XRD, D8 ADVANCE, Bruker) at a scanning speed of 0.02°/step. Surface element was detected by X-ray phosphorescence (XPS, ESCALAB 250Xi, Thermo Fisher) equipped with a radiation source of Al Kα (hν = 1486.6 eV), and peak deconvolution was implemented to confirm FAS17 grafting on the coating surface.

WCA and WSA were measured using a video-based optical instrument (JC2000D) with 5 μL deionized water droplets at room temperature. Microhardness was tested using a microscopic hardness meter at a load of 100 g and dwell time of 10 s. Five points were tested for each coating. Wear resistance of the superhydrophobic coatings was evaluated by a scratching test vs. 1000 grit sandpapers. The coatings were dragged on a rail covered by sandpapers with 5 mm width and 20 cm length, and the coating surface faced to the sandpaper. 10, 50, and 200 g weights were loaded on the samples. The WCA and WSA were measured for every wear distance until WSA reached 90°.

3. Results and discussion

3.1. Surface morphology observation

Appropriate surface features and low surface energy [1] are two main requirements to form a superhydrophobic surface; therefore, in this study, we first investigated the surface morphology. Fig. 1 shows the surface micrographs of all the as-sprayed coatings observed by SEM, and the corresponding WCA photos captured using a JC2000D. Fig. 1(a, d), (b, e), and (c, f) corresponds to Runs 1, 2, and 3 coatings, respectively. From a general view of Fig. 1(a), (b), and (c), the surface of plasma sprayed Fe-based amorphous alloy coatings has a relatively large roughness, because of the papillas with inhomogeneous distribution. Fig. 1(d), (e), and (f) shows the magnifying regions in the contour of Fig. 1(a), (b), and (c), respectively. For Run 1, the papilla was constituted by adherent partially flattening (e.g., Point A) and no-flattening (e.g., Point B) particles, as shown in Fig. 1(d), so that the coating has a roughness in tens of micron and is mainly determined by the particle size. When the spray power increased to 22.5 kW (i.e., Run 2), sub-scale structure appeared on the papillas. This structure consists of adherent smaller particles mainly caused by splashing of molten particles, e.g., Point C. For Run 3 at 30 kW, some nano oxides grew on the entire surface, especially on the papillas. The appearances of oxides make the coatings with hierarchical topography. At a part of papillas, e.g., the point D in Fig. 1(f), there is triple-level hierarchical surface, constituted of no-flattening particle as the first level in dozens of micrometers, adherent tiny particles as the second level in several micrometers, and oxides level in nanometer dimension.

Surface roughness was measured by laser scanning confocal

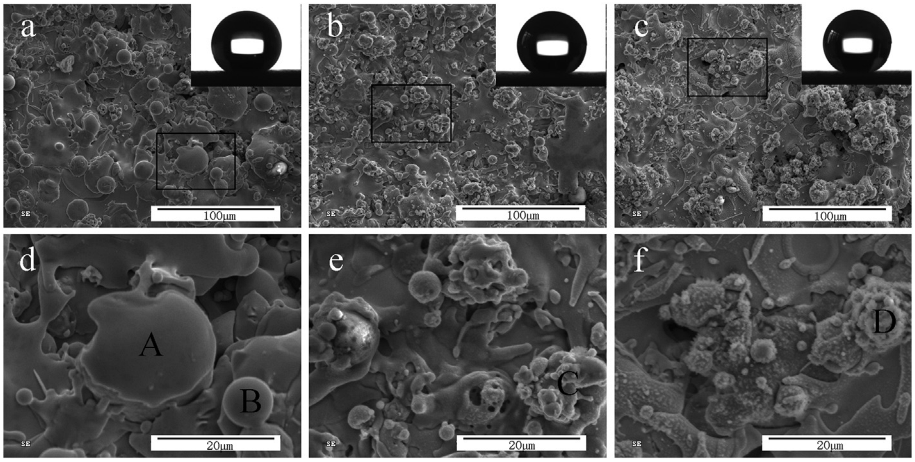

Fig. 1. SEM surface micrographs of (a, d) Run 1, (b, e) Run 2, (c, f) Run 3 as-sprayed coatings and the corresponding static WCA photos. The Figs. (d), (e), and (f) correspond to the contoured regions of (a), (b), and (c), respectively.