Fabrication of Durable and Renegerable Superhydrophobic Coatings on Metallic Surfaces for Potential Industrial Applications

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Abstract— Fabrication of anti-corrosion and self-cleaning superhydrophobic coatings for metallic surfaces which are regenerable and durable in the aggressive conditions has shown tremendous interest in materials science. In this work, the superhydrophobic coatings on metallic surfaces (aluminum, steel, copper) were prepared chemical etching process. Thermal, mechanical, ultra-violet stability of these coatings was also tested. Along with this, regeneration of coatings and self-cleaning, corrosion resistance and water repelling characteristics were also studied. The surface morphology shows the presence of rough microstructures on the treated surfaces and the contact angle measurements confirm the superhydrophobic nature. Superhydrophobic surfaces show the excellent self-cleaning and anti-corrosion behaviour. Water jet impact, floatation on water surface, and low temperature condensation tests proves the excellent water-repellent nature of the coatings. Additionally, these coatings are found to be thermal, mechanical and ultra-violet stable. Further, these surfaces are reproducible. These durable superhydrophobic metallic surfaces have potential industrial applications.

Keywords- Superhydrophobic; Water-repellent; Anti-corrosion; Self-cleaning

I. INTRODUCTION

Superhydrophobicity is defined as when the contact angle of water droplet on surface is greater than 150° with a negligible hysteresis. **S**uperhydrophobic surfaces also behave as self-cleaning, water repellency anti-corrosive, anti-icing, anti-scratching, anti-fouling, anti-bacterial, and anti-aging surfaces. In nature, especially water striders [1] and lotus [2] are known for excellent superhydrophobic properties. Conventionally, superhydrophobic surfaces are produced by grafting a low-surface energy material on the roughened surface [3]. Over the past two decades, tremendous research has been carried to develop artificial superhydrophobic coatings on different substrates such as glass [4], polymers [5], mesh [6], papers [7], textiles [8], metals [9], and wooden [10] for anti-scratching, self-cleaning, anti-icing, drag-reduction, oil-water separation and anti-corrosive applications. Furthermore expansion of superhydrophobicity research field is attracting to researcher due to its outstanding industrial applications. Metals have tremendous applications in industries and household activities, but these applications are limited due to corrosion. However, superhydrophobic coatings on metallic substrate can slow down the process of corrosion because of their self-cleaning and water-repellent properties. The etching of metals in acid and/or alkaline solutions can simply create rough surface. Few studies on creating superhydrophobic coatings on surfaces using chemical etching technique have been done [11-19]. Despite having excellent properties like self-cleaning, anti-corrosive, anti-icing, etc., superhydrophobic surfaces are not widely industry applicable because of lack of mechanical, thermal, and chemical stability and regenerability. In current work, regenerable and durable superhydrophobic coatings on metallic surfaces were prepared by chemical etching technique.

II. EXPERIMENTAL DETAILS

Cleaned aluminum and steel substrates were immersed in NaOH and solution of HNO_3 and HCl (ratio 1:3) for 60 minutes, respectively. Afterward, etched aluminum, etched steel, and untreated copper samples were immersed in 20 gm/liter ethanol solution of lauric acid for varying time 30 min, 24, and 72 hours, respectively. Then they were dried in air for 24 hours. Surface morphologies of the prepared samples were examined with scanning electron microscopy (SEM) (Nova NanoSEM, FEI).

Contact angle measurement was done at room temperature through sessile drop method using Drop Shape Analyser (DSA) (25, Kruss, Germany) with droplet of distilled water of 7-10 μL drop volume. Additionally, durability for UV exposure, heat treatment, and mechanical disturbances on superhydrophobic coatings was studied. Further, regeneration of coatings was also done. Along with, self-cleaning, corrosion-resistant, and water repelling characteristics were also studied.

In thermal analysis, a simple thermal test was carried out in a hot air oven at varying temperature. Contact angles were measured after heating the samples.

The corrosion test was carried out by simply immersing the superhydrophobic surface in acetic acid solution and sodium chloride solution and their contact angles were measured and effect of these solution on the superhydrophobic surface was analyzed.

The self-cleaning test was carried out by simply sprinkling small amount of graphite powder taken from a pencil on the untreated surface and the superhyhydrophobic surface.

In adhesive peeling test, it was carried out by using commercially purchased insulation tape and the peeling was done on the superhydrophobic surface until it lost its superhydrophobicit

Floatation on water surface test is carried out by keeping the two superhydrophobic samples prepared from different etchants on the water surface in a petri dish and it was observed that how long the prepared samples remain afloat.

Water jet impact test was carried out by allowing the prepared sample surfaces and the untreated metallic surface to face the water jet which is released from a syringe and the interaction between the water jet and the sample surfaces is observed. It was carried out for 1 min.

The samples are simply bent from different directions and the water droplets are dropped on different positions on the bent surfaces to study if the bending has affected the superhydrophobic surface or not. Here repeated folding of samples were carried out.

Ultraviolet irradiation test was carried out by placing the samples in a UV curer(UltraV-C1, Apex Instruments Co.Pvt.Ltd, India) and exposing it to a ultraviolet light of wavelength 254 nm.

III. RESULTS AND DISCUSSION

Chemical reactions of NaOH with aluminium and HNO_3+HCl acidic solution with steel result in an etching process leading to a rough microporous structure on the surface. After etching aluminium and steel substrates, the samples were immersed in lauric acid solution which results in the formation of sponge like layer on the surface as shown in fig 1 (a, b). This happens because the carboxyl in the positive end of the lauric acid reacts with the hydroxyl or the steel/aluminum atom through dehydrating process.

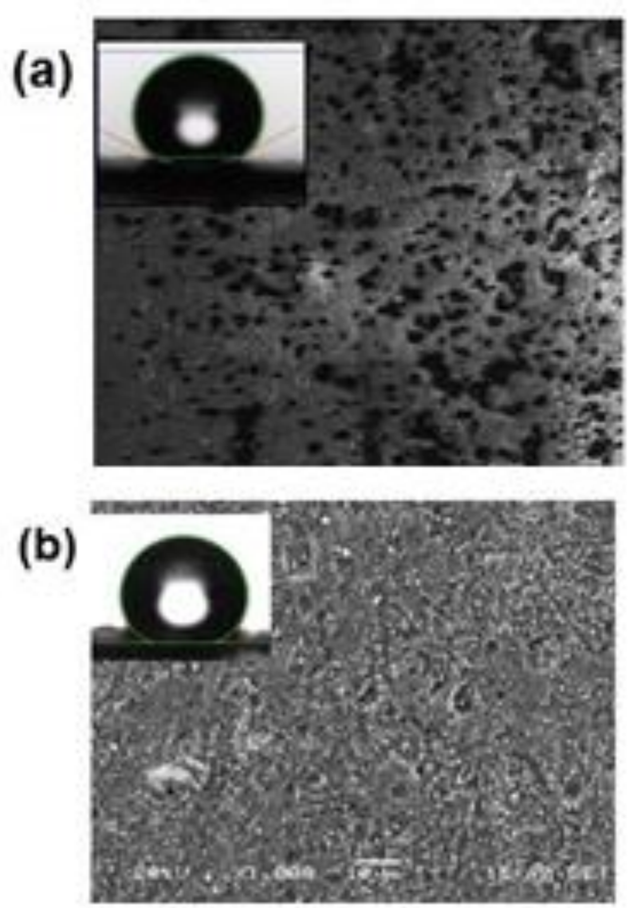

Fig. 1. SEM images of superhydrophobic coatings on (a) aluminium, and (b) steel surfaces. Insert shows a water drop image on corresponding surface.

The copper surfaces were immersed in lauric acid solution which results in the formation of flowerlike microclusters on the surface as shown in fig 2. Copper ions are released continuously from the copper surface in fatty acid solution; these ions immediately are captured by carboxyl in the positive end of the lauric acid. The formation of a rough micro-cratered surface, in combination with a modified surface chemistry arising from lauric acid, contributes to the creation of superhydrophobic and water contact angles for all three are found to be more than 150°.

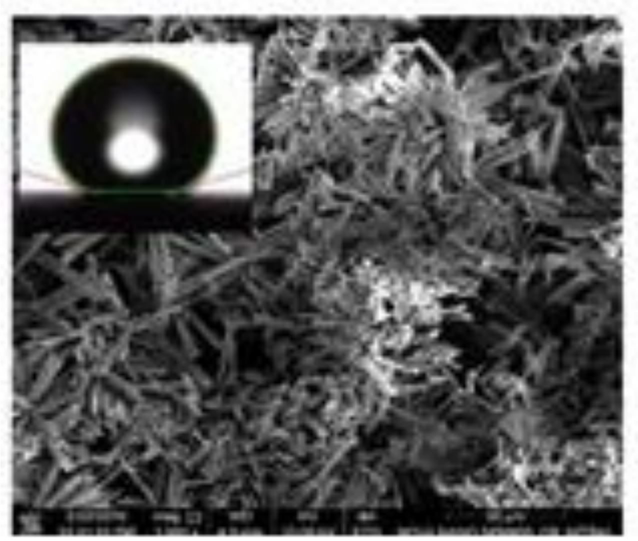

Fig. 2. SEM images of superhydrophobic coatings on copper surfaces. Insert shows a water drop image on corresponding surface.

For practical purposes, these metallic surfaces are to be exposed to elevated temperature. Superhydrophobic samples were annealed in an oven for 1 hour at elevated temperatures varying from 40 to 300 °C. Superhydrophobicity aluminum remains stable and is unaffected upto 170 ºC, after this contact angle starts decreasing and no longer remains superhydrophobic after 250 ºC (Fig. 3).

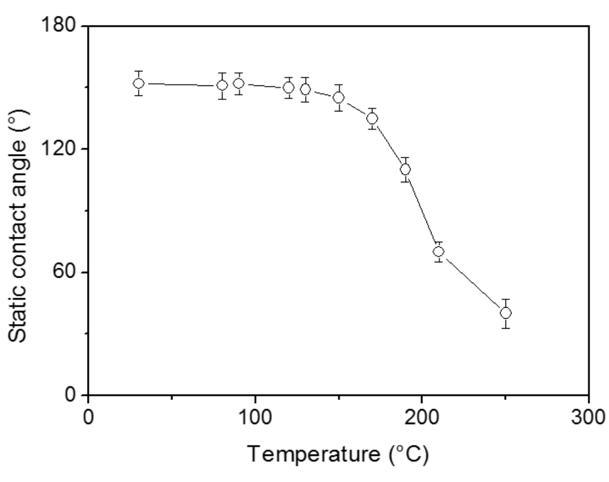

Fig. 3. Effect of temperature on the superhydrophobic surfaces which were heated for 1 hr.

It is observed that when the elevated temperature is between 40 and 120 ºC, the water contact angle of the steel and copper samples remain constant that there is not much change which means that the surface superhydrophobicity remains stable and is unaffected within this temperature range. Metallic surfaces comes in humid conditions or comes in contact of water for longer time, they becomes corrode. The superhydrophobic samples were kept in acidic medium of acetic acid having a 5% v/v concentration for varying time from 1 hour to 100 hours. Alumnium, steel, and copper coatings are unchanged for 24, 6, and 12 hours in acetic acid solution (Fig. 4), respectively. Superhydrophobic surfaces are also found to be UV stable for several hours.

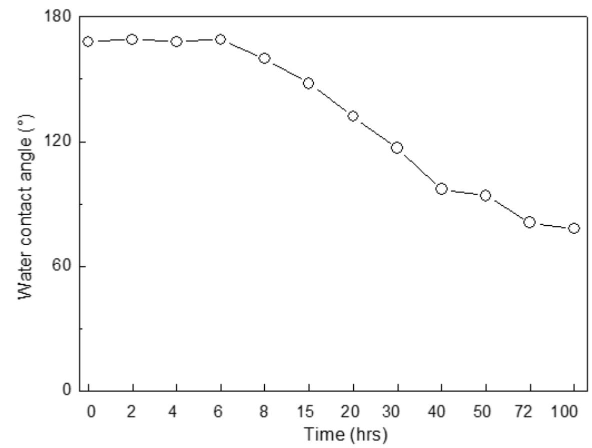

Fig. 4. Effect of immersion time in acetic solution on the superhydrophobic copper surface.

Coating shows the excellent self-cleaning properties as shown in fig. 5. The untreated metallic samples do not have self-cleaning property as few drops of water are dropped on it the graphite powder still sticks to the untreated metallic surfaces. While it can be observed that the water droplets clean the surface by carrying the powder along with them as they slide down the surface displaying the self-cleaning nature of the prepared superhydrophobic surfaces.

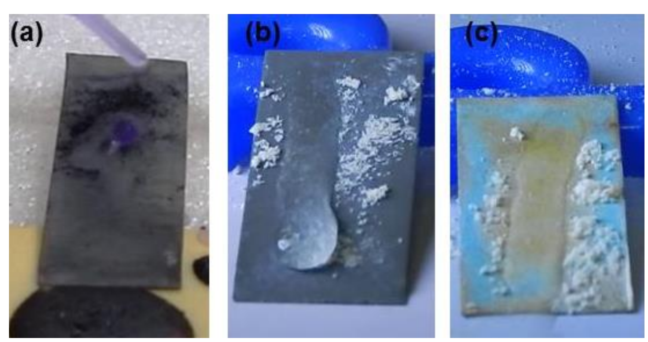

Fig. 5. Optical images of self-cleaning behavior of superhydrophobic coating on (a) aluminium, (b) steel, and (c) copper surfaces.

It is experimentally observed that coating sustains several times of adhesive peeling test. It is observed that superhydrophobicity of coating remains unchanged and water droplets fall off the surface till several cycle of adhesive tape peeling. After that, coating degrades and achieves sticky superhydrophobicity.

Also, mechanical disturbances due to bending and folding have not much effect on the superhydrophobicity (Fig. 6). The surfaces are bent to study its effect on the superhydrophobic surface. The samples were taken for the bending test and after that water droplets were released on different positions of the bent surfaces. It was observed that upto several bends the water droplets maintain their spherical shape and bounce off but after that the droplets stick to the surface for both the samples.

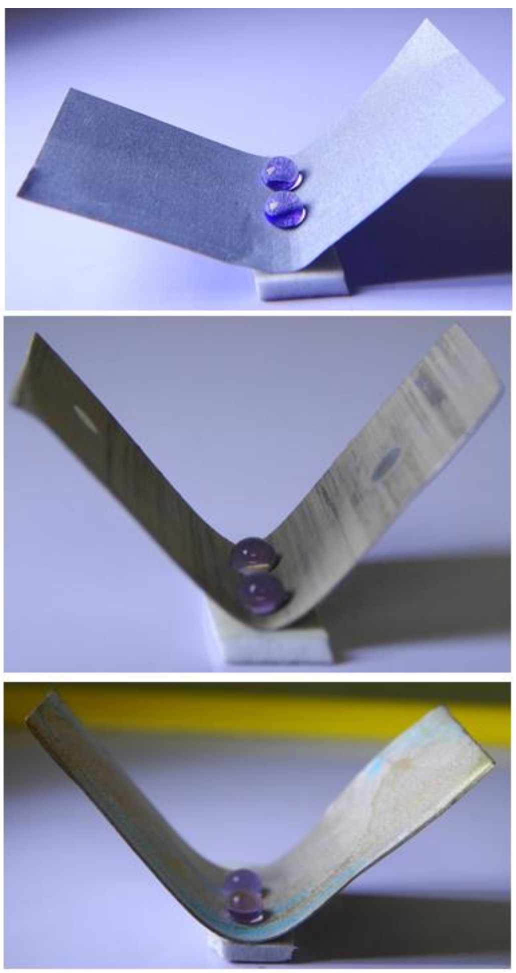

Fig. 6. Optical images of surface bending of superhydrophobic coating on aaluminium, steel, and copper surfaces.

Regeneration of superhydrophobic coating is very important for its practical application because often surface undergoes in extremely harsh conditions and surface can easily damage. For instance, when coated sample was continuously annealed at 300 °C for 6 hours, water contact angle is also found to be less than 10°, i.e. surface was completely damaged due to high and continuous heating and superhydrophobicity of surface is switched to superhydrophilicity. For regeneration of the coating the damaged superhydrophobic coating sample was again immersed in ethanol solution of lauric acid for 30 min and then air dried for 24 hours. The coating regenerated and restored its superhydrophobicity. The surface regains its superhydrophobic characteristic, confirming that this coating is regenerable.

By performing low temperature condensation, water jet impact, and floating tests on above superhydrophobic coatings, it is asserted that coatings have excellent water repelling nature. Impact of high speed water jet on superhydrophobic aluminum, steel and copper surfaces were observed and compared with impact on as-received metallic surfaces. On spraying water, it spreads immediately on as-received metallic surfaces but it bounces off the superhydrophobic metallic surface in the opposite direction as shown in Fig. 7 and this bouncing of water was continuously seen for several minutes.

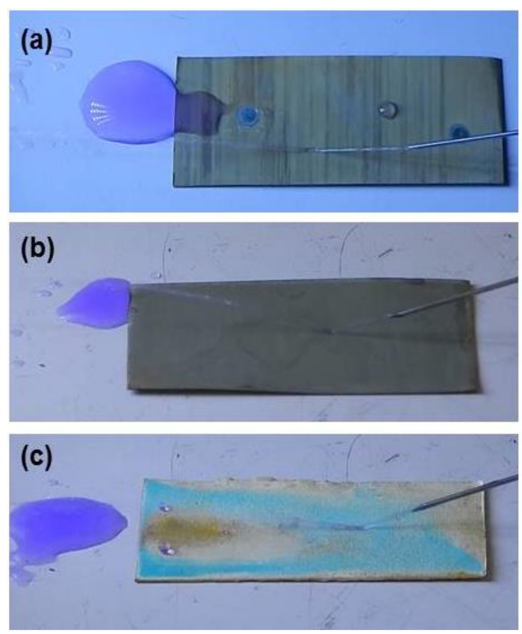

Fig. 7. Optical images of water jet impact on (a) aluminium, (b) steel, and (c) copper superhydrophobic surfaces.

IV. SUMMARY

In this paper, superhydrophobic coatings on metallic surfaces have been synthesized by chemical etching process. Wettability and surface morphology of modified surfaces were characterized using contact angle measurement technique, and SEM, respectively. Mechanical stability, thermal stability, UV stability, water repellent, self-cleaning, and corrosion tests were also performed. SEM results confirm the presence of a rough microstuctures on the treated surfaces and the contact angle measurements reveal the superhydrophobicity. Water jet impact, water floatation, and condensation tests assert the excellent water repellent nature of coatings. Also thermal, mechanical and UV stabilities of coatings are also evaluated. Further, coating shows the excellent self-cleaning and corrosion-resistant property. These mechanical, thermal and UV stable and regenerable superhydrophobic metallic surfaces with excellent water repellent properties are having potential application in anti-corrosion and self-cleaning applications.

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