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Regular Article

Fabrication of bioinspired, self-cleaning superliquiphilic/phobic stainless steel using different pathways

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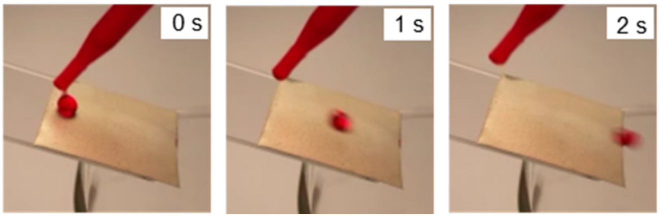
GRAPHICAL ABSTRACT

Superliquiphobic nanocomposite coating on a stainless steel substrate surface



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ABSTRACT

The mechanical properties, corrosion-resistance, and aesthetics of stainless steel make it one of the most important and widely used materials worldwide in the construction, food, and transportation industries just to name a few. In this paper we demonstrate how these properties can be further enhanced by changing the hydrophilic stainless steel surface to be superhydrophilic, superhydrophobic, or superliquiphobic. Creation of these functional surfaces requires hierarchical roughness and chemistry. Roughness is created using various pathways including sandblasting, chemical etching, and nanocomposite coatings. Surface chemistry is controlled using methylchlorosilane, nanoparticles in methylphenyl silicone, and fluorosilane treatment. The broad approach allows for direct comparisons of these pathways. Resulting treatments can create stainless steel surfaces with a hexadecane contact angle of 155° and tilt angle of 7–10°. Discussions of rust-avoidance and coating through condensation reactions are included. Enhanced properties of self-cleaning behavior, anti-icing behavior, wear resistance, and bending resistance are demonstrated on stainless steel 304 L. Stainless steel 430, which is more corrosion prone than stainless steel 304 L, is then used to demonstrate transferability of the treatments and corrosion resistance imparted through superliquiphobicity.

1. Introduction

Innovations to smelting technology around 1200 BC allowed steel, an iron-carbon alloy, to bring the Bronze Age to an end. Over the ages, steel innovations have continued in terms of both alloys, such as Wootz and shear steel, and production methods, such as the use of blast furnaces and Bessemer or Siemens steelmaking processes [20]. Another major innovative milestone, resulting in a new class of material, came with the observation that steel high in chromium content was resistant to some acids. This observation, first made by Berthier in 1821, resulted in chromium-rich,

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corrosion-resistant steel known as stainless steel (SS). A series of discoveries advanced this work, culminating with Harry Brearley producing the first commercial martensitic stainless steel while improving gun barrels in 1913 [14].

Stainless steel has chromium content greater than about 10.5 wt%. The chromium imparts corrosion resistance on stainless steel through its ability to form highly adherent, impervious chromium oxide layers on the steel surface. This layer, only a few atoms in thickness, protects (passivates) the underlying metal. Additionally, this ability allows for the surface of the steel to be treated for aesthetics (i.e. brushed or polished). The combination of mechanical properties, chemical corrosion resistance, and aesthetics has made stainless steel prevalent throughout society, and the following examples represent just a few of the many uses. In construction, stainless steel imparts advantageous properties of durability, aesthetics, ductility, and corrosion resistance [2]. Stainless steel meets the harsh environmental demands of chemical transport, such as piping or rail cars. Stainless steel is prevalent in the food industry due to its ability to be more easily cleaned and disinfected [8]. Due to the worldwide scale of usage of stainless steels, all innovation has the potential for a very large impact, and one area of interest has been through surface modification. One can imagine the usefulness of naturally liquid repellant and anti-fouling tabletops, tar repellant railroad car transports, anti-icing airplanes and windmills, or drag reduction in pipe flows.

Surface modification in this instance refers to the ability to control a surface's wettability. At the extremes of the wettability spectrum, superliquiphilic surfaces and superliquiphobic surfaces can enhance desirable properties or impart new ones. Examples include making or giving a surface a surface liquid-repellency (oil and water), self-cleaning, drag-reduction, anti-smudge, and/or anti-icing behaviors. The ability to control the wettability of a surface relies on the ability to create hierarchical roughness and to control the surface chemistry. This has been learned from nature through the observation of functional surfaces such as the superhydrophobic lotus leaf [33], [5]. Hierarchical roughness can change a hydrophobic surface with a water contact angle (CA) $\approx 110^\circ$ to superhydrophobic with a water contact angle $>160^\circ$ and water tilt angle (TA) $< 10^\circ$. Similarly, hierarchical roughness combined with a hydrophilic surface results in superhydrophilicity (water CA $< 10^\circ$). When a low enough surface energy is achieved, even droplets of low surface tension liquid (e.g. oils) are repelled and the surface is known as superliquiphobic (oil CA $> 150^\circ$, oil TA $< 10^\circ$).

Table 1 presents a literature review of existing methods of producing superhydrophobic and superliquiphobic behavior on steel surfaces. The combination of hierarchical morphology and surface chemistry is required in both cases, and researchers have utilized a variety of chemical and physical methods to achieve them. Both superhydrophobicity and superliquiphobicity sections are broken into subsections based on these methods; chemical etching and coating, mechanical abrasion and coating, laser machining and coating, plasma etching and coating, and coatings only. Within each of these subsections, for each reference, the experimental details are given. The following columns offer the resultant surface morphology, contact and tilt angles (or contact angle hysteresis), and comments/results.

One can see that superhydrophobicity has been achieved through a variety of pathways. A variety of chemicals such as nitric acid, hydrofluoric acid, iron trichloride, pirhana solution, cupric chloride, sulfuric acid, have been used create roughness, which was then combined with a hydrophobic coating such as polydimethylsiloxane or a fluoro-compound [35,7,22,23,26,21,39]. Mechanical abrasion in the form of sandblasting has been another technique commonly used to create roughness followed by a hydrophobic coating [11,3,16,36,25]. Nano- and femtosecond laser machining combined with silanization has been shown as well [40,12]. Her et al. [18] make use of plasma etching to create roughness followed by siloxane deposition. Another route to creating roughness has been to add it to the substrate through coating, achieved through self-assembly [41], electroless deposition of Ag [17], electrodeposition of metals such as Ni or Zn [24,9], or aluminum arc spray [13].

Superliquiphobic surfaces are much more difficult to create and success in this area has been limited. Meng et al. [29] used a one-step chemical etching process. Perfluorocarboxylic acid was used to etch and treat iron, but the resulting surfaces did not meet the 150° threshold for superliquiphobicity. Additionally, no data was presented on the durability of the surfaces. Motlagh et al. [30,31] combined different mechanical abrasions with nanocomposite spray coating to achieve superliquiphobicity. However, the resulting surfaces were only superliquiphobic with higher surface tension liquids such as ethylene glycol. The surfaces did not show superliquiphobicity when lower surface tension liquids such as fuel oil were used. Huang et al. [19] achieved superliquiphobicity by depositing a new Ni surface and then modifying it, but did not provide any data on the durability of the coating. Overall, we find that existing technology to create superliquiphobicity on stainless steels is limited in multiple areas. Only one method used hexadecane as the test oil, with the others requiring higher surface tension oils to meet the standards of CA $> 150^\circ$ and TA $< 10^\circ$. Huang et al. [19] use hexadecane, but lack in the area of durability data.

In this study we impart superhydrophilicity, superhydrophobicity, and superliquiphobicity on stainless steel 304 L using various pathways including sandblasting, chemical etching, and nanocomposite coatings to create roughness. Coatings necessary to create superhydrophobicity and superliquiphobicity use methylchlorosilane, nanoparticles in methylphenyl silicone, and fluorosilane [38,5,27]. Various pathways provide competing methods of imparting superliquiphilicity or superliquiphobicity. The varying levels of success between the methods offer insight into altering surface roughness and coating methods. Surfaces are characterized by contact angle and tilt angle and are analyzed for self-cleaning and anti-icing behaviors and then for durability through wear-resistance and bending. Procedures used to create various wetting regimes on stainless steel 304 L are then verified on stainless steel 430. Last, stainless steel 430 (less corrosion resistant than 304 L) is used to test corrosion resistance imparted by the superliquiphobic surface modification.

2. Experimental details

In order to impart superhydrophilicity, superhydrophobicity, or superliquiphobicity on a stainless steel surface, roughness and the desired surface chemistry are necessary. The first step is to impart roughness onto the surface. The three pathways utilized on the stainless steel substrates are shown in Fig. 1. The first two, shown on the left, are sandblasting and chemical etching. These two pathways aim to create roughness out of the substrate itself. Etching utilizes acids to eat away at the substrate's surface at different rates, leaving behind roughness. Sandblasting does not remove the substrate, but deforms it using a highly pressurized particulate spray. The third pathway to creating roughness is adding to the substrate, coating using a nanoparticle/binder system, and is shown to the right in Fig. 1. Once the roughness has been created, the surface chemistry must be controlled to achieve superhydrophilicity, superhydrophobicity, and superliquiphobicity.

Steel is naturally hydrophilic, so simply imparting roughness moves it toward being superliquiphilic. When using the nanoparticle/binder system, choosing a hydrophilic nanoparticle in a methylphenyl silicone binder results in superhydrophilicity.