

Advanced materials for condensing heat transfer

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ABSTRACT

The wetting of solids by liquids is an important consideration for heat exchangers as it can have a dramatic impact on heat transfer efficiency. The use of superhydrophobic materials, surfaces or coatings is expected to give rise to next-generation high efficiency heat exchanger designs, and this is particularly the case for geothermal heat exchangers where heat exchanger materials interact with highly corrosive fluids.

In order to address this challenge, a material-by-design approach has been adopted, where nanoscale metal oxides were designed and fabricated to provide improvements to the performance of conventional hydrophobic coatings, as well as bare base materials. Novel superhydrophobic coatings were developed, consisting of a polysiloxane matrix, which provides an inherently water repellent film, and functionalized silica nanoparticles, providing bottom-up roughness. Coatings were applied to aluminum Q-panels, which had top-down engineered roughness, providing a composite structure with dual-scale roughness, necessary for superhydrophobicity. The introduction of coatings with multiple functionalities has resulted in the development of both mechanically resilient and highly repellent coatings for heat transfer applications. The novel coatings survived under prolonged immersion in an acidic water solution without changing their superhydrophobic properties, demonstrating their potential for heat exchanger applications and other applications involving moderately corrosive environments.

Key words: Superhydrophobic, silica particles; heat exchangers; coatings

INTRODUCTION

Geothermal energy is an excellent source of renewable clean power generation, as well as for heating and cooling. Unlike other renewable energy sources, it is unaffected by local climate conditions. However, the heat exchangers used in geothermal power plants are under constant threat of scale formation and corrosion due to the harsh operational conditions to which they are exposed. Therefore, surface modifications to heat exchanger materials, for example through coatings, are necessary to improving the efficiency and durability of geothermal plant. Coatings with superhydrophobic properties are highly desirable for protecting the base metal/alloy due to their unique self-cleaning, anti-fouling and corrosion inhibition properties. These properties also help to reduce the operational and maintenance costs of the equipment.

The interaction between the solid surface and working liquid significantly influences the efficiency of a heat exchanger. Many studies suggest that introducing micro- or nano-engineered features can alter the wettability of the surface and hence improve heat transfer efficiency [1]. For condensation heat transfer, where a superheated vapour comes into contact with a cooled surface/wall, heat transfer takes place through either filmwise or dropwise condensation. Filmwise condensation is undesirable because additional thermal resistance is generated due to liquid film formation between wall and vapour, decreasing heat transfer. Dropwise condensation results in droplets with various size being formed, which continuously leave the surface due to gravitational or flow forces, vacating the surface area for new droplet formation. Therefore thermal resistance is low when this mechanism is active, leading to better heat transfer between vapour and wall. Despite its benefits, dropwise condensation is challenging to promote and maintain, and requires that liquid droplets do not wet the wall surface or be anchored to it. Coatings with hydrophobic (hydrophobic/oleophobic) properties, i.e. forming a high equilibrium surface angle between the surface and droplet, are of interest for this application [2].

This study focuses on achieving hydrophobic surfaces on an aluminium substrate by introducing dual-scale roughness to improve heat transfer efficiency. To generate micro-scale roughness, pretreatment of the aluminium substrate was done via etching, anodization and grit blasting. Nano-scale roughness was achieved by reinforcing hydrophobic coatings with functionalized SiO₂ nanoparticles. Application of these modified coatings on the pretreated aluminium substrates was undertaken to achieve the desired dual-scale roughness. The wettability and durability of the developed coatings were examined, as well as the corrosion performance of selected candidate coatings, to indicate their performance for geothermal heat exchanger applications.

EXPERIMENTAL PROCEDURE

Materials and Methods

Substrate: Aluminum Q-panels (3003 H14) were degreased by immersing in a cleaning solution for 15 minutes at 65 °C.

Pretreatment of substrate: Three pretreatment methods were used:

- Method A: Etching and anodizing (hereinafter called EA)
- Method B: Grit blasting, followed by the same steps as in Method A
- Method C: Method A followed by an extra etching step (carried out in the same manner as the first etching step) (EAE)

Grit blasting was performed to provide microroughness, using aluminum oxide grit (#100) with 30 psi applied pressure in a position of 45°, 10 cm away from the nozzle. For etching, samples were immersed in sulfuric acid and sodium dichromate solution in a thermal bath at 65 °C for 30 minutes. Anodization of aluminum substrates was done in orthophosphoric acid solution for 20 minutes at 10 V (referred to as 10V20M) or 20 V (referred to as 20V20M).

Coating application: Two commercial coatings were used, Table 1, both of which were polysilazane based formulations which react with the surface and moisture from the atmosphere to cure; neither contained fluorine. Silica nanoparticles were used as reinforcing material in these coating formulations to create the nanoscale bottom-up roughness. Two different types of functionalized silica nanoparticles were used to provide the nano-scale roughness:

- Commercial: Fully dense, pyrogenic silica particles, with a particle diameter of 20 nm, surface treated with hexamethyldisilazane (HMDS) to increase their hydrophobicity (referred to as PyroSiO₂).
- Lab-made: A modified Stöber method was used to prepare mesoporous, monodispersed silica nanoparticles [3]. In short, a mixture of tetraethoxysilane (TEOS), methylated spirit (alcohol), water and ammonia was prepared and stirred for four hours. The solution mixture was left at room temperature for at least 24 hours before any further steps. Later, ammonia, water and alcohol were evaporated, and the removed solvent was replaced with fresh ethanol. This step was repeated twice to obtain the final product. The obtained particle size distribution was monomodal with an average size of 35 nm (referred to as SMS35).

Further, functionalization of the SMS35 nanoparticles was undertaken using a silane coupling agent that exchanged the surface silanol groups with aliphatic hydrocarbon or fluorocarbon groups, reducing the surface energy and increasing the hydrophobicity. Typically, silica nanoparticles were mixed with a silane reagent and catalyst, and left overnight at 65 °C.

Two types of functionalisation were performed:

- Single: with HMDS only (referred to as Single Stöber).
- Dual: with Trimethoxy(3,3,3-trifluoropropyl)silane (333) and HMDS (referred to as Dual Stöber).

A total of twelve different surface preparation methods were compared (Table 1). Six of the coating systems achieved hydrophobicity via surface chemistry only, whilst the remainder achieved hydrophobicity via a combination of surface chemistry and hierarchical roughness:

Characterization

Wettability measurement: Coating wettability was examined using a drop shape analyzer (DSA100 from KRÜSS[†]), where DI water and diiodomethane were used as standardised test liquids, and triplicate measurements were taken. A fine auto-metered syringe placed 2 µL droplets of the test liquids onto the solid surface of the coatings and high-resolution images were taken. The droplet volume was small enough that gravitational effects could be neglected. After the equilibrium state was achieved (when there was no visible change in the droplet width), the goniometer was used to measure the droplet contact angle every 0.1 s for 5 s of measurement. The total surface energy was then calculated based on the OWRK method (Owens, Wendt, Rabel and Kaelble) [4, 5].

The tilting table facility of the DSA100 was used to undertake dynamic measurements of the test liquids. The difference between the advancing and receding contact angles, (θ_{ACA} and θ_{RCA} respectively) at the maximum tilt angle, or at the point of the droplet moving was measured. This value is called the contact angle hysteresis and was measured for selected surfaces. The larger this hysteresis the more film forming the behavior of the droplets and the greater the adherence of drops to the surface. The angle at which droplets move across the surface under the action of gravity when the sample is tilted is called the sliding angle, SA. This value was also measured, and the lower the value of the sliding angle the lower the adhesion between the droplet and the surface.

[†] Trade name.

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Table 1: Test specimen prepared for examination

Sample name	Surface preparation	Coating type	Silica nanoparticle functionalization
Bare Al	Degreasing with IPA	None	None
10V20M PS_1	Method A (10V 20M)	Sharc® Sapphire [†]	None
20V20M PS_1	Method A (20V 20M)	Sharc® Sapphire [†]	None
10V20M PS_2	Method A (10V 20M)	Tutoprom™ Bright [†]	None
20V20M PS_2	Method A (20V 20M)	Tutoprom™ Bright [†]	None
20V20M PS_1 EAE	Method C (20V 20M)	Sharc® Sapphire	None
20V20M PS_2 EAE	Method C (20V 20M)	Tutoprom™ Bright [†]	None
PS_2 PyroSiO ₂ 50:50	Method B (#100)	Tutoprom™ Bright [†]	Gelest [†] silica nanoparticles
PS_2 Single Stöber 50:50	Method B (#100)	Tutoprom™ Bright [†]	SMS35 HMDS
PS_2 Dual Stöber 50:50	Method B (#100)	Tutoprom™ Bright [†]	SMS35 333/HMDS
PS_1 Dual Stöber 50:50	Method B (#100)	Sharc® Sapphire [†]	SMS35 333/HMDS
PS_1 Dual Stöber 25:75	Method B (#100)	Sharc® Sapphire [†]	SMS35 333/HMDS
PS_1 Single Stöber 25:75	Method B (#100)	Sharc® Sapphire [†]	SMS35 333/HMDS

Adhesion analysis: Tape adhesion tests, based on the cross-hatch tape test in accordance with ASTM⁽¹⁾ D 3359, and dolly pull-off tests based on ASTM⁽¹⁾ D4541 [6, 7], were used to examine the coating adhesion to the surface. The level of adhesion was assessed according to the standard (Part B) using the 5-point scale, where 5 points correlates to perfectly smooth lattice cut, and 0 points are assigned when more than 65 % of the area was affected.

The pull-off test was performed using an Elcometer 510[†] Automatic Pull-Off Adhesion Gauge. A metal dolly with 20 mm diameter was placed on the test area and stuck to the surface using LOCTITE 4061[†] (ethyl cyanoacrylate) adhesive. After the adhesive was cured (1 h drying in lab conditions), the dolly was attached to the pull-off equipment, hydraulic pressure was applied and increased gradually until the dolly was completely pulled-off from the surface.

Surface roughness analysis: Surface roughness was measured with Alicona[†] Imaging equipment. The examined parameters included: the mean roughness [Ra], the root-mean-square roughness [Rq], the mean roughness depth [Rz], kurtosis [Rku] and skewness [Rsk].

Scratch resistance/durability: A Sclerometer Hardness Tester (Elcometer 3092[†]) was used to test the scratch resistance of the candidate coatings. The body of the gauge contains a spring-loaded tool fitted with a tungsten carbide tip. The tip was pressed against the surface being tested and the gauge was moved a short distance in an attempt to scratch the coating. The coating was inspected and the spring loading was increased until the tip left a mark or destroyed the coating. The spring loading was adjusted to apply loads from 1 N to 10 N. Additionally, on a fresh area of the coating the loading was decreased to find the point whereby the tip did not destroy the coating. The gauge was placed perpendicular to the surface being tested, and sufficient downward force was applied to compress the spring by approximately 2 mm. The gauge was then moved across the surface to produce a linear scratch approximately 10 mm in length. If the surface was marked, the spring loading was reduced until surface marking was not detected.

[†] Trade name.

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⁽¹⁾ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

Corrosion performance: To analyze the corrosion performance of the developed coatings, samples of size 40 x 40 mm were immersed into a 3.5 wt.% NaCl solution, at pH 4, for seven days, at room temperature. Before immersion, uncoated surfaces were covered using Belzona-4911[†]. Further, cross-sections of samples were prepared after removing them from the NaCl solution and SEM analyses were undertaken.

RESULTS

Wettability characteristics – static contact angles

Static water and diiodomethane contact angles of test specimens are presented in Figure 1. Uncoated substrates showed hydrophilic behavior, whilst increases in both water and diiodomethane contact angles were observed after the application of all the candidate surface treatments.

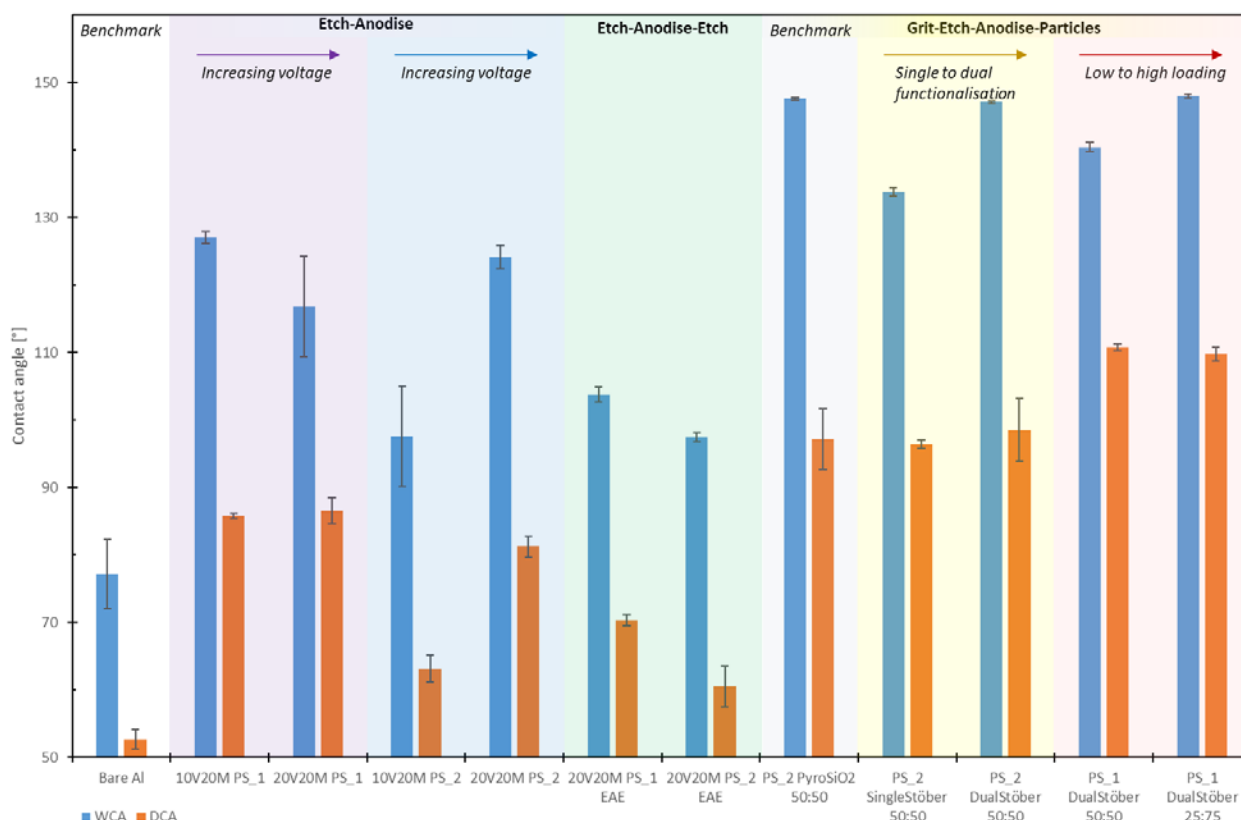


Figure 1: Static contact angles with water and diiodomethane as the probe liquids.

The best performing coatings were subjected to wettability measurements under dynamic conditions. Table 2 presents the values of the dynamic contact angle parameters, which include roll-off tilt, receding [R] and advancing [A] contact angles and contact angle hysteresis (CAH) for water and diiodomethane as test liquids. Results are also shown visually in Figure 2.