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Development of hydrophobic cupronickel surface with biofouling resistance by sandblasting

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ABSTRACT

The paper focuses on a novel method for enhancing the biofouling resistance of cupronickel (90-10 Cu-Ni) alloy by surface modification involving sand blasting, pickling and coating with silane. After optimizing the experimental parameters for polishing, pickling and sandblasting in order to develop a hydrophobic surface, the surface morphology and the wetting properties of the modified surface were characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM), confocal laser scanning microscopy (CLSM) and contact angle meter. The enhancement in resistance to bacterial adhesion was demonstrated by adhesion studies on *Pseudomonas* sp., the major biofilm former in marine environment. The silane based coating on the sand blasted surface of cupronickel alloy brought about two order reduction of bacterial attachment as compared to the control sample.

1. Introduction

Copper nickel alloys [1–3] are used in a wide range of applications as pipes and condenser tubes in sea water cooled systems because of their resistance to localized corrosion, particularly erosion corrosion and microbiologically induced corrosion (MIC). Copper is reported to resist biofouling due to copper toxicity to microbes [4]. Copper oxide and silica based functional coatings are used as biocidal functional coatings to kill *E. coli* [5]. Wire arc sprayed copper coatings on 316 L SS are found to have antibacterial property against *Escherichia coli* and *Staphylococcus aureus* [6]. Antifouling performance was demonstrated by polyethylene-copper based organic/inorganic coatings when exposed to *Bacillus* sp. [7]. However, copper resistant microbes can form biofilms and can lead to microbiologically induced corrosion of Copper alloys during prolonged service in sea water. Metabolic products of microbes like CO, HS, NH_3, many organic and inorganic acids as well as sulfur compounds such as mercaptans, sulphides and disulfides can cause localized corrosion. Extensive investigations have revealed that no material is completely immune to bio-fouling which may further lead to MIC. The copper resistance behavior of the Gram negative bacteria, *Pseudomonas* to copper was reported in literature [8,9]. Thus, toxicity alone cannot guarantee long term resistance of copper or cupronickel alloys towards biofouling or MIC. Hence, it is desirable to develop surface modification techniques that can enhance biofouling resistance of cupronickel alloys.

Bacterial adhesion to a solid surface is a crucial step in the process of biofilm formation. As microbes like bacteria move towards a solid surface, the initial interaction between the cell and the surface is governed by long and medium range forces, primarily van der Waals and electrostatic forces [10]. These forces depend on the physiochemical properties of the substrate and the bacterial surface such as hydrophobicity, surface charge [11] and surface free energy [12]. Therefore, prevention of biofouling is of paramount importance which can be achieved by employing a coating that forms a barrier between the material to be protected and the microbial environment. Most of the conventional anti-fouling coatings and paints like tributyl tin (TBT) available in the market have serious environmental issues [13] and have been banned. Thus, environmental friendly coating that can provide long term protection to the material from bio-fouling is necessary. In this regard, superhydrophobic (SHP) coatings have gained much attention in recent times due to their wide ranging applications.

Generally, surfaces whose water contact angles (WCA) exceed 90° are called hydrophobic and those with WCA above 150° are known as SHP surfaces. Lotus leaves are a typical example of SHP surface with water contact angle > 150°. Detailed studies of lotus leaf surface have confirmed the surface morphology with micro and nano scale roughness [14,15] along with wax coating using a low surface energy material lead to apparent WCA > 150°. Our earlier studies involved the

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detailed microscopic evaluation of the natural lotus leaves [16] using scanning electron microscope (SEM) and atomic force microscope (AFM). The information thus obtained served as the input for the development of SHP coatings on different substrates. Attempts were made to develop lotus effect based SHP coatings to enhance the corrosion resistance of materials in chloride and nitric acid media and to reduce bacterial adhesion. The SHP coatings have been developed on a wide variety of materials including titanium [16–19], chrome-moly steels [20,21], glass slides [22] and marine steels [23]. SHP coatings become highly relevant in the case of these materials because there is an increasing demand for their improved corrosion and biofouling resistance.

Traditionally methods such as chlorination have been used in the prevention of biofouling in cooling water systems. In the recent past there have been efforts to employ SHP surfaces and coatings to mitigate bacterial adhesion. In 1994, Callow and Fletcher [24] listed the various works on the adhesion of microfouling slimes and algae on low surface energy material surfaces. There are reports in which authors have demonstrated less number of bacteria on low energy substrates [25,26] whereas in some other reports hydrophobic surface seem to be the preferred surfaces for bacterial adhesion [27,28]. The difference is attributed to various factors including the fact that the studies have been carried out with different strains of bacteria cultured under different laboratory conditions [29]. James Chapman et al., [30] reported the use of biocidal nanoparticles such as silver along with a SHP self-assembled monolayer (SAM) for effective protection against biofouling in marine environments. Lotus leaf inspired surfaces [31] and micro-textured polydimethyl siloxane (PDMS) surfaces [32] were shown to have reduced protein adsorption. SHP antibacterial copper coated PDMS polymer films [33] were shown to be effective in reducing the bacterial adhesion.

The objective of the present study is to modify the surface of cupro-nickel alloy using sandblasting so that the surface becomes hydrophobic and then coating with a low surface energy material thereby reducing the bacterial adhesion on the same when exposed in sea water. In the present study, the antibacterial property of the as-developed hydrophobic Cu-Ni surfaces is studied in the culture of *Pseudomonas* sp., which is the predominant biofilm former in the coastal waters of Kalpakkam. The role of various surface treatments such as polishing, pickling, sand blasting and silane coating on the wettability and bacterial adhesion is discussed in detail.

2. Materials and methods

2.1. Sample preparation

The detailed composition of cupronickel in the form of a 3 mm thick sheet used in the present study is shown in Table 1. Cupronickel sheets were cut into small coupons of size 30 × 20 × 3 mm and a 2 mm diameter hole was drilled at the centre of the top end. The as-received samples were ultrasonically cleaned in acetone for 5 min and were labeled as Sample A. The cupronickel samples were polished using SiC paper from grade 80 to 1000. The polished samples were pickled in a solution of 0.5 g of $Na_2Cr_2O_7$ in 15 mL of H_2SO_4 for about 5 min with constant agitation. Pickling here refers to the process in which surface impurities and scales are removed from the sample and in addition contributes to increased surface roughness [23]. The samples were then rinsed in de-mineralized (DM) water and dried in air. The dried samples were dip coated in perfluoro octyl triethoxy silane (PFOTES, Alfa Aesar, 97% purity) solution. The detailed procedure for silane solution preparation and dip coating was discussed elsewhere [19]. The silane solution was prepared by mixing 1·5 wt% of 0·1 N HCl, 88 wt% ethanol, 10 wt% DM water and 0·5 wt% silane. The solution was stirred for about 4 h at room temperature. The cupronickel samples were dip coated (Single Dip Coating Unit, SDC-2007C, Apex Instruments, Kolkata) in silane solution, with dipping and lifting speed of 50 mm/min, and the samples were allowed to remain for a minute in silane solution before lifting. The samples were subsequently baked in a hot air oven at 110 °C for 30 min. The samples that were polished, pickled and dip coated in silane solution were labeled as Sample B. Coupons of cupronickel in as received condition (Sample A) were subjected to sandblasting in an industrial setup. The parameters for sandblasting are presented in Table 2. After sandblasting, the samples were pickled in a solution of $Na_2Cr_2O_7 + H_2SO_4$ for about 5 min with constant agitation. The samples were then rinsed in de-mineralized (DM) water and dried in air. The dried samples were dip coated in silane solution as described above. The samples were subsequently baked in a hot air oven at 110 °C for 30 min. The samples that were sandblasted, pickled and dip coated in silane solution were labeled as Sample C.

Table 1
Composition of cupronickel samples.

Element	Ni	Fe	Mn	Zn	C	Pb	S	Cu
Wt%	9.20	1.06	0.53	0.27	0.02	0.01	0.30	Bal

Table 2
Parameters used for sand blasting of cupronickel samples.

Type of process	Pneumatic assisted sand blasting
Size of particle	100 to 200 μm
Type of nozzle	Variable flow
Pneumatic pressure	6.0 to 6.5 kg/cm^2

2.2. Surface characterization studies

The morphology of as-prepared samples was characterized by scanning electron microscope (Desktop Mini-SEM, SNE 3000M, Korea) and atomic force microscope (NT MDT Solver Pro ECAFM, Russia). The chemical composition of the coatings was analyzed using energy dispersive X-ray spectroscopy (EDS) coupled with SEM. The surface modified samples were examined using Confocal Laser Scanning Microscope (Carl Zeiss, LSM880). Water contact angles on the as-synthesized samples were measured using video based contact angle meter (OCA15EC, Data Physics Instruments, Germany). The dosing volume was 5 μL and the dosing rate was 1 μL/s for all the experiments. WCA values were recorded at five different locations on each sample and the average WCA value was reported. DM water was used in all these experiments.

2.3. Bacterial adhesion studies

Pseudomonas sp., Gram-negative bacteria was selected for the present study as it was found to be one of the major biofilm formers in the Bay of Bengal coastal waters of Kalpakkam. The characterization and identification of *Pseudomonas* up to genus level was reported elsewhere [34]. This bacteria was cultured in 10% (dilute) nutrient broth (Peptic digest: 5 g/L; NaCl: 5 g/L; Beef extract: 1.5 g/L; Yeast extract: 1.5 g/L; pH: 7.4 ± 0.2) for about 24 h. The bacterial adhesion studies are carried out for triplicate samples for each condition i.e., 3 as received samples, 3 polished, pickled and dip coated samples and 3 sand blasted, pickled and dip coated samples. Initially the control and surface modified cupronickel samples were sterilized using UV visible light inside a Klenzaids Laminar Air Flow Chamber for 2 h. The surface sterilized samples were exposed to a culture of *Pseudomonas* sp. for about 24 h. Then the samples were taken out and rinsed in distilled water, flooded using Acridine orange (0.1% solution in distilled water). After 10 min, the excess stain was drained off and the coupons were rinsed in distilled water and dried in the dark. Acridine orange, is a fluorescent dye which differentially stains single stranded RNA and double stranded DNA,