

Non-Wetting Nickel-Cerium Oxide Composite Coatings with Remarkable Wear Stability

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ABSTRACT

Engineered non-wetting surfaces inspired by biological species are of interest in the industry due to their potential applications such as water repelling, self-cleaning, anti-icing, anti-corrosion, anti-fouling, and low fluid drag surfaces. However, the adoption of non-wetting surfaces in large scale industrial applications has been hampered by synthesis techniques that are not easily scalable and the limited long term stability and wear robustness of these surfaces in service. In this study, we demonstrate a simple, low cost, and scalable electrochemical technique to produce robust composite coatings with tunable non-wetting properties. The composite coatings are composed of an ultra-fine grain nickel matrix with embedded hydrophobic cerium oxide ceramic particles. Comprehensive characterization, including wetting property measurements, electron microscopy, focused ion beam analysis, hardness measurements, and abrasive wear testing were performed to establish the structure-property relationships for these materials. The grain refinement of the nickel matrix contributes to the high hardness of the composites. As a result of the bimodal CeO₂ particle size, hierarchical roughness is present on the surface of the composite, leading to remarkable non-wetting properties, even after 720 m of abrasive wear.

INTRODUCTION

Non-wetting, water repelling surfaces were first observed in nature, with the lotus leaf being the most prominent example. The surface of the lotus leaf has a hierarchical roughness, composed of nanoscale wax crystals superimposed on microscale papillae. Generally, these surfaces are hydrophobic or superhydrophobic, where the water contact angles are $>90^\circ$ and $>150^\circ$, respectively [1]. These surfaces often exhibit self-cleaning [2], anti-corrosion [3], anti-icing [4], and improved surface transport condensation properties [5] which are beneficial in many industrial applications. Currently, the widespread adoption of these surfaces for industrial applications is limited by complex synthesis

techniques and the long term wear stability of these surfaces. A recent study has demonstrated that hard and thermally stable rare earth oxide ceramics are hydrophobic due to their unique electronic structure [6]. In this work, we incorporate hydrophobic cerium oxide particles in a nickel matrix to produce a robust, non-wetting composite coatings. The synthesis approach to produce these materials is electrodeposition. Electrodeposition is a well-established industrial coating technology to produce non-wetting metal and metal matrix composite coatings on a conductive substrate [7,8].

EXPERIMENTAL DETAILS

Ni-CeO₂ composite coatings were electrodeposited onto polished 2 x 2 cm copper substrates in an aqueous solution containing 300 g/L NiSO₄·6H₂O, 45 g/L NiCl₂·6H₂O, 45 g/L H₃BO₃, and 50 g/L CeO₂ particles. The pH and temperature of the solution were kept at 3.5 – 4.0 and 60°C, respectively. The anode was a chemically inert Ti-basket containing Ni rounds. Only one side of the copper substrate was plated. Electrodeposition was carried out at for 20 min at a current density of 50 mA/cm². After deposition, the samples were rinsed with deionized (DI) water and ultrasonically cleaned in ethanol to remove loosely attached CeO₂ particles. The samples were placed in a vacuum chamber as described earlier [9]. Static water contact angles (WCA) were determined by placing 5 μL DI water droplets on the surface.

The surfaces of the coatings were characterized by scanning electron microscopy. Energy dispersive X-ray spectroscopy (EDXS) was performed to determine the composition of the composites. Cross-sections of the coatings were analysed by the focused ion beam (FIB) milling technique. Cross-cut tape tests (ASTM D3350-09) were performed to evaluate the coating adhesion to the substrate. Vickers microhardness was evaluated by using a 50 g load. Abrasive wear stability of the composite coatings were evaluated by linear abrasion test on 800 grit SiC abrasive paper [10]. The specimens were abraded in a reciprocating motion with a stroke length of 0.15 m and an applied pressure of 4000 Pa. After every 72 m of abrasion, the SiC abrasive paper was replaced.

In addition to Ni-CeO₂, the wear stability of electrodeposited Ni-PTFE composite [11] and NeverWet™, a commercial superhydrophobic spray-on treatment (CSHST) applied on polished copper substrate were also investigated for comparison.

RESULTS AND DISCUSSION

A secondary electron (SE) micrograph of as-deposited Ni-CeO₂ composite coating is shown in Figure 1a. The composite is composed of CeO₂ particles (55vol.%) with bimodal particle size distribution (30 μm, 5 μm) embedded in a Ni matrix. The bimodal particle size distribution allows high packing of the particles; smaller CeO₂ particles were embedded between the larger particles. As a result, hierarchical surface roughness was achieved which may be beneficial in the long term wear stability of this coating as the larger particles will protect the lower lying particles from damage to maintain the non-wetting properties. Similarly, the as-deposited Ni-PTFE composite control coating (Figure 1b) also has a hierarchical surface roughness formed by the bimodal sized PTFE particles (8 μm, 0.6 μm) co-

deposited (69vol.%) into the Ni matrix. The CSHST control coating (Figure 1c) has a different structure compared to the Ni-based electrodeposited composites; a porous structure is visible at low magnification. At high magnification (Figure 1c inset), it is visible that the porous structure of the coating is formed by clusters of nanoparticles. According to the material safety datasheet of the CSHST, the coating contains silicone and silica, so it is likely that the nanoparticles are silica particles held by hydrophobic silicone.

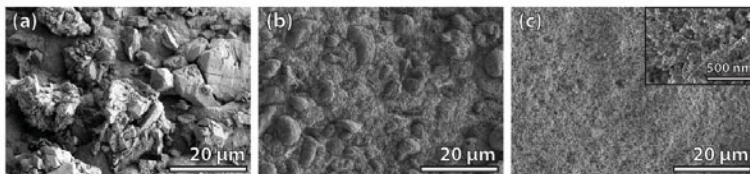


Figure 1. Secondary electron micrographs of as-deposited (a) Ni-55vol.% CeO₂ composite coating, (b) Ni-69vol.% PTFE composite control coating, (c) CSHST control coating.

Cross-section analysis of the Ni-CeO₂ composite coating was performed by FIB milling to verify that co-deposition of CeO₂ particles is not just limited to surface. As demonstrated in Figure 2, the CeO₂ particles are indeed embedded in the Ni matrix and the particles will not be easily removed when the composite coatings are utilized in applications that involve abrasive wear. Furthermore, the image of the cross-section surface revealed that the Ni matrix has an ultra-fine grain structure (average grain size: 310 nm) that gives rise to high hardness of the composite (366 HV) due to Hall-Petch strengthening.

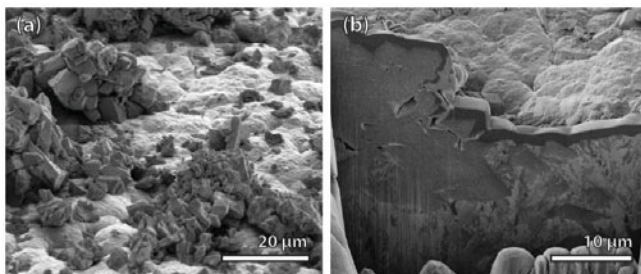


Figure 2. Cross-section analysis of Ni-CeO₂. (a) SE micrograph of the surface of Ni-CeO₂ composite before FIB milling (incident beam: electron). (b) SE micrograph of the cross-section surface (incident beam: focused Ga⁺ ion). The CeO₂ particles are indeed embedded in the Ni matrix.

Cross-cut tape tests were conducted to verify that all coatings are well adhered to the Cu substrate. Optical micrographs of the Ni-CeO₂, Ni-PTFE, and CSHST before and after the tape test are shown in Figure 3. Based on the results, none of the squares of the lattice were detached for all coatings, indicating excellent

adhesion of the coatings to the Cu substrates. Based on the ASTM D3350-09 guidelines, an adhesion classification of 5B was assigned for all three specimens.

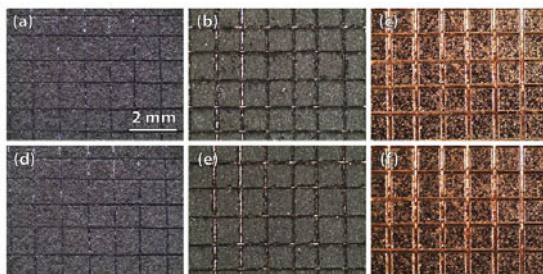


Figure 3. Optical images of (a) Ni-55vol.% CeO₂ composite coating, (b) Ni-69vol.% PTFE composite control coating, and (c) CSHST control coating before the tape test. No significant changes were observed on the lattice grids after the tape test; (d) Ni-CeO₂, (e) Ni-PTFE, and (f) CSHST coating.

As shown in Figure 4, all pristine specimens were hydrophobic or superhydrophobic (Ni-CeO₂: 132°, Ni-PTFE: 156°, CSHST: 155°). Between the three specimens, the degradation rate of CSHST in the context of hydrophobicity is the highest as shown by steep curve in Figure 4. Conversely, the degradation rate of Ni-CeO₂ remained low as depicted by the flat curve and the WCA did not significantly change even after 720 m of abrasion (WCA = 127°). Beyond 84 m and 48 m, the WCA of Ni-PTFE composite and CSHST coating, respectively, were lower than Ni-CeO₂ composite. Representative SE images of the coatings after 24 m of abrasion are demonstrated in Figure 5. No significant changes to the surface morphology was observed for the Ni-CeO₂ composite due to the high hardness and wear resistance of the co-deposited ceramic particles (Figure 5a). On the other hand, wear tracks and deformed micron size PTFE particles caused by the abrasion was observed for the Ni-PTFE composite (Figure 5b). Due to the bimodal particle size distribution, the PTFE particles in the recessed area remained intact and the WCA remained above 150°. For the CSHST coating, surface morphology was changed significantly; delamination wear and flattening of the coating was observed (Figure 5c). As a result, a rapid decrease in WCA was observed (Figure 4).

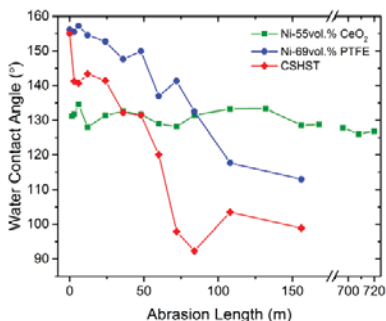


Figure 4. Wear stability of non-wetting surfaces.

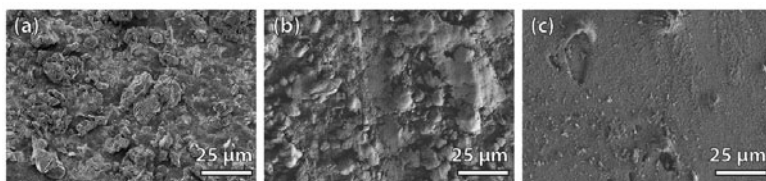


Figure 5. Secondary electron micrographs after 24 m of abrasion on 800 grit SiC abrasive: (a) Ni-55vol.% CeO₂ composite coating; (b) Ni-69vol.% PTFE composite control coating, wear groove marks are visible; (c) CSHST control coating showing delamination wear and surface smoothing.

CONCLUSIONS

Robustness of the Ni-CeO₂ composite coatings was evaluated by a linear abrasion test. Compared to other non-wetting surfaces including Ni-PTFE composite and CSHST coating, Ni-CeO₂ composite coatings demonstrated superior non-wetting characteristics after significant abrasion on the surface due to the high hardness of the embedded CeO₂ particles and hierarchical surface roughness. The findings of this study establish the feasibility of applying non-wetting Ni-CeO₂ composites coatings in applications that demand high wear stability, such as condenser tubes and plates for power generation and desalination.

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