

## Ni-Fluoropolymers Composite Coatings Obtained via Electroless Plating for Anti-Icing Application

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Electroless pure nickel plating was used as a manufacturing technique to produce Ni-fluoropolymers composite coatings on Ti6Al4V substrates. To evaluate the influence of the surface roughness on the water drop contact angle, four different coating architectures (Ni, Ni+FEP, Ni polished and Ni+FEP polished) have been proposed and implemented. Firstly, as a coating reference, a single layer of pure Ni coating was deposited (thickness around 10  $\mu\text{m}$ ); then, Ni+FEP single layer was deposited with the help of a surfactant added to the nanoparticles solution to avoid the agglomeration of the filler. Water drop contact angles as a function of time were studied for the different samples and it turns out that the presence of the fluoropolymer fillers inside the matrix deeply modify the wettability of the Ni matrix surface. These results show how coatings obtained by this synthesis technique can be used as possible candidates for passive anti-icing systems.

### 1. Introduction

Nowadays, cold weather conditions are considered a critical factor in the design, analysis, and performance tests of airplane aerodynamic surfaces. Only from 1990 to 2005, there have been 240 reports of aviation accidents due to icing (Egast, 2018), and most of them included icing on aircraft wings (Pouryoussefi et al., 2016). Just to cite one of the most recent tragic events, 50 people died in an aircraft accident (Continental Connection Flight 3407) in the area of Buffalo in February 2009: the aircraft stalled and crashed, after flying in severe icing conditions.

In recent years, considerable efforts have been directed toward the development of novel materials and coating techniques to enhance anti-icing performance (Belaud et al., 2021; Y. Cao et al., 2018; Grishaev et al., 2021; Zhou et al., 2023). One promising approach involves the use of composite coatings comprising nickel (Ni) and fluoropolymers, which have demonstrated excellent anti-icing properties. (Samsun et al., 2023; Shiverskii et al., 2023; Zhang et al., 2022; Zhao et al., 2022) Fluoropolymers, known for their low surface energy and non-stick characteristics, offer inherent ice-repellent properties. However, the limited mechanical strength and adhesion of pure fluoropolymers pose challenges for their direct application as coatings. By combining fluoropolymers with a reinforcing layer of Ni, it is possible to achieve enhanced mechanical properties and adhesion while preserving the ice-repellent characteristics.

Electroless plating, a widely employed deposition technique, has gained considerable attention for the synthesis of Ni-fluoropolymer composite coatings. Unlike electroplating, electroless plating does not require an external power source, making it suitable for coating complex geometries and non-conductive substrates. The process involves the autocatalytic deposition of a metal layer from a chemical bath onto a substrate surface, ensuring uniform coating thickness and good adhesion.

This technique allows depositing a pure nickel coating or a polymer composite coating, which thanks to their surface morphology and wettability properties can offer ice-phobic properties. This coating is naturally hydrophobic, and it aims to use this property to decrease or avoid the water accumulation on the aerodynamic surfaces before the freezing of the water itself (Song et al., 2020). Meanwhile, the use of this coating could help to decrease the shear stress needed to remove ice from the structure, which can then be detached by exploiting

external forces such as gravity or aerodynamic forces which in this way may exceed the adhesion force that bond the ice to the structure. The knowledge gained from this research will contribute to the development of highly efficient and durable anti-icing coatings, with potential applications in aviation, power transmission, marine systems, and other industries where ice accumulation poses significant challenges. (Antonini et al., 2011)

## 2. Materials and methods

Electroless nickel plating and Ni-fluoropolymers coatings were conducted on squared specimens of Ti6Al4V with dimensions of 12 mm x 12 mm x 2 mm. Since the samples must be dipped in the solution, the presence of a hole, practiced through a drill press, is required to allow them to be hung with a nylon thread. All chemicals were purchased by Alfa Aesar (Thermo Fisher Scientific) and used without any further purification.

### 2.1 Coating preparation and Characterization

Specimens were pre-treated before plating by sandblasting with corundum (mesh 80) to increase the roughness and by rinsing in ultrasonic cleaning in acetone to remove the contaminants from the surface. The composition and the preparation of the solution are reported in a previous work (Genova et al., 2017a, 2019) and concentrations are reported in Table 1. Fluoropolymers nano-coatings were obtained using commercial fluorinated ethylene propylene (FEP) water solution purchased by 3M Dyneon. The dispersion has a solids content of around 55 wt%. The almost spherical, hydrophobic polymer particles have an average size of around 150 nm. Nanoparticles agglomeration was avoided by dispersing the polymer particles with a cationic surfactant capable of forming micelles in aqueous solution; 0.75 g of Cetyltrimethylammonium bromide (CTAB) were dissolved into 25 ml of water and sonicated until the solution was clear; then 12 ml of FEP was added to the CTAB solution and sonicated for 1 hour before introduction in the electroless plating solution. All the depositions were conducted in 300 ml of solution per sample.

Table 1: Plating solution composition (mol/L).

Compound	Function	Chemical formula	Concentration (mol/L)
Nickel chloride	Source of Ni <sup>2+</sup>	NiCl <sub>2</sub>	0.08
Hydrazine	Reducing agent	N <sub>2</sub> H <sub>4</sub> x H <sub>2</sub> O	0.4
Lactic acid	Complexing Agent	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	0.15
Disodium EDTA	Complexing Agent	Na <sub>2</sub> [C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O <sub>8</sub> ]	0.016
Sodium hydroxide	Buffer	NaOH	0.25

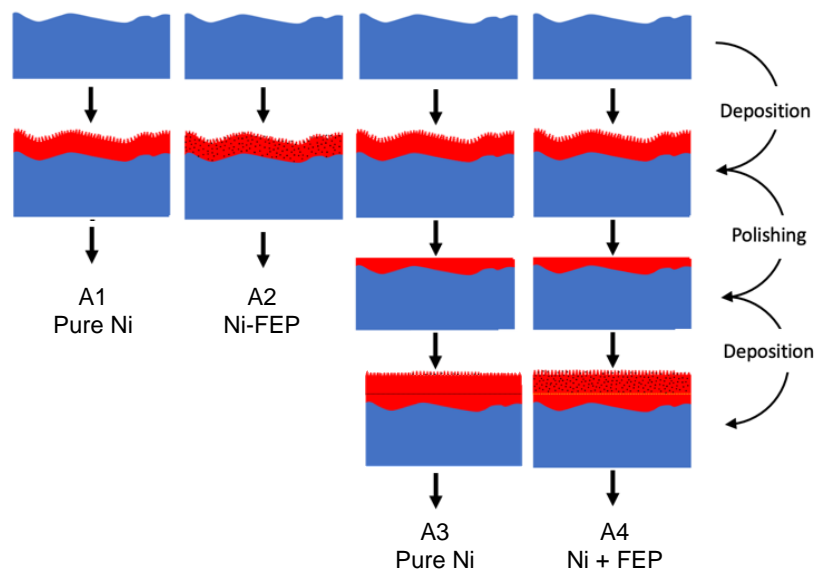


Figure 1: Schematic process to produce the ice-phobic coatings.

In Figure 1 is shown the schematic process to obtain all the different coatings; Section a is referred to the nanocomposite coating directly coated onto the substrate surface (sample A1). In this case, the rugosity of the sample is to be considered micro (from the sandblasting) and nano (from the typical surface of the electroless

pure Ni plating). To study the influence of the roughness on the wettability, coatings with and without fluoropolymers were polished with a p4000 SiC paper (section *b*, sample A2) and then a second deposition with Ni-fluoropolymers was conducted on the polished pure Ni surface (sample A3). In Table 2 are summarized the composition and the number of layers for the different coatings studied in this work. Water drop contact angles (CA) on solid surfaces were studied by an ad-hoc experimental apparatus. The structure of the test rig is similar to the typical contact angle test. The high-resolution camera Dino-Lite AM4113ZT equipped with a 1.3 Megapixels sensor allowed to capture the binarized pictures of the water drops at different times of air lab exposure. A measured water drop is generated by the needle tip of a micropipette using deionized water to minimize the effect of different surface energy coming from the impurities in the water. ImageJ software equipped with an additional plugin allowed to elaborate the contour of the drop itself and extrapolate the value of the contact angle. The evolution of the contact angle was measured as a function of the air lab exposition for each coating. Three measurements were carried out for each sample, averaged, and repeated over time to obtain additional information on the modification of wettability.

Surface morphology and composition of the coatings were determined with a FEG-SEM Tescan Mira3 (Tescan, Brno, Czech Republic) equipped with an Edax Octane Elect detector for energy-dispersive X-Ray spectroscopy (EDS).

Table 2: Design of experimental coatings.

Coating	Composition	Layer	Rugosity
A1	Ni	1	micro and nano
A2	Ni + FEP	1	micro and nano
A3	Ni / Ni	2	nano
A4	Ni / Ni + FEP	2	nano

### 3. Results and discussion

A cross-section image of the Ni-fluoropolymer nanocoating is reported in Figure 2. The strategy of using a surfactant to disperse the polymeric nanoparticles gave some important results: the coating is homogeneous and conforms to the irregularities of the substrate; the nanoparticle reinforcement is well dispersed throughout the thickness of the coating; however, the presence of surfactant influences the deposition rate which is decreased (around 10  $\mu\text{m}/\text{h}$ ) compared to the values reported in the literature for the pure Ni system (Genova et al., 2017b). This phenomenon was already observed in literature by B.H. Chen et al. 2002 for the system Ni-P electroless plating. All the samples were coated with around 10  $\mu\text{m}$  of Ni (with and without nanoparticles) for the single-layer samples. Since it is hard to measure the quantity of the first Ni layer after the polishing procedure, the thickness of the second layer was set at 5  $\mu\text{m}$ .

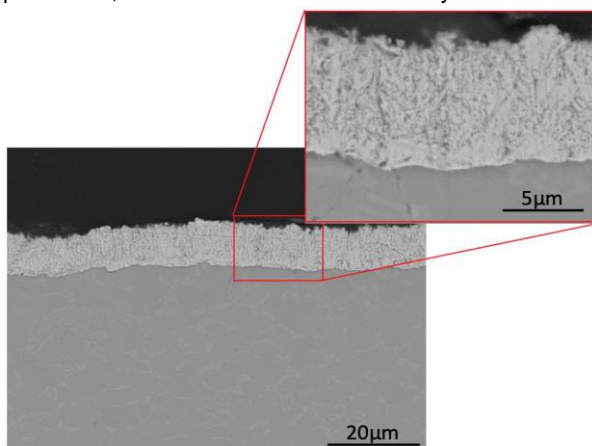


Figure 2: Cross-section image of the Ni-fluoropolymer nanocoating (sample A1).

A comparison of the four different configurations presented in this work with the respective sketches are reported in Figure 3(a-d). In particular, Figures 1a and 1c show the coating obtained by directly depositing, respectively, pure Ni without and with nanoparticles (samples A1 and A2). As previously mentioned, the effect of roughness, in this case, is to be considered as the sum of the contribution of the roughness deriving from the preparation (sandblasting) and the peculiar nano-roughness typical of the coatings obtained by electroless pure nickel. As

far as nano-roughness is concerned, AFM measurements were conducted in previous work for the electroless pure nickel system (Genova et al. 2019) while the roughness values relating to the pre-treatment were measured using a profilometer (Talyscan 150, Taylor-Hobson) equipped with a cantilever which did not show evident differences in the samples with and without polymeric nano reinforcement ( $R_a [\mu\text{m}] 1.75 \pm 0.0881$ ). Since the electroless plating is capable to deposit a conformal coating, the roughness is strongly influenced by the sandblasting pre-treatment. For this reason, in samples A3 and A4, the fine lapping step was introduced between the first and second deposition. As can be seen in Figure 3c, there is no discontinuity between the first and second deposition (the recovery zone of the coating is imperceptible in the SEM image). This confirms that it is possible to obtain a tailorable roughness simply by using the first deposition step to eliminate the imperfections of the sample due to the preparation. In the case of the nickel-FEP coating, in this case, the second coating is more evident because the nanoparticle dispersion allows the two coatings to be distinguished.

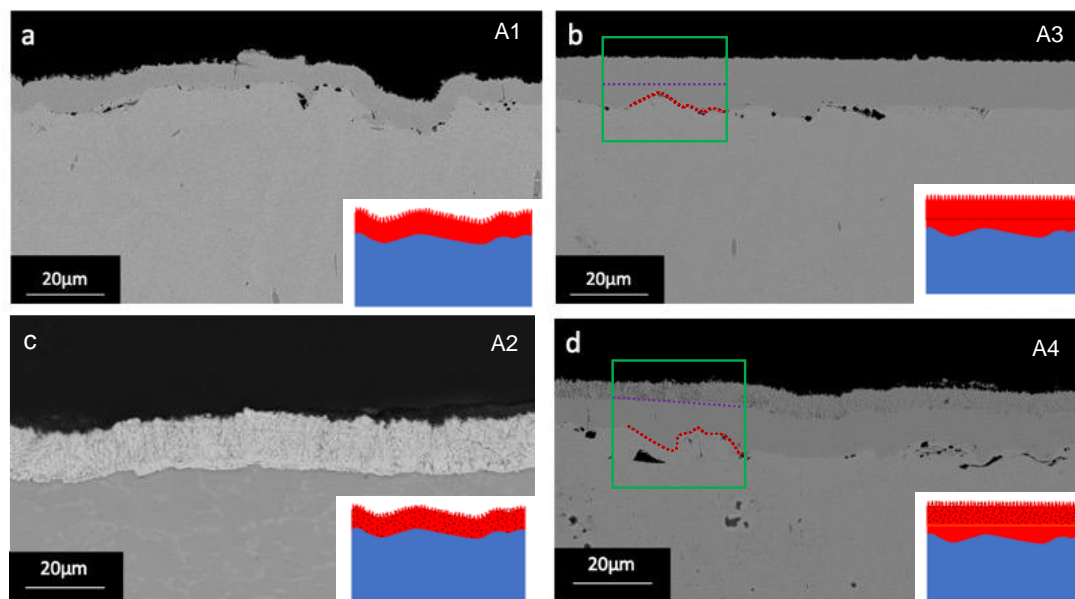


Figure 3: Cross-section images and respective sketches of the coatings studied; in particular: sample A1 (a), sample A2 (b), sample A3 (c), and sample A4 (d).

Wettability evolution by exposing the samples to the lab air was measured up to 200h. The results for all the samples are shown in Figure 4a-d. Sample A1 (single layer, Ni pure) shows the same behavior observed in previous work (Genova et al. 2019). Briefly, the surface of the sample is super hydrophilic ( $CA < 5^\circ$ ) thanks to the contribution of the micro-nano-structured hierarchical structure, typical of electroless deposition. As can be seen from the graph, once the superhydrophobic state was reached after about 100h, the measurements were conducted with a lower frequency to evaluate possible significant variations (fig. 1-a). This transition, which can be interpreted thanks to the Cassie-Baxter model (Cassie, 1944), can be attributed to surface adsorption of volatile organic compounds (Marmur, 2003) naturally present in the air, intrinsically modifying the wettability value of the surface and thus justifying the clear transition between the two states (super hydrophilic in the case of "as coated" coatings and superhydrophobic after about 100h of exposure). Sample A2, obtained by direct deposition of Ni + FEP, shows a different behavior from sample A1: the difference lies in the CA values obtained in the first hours of exposure to laboratory air. While the plain coating had a  $CA < 5^\circ$  just deposited, in the case of the nanocomposite coating there is an influence of the polymeric reinforcement which modifies the surface wettability value. Since the polymeric material is naturally hydrophobic, its addition to the metal matrix modifies the behavior of the surface making it naturally hydrophobic. As the exposure time increases, an increase in the hydrophobic behavior is observed, probably due to partial adsorption of the volatile organic molecules already mentioned above (fig. 1-b). Figures 1-c and 1-d show the evolution of CA over time for the double layer samples A3, and A4 (with the first layer in both cases of pure Ni, while the second layer is, respectively, pure Ni and Ni + EFF). The double layer in pure Ni shows a higher initial CA than in the case of the monolayer. Considering the manufacturing process, it can be concluded that the contribution of the surface roughness to the CA value, in this case, depends exclusively on the nanostructured surface of the pure Ni (Kubiak et al., 2011). To demonstrate this, the same measurement was carried out on a polished A1 sample (single layer of pure Ni). In this case, the CA value is constant over time (with a value of about  $70^\circ$ , in line with the literature (Yue et al.,

2022) since the previously discussed transition is not favored as there is no nanostructured surface in which the volatile organic compounds can adsorb.

In the case of sample A4 (figure 1-d), the behavior is similar, but the CA value is higher and, also in this case, this increase can be traced back to the presence of the fluoropolymer reinforcement. In both cases, however, the evolution of CA over time shows a similar behavior, with an increasing trend that reaches a plateau value in the superhydrophobicity condition (L. Cao et al., 2009) (with CA values similar to coatings A3 and A4).

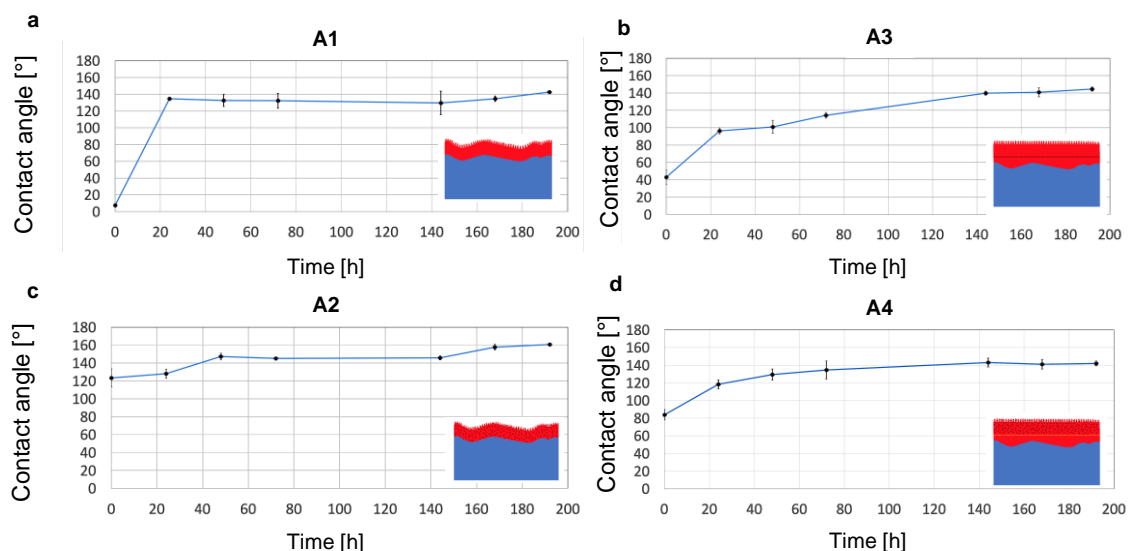


Figure 4: Water drop contact angles as a function of time for the samples: A1 single layer, Ni pure(a); A3 double layer, Ni pure(b); A2 single layer, Ni + FEP (c); A4 double layer, Ni pure + Ni + FEP (d).

#### 4. Conclusions

In this study, Ni-fluoropolymers composite coatings were successfully produced on Ti6Al4V substrates using electroless plating. The influence of surface roughness on water drop contact angle was investigated by implementing different coating architectures. To obtain an excellent dispersion of the nanoparticles inside the matrix, a cationic surfactant (CTAB) was introduced in the deposition bath, allowing to obtain a coating with a good degree of dispersion of the nanoparticles. Cross-sectional SEM analysis confirmed this hypothesis. The evolution of the contact angle as a function of the exposure time in laboratory air was evaluated for all the samples obtained. The results showed that the addition of nanoparticles leads to a decrease in wettability (CA = 120°) for the modified as-coated samples. The results demonstrated that the presence of fluoropolymer fillers significantly altered the wettability of the Ni matrix surface, indicating the potential of these coatings as passive anti-icing systems. Further studies can explore the durability and long-term performance of these anti-icing coatings to optimize their effectiveness and broaden their practical applications.

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