

Review: Superhydrophobic Nickel Coatings for Corrosion Protection by Electrodeposition

Sri Ramadhani¹, Rini Riastuti¹, Nono Darsono²

Author Affiliations

¹ *Department of Metallurgy and Material Engineering, Universitas Indonesia, Depok 16424, West Java, Indonesia*

² *Research Center of Material Science and Metallurgy, The National Research and Innovation Agency (BRIN), Kawasan Puspiptek Serpong, South Tangerang 15314, Banten, Indonesia*

Author Emails

sriramaadhani@gmail.com

Abstract. Metals that come into contact with a humid atmosphere containing corrosive compounds including chloride, oxygen, carbon dioxide, hydrogen sulfide, and others will corrode and cause material degradation. If corrosion is not managed, it can result in business losses and risk safety. These coatings have proven to be excellent candidates for preserving metals against corrosion because they offer a barrier between the metal and its environment. Nickel is a hydrophilic metal (likes water), it requires a superhydrophobic coating that uses the lotus effect to clean the substrate of impurities while also preventing the formation of a moisture layer on the surface due to its angle. Increase the roughness of the surface structure in the micro-nano hierarchical and reduce the surface tension to increase the water contact angle to achieve a surface with good superhydrophobic qualities. Several researchers, However, several researchers have succeeded in generating superhydrophobic nickel layers on a diverse matrix in a variety of ways, one of which is the electrodeposition method. This method is useful since it does not take long and provides a superhydrophobic layer that is uniform.

Keyword. Superhydrophobic, Nickel, Electrodeposition, Protection Corrosion

INTRODUCTION

Metals and their alloys are widely employed in a variety of industrial applications due to their superior qualities over other materials, mainly in the oil and gas industry. Electrochemical interactions with the environment make them more susceptible to corrosion. Corrosion is a type of material degradation caused by the interaction of materials, particularly metals, with their environment. This issue is critical because it has the potential to result in corporate losses, environmental harm and security, human safety, and the government's image in the fight against industrial accidents.

Corrosion of metals has a significant economic impact and is a major cause of concern all over the world [1], corrosion management costs roughly 4-5 percent of GDP in industrialized countries, and corrosion control costs cover everything from design to maintenance and treatment [2]. The entire cost of corrosion damage in the oil and gas sector is anticipated to be 1.372 billion dollars per year in terms of property damage, surface pipeline, capital expenditures, and downhole tubing [3]

Air pollution levels, temperature, humidity, and the presence of corrosive compounds are all examples of aggressive environmental conditions that can cause corrosion issues in metals. Metals and their alloys are protected from corrosion by a variety of means, including coatings. By possessing excellent bond strength, abrasion resistance, and anti-corrosive characteristics, the protective layer is meant to provide long-term protection for the structure. Nickel is one of the most often utilized metals to protect steel from corrosion due to its advantageous properties such as exceptional hardness, high wear resistance, and outstanding corrosion performance [4].

When nickel coatings are paired with superhydrophobicity, they can offer distinct benefits, allowing them to be employed in a variety of applications such as corrosion and contamination-resistant materials. Up to now,

various methods and equipment have been proposed and designed to obtain superhydrophobic nickel coating surfaces including scanning deposition [5], selective laser melting [6], and electrodeposition [7]. The electrodeposition method is a high-efficiency, low-cost, simple technique that can be used in large-scale industries [8]. A few researchers [9-11] have looked at the preparation of superhydrophobic nickel surfaces using electrodeposition and chemical modification. Chen et al created a superhydrophobic nickel coating with chemical modification stearic acid exhibiting an increased water contact angle [9]. Yu et al fabricated superhydrophobic Ni-Cu-P alloy coatings with high mechanical strength and good adhesion [10] Jena et al a nickel (Ni)-reduced graphene oxide (rGO)-myristic acid superhydrophobic coating with improved corrosion resistance and self-cleaning ability was created on a carbon steel surface [11].

Characteristics Superhydrophobic Surface

Inspired by natural phenomena such as the self-cleaning capabilities of lotus leaves, rose petals, butterfly wings, and insects. For example, water striders have anti-wet feet that enable them to walk on water [12,13]. Superhydrophobic surfaces which have a contact angle (CA), a low sliding angle (SA < 10°), and a low contact angle hysteresis (CAH), have gotten a lot of attention because of their unique properties enhanced corrosion performance [14], anti-fouling [15], anti-icing [16] drop splitting [17].

Superhydrophobic characteristics are imparted to a metal surface via an effective corrosion prevention technology. Due to its inability to hold onto a surface even at the tiniest tilt angles, no moisture layer can form on such a surface. Surface wettability is determined by the chemical composition of the surface layer as well as the microstructure of the topography.

It is well understood that the surface must have low surface energy as well as a developed shape in order to obtain superhydrophobic characteristics. Most of the time, this is accomplished by using compounds with the appropriate qualities, such as water-repellent substances. However, well-developed morphology is the most important prerequisite for ensuring superhydrophobicity [18,19], and chemical modification [20] can be avoided in some circumstances by providing the required polymodal roughness corresponding to nanoscale and submicroscopic features. As a result, superhydrophobic surfaces can be created in one, two, or three steps, with nickel coatings being one of them.

The contact at the solid surface determines a surface's wettability. The contact angle (θ) is the angle created by a tangent to the liquid at the point of contact and a line across the drop's bottom, Solid surfaces are divided into four types based on contact angles and wetting characteristics measurements as shown fig 1.

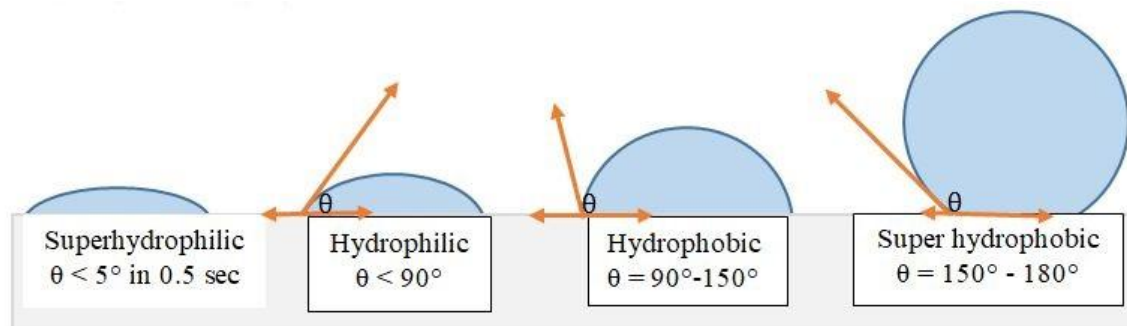


FIGURE 1. Schematic illustration of hydrophilic, superhydrophilic, hydrophobic, and superhydrophobic surfaces [21].

The traditional models for solid/liquid/gas interfaces are indicated by two important theories based on the Wenzel and Cassie-Baxter theorems [22,23]. Wenzel methods when the droplets are placed on a rough surface, except that the droplet water will fill the roughness of the surface and that the droplet will attach to the surface extremely well as shown fig 2a. The roughness element was later introduced by Wenzel.

$$\cos \theta_w = r_s \times \cos \theta \tag{1}$$

The roughness factor $r_s > 1$ is a dimensionless quantity that is always greater than one and is restricted to a uniformly rough surface. The real surface area and the anticipated surface area are the same things. Wenzel's equation predicts that the angle of contact can be increased by hardening the surface because such hardening will increase [24]. Cassie and Baxter extended Wenzel's theory further. Due to the presence of air pockets beneath the water droplets in the Cassie-Baxter state do not fill the full surface. Only the top of the surface is touched by the water droplets. While a small portion of the water contact makes contact with the rough surface's top, trapped air pockets result. This creates a slick surface that promotes water droplet mobility as shown fig 2b, allowing water to readily travel or roll across the surface.

$$\cos \theta_{CB} = f_s \times \cos \theta - (1 - f_s) \quad (2)$$

Where θ_{CB} is the Cassie-Baxter contact angle and f_s is the fraction of the surface area that comes into contact with liquid droplets. According to the Cassie-Baxter model, the angle of contact is proportional to the percentage of solids that come into contact with the droplets. The moisture content of heterogeneous (porous) surfaces decreases as the soaked portion of the surface increases.

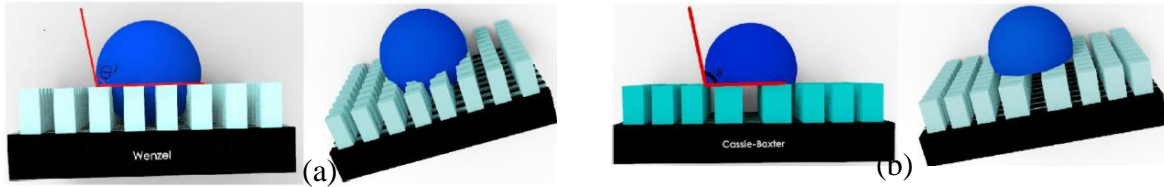


FIGURE 2. Wetting regime for (a) Wenzel model and Cassie-Baxter (b) [25].

Electrodeposition Nickel Coating

Electrodeposition is a method of depositing a substance by dissolving metal ions from the desired material in a solution (electrolyte) and storing them as a thin layer on the substrate's surface using a direct electric current. This is an easy preparation method with numerous benefits, including low cost and consistent coating [26]. The transfer of ions from the electrolyte to the electrode surface and discharge is followed by atoms entering the lattice and crystal formation in the electrodeposition of metals process. Many parameters influence the electrodeposition process for the superhydrophobic surface, including the pH value of the electrolyte solution, time, temperature, and current density [27,28].

The electrolyte solution used in the electrodeposition process typically contains the following components: the main salt, which provides salt ions deposited on the cathode; the conductive salt, which improves the solution's conductivity; the buffer, which is used to stabilize the pH of the solution, particularly the pH near the cathode; the anode activator, which eliminates or reduces anodic polarization and ensures normal anode dissolution; and small adsorbents. Coating morphology is an important factor affecting wettability, and it has recently been discovered that some reagents can regulate the crystal growth process and induce the formation of micro-nano dual-scale structures, thus regulating the morphology of the coatings, in the practice of electrodeposition preparation of superhydrophobic coatings. These compounds are known as crystal modifiers, and they aid in the realization of superhydrophobicity.

In addition, Table 1 lists the successful cases of metal electrodeposition preparation of several superhydrophobic coatings on the substrate in the last six years. To summarize, metal electrodeposition was used to create several superhydrophobic coatings on diverse substrates to produce a good anti-corrosion effect. However, in most circumstances, surface modification is required, and because hydrophobicity is dependent on the surface's micro-nano dual-scale structure, the coating's wear resistance and durability must be increased further.

TABLE 1. Examples of superhydrophobic coatings by metallic electrodeposition.

Matrix	Coating	Electrolyte Composition	Process conditions	WCA	SA	ref
Stainless steel	Ni	Plating solution NiCl ₂ + H ₃ BO ₂ +lauryl sodium sulfate modification : FAS-13	5A/dm ²	165°	1	[29]
H26 Brass	Ni	Etching liquid: FeCl ₃ Plating solution: NiCl ₂ Modification : trichloro silane	Chemical etching(17 min) + 0.05A/cm ² (15 min), 35 °C+	159.5 ± 1.7°	3.3 ± 0.6°	[30]
Mild steel	Ni-Cr	NiCl ₂ +CrCl ₂ Modification : myristic acid	15A/dm ² (the20s)	167,9°	4,7°	[31]
Stainless steel	Cu-Ni	NiSO ₄ +CuSO ₄ +Na ₂ SO ₄ +NDM+do pamine hydrochloride	0.6A/dm ² (20 min), 35°C	162°	-	[32]

Rahimi et.al reported the effects of boric acid on nickel electrodeposition to determine the crystal growth mechanism. Due to the low self-buffering power of the solution, the presence of boric acid in the nickel chloride solution allows for a higher dissolving degree of nickel chloride. These various mechanisms provide a rougher hierarchical microstructure (cone or pyramidal microstructure) and after 16 days of exposure to air in a 3.5 wt% NaCl solution, the superhydrophobic nickel film showed good corrosion resistance [36]. In another report from Hashemzadeh et.al ammonium chloride is utilized in nickel electrodeposition as a crystal modifier, The addition of ammonium chloride to the plating bath changes the micro-cone structure and results in an appropriate micro-nano cone, with a contact angle of 150-160°[37].

The influence of current density on coating morphology and wettability has been explored by a number of researchers [38,39]. Xiang et.al investigated how nickel plating current density affected low carbon steels. The morphological results indicate a hierarchical structure from prismatic stones to starfishes when the current density is varied from 2, 4, 6, and 8 A/dm². There are pores, however, at high current densities. This shows that current density can alter crystal orientation, and the findings of the potentiodynamic and EIS polarization curves demonstrate that low carbon steel has corrosion resistance [38]. The same phenomenon was also reported by Tan et.al, the contact angle on the superhydrophobic Ni surface changed significantly with increasing current. The contact angle density of steel modified by stearic acid is only 95.4°; when the current density was increased to 60 A/dm² showed the best superhydrophobicity with a contact angle of 154.4° and a sliding area of approximately 2.0°, and the contact angle began to decrease as the current increases when the current density exceeds 80 A/dm² contact angle is less than 120°. As a result, the current density of electrodeposition has a significant impact on the surface hydrophobic characteristics [39].

There is an ideal deposition time in terms of the effect of electrodeposition time on the hydrophobic performance of the coating. Before this critical threshold, the hydrophobicity grows as the deposition time increases, however, after this point, the hydrophobic effect decreases as the deposition time increases. The influence of deposition time on wettability is precisely achieved by modifying the coating morphology, and superhydrophobicity is dependent on the suitable surface morphology.

Copper	Ni/PTFE	NiSO ₄ +NiCl ₂ +H ₃ BO ₃ + PTFE particles	100 mA/cm ² (15 min), 60 °C	≈155°	-	[33]
Mild steel	Ni/WS ₂	NiSO ₄ +NiCl ₂ +H ₃ BO ₃ + CTAB + WS ₂ +Saccharin	4 A/dm ² (20 min), 40 °C	158.3°	7.7°	[34]
Carbon steel	Ni/WC	NiSO ₄ +NiCl ₂ +H ₃ BO ₃ + CTAB + WC	6 A/dm ² (30 min), 40 °C	164.3°	0°	[35]

CONCLUSION

.The material from corrosion and nickel can give strong corrosion resistance on metal surfaces. Superhydrophobic surfaces have a water contact angle (CA) of more than 150 degrees and a slide angle (SA) of less than 10 degrees. Surface energy and surface roughness are two significant aspects to consider while fabricating superhydrophobic surfaces. Surface roughness can be achieved by adjusting electrodeposition process parameters such as current density d pH and time. The superhydrophobic coating provides corrosion protection by forming a barrier layer so that there is no wettability of the surface. A nano-micro hierarchical structure emerges as a result. The existence of roughness on the surface increases the contact angle, causing the water that is dropped on the surface to be spherical and easy to slip, allowing impurities to be carried away and the surface to become clean, as Cassie-Baxter predicted. This technology is simple, environmentally friendly, and energy-efficient, and it offers a new perspective on the use of superhydrophobic coatings in metal corrosion protection.

REFERENCE

1. Fihri, E. Bovero, A. Al-Shahrani, A. Al-Ghamdi, G. Alabedi, Colloids Surface, Physicochem. Eng. Aspects., 520, 378–390 (2017)
2. M. Natesan, N. Palaniswamy, Corros. Rev. 27 (2009)
3. P, L.T, Grema, A.S, Latinwo, G.K, Gutti, B. Int. J. Ind. Chem. 4, 35 (2013)

4. S. Esmailzadeh, S. Khorsand , K. Raeissi, F. Ashrafizadeh, *Surface & Coatings Technology*, 283, 337-346 (2015)
5. Z.Wang, L.shen, W.Jiang, M.Fan, D.Liu, J.Zhao, *Surface & Coatings Technology* 377,124886 (2019)
6. D.Iacovetta, J.Tam, U.Erb, *Surface & Coatings Technology*, 279, 134-141 (2015)
7. L. Feng, S.H. Li, Y.S. Li, H.J. Li, L.J. Zhang, J. Zhai, Y.L. Song, B.Q. Liu, L. Jiang, D.B. Zhul, *Adv. Mater.* 14, 1857–1860 (2002)
8. N.A. Polyakov, I.G. Botryakova, V.G. Glukhov, G.V. Red'kina, Yu.I. Kuznetsov, *Chemical Engineering Journal* 421, 127775, (2021)
9. Z. Chen, F.Tian, A.Hu, M. Li, *Surface & Coatings Technology* 231, 88–92 (2013)
10. 10Q. Yu, Z.Zeng, W.Zhao, M.Li, X.Wu, Q.Xue, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 427, 1– 6 (2013)
11. G.Jena,, C. Thinaharan, R.P. George, J.Philip, *Surface & Coatings Technology* 397, 125942 (2020)
12. L.Feng, H.Zhang, Z.Wang, Y.Liu, *Colloids Surface, Physicochem. Eng. Aspects*, 441, 319-325 (2014)
13. P.P. Goodwyn, E.D. Souza, K. Fujisaki, S. Gorb, *Acta Biomater.* 4, 766–770 (2008)
14. K. An, C. Long, Y. Sui, Y. Qing, G. Zhao, Z. An, L. Wang, C. Liu, *Surface & Coating. Technology.* 384, 125-312 (2020)
15. X. He, P. Cao, F. Tian, X. Bai, C.Yuan, *Surface & Coating. Technology*, 357, 180–188 (2019)
16. Y. Shen, G. Wang, C. Zhu, J. Tao, Y. Lin, S. Liu, M. Jin, Y. Xie, *Surface & Coating. Technology*, 319, 286–293 (2017)
17. K. Seo, M. Kim, *Carbon* 68, 583–596 (2014)
18. Y.T. Cheng, D.E. Rodak, C.A. Wong, C.A. Hayden, *Nanotechnology* ,17 (5) 1359–1362 (2006)
19. M. Yamamoto, N. Nishikawa, H. Mayama, S. Yokojima, S. Nakamura, K. Uchida, *Langmuir*, 31, 7355–7363 (2015)
20. C. Chen, S. Yang, L. Liu, H. Xie, H. Liu, L. Zhu, X. Xu, *J. Alloy. Compd.* 71, 1506–513 (2017)
21. J.jeeyahan, M.Chandrasekaran, G.Britto Joseph, R.B.Durairaj, and G.Mageshwaran, *J.Coating Technology, Res*, Vol 15, no. 2, pp. 231-250 (2018)
22. A. Cassie, S. Baxter, *Trans. Faraday Soc.* 40, 546–551 (2014)
23. A. Carré and K. L. Mittal, *Superhydrophobic Surface*, vol. 65, no. 6. CRC Press (2009)
24. D.Zhang, L.Wang, H.Qian, X.Li. *Journal of Coatings Technology and Research*, Volume 13, pages 11–29 (2016)
25. Q. Liu, Z.X. Kang, *Mater. Lett.* 137, 210–213 (2014)
26. F. Su, K. Yao, *ACS Applied Materials & Interfaces*, 6, 8762-8770 (2014)
27. G. He, S. Lu, W. Xu, S. Szunerits, R. Boukherroub, H. Zhang, *Physical Chemistry Chemical Physics*, 17, 10871-10880 (2015)
28. T.F. Xiang, S.B. Ding, C. Li, S.L. Zheng, W. Hu, J. Wang, P.J. Liu, *Material and Design.* 114, 65–72 (2017)
29. J. Liang, D. Li, D. Wang, K. Liu, L. Chen, *Appl. Surf. Sci.* 293, 265–270 (2014)
30. Yu, C. Zhou, R. Liu, Q. Zhang, J. Gong, D. Tao, Z. Ji, *Colloids Surf, Physicochem. Eng. Aspects* 589, 124475 (2020)
31. T. Xiang, D. Chen, Z. Lv, Z. Yang, L. Yang, C. Li, , *J. Alloys. Compd.* 798, 320–325 (2019)
32. M. Xiang, M. Jiang, Y. Zhang, Y. Liu, F. Shen, G. Yang, Y. He, L. Wang, X. Zhang, S. Deng , *Appl. Surf. Sci.* 434, 1015–1020 (2018)
33. J. Tam, J.C.F. Lau, U. Erb, , *Nanomaterials* 9, 9010002 (2018)
34. G. Zhao, Y. Xue, Y. Huang, Y. Ye, F. Walsh, J. Chen, S. Wang, *RSC Adv.* 6 ,59104 (2016)
35. G. Zhao, J. Li, Y. Huang, L. Yang, Y. Ye, F.C. Walsh, J. Chen, S. Wang, *RSC Adv.* 7, 44896–44903, (2017)
36. E. Rahimi, A. Rafsanjani-Abbasi, A. Kiani-Rashid, H. Jafari, A. Davoodi, *Colloids Surface, Physicochem. Eng. Aspects.*, 547, 81–94 (2018)
37. M. Hashemzadeh, K. Raeissi, F. Ashrafizadeh, S. Khorsand, *Surface & Coating Technology*, 283, 318-328 (2015)
38. T.F. Xiang, S.B. Ding, C. Li, S.L. Zheng, W. Hu, J. Wang, P.J. Liu, *Material and Design.* 114, 65–72 (2017)
39. J.Tan, J.Hao, Z.An, C.Liu, *International Journal of Electrochemical* 12, 40 – 49 (2017)