

Fabrication of superhydrophobic surfaces on copper substrates via flow plating technology

Jing Sun¹, Long Wang¹, Ke Hu², Jinlong Song^{1,3}, Xin Liu¹

¹Key Laboratory for Precision and Non-traditional Machining Technology of the Ministry of Education, Dalian University of Technology, Dalian 116023, People's Republic of China

²Shenyang Blower Works Group Corporation, Shenyang 110869, People's Republic of China

³Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, USA
E-mail: xinliu@dlut.edu.cn

Published in Micro & Nano Letters; Received on 17th July 2014; Accepted on 10th November 2014

The preparation of superhydrophobic surfaces on hydrophilic metal substrates depends on both surface microstructures and low surface energy. Composite electro-brush flow plating technology was developed to prepare appropriate microstructures leading to superhydrophobicity on copper surfaces. The effects of plating voltage and plating time on the coating surface structures and hydrophobicity were discussed. The surface morphology and chemical composition were characterised by scanning electron microscopy and energy-dispersive X-ray spectroscopy. The results demonstrate that the prepared surfaces have the appearance of micro-nano hierarchical structures composed of submicron papilla-like Ni structures and nanoscale Al_2O_3 particles. After fluoridation, the coating surfaces prepared by proper parameters show superhydrophobicity with a water contact angle of 162° and a sliding angle of less than 10° . Tests of micro hardness, wear resistance and persistence show that the obtained superhydrophobic $n\text{-Al}_2\text{O}_3/\text{Ni}$ coating surfaces have outstanding mechanical properties and stability. This sample preparation technique has prospective application in the large-scale and continuous production of superhydrophobic engineering materials.

1. Introduction: Wettability, commonly measured using the liquid contact angle (defined as the angle that a liquid makes with a solid), is one of the most important properties of solid surfaces. A solid surface with a water contact angle larger than 150° is called a super-hydrophobic surface [1]. To become more capable of adapting to nature, many organisms have evolved with superhydrophobic surfaces with strong repellence of water, such as lotus leaves, rice leaves [2, 3], water strider legs [4], butterfly wings [5] etc. Superhydrophobic surfaces have widely promising applications in industrial and agricultural production because of their peculiar properties such as self-cleaning, corrosion resistance, anti-oxidation, drag reduction, anti-fog, repellence of snow or ice, directional transportation, oil-water separation and so on [6–12]. Copper, with its excellent electric and thermal conductivity, plays a vital role in a range of fields such as electric power, mechanical manufacturing, building industry and defence industry. As a typical metal, copper has high surface energy which can lead to the accumulation of water molecules on its surface, causing corrosion and sticking of ice or snow. It is significant to prepare superhydrophobic surfaces on copper substrate to keep it clean and prevent it from corrosion of accumulated ice and snow.

To date, researchers have successfully developed various methods to obtain superhydrophobicity based on copper. Common methods include chemical etching [13–15], electroless galvanic deposition [16–19], electrochemical deposition [20, 21], one-step immersion [22, 23] and surface oxidation [24, 25]. Although great development has been made in preparing superhydrophobic surfaces, there are still some limitations remaining, such as being environmentally unfriendly, having poor mechanical property, the high cost and the unpredictable process of the reaction. As a typical electrochemical deposition method, the brush-plating technique, with a moving electro-brush, makes it possible to fabricate large-area coating, which is limited by the fixed cathode and anode in traditional electrochemical deposition.

In our previous research, the composite brush electroplating technique developed by adding nanoparticles in the plating solution was

used to prepare the hierarchical micro/nanostructures on typical metal substrates [26, 27]. However, the problem that the graphite anode is easily damaged has existed for a long time in the previous device. Graphite, with layered structures combined with molecular force, easily disintegrates after a long time at high plating current. It is worse if the volume of disintegrated graphite is larger than the intact graphite, causing a decrease of the gap between the graphite anode and the substrate, and then the substrate (especially soft metal, such as copper) would be scratched easily by the moving brush. To solve this problem, an improved experimental device for flow plating technology was designed in this study. The graphite anode was replaced by austenitic stainless steel 1Cr18Ni9Ti, by which the experiment process was stable and continuous, and hence, the results of the experiments exhibited good reproducibility.

Based on the improved device, we explored a suitable type of nanoparticles which were added to the bath to fabricate a composite coating with high hardness on the copper substrate, as high hardness can enhance the mechanical strength of the plating coating. By adding Al_2O_3 nanoscale particles into the nickel electroplating bath, $n\text{-Al}_2\text{O}_3/\text{Ni}$ composite coatings with hierarchical micro/nanometer-scale structures were finally obtained. The microhardness value and wear resistance of the $n\text{-Al}_2\text{O}_3/\text{Ni}$ composite coatings were higher than the previous $n\text{-SiO}_2/\text{Ni}$ coating. After modification of low surface energy material, a superhydrophobic surface with a static water contact of about 162° and a sliding angle of less than 10° was obtained.

2. Experiment

2.1. Materials: A copper plate with purity of 99% was obtained from Tianjin Kermel Chemical Reagent Co., China. Fluoroalkylsilane (tridecafluorooctyltriethoxysilane (FAS), $\text{C}_{18}\text{F}_{31}\text{H}_{43}\text{Si}(\text{OCH}_2\text{CH}_3)_3$) was obtained from Degussa Co., Germany. The mean diameter of $n\text{-Al}_2\text{O}_3$ is 15 ± 5 nm and the specific surface area (Brunauer–Emmett–Teller) is about $200 \text{ m}^2/\text{g}$. A rapid solution of nickel brush plating were prepared with deionised water, pH was controlled to about 7.5, and measured at

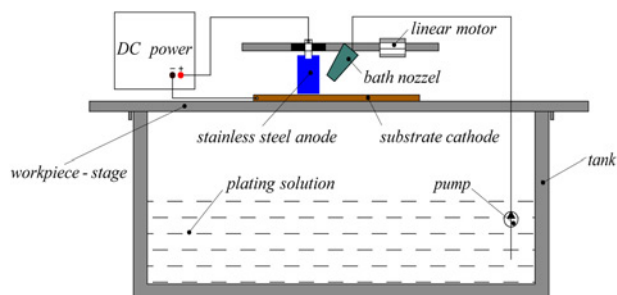
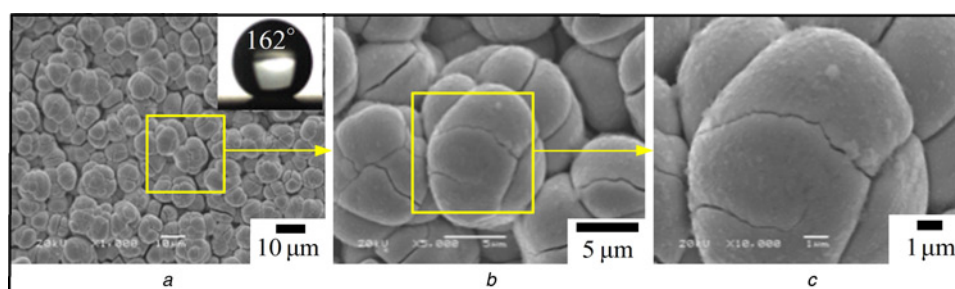
Table 1 Ingredients of nickel plating solution reagent

Reagent	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{O}_7(\text{NH}_4)_3$	$\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%)	$n\text{-Al}_2\text{O}_3$
content, g/l	256	55	105	proper

room temperature (25°C). The other chemicals (as shown in Table 1) used were of analytical grade (Tianjin Kermel Chemical Reagent Co., China).

2.2. Experimental device: As shown in Fig. 1, the copper substrate fixed on the workpiece stage was used as the cathode, whereas 1Cr18Ni9Ti stainless steel was used as the anode. The substrates were rubbed out by the reciprocating moving electro-brush, which was driven by the linear motor. Meanwhile, the pump made the plating solution circle through the brush constantly to ensure a continuous reaction.

2.3. Sample preparation: A $15 \times 50 \times 1 \text{ mm}^3$ copper plate was first polished mechanically using 500# and 1000# metallographic abrasive papers to remove the oxide layer. Then the substrate was cleaned ultrasonically in sequence with alcohol and deionised water for about 1 min. After the process of electrolytic degreasing and under layer plating on the copper substrate, composite electro-brush flow plating technology based on the experimental devices was used to obtain composite coating. The plating solution composition is shown in Table 1. Specifically, by ultrasonic vibration and mechanical stirring, $n\text{-Al}_2\text{O}_3$ can be made to suspend in the brush-plating solution evenly. After being ultrasonically rinsed in deionised water and subsequently dried, the sample was immersed in 1 wt% ethanol solution with fluoroalkylsilane for 1 h (25°C) followed by heat treatment at 120°C for 40 min to reduce the surface energy.

**Figure 1** Experimental devices used to prepare superhydrophobic surface**Figure 2** SEM images of the coating surface on the copper substrates after flow plating for 4 min at 12 V DC voltage

a SEM image of 1000 times magnification
b SEM image of 5000 times magnification
c SEM image of 10 000 times magnification

2.4. Characterisation: The morphological and elemental analyses of the samples were observed using scanning electron microscopy (SEM; JSM-6360LV, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS; INCA Energy, Oxford Instruments, UK). Water contact angles and sliding angles were measured using a contact angle system OCA 20 (DataPhysics Instruments GmbH, Germany) with a water droplet of 5 μl at the ambient temperature (25°C). The average value of five measurements at different positions of the sample was adopted as the final contact angle. The sliding angle is defined as the angle at which the droplet begins to slide away down the inclined surface.

3. Results and discussion

3.1. Microstructures and wettability on $n\text{-Al}_2\text{O}_3/\text{Ni}$ composite coating surface: Figs. 2a–c show the SEM images of a superhydrophobic composite coating surface on the copper substrate after flow plating for 4 min with 12 V DC voltage, as well as the water droplet on the prepared coating surface. The coating surface has the appearance of the uniform papilla-like structures resulting from flow brush electroplating, as shown in Fig. 2a. The papilla-like structures at different space locations hold together to form many pit structures with sizes of 10–30 μm . From the SEM images with large magnifications, it can be clearly seen that the papilla-like structures are covered with nanoscale grains and crack structures, as shown in Figs. 2a and b. Thus, the coating surfaces with the binary rough structures constructed by micrometer-scale papilla-like structures, nanoscale globular particles and crack structures are very rough, and play a crucial role in the generation of superhydrophobicity on the copper substrate. Before fluorination treatment, the obtained $n\text{-Al}_2\text{O}_3/\text{Ni}$ composite coating surfaces exhibit superhydrophilic properties, and the water droplets spread on the surface completely with a contact angle of nearly 0°. This phenomenon conforms to Wenzel's theory [28] that roughness enhances the hydrophilicity of hydrophilic surfaces. However, a 5 μl water droplet exhibits a typical spherical shape with a contact angle of 162° and sliding angle of less than 10° on the composite coating surfaces after being modified by FAS. The combination of hierarchical micro/nanometer-scale structures and material with low surface energy makes a water droplet on the coating surface exhibit the Cassie–Baxter contact state [29]. A large amount of air is trapped between surfaces and water droplets, thus leading to a high water static contact angle and a low sliding angle.

3.2. Analysis of micro/nanometer-scale binary structures: Fig. 3 shows the elemental composition of the $n\text{-Al}_2\text{O}_3/\text{Ni}$ coating surface analysed using EDS. It clearly demonstrates that the distinct peaks of oxygen, aluminium and nickel exist collectively in the prepared $n\text{-Al}_2\text{O}_3/\text{Ni}$ coating surface before fluorination treating. According to the mass fraction and atomic fraction, the main components of the coating are Ni and $n\text{-Al}_2\text{O}_3$.

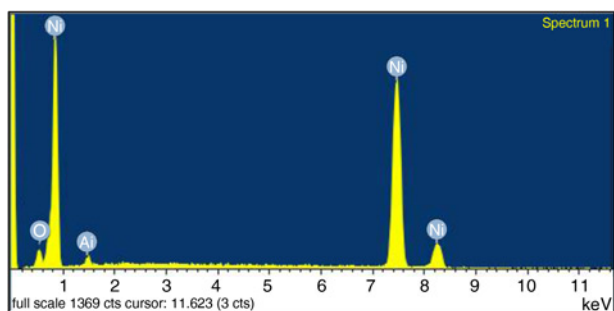


Figure 3 Energy spectrum analysis diagram of Ni/Al₂O₃ coating surfaces before fluorination

By applying an electric field, Ni²⁺ in the plating solution obtains electrons and turns into Ni particles while contacting with the brush. The formed Ni particles, having quite good preferential adsorbability to nanoparticles, deposite on the samples mixed with the insoluble nanometer-scale *n*-Al₂O₃ particles. As the processing time extends, the coating becomes thicker and finally the *n*-Al₂O₃/Ni composite coating with micro/nanometer-scale binary structures is obtained.

3.3. Effects of processing voltage on hydrophobicity: Fig. 4 shows the variation in the water contact angle and sliding angle with the plating voltage. The copper surface was processed by flow plating for 4 min at room temperature. The processing voltage varied from 0 to 15 V. When the voltage was 0 V, owing to the lack of micro/nanometer-scale binary structures, the water contact angle of the original copper surface after mechanical polishing and fluoridation was only 95° (Fig. 5a). At 5 V, the contact angle of the plating coating surface after fluoridation increased to 115°. Owing to the low voltage, only a few papilla-like structures were formed on the surface (Fig. 5b). As the plating voltage increased, crystal nucleus in the plating solution grew and formed quickly, leading to more papilla-like structures holding together to form lots of pit structures (Fig. 5c). When the voltage reached 12 V, the papilla-like structure surfaces were covered with nanoscale Al₂O₃ grains (Fig. 5d). The superhydrophobic surface with a water contact angle of 162° and sliding angle smaller than 10° was obtained. When the voltage exceeded 12 V, the water contact angles and sliding angles remained stable, and the obtained micro–nano hierarchical structures changed little as well (Fig. 5e).

3.4. Effects of plating time on hydrophobicity: Fig. 6 shows the variation in the water contact angle and sliding angle with the plating time. The copper surface was processed by flow plating at 12 V for different times at room temperature. At a plating time of 0.5 min, papilla-like structures were not apparent as crystal particles had not reached a certain size (Fig. 7a). Although the

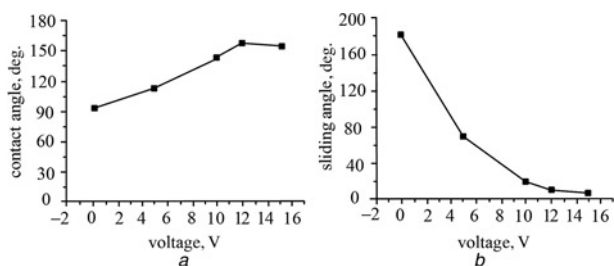


Figure 4 Relationship between the brush-plating voltage and super hydrophobicity of the coating surface on the copper substrates
a Relationship between plating voltage and water contact angle
b Relationship between plating voltage and water sliding angle

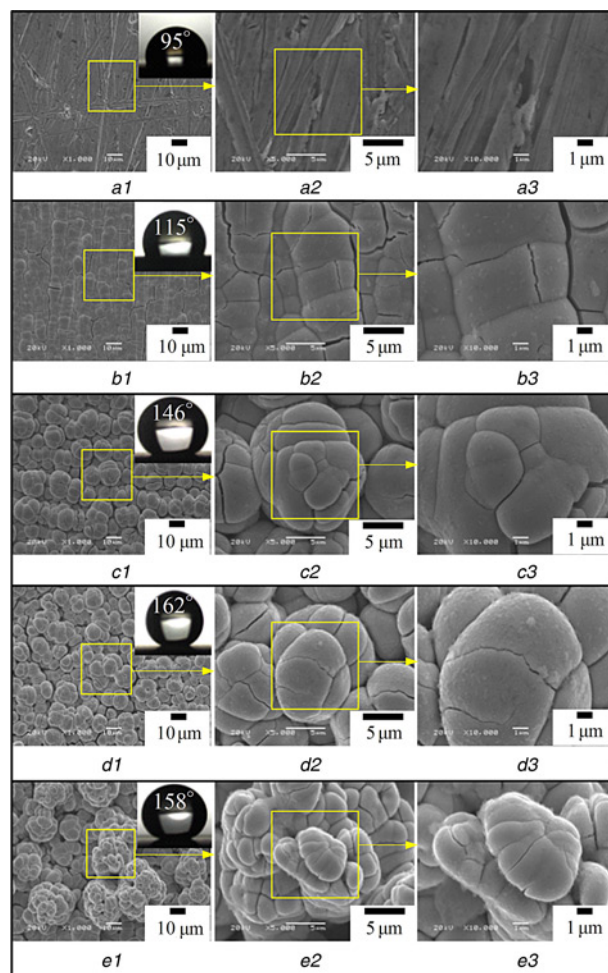


Figure 5 SEM images of Ni/Al₂O₃ composite coating surface under different brush-plating voltages
a1–a3 SEM images of coating surface under plating voltage of 0 V
b1–b3 SEM images of coating surface under plating voltage of 5 V
c1–c3 SEM images of coating surface under plating voltage of 10 V
d1–d3 SEM images of coating surface under plating voltage of 12 V
e1–e3 SEM images of coating surface under plating voltage of 15 V

contact angle of the plating coating surface after fluoridation increased to nearly 140°, the sliding angle was very large. As the plating time extended, the crystal nucleus gradually grew. Preferentially, growing and tip effect of firstly formed Ni crystal nucleus could lead to the formation of papilla-like structures and pit structures encapsulated with nanoscale Al₂O₃ particles (Figs. 7b–e). Al₂O₃ particles added could promote grain refinement, making it easy for crystal nucleation to occur. When the plating time was extended to 2 min, the water contact angle of

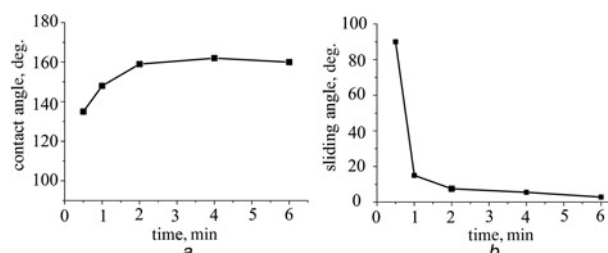


Figure 6 Relationship between the brush-plating time and superhydrophobicity of the coating surface on the copper substrates
a Relationship between plating time and water contact angle
b Relationship between plating time and water sliding angle

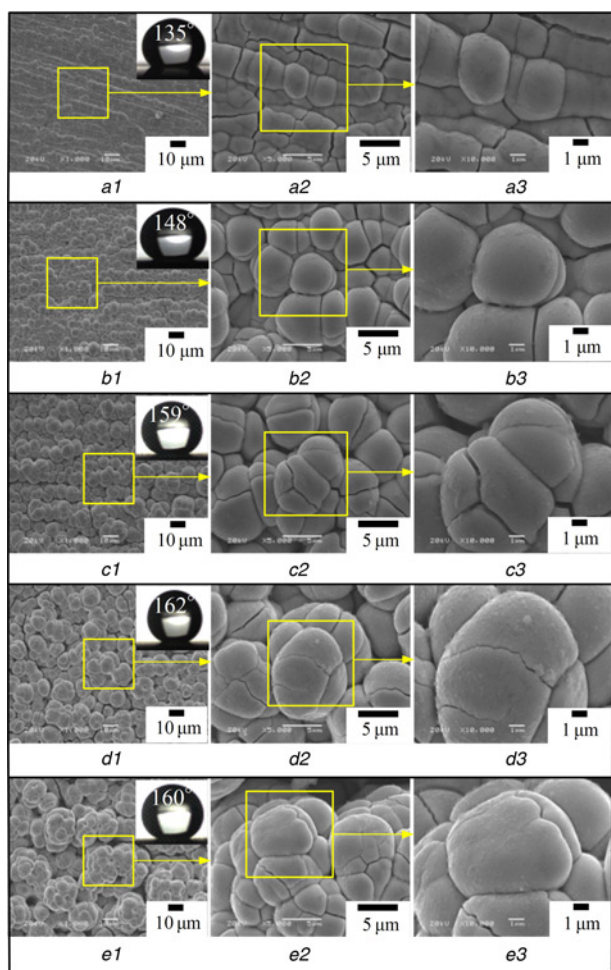


Figure 7 SEM images of $\text{Ni}/\text{Al}_2\text{O}_3$ composite coating surface under different brush-plating times

a1–a3 SEM images of coating surface under plating time of 0.5 min
b1–b3 SEM images of coating surface under plating time of 1 min
c1–c3 SEM images of coating surface under plating time of 2 min
d1–d3 SEM images of coating surface under plating time of 4 min
e1–e3 SEM images of coating surface under plating time of 6 min

the coating reached 159° and the sliding angle was less than 10° , then contact angles and sliding angles appeared to fluctuate little as time continued to increase. At the plating time of 4 min, the papilla-like structure surfaces were covered with nanoscale Al_2O_3 grains (Fig. 7d). The formation of micro/nanoscale binary

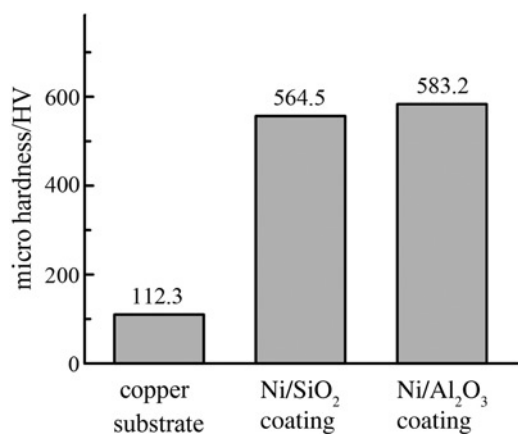


Figure 8 Comparison chart of microhardness

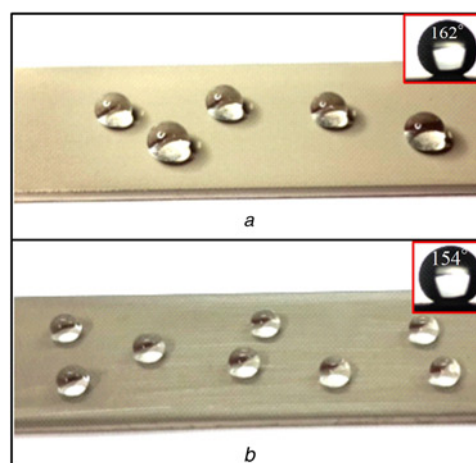


Figure 9 Water contact angles of $\text{Ni}/\text{Al}_2\text{O}_3$ composite coating
a Before friction test
b After friction test

structures constructed of $n\text{-Al}_2\text{O}_3$ and Ni caused superhydrophobicity after fluoridation. When the plating time exceeded 4 min, super-hydrophobicity remained stable and structures of coating appeared almost unchanged (Fig. 7e).

3.5. Analysis of microhardness, wear resistance and persistence of prepared coating: As an important index of plastic deformation resistance, the microhardness of the prepared coating needs to be tested. As the coating is very thin and measurement results might be influenced by the copper substrate, a vertical section of the coating was selected as the measurement position. A microhardness tester was used and are average value of five measurements at different positions of the sample was adopted as the final value of microhardness. Under pressure of 100 g applied for 15 s, the microhardness of the coating was 583.2 HV, which was higher than the $n\text{-SiO}_2/\text{Ni}$ composite coating obtained before (Fig. 8). Compared with the hardness of the original copper surface (112.3 HV), the microhardness of the $n\text{-Al}_2\text{O}_3/\text{Ni}$ composite coating had remarkably improved. Superhydrophobicity, combined with improved microhardness, can heavily broaden the application field of copper.

As is shown in Fig. 9a, the water contact angle of coating surface was 162° before polishing. After polishing five times with 1000# metallographic abrasive paper with a load of 4.5 KPa, the superhydrophobicity of the coating could remain, although a few scratches appeared on the coating surface (Fig. 9b). This test indicates that the $n\text{-Al}_2\text{O}_3/\text{Ni}$ composite coating obtained has high wear resistance. Furthermore, the wear resistance of the $n\text{-Al}_2\text{O}_3/\text{Ni}$ composite coating is higher than the $n\text{-SiO}_2/\text{Ni}$ composite coating that was obtained before.

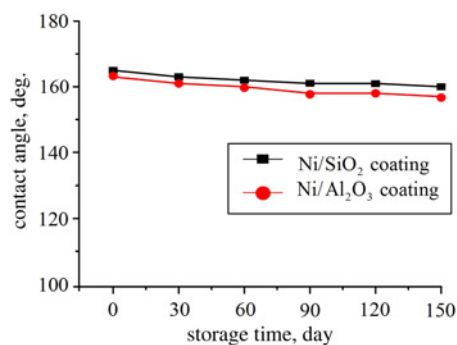


Figure 10 Relationship between water contact angles and storage time

Fig. 10 shows the variation of the water contact angles with the storage time. We can see that the as-fabricated $n\text{-Al}_2\text{O}_3/\text{Ni}$ coating surface, as well as the $n\text{-SiO}_2/\text{Ni}$ coating surfaces obtained before, can still remain superhydrophobic during exposure in air for 150 days, showing that the superhydrophobicity of composite coating has excellent persistence.

4. Conclusion: A superhydrophobic $n\text{-Al}_2\text{O}_3/\text{Ni}$ composite coating was successfully fabricated on a widely applied engineering material-copper substrate. The preparation method used is the novel composite electro-brush flow plating technology, which is relatively simple and effective. Many microscale papilla-like structures, pits structures and nanoscale Al_2O_3 particles jointly formed micro-nano hierarchical structures, which are the key to achieving superhydrophobicity. The optimum processing conditions were obtained by investigating their effects on the surface micromorphology and superhydrophobicity. The measurements indicate that the composite coating surfaces have superhydrophobicity with a water contact angle of 162° and a sliding angle of less than 10° after subsequent fluorination. The addition of Al_2O_3 particles enhances the mechanical strength of the obtained superhydrophobic coating. The tests of microhardness, wear resistance and persistence show that the prepared superhydrophobic $n\text{-Al}_2\text{O}_3/\text{Ni}$ composite coating surfaces have an excellent mechanical property and stability. The improved device, especially the employment of austenitic stainless steel 1Cr18Ni9Ti anode, will enable the large-scale and continuous production of superhydrophobic engineering materials with new industrial applications.

5. Acknowledgments: The work was financially supported by the Doctor Startup Fund of Liaoning Province (grant no. 20121018), a Scholarship Award for Excellent Doctoral Students granted by the Ministry of Education and project funded by the China Postdoctoral Science Foundation.

6 References

- [1] Li X., Reinhoudt D., Crego-Calama M.: 'What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces', *Chem. Soc. Rev.*, 2007, **8**, pp. 1350–1368
- [2] Barthlott W., Neinhuis C.: 'Purity of the sacred lotus, or escape from contamination in biological surfaces', *Planta*, 1997, **1**, pp. 1–8
- [3] Guo Z.G., Liu W.M.: 'Biomimic from the superhydrophobic plant leaves in nature: Binary structure and unitary structure', *Plant Sci.*, 2007, **6**, pp. 1103–1112
- [4] Gao X.F., Jiang L.: 'Water-repellent legs of water striders', *Nature*, 2004, **7013**, p. 36
- [5] Wang H., Tang L.M., Wu X.M., Dai W.T., Qiu Y.P.: 'Fabrication and anti-frosting performance of super hydrophobic coating based on modified nanosized calcium carbonate and ordinary polyacrylate', *Appl. Surf. Sci.*, 2007, **22**, pp. 8818–8824
- [6] Shi F., Niu J., Liu J.L., ET AL.: 'Towards understanding why a superhydrophobic coating is needed by water striders', *Adv. Mater.*, 2007, **17**, p. 2257
- [7] Kulinich S.A., Farzaneh M.: 'Ice adhesion on super-hydrophobic surfaces', *Appl. Surf. Sci.*, 2009, **18**, pp. 8153–8157
- [8] Tourkine P., Le Merrer M., Quere D.: 'Delayed freezing on water repellent materials', *Langmuir*, 2009, **13**, pp. 7214–7216
- [9] Shirtcliffe N.J., McHale G., Newton M.I., Perry C.C.: 'Wetting and wetting transitions on copper-based super-hydrophobic surfaces', *Langmuir*, 2005, **3**, pp. 937–943
- [10] Zhang S., Lu F., Tao L., ET AL.: 'Bio-inspired anti-oil-fouling chitosan-coated mesh for oil/water separation suitable for broad pH range and hyper-saline environments', *ACS Appl. Mater. Interfaces*, 2013, **22**, pp. 11971–11976
- [11] Yang X., Song J., Xu W., Liu X., Lu Y., Wang Y.: 'Anisotropic sliding of multiple-level biomimetic rice-leaf surfaces on aluminium substrates', *Micro Nano Lett.*, 2013, **8**, pp. 801–804
- [12] Jin M.H., Feng X.J., Feng L., ET AL.: 'Superhydrophobic aligned polystyrene nanotube films with high adhesive force', *Adv. Mater.*, 2005, **16**, p. 1977
- [13] Qian B.T., Shen Z.Q.: 'Fabrication of superhydrophobic surfaces by dislocation-selective chemical etching on aluminum, copper, and zinc substrates', *Langmuir*, 2005, **20**, pp. 9007–9009
- [14] Liu L.J., Xu F.Y., Ma L.: 'Facile fabrication of a superhydrophobic Cu surface via a selective etching of high-energy facets', *J. Phys. Chem. C*, 2012, **35**, pp. 18722–18727
- [15] Pan L., Dong H., Bi P.: 'Facile preparation of superhydrophobic copper surface by HNO_3 etching technique with the assistance of CTAB and ultrasonication', *Appl. Surf. Sci.*, 2010, **5**, pp. 1707–1711
- [16] Safaei A., Sarkar D.K., Farzaneh M.: 'Superhydrophobic properties of silver-coated films on copper surface by galvanic exchange reaction', *Appl. Surf. Sci.*, 2008, **8**, pp. 2493–2498
- [17] Larmour I.A., Bell S.E.J., Saunders G.C.: 'Remarkably simple fabrication of superhydrophobic surfaces using electrodeless galvanic deposition', *Angew. Chem.*, 2007, **10**, pp. 1740–1742
- [18] Song W., Zhang J.J., Xie Y.F., Cong Q., Zhao B.: 'Large-area unmodified superhydrophobic copper substrate can be prepared by an electrodeless replacement deposition', *J. Colloid Interface Sci.*, 2009, **1**, pp. 208–211
- [19] Xu X., Zhang Z., Yang J.: 'Fabrication of biomimetic superhydrophobic surface on engineering materials by a simple electrodeless galvanic deposition method', *Langmuir*, 2010, **5**, pp. 3654–3658
- [20] Shirtcliffe N.J., McHale G., Newton M.I., Chabrol G., Perry C.C.: 'Dual-scale roughness produces unusually water-repellent surfaces', *Adv. Mater.*, 2004, **21**, p. 1929
- [21] Xi J.M., Feng L., Jiang L.: 'A general approach for fabrication of superhydrophobic and superamphiphobic surfaces', *Appl. Phys. Lett.*, **92**, (5), pp. 053102–053102-3
- [22] Wu W., Chen M., Liang S., Wang X., Chen J., Zhou F.: 'Superhydrophobic surface from Cu–Zn alloy by one step O_2 concentration dependent etching', *J. Colloid Interface Sci.*, 2008, **2**, pp. 478–482
- [23] Wang S.T., Feng L., Jiang L.: 'One-step solution-immersion process for the fabrication of stable bionic superhydrophobic surfaces', *Adv. Mater.*, 2006, **6**, p. 767
- [24] Lee S., Kim K., Pippel E., Kim S., Kim J., Lee H.: 'Facile route toward mechanically stable superhydrophobic copper using oxidation-reduction induced morphology changes', *J. Phys. Chem. C*, 2012, **4**, pp. 2781–2790
- [25] Liu X.L., Jiang Z.H., Li J., Zhang Z.H., Ren L.Q.: 'Super-hydrophobic property of nanosized cupric oxide films', *Surf. Coat. Technol.*, 2010, **20**, pp. 3200–3204
- [26] Song J., Xu W., Lu Y., Luo L., Liu X., Wei Z.: 'Fabrication technology of low-adhesive superhydrophobic and superamphiphobic surfaces based on electrochemical machining method', *J. Micro Nanomanuf.*, 2013, **2**, p. 21003
- [27] Hu K., Xu Q.X., Yang X.L.: 'Fabrication of superhydrophobic surfaces on copper substrates via brush plating technique', *Adv. Mater. Res.*, 2014, **834–836**, pp. 662–669
- [28] Wenzel R.N.: 'Resistance of solid surfaces to wetting by water', *Ind. Eng. Chem.*, 1936, **8**, pp. 988–994
- [29] Cassie A.B.D., Baxter S.: 'Wettability of porous surfaces', *Trans. Faraday Soc.*, 1944, **40**, pp. 546–551