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Durability study of super-hydrophobic surfaces according to surface morphology and material type

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1. Introduction

The concept of superhydrophobic surfaces was initially inspired by the morphology of lotus leaves found in nature [1]. Superhydrophobic surfaces are typically defined as surfaces with water contact angles of 150° or greater, achieved through a combination of surface structures and surface energy considerations. Due to their high contact angles, superhydrophobic surfaces have gained attention in various applications such as anti-fouling surfaces [2], self-cleaning surfaces [3], and anti-icing materials [4]. However, the primary challenge in utilizing superhydrophobicity in industrial applications is durability. Extensive research efforts have been directed toward enhancing the robustness of superhydrophobic surfaces. One approach to improve the durability of superhydrophobic surfaces is to rely solely on the intrinsic surface structure of the material, without the need for additional coatings or surface energy modification. This approach offers the advantage of maintaining surface properties even in the presence of surface wear and tear, as the material composing the surface remains unchanged. However, it comes with the limitation of being applicable to a limited range of materials. Numerous studies have evaluated the robustness of various surfaces using methods such as finger-wipe tests, tape peeling, blade scratching, sandpaper abrasion, and the sandblasting method. However, the absence of established standardized criteria for assessing wear resistance has made it challenging to compare the durability of different coatings. In this study, we selected Al, Cu, and Ti as the experimental materials, which are widely utilized in various industries and have been actively researched for surface modification. To implement surface properties on a macroscopic curved surface, we employed the electrochemical etching method for all processes. A superhydrophilic surface was created by forming microstructures on the surfaces of Al, Cu, and Ti, and then coated with a hydrophobic material as a Self-Assembled Monolayer (SAM) to create a superhydrophobic surface. Surface structures and wetting behavior were observed. The conventional sandpaper abrasion test is a widely used laboratory method to evaluate the mechanical durability of superhydrophobic surfaces. It assesses the resistance to wear under a given stress by comparing the number of wear cycles or the length of wear distance that a superhydrophobic surface can endure. Hence, a straightforward comparison of wear cycles or wear distances to evaluate the wear resistance of superhydrophobic coatings is inaccurate. In this research, we conducted wear experiments on the fabricated superhydrophobic surfaces of each metal type by applying vertical pressure using a roller. Subsequently, we investigated the contact angles and self-cleaning capabilities, thereby evaluating the robustness based on microstructure variations and observed the wear morphology through SEM imaging.

2. Experimental procedure

To test the robustness of the specimen, a standardized rolling wear tester was designed and a wear test was performed as depicted in Figure 1. The rubber roller reciprocated over the specimen at a speed of 5.3cm/s, and a load of 21.98N was applied to the specimen using two 1kg weights. Rolling wear tests were conducted on Cu, Al, and Ti specimens, respectively, and the experiment was conducted based on a contact angle of 110°. A rolling wear test was performed 100 times for Cu specimens and 1000 times for Al and Ti specimens, and contact angle measurements were performed to check the change in contact angle at each cycle. The rationale for selecting each test cycle of each superhydrophobic specimens were determined by preliminary experiments prior to the main experiment. In the preliminary experiments, it was found that the superhydrophobic Cu specimen has a durability of about 4000 cycles. For superhydrophobic Al and Ti, the number of cycles was selected to check the degradation of contact angle at about 20000 and 30000 cycles, respectively. After the rolling wear test we determine the degree of material transfer that occurred in the material before and after the experiment, EDS analysis was performed by comparing the two cases of a superhydrophobic specimen that did not undergo a rolling wear test and a superhydrophobic specimen that completed the rolling wear test. To compare the self-cleaning ability, experiments were conducted on specimens with superhydrophobic surfaces, before and after rolling wear test. The deposition material used in the experiment was Arizona Test Dust, and the ATD was shaken through a sieve and filtered before and after untreated specimens and rolling wear test. After and after the wear test, it was deposited on a specimen with an intermediate value. The experimental equipment includes a device that tilts and fixes the specimen at an angle of 10 degrees and a pump that supplies DI water to the surface of the specimen. To wash the specimen, it was washed with DI water at a flow rate of 1 ml/min.

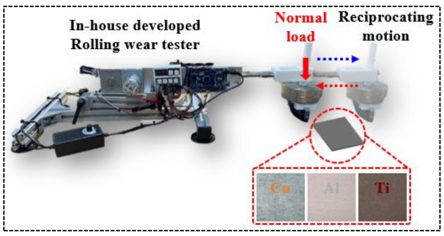

Fig. 1 In-house developed rolling wear tester

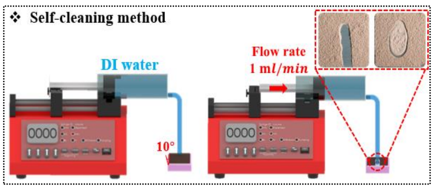

Fig. 1 Self-cleaning test process

3. Results and discussion

The results of the wear experiment until the contact angle for each specimen becomes less than 110 degrees are shown in Figure 3. Cu contact angle of less than 110 degrees at 4,300 cycles, Al at 21,000 cycles, and Ti at 32,000 cycles. In the case of Cu, it can be seen that the Cu nanowires are pressed relatively evenly when a load is applied to the surface due to the nanowire structure having a relatively uniform structure and a small height difference. In the case of Al, there is a difference in height, it can be seen that the cubic structures that exist in a relatively low position have a lower degree of deformation or almost no deformation than the cubic structures that exist in a relatively high position. In the case of Ti, it is a nano-net structure over micro-pits, and the structure in areas not dug into micro-pits acts as a guard, so it can be seen that the deformation period of the structure inside the pits is later than that of Al. The self-cleaning rate was measured by percent of subtracting the area of sand remaining from the area covered by water. As a result of the self-cleaning experiment, the superhydrophobic Cu specimen after 5,000 wear tests showed a cleaning rate of 11.9%, and the superhydrophobic Cu specimen before a wear test showed a cleaning rate of 98.2%. The superhydrophobic Al specimen after 25,000 wear tests showed a cleaning rate of 40.9%, and superhydrophobic Al specimen before the wear test showed a cleaning rate of 98.4%. The superhydrophobic Ti specimen after 35,000 wear test showed a cleaning rate of 21.3%, and superhydrophobic Ti specimen before wear test showed a cleaning rate of 94.7%. The results between contact angle increase and cleaning rate are shown in Figure 4.

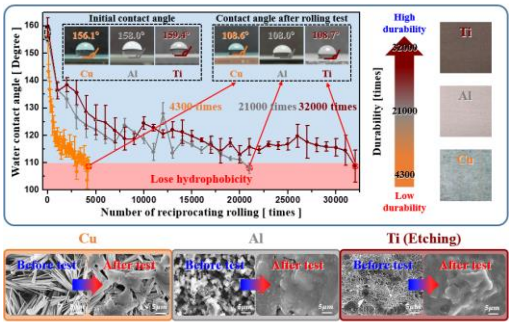

Fig. 3 Contact angle degradation of superhydrophobic surfaces

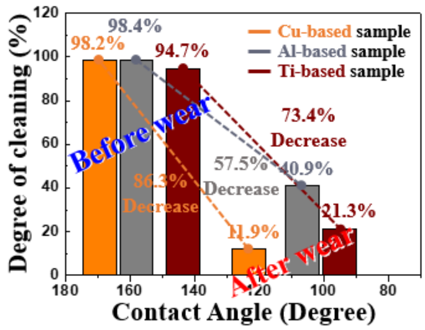

Fig. 4 Self-cleaning degradation

Conclusion

This study focused on evaluating and comparing the durability of commercially available superhydrophobic surfaces based on Cu, Al, and Ti using an in-house developed rolling wear tester. The results showed that the order of the most durable surfaces are Ti, Al, and Cu. In addition to mechanical properties of the material, we found that it is more closely related to the morphology of structure created in the fabrication of the superhydrophobic surface. The reason for this is that Cu has a needle-like nanopillar structure and is therefore weak in bending. This causes the nanopillar to break down under load, revealing the hydrophilic surface of the Cu, which quickly loses its hydrophobicity. Al, on the other hand, has a cubic structure and is a ductile metal, so when it is loaded, the surface changes to a pressed surface rather than a cracked or broken surface. Therefore, hydrophilic surface is not revealed. Finally, Ti has the best stiffness compared to Al and Cu. It has the best robustness because it has the effect of distributing the load due to its net structure. We analysis and compared each structure in Abaqus, a finite element method analysis program, through simulation analysis. In this study, we found that the self-cleaning efficiency is related to the contact angle. Before the rolling wear test, the specimens had an air layer formed by the structures, resulting in a contact angle of more than 150 degrees, and the self-cleaning efficiency was more than 94% for all three specimens. After the rolling wear test, the structures collapsed and compressed, the air layer disappeared, and the self-cleaning efficiency dropped to 10% for Cu and Ti and 40% for Al. We found that the contact angle of the surface decreases as the structure collapses, and as the contact angle decreases, the self-cleaning ability decrease.

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