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Study on the Super Lubricated and Tribological Properties of Triethanolamine Borate as a New Lubricant Additive

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Abstract

As a new green water-based complete synthetic cutting fluid additive, the anti-rust properties of triethanolamine borate have been extensively studied, but its tribological properties in the cutting process have not yet been reported. In this paper, the super-lubricity theory is applied to the study of lubricating additives. Based on the occurrence mechanism and realization conditions of super-lubricity, founding that the triethanolamine borate has super lubricated properties through analyzing its molecular structure; the tribological properties of triethanolamine borate were further studied based on a large number of experiments. The friction coefficients of triethanolamine borate, glycerol and polyethylene glycol 400 were measured by the friction and wear tester, and the friction coefficient variation rule was obtained and the friction reduction ability of triethanolamine borate was analyzed; by analyzing physical quantities such as friction coefficient, lubrication stability, outline and morphology of wear scar, the tribological properties of aqueous solutions of triethanolamine borate with different contents were studied, and the influence rule of additive content on tribological properties was obtained. The research results show that triethanolamine borate has excellent anti-friction and anti-wear properties compared with the traditional lubricating additives glycerol and polyethylene glycol 400, its friction coefficient and the width and depth of the wear scar are the lowest among them; the anti-friction and anti-wear ability of triethanolamine borate increases with the increase of its content in the aqueous solution.

Keywords

Super-lubricity; Lubricating additive; Triethanolamine borate; Tribological properties.

1. INTRODUCTION

With the development of industry, some fields have increasingly higher requirements on mechanical and mechanical properties of parts. For example, the lightweight and high-strength evolution of aerospace parts have made the application of difficult-to-machine materials such as titanium alloys more extensive [1-2]. However, such materials are very likely to cause tool wear [3-4] in the processing process and affect the machining quality of the workpiece, so the use of cutting fluid is essential in the processing. Previous studies have shown that tool wear caused by thermal and chemical effects is the main part of titanium alloy processing, and it is more appropriate to use water-based complete synthetic cutting fluid with the good cooling performance [5-7].

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In recent years, metal cutting fluid has been developing towards the direction of green and environment-friendly water-based complete synthetic cutting fluid, which not only satisfies lubrication, cooling, cleaning and rust protection, but also causes less and less harm to the human body and environmental pollution [8-9]. Water-based complete synthetic cutting fluid relies on various additives to obtain excellent performance. The choice of additives is varied, including a surfactant, extreme pressure lubricant, rust inhibitor, etc., among which extreme pressure lubricant is related to the lubrication and anti-wear performance of cutting fluid [10]. Traditional extreme pressure lubricants contain elements such as sulfur, phosphorus and chlorine. Although they have excellent anti-wear properties, they do great harm to the human body and the environment [11]. With the development of science and technology, boron extreme pressure lubricants mainly composed of organic borate have gradually attracted people's attention. Organic borate has good anti-friction and anti-wear properties, high oil film strength and non-toxic [12]. With triethanolamine borate has been widely studied because of its excellent anti-rust performance [13], but there are few reports on other properties except anti-rust performance, especially the lack of investigations of the lubrication effect between metal, so from the field of tribology probe into its anti-friction and anti-wear effect between metal is of great significance, which is expected to make triethanolamine borate break the limitation of rust inhibitor and become new cutting fluid lubrication additives.

Super-lubricity is one of the most promising advanced scientific theories in the field of modern tribology. It refers to the lubrication state with a friction coefficient of 0.001 or lower. Super-lubricity was proposed in the late 1980s. Hirano et al. [14], a Japanese scholar, conducted molecular dynamics simulation of the relative sliding of two smooth crystal surfaces, and found that the friction completely disappeared. Therefore, they defined this special lubrication state as super-lubricity. Subsequently, scholars and research institutions at home and abroad have carried out a large number of studies on super-lubricity [15-18]. The present progress, on the one hand, studies the generation and existence mechanism of super-lubricity theoretically, and on the other hand, explores the properties and existence conditions of super lubricated materials experimentally.

By analyzing the molecular structure of triethanolamine borate and combining with the mechanism of super-lubricity, it is found that triethanolamine borate has super lubricating properties. On this basis, the frictional properties of triethanolamine borate were studied based on a large number of experiments, and the lubrication mechanism of triethanolamine borate was revealed. This study lays a foundation for the application of triethanolamine borate as a new lubricant additive in cutting fluid.

2. STUDY ON SUPER LUBRICATED PROPERTIES OF TRIETHANOLAMINE BORATE

2.1. Occurrence Mechanism and Realization Conditions of Super-lubricity

Luo and his team at Tsinghua University came up with an acid-based and alcohol-based super lubricated system, and they found that three conditions need to be met to achieve super-lubricity. The first condition requires that the friction pair must have silicon hydroxide bonds, the second condition requires sufficient hydrogen ions in the solution, and the third condition requires that the solution must contain sufficient polyhydroxy molecules [19-20]. The occurrence mechanism of super-lubricity is that hydrogen ions adsorbed on the surface of the friction pair are positively charged to form a double electric layer, and polyhydroxy molecules react with water to form a hydrogen bond network structure, which together with water molecules forms a three-layer structure to achieve super-lubricity, namely, the double electric layer - hydrogen bond network structure - hydrated water [21-22]. Its super lubricated structure is shown in Figure 1:

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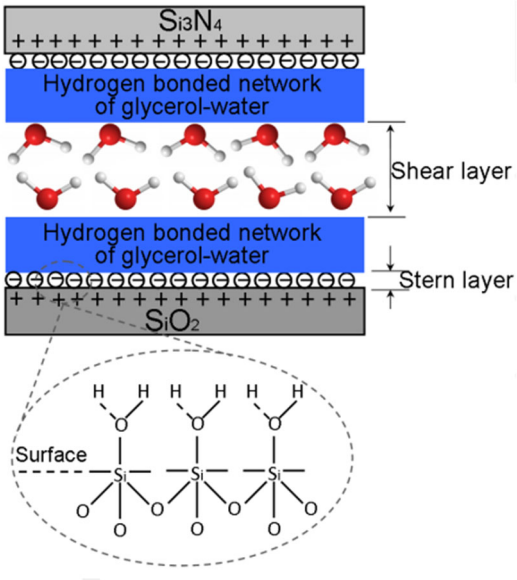

Figure 1. Superlubrication architecture of acids and alcohols

2.2. Super Lubricated Property of Triethanolamine Borate

The molecular formula of triethanolamine borate is C6H12BNO3, and its structure is shown in Figure 2:

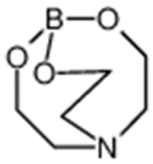

Figure 2. Molecular structure of triethanolamine borate

Triethanolamine borate is produced by the reaction of boric acid and triethanolamine under the action of a water-bearing agent. The reaction formula is shown in Figure 3 [23]. During the reaction, the hydroxyl group in boric acid and the hydrogen atom in the triethanolamine hydroxyl group produce water, and the boron atom directly combines with the oxygen atom in the triethanolamine hydroxyl group, and the water-carrying agent continuously takes away the water and finally forms triethanolamine borate. The three-dimensional molecular structure of triethanolamine borate is shown in Figure 4. Triethanolamine borate is a cage-shaped heterocyclic compound and belongs to nitrogen-containing borate in terms of composition [24]. The purpose of synthesizing triethanolamine borate is to introduce nitrogen atoms into the borate to form a coordination bond between nitrogen and boron, increase steric hindrance and enhance the hydrolytic stability of the borate. So as to solve the problem of easy hydrolysis of boric acid ester due to the electron deficiency of boron atom [25]. Also, boron and nitrogen have extreme pressure lubrication performance, which can be further enhanced by using the hydrocarbon as the carrier.

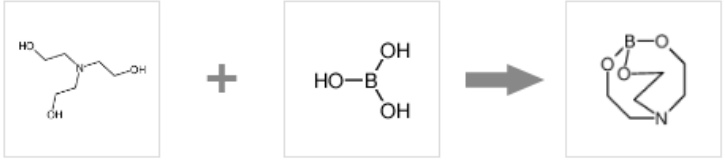

Figure 3. The reaction formula for generating triethanolamine borate

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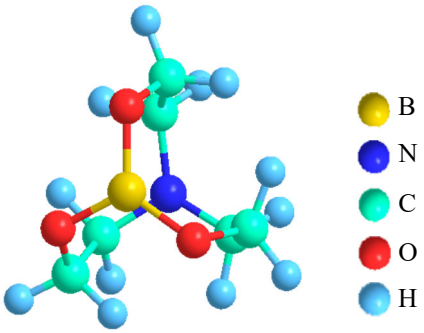

Figure 4. 3D molecular structure of triethanolamine borate

By analyzing the molecular composition of triethanolamine borate and combining with the occurrence mechanism and realization conditions of super-lubricity, we found that triethanolamine borate has the conditions to realize super-lubricity, that is, it contains hydrogen ion and the hydroxyl group at the same time, and has certain super lubricating properties. In cutting conditions, especially in the first contact area, a part of triethanolamine borate molecules will be squeezed to break the molecular chain, leading to more free activities of nitrogen and boron atoms. Due to the high-temperature characteristics during cutting, nitrogen atoms and boron atoms can combine to form tiny hexagonal boron nitride particles [26], which have a layered structure similar to graphite and excellent properties of lubrication and heat conduction. The tiny hexagonal boron nitride particles may exist in the cutting fluid in the form of nano solid super lubricated molecules [27] to enhance the properties of lubrication and heat conduction. According to this inference, triethanolamine borate is superior to glycerin and polyethylene glycol as lubricant additives in cutting fluids.

3. THE EXPERIMENT DESIGN

3.1. The Experimental Materials

Carbide ball: YG8, diameter: 9.525mm, density: 14.5~14.9g/cm3, hardness: HRA89.5; titanium alloy plate: TC4, diameter: 54mm, thickness: 2mm, density: 4.51g /cm3, hardness: HRC 31; triethanolamine borate: light yellow transparent liquid, 20°C density: 1.25, molecular weight: 157, purchased from Wuxi Yatai United Chemical Co, LTD; glycerol: commonly known as glycerin, clarified viscous liquid, analyzed pure AR, and purchased from Xilong Scientific Co, LTD, with a relative molecular weight of 92.09; polyethylene glycol 400: referred to as "PEG - 400", colorless viscous liquid, average molecular weight: 370~400, purchased from Xilong Scientific Co, LTD.

The experimental solution was configured according to the content of additives. Triethanolamine borate aqueous solution with 10% content was prepared by the mixture of triethanolamine borate and deionized water at the volume ratio of 1:9. Keep the total volume of the solution after mixing unchanged, and configure a triethanolamine borate aqueous solution with a content of 10% to 100%, respectively.

3.2. Experimental Equipment and Methods

3.2.1 Friction and wear test

The MFT-EC4000 electrochemical corrosion friction and wear tester developed by the Lanzhou Institute of Chemical Physics was used to measure the friction coefficient. The experimental equipment was shown in Figure 5. During the test, the titanium alloy disc and cemented carbide ball were fixed on the instrument, and then the solution to be measured was dropped into the contact area. The motion mode was reciprocating. The solution was moved for

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10 minutes under a certain load at a frequency of 2HZ to measure the friction coefficient of the solution under the friction pair of titanium alloy and cemented carbide.

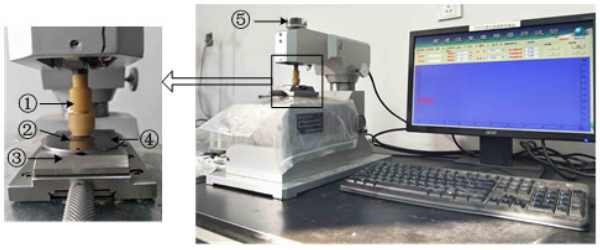

Figure 5. MFT-EC4000 electrochemical corrosion friction and wear tester. ①upper sample fixture; ②lubricating fluid; ③lower sample fixture; ④lower sample tray; ⑤weight

3.2.2 Observation of wear scar morphology

The optical microscope was used to observe the morphology of the wear scar and measure the width of the wear scar. The workpiece to be measured was cleaned by ultrasonic before measurement, and the vertical line measurement method was used to reduce the error during measurement. TIME3220 roughness tester is used to measure the wear scar profile to get the depth of the wear scar. During the measurement, the motion direction of the roughness tester probe is perpendicular to the direction of the wear scar, and the depth of the wear scar is obtained by processing the measured original data.

4. ANALYSIS OF EXPERIMENTAL RESULTS

4.1. Experimental Study on Anti-friction and Anti-wear Properties

4.1.1 Comparative study on anti-friction properties

At present, the main lubricating components of water-based cutting fluids on the market are glycerin or polyethylene glycol, etc. To study the lubricating properties of triethanolamine borate, it is compared with glycerin and polyethylene glycol 400. The friction and wear tests of the three solutions were carried out under different loads, and the variation curves of the friction coefficients were obtained. Figure 6 shows the variation curve of the friction coefficient of triethanolamine borate, glycerol and polyethylene glycol 400 under different loads. It can be seen from the figure that when the load is lower than 10N, the friction coefficients of the three solutions are, from low to high, glycerol, triethanolamine borate and polyethylene glycol 400 in sequence. When the load is greater than 10N, the friction coefficient of triethanolamine borate is the lowest. Among them, the friction coefficient of polyethylene glycol 400 varies less under different loads, and the friction coefficient of triethanolamine borate and glycerol varies more. The results show that the lubrication property of triethanolamine borate is better when the load is more than 10N.

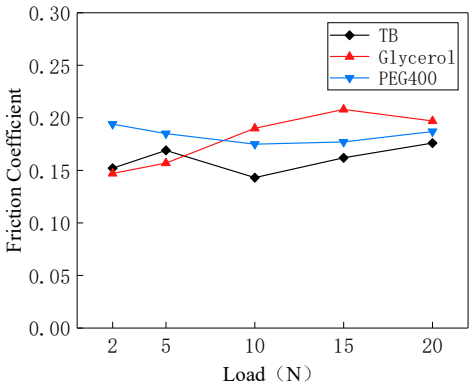

Figure 6. Comparison of friction coefficients of three solutions under different loads

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4.1.2 Comparative study on anti-wear properties

The width and depth of the wear scar of the three solutions under different loads were measured. The results are shown in Figure 7 and Figure 8. Figure 7 shows the width of the wear scar of the three solutions under different loads. As can be seen from the figure, the width of the wear scar increases with the increase of the load. Under the same load, the width of the wear scar of the three solutions is not different, but the width of the wear scar of PEG 400 solution is always the largest. At loads of 2N to 10N, the wear scar width of glycerol is lower than that of triethanolamine borate, whereas at 15N and 20N the results are reversed. Figure 8 shows the wear scar depth of the three solutions under different loads. As can be seen from the figure, the wear scar depth also increases with the increase of the load. When the load is 2N and 5N, the wear scar depth of triethanolamine borate solution is relatively larger, while the wear scar depth of triethanolamine borate solution is the smallest under the load of 20N. The width of the wear scar and the depth of the wear scar reflect the anti-wear performance of the solution, so it can be seen that for the friction pair of titanium alloy, the anti-wear performance of triethanolamine borate is close to that of glycerol and polyethylene glycol 400, and the anti-wear performance of triethanolamine borate is even better than the other two solutions under a relatively large load. Combining the friction coefficient and the width and depth of wear scars, triethanolamine borate can be used as a lubricant additive for titanium alloy cutting fluids.

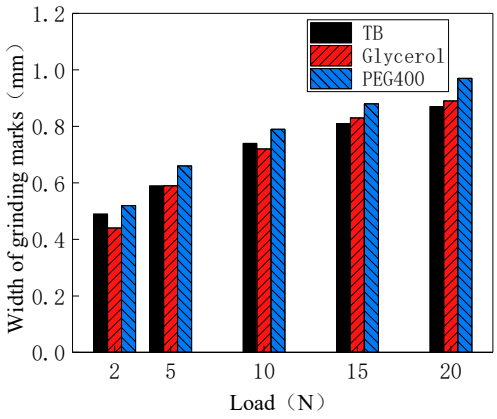

Figure 7. The wear scar width of the three solutions under different loads

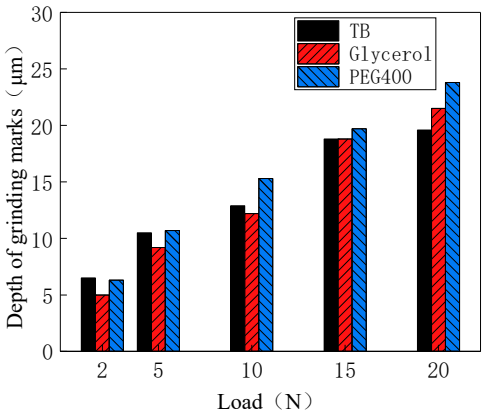

Figure 8. The wear scar depth of the three solutions under different loads

4.2. Effect of Additive Content on Tribological Properties

Water-based cutting fluid is composed of various additives and water, so it is particularly important to mix triethanolamine borate ester with water to prepare an aqueous solution of triethanolamine borate ester with different contents, and then analyze the effect of additive

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content on tribological properties. Triethanolamine borate's tribological properties as lubricant additive of cutting fluid were studied by analyzing the friction coefficient, lubrication stability, profile and morphology of the wear scar and other parameters, to provide a reference for the final synthesis of cutting fluid.

4.2.1 Effect of additive content on anti-friction properties

The anti-friction properties of triethanolamine borate aqueous solutions with different contents for the friction pair of titanium alloy and hard alloy were investigated through friction and wear tests. Figure 9 shows the relationship between the friction coefficient and the content of triethanolamine borate. The abscissa represents the content of triethanolamine borate in the solution. When the content is 0%, it is pure deionized water; when the content is 100%, it is pure triethanolamine borate solution. Three groups of tests were measured under the load of 10N, and the variation range of friction coefficient of each group was respectively 0.241~0.269; 0.098 ~ 0.267; 0.125 ~ 0.261. It can be seen from the figure that when the content is less than 40%, the triethanolamine borate solution's friction coefficient is the same as that of deionized water. The friction coefficient of the solution changed significantly when the content was between 50% and 90% compared with the content below 40%. The test results of the first and third groups show that when the content of triethanolamine borate is 50%, the friction coefficient significantly decreases, and tends to slow decrease when content increased to 90%, while the second group of experimental data shows that the friction coefficient of the solution gradually declines when the content increases from 40% to 90%. When the content of triethanolamine borate in the solution increases from 90% to 100%, the friction coefficient of the three groups of experimental data decreases significantly. It is concluded that triethanolamine borate aqueous solution has an effective lubrication effect on friction pair of YG8 carbide and TC4 titanium alloy. The lubrication effect is low when the content of triethanolamine borate in solution is less than 40%, good when the content is between 50% and 90%, and best when the content is 100%. The friction coefficient reflects the anti-friction performance of the solution. For friction coefficient, if triethanolamine borate is added as a lubricant to the water-based cutting fluid, its content is between 50% and 90%, and the cost-effectiveness is optimal, while the content is less than 40%, it has almost no lubrication effect. This phenomenon may be the reason why triethanolamine borate is used only as an anti-rust additive and not as a lubricant additive.

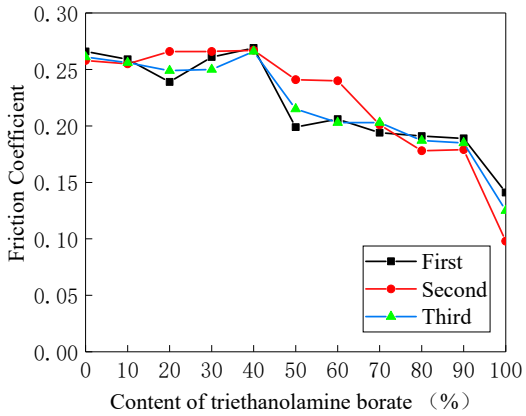

Figure 9. Relationship between friction coefficient and the content of triethanolamine borate

4.2.2 Effect of additive content on lubrication stability

The stability of the lubrication effect of triethanolamine borate aqueous solutions with different contents in the friction process was investigated through friction and wear tests. Figure 10 shows the variation curve of the friction coefficient of the aqueous solution of

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triethanolamine borate with different contents over time. It can be seen from Figure 10 that the friction coefficient curve fluctuates greatly in the first four small graphs, while the friction coefficient curve fluctuates little in the last two small graphs. It can be inferred that triethanolamine borate has stable lubrication property between titanium alloy and hard alloy. For the triethanolamine borate aqueous solution, the stability is close to that of pure triethanolamine borate solution when the content is higher than 80%, but the stability is poor when the content is lower than 60%, which is similar to that of deionized water. In conclusion, if triethanolamine borate is added to the water-based cutting fluid as an extreme pressure agent, the lubrication stability will increase with the increase of triethanolamine borate content, but the factor of lubrication stability has little effect on the performance of the cutting fluid.

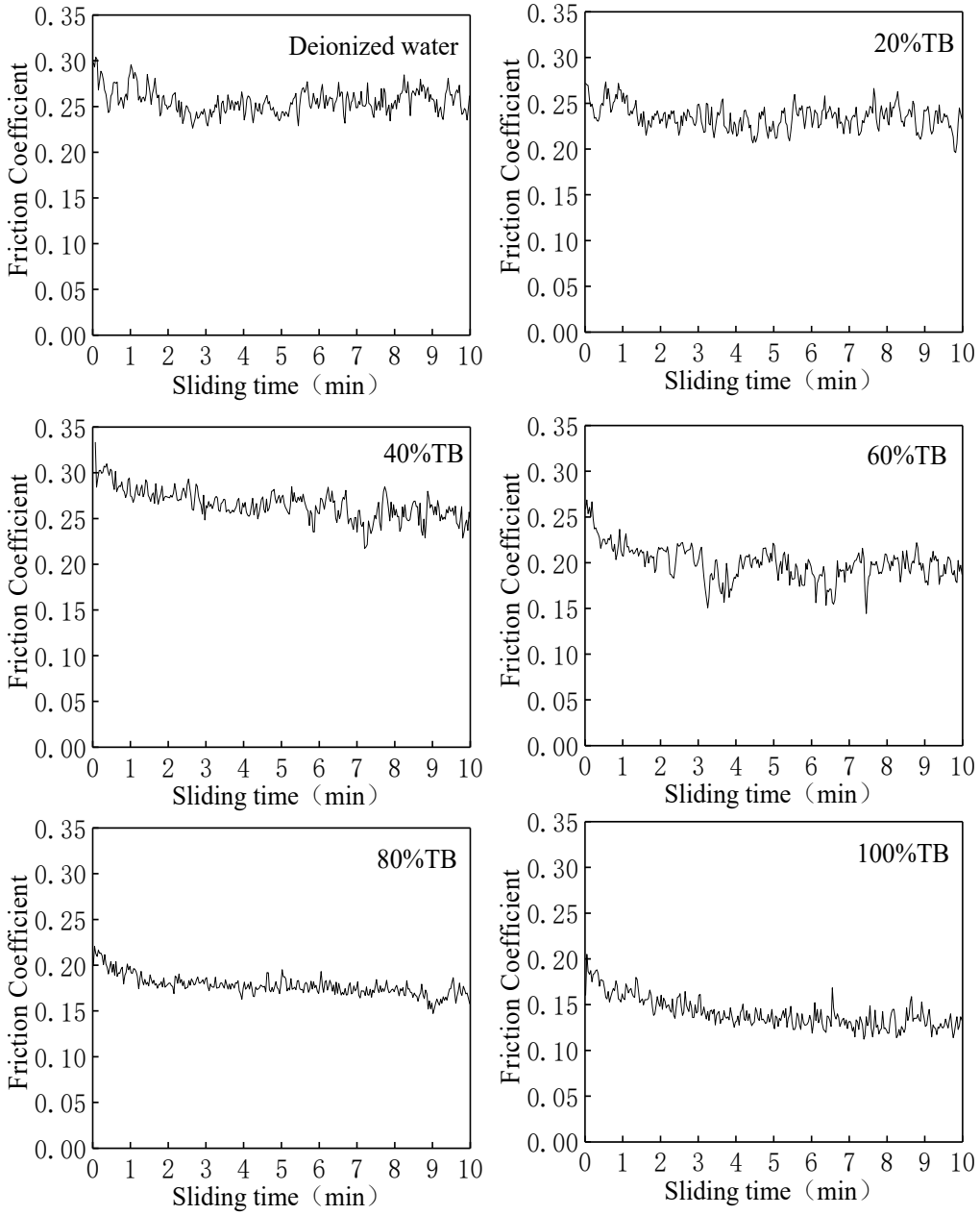

Figure 10. Variation of friction coefficient of triethanolamine borate aqueous solution with different contents with time

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4.2.3 Effect of additive content on anti-wear properties

By observing the width and depth of the wear scar, the anti-wear performance of the triethanolamine borate aqueous solution with different contents on the friction pair of titanium alloy was analyzed. Figure 11 shows the relationship between the content of triethanolamine borate and the width and depth of the wear scar. In the figure, the range of wear scar width is 0.65~0.79 mm, and the range of wear scar depth is 10~17.4 microns. Among them, the width and depth of the wear scar show irregular changes when the content of triethanolamine borate is less than 90%. The change range is relatively large when the content of triethanolamine borate is less than 70%, while the change range is relatively small when the content of triethanolamine borate is between 70% and 90%. When the content of triethanolamine borate increases from 90% to 100%, both the width and depth of the abrasion decrease significantly. It can be concluded that the content of triethanolamine borate in the solution has little effect on the width and depth of the wear scar, but when the triethanolamine borate is made into cutting fluid, the content should be as high as possible to ensure the surface quality of titanium alloy after processing.

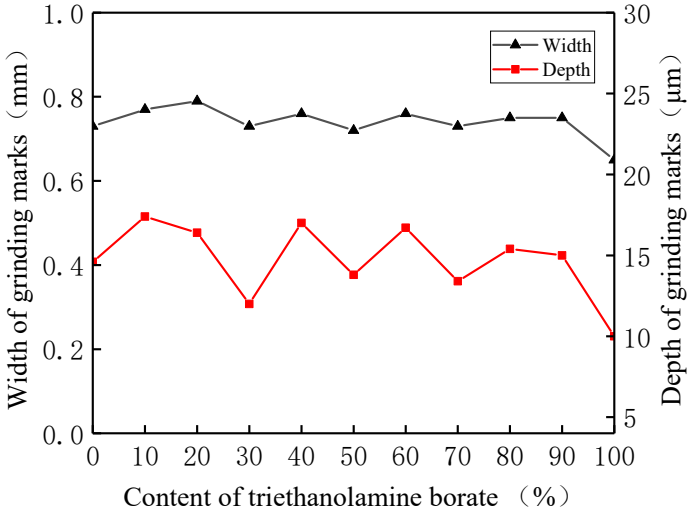

Figure 11. Relationship between width and depth of wear scar and the content of triethanolamine borate

4.2.4 Effect of additive content on wear scar morphology

The anti-wear performance of aqueous solution of triethanolamine borate with different contents was analyzed by observing the wear scar morphology of titanium alloy surface, Figure 12 shows the wear scar morphology of titanium alloy surface when the content of triethanolamine borate in the solution is even. As shown in the figure, when the solution is pure deionized water, the wear scar morphology is very rough and shows the phenomenon of scratch extrusion bulge, thus making the furrow intermittent. When the content of triethanolamine borate in the solution was 40%, the wear scar morphology was similar to that of deionized water lubrication, but with the increase of the content, it became less and less. When the content is higher than 60%, the wear scar morphology appears more delicate, the extrusion phenomenon has disappeared, and the furrows are thin and dense and visible. It can be seen that with the increase of the content of triethanolamine borate in the solution, the anti-wear property of the solution is gradually enhanced, especially when the content reaches 60%, the quality of anti-wear marks has been significantly improved. The influence of the content of triethanolamine borate on the wear scar morphology and the effect on the friction coefficient correspond to each other, which shows that only when the content of the triethanolamine borate reaches above 40%, its lubrication property to the solution can be clearly shown.

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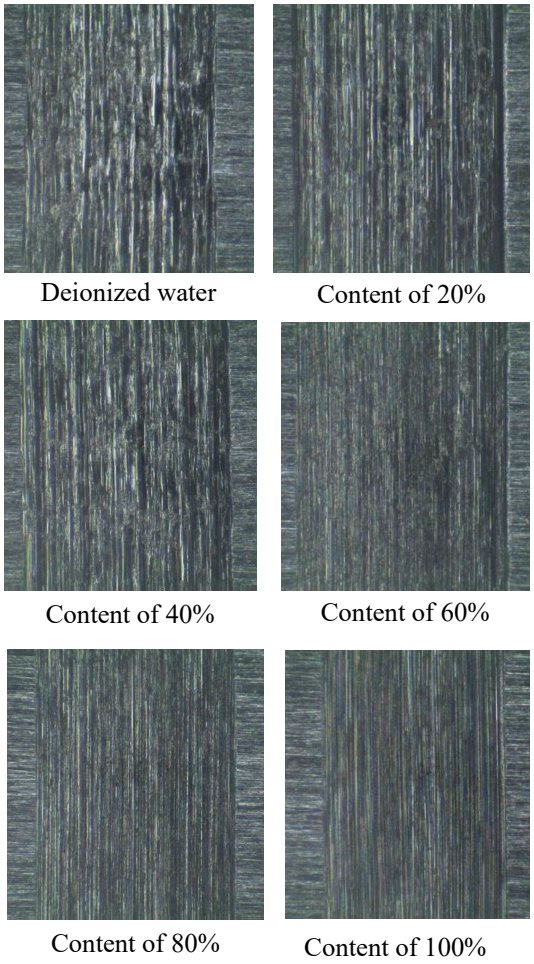

Figure 12. Wear scar morphology of different content of triethanolamine borate aqueous solution

5. CONCLUSION

(1) The super-lubricity theory is applied to the study of lubricating additives. By analyzing the molecular composition of triethanolamine borate and combining the occurrence mechanism and realization conditions of super-lubricity, it is found that triethanolamine borate has the conditions to realize super-lubricity, that is, it contains hydrogen ion and the hydroxyl group at the same time, and has certain super lubricating properties.

(2) The friction coefficients of triethanolamine borate, glycerol and polyethylene glycol 400 were measured by the friction and wear tester, and the friction coefficient variation rule was obtained and the friction reduction ability of triethanolamine borate was analyzed; by analyzing physical quantities such as friction coefficient, lubrication stability, outline and morphology of wear scar, the tribological properties of aqueous solutions of triethanolamine borate with different contents were studied. The research results show that triethanolamine borate has anti-friction and anti-wear ability as glycerin and polyethylene glycol under the friction pair of titanium alloy and hard alloy. The anti-friction and anti-wear ability of triethanolamine borate increases with the increase of its content in aqueous solution; the anti-friction and anti-wear ability of triethanolamine borate increases with the increase of its content in aqueous solution.

(3) At present, the excellent anti-rust performance of triethanolamine borate is widely studied and applied, but there is a lack of research on the lubricating effect of metals. This study is based on the super-lubricity theory and combined with a large number of experiments to reveal the lubrication mechanism of the triethanolamine borate and clarify that it has good anti-

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friction and anti-wear ability. This research result is expected to make triethanolamine borate break the limitation of rust inhibitor and become new cutting fluid lubrication additives.

(4) Triethanolamine borate, like glycerin and other lubricants, has the potential to become a lubricant additive for water-based complete synthetic cutting fluid. This study provides a theoretical basis for the development of green cutting fluid based on the triethanolamine borate.

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