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Research Article

Preparation and Tribological Properties of Dual-Coated TiO_2 Nanoparticles as Water-Based Lubricant Additives

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Titanium dioxide nanoparticles (TiO_2) were synthesized and then dual-coated with silane coupling agent (KH-570) and OP-10 in sequence in order to be dispersed stably in water as lubricant additives. The tribological properties and the application performance in Q235 steel machining of the nanoparticles as water-based lubricant additives were investigated on an MSR-10D four-ball tribotester and on a bench drilling machine, respectively. Scanning electron microscope (SEM) and atomic force microscope (AFM) were used to analyze the worn surface. The results show that the surface-modified TiO_2 nanoparticles can remarkably improve the load-carrying capacity, the friction reducing, and anti wear abilities of pure water. The wear scar diameter and the coefficient of friction of the water-based lubricating fluids with TiO_2 nanoparticles decreased, and the thick deep furrows on the surface of wear scar also decreased obviously with the increase of TiO_2 concentration. The power consumption in drilling process was lower and the cutting surface was smoother using the water-based lubricating fluids added TiO_2 nanoparticles compared to the fluid without addition. The reason for nanoparticles improving tribological properties of water based lubricating fluid might be the formation of a dynamic deposition film during rubbing process according to analysis of the worn surface.

1. Introduction

Environment protection and energy conservation are becoming very important issues in modern industrial production. The main cause of energy loss in a mechanical system is friction [1]. The conventional choice is use of a mineral oil-based lubricant to reduce wear and friction in mechanical systems [2]. However, due to the inherent toxicity and the nonbiodegradable nature of oil-based lubricants, developing environment-friendly water-based lubricating fluids is meaningful for resource conservation society [3, 4]. Nevertheless, the poor tribological properties of water-based lubricating fluids [5] make it unacceptable for most of tribological applications. In order to adjust the performance and to improve the properties of water based lubricants, high-quality additives are used [6]. Liu et al. synthesized poly(N-isopropylacrylamide) brush as water-soluble additive and found that the additive helped decrease the friction coefficient of the lubricant to 0.03 due to its physical adsorption of the polymer chains [7]. Zhang et al. investigated the friction and wear behaviours of a (Ca, Mg)-sialon/SAE 52100 steel pair under the lubrication of various polyols in water and found that the friction coefficient was much lower than that of pure water [8]. Duan Biao in his research on colloidal PSt as a new additive for water-based lubrication found that it can improve the base fluid's antiwear and extreme pressure performance [9]. Among all of the studies on water-based lubricant additives, nanoparticles arouse our interest because there have been a lot of researches on nanoparticles as additive in traditional oil-based lubricant and the nanoparticles exhibit good antiwear and friction reducing properties [10–18]. Some researchers have found that Fe_2O_3, CeO_2, and diamond nanoparticles as water-based lubricating additives can significantly reduce the friction coefficients and improve anti-wear properties [19–21]. But the studies on nanoparticles as additive in water and, especially, on the application of nanoparticles in water-based machining liquid are still scare and should be further investigated due to their difficulty of dispersion and stability in water [22, 23].

Among all nanoparticles as lubricant additives, TiO_2 nanoparticle is a promising additive to water-based lubricating fluids because of its excellent comprehensive properties, such as nontoxicity, white color, low density, and good tribological properties [24–26].

In this paper, titanium dioxide (TiO_2) nanoparticles were synthesized using the homogeneous precipitation method. The surface of TiO_2 nanoparticles was modified by dual coatings with silane coupling agent (KH-570) and OP-10 in sequence in order to improve its dispersion and stability in water. Zeta potential of TiO_2 nanoparticles in water was measured to analyse its dispersion stability. Tribological properties of TiO_2 nanoparticles as lubricant additive in water were investigated using a four-ball tester. And Q235 steel-drilling test on a bench drilling machine was carried out using water-based cutting fluids with TiO_2 nanoparticles in order to explore TiO_2 nanoparticles action on machining application. The antiwear and friction reducing mechanism of the dual-coated TiO_2 nanoparticles as water-based lubricant additive was discussed according to SEM and AFM analysis of the worn surfaces.

2. Experimental Method

2.1. TiO_2 Nanoparticle Synthesis. TiO_2 nanoparticles were synthesized by homogeneous precipitation (urea as precipitant) method in this paper. All chemical reagents were reagent grade without further purification. The typical preparation procedure is as follows: the solutions of titanous sulfate and sodium dodecyl benzene sulfonate (LAS) were prepared and mixed under stirring, and then an aqueous solution of urea (PH = 1.5) was added into the above mixture at 343 K, and the molar composition of urea to $TiOSO_4$ was 10 : 1. After completing precipitation, white precipitated powders were cleaned by deionized water, dried in a vacuum drying oven for 3 hours, calcined in a furnace at 650°C for 5 h, and then ground into powders in absolute ethyl alcohol-added KH-570 using a ball-grinding mill. And the KH-570 surface-modified TiO_2 powders were coated again by OP-10 in water at 343 K under ultrasonic vibration and mechanical stirring. The obtained powder was analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The zeta potential of the dual-coated TiO_2 nanoparticles in the water was examined by a Zetasizer Nano ZS ZEN 3600 particle-size analyzer to determine its surface charge.

2.2. Tribological Test and Surface Analysis. In this study, deionized water was used as pure water. Water-based lubricants with different concentration of 0.1 vt.%, 0.2 vt.%, 0.4 vt.%, 0.8 vt.%, and 1.6 vt.% TiO_2 nanoparticles were prepared.

Experiments of measuring friction reduction and antiwear properties of the cutting fluids with nanoparticles were carried out with an MSR-10D four-ball tribotest at a rotating speed of 1440 rpm under the applied loads of 147 N for 10 min. The steel ball (Φ 12.7 mm, HRC 62–64) was made of GGr15 bearing steel (AISI 52100 steel). Same tests were performed for three times so as to minimize data scattering. At the end of each test, wear scar diameters on the three stationary balls were measured, and an average wear scar diameter of the three tests was calculated. Scanning electron microscope (SEM), atomic force microscope (AFM), and energy dispersive spectrometry (EDS) were used to examine the morphology and chemical composition of the wear scars and to study possible tribochemical changes involved in the friction process.

2.3. The Application of the Water-Based Cutting Fluids Added TiO_2 Nanoparticle. The application performance of water-based cutting fluids added TiO_2 nanoparticles was explored by drilling test. A bench drilling machine (Z516-A) was used to measure the power consumption of drilling at 1800 rpm and room temperature for evaluating lubricating properties. The power consumption was calculated by the following formula:

$$\frac{\Delta \mathrm{P}}{P} = \frac{(P - P_0)}{P_0} * 100\%, \tag{1}$$

where P_0 is the input power when the drilling machine is in idle, yet the P is the actual input power during the drilling process.

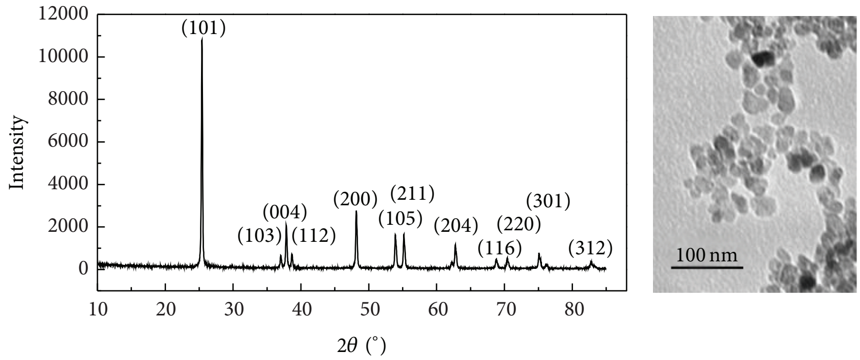
The applied steel plates in all tests were made of Q235 steel, and the diameter of drill bit was 10 mm. The addition concentration of dual-coated TiO_2 nanoparticles in pure water was 2 vt.%, 4 vt.%, 6 vt.%, and 10 vt.%, respectively considering actual situation of drill processing. The water-based cutting fluids without nanoparticles used in the experiment were pure water mixed with an amount of KH-570 and OP-10 in order to exclude the effect of surfactant on TiO_2 nanoparticles action.

The machining surfaces of inside wall of the holes were analyzed after the experiments.

3. Results and Discussion

3.1. TiO_2 Nanoparticle Characterization. Figure 1 presents the XRD pattern and TEM images of TiO_2 nanoparticles. It can be seen that the prepared particles are pure TiO_2 particles with single anatase phase (Figure 1(a)). The dual-coated TiO_2 nanoparticles have spherical shape, take on homogeneous dispersion, and have no obvious aggregation, and the average size of the prepared particles is about 20 nm in diameter as shown in Figure 1(b). The surface modification agents are adsorbed on the surface of nanocrystalline, which can reduce the surface energy of nanocrystalline and prevent nanoparticles from aggregating. The zeta potential value of pure TiO_2 nanoparticles in water is measured to be −5.44 mV, and the zeta potential value of dual-coated nano-TiO_2 increases to −24.6 mV. The modified nanoparticles in water show relatively higher dispersion stability because the zeta potential value of dual-coated nano-TiO_2 is more than three times higher than that of pure TiO_2 nanoparticles.

3.2. Experimental Results of Four-Ball Test. Maximum nonseizure load (P_B values) of the lubricants containing the dual-coated TiO_2 nanoparticles is shown in Figure 2. In general, the P_B value of the lubricant increases with the increase of nanoparticles addition concentration, but the concentration of nanoparticles is 0.4 vt.%, and the P_B value reaches the



(a) (b)

FIGURE 1: (a) X-ray diffraction spectra of the TiO_2 nanoparticles; (b) TEM image of the TiO_2 nanoparticles.

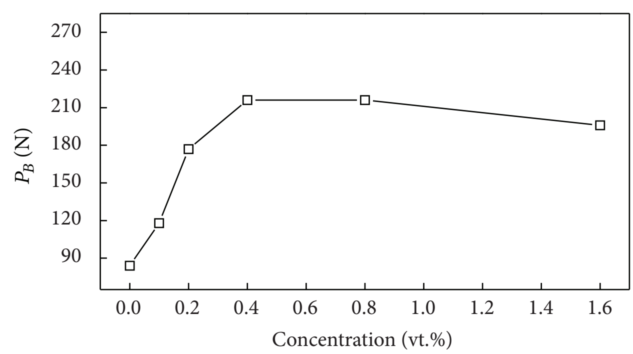


FIGURE 2: The maximum nonseizure load (P_B values) of lubricants with different additive concentration.

maximal value. At that concentration, the P_B value of the lubricants with TiO_2 nanoparticles is improved maximally by 157%. So it can be thought that the dual-coated TiO_2 nanoparticle has good load-carrying capacity and excellent extreme pressure property.

The wear scar diameter and friction coefficient are functions of the additive nanoparticle concentration in water, as presented in Figure 3. Figure 3(a) shows wear scar diameter (WSD) of steel balls lubricated by base water containing different amounts of TiO_2 nanoparticles. Results show that TiO_2 nanoparticles can improve the antiwear properties (reduce WSD) of the base water obviously, even at a low concentration of 0.1 vt.%. When the concentration of nanoparticles in water increases, the value of WSD decreased. The WSD of the lubricants with TiO_2 nanoparticles is reduced by 34.8% maximally.

The coefficient of friction is a demonstration of energy loss caused by friction. Figure 3(b) shows the friction reducing property of the TiO_2 nanoparticles at different additive concentration in base water. It can be seen from Figure 3(b) that the friction coefficient of the water-added TiO_2 nanoparticles is decreased dramatically compared to the lubricant without nanoparticles with the friction coefficient of 0.17; the minimum value of friction coefficient of the water containing nanoparticles reaches 0.04 as the addition concentration of nanoparticles in water is 1.6 vt.%, which indicates that dual-coated TiO_2 nanoparticles as water-based lubricant additive have excellent friction reducing property.

Figure 4 gives SEM images of the rubbed surface lubricated with pure water and water-added TiO_2 nanoparticles of 0.1 vt.%, 0.8 vt.%, and 1.6 vt.%, respectively. The worn surface lubricated with pure water presented in Figure 4(a) is rough with many thick and deep furrows due to strong adhesion and ploughing between contacted asperities on the rubbed surface of tribopairs. The worn surface lubricated with water-added TiO_2 nanoparticles is smoother than that lubricated with pure water. And with the increase of addition concentration of TiO_2 nanoparticles in pure water, the thick and deep furrows on wear scar surfaces become less and shallower.

3.3. Experimental Results of Drilling Test. Figure 5 plots the variation of power consumption of drilling with addition concentration of TiO_2 nanoparticles in cutting fluids. In this figure, it can be seen that with the increase of TiO_2 nanoparticles in cutting fluids, the power consumption of drilling firstly decreases to the minimum value and then increases. The optimal addition concentration is 6 vt.%, and

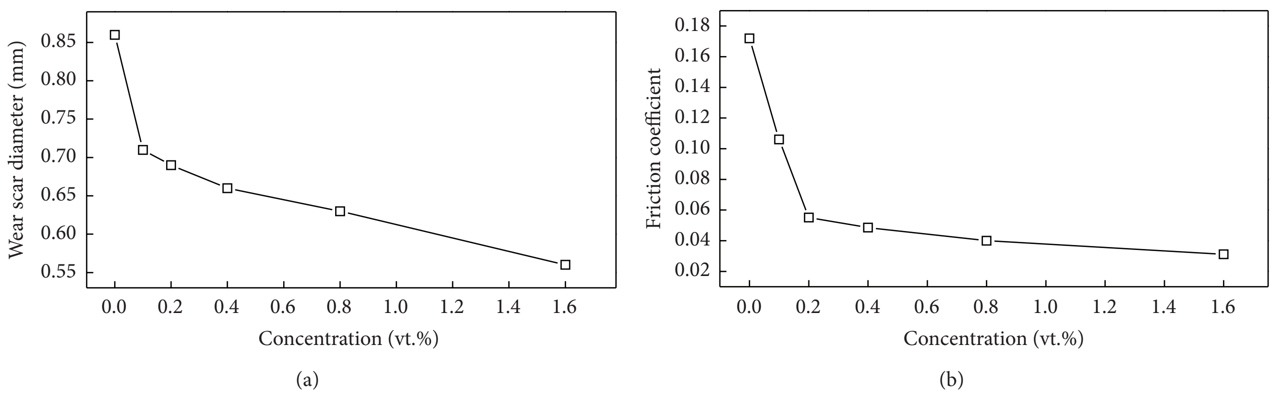


Figure 3: Wear scar diameter (a) and friction coefficient (b) as a function of additive concentration.

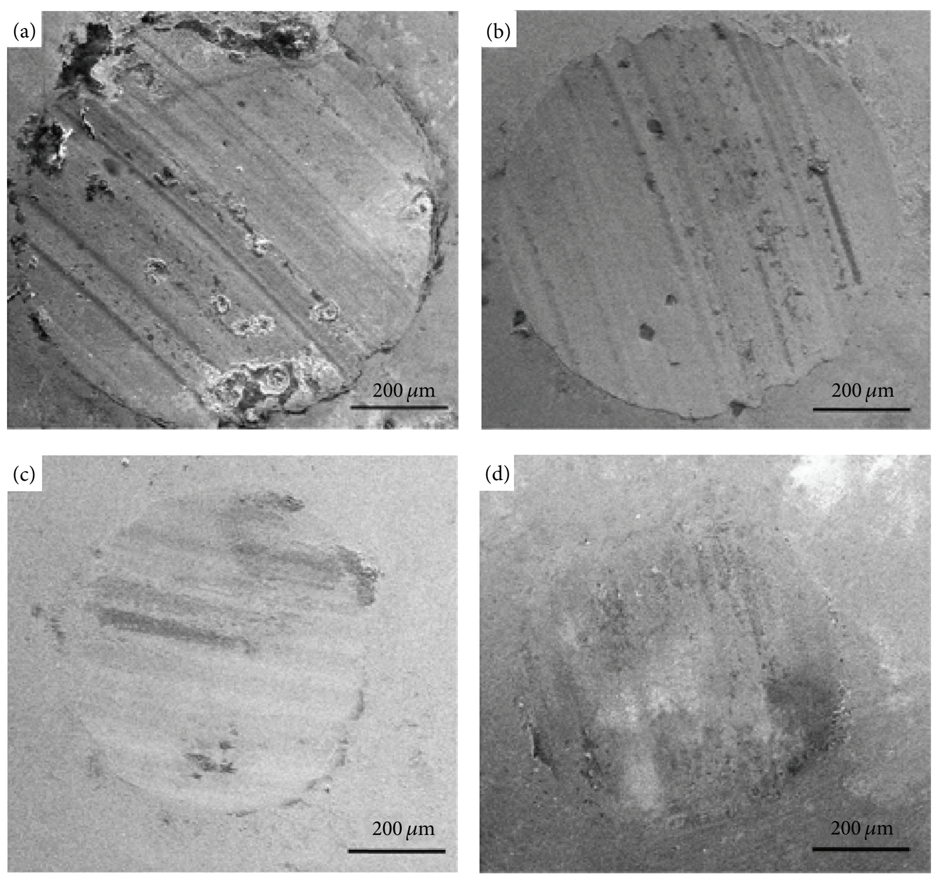


Figure 4: SEM micrographs of wear scar surfaces lubricated with different concentration of nanoparticles: (a) no addition, (b) 0.1 vt.%, (c) 0.8 vt.%, and (d) 1.6 vt.%.

under this concentration, the power consumption of drilling is 35.4% less than that without TiO_2 addition.

Figure 6 presents SEM images of the machined inside surface of drilling hole lubricated without lubricant liquid, using cutting fluids without nanoparticles and using cutting fluids with 2 vt.% and 6 vt.% nanoparticles.

The machined inside surface lubricated without lubricant liquid presented in Figure 6(a) is evidently rough with many built-up edges and some thick deep furrows because of severe adhesion and ploughing. In Figure 6(b) the machined inside surface lubricated with cutting fluids without nanoparticles is also rough with many thick and deep furrows but without built-up edge. In Figures 6(c), and 6(d), the machined inside surfaces lubricated with cutting fluids with 2 vt.% and 6 vt.% nanoparticles, respectively, are smoother than that lubricated with the cutting fluids without nanoparticles, and the furrows of surface are less and shallower.

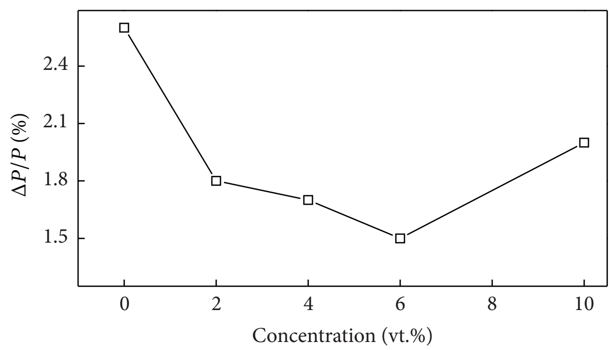


FIGURE 5: The power consumption of drilling as a function of additive concentration.

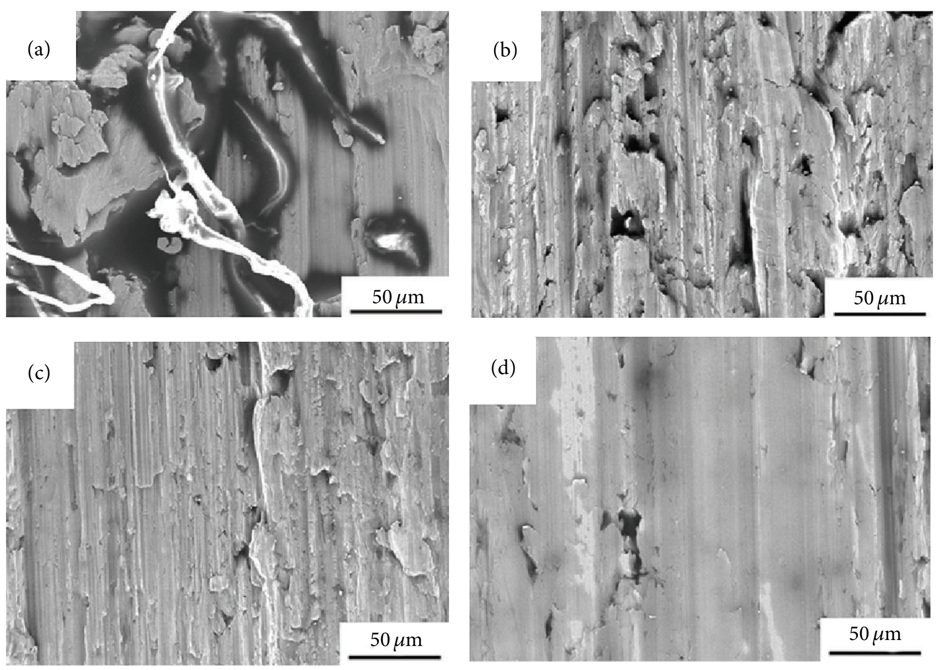


FIGURE 6: SEM image of the machined inside surface of drilling hole lubricated (a) without lubricant liquid; (b) using cutting fluids without nanoparticles; (c) using cutting fluids with 2 vt.% nanoparticles; (d) using cutting fluids with 6 vt.% nanoparticles.

3.4. Tribological Mechanism Analysis of Nanoparticles as Water-Based Additive. Figure 7 presents the tribological model of nanoparticles as water-based lubricant additive according to the above experimental results.

The antiwear and friction reducing mechanism of nanoparticles as water-based additive might be understood better due to the separation effect of nanoparticles as deposition film to the asperities on the contacting surface of the tribopairs. When lubricated with the water without nanoparticles addition as shown in Figure 7(a), many asperities on the rubbing surface of tribo-pairs might directly be in contact due to poor separation of pure water to the asperities, which leads to strong adhesion and ploughing between contacted asperities on the rubbed surface of tribo-pairs [27], and many thick and deep furrows on the worn surface are found as shown in Figures 4(a) and 6(b). When a trace amount of nanoparticles were added into the water as lubricant additive as shown in Figure 7(b), the nanoparticles might be deposited on the rubbing surface, which separates apart asperities on the contacting surface and reduces the thick deep furrows on the worn surface as shown in Figures 4(b) and 6(c), due to reduction of the area of contacted asperities on the rubbing surfaces. When lubricated with the water added with an appropriate amount of nanoparticles as shown in Figure 7(c), the nanoparticles separate all asperities on the contacting surface and the thick deep furrows on the worn surface cannot be found as shown in Figures 4(c), 4(d), and 6(d). At the same time, the worn surface became smoother compared to that lubricated without nanoparticles.

In order to further explore the nanoparticles action as water-based lubricant additive in rubbing process, atom force microscope (AFM) is used to analyze the worn surface of steel ball lubricated with the water-added 1.6 vt.% nanoparticles after ultrasonic washing for 5 minutes as shown in Figure 8.

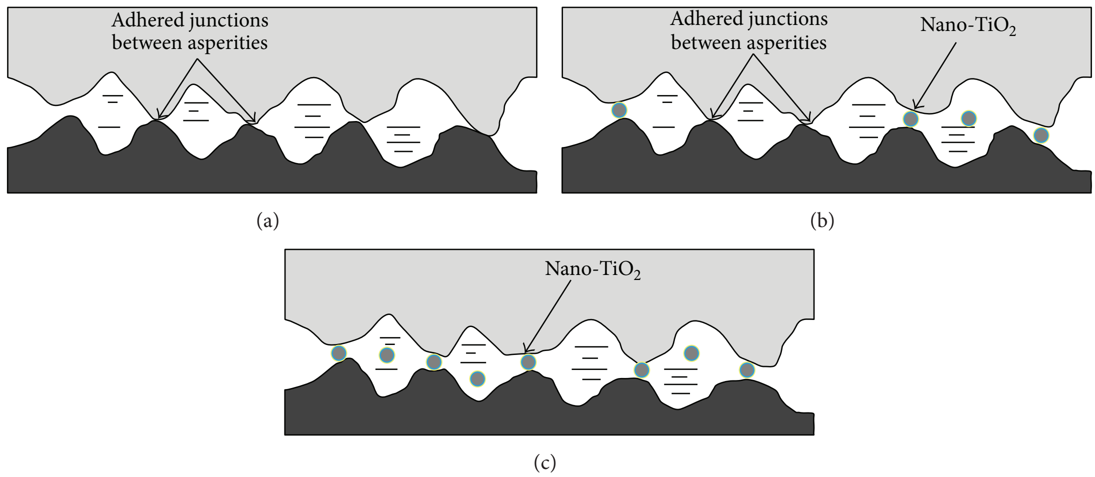


Figure 7: Schematic diagram showing separation effect of nanoparticles during rubbing lubricated (a) pure water without nanoparticle; (b) the water with a trace amount of nanoparticles; (c) the water with an appropriate amount of nanoparticles.

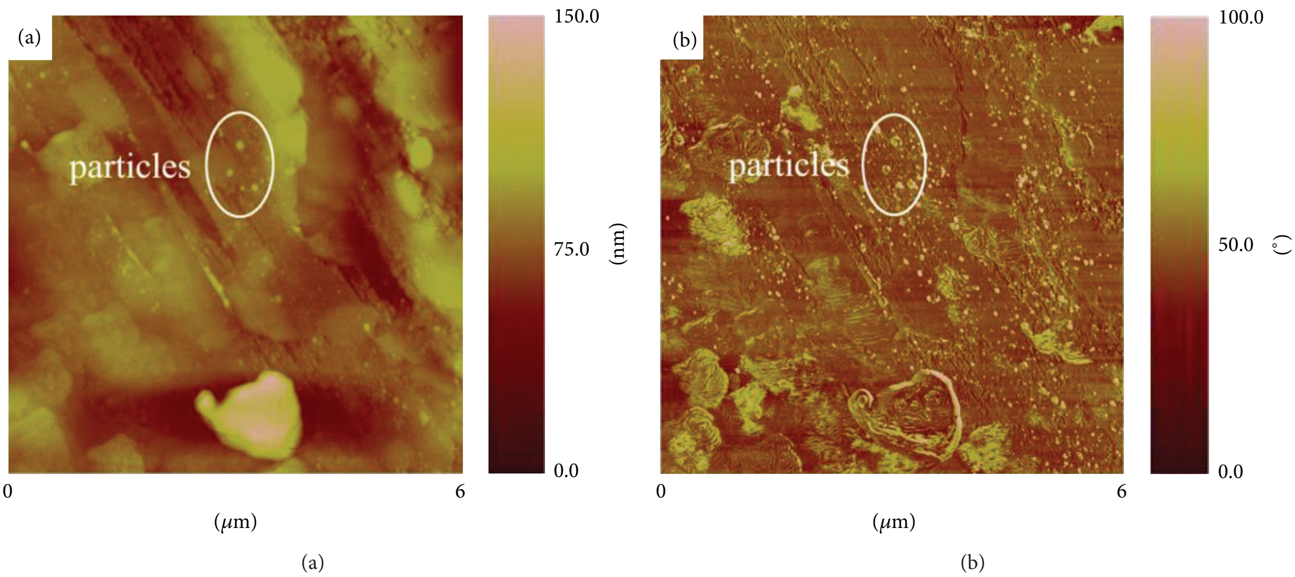


Figure 8: AFM analysis of the worn surface of steel ball after four-ball test lubricated by the water with 1.6 vt.% TiO_2 nanoparticles with ultrasonic washing for 5 minutes (a) height image; (b) phase image.

The nanoparticles are found on the surface of asperities. However, the amount of nanoparticles found on the surface of asperities is little and cannot separate the contacted asperities completely, so cannot perform excellent tribological properties.

Figure 9 presents the EDS analysis of worn surface after four-ball test lubricated by the water-added 1.6 vt.% TiO_2 nanoparticles without ultrasonic washing and with ultrasonic washing for 2 minutes and 5 minutes, respectively. It can be seen that with the increase of washing time, weight percent of Ti element on the worn surface decreases gradually, and Ti element is not found on the worn surface after ultrasonic washing for 5 minutes.

The reasonable explanation might be a dynamic deposition film formed by nanoparticles during rubbing process which might separate effectively the direct contact of asperities, alleviate the strong adhesion and ploughing between asperities, and result in the decrease of the wear scar diameter and the friction coefficient obviously during four-ball test as shown in Figure 3 and the significant reduction of the power consumption during drilling test as shown in Figure 5.

4. Conclusion

(1) Dual-coated TiO_2 nanoparticles with KH-570 and OP-10 in sequence exhibit good dispersity and stability in pure water.

(2) Dual-coated TiO_2 nanoparticles as water-based lubricant additive provide more excellent tribological

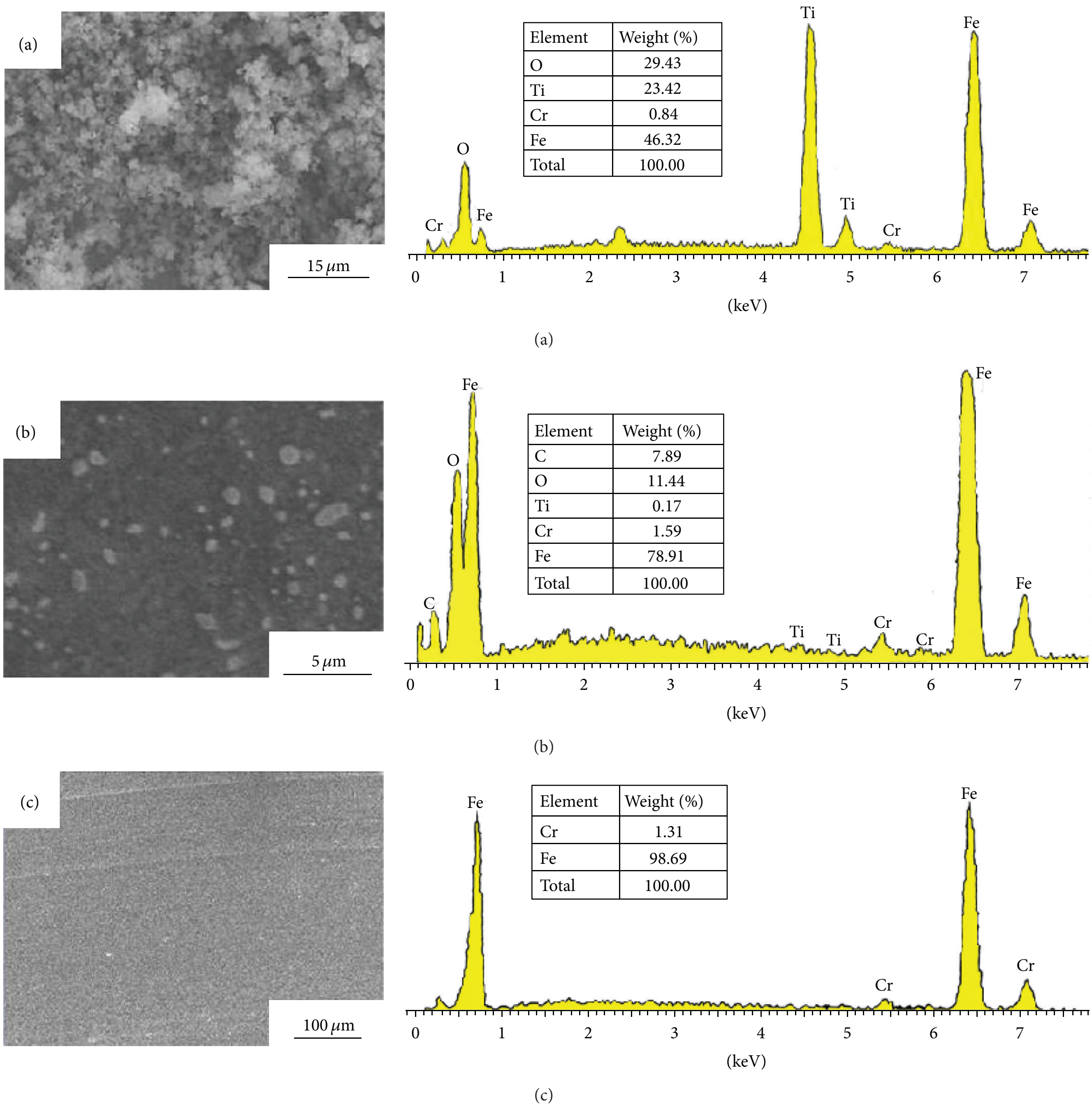


FIGURE 9: SEM and EDS analysis of worn surface of steel ball after four-ball test lubricated by the water-added 1.6 vt.% TiO_2 nanoparticles. (a) Without ultrasonic washing; (b) with ultrasonic washing for 2 minutes; (c) with ultrasonic washing for 5 minutes.

properties than pure water in terms of load-carrying capacity, antiwear, and friction reducing.

(3) Dual-coated TiO_2 nanoparticles as cutting fluids additives also exhibit better friction reducing property. The power consumption in drilling process lubricated with TiO_2 nanoparticles is lower than that of the fluid without nanoparticle addition. The optimal concentration is about 6 vt.%.

(4) The antiwear and friction reducing mechanism is that TiO_2 nanoparticles can form a dynamic deposition film on the worn surface and separates the direct contact between the asperities of the rubbing surfaces according to the analysis of SEM, AFM, and EDS of worn surfaces.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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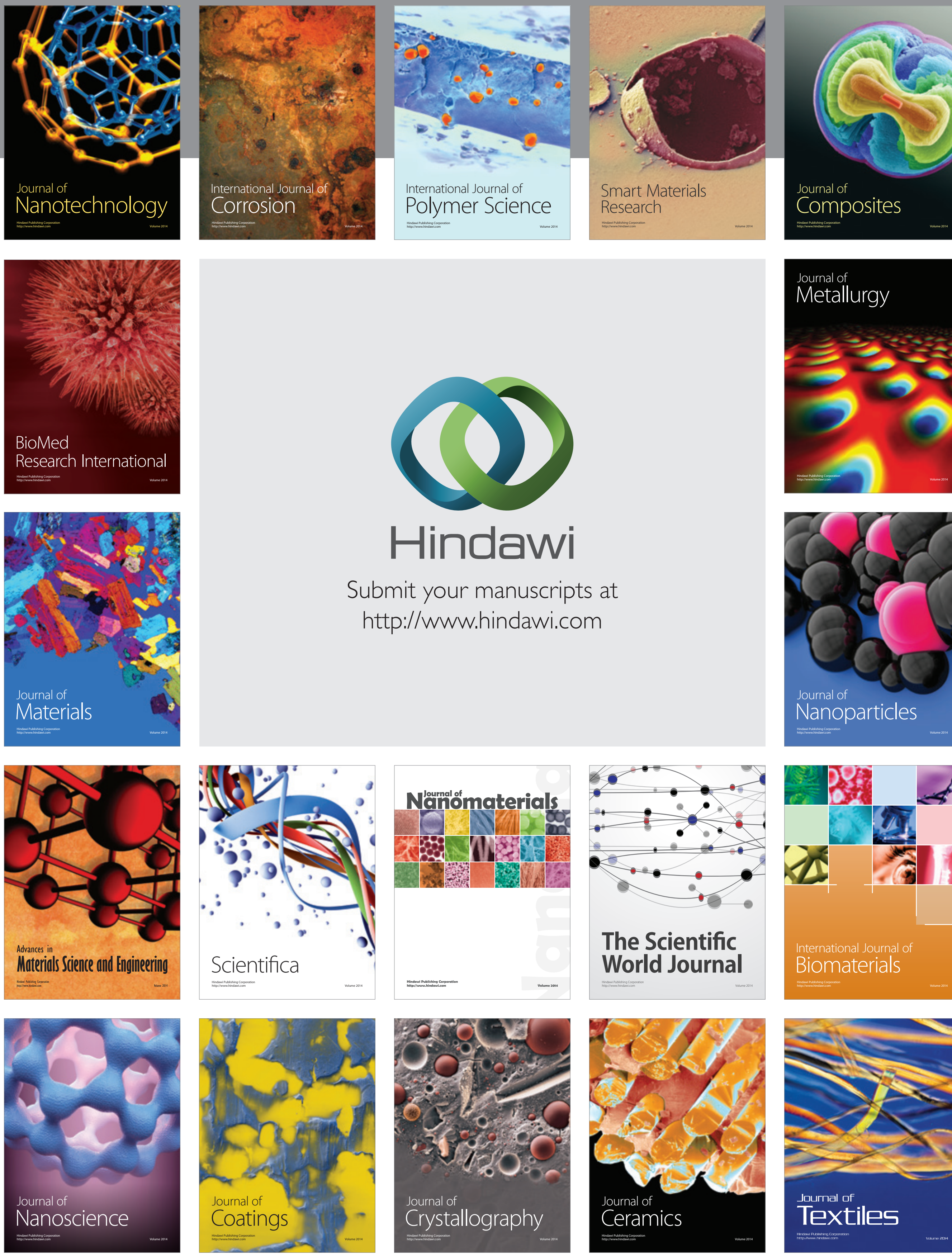
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