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# Investigation of 1,3-Diketone and Nano-Copper Additives for Enhancing Boundary Lubrication Performance

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**Abstract:** In this work, 1,3-diketone synthesized via the Claisen condensation method and nano-copper particles modified by the Brust–Schiffrin method were added into a commercial marine medium-speed diesel engine cylinder piston oil to evaluate their effects on boundary lubrication performance. Friction and wear tests conducted on CKS-coated piston ring and cast-iron cylinder liner samples demonstrated significant reductions in both friction and wear with the addition of 1,3-diketone and nano-copper particles. Compared to the original oil without additives, the friction force was reduced by up to 16.7%, while the wear of the piston ring and cylinder liner was decreased by up to 21.6% and 15.1% at 150 °C, respectively. A worn surface analysis indicated that the addition of 1,3-diketone and functionalized nano-copper particles influenced the depolymerization and tribo-chemical reactions of the anti-wear additive ZDDP (zinc dialkyldithiophosphate) in the original engine oil. This modification enhanced the oil's anti-friction and anti-wear properties, offering valuable insights into the development of eco-friendly lubricants for energy-efficient systems.

**Keywords:** lubricating oil; diketone; nanoparticles; tribofilm

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## 1. Introduction

The International Maritime Organization (IMO) has implemented rigorous measures to reduce Global Greenhouse Gas (GHG) emissions [1], establishing higher standards for the sustainable development of the shipping industry. The adoption of clean fuels such as methanol and ammonia, either as full or partial replacements for traditional fossil fuels in marine engines, has emerged as a key strategy to meet these environmental goals [2]. However, the application of these clean fuels results in a significant increase in combustion chamber pressure [3,4], which worsens the lubrication conditions between tribo-pairs in marine engines [5]. The piston ring and cylinder liner, especially, are subjected to harsher working conditions. Elevated loads and temperatures lead to thinner or discontinuous lubricating films [6], which may cause abnormal wear and even scuffing between the piston ring and cylinder. This severely affects the reliable operation of the vessel. Therefore, enhancing the boundary lubrication performance of existing lubricants and preventing the abnormal wear of key tribo-pairs including the piston ring-cylinder liner are crucial for the transition to green shipping and the reliable operation of ships.

Zinc dialkyldithiophosphate (ZDDP) is a widely used anti-wear additive in engine lubricants, offering additional antioxidant and anti-corrosion properties. It is a key ingredient in modern lubricant formulations. Although ZDDP contributes to sulfur and phosphorus pollution and faces increasing usage restrictions due to tightening emission regulations, it remains one of the most cost-effective anti-wear agents available and cannot be easily replaced in the short term. In the future, combinations of additives (e.g., ZDDP with new additives) or nano anti-wear materials may gradually supplement or replace the functions of ZDDP. For instance, some studies have explored the use of ionic liquid additives to synergistically enhance the extreme pressure performance of ZDDP, addressing the intensified lubrication issues [7].

1,3-diketone is a promising and environmentally friendly additive for lubricating oils. Initially, 1,3-diketone was expected to enhance friction reduction and wear resistance by functioning as mesogenic fluids [8,9]. Later, Li et al. [10] demonstrated that ultralow friction resulted from a tribo-chemical reaction between the diketone and the steel surface. In 2018, Li et al. [11] further discovered the superlubricity of 1,3-diketone, attributed to their ability for autonomous viscosity control. They identified the load and velocity boundaries for oil-based superlubricity using 1,3-diketone [12]. The achievement of this superlubricity phenomenon requires a smooth surface with a roughness below tens of nanometers, which exists at a distance from the roughness typically found at the engineering scale. Subsequently, macroscale oil-based superlubricity was achieved on the typical engineering surface (Sa = 0.2 μm); however, it was not obtained on surfaces with a higher roughness due to the excessive consumption of oil and the generation of large abrasive particles rather than iron-complex ones [13]. Based on the above research results, 1,3-diketone, as an environmentally friendly anti-friction and anti-wear additive, may have potential for use in combination with ZDDP to improve the boundary lubrication performance and reduce the phosphorus content.

The addition of nanoparticles into lubricants has been verified, which can greatly reduce friction and wear [14]. Li et al. [15] investigated the synergistic effect of 1,3-diketone and carbon-based nanoparticles as hybrid eco-friendly additives in polyalphaolefin oil, but the combination exhibited limited tribological performance. However, this study offers new insights for designing high-performance 1,3-diketone composite lubricant additives. Metallic nanoparticles, such as Cu, Ag, Fe, and Ni, possess unique physicochemical properties and small-size effects, making them widely applied in lubricant oils [16]. Among these, Cu nanoparticles with a low shear force, and eco-friendly nature, contribute to enhanced friction reduction, wear resistance, and extreme pressure performances [17]. Therefore, nano-copper particles, as auxiliary materials to 1,3-diketone, are expected to further improve synergistic lubrication effects. Nevertheless, when introducing the composite additive of 1,3-diketone and nanoparticles, it is crucial that we determine whether their synergistic effect will interfere with the normal reaction process of ZDDP or further enhance the lubrication performance. Clarifying these issues is essential for optimizing the composite additive formulation. However, there is currently a lack of research on such problems, presenting multi-dimensional technical challenges for formulation optimization.

To enhance the reliability of marine engines and support green development, novel eco-friendly lubricant additive systems must be developed to improve the boundary lubrication performance and reduce friction and wear in key moving parts. In this work, we incorporated 1,3-diketone additives and composite additives of 1,3-diketone and functionalized nano-copper into a commercial marine medium-speed diesel engine cylinder piston oil and investigated their lubrication performance. To realistically evaluate the properties of modified lubricants in practical applications, the commonly used piston ring coated with a chromkeramikschicht (CKS) layer and cast-iron cylinder liner in marine diesel engines were selected as the research subjects. A self-designed friction and wear tester was used. The tester has been confirmed to effectively simulate the boundary lubrication conditions and is well-correlated with the bench test results. The enhancement in the boundary lubrication performance through the synergy of 1,3-diketone and functionalized nano-copper particles was confirmed. The morphology and chemical composition of the worn surfaces were analyzed to investigate the lubricant behavior of the hybrid lubricant additives. These findings provide a new perspective for developing eco-friendly and high-performance lubricants to meet increasingly stringent boundary lubrication requirements.

## 2. Materials and Methods

### *2.1. Materials*

The tested specimens were cut from an actual piston ring and cylinder liner used in an internal combustion engine. Figure 1a exhibits a micrograph of the piston ring electroplated with a chromkeramikschicht (CKS) layer (ASIMCO Shuanghuan Piston Ring (Yizheng) Co., Ltd, Yangzhou, China). The surface of the CKS piston ring exhibits densely packed crosshatch patterns with irregularly shaped cracks, which is a typical morphology of the CKS coating. The surface hardness and roughness (Sa) were 1068.2 HV and 0.31 μm, respectively. Figure 1b shows the morphology of the cylinder liner that was made from cast iron (Yantai Vast Co., Ltd, Yantai, China). The surface of the cast iron is characterized by a distribution of coarse and fine honing marks. The surface hardness and roughness (Sa) were 356.6 HV and 11.27 μm, respectively.

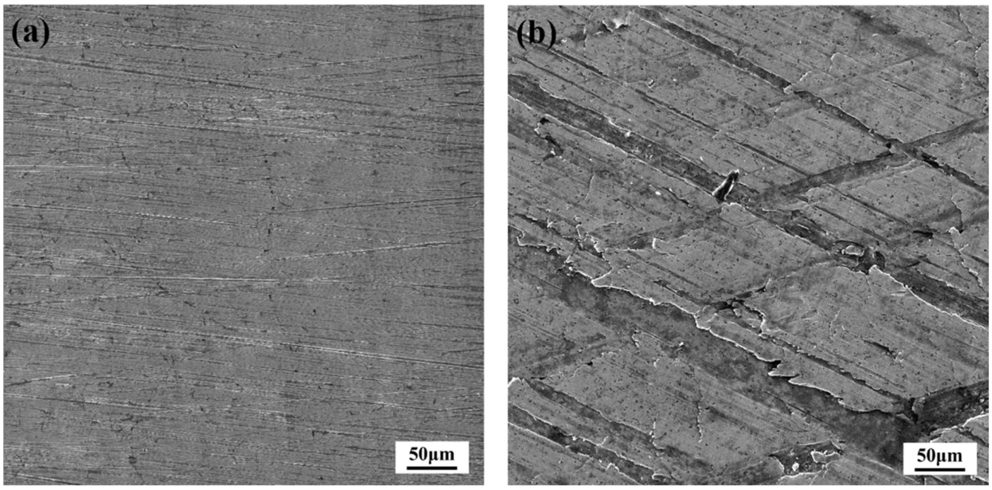
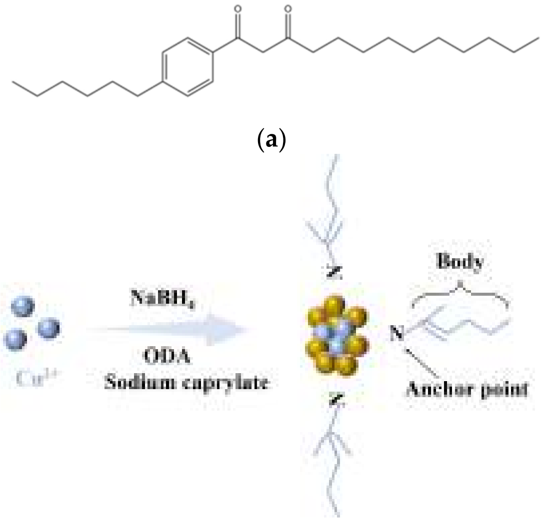


**Figure 1.** Micrographs of CKS coating (**a**) and cast iron (**b**).

A commercial marine medium-speed diesel engine cylinder piston oil (DCB3015, PetroChina Lubricating Oil Company, Beijing, China) was chosen as the lubricant to be modified, designated as BO. According to the SAE oil viscosity grade standard, this oil belongs to the SAE 30 viscosity grade, with a kinematic viscosity of 11.23 $mm^2/s$ at 100 °C. The 1,3-diketone additive was synthesized via Claisen condensation method, and its molecular structure is presented in Figure 2a. 1,3-diketone with a mass fraction of 2.25% was added into the BO and underwent ultrasonic treatment, labeled as MO1. To further enhance the properties of the modified lubricant, nano-copper particles were introduced into MO1. The dispersion of nanoparticles in lubricants presents significant challenges. Additionally, nano-copper may chelate with 1,3-diketone, potentially hindering the reaction between 1,3-diketone and tribo-pairs. To address these issues, the nano-copper particles were modified by octadecylamine (ODA) using Brust–Schiffrin method, as shown in Figure 2b. This modification improved the dispersibility of the nanoparticles in the lubricant and prevented chelation with 1,3-diketone. The modified lubricant, containing 2.25% 1,3-diketone and 0.2% ODA-modified nano-copper particles, was marked as MO2. The kinematic viscosities of MO1 and MO2 were measured to be 10.79 and 10.80 $mm^2/s$ at 100 °C, respectively, which are at the same viscosity grade as BO.



(**a**)

(**b**)

**Figure 2.** (**a**) Molecular structure of 1,3-diketone additive, and (**b**) octadecylamine (ODA) modified copper nanoparticles.

### 2.2. Friction and Wear Test

1,3-diketone has shown great potential in achieving micro- and macro-level superlubricity as mentioned above. However, an enormous gap between theoretical research and practical engineering applications still exists due to the complexity of environmental and interfacial parameters. In this work, the modified lubricants were tribologically investigated using a self-designed friction and wear tester. This apparatus has been verified to strongly correlate with real engine operating conditions [18]. The test rig provides a 30 mm reciprocating stroke, and the temperature between the tribo-pairs can be heated up to 300 °C. During testing, the tribo-pairs were fully immersed in an oil reservoir containing the lubricants. The image of the friction and wear apparatus is shown in Figure 3.

The typical combustion pressure after top dead center is approximately 20 MPa [19]; therefore, a load of 40 MPa (1000 N) was applied to the tribo-pairs to accelerate and intensify the wear process. The maximum friction force per reciprocating cycle between the tribo-pairs under variable working conditions were measured and recorded online, and the corresponding friction coefficients were calculated by dividing the friction forces by the applied load during the stable wear stage. The interface temperature between the piston ring and cylinder liner at dead center typically reaches around 150 °C [20]. To comprehensively evaluate the effect of variable temperature levels on lubricant performance, the tests were conducted at 30, 90, and 150 °C. Existing study has shown that the sliding speed of the piston ring around dead center is less than 0.9 m/s [21]. To replicate the speed conditions at the top dead center and deteriorate lubricated condition, the average reciprocating speed was set to 0.3 m/s. The above parameter settings effectively simulate the boundary lubrication conditions of the piston ring-cylinder liner near the top dead center and were employed to evaluate the boundary lubrication performance of the lubricant. Before each test, the samples were ultrasonically cleaned in an alcohol solution. Each working condition was tested in at least three repeated experiments to ensure the reliability of the results.

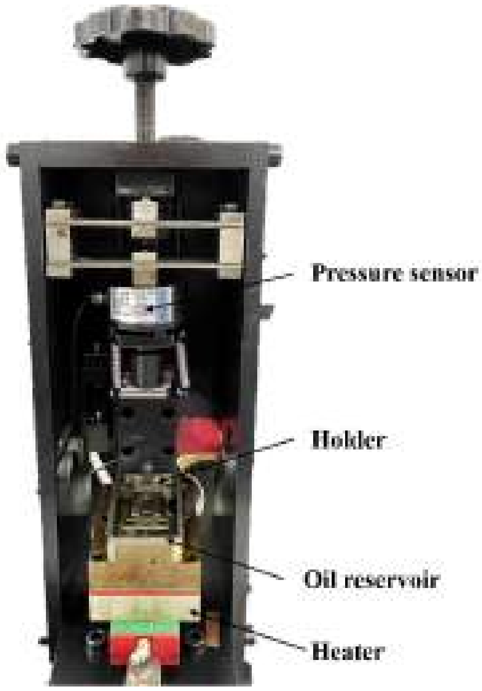


**Figure 3.** Image of friction and wear apparatus.

### 2.3. Characterization

Capillary method was used to measure the kinematic viscosities of varying lubricants. Scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM) were employed to analyze the worn surface morphologies of tribo-pairs. And wear loss is represented by the step difference between the worn and unworn areas. Atomic force microscopy (AFM) was used to examine the microstructures of tribo-films generated on the worn surfaces. The chemical composition of the worn surfaces of the cylinder liners was analyzed using X-ray photoelectron spectroscopy (XPS). The worn surfaces were sputtered using Ar iron source. Casa XPS 2.3 software was used to conduct the data processing.

## 3. Results and Discussion

### 3.1. Friction and Wear Tests

The friction and wear results obtained using different lubricants at various temperatures are presented in Figure 4. Analyzing the friction force curves (Figure 4a) and corresponding friction coefficients (Figure 4b) reveals that the friction between the tribo-pairs decreased with increasing temperature. Especially, the lubricants modified by the 1,3-diketone and nanoparticles exhibited significant friction reduction across all tested temperatures. In addition, as shown in Figure 4a, the friction force initially decreased gradually and then stabilized as the test progressed, which can be attributed to the running-in process between the tribo-pairs. Notably, under the same temperature condition, the lubricant tailored by the 1,3-diketone and nanoparticles exhibited the shortest running-in time, followed by the lubricant modified by 1,3-diketone alone. And the commercial lubricant before modification required a longer time to achieve a stable friction force. A previous finding has demonstrated that 1,3-diketone can chelate with iron substrates under complex friction conditions, facilitating a rapid running-in [13]. On this basis, the incorporation of nano-copper significantly shortens the running-in period, possibly because of its deposition and filling effects, which further enhance lubrication and surface protection. Figure 4c illustrates the wear losses of the tribo-pairs using different lubricants at varying temperatures. As the temperature increased, the wear of the friction pairs lubricated with different oils generally showed a decreasing trend. And the addition of 1,3-diketone and nano-copper provided further surface protection, resulting in the least wear. These results indicate that the incorporation of 1,3-diketone and nano-copper enhances the boundary lubrication performance.

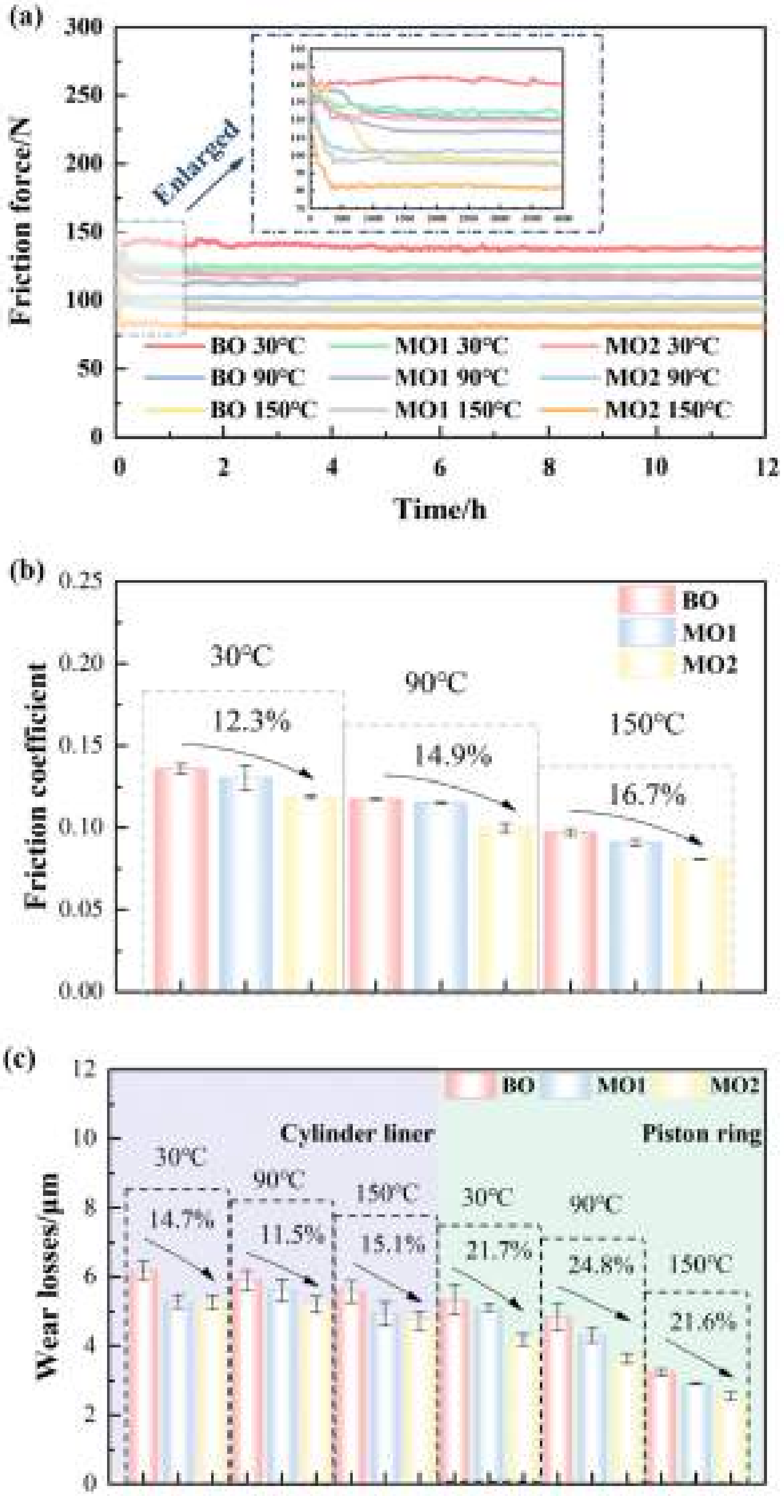


**Figure 4.** Friction and wear results of tribo-pairs under different temperatures: (**a**) friction forces versus time; (**b**) friction coefficient; and (**c**) wear losses of tribo-pairs.

### *3.2. Morphology Analysis of Worn Surfaces*

Figure 5 illustrates the confocal morphologies of the worn surfaces of CKS-electroplated piston ring specimens lubricated with different oils. For the commercial oil without modification, the piston ring surface exhibited severe wear marks, and the electroplating pattern became indistinct at a temperature of 30 °C (Figure 5a). Additionally, a blue color was observed on the wear scar along the sliding direction. Existing studies have shown that ZDDP tribo-films on iron-based surfaces typically appear blue or brown [22–24]. The blue color observed on the worn piston ring surface may also be attributed to the tribo-chemical reaction of ZDDP, but the uneven distribution suggests that the decomposition of the ZDDP additive was limited at 30 °C. As the temperature increased to 90 °C, the blue color appears to cover almost the entire worn surface (Figure 5b), resulting in a lower wear degree compared to that at 30 °C as shown in Figure 4c. At 150 °C, the worn surface primarily appeared brownish-black as shown in Figure 5c. Given that the wear amount was the lowest at this temperature, it can be inferred that higher temperatures further promoted the decomposition and tribo-chemical reaction of the ZDDP additive. After adding 1,3-diketone, the wear marks are relatively light under all temperature conditions, and the electroplated pattern on the original coating surface remains clearly visible (Figure 5d–f), which is consistent with the wear results shown in Figure 4c. However, unlike when using the unmodified commercial oil, there was no significant area of blue on the worn surface at 90 °C as shown in Figure 5e. This suggests that, under the effect of 1,3-diketone, ZDDP does not undergo extensive consumption and form a large amount of blue tribo-film during the friction process. As the temperature rises to 150 °C, a distinct blue friction film can be observed on the worn surface of the piston ring (Figure 5f), indicating that ZDDP and diketone work synergistically. Under the influence of the high temperature, the two undergo tribo-chemical reactions that reduces wear and protects the piston ring coating. After adding 1,3-diketone and nano-copper particles, no large-area blue tribo-film was generated (Figure 5g–i). This indicates that the ZDDP additive in commercial oil was not fully activated to form a protective film on the worn surface. On the other hand, although the wear losses were the lowest with the addition of both 1,3-diketone and nanoparticles, the electroplated patterns on the original coating surface appeared less distinct compared to the other two cases. This may be due to the nano-copper deposition filling the electroplated fine lines under the reciprocating friction. Given that the deposited nano-copper film itself has a low shear strength, this eventually results in fine and uniform wear marks. These findings demonstrate that both 1,3-diketone and nanoparticles contributed to reducing friction and wear, and enhancing the boundary lubrication performance.

Figure 6 presents SEM micrographs of the worn cylinder liner surfaces at different temperatures using various lubricants. For unmodified commercial lubricant oil, the material at the edge of the honing grooves underwent significant plastic flow and filled the honing grooves, making the original honing marks on the cylinder liner surface indistinguishable at 30 °C (Figure 6a). Additionally, material spalling was clear on the worn plateau surface. After the addition of 1,3-diketone, plastic flow also occurred at the edges of honing grooves; however, the coarse honing marks were well-preserved at 30 °C (Figure 6d). This indicates that the addition of 1,3-diketone effectively protects the friction pair surface and helps reduce the wear of the cylinder liner, which is consistent with the results in Figure 4. Additionally, color changes were observed on the worn plateau surface, which may correspond to the formation of a tribo-film. After adding 1,3-diketone and nanoparticles, the wear marks on the worn surface were lighter, and the fine honing marks were also well-retained (Figure 6g), indicating a further enhancement in lubrication performance. When the temperature raised to 90 °C, the wear on the cast-iron surface was noticeably milder compared to that at 30 °C for BO and MO2, while it was more pronounced for MO1, which aligns with the wear results presented in Figure 4c. As the temperature increased to 150 °C, the wear marks appeared relatively mild across all cases. The findings demonstrate that elevated temperatures significantly promote the tribo-chemical reactions between ZDDP/1,3-diketone additives and the friction pair surface. Moreover, the incorporation of nano-copper particles can further form an effective boundary protection film, leading to enhanced wear resistance.

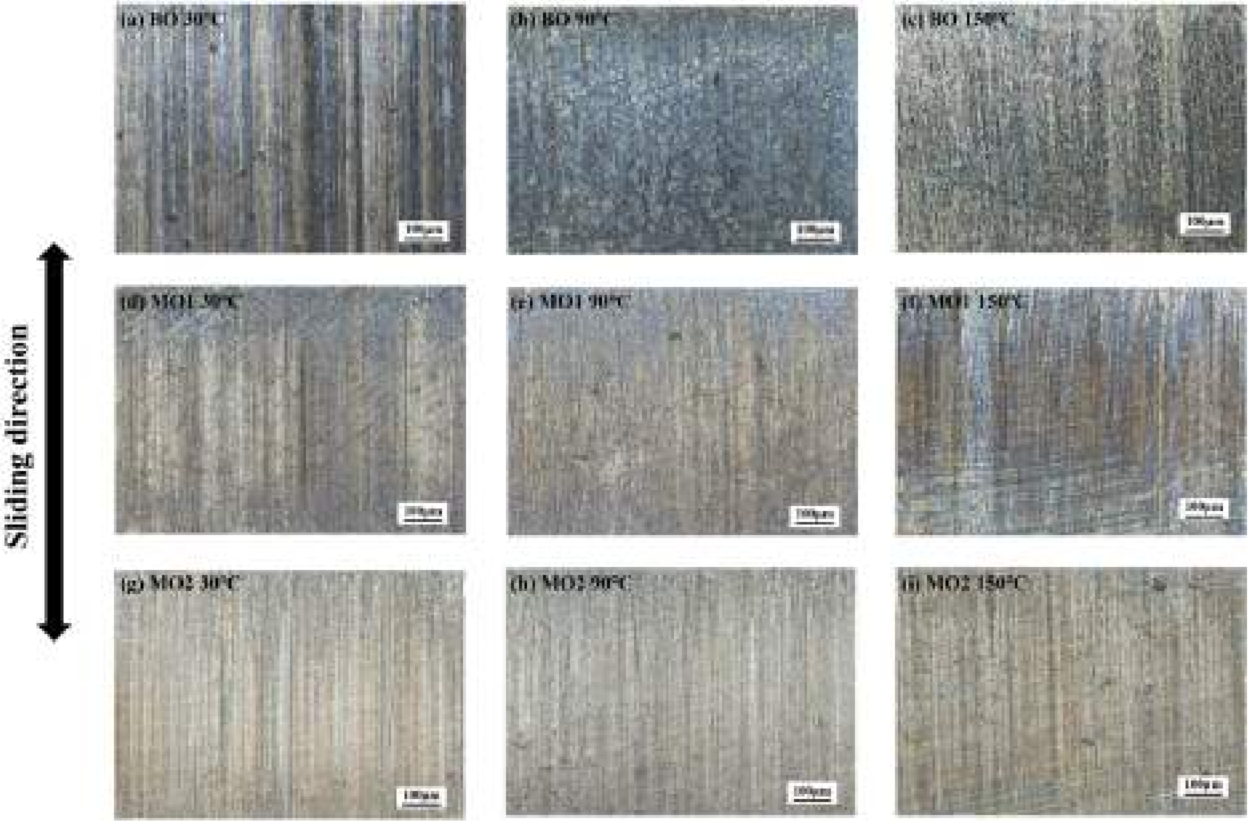


**Figure 5.** Confocal morphology of worn piston ring specimens coated with CKS using different lubricants under different temperature conditions: lubricated with BO under (**a**) 30 °C, (**b**) 90 °C, and (**c**) 150 °C; lubricated with MO1 under (**d**) 30 °C, (**e**) 90 °C, and (**f**) 150 °C; and lubricated with MO2 under (**g**) 30 °C, (**h**) 90 °C, and (**i**) 150 °C.

The AFM images in Figure 7 illustrate the morphological characteristics of tribo-films formed on the worn cylinder liner surfaces lubricated by different oils at 150 °C. For the commercial oil, the non-uniform tribo-film with a relatively rough morphology was observable on the worn surface, corresponding to the rougher topography characteristics of the ZDDP tribo-chemical reaction film [23,25]. After adding the 1,3-diketone material to the lubricating oil, the roughness of the worn surface significantly decreased, indicating that a chelation reaction occurred between the cylinder liner and the diketone, making the wear plateau smoother and greatly reducing friction and wear. When nano-copper particles were further added into the modified oil, the surface roughness was further reduced, possibly because the nano-copper filled the micro-pits on the surface.

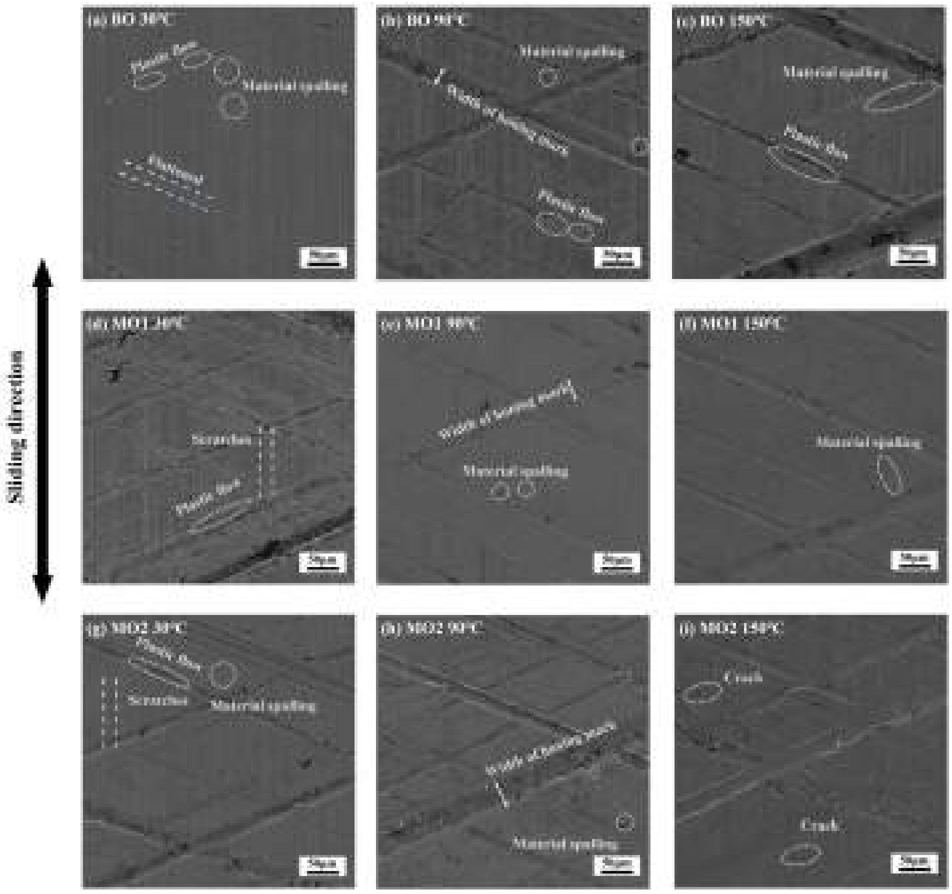


**Figure 6.** Worn morphologies of cylinder liners at different temperatures using various lubricants: lubricated with BO under (**a**) 30 °C, (**b**) 90 °C, and (**c**) 150 °C; lubricated with MO1 under (**d**) 30 °C, (**e**) 90 °C, and (**f**) 150 °C; and lubricated with MO2 under (**g**) 30 °C, (**h**) 90 °C, and (**i**) 150 °C.

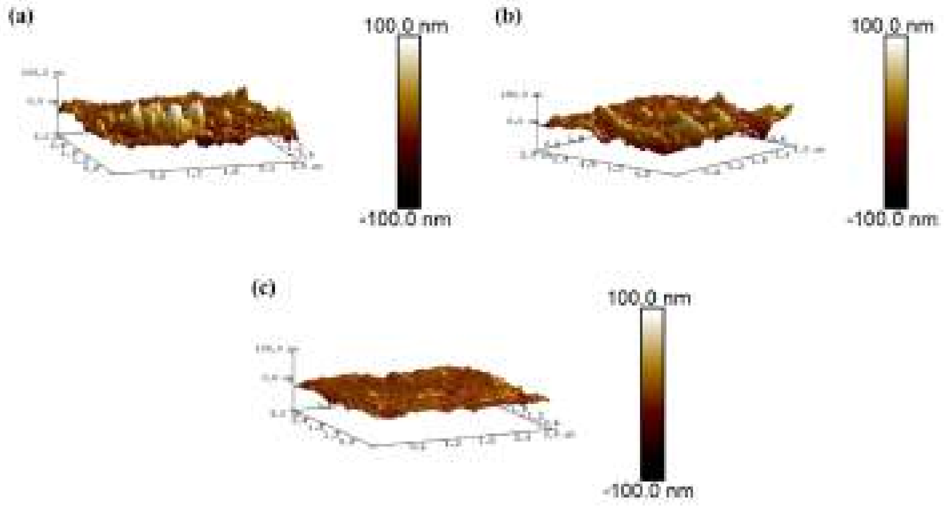


**Figure 7.** AFM micrographs of tribo-films on the worn cylinder liner surfaces using different lubricants under 150 °C: (**a**) BO, (**b**) MO1, and (**c**) MO2.

### 3.3. XPS Analysis of Worn Surfaces

Figure 8 presents the XPS analysis results of the worn cylinder liner surfaces using different lubricants at 150 °C. Figure 8a–c presented the C 1s high-resolution spectra of the worn cylinder liner surfaces lubricated with different oils. In the case of the unmodified commercial oil, the spectral fittings reveal the presence of the C-C/C-H, C-O, and C=O components on the worn surface. When using the lubricating oil containing 1,3-diketone, the main peaks at 283.5 and 286 eV were considered to be metal carbide and C-C=O [26–28], respectively. This observation suggests that 1,3-diketone molecules adsorb on the cast-iron surface and may react with it to form metal carbides. Furthermore, on the worn surface lubricated by the modified oil containing 1,3-diketone and functionalized nano-copper particles, C-C=O and metal carbides were also fitted, suggesting that similar adsorption and reaction processes occurred, as when only diketone was added. Figure 8d–f illustrate the O 1s high-resolution spectra of the worn cast-iron cylinder liner surfaces using different lubricants. For the commercial oil without modification, the main peak at 530.2 eV is attributed to the formation of metal oxides. Additionally, two phosphate-related peaks can be fitted. The first at 531.6 ± 0.3 eV was considered to be non-bridging oxygen (NBO) in phosphates, and the second at 533.3 ± 0.3 eV was assigned to bridging oxygen (BO) in phosphates [29]. The intensity ratio of the BO to NBO peaks (BO/NBO) can be used to evaluate the phosphate species and the chain length [5]. The calculated BO/NBO was 0.13, indicating that the glassy phosphate film formed on the worn surface mainly exists in the form of pyrophosphate. After adding 1,3-diketone, in addition to the peaks associated with metal oxides and phosphates, the presence of C=O (closed to the benzene ring structure) was also identified [26–28], confirming the chelation between 1,3-diketone and cast iron. Additionally, the incorporation of diketone additives led to an increase in the BO/NBO ratio to 0.2, indicating the formation of long-chain phosphates. It may be that the presence of diketone molecules is not conducive to the depolymerization of ZDDP, thereby preventing the formation of short-chain phosphates with a superior durability and wear resistance. When both 1,3-diketone and nano-copper particles were added, the worn cylinder liner surface can also be fitted with a C=O ring structure similar to the benzene ring structure. The addition of nano-copper did not affect the adsorption and chelation of diketone molecules on the cast-iron cylinder liner. The BO/NBO ratio increased to 0.22, signifying a further reduction in the depolymerization of ZDDP. Figure 8g–i present the S 2p, P 2p, and Zn 2p spectra for the worn cylinder liner surfaces. With the addition of 1,3-diketone and nano-copper particles, the intensities of S 2p, P 2p, and Zn 2p decreased, accompanied by noticeable noise peaks, indicating a reduction in the content of primary constituent elements such as S, P, and Zn in the ZDDP tribofilm. This suggests that the introduction of diketone and nano-copper additives may inhibit the adsorption and depolymerization of ZDDP additives, which is consistent with the BO/NBO results in Figure 8d–f. The significant improvement in friction and wear performance upon the addition of diketone and nano-copper additives demonstrates their effective role in reducing friction and wear, thereby alleviating interfacial thermal and mechanical conditions. Since ZDDP typically undergoes tribo-chemical reactions under high thermal and mechanical stresses to form a protective film with friction-reducing and wear-resistant properties, its role was not fully exerted after the modification of the lubricating oil. Future research could explore the possibility of completely replacing ZDDP additives with a combination of diketone materials and nano-particle additives.

### *3.4. Lubrication Effect of 1,3-Diketone and Nano-Copper Particles*

Based on the experimental and analytical results, the lubrication behaviors of the three tested oils designated as BO (original commercial marine medium-speed diesel engine cylinder piston oil), MO1 (modified with 1,3-diketone), and MO2 (modified with a combination of 1,3-diketone and nano-copper particles) are illustrated in Figure 9. This figure demonstrates the changes in the worn cylinder liner surface, providing insight into the effects of different lubricant formulations on surface wear and lubrication performance.

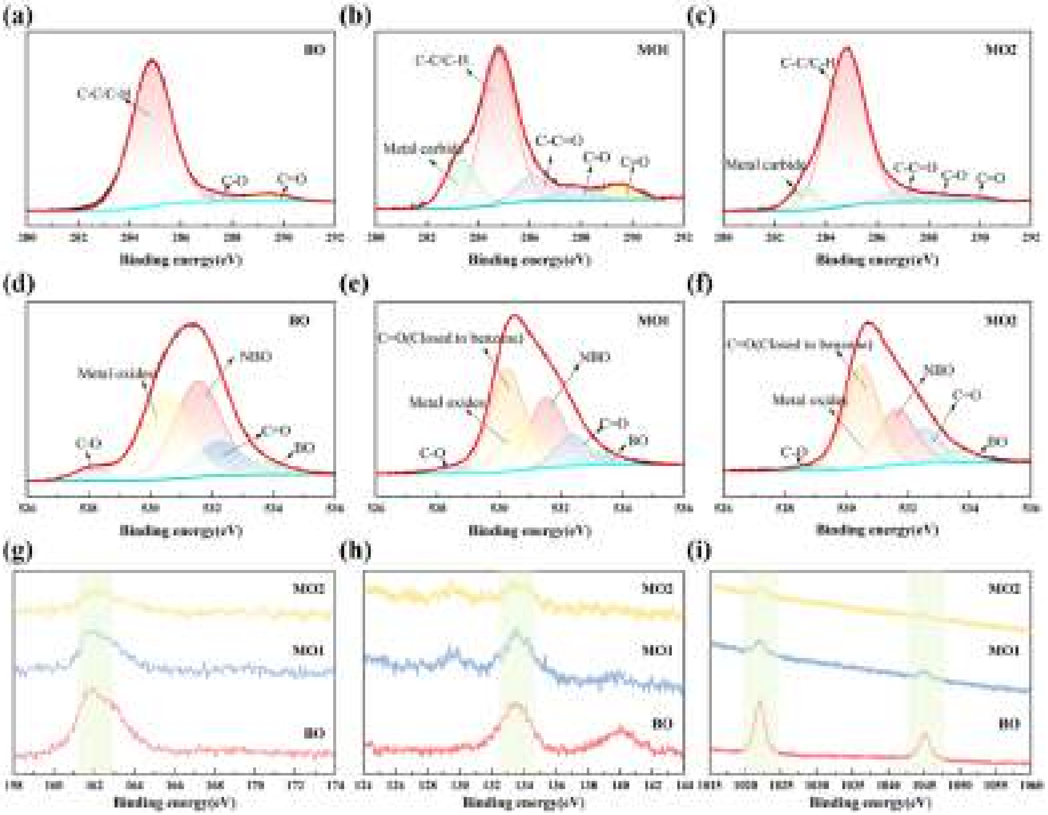


**Figure 8.** XPS analysis of worn cylinder liner surfaces using different lubricants at 150 °C: (**a**–**c**) C 1s, (**d**–**f**) O 1s, (**g**) S 2p, (**h**) P 2p, and (**i**) Zn 2p.

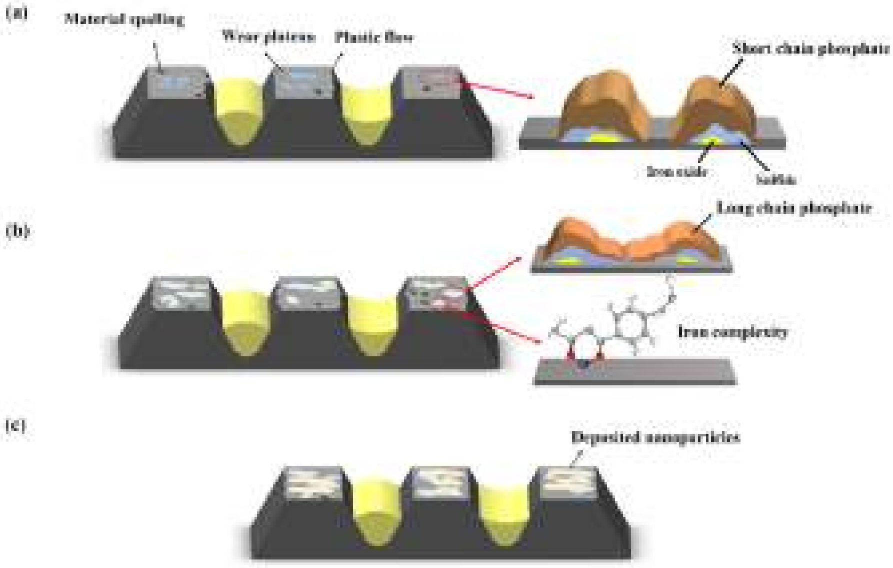


**Figure 9.** Schematic diagram of lubricant mechanism: (**a**) BO, (**b**) MO1, and (**c**) MO2.

During the friction process, the surface material of the cylinder liner undergoes plastic deformation under the applied force as shown in Figure 9a. At the intersections of the honing lines, the plastic flow layer is extruded from the honing platform and fills the grooves. Additionally, some material is sheared and peeled off to form abrasives due to the effects of reciprocating friction. As the temperature and load at the friction interface increase, the ZDDP anti-wear additive in the oil decomposes and adsorbs onto the worn surface, initiating a tribo-chemical reaction. The resulting tribo-film effectively reduces friction and wear, thereby enhancing the lubrication performance. As shown in Figure 9a, the ZDDP tribo-film is distributed discontinuously across the wear platform. Previous studies have reported that the microscopic morphology of ZDDP tribo-films typically appears as island-shaped or pad-shaped structures [23,25]. Near the substrate, these films primarily consist of sulfides such as iron sulfide and zinc sulfide, or metal oxides, which are further covered with a glassy phosphate layer. Due to the distribution and morphological characteristics of the ZDDP tribo-film, its surface appears relatively rough, which aligns with the results shown in Figure 7a. The BO/NBO ratio obtained from the O 1s high-resolution spectrum in Figure 8d indicates that the phosphate primarily exists in the form of short-chain pyrophosphate. Gosvami et al. [30] demonstrated that the growth of pad-like ZDDP tribo-film is influenced by stress and thermal activation. More severe friction conditions, such as a high load and temperature, facilitates the depolymerization of the ZDDP additive, leading to the formation of a short glassy film [5].

After the addition of 1,3-diketone, the changes in the worn cylinder liner surface during the friction process are shown in Figure 9b. In addition to the tribo-chemical reaction of ZDDP, 1,3-diketon underwent a chelating reaction with the cast-iron cylinder liner, forming an iron chelate. This reaction smoothed the wear plateau and significantly reduced friction and wear. The presence of a detected C=O bond (adjacent to the benzene ring structure) in Figure 8e further confirms the chelation between 1,3-diketone and the cylinder liner. Moreover, this process contributed to a shortened running-in period. On the other hand, a reduction in the content of primary elements such as S, P, and Zn in the ZDDP tribo-film was confirmed, according to the XPS results shown in Figure 8. Additionally, the O 1s fine spectrum revealed that the glassy phosphate film detected on the worn surface exhibited a longer chain length compared to that when BO was used as the lubricant. This suggests that the tribo-chemical reaction of 1,3-diketone provides an effective lubricating effect at the friction interface, reducing localized heat and stress. As a result, the depolymerization of ZDDP may be inhibited.

After the addition of 1,3-diketone and modified nano-copper particles, iron chelates were also detected on the worn surface, as shown in Figure 8, indicating that the incorporation of nano-copper did not interfere with the adsorption and chelation of diketone molecules on the cast-iron cylinder liner. Furthermore, the types and chain length of phosphates detected on the worn surface remained unchanged compared to those observed with the addition of 1,3-diketone alone, suggesting that the depolymerization of ZDDP may also be inhibited. The nanoscale morphology of the worn cylinder liner surface after the friction and wear test, shown in Figure 7c, revealed a remarkably smooth surface. This can be attributed to the accumulation of frictional heat between the tribo-pairs, which facilitated the deposition of nano-particles onto the worn surface, forming a protective deposition film, as depicted in Figure 9c. This film repairs surface irregularities, minimizes the direct contact between the micro-asperities of the friction pairs, and reduces the shear strength between the sliding surfaces [31]. Hence, the combination of 1,3-diketone and functionalized nano-copper particles provides a synergistic effect in improving the boundary lubrication performance. Notably, this enhancement is not based on the effect of ZDDP. Instead, it suppresses the depolymerization and reaction of ZDDP, offering a novel approach for developing environmentally friendly, high-performance lubricant systems.

## 4. Conclusions

In this work, 1,3-diketone and modified nano-copper particles were synthesized and incorporated into a commercial marine medium-speed diesel engine cylinder piston oil to enhance its lubrication performance. Friction and wear tests were conducted using a self-designed tribological tester to evaluate the boundary lubrication properties of the modified oils. The following conclusions were drawn:

(1) A remarkable enhancement in boundary lubrication performance was achieved when using lubricating oil containing 1,3-diketone and nano-copper particles. Especially at high temperatures, compared to the commercial oil, the friction force was reduced by up to 16.7%. The wear of the piston ring was decreased by 21.6%, while the wear of the cylinder liner was reduced by 15.1% at 150 °C.

(2) The presence of 1,3-diketone and nano-copper accelerates the running-in process between the friction pairs, allowing the friction force to stabilize more rapidly at a lower level. This effect is attributed to the chelation of 1,3-diketone with iron substrates under complex friction conditions, while the deposition and filling effects of nano-copper further enhance the lubrication and surface protection, promoting a smoother and more efficient running-in process.

(3) The addition of 1,3-diketone and functionalized nano-copper particles influenced the depolymerization and tribo-chemical reactions of the anti-wear additive ZDDP, offering a novel approach for developing environmentally friendly, high-performance lubricant systems.

Although the lubricant modified with 1,3-diketone and nano-copper composite additives in the simulation test in this paper is superior to the standard commercial lubricant in friction reduction and wear resistance, it is still necessary that we systematically evaluate its key performance indicators such as oxidation stability, detergency, and extreme pressure performance before it is used in engineering applications to reduce or replace ZDDP. On the other hand, our tests were conducted on a sample-level tribological system, which can never fully replicate the dynamic thermal and mechanical stresses encountered in actual marine engines. Moreover, with the application of new fuel engines, the impact of combustion products may also be a research focus for future lubricant development. In the future, we will develop a test bench to conduct relevant research and address the above issues.

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