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Improvement of Tribological Properties of ZnO Nanoemulsion Lubricant for Zirconium Alloy Cold Rolling by Hydroxyethyl Cellulose (HEC)

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Keywords：cold rolling, ZnO nanoparticle, nanoemulsion, anti-friction and anti-wear, HEC.

ABSTRACT

Zirconium alloy' s surface often sticks and peels off during the cold process, which has a serious impact on the surface quality of the workpiece and the mold's service life. In this paper, lard was used as the oil phase to create the nano-lubricating emulsion, while Span 80 was used as the dispersant to distribute the ZnO nanoparticle using a strong ultrasonication. The addition of HEC improved the dispersion and stability of the emulsion particles by forming a network structure in solution as a result of its mutual crosslinking. Compared with the emulsion without HEC, the friction and wear were reduced by up to 85.24%. SEM showed that the surface of HEC nanoemulsion as lubricant was smooth after friction test, which greatly reduced the occurrence of adhesive wear. Furthermore, with the addition of HEC, the film thickness increased, which facilitated the entry of the nanoemulsion and improved the bearing capacity after friction demulsification. Moreover, HEC nanoemulsion can be adapted to friction under various working conditions with excellent anti-friction and anti-wear ability, which is expected to improve the surface adhesive wear of Zr alloy caused by cold rolling and the surface processing quality.

INTRODUCTION

Zirconium alloys are corrosion resistant materials and biocompatible for in body implantation.

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In medical surgery, Zr alloys can be used as knee or hip implants, reducing friction and increasing wear resistance while maintaining overall properties (manufacturability, fracture toughness and ductility et al.), and it is considered as a good solution for medical implants (Zhang et al., 2021). Currently, the main processing method of Zr alloy products is cold rolling. A Smooth machining surface is very important for both the workpiece and mold (dos Santos et al. 2021). However, Zr alloys are easy to stick to the die during cold rolling, causing spalling and fatigue cracking failure, which seriously affects the quality and stability of Zr alloy products. This leads to an increase of production costs and reduces production efficiency. In order to solve the problems in Zr alloy rolling process, it is necessary to adopt a more effective lubrication method to form a stable lubricating film between the roll and the rolling piece (Meng et al., 2020; Chang et al.,2019), reducing the friction between the contact surfaces, and thus the adhesive wear of the Zr alloy.

Due to the large amount of deformation and friction heat (Chang, 1999; Chang et al., 2019), emulsion or water-based lubricating fluid is often used as rolling lubricant (Hajshirmohammadi et al., 2019; Lo et al., 2010). Water is widely used as a coolant in the rolling process due to its large specific heat capacity, low cost and high heat absorption rate. On the other hand, grease is easily adsorbed on the metal surface to form a lubricating film to improve tribological properties. Emulsifiers that combine the advantages of both liquids are ideal for rolling lubrication. For oil-in-water emulsions, the occurrence of depleted oil mainly depends on the concentration of the emulsion and the particle size of the oil phase particles (Reich et al., 2001; Azushima et al., 2009). In order to ensure the stability of emulsion particle size, different surfactants, biopolymer stabilizing emulsifiers and nanoparticle emulsifiers are used to adjust and control the size of oil phase particles and improve dispersion (Chaudhari et al., 2015; Sakazaki et al., 2019). The nanoparticles in the emulsion can also act as a lubricant to improve the bearing capacity and reduce friction and wear. Many scientific researchers add TiO_2, SiO_2, Al_2O_3, MoS_2, carbon nanocapsules and other nanoparticles to the emulsion to play a good anti-friction and anti-wear effect (Wu et al., 2017; Sharma et al., 2018; Bao et al., 2022). They use the nanoparticle micro-bearing effect, surface repair effect, etc. to reduce the shear force between the frictional contact surfaces, thereby improving the quality of the rolled workpiece and improving the process efficiency (Bao et al., 2017; Kong et al., 2017).

Zinc oxide (ZnO) is a highly adaptable material that can be used in different environments through the design of porosity, size, and morphological characteristics (Alenezi et al., 2018). Under natural conditions, ZnO exists as a single stable hexagonal wurtzite structure (Jiang et al., 2012). In recent decades, ZnO has been widely used in many fields such as photocatalysis, antibacterial, and material modification due to its good piezoelectricity, room temperature ferromagnetism, and chemical sensing effect (Paul et al., 2019; Liu et al., 2017; Vatansever et al., 2010). In tribological applications, ZnO nanoparticles are usually added to polymers such as PE, PTFE, and PEEK to improve the mechanical properties and wear resistance of the material (Sharma et al., 2014; Mu et al., 2015; Wu et al., 2022). In addition, studies have shown that ZnO nanoparticles as additives have good anti-wear effect under extreme pressure conditions (Battez et al., 2006). ZnO nanoparticles are adsorbed on the friction interface when the friction pair are in relative motion, improving the contact condition by reducing and repairing the surface roughness to increase the surface quality (Marino et al., 2022). It can be seen from the above studies that ZnO has a great potential in improving the tribological properties of materials, and can act as a nanodispersant for emulsions due to its clean, safe, and controlled qualities during preparation as well as its microscopic morphology. However, there are still few studies on the lubrication synergy of ZnO in emulsions.

To enhance tribological properties of rolling lubricant emulsion, nano-sized ZnO particles were prepared by using zinc acetate as a precursor and polyvinylpyrrolidone (PVP) as a surfactant. Using Span 80 as the dispersant and lard as the oil phase, the ZnO was dispersed in the oil by a facile one-step nanoemulsion method (Wang et al., 2019), and then the oil-water phase was mixed using strong sonication to prepare the O/W emulsion. Hydroxyethyl cellulose (HEC) was added to adjust the viscosity and improve the stability of the emulsion by the network structure formed by its cross-linking in the aqueous solution. The tribological properties of the prepared nanoemulsion were tested by a tribometer, and the wear marks were analyzed by SEM, EDS and XPS. The composition of the surface facial mask was detected to clarify the mechanism.

EXPERIMENTAL

Nanoemulsion preparation

The morphology of nano-particles has a great relationship with the crystal plane energy of each crystal plane. The size of crystal plane energy determines the growth rate of crystal plane. Generally, the crystal surface energy can be adjusted and changed by adding surfactants in the reaction environment. By different adsorption states on different crystal surfaces, the growth of nanocrystals can produce preferred orientation. As shown in Fig.1, in reaction solution, PVP hydrolysis had positive points and was adsorbed on the negative polar surface [000-1]. In the alkaline environment, part of PVP binded OH^- ions with negative charges and was adsorbed on the positive polar surface [0001], which inhibited the adsorption of $Zn(OH)_4^{2-}$ ions on the two surfaces and caused the six sides to grow rapidly (Xie et al., 2012). Then, the particle size was adjusted by controlling the aging time.

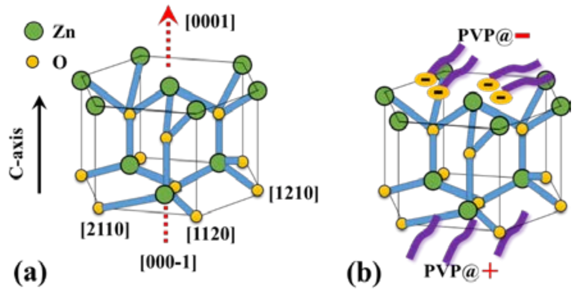

Fig. 1 Structural diagram of zinc oxide

The preparation process of ZnO nanoemulsion is shown in Fig. 2. By using zinc acetate (Shanghai Aladdin Biochemical Technology Co., Ltd.,China) as the precursor solution, polyvinylpyrrolidone (PVP, Shanghai Aladdin Biochemical Technology Co., Ltd.,China) as the surfactant, and adjusting the pH to 11 with 0.1 mol/L NaOH solution after stirring, nano-scale ZnO particle suspension was obtained. PVP was used as a surfactant, in which the lipophilic group and the $-CH_3$ of the acetate ion are linked due to the van der Waals force, so that PVP has a negative charge. In addition, due to the electrostatic effect, PVP was adsorbed to the positive surface of ZnO crystal, inhibiting its growth in the c-axis direction. Simultaneously, PVP adsorbs on the non-polar surface of ZnO crystal due to the van der Waals effect, which also inhibits the radial growth to a certain extent. After aging treatment in a 30°C thermostat for 6 hours, the prepared product was repeatedly centrifuged-cleaned, and finally dried at 80°C in a drying oven to obtain nano-ZnO powder. According to the negative ion coordination polyhedron growth unit, during the crystallization process of ZnO, there was particle aggregation and growth, which is the superposition of coordination tetrahedra at the interface, and its growth unit is the complex $Zn(OH)_4^{2-}$. The reaction equation for the preparation of ZnO nanoparticles is shown below (Ma et al., 2008).

(1) Formation process of growth unit:

$$Zn^{2+} + 2OH^{-} + 2H_2O = Zn(OH)_4^{2-} + 2H^{+}$$

(2) The process that growth elements are superimposed on the crystal interface through dehydration reaction:

$$Zn_mO_p(OH)^{n(n+2p-2m)-}(\text{crystal}) + Zn(OH)_4^{2-} =$$
$$Zn_{m+1}O_{p+1}(OH)^{n(n+2p-2m+2)-} + H_2O$$

When preparing the emulsifier, lard was used for the oil phase, and 0.5 g of Span80 was weighed as a dispersant to disperse 0.04 g of ZnO particles in the oil phase for 1h using an ultrasonic device. Afterwards, the oil phase was poured into 5 g of water, and triethanolamine oleate (Tianjin Shengao Chemical Reagent Co., Ltd., China) was used as an emulsifier for 30 min of strong ultrasonic emulsification, and then a certain quantity of hydroxyethyl cellulose (HEC, Tianjin Shengao Chemical Reagent Co., Ltd., China) was added, and an emulsion containing ZnO nanoparticles was obtained after stirring uniformly.

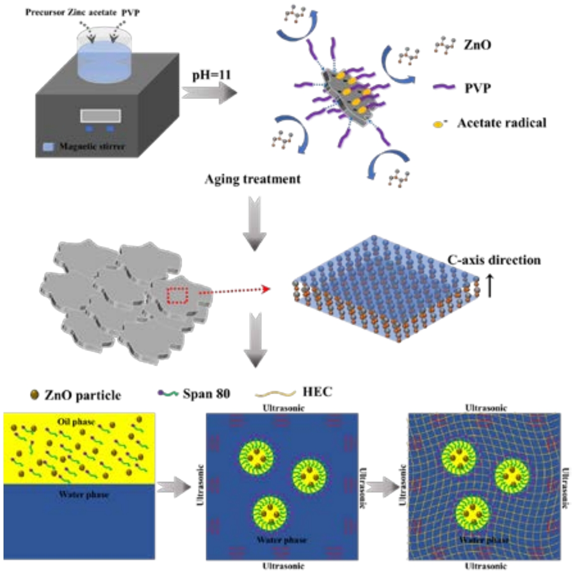

Fig. 2 Preparation process of ZnO nanoemulsion

Tribological tests

The tribological properties of ZnO nanoemulsion were tested and evaluated using the ball-on-disk reciprocating module with a tribometer. The bearing steel ball (Diameter 9.525 mm, Ra 0.008 μm, Poisson's ratio 0.30, Elastic Modulus 219 GPa, SKF Ball Bearing Manufacturing Company, Sweden) was used as the upper friction pair, and the Zr-4 alloy (Poisson's ratio 0.33, Elastic Modulus 95.2 GPa, State Nuclear Bao Titanium and Zr Industry Co., Ltd., China) was chosen as the lower friction sample. Before tests, the zirconium alloy rod was cut into Φ10 mm×3 mm discs, which were ground and polished until the surface roughness Ra is less than 0.019 μm. Moreover, bearing steel balls and Zr alloy discs were ultrasonically cleaned in absolute ethanol solution for 10 minutes to remove contaminants such as oil stains on the surface. According to the actual processing conditions of Zr alloy, the test load can be set in the range of 5-30 N and the experimental frequency was 2 Hz by converting the load and processing speed into experimental parameters. During test, the reciprocating stroke was 6mm, and the air humidity was kept at 30±2%. Except for the high temperature condition, the experiment was carried out at room temperature (25ºC). The duration of each friction test was 10 minutes. In order to ensure the accuracy of the data, the friction coefficient (COF) test was repeated three times.

Characterization methods

The optical microscope (CX40M, Sunny Optical Technology Co., Ltd., Ningbo, China) equipped with warm white LED light was used to observe the worn surfaces and wear spots of Zr-4 surfaces. The internal structure and surface morphology of the nanomaterials were observed by transmission electron microscopy (TEM, JEOL JEM-2100, Nippon Electronics Co., Ltd., Japan) and field emission scanning electron microscopy (SEM, GeminiSEM 500, Carl Zeiss AG, Germany), respectively. The crystal phase composition of the sample was characterized by X-ray diffraction (XRD, Bruker D8 ADVANC, Bruker Instruments Ltd., Germany), and the results were compared with the standard crystal phase to determine the crystal phase structure of the prepared product. The size of the prepared ZnO nanoemulsion was measured using ZETA potential and nanometer particle size analyzer (Zetasizer Nano ZSE, Malvern Instruments Ltd., UK). The functional groups and inorganic compound in the friction area of the sample were tested and analyzed by Raman spectroscopy (DXR2xi, Thermo Fisher Scientific, USA) and X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB Xi+, Thermo Fisher Technology (China) Co., Ltd., China) to analyze the mechanism of anti-friction and anti-wear. The dispersion and fragmentation of nanoemulsion were achieved by an ultrasonic pulverizer (USAC35-1200, Ningbo Weicheng ultrasonic equipment Technology Co., Ltd., China). Tribological performance tests of nanoemulsion were carried out by using a ball-on-disk tribometer (UMT-2, CETR Co. Ltd., USA). The kinematic viscosity of lubricating fluids at room temperature was measured using a Cannon-Fensk capillary viscometer (Guangdong Saituo Instrument Technology Co., Ltd., China), and the density of the lubricant was measured by a specific gravity meter (Jining Hanye Machinery Equipment Co., Ltd., China).

RESULTS AND DISCUSSION

Characterization of ZnO nanoemulsion

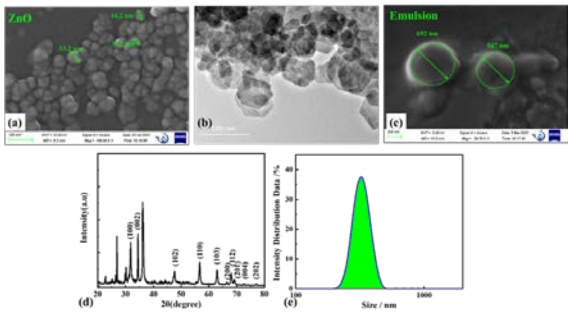

Fig. 3 Characterization of Surface Morphology of ZnO and its nanoemulsion (a) SEM image of ZnO nano particles; (b) TEM image of ZnO nano particles; (c) SEM image of emulsion; (d) XRD analysis of ZnO; (e) Particle size distribution data of emulsion

The SEM images of ZnO nanoparticle prepared by solution method and its nanoemulsion particles obtained after freeze-drying are shown in Fig. 3. When zinc acetate is dissolved in water, it produces an acetate ion with -CH_3 functional group, and as a surfactant, PVP possess both lipophilic group -CH_3 and hydrophilic group -C=O. The oil-philic and acetate ion -CH_3 are connected by the van der Waals force, giving PVP a negative charge. Therefore, PVP can be adsorbed on the positive surface of ZnO crystals due to electrostatic action, which prevents the crystals from growing along the C-axis direction. Meanwhile, PVP can be also adsorbed on the non-polar surface of ZnO crystals due to van der Waals action and inhibit the radial growth to a certain extent. From the aforementioned factors, smaller ZnO nanoparticles can be obtained as shown in Fig. 3a. The overall size of ZnO nanoparticles remains below 50 nm and the morphology is nearly sheet-like structure (Fig. 3b). The prepared ZnO particles were analyzed by X-ray diffraction and compared with the standard (JCPDS No.36-1451). Its main peak position corresponds to the crystal planes of (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) of the standard value, and it is in hexagonal wurtzite. There are no diffraction peaks of other impurities in the figure, indicating its high purity and good crystallinity (Fig. 3d). After the nano-emulsion was prepared, the particle size of the emulsion was about 400-700 nm through SEM and nano-particle size analysis data. After ZnO was added to the emulsion to prepare the nano-emulsion, the particle size of the emulsion was about 400-700nm through SEM and nano-particle size analysis data (Fig. 3c and e).

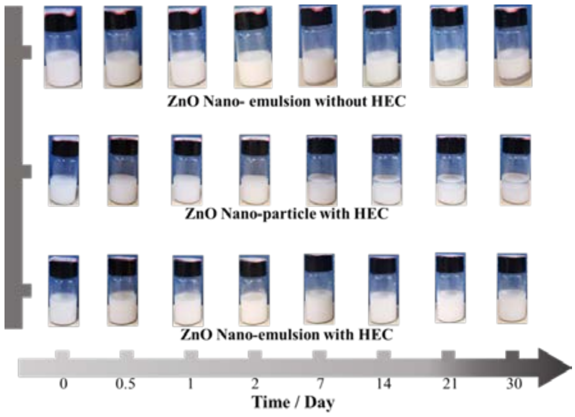

Fig. 4 ZnO nanoemulsion dispersibility test

The stability of the nano-emulsion was evaluated by gravity sedimentation method for the invariable water-oil matching ratio of the nanoemulsion. At room temperature, photographs were taken with a camera to record the sedimentation process, and the result was shown in Fig. 4. The nanoemulsion without HEC can maintain the dispersion stability for one week, and then the emulsion began to subside gradually, and an obvious water layer appeared in lower part of the bottle. The ZnO water base suspension liquid with 0.6 wt% HEC began to lose stability after 2 days. Zinc oxide particles gradually sink due to high density, and with the increase of time, the supernatant increases. After 30 days of natural sedimentation, there has been an obvious stratification phenomenon, which indicates that the ZnO nanoparticle solution containing HEC has poor dispersion. It can be seen from the photos at different times that during the sedimentation process, the nanoemulsion containing HEC can ensure that there is no obvious aggregation and stratification phenomenon for 30 days, showing good dispersion stability. This is because HEC forms a hydrated molecular layer in water and long chains are cross-linked to each other to form a network structure. On the one hand, it improves the viscosity of emulsion, limits the movement of oil droplets and reduces collisions; On the other hand, the network structure has a binding effect on the emulsion nanoparticles, so that they remain in a stable position and do not contact each other to form large particles, resulting in the separation of oil and water.

Friction and wear analysis

Tribological tests were carried out using different lubricants under 5 N load and 2 Hz frequency working conditions, and 20 μL of nanoemulsion was quantitatively added as lubricant during friction test. The obtained friction coefficient variation curves and optical microscope pictures of the worn surfaces of different samples are shown in Fig. 5. According to the test results, the anti-friction and anti-wear effects of HEC solution and O/W emulsion were not satisfactory. Under the test conditions, the COF was high, and the surfaces of the Zr alloy and steel ball mating pairs were severely worn. Adding different concentrations of HEC into the O/W emulsion greatly improved the tribological properties of the lubricant. Furthermore, with the increase of HEC concentration, the COF first decreased and then increased. In the nanoemulsion with HEC concentration of 0.6 wt%, the COF was the smallest about 0.032, which was about 85.24% lower than that of the emulsion without HEC (Fig. 5a). Fig. 5b shows the wear surface topography of the friction contact area after the friction pairs experimented with different lubricants. It can be clearly seen that the wear marks were reduced after the addition of HEC, indicating that the nanoemulsion had good anti-wear properties. When the additional HEC concentration was increased, the wear scar width and diameter both decreased, according to a comparison of the two measurements. When 0.8 wt% HEC was added, the wear scar width and wear scar diameter were only 68.03 μm and 78.42 μm.

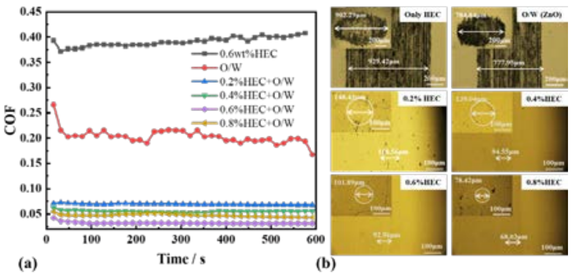

Fig. 5 Friction coefficient (a) and wear surfaces (b) of nanoemulsions with different concentrations of HEC

In order to further explore the tribological properties of nanoemulsion, the nanoemulsion containing 0.4wt% HEC was selected as the lubricant, and the reciprocating frequency was set to 2Hz. Tribological tests were carried out under different loads and temperatures with 20 μL lubricant. The results are shown in Fig. 6. Fig. 6 a and b are the graphs of COF and load variation at a temperature of 20ºC. Under low load (5~15 N), as the load increases, the thickness of the lubricating film becomes smaller, while the contact ratio of the friction pairs did not change much, so the shear force did not increase significantly during the movement, and the COF decreased. Under high load, the lubrication state changed to boundary lubrication. At this point, the COF increased as the contact ratio, and the shear force increased, and the demulsification lubricant and ZnO nanoparticles were mostly lubricated together. Fig. 6 c and d are the COF curves at different temperatures obtained from tribological tests under a 5 N load. When the temperature were 40°C and 80°C, the COF curve had a mutation point. It can be seen from the Fig. 6c that 40°C occurs later than 80°C. This mutation point may correspond to the moment when all the water phase evaporates. With the increase of temperature, the evaporation rate of the hydrated molecular layer accelerated. When the water molecules evaporated, only the oil phase containing nanoparticles existed at the lubricating interface, which would lead to the sudden change of the COF within the test time. However, since 120°C and 160°C exceed the boiling point of the water phase, the evaporation rate was extremely fast, so the sudden change could not be captured in the figure. The average COF decreased with the increase of temperature, which may be because the increase of temperature was favorable for the lubricating fluid to form strong chemical adsorption on the metal surface, decreasing the COF.

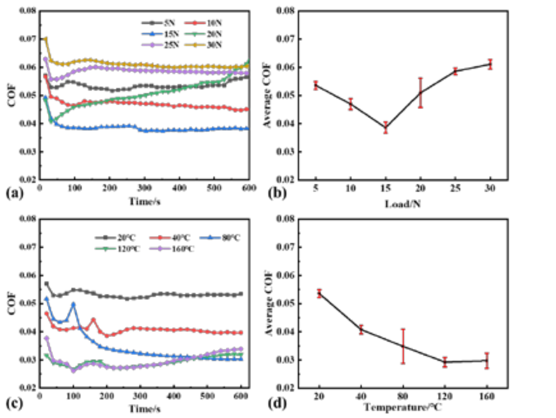

Fig. 6 Variation of friction coefficient of nanoemulsions under different loads (a and b) and temperatures (c and d)

Fig. 7 shows the surface morphologies of the wear scar of the steel balls and the Zr alloy discs under different loads and temperatures. Overall, the wear scar increased gradually with the increasing of the load. When the load was 5 N, the wear scar width and wear spot diameter were only 92.96 μm and 101.89 μm, respectively. However, when the load reached 30 N, the wear scar width and wear spot diameter reached 256.14 μm and 292.91 μm, respectively. It can be seen from the optical microscope images that the surface of the worn surfaces under 5~25 N was relatively flat and light. When the load was 30 N, there was obvious abrasive wear at the center of the wear spot and wear mark surface, which was due to the increase of the contact stress on the contact surface, resulting in the increase of the actual surface contact area of the friction pair, thereby increasing the wear. It can be seen from Fig. 8 that with the increase of HEC concentration, the viscosity increased significantly, and under the same load, the change of the contact ratio (the calculation process is attached in Appendix part) was obviously related to the HEC concentration. The contact fraction was extremely small at high concentrations and low loads, indicating that little wear occured on the friction surfaces. Under the load of 30N, the friction contact ratio under 0.4wt%HEC lubrication was 0.75%, so the surface of Zr alloy would have larger wear in comparison. In addition, with the increasing of temperature, the wear size changed slightly, and the wear scar width and wear spot diameter were maintained at 200 μm and 150 μm, respectively, and only slight abrasive wear occurs, which proved that the prepared ZnO nanoemulsion had good tribological properties and can meet the lubrication requirements under normal processing conditions.

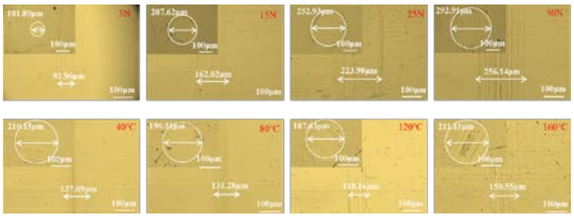

Fig. 7 Zr alloy wear surfaces lubricated by nanoemulsion at different loads and temperatures

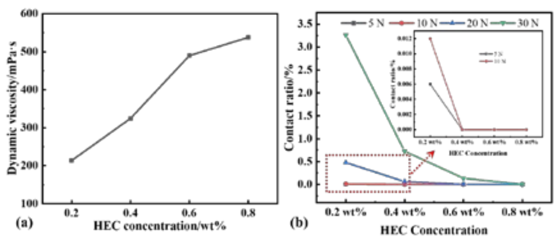

Fig. 8 (a) HEC viscosity at different concentrations; (b) contact ratio at different HEC concentrations under various conditions

SEM and EDS anslysis

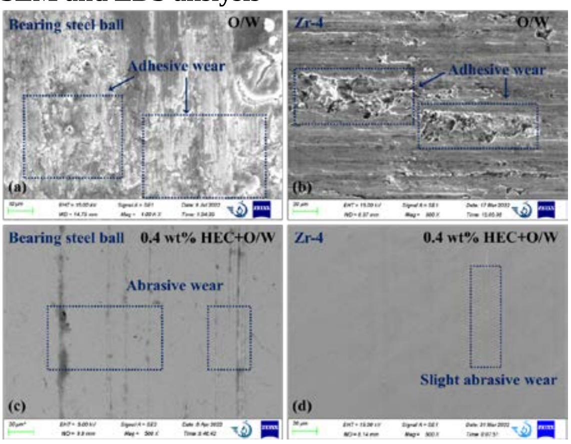

Fig. 9 SEM images of worn surfaces under the lubrication of O/W emulsion (a and b) and 0.4 wt% HEC+ O/W emulsion (c and d)

The surface wear morphology of the friction pair is one of the important criteria to measure the friction performance of lubricants. Therefore, SEM was used to detect the surface of the friction pair under the lubrication of O/W emulsion with and without HEC, and the images are shown in Fig. 9. There were a lot of adherents in the friction area of the steel ball lubricated with O/W, accompanied by a small amount of furrow wear. Simultanouesly, there were also many peeling marks on the Zr alloy surface of the corresponding friction pair. This phenomenon seriously affected the surface quality of the machined workpiece and the service life of abrasive tools in production (Fig. 9a and b). The addition of HEC did not only improve the stability of the emulsion, but also significantly improved the tribological properties. It can be seen from Fig. 9c and d that under the lubrication of O/W emulsion containing 0.4wt% HEC, there was only a small amount of abrasive wear on the surface of the friction pair of the steel ball, while the friction surface of the Zr alloy pair was very smooth with almost no wear marks.

Then the EDS analysis was carried out on the adhesion at the friction interface of the steel ball, and the element distribution map and element content weight obtained are shown in Fig. 10. The main adhesive on the surface of the steel ball using O/W emulsion as lubricant was Zr alloy, in which Zr element accounted for up to 45.22wt% on the wear surface, while the content of Zn element was 0, indicating that the nanoemulsion did not form a stable lubricating film. However, under the lubrication of the nanoemulsion containing HEC, the element content analysis of the ball wear surface (Fig. 10b) showed that the surface contained 0.3wt% Zn element, and no Zr element was detected, indicating that under the action of this lubricant, nanoemulsion particles could smoothly enter the friction gap and participate in the friction process, and there was no adhesive wear on the friction surface. Therefore, the tested Zr produced a superior surface finish, and it was difficult to see the wear trace.

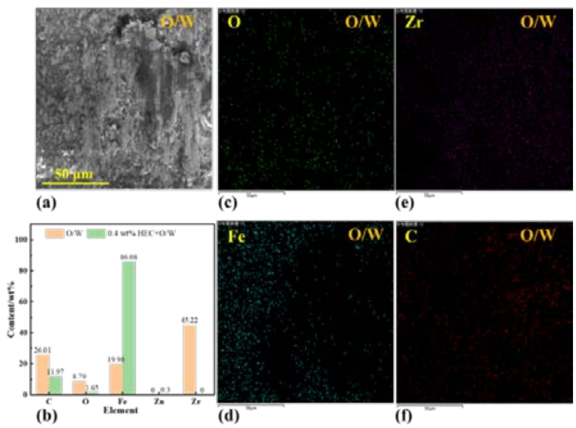

Fig. 10 EDS analysis of ball worn surfaces under the lubrication of O/W emulsion and 0.4 wt% HEC+ O/W emulsion

Since HEC is intertwined in the water phase to form a network structure, the stability of the particles is improved, and the hydrated molecular layer formed by HEC is easily adsorbed on the friction interface, which increases the thickness of the lubricating film, making it easier for the nanoemulsion particles to enter the interface. After demulsification under high load, the surface repairing effect and the low shear force of ZnO nanoparticles as well as adsorption of oil phase on the friction interface jointly form a stable lubricating film, which reduces friction and wear.

Mechanism analysis

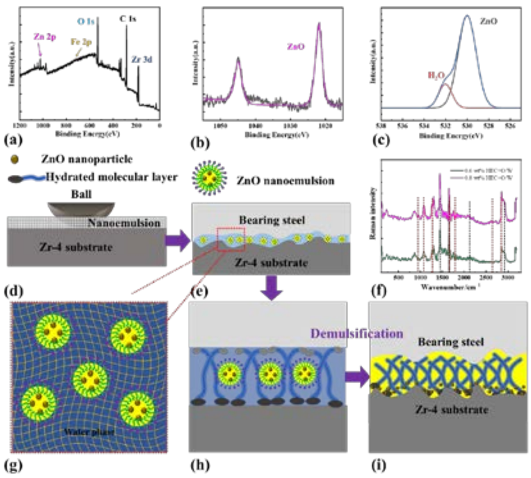

Fig. 11 Schematic diagram of HEC hydration lubrication mechanism of ZnO nanoemulsion

In order to further explore the friction reduction mechanism of O/W nanoemulsion containing HEC, the surface of Zr alloy disk was analyzed by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, as shown in the results of Fig. 11a, b, c and f. XPS showed that Zn elements on the friction surface had existed in the form of Zn^{2+}, indicating that the surface contained ZnO, and the electronic binding energy of O1s also indicated the existence of ZnO. The Raman spectra of the worn surface showed characteristic peaks at 2897, 2446, 1587 and 1450 cm^{-1}, corresponding to CHO, CH, heterocyclic and CH_2 groups, respectively. The above four groups are the characteristic groups of HEC (Sheng et al. 2019). The peak around 871 and 1743 cm^{-1} corresponded to phospholipids and stretching vibration of triglyceride ester chains, and the bands at 1444 cm^{-1} was caused by $\delta(CH_2)$sc methylene scissor deformation, which were the characteristic groups of lard (Taylan et al., 2020). In addition, lard fat had an obvious band at 1271 cm^{-1}, which was attributed to bending vibration of δ(C-H) at the cis double bond in R-HC=CH-R (Czamara et al., 2015; Nedeljkovic et al., 2016). According to the analysis of the tribological mechanism of ZnO nanoemulsion according to the test results, it can be seen that when the friction contact pair was in relative motion, the hydrated molecular layer of HEC caused a larger film thickness during friction. Based on the dynamic concentration theory, the oil particles coated with ZnO nanoparticles entered the contact zone, and the action of the load caused the oil particles to be flattened, making the surfaces of the oil particles contact each other, and then the oil phase became a continuous phase (Fig. 11e, h and i). It was gradually adsorbed on the surface of the friction contact pair, so that the original oil-in-water was converted into water-in-oil (Azushima et al., 2011; Guillaument et al., 2011). At the same time, a large number of ZnO nanoparticles were driven to settle on the surface of the disk, which promoted the formation of the ZnO protective film and effectively reduced the surface wear of the friction contact pair. In addition, the ZnO particles had a sheet-like structure, which was easy to slip between sheets, and thus had good friction-reducing properties. At high temperature, although the evaporation of the hydrated lubricating layer led to a certain increase in the COF, the existence of the oil phase could still maintain the good anti-friction and anti-wear properties of the lubricating fluid. Under real-world working circumstances, this nanoemulsion can fulfill the application. It should address the issue of adhesive wear during zirconium alloy processing.

CONCLUSION

In this paper, by using lard as oil phase and Span 80 as dispersant, ZnO nanoparticles were dispersed in oil, O/W emulsion was prepared using powerful ultrasonication, and HEC was added to improve the dispersion of emulsion particles. The tribological properties of the nanoemulsion under different working conditions were tested by a tribometer, and the wear surface morphological characteristics and composition of the friction film of the steel ball and zirconium alloy were observed, and the following conclusions could be drawn.

1) The prepared ZnO nanoparticles have a particle size of 30-50nm, the main component is hexagonal wurtzite, and the particle size of the emulsion is 400-700nm. After adding HEC, the stability of the emulsion can be improved, and it can be maintained for 30 days without obvious coagulation.

2) After adding HEC to the nanoemulsion, the COF and wear amount decrease greatly, and with the increase of HEC, the wear amount continues to decrease, and the COF first decreases and then increases slowly. In the nanoemulsion with HEC concentration of 0.6 wt%, the COF is the smallest approximately 0.032, which is about 85.24% lower than that of the emulsion without HEC. In addition,

when 0.8 wt% HEC is added, the minimum values for the wear width and wear diameter are only 68.03 μm and 78.42 μm.

3) The nanoemulsion containing HEC can exhibit good tribological properties under multiple working conditions. With the increase of load from 5N to 30N, the COF first decreases and then increases, and the wear amount remains almost unchanged. And as the test temperature increases, the average COF keeps decreasing, and the wear is severe at high temperature.

4) Through EDS detection and analysis, as long as it is adhesive wear under O/W emulsion lubrication, a large amount of Zr adheres to the wear surface of steel balls. After adding HEC, under the joint action of hydrated molecular layer, oil phase layer and ZnO particles, a stable lubrication layer is formed on the friction surface, which greatly reduces wear.

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REFERENCES

Alenezi, M.R., "Hierarchical Zinc Oxide Nanorings with Superior Sensing Properties," *Materials Science and Engineering B-Advanced Functional Solid-State Materials*, Vol.236, pp.132-138 (2018).

Azushima, A., Inagaki, S., Ohta, H., "Plating Out Oil Film Thickness on Roll and Workpiece During Cold Rolling with O/W Emulsion," *Tribology Transactions*, Vol.54, pp.275-281 (2011).

Azushima, A., Inagaki, S., Ohta, H., "Starvation Behavior in Cold Rolling of Aluminum with Oil-in-Water Emulsion," *Tribology Transactions*, Vol.52, pp.744-749 (2009).

Bao, Y., Liu, K., Zheng, Q., et al., "A Review of Preparation and Tribological Applications of Pickering Emulsion," *Journal of Tribology-Transactions of the Asme*, Vol.144, No.1 (2022).

Bao, Y.Y., Sun, J.L., Kong, L.H., "Effects of Nano-SiO_2 as Water-based Lubricant Additive on Surface Qualities of Strips after Hot Rolling," *Tribology International*, Vol.114, pp.257-263 (2017).

Battez, A.H., Rico, J.E.F., Arias, A.N., et al., "The Tribological Behaviour of ZnO Nanoparticles as an Additive to PAO6," *Wear*, Vol.261, pp.256-263 (2006).

Chang, D.F., "Thermal Stresses in Work Rolls During the Rolling of Metal Strip," *Journal of Materials Processing Technology*, Vol.94, No.1, pp.45-51 (1999).

Chang, L., Jeng, Y.R., "A Model for Surface-Film Lubricated Cold Rolling Incorporating Interdependence of Mechanics, Heat Transfer, and Surface-Film Lubrication," *Journal of Tribology- Transactions of the Asme*, Vol.141, No.1 (2019).

Chang, L., Jeng, Y.R., "On the Feasibility of Surface-Film Lubricated Cold Rolling Without Liquid-Phase Cooling," *Journal of Tribology-Transactions of the Asme*, Vol.141, No.5 (2019).

Chaudhari, A., Pan, Y., Nitin, N., "Beverage Emulsions: Comparison Among Nanoparticle Stabilized Emulsion with Starch and Surfactant Stabilized Emulsions," *Food Research International*, Vol.69, pp.156-163 (2015).

Czamara, K., Majzner, K., Pacia, M.Z., et al., "Raman Spectroscopy of Lipids: A Review," *Journal of Raman Spectroscopy*, Vol.46, pp.4-20 (2015).

dos Santos, F.F., Silva, Sd.C., Abrao, A.M., et al., "Influence of the Carbon Content on the Surface Integrity of Deep Rolled Steels," *Journal of Tribology-Transactions of the Asme*, Vol.143, No.8 (2021).

Guillaument, R., Vincent, S., Caltagirone, J.P., et al. "Plate-out Modelling for Cold-rolling Systems Lubricated with Oil-in-Water Emulsions," *ARCHIVE Proceedings of the Institution of Mechanical Engineers Part J Journal of Engineering Tribology*, Vol.225, No.J9, pp.905-914 (2011).

Hajshirmohammadi, B., Forouzan, M.R., Heidari, A., "Effect of Interstand Tensions on Lubrication Regime in Cold Strip Rolling with O/W Emulsion," *Tribology Transactions*, Vol.62, pp.548-556 (2019).

Jiang, Q.P., Liu, Y.J., Kan, H., et al., "Microwave-assisted Synthesis of Hexagonal Structure ZnO Micro-tubes," *Materials Letters*, Vol. 81, pp.198-201 (2012).

Kong, L.H., Sun, J.L., Bao, Y.Y., "Preparation, Characterization and Tribological Mechanism of Nanofluids," *Rsc Advances*, Vol.7, pp.12599-12609 (2017).

Liu, Y.X., Song, H., Zhu, K.N., et al., "Microwave-assisted Synthesis of Zinc Oxide and its Performance in Photodegradation of CTMAB," *Research on Chemical Intermediates*, Vol.43, pp.971-982 (2017).

Lo, S.W., Yang, T.C., Cian, Y.A., et al., "A Model for Lubrication by Oil-in-Water Emulsions," *Journal of Tribology-Transactions of the Asme*, Vol.132, No.1 (2010).

Ma, Z.X., Yan, P.K., Ma, Z.J., et al. "Formation Mechanism of Nano-ZnO Prepared by Using One-step Method," *Journal of Synthetic Crystals*, Vol.37, No.2, pp.305-310 (2008).

Marino, F., Lopez, E.R., Arnosa, A., et al., "ZnO Nanoparticles Coated with Oleic Acid as Additives for a Polyalphaolefin Lubricant," *Journal of Molecular Liquids*, Vol. 348 (2022).

Meng, W., Sun, J., Wang, C., et al., "pH-dependent Lubrication Mechanism of Graphene Oxide Aqueous Lubricants on the Strip Surface During Cold Rolling," *Surface and Interface Analysis*, Vol.53, No.4, pp. 406-417 (2020).

Mu, L.W., Zhu, J.H., Fan, J.D., et al., "Self-Lubricating Polytetrafluoroethylene/Polyimide Blends Reinforced with Zinc Oxide Nanoparticles," *Journal of Nanomaterials*, Vol.2015 (2015).

Nedeljkovic, A., Rosch, P., Popp, J., et al., "Raman Spectroscopy as a Rapid Tool for Quantitative Analysis of Butter Adulterated with Margarine," *Food Analytical Methods*. Vol.9, pp.1315-1320 (2016).

Paul, S.K., Dutta, H., Sarkar, S., et al., "Nanosized Zinc Oxide: Super-Functionalities, Present Scenario of Application, Safety Issues, and Future Prospects in Food Processing and Allied Industries," *Food Reviews International*, Vol.35, pp.505-535(2019).

Reich, R., Panseri, N., Bohaychick, J., "The Effects of Lubricant Starvation in the Cold Rolling of Aluminum Metal When Using an Oil-in-Water Emulsion," *Lubrication Engineering*, Vol.57, pp.15-18 (2001).

Sakazaki, Y., Schmitt, V., Olsson, U., "Particles with Tunable Wettability for Solid-Stabilized Emulsions," *Journal of Dispersion Science and Technology*, Vol.40, pp. 219-230 (2019).

Sharma, A.K., Singh, R.K., Dixit, A.R., et al., "An Investigation on Tool Flank Wear Using Alumina/MoS_2 Hybrid Nanofluid in Turning Operation," *International Conference on Manufacturing Engineering and Materials (ICMEM)*, Novy Smokovec, SLOVAKIA, pp.213-219 (2018).

Sharma, R.K., Balani, K., "Mechanics of ZnO Micro-rod and ZnO Nanoparticle Reinforcement in Ultra-high Molecular Weight Polyethylene Biocomposite," *Journal of Physics D-Applied Physics*, Vol.47 (2014).

Sheng, D.Z., Zhang, H.C., "Tribological Properties of Titanium Alloy in Water-based Lubricating Process of Hydroxyethyl Cellulose," *Rare Metal Materials and Engineering*, Vol.8 (2019).

Taylan, O., Cebi, N., Yilmaz, M.T., et al., "Detection of Lard in Butter Using Raman Spectroscopy Combined with Chemometrics," *Food Chemistry*, Vol.332, (2020).

Vatansever, N., Polat, S., "Effect of Zinc Oxide Type on Ageing Properties of Styrene Butadiene Rubber Compounds," *Materials & Design*, Vol.31, No.3, pp.1533-1539 (2010).

Wang, C.M., Zhang, X.R., Jia, W.B., et al. "Preparation and Tribological Properties of Modified Field's Alloy Nanoparticles as Additives in Liquid Poly-alfa-olefin Solution," *Journal of Tribology-Transactions of the Asme*, Vol.141 (2019).

Wu, H., Zhao, J.W., Xia, W.Z., et al., "Analysis of TiO_2 Nano-Additive Water-Based Lubricants in Hot Rolling of Microalloyed Steel," *Journal of Manufacturing Processes*, Vol.27, pp.26-63 (2017).

Wu, T., Zhang, X.Y., Chen ,K., et al. "The Antibacterial and Wear-Resistant Nano-ZnO/PEEK Composites Were Constructed by a Simple Two-Step Method," *Journal of the Mechanical Behavior of Biomedical Materials*, Vol.126 (2022).

Xie, Q.S., "Preparation, Structure and Property of Zinc Oxide with Different Morphology," *Lanzhou University*, (2012).

Zhang, T.M., Ou, P.H., Ruan, J.M., et al., "Nb-Ti-Zr Alloys for Orthopedic Implants," *Journal of Biomaterials Applications*, Vol.35, pp.1284-1293 (2021).

APPENDIX

The mating surfaces under the test conditions in this paper have a certain roughness and are mainly in the state of mixed lubrication in the process of movement. Reynolds equation is usually used to solve the problem of mixed fluid hydrodynamic lubrication. The purpose of this section is to conduct a basic theoretical study of the load-bearing properties of HEC nanoemulsions, which are mainly based on the lubrication conditions of the fluid under the condition of constant temperature, that is, the changes in the viscosity and density of the lubricating fluid with temperature are not considered. The expression of the basic Reynolds equation is as follows:

$$\frac{\partial}{\partial x}\left(\rho h^3 \frac{\partial p}{\partial x}\right)+\frac{\partial}{\partial y}\left(\rho h^3 \frac{\partial p}{\partial y}\right)=6\eta\left[\frac{\partial}{\partial x}(U\rho h)+\frac{\partial}{\partial y}(V\rho h)+2\rho\frac{\partial h}{\partial t}\right] \quad \text{(SEQ-1)}$$

Where, η -- Dynamic viscosity of lubricant/Pa·s; ρ -- Density of lubricant/kg·m^{-3}; t -- Movement time/s; p -- Oil film surface pressure/Pa; U -- along x Direction speed/m·s^{-1}; V -- Movement speed in the y direction/m·s^{-1}.

The friction balls and friction discs tested in this paper have a certain degree of roughness, so there is an oil-depleted area or a cavitation area during the relative motion of the friction pair, which causes a partial gap between the friction pairs. Therefore, it is necessary to correct the Reynolds equation. Adding the oil film proportional variable θ, which describes the spent oil and cavitation area, into the equation, the modified equation can be expressed as:

$$\frac{\partial}{\partial x}\left(\frac{\rho h^3}{\eta}\frac{\partial p}{\partial x}\right)+\frac{\partial}{\partial y}\left(\frac{\rho h^3}{\eta}\frac{\partial p}{\partial y}\right)=12u_e\frac{\partial}{\partial x}(\rho\theta h) \quad \text{(SEQ-2)}$$

Where, Oil film proportional variable θ -- The ratio of inlet oil layer thickness h_{oil} to clearance h; u_e - sliding speed/m·s^{-1}. In order to better simulate the actual working conditions, cavitation may occur when the ball-on-disk contact pressure is large, so JFO cavitation algorithm is adopted, as shown in formula (SEQ-3):

$$\begin{cases} 0\le\theta<1 & p=0 \\ \theta\ge 1 & p>0 \end{cases} \quad \text{(SEQ-3)}$$

The gap h includes the roughness peak height, elastic deformation and initial gap height, and the formula is as follows:

$$h=h_0+\frac{x^2}{2R_x}+\frac{y^2}{2R_y}+\delta(x,y)+v(x,y) \quad \text{(SEQ-4)}$$

Where, h_0 -- initial gap height; δ(x, y) -- surface roughness peak height; v(x, y) -- elastic deformation perpendicular to the surface, and it can be expressed in terms of the pressure-dependent Boussinesq integral:

$$\mathrm{v}(x,y)=\frac{2}{\pi E^*}\iint\frac{\mathrm{p}(\xi_1,\xi_2)}{\sqrt{(x-\xi_1)^2+(y-\xi_2)^2}}d\xi_1 d\xi_2 \quad \text{(SEQ-5)}$$

To improve the computational efficiency of elastic deformation, the Fast Fourier Transform (FFT) method is adopted. The pressure distribution can be obtained from formula (SEQ-2), so the dimensional elastic deformation of each specific node can be calculated by the following formula:

$$\mathrm{V}(x_i,y_j)=IFFT\left(FFT\left(\mathrm{D}(x_i,y_j)FFT\left(\mathrm{P}(x_i,y_j)\right)\right)\right) \quad \text{(SEQ-6)}$$

Where, $V(x_i, y_j)$ -- nodal deformation at point (x_i, y_j); $P(x_i, y_j)$ -- hydrodynamic pressure or contact pressure when the film thickness is less than the threshold value; $D(x_i, y_j)$ -- Influence factor.

To obtain the true pressure distribution and film thickness distribution under a given load, the load balance equation can be expressed as:

$$\mathrm{w}=\iint \mathrm{p}(x,y)\mathrm{d}x\,dy \quad \text{(SEQ-7)}$$

The value of oil film thickness H in different friction areas is obtained through the oil film thickness equation, and the relationship between friction clearance and oil film thickness is judged point by point. If it is less than the oil film thickness, it indicates that there is micro convex contact here. Finally, the total contact area S_c of the whole friction area is obtained by adding the contact areas. Therefore, the calculation formula of contact ratio is as follows.

$$contactratio=\frac{S_c}{S}\times 100\% \quad \text{(SEQ-8)}$$

The convergence criterion of pressure and load is:

$$\sigma_1=\frac{\left|\sum_{N}^{i=1}\sum_{N}^{j=1}P^k(i,j)-\sum_{N}^{i=1}\sum_{N}^{j=1}P^{k-1}(i,j)\right|}{\sum_{N}^{i=1}\sum_{N}^{j=1}P^{k-1}(i,j)} \quad \text{(SEQ-9)}$$

$$\sigma_2=\frac{\left|\sum_{N}^{i=1}\sum_{N}^{j=1}\mathrm{P}^k(i,j)\mathrm{DXDY}-\sum_{N}^{i=1}\sum_{N}^{j=1}\mathrm{P}^{k-1}(i,j)\mathrm{DXDY}\right|}{2\pi/3} \quad \text{(SEQ-10)}$$

Where, N -- the number of grid nodes; σ_1 and σ_2 -- the convergence accuracy. When $\sigma_1 \le 1\times10^{-6}$, $\sigma_2 \le 1\times10^{-5}$, the iterative process ends.

羥乙基纖維素（HEC）改善鋯合金冷軋 ZnO 納米乳液的摩擦學性能研究

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摘 要

鋯合金在冷軋過程中易發生粘脫現象，嚴重影響工件的表面質量和模具的使用壽命。在本文中，使用豬油作為油相、Span80 作為分散劑來製備納米潤滑乳液，並用強超聲分散 ZnO 納米顆粒。加入 HEC 會提高了乳液顆粒的分散性和穩定性。用摩擦試驗機測試了納米乳液在不同工況下的摩擦學性能。與未添加 HEC 的乳液相比，磨損減少了 85.24%。SEM 顯示，HEC 納米乳液作為潤滑劑，摩擦試驗後表面光滑，大大減少了粘著磨損的發生。此外，HEC 納米乳液可以適應各種工作條件下的摩擦，具有優異的減摩抗磨能力，有望改善鋯合金冷軋引起的表面粘著磨損和表面加工質量。