Microstructures, mechanical properties, and grease-lubricated sliding wear behavior of Cu–15Ni–8Sn–0.8Nb alloy with high strength and toughness

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Received: 02 January 2020 / Revised: 23 April 2020 / Accepted: 06 May 2020

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Abstract: Alloys used as bearings in aircraft landing gear are required to reduce friction and wear as well as improve the load-carrying capability due to the increased aircraft weights. Cu–15Ni–8Sn–0.8Nb alloy is well known for possessing good mechanical and wear properties that satisfy such requirements. In this study, the microstructure, mechanical properties, and grease-lubricated sliding wear behavior of Cu–15Ni–8Sn–0.8Nb alloy with 0.8 wt% Nb are investigated. The nanoscale NbNi₃ and NbNi₂Sn compounds can strengthen the alloy through the Orowan strengthening mechanism. A Stribeck-like curve is plotted to illustrate the relationship among friction coefficient, normal load, and sliding velocity and to analyze the grease-lubricated mechanism. The wear rate increases with normal load and decreases with sliding velocity, except at 2.58 m/s. A wear mechanism map has been developed to exhibit the dominant wear mechanisms under various friction conditions. When the normal load is 700 N and the sliding velocity is 2.58 m/s, a chemical reaction between the lubricating grease and friction pairs occurs, resulting in the failure of lubricating grease and an increase in wear.

Keywords: Cu–15Ni–8Sn–0.8Nb alloy; microstructure; mechanical properties; grease-lubricated wear behavior

1 Introduction

Bronze–beryllium (Cu–Be) alloys are widely used as bearing materials owing to their high strength and hardness, excellent thermal conductivity, and good wear resistance [1, 2]. However, the fumes produced by Cu–Be alloys during processing and the debris derived from friction are harmful to human health. Furthermore, Be is very expensive compared to other elements, such as Ni, Sn, Ti, and Al [3]. To overcome these problems, alternative materials are being investigated. Age-hardenable Cu–Ni–Sn alloys are considered the most probable substitutes for Cu–Be alloys from the perspectives

of strength, wear resistance, production cost, and environmental protection [4]. Cu–Ni–Sn alloys have gained considerable attention since the Bell Telephone Laboratory developed them in the 1970s [5]. Currently, many types of Cu–Ni–Sn alloys have been included in American standards, such as Cu–4Ni–4Sn (UNS C72600), Cu–9Ni–6Sn (UNS C72700), Cu–10Ni–8Sn (UNS C72800), and Cu–15Ni–8Sn (UNS C72900). Among them, Cu–15Ni–8Sn alloy has the optimal mechanical properties [6, 7], which might be close to those of Cu–Be alloy [8]. However, the Cu–Ni–Sn alloys used in bearings for engines and aircraft landing gear must possess both excellent mechanical properties and good wear resistance.

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Many studies have been conducted on the wear behavior of Cu–15Ni–8Sn alloy in recent years. Singh et al. [9, 10] and Zhang et al. [11] studied the wear behavior of Cu–15Ni–8Sn alloy under a dry-sliding condition. Zhang et al. [12, 13] investigated the wear behavior of Cu–15Ni–8Sn alloy under an oil-lubricated condition. Singh et al. [10] found that oxides formed in the dry-sliding process were derived in the transfer layer, improving the wear resistance of Cu–15Ni–8Sn alloy. Zhang et al. [11, 12] studied the effect of hardness on the wear behavior of Cu–15Ni–8Sn alloy and found that the friction coefficient (CoF, μ) was not affected by the hardness. In addition, they observed that the increase in hardness could improve the wear resistance of the alloy. When the wear test was carried out under an oil-lubricated condition, the minimum wear rate was obtained at the maximum hardness, however, it slightly deviated when the wear test was conducted under a dry-sliding condition. Zhang et al. [13] reported that the wear rate and CoF increased with the applied load when Cu–15Ni–8Sn alloy slid against GCr15 steel in lubricating oil. However, for bearings employed in aircraft, aviation lubricating grease is generally used as a lubricant [14]. Grease is a colloid substance that primarily includes a base oil and a thickener [15, 16]. The main advantages of using grease instead of oil as a lubricant are less leakage, ease of use, and no requirement for supply accessories [17]. However, research on the wear behavior of Cu–15Ni–8Sn alloy under grease-lubricated conditions has rarely been reported.

Increasing the strength and toughness of Cu–15Ni–8Sn alloy has been the direction of efforts. The addition of micro-alloying elements to Cu–15Ni–8Sn alloy is an effective method of simultaneously improving its strength and toughness [18]. For example, the addition of Nb can simultaneously improve the strength and toughness of Cu–15Ni–8Sn alloy [19, 20]. Ouyang et al. [20] observed some intergranular precipitates through high-angle annular dark-field imaging analysis in Cu–15Ni–8Sn alloy enriched with Ni, Sn, and Nb. They thought that these precipitates would help improve the strength and toughness. Moreover, Gao et al. [21] found that Nb addition could refine the grains and form NbNi₃

compounds that enhance the strength and toughness of Cu–9Ni–6Sn alloy. However, Gallino et al. [22] held a different view on the types of compounds enriched with Nb, Ni, and Sn, believing that Nb would react with Ni and Sn to form NbNi₃ and NbNi₂Sn compounds.

In this study, the microstructures, mechanical properties, and grease-lubricated sliding wear behavior of Cu–15Ni–8Sn alloy with 0.8 wt% Nb fabricated by powder metallurgy and hot extrusion are investigated. Because 300M steel is commonly used in aircraft landing gear [23], it is selected as a counterpart. Aviation wide-temperature grease 7031A, which complies with the MIL-G-81322 technical specification, is a special lubricating grease for aircraft landing gear [24]; therefore, it is chosen as the lubricant. This work mainly focuses on the following aspects: 1) the form of Nb in the Cu–15Ni–8Sn alloy, 2) the effect of Nb on the microstructures and mechanical properties of Cu–15Ni–8Sn alloy, and 3) the grease-lubricated sliding wear behavior of the peak-aged Cu–15Ni–8Sn–0.8Nb alloy against 300M steel.

2 Experimental

A Cu–15Ni–8Sn–0.8Nb alloy rod with a chemical composition of 15.8 wt% Ni, 7.94 wt% Sn, 0.78 wt% Nb, and Cu in the balance was fabricated by cold isostatic pressing, vacuum sintering, and hot extrusion. Cu–15Ni–8Sn–0.8Nb alloy powders were prepared by gas (N₂) atomization method, with a particle size of less than 100 μ m. These alloy powders were processed by cold isostatic pressing under a pressure of 200 MPa for 20 min. The green ingot was sintered at 850 °C for 4 h in a vacuum of approximately 10^{−3} Pa. The sintered-rod was homogenized at 830 °C for 6 h and then extruded at 830 °C with a hot extrusion ratio of 9.5:1. The hot extrusion velocity was 30 mm/s. The as-extruded alloy was solid solution heat-treated at 850 °C for 1 h in a H₂ atmosphere and rapidly quenched in water. The solid solution-treated alloy was aged at 400 °C for 2.5 min to 6 h using a NaNO₃ salt bath furnace and then quenched rapidly in water. For comparison, a Cu–15Ni–8Sn alloy with a chemical composition of 15.3 wt% Ni, 8.04 wt% Sn, and Cu in the balance was fabricated using the

same preparation procedure as that the Cu–15Ni–8Sn–0.8Nb alloy. According to the ASTM E8/E8M–11 standard, in which the ratio of gauge length to gauge diameter was 5:1 for rod specimens, the tensile tests were performed at 25 °C using an Instron 8802 testing machine at a rate of 2 mm/min and the reported results were derived from the average of five separate samples. Hardness tests were conducted on a Micromet 5104 tester (Buehler, USA), with a load of 100 gf (0.98 N) and a holding time of 10 s. The hardness reported herein was derived from the average of 10 random measurements. The hardness of 300M steel was 581 HV.

The grease-lubricated sliding wear behavior of the peak-aged Cu–15Ni–8Sn–0.8Nb alloy against 300M steel (Haichuan Non-ferrous Metal Materials Co., Ltd., China) was evaluated using a block-on-ring tester (MRH-1, Yihua Tribology Testing Technology Co., Ltd., China) at 25 °C within a wide normal load and sliding speed range (normal load: 50–700 N; sliding velocity: 0.13–2.58 m/s). Each wear test lasted for 120 min. A representative schematic of the friction pairs is shown in Fig. 1(a). Wear specimens (Cu–15Ni–8Sn–0.8Nb alloy) were cut into blocks of 12.30 mm × 12.30 mm × 19.05 mm using wire electrical discharge machining. The wear specimens were ground and polished until all scratches were removed. Before testing, rings with outer diameters of 49.22 mm and the wear specimens were immersed into an acetone solution and cleaned using an ultrasonic bath for 15 min to remove the residual abrasive paste. Before the wear test, 1.0 g of lubricating grease (7031A, Sinopec Co., Ltd., China) was coated uniformly on the block–

ring contact surface. The CoF was continually recorded during the wear test. The average CoF was calculated for each wear test within 120 min. The width of the wear track on the block was measured using an optical microscope (Leica DM4500P, Germany). A schematic of the cross-sections of the worn block is displayed in Fig. 1(b). The volumetric wear loss was calculated by the formula given in the Chinese Standard GB/T 12444-2006:

$$V = \frac{D^2}{8} c \left[2 \sin^{-1} \frac{b}{D} - \sin \left(2 \sin^{-1} \frac{b}{D} \right) \right] \quad (1)$$

where V is the volumetric wear loss (mm³), D is the outer diameter of the ring (mm), b is the width of the wear track on the block (mm), and c is the width of the block (mm). The wear rate was calculated as $W = V/L$, where W is the wear rate (mm³/mm) and L is the sliding distance (mm) [25]. The surface temperature of the specimens at the end of the wear test was observed by a handheld infrared thermometer. All wear tests under the same conditions were carried out three times to ensure repeatability, and the average of the tests was reported.

The suitable service temperature of aviation grease 7031A is from –54 to +170 °C. Its viscosities at different temperatures (20 °C: 119.2 Pa·s; 35 °C: 10.97 Pa·s; 50 °C: 4.231 Pa·s; 100 °C: 3.44 Pa·s) were detected using a rotational rheometer (ARES, TA, USA). To analyze the thickener and additive of aviation grease 7031A, a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) fitted with an energy dispersive X-ray spectrometer (EDS) was used. The lubricating grease was isolated by centrifugation

Fig. 1 Schematic of (a) friction pairs and (b) volumetric wear loss calculated by the average width of the wear track.

and then washed using a tetrachloroethylene solution to minimize the base oil. The centrifuged lubricating grease was dispersed with an acetone solution and deposited onto an ultrathin carbon wafer with a diameter of 3 mm for TEM characterization. TEM images and EDS analysis of the centrifuged lubricating grease are depicted in Fig. 2. We can observe short fibers and mesh structures in the centrifuged lubricating grease. The short fiber should be the saponifier as thickening the base oil, and the mesh structure could be the solid lubricating additive as enhancing the tribological properties [26]. Mg, Al, and Si were detected besides C, N, O, and F according to the corresponding EDS analysis.

Surface morphologies of the Cu–15Ni–8Sn–0.8Nb alloy were captured by a scanning electron microscope (SEM, FEI, USA). Before testing, the alloy surface was ground and polished to mirror finish. The polished alloy was etched by a mixture consisting of 5 g FeCl_3 , 20 mL concentrated HCl solution, and 100 mL alcohol solution. The sizes of 400 grains were measured using Nano Measurer 1.2 software to calculate the average value [20]. The distribution of the alloying elements was analyzed by electron probe microanalysis (EPMA, JXA-8530F, Japan). The microstructure of Cu–15Ni–8Sn–0.8Nb alloy was detected by TEM (FEI Titan G2-300, USA). First, a TEM sample was produced by mechanically polishing coupons to a thickness of 60 μm . Next, a thin foil with a diameter of 3 mm was punched

from the coupons. Finally, the thin foil was thinned using twinjet electro-polishing in a mixture consisting of 30% concentrated HNO_3 and 70% methyl alcohol to obtain a wedge-shaped depression and hole. The temperature of the electro-polishing solution was -30 ± 4 °C and the applied voltage was 7–10 V. The phase composition of the Cu–15Ni–8Sn–0.8Nb alloy was determined by X-ray diffraction (XRD, TTRIII, Rigaku, Japan) using a Cu $K\alpha$ radiation within the range of $2\theta = 20^\circ$ – 100° . The scanning rate was 4 ($^\circ$)/min. The worn-surfaces, cross-sections, and wear debris were studied by SEM equipped with an EDS. The ultrafine wear debris was analyzed by TEM (JEM-2100F, JEOL, Japan). The chemical states of the elements on worn tracks were examined by X-ray photoelectron spectroscopy (XPS-Escalab210).

3 Results and discussion

3.1 Microstructure

Figures 3(a) and 3(b) illustrate the microstructure of Cu–15Ni–8Sn and Cu–15Ni–8Sn–0.8Nb alloys after solid solution treatment, respectively. The average grain size of Cu–15Ni–8Sn alloy decreases from 32 to 7 μm after adding 0.8 wt% Nb, indicating that the addition of Nb refines the grains. Figures 3(c)–3(g) present the SEM image and corresponding elemental distribution of the Cu–15Ni–8Sn–0.8Nb

Fig. 2 (a, b) TEM images and (c) EDS analysis of the thickener of 7031A grease.

alloy after solid solution treatment. Nb is mainly distributed at the grain boundaries and may react with Ni and Sn to form corresponding compounds.

TEM analysis and XRD patterns of Cu–15Ni–8Sn–0.8Nb alloy after solid solution treatment are required to determine the types of compounds containing Nb, and the results are exhibited in Fig. 4. It can be observed that a large number of nanoparticles are distributed in the grains. These nanoparticles are NbNi₂Sn (cubic crystallographic structure with space group *Fm-3m*) and NbNi₃ (orthorhombic crystallographic structure with space group *Pmmn*) through high-resolution TEM analysis. In addition, NbNi₂Sn and NbNi₃ were also detected by XRD analysis, as depicted in Fig. 4(e). According to the semi-empirical Miedema's model [27] and Toop's

model [28], the formation enthalpies of NbNi₃ and NbNi₂Sn compounds were calculated, which are –25.07 and –28.02 kJ/mol, respectively. Compared to the NbNi₃ phase, the NbNi₂Sn phase is easier to form. These phases containing Nb will have a crucial influence on the properties of the alloy, especially strength and toughness.

3.2 Mechanical properties

Figure 5 illustrates the stress–strain curves and fracture morphologies of the Cu–15Ni–8Sn and Cu–15Ni–8Sn–0.8Nb alloys after solid solution treatment. The fracture images of the studied alloys after tensile tests were taken to analyze the fracture mechanisms. The Cu–15Ni–8Sn alloy exhibits an ultimate tensile strength of 457 MPa, yield strength of 264 MPa,

Fig. 3 Optical, SEM, and corresponding elemental mapping images of the alloys after solid solution treatment: optical images of (a) Cu–15Ni–8Sn and (b) Cu–15Ni–8Sn–0.8Nb alloys, (c) SEM and (d–g) corresponding elemental mapping images of Cu–15Ni–8Sn–0.8Nb alloy.

Fig. 4 TEM images and XRD patterns of the Cu–15Ni–8Sn–0.8Nb alloy after solid solution treatment: (a, b) bright-field TEM, (c, d) high-resolution TEM, and (e) XRD. *d* is the diameter of grain.

and an elongation of 48.3%. After adding 0.8 wt% Nb to the Cu–15Ni–8Sn alloy, the ultimate tensile strength, yield strength, and elongation increased to 590 MPa, 368 MPa, and 56.8%, respectively. This indicates that adding 0.8 wt% Nb to Cu–15Ni–8Sn alloy improves its mechanical strength and toughness simultaneously. A large number of dimples can be observed on the fractures of both these alloys, indicating that their fracture mechanism is a typical ductile fracture. The strength mechanism of Cu–15Ni–8Sn alloy is by solid solution strengthening. However, the strength mechanisms of Cu–15Ni–8Sn–0.8Nb alloy have grain boundary strengthening and precipitation strengthening, in addition to solid solution strengthening. According to the Hall–Petch relationship [29], $\Delta\sigma_{\text{HP}} = K^{\text{HP}}d^{-1/2}$, where $\Delta\sigma_{\text{HP}}$ is the increase in yield strength because of grain boundary strengthening, and K^{HP} is a constant for pure Cu (0.15 MPa·m^{1/2} [30]). The increase in yield strength of Cu–15Ni–8Sn–0.8Nb alloy is 53 MPa resulting from grain boundary strengthening. In general, the deformation inhomogeneity and stress concentration are both small when the grains are fine, increasing the difficulty of cracking the alloy. Moreover, a large number of twists at the grain boundaries in the fine grains will be unfavorable to the propagation of cracks, making the grains bear a large plastic deformation before fracture [31, 32]. Therefore, the addition of Nb realizes simultaneous improvements in the strength and toughness of Cu–15Ni–8Sn alloy through refining the grains. Precipitation

strengthening will play an important role in enhancing the strength of the alloy. The average radius and volume fraction of the particles containing Nb element (NbNi₂Sn and NbNi₃) are 60.2 nm and 1.45%, respectively. Based on the Orowan–Ashby equation [33], the shear strength increase, τ_{ppt} , is 20.94 MPa in this study. The increase in yield strength caused by the precipitation mechanism, $\Delta\sigma$, can be expressed as $\Delta\sigma = M \cdot \tau_{\text{ppt}}$ [30], where M is the Taylor factor of 3.1 [34]. Therefore, the increase in yield strength of Cu–15Ni–8Sn alloy with 0.8 wt% Nb is 64.9 MPa due to precipitation strengthening. The total increase in yield strength of Cu–15Ni–8Sn–0.8Nb alloy caused by grain boundary strengthening and precipitation strengthening is 117.9 MPa through calculation. According to the experimental data, the yield strength of the solid solution-treated Cu–15Ni–8Sn alloy has increased by 104 MPa after adding 0.8 wt% Nb, which is close to the calculated value. Therefore, the increase in yield strength of the Cu–15Ni–8Sn alloy by adding Nb is mainly caused by grain boundary and precipitation strengthening.

With the development of large aircraft, the materials used as bearings in aircraft landing gear must have excellent carrying capacity. The ideal bearing material should have enough strength and toughness to withstand deformation from static and suddenly imposed normal loads in service [35]. Therefore, the next work mainly focuses on the grease-lubricated sliding wear behavior of Cu–15Ni–8Sn–0.8Nb alloy. According to the theory of adhesive wear [36], the

Fig. 5 Stress–strain curves and fractures of the studied alloys after solid solution treatment: (a) stress–strain curves, (b) fracture of Cu–15Ni–8Sn–0.8Nb alloy, and (c) fracture of Cu–15Ni–8Sn alloy.

wear resistance of materials is mainly related to its hardness. In general, wear resistance increases with hardness. The hardness variation versus the aging time of Cu–15Ni–8Sn–0.8Nb alloy aged at 400 °C is presented in Fig. 6. It can be found that the peak aging hardness occurs when the alloy is aged at 120 min, with a peak-age hardness of 347 HV. This peak-aged Cu–15Ni–8Sn–0.8Nb alloy was selected as the final studied object.

Fig. 6 Hardness variation versus aging time of Cu–15Ni–8Sn–0.8Nb alloy.

Fig. 7 (a, b) CoF curves, (c) average CoFs, and (d) wear rates of Cu–15Ni–8Sn–0.8Nb alloy sliding against 300M steel under a grease-lubricated condition at different normal loads and sliding velocities.

3.3 Grease-lubricated sliding wear behavior

3.3.1 Friction and wear

Figures 7(a) and 7(b) display the representative curves of the evolution of the CoF of Cu–15Ni–8Sn–0.8Nb alloy at sliding velocities of 0.13 and 2.58 m/s, respectively, and at different normal loads under a grease-lubricated condition. It can be observed that the CoFs are fluctuating, especially at low sliding velocities. This can be explained as follows: First, the lubricating grease cannot be spread uniformly on the contact surfaces when the sliding velocity is low, resulting in the formation of an uneven lubricating film during friction. Second, wear debris generated at low sliding velocities may remain in the lubricating grease, which increases the inhomogeneity of the formed lubricating film, causing fluctuations in the CoFs. Third, a protective oxide film can be more difficult to form on the worn-surface of the Cu–Ni–Sn alloy at low sliding velocities than that at high sliding velocities [37]. The above analysis illustrates that direct contact

between friction pairs may be dominant at low sliding velocities, which leads to the occurrence of fluctuations during the friction process. The frictional heat generated in the friction process can be expressed as $Q = \mu P v t$, where Q is the frictional heat (J), P is the normal load (N), v is the sliding velocity (m/s), and t refers to the sliding time (s). Therefore, frictional heat increases with sliding velocity and normal loads. The lubricating grease may fail due to the high frictional heat during sliding, resulting in the occurrence of dry sliding and seizure. The friction of the alloy under a normal load of 700 N and a sliding velocity of 2.58 m/s resulted in seizure after approximately 14 min due to the high frictional heat, forcing the test to stop (Fig. 7(b)). Therefore, the average CoF of the alloy, in this case, was not calculated.

Figure 7(c) indicates the average CoFs of Cu–15Ni–8Sn–0.8Nb alloy under different friction conditions. The CoF decreases with the sliding velocity, which may be related to the lubrication regime of the lubricating grease. In contrast, the CoF increases initially and then decreases with the normal load. At the same sliding velocity, the minimum CoF is achieved when the normal load is 50 N, and the maximum value is obtained when the normal load is 200 N. In general, the relationship between CoF and normal load can be expressed as $\mu = SA/P$, where A is the apparent contact area and S is the shearing stress [38] (which is a constant for a given material). Therefore, the CoF decreases with the increase in normal load based on the above relation. Moreover, when the normal load increases, a tribochemical reaction may occur, and the formed reaction film can provide an anti-wear and friction-reducing function further [39]. However, the lubricating film formed during the friction process is difficult to destroy under a relatively low normal load (such as 50 N), and the friction is mainly three-body wear. Therefore, the CoFs of the alloy at a normal load of 50 N is the lowest compared with those at other normal loads in this study.

The variation of the wear rate of Cu–15Ni–8Sn–0.8Nb alloy at various sliding velocities and normal loads under a grease-lubricated condition is displayed in Fig. 7(d). It can be observed that the wear rate

increases with the normal load and decreases with the sliding velocity. This phenomenon is attributed to the following reasons. (i) The real contact area increases due to the increase in normal load, causing an increase in wear [39]. (ii) The shear stress borne by the lubricating film increases with normal load. Furthermore, the lubricating film will be broken when the shear stress reaches or exceeds its bearing capacity, resulting in the occurrence of two-body wear. (iii) As the normal load increases, more wear debris is generated during the friction process. The generated wear debris cannot be removed timely by the lubricating grease and maybe aggregated between friction pairs, leading to deterioration of the lubricating film. (iv) The increase in sliding velocity can accelerate the formation of a lubricating film and reduce the wear [36]. However, the worn-surface temperature of the specimen after the wear test (detected by a handheld infrared thermometer) increases dramatically under a normal load of 700 N and a sliding velocity of 2.58 m/s, as shown in Fig. 8. Therefore, the lubricating grease fails quickly and direct contact is established in this case, leading to a sharp increase in wear rate.

The wear rate of the peak-aged Cu–15Ni–8Sn–0.8Nb alloy against 300M steel under a grease-lubricated condition varies from 1.15×10^{-7} to 5.12×10^{-6} mm³/mm. According to Ref. [36], when the wear rate is less than 5×10^{-6} mm³/mm, the wear regime belongs to mild wear. In general, mild wear is considered as an

Fig. 8 Worn-surface temperature of Cu–15Ni–8Sn–0.8Nb alloy under different normal loads and sliding velocities after wear tests.

acceptable form of wear regime in many applications, such as bearings in aircraft shaft sleeves. In this study, based on the obtained wear rates, the wear can be divided into three wear regimes: ultra-mild wear $< 1 \times 10^{-6} \text{ mm}^3/\text{mm}$, $1 \times 10^{-6} \text{ mm}^3/\text{mm} < \text{mild wear} < 5 \times 10^{-6} \text{ mm}^3/\text{mm}$, and severe wear $> 5 \times 10^{-6} \text{ mm}^3/\text{mm}$. The transition of wear regimes is determined by the two green dividing dashed lines marked at values of 1×10^{-6} and $5 \times 10^{-6} \text{ mm}^3/\text{mm}$, as shown in Fig. 7(d).

3.3.2 Grease-lubricated mechanism

To understand the grease-lubricated mechanism of the peak-aged Cu–15Ni–8Sn–0.8Nb alloy/300M steel tribo-pair, the data in Fig. 7(c) was arranged. The variation of CoF versus the Sommerfeld number [39] $S_0 = \eta v / P$ (η is the viscosity of lubricating grease) is plotted in a Stribeck-like curve, as depicted in Fig. 9. By non-linear fitting (origin 9.0) of the experimental data, the relationship between μ and S_0 can be expressed as follows:

$$\mu = 3.01 \times 10^{-5} \left(\frac{\eta v}{P} \right)^2 - 2.88 \times 10^{-3} \left(\frac{\eta v}{P} \right) + 7.64 \times 10^{-2} \quad (2)$$

The CoF decreases gradually to 0.0077 and then increases slowly with the Sommerfeld number. The lubrication mechanism changes from boundary lubrication (BL) to mixed lubrication (ML) and then to hydrodynamic lubrication (HL).

Fig. 9 Stribeck-like curve of Cu–15Ni–8Sn–0.8Nb alloy/300M steel tribo-pair under grease-lubricated conditions.

The boundary line between ML and HL is $S_0 = 47.78 \times 10^{-3}$. In addition, according to the theory of lubrication [36], the range of CoF is between 0.1 and 0.15 under the BL condition. The corresponding partitions of the lubrication mechanisms are exhibited in Fig. 9.

3.3.3 Characterization of worn-surface and cross-section

For a deeper understanding of the effect of normal load and sliding velocity on the wear mechanism, worn-surfaces of the peak-aged Cu–15Ni–8Sn–0.8Nb alloy under different friction conditions were analyzed using SEM with EDS, as displayed in Fig. 10. It can be observed that the morphologies of the obtained worn-surfaces under different friction conditions are different. Some black regions with high oxygen content are found when the sliding velocity is 2.58 m/s, indicating that the worn-surfaces are oxidized during the friction process. In addition, some micro-ploughs are found when the normal load is 50 N, while many deep grooves and cracks (even peelings) are observed when the normal load is 700 N. In general, the black region with high oxygen content, micro-ploughs or grooves, and cracks or peelings can be regarded as evidences of oxidation wear, abrasive wear, and delamination, respectively [40]. Therefore, there are different wear mechanisms for the investigated alloy under different sliding conditions. This can be illustrated from the following aspects. First, under low sliding velocity conditions, such as a sliding velocity of 0.13 m/s, the lubricating grease cannot be spread uniformly onto the worn-surface to form a continuous lubricating film, leading to the occurrence of solid-to-solid contact. Moreover, the lubricating film can be easily broken under high normal load conditions, resulting in serious wear. Furthermore, owing to the non-flowability of the lubricating grease, the generated wear fragments during the friction process may remain between contact surfaces and act as new abrasive particles. Therefore, deep grooves can be observed under a normal load of 700 N and a sliding velocity of 0.13 m/s, as illustrated in Fig. 10(c). Second, under high sliding velocity conditions, such as at 2.58 m/s, a continuous lubricating film may be formed easily, preventing the occurrence of two-body wear. Moreover, the

worn-surface temperature of the investigated alloy after wear test increases dramatically with the sliding velocity, as presented in Fig. 8. For example, the worn-surface temperature is 35 °C under a normal load of 700 N and a sliding velocity of 0.13 m/s, while it can reach 150 °C under a normal load of 700 N and a sliding velocity of 2.58 m/s. A tribo-chemical reaction may occur with the increase in surface temperature during friction to form a corresponding chemical reaction film, which can further provide an anti-wear function [26]. Under a normal load of 50 N and a sliding velocity of 2.58

m/s, the lubricating film and chemical reaction film are both difficult to destroy due to a small contact pressure, resulting in slight wear. Generally, the flash temperature during friction is higher than the worn-surface temperature detected after the wear test. Therefore, the flash temperature of the investigated alloy can exceed 150 °C during friction under a normal load of 700 N and a sliding velocity of 2.58 m/s, failing the lubricating grease and occurrence of two-body wear. The wear is aggravated significantly and more cracks appear, as exhibited in Figs. 10(d) and 10(e).

Fig. 10 SEM images of worn-surfaces of Cu-15Ni-8Sn-0.8Nb alloy under different sliding conditions: (a) 50 N, 0.13 m/s; (b) 50 N, 2.58 m/s; (c) 700 N, 0.13 m/s; and (d, e) 700 N, 2.58 m/s. Insets show EDS analysis of the corresponding worn-surfaces. ZAF correction includes the correction factors of atomic number (Z), absorption (A), and fluorescence (F).

To investigate the interaction between the lubricating grease and friction pairs in more detail, XPS analysis was performed on the worn tracks of the peak-aged Cu–15Ni–8Sn–0.8Nb alloy. The full XPS spectra curves prove the presence of copper, nickel, tin, silicon, nitrogen, and oxygen, as shown in Fig. 11. The Si 2p peak at 103.0 eV and Si 2s peak at 154.3 eV both illustrated the existence of silicon dioxide. SiO₂ nanoparticles are commonly used as additives for anti-wear and extreme-pressure grease [41].

The spectra of Cu 2p, Ni 2p, and Sn 3d of the worn tracks on the specimens were analyzed by XPS peak-fitting method, as displayed in Fig. 12. Under a normal load of 50 N, it can be observed from Fig. 12(a1) that the copper Cu 2p_{3/2} signal has

Fig. 11 Full XPS spectra of worn tracks on Cu–15Ni–8Sn–0.8Nb alloy under different sliding conditions.

Fig. 12 Cu 2p, Ni 2p, and Sn 3d spectra of the worn tracks on Cu–15Ni–8Sn–0.8Nb alloy under different sliding conditions using the XPS peak-fitting method.

three peaks at 933.4, 932.1, and 932.8 eV, which are attributed to CuO, Cu₂O, and Cu, respectively. The nickel Ni 2p_{3/2} signal has two peaks at 861.6 and 856.2 eV attributed to NiO and Ni₂O₃, respectively. The peaks of tin Sn 3d_{5/2} are detected at 487.5 and 486.4 eV due to the formation of SnO₂. The peak at 486.9 eV illustrates the existence of SnO. However, it can be seen from Figs. 12(a2), 12(b2), and 12(c2) that NiCO₃ and [Sn₂(C₆H₅)₆] are also detected by the peak-fitting method on the worn tracks, besides Cu, CuO₂, NiO, Ni₂O₃, SnO, and SnO₂. The formation of NiCO₃ and [Sn₂(C₆H₅)₆] confirms the occurrence of a tribo-chemical reaction between the lubricating grease and friction pairs, causing a rapid failure of the lubricating grease and accelerated wear.

SEM images of cross-sections of the peak-aged Cu–15Ni–8Sn–0.8Nb alloy under different sliding conditions are depicted in Fig. 13. It can be observed that the cross-sections under a normal load of 50 N are smooth regardless of the sliding velocity, indicating that the alloy is only subjected to ultra-mild wear. However, when the normal load is 700 N, a large number of cracks appear on the cross-sections, illustrating the occurrence of delamination.

3.3.4 Characterization of wear debris

Typical micrographs of the wear debris obtained at a sliding velocity of 2.58 m/s under different normal loads are presented in Fig. 14. Under a normal load of 50 N, the wear debris is coated by lubricating grease. The corresponding diffraction patterns consist of halos, confirming the presence of amorphous phases. In general, the amorphous phase can improve the wear resistance of a material [37]. Thus, the wear rate of the peak-aged Cu–15Ni–8Sn–0.8Nb alloy obtained under a normal load of 50 N and a sliding velocity of 2.58 m/s is the minimum. Under a normal load of 700 N, it can be observed that the wear debris is not coated by lubricating grease, while C, Mg, Si, Al, and Ca elements, which come from the lubricating grease, can be detected by EDS. To further ascertain the existence of a chemical reaction between the lubricating grease and friction pairs, in this case, the wear debris was investigated by TEM and selected area electron diffraction, as exhibited in Fig. 14(d). SiO₂, CuO, Fe₂O₃, and NiCO₃ phases can be observed in Fig. 14(d). It should be emphasized here that none of the phases observed

Fig. 13 SEM images of the cross-sections of Cu–15Ni–8Sn–0.8Nb alloy under different sliding conditions: (a) 50 N, 0.13 m/s; (b) 50 N, 2.58 m/s; (c) 700 N, 0.13 m/s; and (d) 700 N, 2.58 m/s.

Fig. 14 (a, b) SEM and (c, d) TEM images of wear debris under different normal loads at a sliding speed of 2.58 m/s, with the insets showing EDS and selected area electron diffraction: (a, c) 50 N and (b, d) 700 N.

in this study are pure phases except for the SiO_2 phase. For instance, the CuO phase is not purely CuO but $(\text{Cu}, \text{Ni}, \text{Sn})\text{O}$ [37]. Certainly, the NiCO_3 phase is also not purely NiCO_3 but $(\text{Ni}, \text{Mg})\text{CO}_3$. The TEM analysis results reconfirmed that a tribochemical reaction occurred during friction when the normal load was 700 N and the sliding speed was 2.58 m/s. The results are following the above XPS analysis.

3.3.5 Wear mechanism map

Based on the above analysis, a wear mechanism map for the peak-aged Cu–15Ni–8Sn–0.8Nb alloy against 300M steel under a grease-lubricated condition was established, as displayed in Fig. 15. The transition of ultra-mild wear and mild wear is determined by the green solid dividing line, whose wear rate is $1 \times 10^{-6} \text{ mm}^3/\text{mm}$. According to thermodynamics, ΔG can be calculated by $\Delta G_T = \Delta H_T + T\Delta S_T$, where ΔG_T is Gibbs free energy change of the reaction at T (K), while ΔH_T and ΔS_T are the enthalpy and entropy differences of the reaction product to the reactants at T (K), respectively [42]. The ΔG values of oxides formed mainly at different temperatures were obtained using HSC Chemistry 6.0, as listed in Table 1. It can be observed that the ΔG values of all oxides in Table 1 are all negative, indicating that Cu–Ni–Sn

alloy can easily oxidize during friction. Evidently, the occurrence of oxidation reactions is affected by the diffusion rate of atoms in addition to thermodynamics. In general, atoms easily diffuse at high temperatures.

Fig. 15 Wear mechanism map for Cu–15Ni–8Sn–0.8Nb alloy against 300M steel under a grease-lubricated condition.

Table 1 ΔG of oxides formed at different temperatures.

Temperature (°C)	Cu ₂ O	CuO	NiO	SnO	SnO ₂
50	−291.87	−251.51	−418.46	−499.01	−514.87
100	−284.24	−242.28	−409.06	−489.44	−504.67
150	−276.6	−233.12	−399.74	−479.95	−494.49
200	−269.03	−224.05	−390.53	−470.51	−484.37

From Fig. 8, the temperature of the worn-surface of the alloy under a normal load of 50 N and a sliding velocity of 2.58 m/s is 50 °C, and oxidative wear has occurred (Fig. 10(b)). Therefore, it can be considered that the alloy has undergone oxidative wear when the surface temperature reaches or exceeds 50 °C. The wear mechanism map is divided into four regions by the two dividing lines, and the corresponding wear mechanisms are presented in Fig. 15.

4 Conclusions

1) Nb addition refines the grains and improves the strength and toughness of Cu–15Ni–8Sn alloy simultaneously. This can be attributed to the formation of NbNi₂Sn and NbNi₃ phases.

2) The difference in strength between the Cu–15Ni–8Sn alloy with and without Nb addition is mainly caused by grain boundary and precipitation strengthening, while the difference in toughness is mainly due to grain refinement.

3) The CoF decreases with sliding velocity, while it increases initially and then decreases with the normal load. The wear rate increases with the normal load and decreases with the sliding velocity (except at 2.58 m/s).

4) A Stribeck-like curve is established by a function of the CoF to the Sommerfeld number. The boundary between ML and fluid lubrication is ascertained using the parabolic-fitting method. The parabolic equation is obtained from the experimental results, explaining the relationship between CoF, sliding velocity, and normal load.

5) Under relatively low normal load and sliding velocity conditions, the dominant wear mechanism is abrasive wear. However, the Cu–15Ni–8Sn–0.8Nb alloy would be subjected to oxidative wear with the increase in sliding velocity, and it would bear delamination wear with the increase in normal load.

6) Under a normal load of 700 N and a sliding velocity of 2.58 m/s, a chemical reaction between lubricating grease and friction pairs occurs, leading to the failure of lubricating grease and an increase in wear.

Acknowledgements

The authors would like to express their gratitude for the financial support provided by the National Key Research and Development Program of China (Grant Nos. 2017YFB0306105 and 2018YFE0306100).

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