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Wear Resistance Mechanism of Sub-Nano Cu_3P Phase Enhanced the Cu-Pb-Sn Alloy

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Abstract: High Cu-Pb-Sn, as the material for bimetallic cylinder block, is widely used in the selection of wear-resistant parts due to its excellent wear reduction, thermal conductivity, fatigue resistance, and strong bearing capacity, such as bearings and bearing bushes, aerospace pump rotor, turbine and guide plate, etc. However, because its wear resistance is not enough to meet the harsh conditions of high temperature, high speed, and heavy load, the research on high wear resistance Cu-Pb-Sn materials has important theoretical significance and application value for the application of bimetallic materials. $ZCuPb_{20}Sn_5$ alloy was taken as the research object to analyze the influence mechanism of its different microstructure and mechanical properties on the friction and wear properties of alloy materials. Friction experiments under two conditions of oil lubrication and dry friction were carried out on the MMW-1A pin-on-disc friction and wear testing machine. The wear resistance and wear mechanism of $ZCuPb_{20}Sn_5$alloy under the action of Cu_3P were discussed, and a high wear-resistant Cu-Pb-Sn alloy for bimetal cylinder block was prepared. The results show that with the increase of P content, both the friction coefficient and wear rate decrease, and the wear reduction of $ZCuPb_{20}Sn_5$ alloy increases. Under oil lubrication conditions, the friction coefficient decreases by 21.4% and the wear rate decreases by 85.5% compared with that without adding P. The friction-reducing and wear-resistant properties of $ZCuPb_{20}Sn_5$ alloy materials are increased. In dry friction and oil lubrication, the mass wear amount of $ZCuPb_{20}Sn_5$ alloy material decreases with the increase of P element addition, and the change rule of alloy wear amount is consistent under the two methods. In the process of friction and wear, adhesive wear occurs, and the wear amount of the alloy material increases. With the increase of P content, the lead particles are refined and evenly distributed, which promotes the formation of a uniform self-lubricating lead film during the friction process and reduces the degree of adhesive wear. The appearance of Cu_3P reduces the contact area of the friction surface and weakens the adhesive wear, so the wear rate is reduced.

Keywords: Cu-Pb-Sn; wear resistance; Cu_3P; friction coefficient; wear rate

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1. Introduction

Lead–bronze is considered to be the most widely used and oldest lining metal material because of its good machinability, wear reduction, fatigue resistance, and strong load-bearing capacity. It is also one of the first choices for solid self-lubricating composite materials [1]. Although the casting performance has been improved in practical applications, the use limit of lubricating oil or grease was exceeded in many harsh working conditions. Traditional wear-resistant metals and some ordinary lubricating micropowders are used as wear-reducing coatings, not meeting the comprehensive performance requirements required by the material [2]. Theoretical regularities related to change in friction and wear parameters in the bearings were used, depending on the used materials and load conditions. The use of copper for manufacturing the bearing shell was determined as one of the promising ways to increasing their quality indicators [3].

In tribology, under the condition that the material bears the same pressure, the friction coefficient of the material with high shear strength is relatively high [4]. During the operation of the part, as the speed increases and the temperature increases, the oxide film is more likely to form so that the viscous area of the contact surface increases, thereby reducing the friction coefficient at the same time under the condition of constant speed and temperature. Common methods for enhancing the friction and wear properties of lead–bronze materials at home and abroad include particle reinforcement, fiber reinforcement, and carbon nanotube reinforcement. Nanoparticles have begun to receive most attention and applications due to their small size effect-enhancing copper-based materials [5]. Therefore, the research of new wear-reducing materials is of great significance to the future development.

Particle reinforcement is to add hard particles with high strength, high modulus, high hardness, wear resistance, and high temperature stability into the high plasticity copper matrix to enhance the performance of the alloy, especially when the performance of ceramic particles is more obvious [6]. Lei Yuanyuan found that the addition of SiC, TiB_2, TiC, B_4C, etc., particles reduced the friction coefficient of the composite by 30% compared to the matrix [7]. The addition of SiC particles improves the wear resistance of copper matrix composites to varying degrees. C. Salvo used the synthesis of novel Ti_2AlN MAX phase to reinforce copper matrix composites (Cu-MAX composites) by hot pressing [8].

Particle reinforcement can not only improve the strength of the alloy material, but also improve its wear resistance [9]. Graphite is a good anti-friction material. The addition of hard particles SiC and graphite has a great influence on the increase of wear resistance and friction reduction of its alloy materials [10].

In 2006, Liu Debao studied the dry friction and wear properties of nitride ceramic particles reinforced copper matrix composites. He found that as the content of nitride particles increased, the wear rate of the material decreased and then leveled off [11]. In 2007, Yuan Chuanyong studied the friction and wear properties of titanium diboride–copper–graphite matrix composites and found that the wear rate of the composites after adding titanium diboride was the highest, and the copper-plated titanium diboride was the lowest [12]. In 2019, Zhang Shengli added TiB_2 particle reinforced particles to copper-based alloy materials to improve the hardness and wear resistance of composites. The friction coefficient and wear amount decreased with the increase of TiB_2 reinforced particle content [13]. In 2020, Fangfang Zhang prepared copper matrix composites with Ti_2SnC particles as a reinforcement phase by exothermic dispersion method and studied the tribological behavior [14]. In 2018, Filip Ilie analyzed the physical–chemical parameters and the suitable processes for initiation and achieving the selective mass transfer (IASMT) for the steel–bronze pair, which, in optimal conditions, a thin layer (tribofilm) forms on the contact predominates copper surfaces [15]. In 2020, Avinash Lakshmikanthan studied the effect of aging temperature and particle size ratio of SiC particles on the mechanical and tribological properties of A357 composites reinforced with dual particle size SiC. He found that the ratio of large particles to small particles also seems to affect the mechanical and tribological properties. The presence of more small particles was found to be good for strength and ductility, whereas more large particles were found to be good for hardness and wear resistance [16]. In 2020, V.V. Monikandan studied the dry sliding tribological behaviors of the mono-composite and hybrid composites as a function of temperature on high temperature pin-on-disc tribotester against EN 31 counterface. The wear protective layer formed on the worn pin surfaces of the Gr-reinforced and MoS_2-reinforced hybrid composites which prevents direct metallic contact of the tribo-couple. Therefore, the wear rate and friction coefficient of the Gr reinforced and MoS_2-reinforced hybrid composites decreased in the temperature range of 30−100 °C due to the combined lubrication offered by the wear protective layer and its solid lubricant phase [17].

The reinforcing phase is uniformly distributed, and the furrows formed by wear are shallow and narrow. The wear performance is relatively stable. In 2021, Ravikumar N. and Tamilarasan T.R. studied friction and wear properties between the friction composite with graphene nanopowder (GNP) and grey cast iron disc alloyed with copper (CuGCI). A pin-

on-disc machine was used under dry sliding condition and compared its performances with the other tribo-pairs formed between friction composites with graphite (Gr), Molybdenum di sulphide (MoS_2), and disc. Results showed that the tribo pair of 10 wt.% GNP-CuGCI and 15 wt.% GNP-CuGCI proved to have good friction and wear performances compared to the other tribo pairs, and were also at par with the performance of the commercial pad tested under the same conditions [18]. Lin Guangyuan systematically investigated the effect of graphene orientation on the friction and wear properties of the composite by both experimental and finite element simulation. The friction test results show that, with only ~0.2 vol% graphene, the maximum anisotropy ratio of wear resistance reaches a level as high as 100-fold in the laminated composite [19].

For friction, the wear rate of high-hardness materials is generally lower, but the friction coefficient is too large, which does not play a role in reducing friction [20]. As mentioned by Zheng Xiaomeng, under the action of load, the deformation of the soft layer on the surface of the material is large, and in the process of friction sliding, although the friction coefficient is small, the wear rate will increase. The hard layer has small deformation under load, small wear rate, but large friction coefficient. However, after combining the soft layer and the hard layer to obtain the basic structure of the multi-layer film, when the load acts, under the support of the hard layer, the contact area between the pair and the soft layer decreases. On the one hand, the soft film layer plays a role in reducing friction and reduces the friction coefficient. On the other hand, under the support of the hard layer, the wear of the soft layer is reduced [21].

On the basis of not changing the self-lubricity of the material, the $ZCuPb_{20}Sn_5$ alloy material was modified. The wear resistance of the alloy is increased by adding different contents of P to make it produce a hard second phase micro-nano particle (Cu_3P) reinforced phase. The soft phase matrix is utilized to ensure the alloy has good embedment and friction compliance. While improving the wear reduction, the raised hard particles can bear the load and increase the wear resistance. Moreover, the lubricating oil can be stored in the gap between the convex hard point and the concave soft base so as to ensure that the friction process has a good oil lubrication effect to reduce the friction coefficient. The wear resistance of $ZCuPb_{20}Sn_5$ alloy was studied under two different working conditions of oil lubrication and dry friction, mainly to improve the wear resistance of alloy materials. By analyzing the friction coefficient, wear rate, and wear morphology of $ZCuPb_{20}Sn_5$ alloy, we judged the influence of P on the friction and wear properties of Cu-Pb-Sn alloy and obtained the wear mechanism. In order to be able to understand more comprehensively the influence, function, and mechanism, clarify the depth or progress achieved by the current research and the existing problems, prepare new materials suitable for high speed and high load wear resistance, and expand the application scope of copper-based self-lubricating materials, which will bring huge economic and social benefits, we firmly believe that it is making future research more targeted. Under the condition of not destroying its room temperature plasticity, it is the ideal result pursued by researchers to improve the strength properties of copper alloy materials and improve the wear resistance of the alloys, which is also the focus of this paper. However, the microscopic mechanism of this synergy is still unclear, and further systematic and in-depth exploration is needed, which also has important theoretical and practical significance for the application of copper alloys in the material science community.

2. Experimental Procedure

$ZCuPb_{20}Sn_{5-x}P$ alloy castings were smelted in a well-type resistance furnace (SG2-12-13) and a 16# graphite crucible. In $ZCuPb_{20}Sn_{5-x}P$ alloy, x = 0, 0.05, 0.1, 0.2, or 0.3). The content of P was determined with reference to the newly compiled practical manual of casting standards [22]. After smelting, samples were taken at the same location for analysis. The friction and wear properties of the samples were tested in MMW-1A pin-on-disc friction (Jinan, China). After the friction test, the microstructure and morphology of the worn surface were observed by a metallographic microscope (AXIO Scope.A1, Taiyuan, China) and

a scanning electron microscope (SEM, SU5000, Taiyuan, China). The element distribution of the worn surface was characterized by an energy dispersive spectrometer (EDS). The main secondary phases, Cu_3P and Ni_3P in the $ZCuPb_{20}Sn_5$ alloy, were determined with an electron probe (EPMA, JXA-8100, Taiyuan, China).

The friction test was carried out on the MMW-1A pin-on-disc friction and wear tester. The friction pin material is $ZCuPb_{20}Sn_5$ alloy material, and the friction disc is high-quality carbon structural steel No. 45 (45# steel) disc. The disc had holes inside and was 19 mm thick for easy installation. During the friction process, the pin rotates, the rotation radius was 23 mm, and the steel plate was fixed. The test temperature of the friction and wear test was room temperature, and the lubrication state was oil lubrication and dry friction. Tests were conducted with the 250 N load and the 1500 r/min or 3.61 m/s rotational speed, the time of the test is 30 min, and the lubricating oil used is 15 W-40#. The experiment was carried out in the oil tank. The changes of friction coefficient, wear rate, and wear morphology were observed by changing the content of P element. The same experiment was repeated three times and averaged, where the value of the coefficient of friction was an average of the 30-min. The friction conditions of dry friction are that the load is 100 N, the rotation speed is 1500 r/min or 3.61 m/s, and the time is 15 min. The experimental conditions of all schemes remain unchanged, and only the content of P element was changed. The same experiment was repeated three times and averaged, wherein the value of the coefficient of friction was an average of the 15-min values. Before the test, each sample was cleaned by rough grinding, fine grinding and polishing to ensure the surface roughness Ra $\leq$ 0.8 μm, and called its quality. After wear, wash with acetone and dry it, and then weigh its mass with a 1/10,000 electronic analytical balance and calculate its wear rate through the weight of wear loss (average of multiple weightings).

The test data was based on the friction curves of Cu-Pb-Sn alloys with different P contents under oil lubrication and dry friction conditions. Thirty points were selected in the oil lubrication state curve, and each point was the average value within the minute. In the dry friction state, 15 points were selected, and each point was the average value within the minute.

In the process of friction, the surfaces of two objects in contact with each other will inevitably appear as wear phenomena such as continuous loss, transfer, or residual strain of the surface material, which will shorten the service life of the material. Therefore, before being used, the calculation of wear rate is very important. The calculation formula of the wear rate A is shown in Equation (1):

$$\text{Wear rate A} = \Delta W \cdot (\rho \cdot S \cdot P) \tag{1}$$

Among them, ΔW is the mass difference before and after friction, unit: $mm^3/(N{\cdot}m)$; ρ is the density of the material, unit: g/cm^3; S is the sliding distance, unit: m; P is the applied load, unit: N.

The quality data of Cu-Pb-Sn alloys with different P contents before and after wear were recorded. According to the wear rate Equation (1) the wear rate under each set of scheme conditions is calculated. The density of $ZCuPb_{20}Sn_5$ alloy was experimentally measured to be 9.47 g/cm^3, and each scheme was repeated three times to obtain the average value.

3. Results and Discussion

3.1. Friction Coefficient

3.1.1. Oil Lubrication

Figure 1 is a graph showing the variation of friction coefficient with time and P contents for $ZCuPb_{20}Sn_5$ alloys under oil lubrication conditions. Figure 1a is the change of friction coefficient with time, and Figure 1b is the relationship between P content and average friction coefficient.

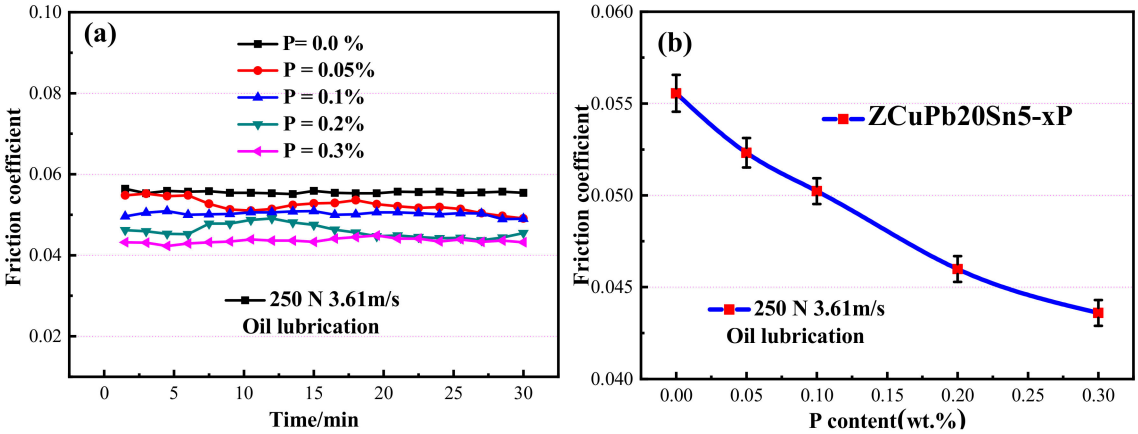

Figure 1. Friction curve of $ZCuPb_{20}Sn_{5-x}P$ alloy under oil lubrication (**a**) time; (**b**) P content.

It can be seen from Figure 1 that with the increase of P content, the friction coefficient of $ZCuPb_{20}Sn_5$ alloy decreases, and it decreases basically linearly. When no P was added, the friction coefficient was 0.056, and when the P content was increased to 0.3%, the friction coefficient decreased to 0.044, a decrease of 0.012. When the P content is 0.1%, the friction coefficient is 0.050, a decrease of 10.7%. When the content of P increased from 0.1% to 0.2% and 0.3%, the decrease rates were 8% and 4.3%, respectively, and the decrease rates gradually decreased. It can be seen from the curve of friction coefficient versus time in Figure 1a that under the condition of oil lubrication, the alloy materials with different P additions are basically stable and fluctuate within a fixed value range during the friction and wear experiment, and the fluctuation range is very small. Approximate the law of linear change. Under the condition of oil lubrication, the friction coefficient of $ZCuPb_{20}Sn_5$ alloy material decreased after adding different content of P, and the overall friction coefficient was between 0.034 and 0.056. With the increase of P content, the friction coefficient of $ZCuPb_{20}Sn_5$ alloy material decreases linearly, and the decrease is basically a fixed value. When the P content is 0.3%, the friction coefficient is the smallest, and the minimum friction coefficient is 0.044. When no P is added, the friction coefficient is the largest, and the maximum is 0.056. It can be seen from Figure 1b that different P changes with time, under oil lubrication conditions. Except for the two cases where 0 wt.%P and 0.05 wt.%P are added, the changes are unstable. The change trend of the friction coefficient is stable. Mainly because the alloy material does not have phosphorous copper or a small amount of phosphorous copper deoxidized and degassed during the melting process, there is no hard micro-nano Cu_3P in the alloy structure, and the distribution of lead is uneven, so it is easy to be in the friction process. There are fluctuations and instability. With the increase of P content, the distribution of lead particles becomes uniform, the structure and properties of the alloy are optimized, and the hard Cu_3P micro-nano particles are precipitated in the alloy, which improves the wear reduction and reduces the friction coefficient.

In conclusion, under the condition of oil lubrication, adding different contents of P to the alloy $ZCuPb_{20}Sn_5$ can reduce the friction coefficient of the alloy material, and with the increase of element content, the friction coefficient decreases.

3.1.2. Dry Friction

Figure 2 is a graph showing the relationship between the friction coefficient of $ZCuPb_{20}Sn_5$ alloys with different P contents and time and different P contents under dry friction conditions in which Figure 2a is a curve diagram of the friction coefficient with time and Figure 2b is the friction coefficient. Graph of the change with P content.

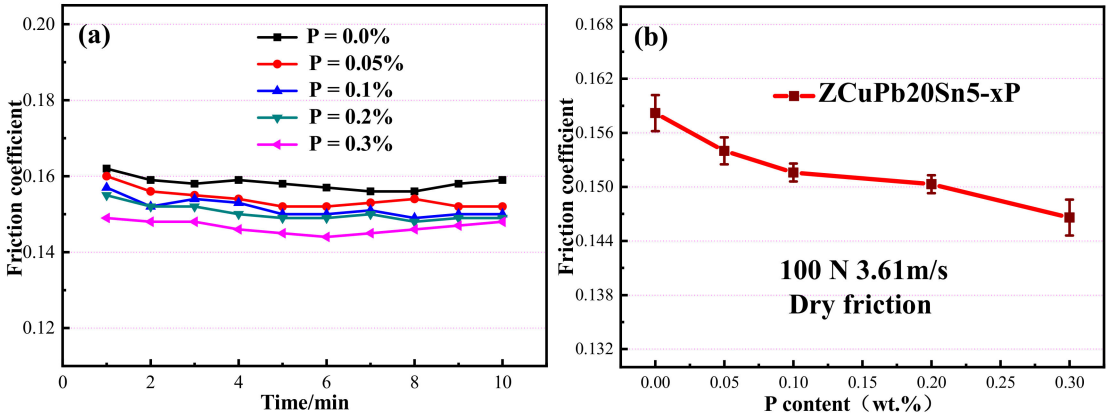

Figure 2. Friction curve of $ZCuPb_{20}Sn_{5-x}P$ alloy under dry friction (**a**) time; (**b**) P content.

It can be seen from Figure 2b that with the increase of P content, the friction coefficient of $ZCuPb_{20}Sn_5$ alloy gradually decreases. Without P, it was 0.158, and when the amount of P was 0.3 wt.%, the friction coefficient was the smallest, which was 0.147, a decrease of 0.011, and a decrease of 69.6%. The variation law of the reduction is consistent with the oil lubrication condition. When the P content is 0.1 wt.%, the friction coefficient is 0.152, which is reduced by 0.002 relative to the friction coefficient of 0.05 wt.%P. When the addition amount of P increases from 0.1 wt.% to 0.2 wt.% and 0.3 wt.%, the friction coefficient reduction is only 0.002 and 0.003, and the change is not obvious. It can be seen from Figure 2a that the friction coefficient changes with time. Under the condition of dry friction, the alloy materials with different contents of P show a state of first decreasing, then increasing, and then maintaining a stable state during the friction and wear experiment, and the fluctuation range is small. When P is not added, the friction coefficient curve fluctuates greatly at first, which belongs to the running-in process between the friction pairs. After the running-in period, it gradually reaches stability. However, with the extension of time, the stable self-lubricating lead film is affected by the individual hard surfaces on the copper pin surface. The particles are destroyed, resulting in an increase in the coefficient of friction.

Under the condition of oil lubrication, the friction coefficient of $ZCuPb_{20}Sn_5$ alloy is 0.056 when no P elements are added. When the P content is 0.3%, it decreases to 0.044; the friction coefficient decreases from 0.158 to 0.131 under the corresponding dry friction condition. Moreover, under the condition of oil lubrication, except for the case of no P and low P (less than 0.05%), the friction coefficient will fluctuate up and down with the extension of time, and the friction process is relatively stable. Under the condition of dry friction, the friction coefficient of the alloy material generally increases first, then decreases, and then tends to be stable with the prolongation of time. At the beginning of the operation of the new friction pair, due to the inevitable large surface roughness value on the surface of the dual material, the actual contact area of the two is small. Although the number of contact points is small, the area of most of the contact points is large, and rapid wear occurs immediately under the load, resulting in serious adhesion of the contact points, so the wear is serious and the friction coefficient increases. However, as the running-in progresses, the micro-bumps on the surface are gradually ground away, which reduces the surface roughness value, increases the actual contact area, increases the number of contact points, and slows down the wear speed, thereby reducing the friction coefficient, and then the wear becomes slow and stable. The friction coefficient remains basically unchanged, which belongs to the normal working stage.

3.2. Wear Rate

3.2.1. Oil Lubrication

After the oil lubrication test was carried out under the condition of 250 N load and 3.61 m/s speed and after the experiment was carried out for 30 min, the $ZCuPb_{20}Sn_5$ alloy

pin samples before and after friction and the 45# steel disc of the grinding disc were cleaned, weighed, and the wear rate was calculated and plotted in Table 1. The change curve is shown in Figure 3.

Table 1. Wear rates of ZCuPb20Sn5 alloys with different P contents under oil lubrication.

No.	Category	Wear (g)	Wear Rate (mm^3/N·m)
P0	pin	0.0331	2.150×10^{-6}
	plate	0.0008	-
P0.05	pin	0.0235	1.528×10^{-6}
	plate	−0.0011	-
P0.1	pin	0.0183	1.189×10^{-6}
	plate	−0.0029	-
P0.2	pin	0.0127	0.825×10^{-6}
	plate	−0.0047	-
P0.3	pin	0.0048	0.312×10^{-6}
	plate	−0.0036	-

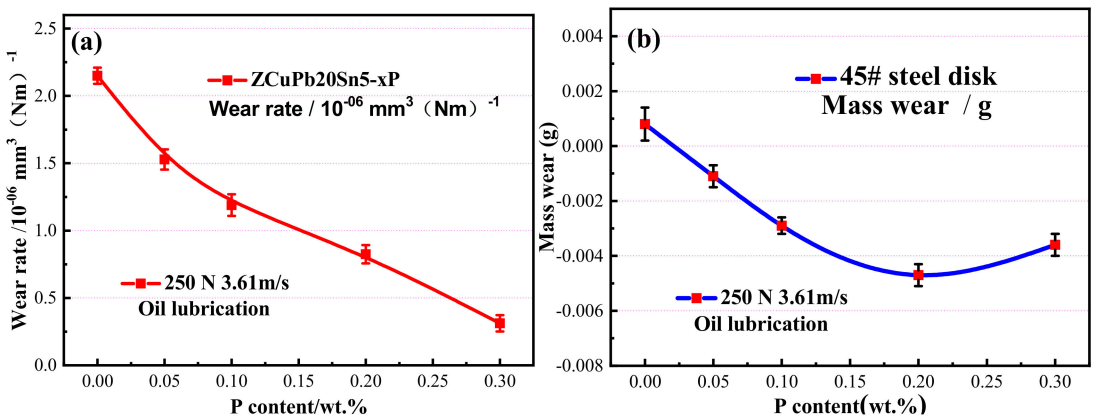

Figure 3. Abrasion of $ZCuPb_{20}Sn_{5-x}P$ alloy and 45 # steel disc under oil lubrication (**a**) wear rate of $ZCuPb_{20}Sn_{5-x}P$ alloy; (**b**) Abrasion of 45#Steel-plate.

Figure 3 is a graph showing the wear rate of $ZCuPb_{20}Sn_5$ alloy pins and 45# steel discs as a function of P content under oil lubrication conditions. Figure 3a is the wear rate of $ZCuPb_{20}Sn_5$ alloy pins, and Figure 3b is the wear of 45# steel discs. It can be seen from the wear rate data. The wear rate of the $ZCuPb_{20}Sn_5$ alloy pin sample decreases with the increase of P content. The main reason is that with the increase of P content, the hardness of $ZCuPb_{20}Sn_5$ alloy material increases linearly, which increases the wear resistance of the alloy. At the same time, due to the addition of P, the structure of the $ZCuPb_{20}Sn_5$ alloy material is refined, the segregation of lead particles is reduced, and the lead particles are evenly distributed in the structure. During the friction and wear test, when the $ZCuPb_{20}Sn_5$ alloy material interacts with the friction pair, With the combined action of frictional heat and deformation and extrusion, the free lead will be gradually extruded from the surface of the alloy material, and a continuous soft lead lubricating film formed on the surface of the friction pair. The soft lead lubricating film reduces the pins and friction pairs. The contact area, the coefficient of friction, and therefore the wear rate reduced. When no P is added, the wear rate is the largest, which is 2.150×10^{-6} mm^3/(N·m). When the P content is 0.3 wt.%, the wear rate is the smallest, and the minimum is 0.312×10^{-6} mm^3/(N·m).

It can also be seen from Figure 3b that the wear quality of the 45# steel disc of the grinding disc changed before and after the experiment. When P is not added, the mass of

the steel plate increases, indicating that in the process of friction, the adhesion phenomenon occurs, and the surface structure of the $ZCuPb_{20}Sn_5$ alloy pin is brought to the surface of the opposite-grinding steel plate during the wear process. From the data, it can be seen that the mass gain of the steel disk increases with the increase of the P content. Since the wear amount of the $ZCuPb_{20}Sn_5$ alloy pin decreases with the increase of the P content, it can be concluded that the main reason for the increase in the quality of the steel plate is the lead particles on the surface of the $ZCuPb_{20}Sn_5$ alloy. The lead particles, evenly distributed in the tissue, form a uniform lead film during the wear process. The film is relatively soft, so it is easily brought to the surface of the steel plate during the friction process, thereby increasing the quality of the rigid plate. Moreover, with the increase of P content, the lead particles on the surface of $ZCuPb_{20}Sn_5$ alloy are numerous and uniform, and the lead film area formed is large. The larger the area, the greater the chance of being taken away, thereby increasing the mass gain of the steel plate. When the P content exceeds 0.2wt.%, the increase in the mass of the steel plate decreases, and the adhesive wear is weakened.

3.2.2. Dry Friction

The oil lubrication test was carried out under the condition of 100 N load and 3.61 m/s speed. After the experiment was carried out for 15 min, the $ZCuPb_{20}Sn_5$ alloy pin samples before and after friction and the 45# steel plate of the grinding disc were cleaned and weighed, and the wear rate was calculated in Table 2 and the change curve was drawn in Figure 4:

Table 2. Wear rates of ZCuPb20Sn5 alloys with different P contents under dry friction.

No.	Category	Wear (g)	Wear Rate ($mm^3/(N{\cdot}m)$)
P0	pin	0.6032	1.30631×10^{-4}
	plate	0.0016	-
P0.05	pin	0.5235	1.13371×10^{-4}
	plate	−0.0015	-
P0.1	pin	0.4883	1.05748×10^{-4}
	plate	−0.0029	-
P0.2	pin	0.3984	8.62786×10^{-5}
	plate	−0.0067	-
P0.3	pin	0.2548	5.51802×10^{-5}
	plate	−0.0041	-

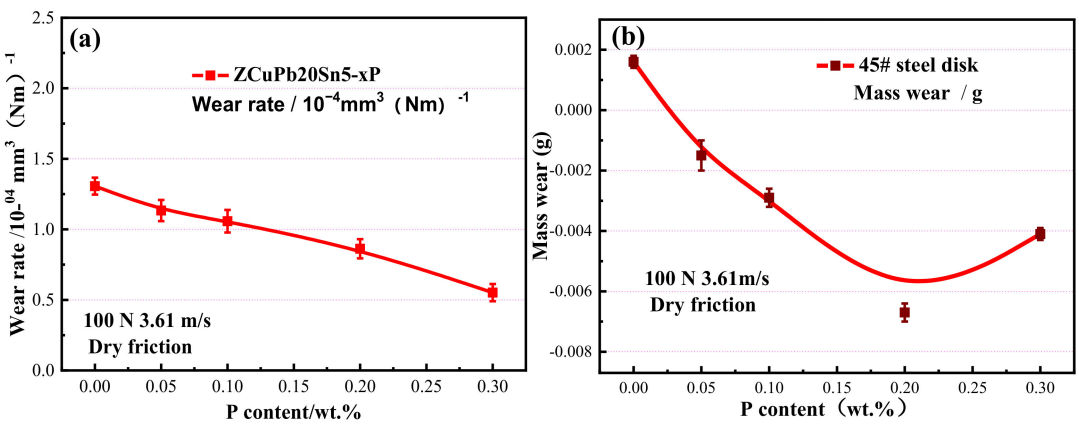

Figure 4. Abrasion of $ZCuPb_{20}Sn_{5-x}P$ alloy and 45 # steel disc under oil lubrication; (**a**) Wear rate of $ZCuPb_{20}Sn_{5-x}P$ alloy; (**b**) Abrasion of 45#Steel-plate.

Figure 4 is a graph showing the change of wear rate of $ZCuPb_{20}Sn_5$ alloy pin and 45# steel disc with P content under dry friction conditions, in which Figure 4a is the wear rate of $ZCuPb_{20}Sn_5$ alloy pin, and Figure 4b is the wear of 45# steel disc rate. It can be seen from Figure 4a that with the increase of P content, the wear amount of $ZCuPb_{20}Sn_5$ alloy decreases linearly. It shows that the addition of P can increase the wear resistance of $ZCuPb_{20}Sn_5$ alloy. From Figure 4b, it can be seen that the mass wear of the 45# steel disc before and after the friction of the abrasive piece is 0.0016 g when phosphor bronze is not added. With the increase of P content, the 45# steel plate quality does not decrease but increases after the steel plate is worn. The increase range first increases and then decreases. When the P content exceeds 0.2 wt.%, the increase increases, indicating that the wear mechanism has changed there. According to the previous analysis of the structure and properties, when the P content exceeds 0.2 wt.%, the number of second-phase hard particles in the structure increases, and the Cu_3P phase appears, which is evenly distributed in the structure, and during the wear process, the asperities form on the friction surface, which reduces the actual contact area between the $ZCuPb_{20}Sn_5$ alloy pin and the 45# steel plate and reduces the adhesive wear, so the wear amount decreases.

By observing the data of the effect of P element on the wear amount of $ZCuPb_{20}Sn_5$ alloy, it can be concluded that the addition of P element can reduce the mass wear amount of the alloy material in both dry friction and oil lubrication methods. With the increase of alloy content, the wear amount has a decreasing trend. The change rule of the alloy wear amount is consistent in the two methods. The addition of P element did not reduce the quality of the steel plate of the alloy material, but increased, indicating that in the process of wear, the alloy pin material was brought to the steel plate with the opposite grinding surface in the process of friction, and adhesive wear occurred, thus reducing the quality of the steel plate. The adhesive wear weakened with the increase of P content.

3.3. Wear Mechanism of $ZCuPb_{20}Sn_{5-x}P$ Alloy

Morphology Analysis after SEM Wear

Figure 5 shows the morphology of the $ZCuPb_{20}Sn_{5-x}P$ alloy pin under the condition of 100 N load and 3.61 m/s speed without oil lubrication after rubbing for 15 min:

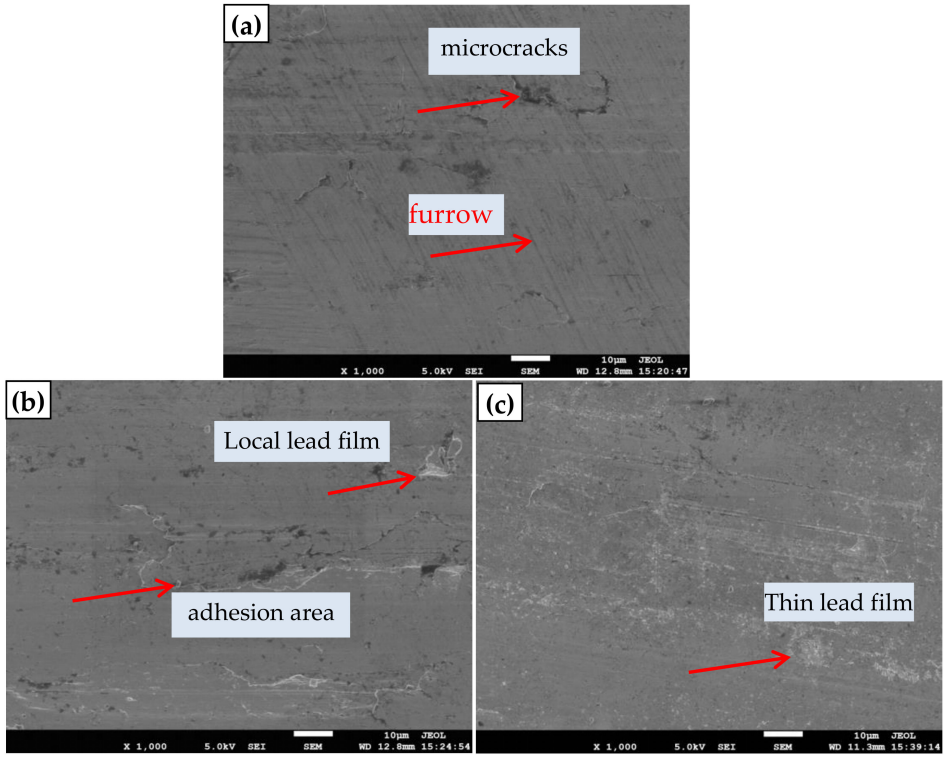

Figure 5. *Cont.*

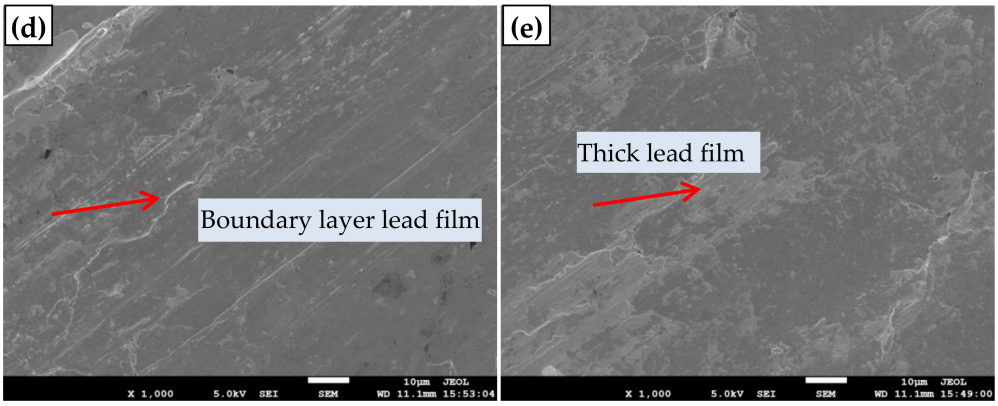

Figure 5. Analysis of friction topographies of $ZCuPb_{20}Sn_{5-x}P$; (**a**) P = 0.0 wt.%; (**b**) P = 0.05 wt.%; (**c**) P = 0.1 wt.%; (**d**) P = 0.2 wt.%; (**e**) P = 0.3 wt.%.

Figure 5 shows the friction and wear morphology of $ZCuPb_{20}Sn_5$ alloy under dry friction conditions after adding different contents of P-Cu. Among them, (a), (b), (c), (d), and (e) represent friction and wear morphology, respectively, of $ZCuPb_{20}Sn_5$ alloy pins that 0 wt.%, 0.05 wt.%, 0.1 wt.%, 0.2 wt.%, and 0.3 wt.% P added. It can be seen from Figure 5 that the wear of the $ZCuPb_{20}Sn_5$ alloy without adding P-Cu is more serious than that with the addition of P-Cu. When P-Cu is not added, there are small furrows, microcracks, and a small amount of debris on the friction surface of $ZCuPb_{20}Sn_5$ alloy, so it can be judged that the wear mechanism of $ZCuPb_{20}Sn_5$ alloy is mainly adhesive wear and abrasive wear. This is because that the friction surfaces mainly come into contact in the form of asperities, resulting in scratches and furrows on the friction surfaces after friction begins. In the process of increasing the friction time, the asperities are ground, and the generated wear debris is brought into the friction surface to cover part of the furrows crack [23]. During the relative sliding process, deformation, slip, and crack nucleation were observed on the counter-grinding surface, resulting in the wear of the alloy material.

With the increase of the content of P element in the $ZCuPb_{20}Sn_5$ alloy, the gray-white block-like film gradually appeared in the structure, and the number and volume of the film increased. The main reason is that with the increase of P content, the second phases Cu_3P appearing in the structure gradually increase and are evenly distributed in the alloy matrix structure, which hinders the aggregation and growth of lead, refines the grains, and strengthens the properties of the alloy. Moreover, the formation of the second phase Cu_3P particles increases the hardness of the alloy. The increasing hardness makes the temperature of the wear surface of the alloy rise rapidly during the friction and wear process, so that the lead particles evenly distributed in the tissue become a soft lead film under the action of hot extrusion during the friction and wear process. The film protects the wear surface of the $ZCuPb_{20}Sn_5$ alloy from being damaged, thereby increasing the wear reduction of the alloy.

With the increase of P content, the friction coefficient decreased successively, and the friction coefficient was stable between 0.05 and 0.06 when the P content was 0.3 wt.%. At the same time, the wear rate decreases with the increase of P content, especially when the P content is greater than 0.05 wt.%, and the wear rate decreases with the increase of P content. The reason is that the increase of P content leads the hardness and wear resistance of the Cu-Pb-Sn alloy to increase. Second, during the friction and wear test, when the Cu-Pb-Sn material interacts with the friction pair, under the combined action of frictional heat and deformation extrusion, the free lead will gradually be extruded to the surface of the material from the alloy, and a continuous soft lead lubricating film is formed on the surface of the friction pair. The soft lead lubricating film reduces the contact area between the pin and the friction pair, thereby reducing the friction coefficient, so the wear rate gradually reduces with the increase of P content.

In order to further analyze the wear mechanism of alloy materials, two schemes with P and no P were selected to carry out EDS data analysis on the wear morphology of alloy pins and grinding discs, as shown in Figures 6 and 7.

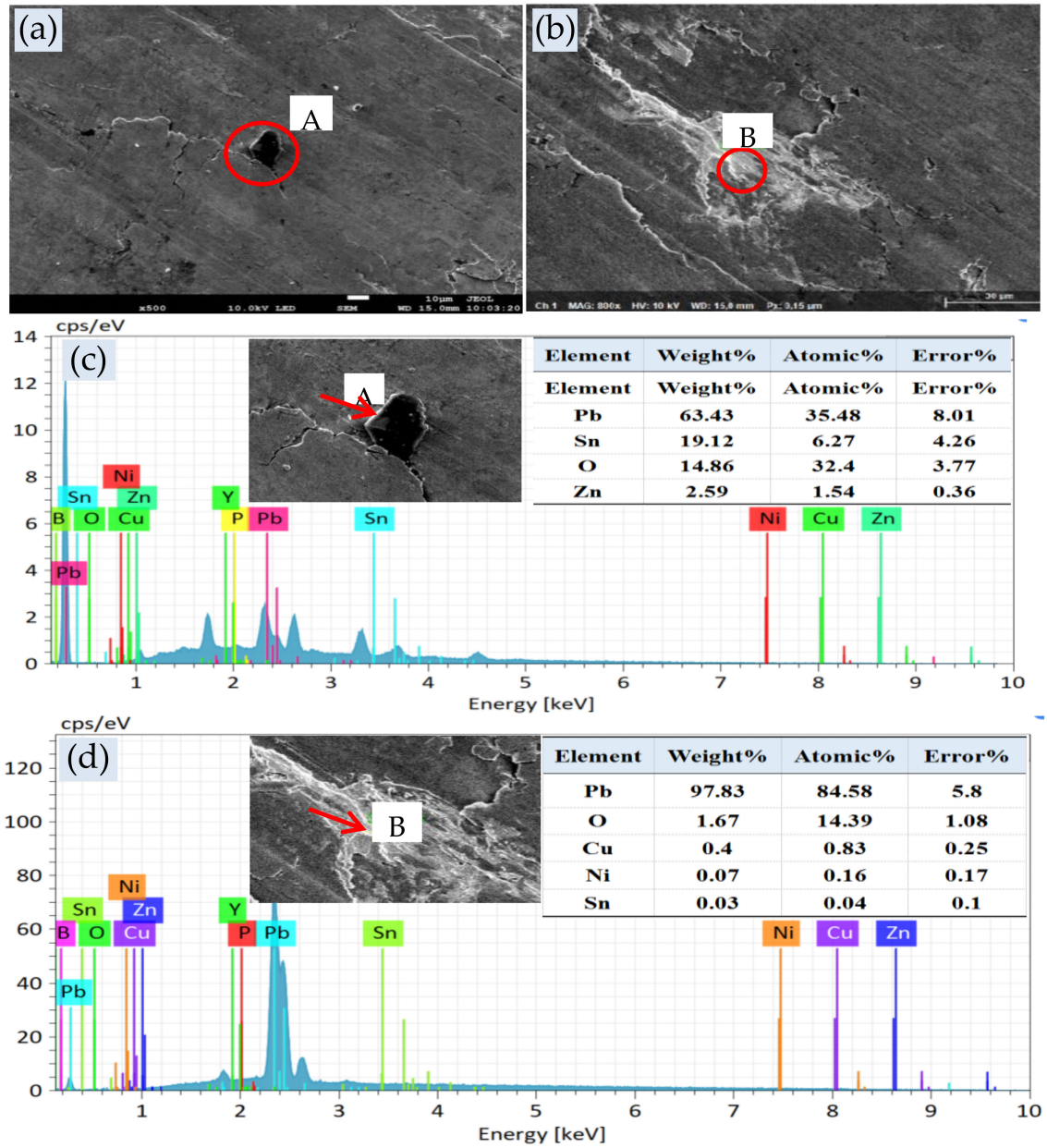

Figure 6. SEM of $ZCuPb_{20}Sn_{5-0}P$ alloy; (**a**) Selection A; (**b**) Selection A; (**c**) EDS of A; (**d**) EDS of B. A is Cu_3P, and the B is Pb.

Figure 7 is the EDS data diagram of the alloy without adding phosphorous copper. From the data analysis in Figure 7, it can be seen that there are oxide particles in the structure, as shown in A of Figure 7, and the particles are impurity particles doped with oxidized lead. Due to its existence, deep pear groove-shaped wear marks appear on the grinding surface during the friction process, as shown in Figure 8.

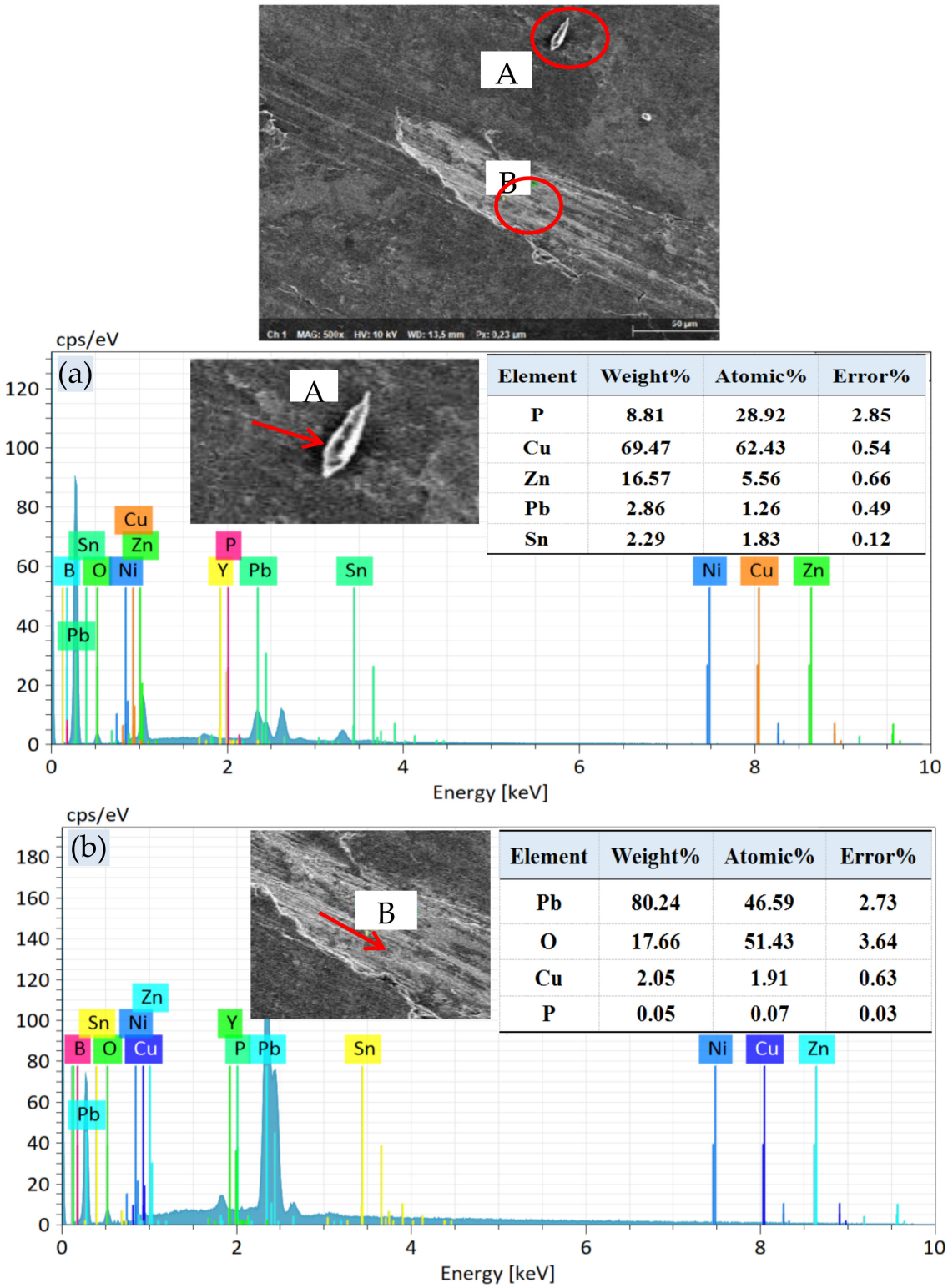

Figure 7. Analysis of friction topographies of $ZCuPb_{20}Sn_{5-0.3}P$: (**a**) EDS of A; (**b**) EDS of B. A is Cu_3P, and the B is Pb

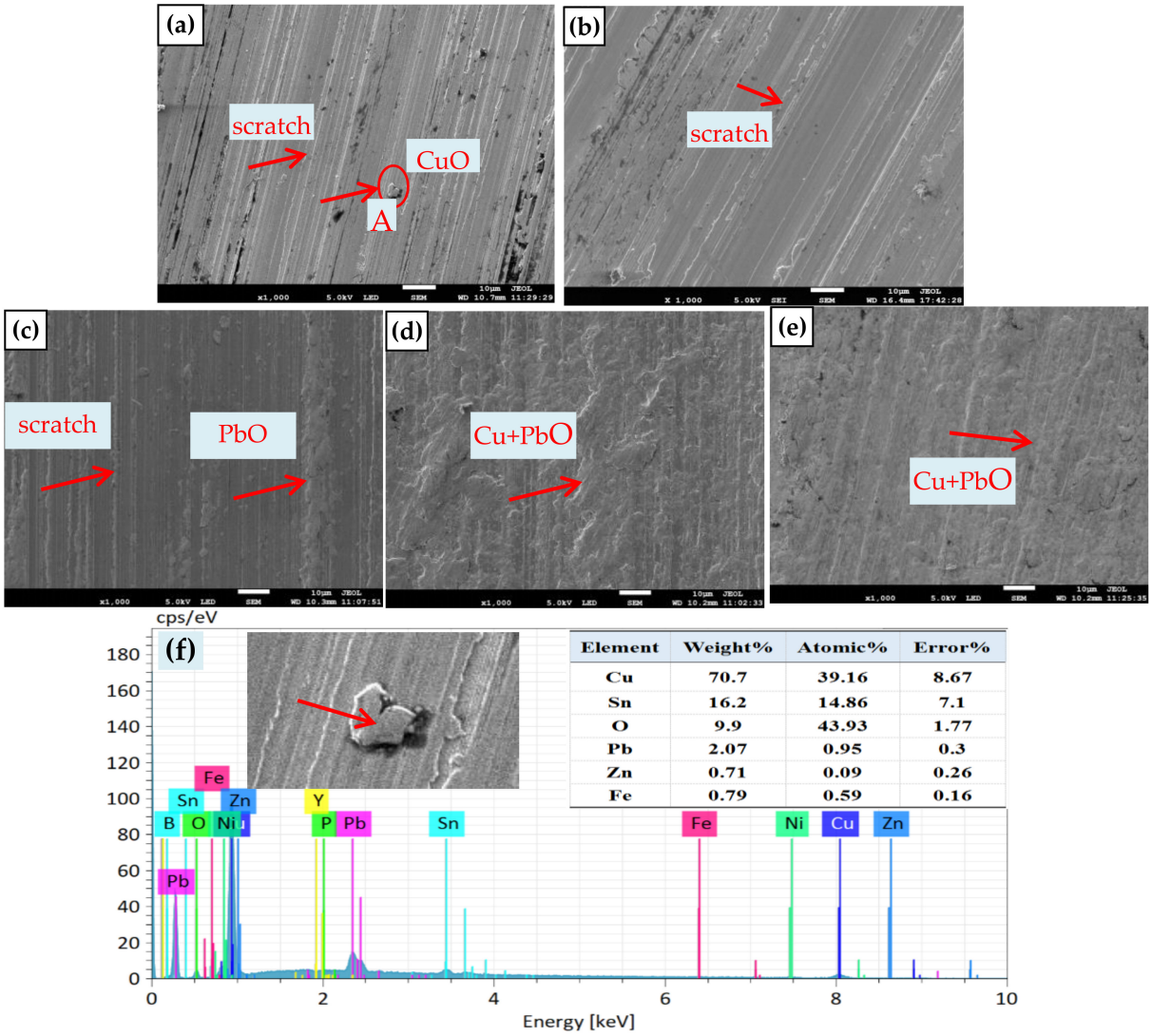

Figure 8. Analysis of friction topographies of 45 steel disks: (**a**) P = 0.0 wt.%, (**b**) P = 0.05 wt.%, (**c**) P = 0.1 wt.%, (**d**) P = 0.2 wt.%, (**e**) P = 0.3 wt.%, (**f**) EDS of A.

Figure 8 shows the morphologies of the $ZCuPb_{20}Sn_5$ alloy pins with different contents of P added to the grinding disc 45# steel, in which Figure 8a is the morphology of the 45# steel after wear without adding phosphorous copper, and Figure 8b–e are the worn morphologies of 45# steel after adding phosphorous copper 0.05 wt.%, 0.1 wt.%, 0.2 wt.%, and 0.3 wt.%, respectively. It can be observed from Figure 8 that with the increase of P content, a layer of gray-white lamellar protective film gradually increases on the surface of the steel plate, which makes the scratches caused by hard particles in the process of wear of the steel plate, that is, the depth of the pear groove, gradually become lighter. Moreover, the thickness and volume of this film increased with increasing P content. The EDS data analysis shows that the film is a lead film. When no P is added, there are granular substances on the surface of the 45# steel plate, and the wear marks are relatively deep and obvious. In the friction process, the asperities on the surface of the $ZCuPb_{20}Sn_5$ alloy are pressed into the surface of the 45# steel plate under the action of pressure, which damages the surface of the sample on the contact surface and forms ravines. During the relative sliding process, deformation, dislocation, and cracks were observed on the counter-grinding surface, resulting in the wear of the 45# steel disc material.

Regarding the judgment of the hard particles, relevant research has been carried out in the previous stage. Combined with the results of the previous experiments [24], the

experimental data with a P content of 0.3 wt.% was determined by using an electron probe, as shown in Table 3.

Table 3. EPMA data of the $ZCuPb_{20}Sn_5$ alloy.

Element	Mass (%)	Atom (%)	K (%)	K-raw (%)	ZAF	Z	A	F
P	2.679	26.3584	1.597	5.341	1.6775	0.9164	1.8313	0.9996
Zn	0.000	0.0000	0.000	0.000	0.0000	0.0000	0.0000	0.0000
Ni	0.186	0.9644	0.190	0.190	0.9772	0.9642	1.0135	1.0000
Cu	14.203	68.1079	13.942	13.943	1.0187	1.0101	1.0085	1.0000
Sn	1.780	4.5694	1.518	1.519	1.1725	1.1111	1.0603	0.9952

It can be concluded that the hard particles in the $ZCuPb_{20}Sn_5P_{0.3}$ alloy material are mainly Cu_3P phase. This phase is a hard and brittle phase, which can increase the hardness and wear resistance of the alloy. Lead acts as a solid lubricant for the material and plays a major role in reducing wear in the material. The compound is hard and uniformly distributed at grain boundaries, inhibiting lead segregation. The Cu_3P particles are uniformly distributed at the grain boundaries and form multiple nuclei during solidification, thereby refining the grains and producing fine-grain strengthening as shown in Figure 9. The blue particles in the red area are Cu_3P, which are uniformly distributed in the tissue. Within a certain range, with the increase of P content, the effect of fine-grain strengthening becomes more obvious, thereby enhancing the ability of the matrix to resist plastic deformation, resulting in increased hardness and wear resistance of Cu-Pb-Sn alloys.

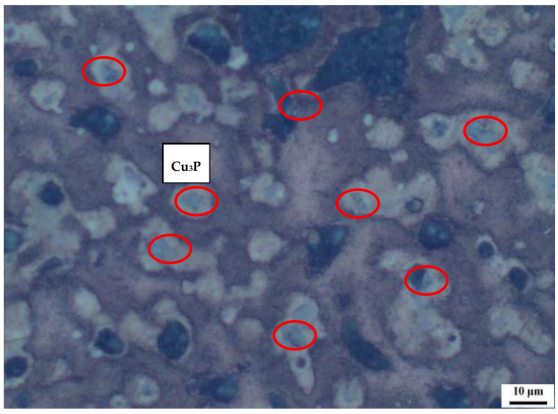

Figure 9. Cu3P topography.

When $ZCuPb_{20}Sn_5$ alloy and 45# steel disc are rubbed under higher hardness conditions, the change of wear rate and friction coefficient between the two contact surfaces and the positive pressure depends on the sliding state, surface morphology, and sliding speed of the sliding surface. During the friction process, the surface of the alloy is easy to fall off, and the surface of the falling surface forms fragments during the friction process and adheres to the wear surface, which makes the wear surface rough and causes the fluctuation of the friction coefficient. With the increase of P addition, the second phase particles of $ZCuPb_{20}Sn_5$ alloy gradually increased, which refined the $ZCuPb_{20}Sn_5$ alloy structure, made the distribution of lead particles uniform, and reduced the surface adhesion of large lead blocks. Therefore, in the process of wear, when the degree of surface shedding decreases, the coefficient of friction decreases slightly, but under high-speed sliding friction the decrease in the coefficient of friction is not obvious.

It can be seen from the analysis that the wear scar on the surface of $ZCuPb_{20}Sn_5$ alloy gradually weakens and the lamellar lead film increases after adding different contents of P to the $ZCuPb_{20}Sn_5$ alloy, as shown in Figure 10. The wear scars on the worn surface of the 45# steel disc are gradually covered by copper and lead films with the increase of P

content. From the perspective of wear mode, the wear mechanism gradually transitions from abrasive wear to adhesive wear. The main wear mechanism is adhesive wear, and some of them have oxidative wear. As the P content continues to increase, the second phase Cu_3P particles appear, which reduces the friction area and reduces the degree of adhesive wear.

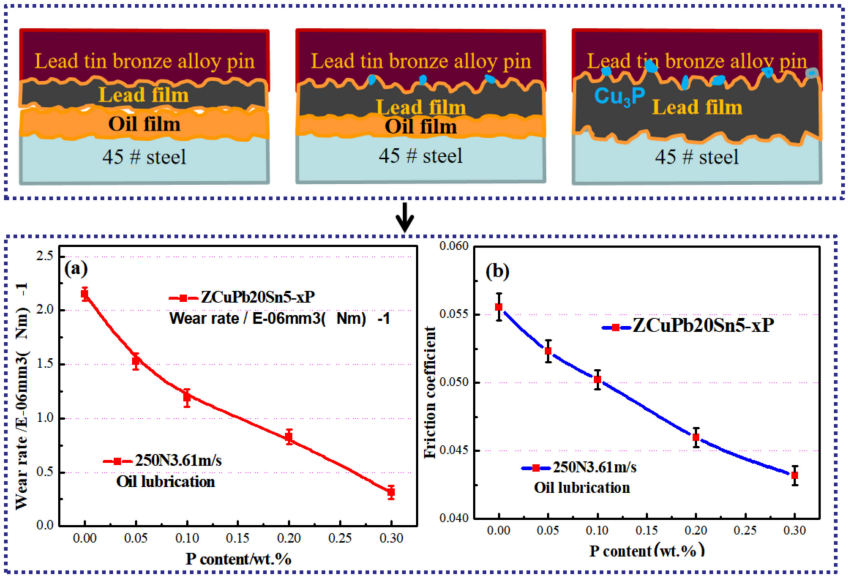

Figure 10. Mechanism diagram of friction and wear; (**a**) the relationship between the wear rate and P content under oil lubrication; (**b**) the relationship between the friction coefficient and P content under oil lubrication.

4. Conclusions

(1) The wear reduction of $ZCuPb_{20}Sn_5$ alloy increases when P is added, and the friction coefficient and wear rate decrease with the increase of P addition. Under the condition of oil lubrication, the addition amount of P is 0.3 wt.%, the friction coefficient and wear rate are the smallest, the friction coefficient is 0.034, and the wear amount is 0.312×10^{-6} $mm^3/(N{\cdot}m)$. Compared with 0.056 when P was not added, it decreased by 0.022. Under the dry friction condition, the friction coefficient decreased from 0.1563 without addition to 0.1436 with P addition of 0.3 wt.%. Under oil lubrication conditions, except for the case of no P and low P (less than 0.05 wt.%), the friction coefficient will fluctuate up and down with the extension of time, and the friction process is relatively stable in other cases. Under the condition of dry friction, the friction coefficient of the alloy material generally increases first, then decreases, and then tends to be stable with the prolongation of time.

(2) In the two methods of dry friction and oil lubrication, the mass wear amount of $ZCuPb_{20}Sn_5$ alloy material decreases with the increase of P element addition, and the two methods make the change law of alloy wear amount consistent. The addition of P element did not reduce the quality of the alloy material steel plate, but increased it, indicating that in the process of friction and wear, the alloy pin material was brought to the opposite grinding surface steel plate in the process of friction, and adhesive wear occurred, thus increasing the wear rate of the alloy material.

(3) After adding P, the main wear mechanism of the alloy under oil lubrication is adhesive wear. The main reason for the enhancement of friction reduction is that with the increase of P content, the lead particles are refined and evenly distributed, which promotes the formation of a uniform self-lubricating lead film in the process of friction and reduces the degree of adhesive wear. At the same time, the appearance of the second phase submicron particles Cu_3P reduces the contact area of the friction surface and weakens the adhesive wear, so the wear rate is reduced.

(4) The addition of P (in the range of 1~0.3 wt.%) can not only improve the mechanical properties of the alloy, but also become a good wear-reducing material, which can reduce the friction coefficient and reduce the wear rate. The optimal limit content of $ZCuPb_{20}Sn_5$ alloy material still needs further research.

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