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THE CHARACTERIZATION OF SILVER COATING ON THE SURFACE OF TIN BRONZE BY ELECTRO-SPARK DEPOSITION

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Silver, as a soft material, is used in the construction of bearings that carry high loads and high speeds, and has good lubrication characteristics, mechanical properties and corrosion resistance. There are many methods of forming a suitable coating, but the process of applying Ag coating to the surface of a tin-bronze bearing sleeve using electrospark deposition (ESD) technology to improve operating conditions has not been sufficiently described. In the article the investigated coating is obtained on a tin bronze substrate, which was formed as a result of ESD with the use of silver as a soft antifriction material. The morphology, composition and properties of the coating were studied. The Ag coating on the surface of tin bronze that was formed by alternately electro-spark deposition applying the soft material of silver. The analysis of deposition on mass transfer, roughness, thickness, surface morphology, elemental composition and tribological properties of the Ag coating were investigated by electronic scales, 3D optical profilometers, scanning electron microscopy (SEM), energy dispersion spectrum (EDS) and tribometer. The results show that the soft material coating of silver is dense, uniformly distributed and metallurgical fusion with the substrate. The coating of silver was deposited on the surface of tin bronze by electro-spark deposition. The optimal process parameter was obtained as follows: the voltage is 60V, the duty cycle is 25%, the efficiency is 1min/cm^2. Under the optimal process parameters, the mass transfer is 25.0mg, the surface roughness of the Ag coating is 15.46μm and the thickness is 15μm. In particular, the layer obtained under the optimal process parameters reduces surface micro-cracks and has a relative smooth and dense surface with good integrity. The Ag coating have a good metallurgical bonding with the substrate, and the microstructure of the deposition is compact. Due to the rapid heating and cooling of the substrate surface by ESD technology, the grains in the deposition layer are very dense, refined, uniformly distributed. The tribological properties of the coating in dry friction show that the lower resistance is exhibited by the Ag coating deposited using the soft antifriction material. The surface friction coefficient is stable after running-in, and becomes stable throughout the test and the minimum friction coefficient of the Ag coating is about 0.31 after running-in stage. The wear mechanism of the Ag coating is dominated by plastic deformation, abrasive wear and slight polishing. Plastic deformation and abrasive wear dominated on the relatively soft Ag coating. Silver and copper have very good wettability, which is conducive to improving the metallurgical bonding performance between metals during ESD. However, the performance of silver as antifriction material coating needs to be further improved.

Key words: *coating, surface, electro-spark deposition (ESD), soft material, tribological properties.*

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Introduction

The bearing tin bronze alloys exhibit better mechanical properties as compared with the Babbitt. Analyzing of their work has shown that the damageability of the bronze pads is exposed in the form of constrained running, high wear and high probability of scoring (Manu et al., 2021; Wang et al., 2018). Thus, there is need to provide for the bronze bearing pads with special coating improving the running conditions.

Tin bronze has good thermal conductivity and can effectively eliminate the heat generated by friction as a substrate material (Tarel'nik et al., 2017; Chen et al., 2021). Soft metal silver is used in the design of bearings bearing high loads and high speeds and has good lubrication performance, mechanical properties and corrosion resistance (Yuan et al., 2020). Silver and copper have very good wettability, which is conducive to improving the metallurgical bonding performance between metals during ESD.

There are many methods to prepare the related coating, but there are few reports on how to deposit the Ag coating on the surface of tin-bronze bearing bush by electro-spark deposition (ESD) technology to improve the operating conditions.

The coating of the tin bronze surface that was formed by ESD applying the soft antifriction material of silver. The analysis of morphology, composition and properties of the coating were investigated.

Materials and research methodology

The material QSn10-1(Cu 89.10%, Sn 9.38%, P 0.72%, Others 0.80%) was cut into size 29mm*25mm*4mm as the substrate. Silver (Ag99.99%) was used to make 3mm in diameter for electro-spark deposition electrode.

The surface of the substrate and the electrodes was ground on silicon carbide grinding papers of different grain size (400, 600, 800, 1200 and 1500 grit) and the roughness of the surface is not greater than 1μm. Prior to deposition of the coating, the substrates and electrodes were cleaned in anhydrous ethanol for 20 minutes by ultrasonic cleaner.

The ESD machine HMT-9500 has a control panel to change the electrical parameters including ESD voltage (20V-100V), duty cycle (20%-100%), rotation speed (150r/min-880r/min) and frequency (50Hz-500Hz). The ESD machine has the ground attachment, the shielding gas outlet and the applicator attachment. The rotation direction can be controlled on the applicator.

Travel speed in both cases was 2mm/s. The rotation speed of the layers was 550r/min and the frequency was 400Hz. Deposition was carried out using a hand-held gun at room temperature with the argon gas (Ar 99%) protection (10L/min flow rate), which avoids contamination of the deposit zone by interstitial elements such as oxygen or nitrogen.

The electro-spark deposition process parameters (electrodes, voltage, duty cycle and efficiency) are shown in Table 1.

Table 1

The ESD parameters of the Ag coating

Specimens	Electrodes	Voltage (V)	Duty cycle (%)	Efficiency (min/cm^2)
1#	Ag	40	20	1
2#	Ag	60	25	1
3#	Ag	80	30	1

The mass transfer data were constructed in weighing the specimens on a Mettler Toledo AL204 balance with an accuracy of 0.1 mg.

Surface roughness and topography measurements were made using 3D optical profilometers of Bruker Contour GT-k1.

ESD treated surface morphology and wear scars were analysed using scanning electron microscopy (SEM) of FEI Quanta 200.The element composition on the surface of the Ag coating was characterized by energy dispersion spectrum (EDS) built into SEM.

Samples for the microstructural analysis were prepared from the cross sections of Ag coating block and mounted in bakelite. After polishing and cleaning, corrosion was applied with 4% nitric acid alcohol. ESD treated cross section morphology of the Ag coating was analysed using metallographic microscopy LECIA DMi8 M.

An assessment of tribological properties was performed in the ball-on-plate reciprocating rig on aMWF-500tribometer. The study is to investigate tribological properties of ESD layers under dry friction conditions. The test temperature was 25°C. The low sliding velocity of 20mm/s was chosen to ensure boundary lubricating conditions and was maintained constant for all the stripes. The track length was 6 mm. The 8 mm diameter bearing steel (GCr15) ball was used as counter-face. The applied loads were 5N, 10N and 15N. For the initial 600 seconds, the applied load was 5N, the following 600 seconds, have more load of 10N, and then to 15N for the final 600 seconds.

Results and analysis

In this study, the analysis of deposition on mass transfer, roughness, and thickness of the Ag coating were investigated, as shown in Table 2.

The electro-spark deposition coating is the result of gradual accumulation through multiple discharge and a large number of deposition points (Wang et al., 2021). The mass transfer is usually regarded as an important index to evaluate ESD (Zhang et al., 2021). At the beginning of deposition, the coating mass increases most obviously. With the increase of deposition time, the mass transfer of electrode to substrate gradually decreases. Finally, with the increase of deposition time, the mass of substrates tops increasing. This is because with the increase of deposition time, the content of oxide or nitride on the surface of the coating increases, the residual stress on the surface increases, the binding force decreases, and the material is more likely to splash during discharge, which impedes the mass transfer in the process of ESD.

In this study, a precision electronic balance with an accuracy of 0.1mg was used to measure the samples and calculate the mass added to the substrate after ESD, as shown in Table 2. From the point of spark discharge rule, the larger of the discharge energy, the mass of the more increase (Umanskyi et al., 2020; Hong et al., 2017), and Table 2 shows that the increase of the mass as the energy increases. When the voltage is 40V, the duty cycle is 20%, the efficiency is 1min/cm2, the minimum value of mass transfer is 16.8mg. When the voltage is 80V, the duty cycle is 30%, the efficiency is 1min/cm2, the maximum value of mass transfer is 32.3mg.

The Bruker Contour GT-K1 3D optical profilometers was used to observe the surface of the deposition layer and measure the surface roughness. As can be seen from Table 2, the roughness increases with the increase of deposition energy. When the voltage is 40V, the duty cycle is 20%, the efficiency is 1min/cm2, the minimum value of the surface roughness is 11.09μm. When the voltage is 80V, the duty cycle is 30%, the efficiency is 1min/cm2, the maximum value of the surface roughness is 23.84μm.

The surface roughness of the Ag coating is not only affected by the deposition parameters, but also affected by the operation technology, the mechanical accuracy of the welding torch and the properties of the deposited materials.

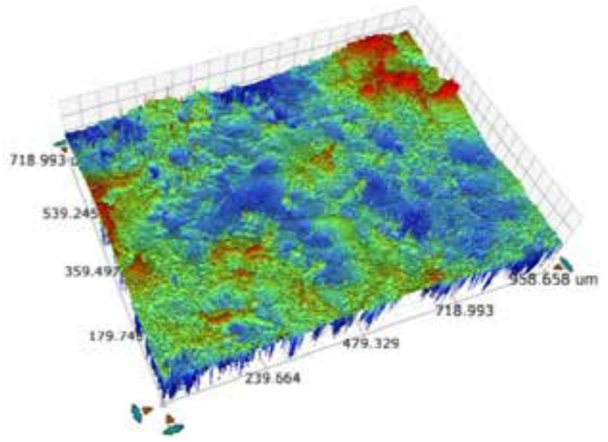
The measured results of the coating surface topography and profile are shown in Fig. 1. It can be seen from the figure that, Fig. 1, **a**, Fig. 1, **b** and Fig. 1, **c**, the surface topography gradually becomes rough, and the change of surface profile curve gradually increases.

The thickness of the Ag coating is the most important index of ESD. As can be seen from Table 2, the coating thickness increases with the increase of deposition energy. When the voltage is 40V, the duty cycle is 20%, the efficiency is 1min/cm2, the minimum value of the thickness is 9μm. When the voltage is 80V, the duty cycle is 30%, the efficiency is 1min/cm2, the maximum value of the thickness is 21μm.

Table 2

The mass transfer, roughness and thickness characteristics of the Ag coating

Specimens	Electrodes	Mass transfer(mg)	Roughness R_a (μm)	Thickness (μm)
1#	Ag	16.8	11.09	9
2#	Ag	25.0	15.46	15
3#	Ag	32.3	23.84	21



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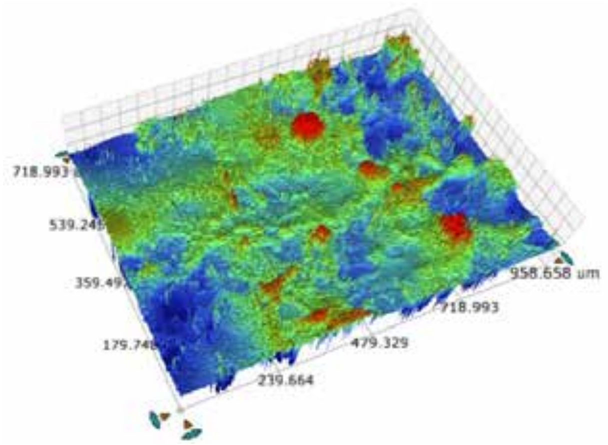

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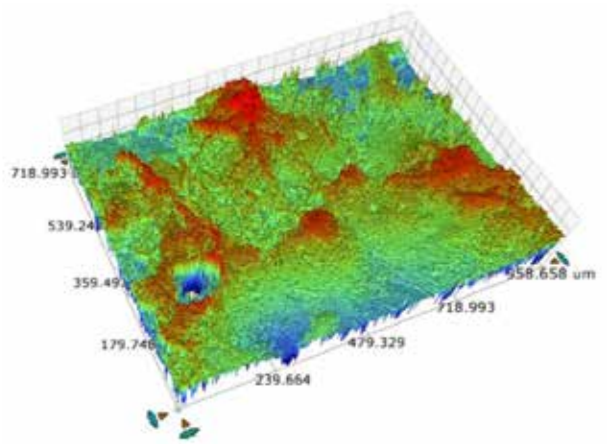

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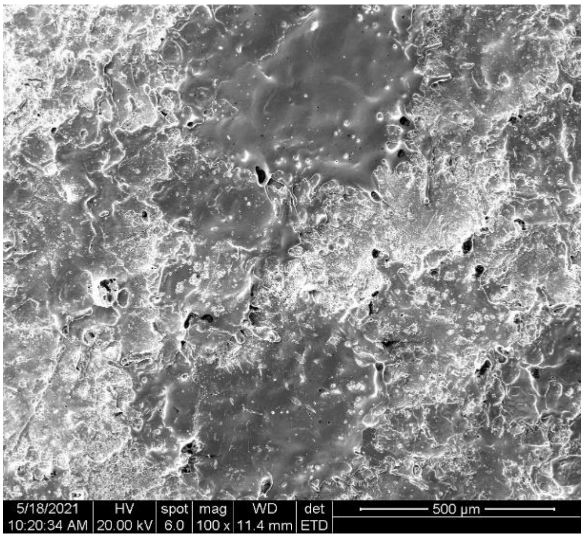
Figure 1. The surface topography and profile of the Ag coating (a-Specimen 1#, b-Specimen 2#, c-Specimen 3#)

The morphology of the Ag coating surface is shown in Fig. 2. It can be seen from the figure that the surface of the deposited coating is sputtering stacking, which is formed by the superposition of many irregular small droplet spots melted by continuous pulse discharge. There are a few microcracks on the surface of the Ag coating, which tend to



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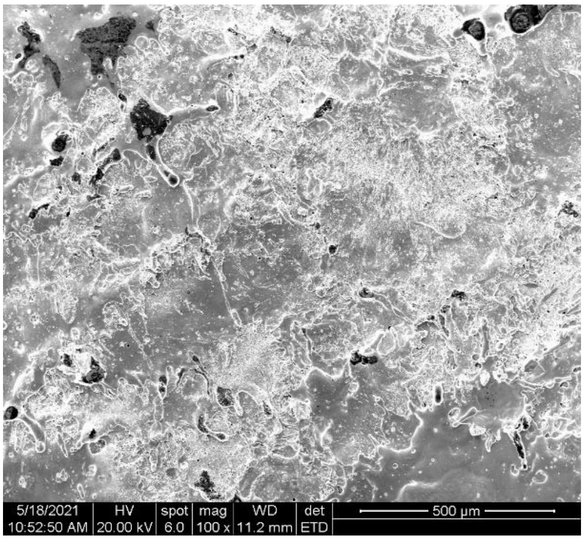

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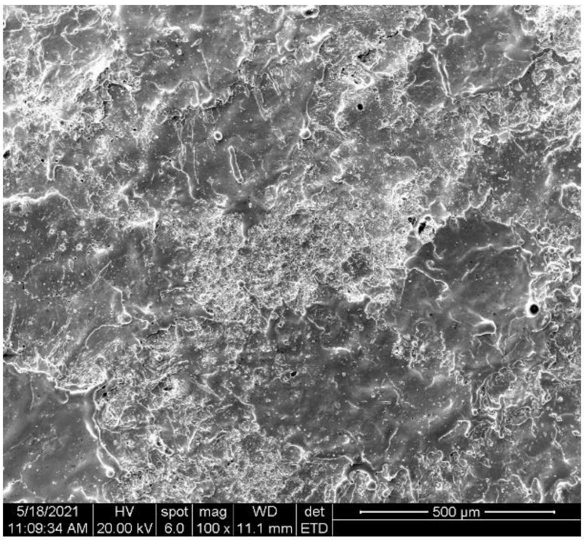

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Figure 2. The morphology of the Ag coating surface (a-Specimen 1#, b-Specimen 2#, c-Specimen 3#)

propagate along the direction perpendicular to the surface of the coating. This is due to the rapid heating and cooling in the process of spark discharge, the residual thermal stress in the coating will exist, leading to the initiation of micro-cracks, and Ag with good plasticity can play a role in relieving the thermal stress, thus reducing the number of cracks. The multilayer structure with a low modulus ratio contributed to reduced stress concentration in harder sub-layer, thereby inhibiting crack initiation.

After deposition, only simple grinding is needed to meet the requirements of surface roughness. The prepared coating surface has a small amount of ferrous metal oxides due to oxidation, which is caused by the oxidation of copper in bronze alloy. It can also be seen from Fig. 2 that the surface of Specimen 1# in Fig. 2, **a** has dense discharge spots and more rough surfaces. With the increase of discharge energy, discharge spots and smooth surfaces increase. That's because the higher the energy, the more molten the metal at the interface, the more fluid it is.

The element composition on the surface of the Ag coating was characterized by energy dispersion spectrum (EDS) in Table 3. As can be seen from the table, with the increase of discharge energy, the content of elements on the surface of the sample changes little and the copper content is relatively high which indicates that the coating thickness is not too thick, and the good wettability between silver and copper can make the metallurgical combination better.

Table 3

The elemental composition of the Ag coating surface

Specimens	P(%)	Cu(%)	Ag(%)	Sn(%)
1#	0.29	40.74	56.46	2.51
2#	0.19	38.14	59.60	2.06
3#	0.18	45.31	51.09	3.41

Electro-spark deposition technology can effectively change the surface of the physical and chemical properties, mechanical properties, so that the tribological properties of the surface changes, which has special properties (Tarelnyk et al., 2018; Cao et al., 2017; Wei et al., 2018).

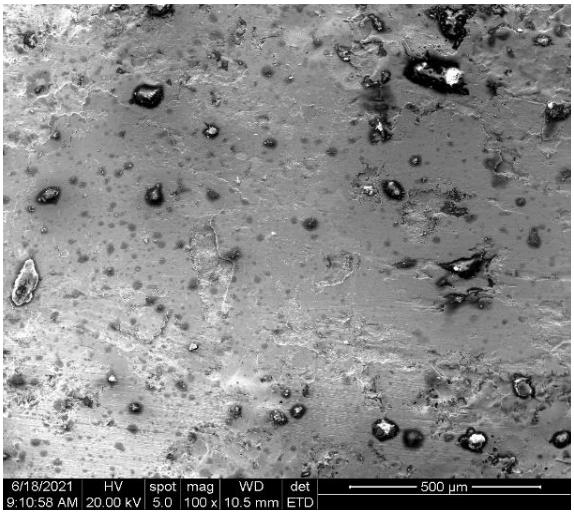
Table 4 compares the evolution of the coefficient of friction at the applied loaded of 5N, 10N and 15N of the ESD modified samples sliding against a GCr15 steel ball in air. For the initial 600 seconds at load of 5N of Specimen 1#, the friction coefficient with an average value of about 0.33. The following 600 seconds at load of 10N, the friction coefficient is about 0.24. And then to 15N for the final 600 seconds, the friction coefficient is about 0.35. The friction coefficient of the coating after running-in is slightly larger mainly because of the thinner coating. For the initial 600 seconds at load of 5N of Specimen 2#, the friction coefficient with an average value of about 0.69. The following 600 seconds at load of 10N, the friction coefficient is about 0.36. And then to 15N for the final 600 seconds, the friction coefficient is about 0.31. The friction coefficient of the coating is slightly larger at the beginning of the run-in mainly because of the increase of the surface roughness of the coating. For the initial 600 seconds at load of 5N of Specimen 3#, the friction coefficient with an average value of about 0.20. The following 600 seconds at load of 10N, the friction coefficient is about 0.22. And then to 15N for the final 600 seconds, the friction coefficient is about 0.31. The reason why the friction coefficient of the coating is small at the beginning of run-in is that the coating thickness increases and the surface is more prone to plastic deformation. The investigation of the tribological properties of the coating in dry friction show that the lower resistance is exhibited by the coating deposited using the soft antifriction material.

From the evolution of the coefficient of friction of the tin bronze substrate with the Ag coating, it is clear that wear process indicated is rather complicated because of the influence of different surface topography and chemical composition during running-in phase (Zhou et al., 2022; Tarelnyk et al., 2012; Xue et al., 2021). For ESD layers, at the beginning of steady stage its friction coefficient shows to some extent direct response to surface roughness and the coating thickness. Because GCr15 with high hardness produce material loss of soft antifriction Ag coating counterpart (with relative low hardness) through dominant abrasion mechanism. With the generation of tribofilm, abrasion of coating-GCr15 sliding couples is transferred to interfacial sliding. Similar to other sliding couples, the steady-state fiction coefficients become more or less independent of surface roughness. The friction coefficient is stable after running-in, and becomes stable throughout the test.

The surfaces of wear traces were analysed in order to understand the friction and wear resistance mechanisms of the coating. The wear scars of the tin bronze substrate with the Ag coating after tribological testing are shown in Fig. 3. It was found from analysis of wear scars in Fig. 3, **a** that the wear mechanism of the Specimen 1# is dominated by abrasive wear and fatigue delamination. The friction surface of Specimen 1# is smooth, the wear marks are fine and shallow, and some materials are spalling and forming spalling pits. The wear mechanism of the Specimen 2# is dominated by abrasive wear and plastic deformation that was found from analysis of wear scars in Fig.3, **b**. However, it can be seen in Fig. 3, **c** that the soft antifriction coating may effectively restrain fatigue delamination, showing plastic deformation, abrasive wear and slight polishing. Plastic deformation and abrasive wear dominated on the relatively soft Ag coating. The initial surface microgeometry was changed during load application and its surface became smooth with fine shallow scratches observed after the wear test. After the smooth surface was formed, the friction and wear stabilised.

The elemental composition of the Ag coating surfaces after tribological testing are shown in Table 5. By comparing Table 3 and Table 5, it can be found that copper content on the surface of specimen 1# decreases from 40.74% to 38.29%, silver content decreases from 56.46% to 46.52%. The tin content on the surface changed little before and after the friction test. In addition, carbon and oxygen elements were detected on the surface, indicating the formation of carbides and oxides after surface wear.

By comparing Table 3 and Table 5, it can be found that after friction test, copper content on the surface of specimen 2# increases from 38.14% to 45.45%, silver content decreases from 59.60% to 46.32%. The tin content on the



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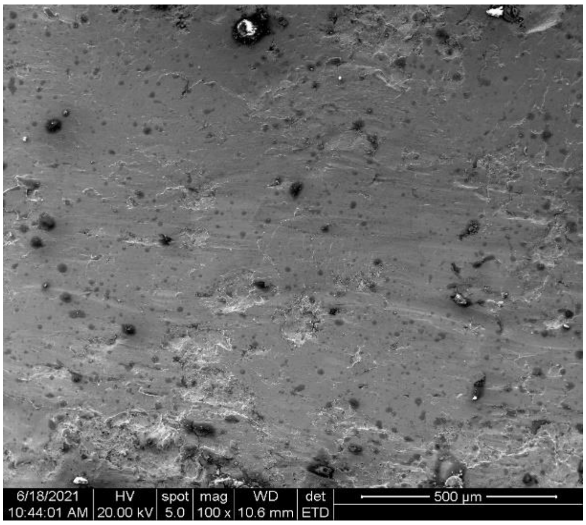

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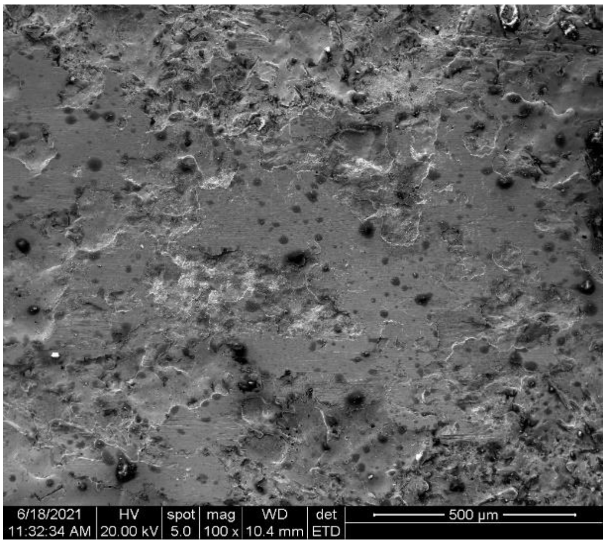

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Figure 3. The wear scars of the tin bronze substrate with the coating after tribological testing (a-Specimen 1#, b-Specimen 2#, c-Specimen 3#)

surface changed little before and after the friction test. In addition, the low content of carbon and oxygen detected on the surface indicates that due to the good stability of silver, less carbides and oxides are produced after surface wear.

By comparing Table 3 and Table 5, it can be found that copper content on the surface of specimen 3# decreases from 45.31% to 41.48%, silver content decreases from 51.09% to 34.72%. The contents of tin on the surface of specimen 3# have little change after friction test. In addition, the higher carbon and oxygen elements content detected on the surface indicates that due to the poor stability of tin and copper, more oxides are generated after ESD. However, due to the large surface roughness, the oxides and carbides on the surface have not been completely removed.

Table 4

The friction coefficient during coating tests at loads of 5 N, 10 N, and 15 N

Specimens	5N	10N	15N
1#	0.33	0.24	0.35
2#	0.69	0.36	0.31
3#	0.20	0.22	0.31

Table 5

The elemental composition of the Ag coating surface after tribological testing

Specimens	C(%)	O(%)	Cu(%)	Ag(%)	Sn(%)
1#	7.63	4.76	38.29	46.52	2.81
2#	1.03	5.52	45.45	46.32	1.68
3#	11.27	11.05	41.48	34.72	1.48

Conclusions

The following conclusions can be drawn from observed results:

(1) The coating of silver was deposited on the surface of tin bronze by electro-spark deposition. The optimal process parameter was obtained as follows: the voltage is 60V, the duty cycle is 25%, the efficiency is 1min/cm^2. Under the optimal process parameters, the mass transfer is 25.0mg, the surface roughness of the Ag coating is 15.46μm and the thickness is 15μm. In particular, the layer obtained under the optimal process parameters reduces surface micro-cracks and has a relative smooth and dense surface with good integrity.

(2) The Ag coating have a good metallurgical bonding with the substrate, and the microstructure of the deposition is compact. Due to the rapid heating and cooling of the substrate surface by ESD technology, the grains in the deposition layer are very dense, refined, uniformly distributed.

(3) The tribological properties of the coating in dry friction show that the lower resistance is exhibited by the Ag coating deposited using the soft antifriction material. The surface friction coefficient is stable after running-in, and becomes stable throughout the test and the minimum friction coefficient of the Ag coating is about 0.31 after running-in stage.

Silver and copper have very good wettability, which is conducive to improving the metallurgical bonding performance between metals during ESD. However, the performance of silver as antifriction material coating needs to be further improved. The wear mechanism of the Ag coating is dominated by plastic deformation, abrasive wear and slight polishing. Plastic deformation and abrasive wear dominated on the relatively soft Ag coating.

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ХАРАКТЕРИСТИКА ПОКРИТТЯ ЗІ СРІБЛА НА ПОВЕРХНІ ОЛОВ'ЯНОЇ БРОНЗИ, СФОРМОВАНОГО МЕТОДОМ ЕЛЕКТРОІСКРОВОГО ОСАДЖЕННЯ

Срібло як м'який матеріал використовується у конструкції підшипників, які несуть високі навантаження і високі швидкості, і має хороші характеристики змащення, механічні властивості та стійкість до корозії. Існує багато методів формування відповідного покриття, але не достатньо описаний процес нанесення Ag-покриття на поверхню олов'яно-бронзової втулки підшипника за допомогою технології електроіскрового осадження (ESD) для покращення умов експлуатації. У статті досліджене покриття, отримане на підкладці з олов'янистої бронзи, яке було сформоване в результаті ESD із застосуванням срібла як м'якого антифрикційного матеріалу. Досліджено морфологію, склад і властивості покриття.

Приведено технологію формування Ag-покриття на поверхні олов'яної бронзи, яке утворене шляхом почергового електроіскрового осадження (ESD) нанесенням м'якого матеріалу срібла. Аналіз впливу осадження на масообмін, шорсткість, товщину, морфологію поверхні, елементний склад і трибологічні властивості Ag-покриття досліджували за допомогою електронних ваг, 3D-оптичних профілометрів, скануючої електронної мікроскопії (SEM), спектру енергетичної дисперсії (EDS) та трибометра. Покриття зі срібла наносили на поверхню олов'яної бронзи електроіскровим напиленням. Оптимальний параметр процесу був отриманий таким чином: напруга 60 В, робочий цикл 25%, продуктивність 1 хв/см^2. За оптимальних параметрів процесу масообмін становить 25,0 мг, шорсткість поверхні Ag-покриття – 15,46 мкм, а товщина – 15 мкм. Зокрема, шар, отриманий *за оптимальних параметрів процесу, зменшує поверхневі мікротріщини і має відносно гладку і щільну поверхню з хорошою цілісністю. Ag-покриття має хороший дифузійний зв'язок із підкладкою, а мікроструктура осадження компактна. Завдяки швидкому нагріванню та охолодженню поверхні підкладки за технологією ESD зерна в шарі осадження дуже щільні, витончені, рівномірно розподілені. Трибологічні властивості покриття при сухому терті показують, що менший опір демонструє Ag-покриття, нанесене з використанням м'якого антифрикційного матеріалу. Коефіцієнт поверхневого тертя стабільний після обкатки і стає стабільним протягом випробування, а мінімальний коефіцієнт тертя Ag-покриття становить приблизно 0,31 після етапу обкатки. У механізмі зношування Ag-покриття переважають пластична деформація, абразивне зношування та незначне полірування. На відносно м'якому Ag-покритті переважали пластична деформація та абразивне зношування. Срібло і мідь мають дуже хорошу «змочуваність», що сприяє покращенню ефективності дифузійного зчеплення між металами під час електростатичних розрядів. Однак ефективність застосування срібла як антифрикційного покриття потребує подальшого покращення.*

Ключові слова: *покриття, поверхня, електроіскрове осадження (ESD), м'який матеріал, трибологічні властивості.*

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