Fretting wear behavior of aluminum coatings

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Received 10/12/2022, Accepted, 15/3/2023, Published 15/4/2023

The aluminum bronze coating is a type of soft solid lubricant film with excellent performance. In this work, to improve the wear resistance and tribological behavior of the aluminum alloy, the aluminum bronze coatings were prepared on aluminum alloy substrates using the High-Velocity Oxygen Fuel (HVOF) system. Fretting wear tests were performed on the coatings at 200 °C with different frequencies to analyze the wear behavior. The worn surface was characterized by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). The results showed that as the frequency increased from 5 Hz to 15 Hz, the coefficient of friction increased from 0.653 to 0.929. It then decreased to 0.890 at 20 Hz. There was an overall trend of the coefficient of friction increasing and then decreasing. The worn surface’s morphology changed from pits to bulges. At a low frequency, the wear mechanism was abrasive wear with delamination. As the frequency increased, adhesive wear was observed and gradually became the dominant wear form. Oxidation occurred on the surface of the worn tracks caused by the high temperature and thermal effect of high-frequency micromotion. Due to the intensification of the oxidation phenomenon, oxidation films formed on the worn surface. The wear rate of the coating was significantly reduced. The oxide was identified as mainly CuO and Cu2O. The presented results confirmed that the aluminum bronze coating fabricated via HVOF exhibited a great resistance performance even at a high frequency.

Keywords: Aluminum coating; Frequency; Wear.
1. INTRODUCTION

Fretting wear is the result of pre-stress or a specific load being applied to the contact surface. The relative motion of two contact surfaces with very tiny amplitudes is produced by the interaction of external vibrations of the contact surface (generally, the displacement amplitude is in the order of microns) [1]. Fretting wear can result in material abrasion or the emergence and growth of fatigue cracks in engineering applications, which can then produce seizure, vibration, abrasion, or part fracture [2]. It is one of the main reasons for severe accidents involving mechanical parts.

Aluminum bronze, a novel type of bronze alloy, has received much attention for its engineering applications. Copper and aluminum are the main components of aluminum bronze. This alloy has great strength and ductility, excellent thermal conductivity, and outstanding wear and corrosion resistance [3]. Aluminum bronze is widely available for use in aerospace, electronic devices, and automotive manufacturing. It is commonly utilized as a wear-resistant material due to its outstanding friction and wear reduction qualities [4]. However, it costs more in commercial applications because of the higher price of copper-based alloys. As a result, aluminum bronze is fabricated for coating using surface engineering techniques. This not only takes advantage of the superior friction and wear resistance of aluminum bronze but also helps to reduce the amount of aluminum bronze needed contributing to reducing the price. For example, the typical nested gray cast iron cylinder liner was successfully replaced by aluminum bronze, which was employed by companies such as the General Electric Company (GE) in the US to provide a wear-resistant and anti-fretting-wear coating on the interior wall of aluminum alloy automotive engine blocks.

The advantages of thermal spraying technology as a typical method of coating manufacturing include low economic cost and excellent preparation efficiency for metallic coatings [5]. It includes primarily atmospheric plasma spraying (APS), arc spraying (AS) and high-velocity oxygen fuel (HVOF) spraying and cold spraying (CS). Each method has its characteristics. For example, APS is stable, and inert gas is typically employed as the working carrier gas during the spraying procedure. The coating oxidizes slowly since the sprayed powder has little interaction with the atmosphere [6]. CS is a solid-state coating deposition process, and no undesirable melting, oxidation, phase transformation, or grain growth occur in the incident particles [14]. Concerning the HVOF process, high-speed flame flow is used to impact particles onto the substrate and create a dense coating. Its benefits are low flame temperature, rapid flame flow, and high deposition efficiency [7]. In addition, HVOF retains the advantages of flame spraying, which fabricates wear-resistant coatings with low porosity, high bond strength to the substrate, and good wear resistance. Meanwhile, it also features high-velocity injection similar to CS, which enables the coating to maintain low oxidation and thermal decomposition [8].

Currently, many studies have been carried out on the wear behavior of aluminum bronze coatings. Alfredo Morales et al. [9] investigated the effect of gas pressure in flame spraying on the properties of aluminum bronze coatings. It has been demonstrated that increased feed pressure, lead to a higher impact velocity, which makes it easier to reduce porous structures and enhance plate adhesion, and is directly connected to coating hardness. The coating fabricated under the highest pressure, 345 kPa O2 and 97 kPa acetylene, had the lowest wear rate. This was related to the samples deposited with the highest impact velocity. Our previous research [17, 18] explored the optimal preparation parameters of aluminum bronze on aluminum alloy substrates via HVOF and studied the fretting wear behavior of the aluminum
bronze coatings at various temperatures. The coatings present excellent fretting wear properties. Literature [10] has investigated the microstructure, phase composition, microhardness, tribological properties, and corrosion resistance of cold sprayed aluminum bronze coatings on Mg-Li alloy. Compared to the Mg-Li alloy substrate, the aluminum bronze coating exhibits higher microhardness and wear resistance. Zhang et al [19] prepared aluminum bronze coatings using a hybrid process of electro-spark deposition (ESD) and ultrasonic surface rolling (USR). USR treatment improved the wear resistance of the ESD coatings. The fretting wear, however, is significantly influenced by friction conditions, especially by frequency.

Most of the studies have focused on the coating composition, sliding friction behavior, and fabrication of aluminum bronze coatings. However, the fretting wear behavior of aluminum bronze coatings has rarely been studied. Our previous studies have demonstrated that the use of HVOF for the fabrication of aluminum bronze has certain advantages and enables the coating to obtain good basic properties [9]. Therefore, fretting wear tests with different frequencies were carried out on aluminum bronze coating/aluminum alloy at 200 °C in combination with our previous good results of using HVOF for the fabrication of aluminum bronze coatings. This study aims to investigate the effect of frequency on fretting wear and understand the wear mechanism of aluminum bronze coatings.

2. EXPERIMENTAL

The aluminum bronze (Beijing General Research Institute of Mining and Metallurgy, China) used for spraying powder is a powder with complete spherical particles fabricated via the atomization comminuting process. Its particle size distribution is 16.6-47.7 μm. It consists mainly of 88.49wt%Cu, 10.34wt%Al, and 1.17wt%Fe. The morphology of the powder is shown in Fig. 1. The ZL114A (6.7wt%Si, 0.52wt%Mg, 0.15wt%Ti, and 92.63wt%Al) aluminum alloy with the size of Ø25.4 mm×6 mm was adopted as the substrate. The surface of the substrates was degreased, grit blasted, and preheated. The coating was then manufactured via HVOF with spraying parameters shown in Table 1. The K2 gun (GTV, Germany) with a flared nozzle was used for the process.
The coating was tested at 200 °C using a fretting wear system (SRV-IV, Optimal, Germany), with a Ø10 mm diameter GCr15 steel ball as the friction substrate. The experimental parameters were selected as a load of 10 N, displacement amplitude of 50 μm, and various frequencies of 5, 10, 15, and 20 Hz with 1250 s. According to the Mindlin model of the slip circle [5], the contact interface of the ball/plane contact of the fretting wear has two regions: the micro-slip region and the adhesion region. Meanwhile, the friction coefficient between the micro-slip and adhesion regions can be greater than 1. Therefore, during the experiment, if the friction coefficient was kept above 2 for more than 30 s, the equipment would start the protection device and automatically stop the experiment. The wear rate \( W \) is the wear volume \( V \) per unit friction distance \( L \) and unit load \( P \). It is calculated according to Equation 1, where \( V \) is the wear volume, \( P \) is the load, \( D \) is the displacement amplitude, \( f \) is the frequency, and \( t \) is the friction time. The wear volume is measured by a 3D profilometer.

The cross-section of the coatings was observed using a field-emission scanning microscope (FEI-SEM, Nova-Nono430, FEI) equipped with energy dispersive X-ray spectroscopy (EDS, Oxford INCAx-sight 6427). The phase composition of the powder and the coatings was determined using an X-ray diffractometer (D8-Advance, Bruker, Germany) with a step of 0.02 ° (Cu-Kα radiation, incident angle 3 °, a range of 10-90 °). The hardness was measured with a microhardness tester (MH-5D, Shanghai Hengyi Company) with a load of 300 g, for a dwell time of 15 s. The hardness values were measured at 10 random locations to obtain the average value. The porosity of the coatings was determined using the ImageJ software after some SEM pictures were randomly obtained. At least 15 measurements were taken for each sample to check the repeatability of the data. Regarding the GB/T 8642-2002 standard, the E-7 adhesive was selected to bond the two counterparts (Ø25.4x38 mm) and the sample, which were fixed under a certain load and placed in a drying oven at 180 °C for 3 h. The bonding strength of the coating and the substrate was measured via an electronic universal testing machine (GP-TS2000M, Shenzhen Gopin Company). The average value was obtained by

Figure 1 SEM morphology of the aluminum bronze powder.
taking 5 parallel specimens under the same experimental conditions.

The three-dimensional morphology of the coated samples after the fretting wear test was carried out using a profiler (DEKTAK XT, Bruker, Germany), to measure the volume of worn tracks. To further investigate the chemical composition, X-ray photoelectron spectroscopy (XPS, Thermo Fisher Nexsa, America) was conducted with an Al Kα (λ=1486.6 eV) X-ray source and an energy step of 0.05 eV.

3. RESULTS AND DISCUSSION

Fig. 2 shows the cross-sectional morphology, EDS analysis of the aluminum bronze coating and the XRD patterns of both the original powder and the as-sprayed coating. The aluminum bronze coating is uniform and dense, with good bonding to the substrate and a small number of holes randomly distributed inside the coating. The porosity of the coating was calculated at 0.10%, bonding strength at 61.63 MPa, and microhardness at 330.33 HV0.3, respectively. EDS analysis indicates that the coating has primarily Cu, Al, and Fe elements which are consistent with the elements contained in the powder.

According to the XRD patterns displayed in Fig. 2 (d), it can be seen that the main phase composition of the powder and the coating is confirmed as α phase (Cu solid solution) and β' phase (AlCu3-based solid solution), and no diffraction peaks of other phases were found [22]. It can be inferred that no significant oxidation occurred during the spraying process due to the low residence time of the particles inside the high-velocity flame. A significant reduction or even disappearance of the intensity of the diffraction peaks of the α and β’ phases in the coating, with the appearance of the "bun" peak, could be found in comparison to the intensity of the diffraction peaks. In the supersonic flame spraying process, the cooling rate of molten particles on the substrate or the surface of the deposited coating was faster, resulting in the generation of an amorphous phase.

The coefficient of friction is an important parameter in the fretting wear process, which can reflect the wear state of the sample and the counterpart at different stages of the wear process. The dynamic curve of the friction coefficient of the aluminum bronze coating and the average friction coefficient with different frequencies at 200 °C are illustrated in Fig. 3.
**Figure 2** Cross-sectional morphology (a-low magnification, b-high magnification) and the EDS analysis (c) of the aluminum bronze coating (4 elements: Cu, Fe, Al, O); XRD patterns of the original aluminum bronze powder and the coating (d).

**Figure 3** Friction coefficient curves (a) and statistics of friction coefficient (b) of all samples.
The early running-in stage, the increasing stage, and the steady stage are the main stages that the friction coefficient transitions through as time passes [23]. It can be seen in Fig. 3 (a) that the coefficient of friction varies considerably at different frequencies. Under the condition of 5 Hz, a lower coefficient of friction is observed. In the initial stage, it goes through a slow running and rising stage until it reaches a stable value and then slowly decreases. After that, the frequency coefficient rises steeply to reach a maximum value and then enters the next falling and rising cycle. The reason for this evolution is due to the protection of passivation film and pollution film on the coating surface. The coefficient of friction is very low under this protection in the early stage of the wear test. With the increase in frequency from 10 Hz to 20 Hz, the friction coefficients of aluminum bronze coated samples increased rapidly at the beginning when the abrasion was more intense due to the higher frequency. The friction coefficients in the stabilization stage are at an identical level, while the friction coefficient of the sample tested at the frequency of 15 Hz showed a tendency to increase with fluctuations. The average friction coefficient was calculated as shown in Fig. 3 (b). The value increases and then decreases with the increase of frequency. The testing sample under 15 Hz exhibits the highest average friction coefficient, indicating that the coating has suffered the most extensive wear.

Based on the results, it can be inferred that the frequency plays a dominant role in the friction coefficient during fretting wear. It was shown that more times of fretting friction for the test per unit time led to more severe abrasive wear and the increased friction coefficient of the samples with the increase in frequency from 5 Hz to 15 Hz. Due to the shearing and squeezing force generated by the GCr15 steel ball contacting the coating surface, under the lower frequency of reciprocating motion, the surface of the coating was destroyed and abrasive wear occurred, resulting in a slow increase in the coefficient of friction [24]. During this period, the two-body contact (coating and counterpart) was the main contact mechanism on a worn surface, and the particles of the broken coating were peeled off.

In the specific case of 15 Hz, it is in a transitional state, where abrasive wear and the generation of an oxide film coexist. The continuous accumulation of abrasive debris formed a laminar third body under the extrusion of the abrasive counterpart, which transformed from a two-body contact to a three-body contact within the worn surface [24, 25]. When the generation of abrasive debris and the formation of the third body reached a dynamical equilibrium, the coefficient of friction changed to a stable pattern. However, when the equilibrium was broken, the third body would be destroyed under shearing and squeezing forces to form new abrasive debris [23]. When the worn surface transitions to a two-body contact, the fluctuation of the friction coefficient will decrease and enter the next fluctuation cycle. This is the reason for having fluctuations in the coefficient of friction at the frequency of 15 Hz. Moreover, there was no oxide film formation when the adhesion effect increased between the counter-abrasive portions and the softened coating with abrasive particles, promoting constant growth of the friction coefficient. Combined with the friction coefficient at 15 Hz frequency, it can be concluded that 15 Hz greatly affects the friction wear of the coating. At 20 Hz, the abrasive debris under repeated friction and extrusion of the counterpart can be formed into an oxide film [26], which offers lubrication and protection to the coating. It leads to a smoother friction coefficient curve and a decrease in the average friction coefficient for the coating tested at the frequency of 20 Hz.

The worn tracks were scanned with a 3D profiler to observe the morphology of the worn surface, as shown in Fig. 4 (a). The depth of the worn tracks was also measured along the white dashed line, and the result is given in Fig. 4 (b). The wear rate was further calculated
using the volume of the worn tracks, which is illustrated in Fig. 4 (c).

**Figure 4** 3D profiles (a) and depth (b) of fretting wear scars; wear rate of all samples (c).

Under the test conditions of 5 Hz, 10 Hz, and 15 Hz, the worn tracks exhibit distinct pits. The deepest worn track is observed under the condition of 5 Hz, where the pits are more elongated and extend along the direction of wear. When the frequency increases to 20 Hz, the worn tracks appear as irregularly shaped bumps. By comparing the wear rate at different frequencies, it can be found that the wear rate decreases with the increase in frequency. The minimum wear rate is detected at the frequency of 20 Hz.

To further analyze and determine the wear mechanism, the overall morphology of the worn tracks was observed and the distribution of oxygen elements on the worn surface was obtained. It shows that there a great deal of fine abrasive debris and a small number of blocky debris on the surface at 5 Hz, while both sides around the center of the worn tracks exhibit traces of plowing along the friction direction. The abrasion between the contact surfaces is
intense at 5 Hz, and wear conditions are aggravated by the continuous peeling off of abrasive debris in the contact region. The wear mechanism in the region is primarily abrasive wear with delamination [27], therefore, its wear rate is the highest. However, with the increase in frequency, the abrasive debris in the contact region was squeezed, leading to the formation of many films [28] on the worn surface and much abrasive debris being expelled from the worn tracks. It can be observed at higher magnification that the scratches in the film along the friction direction are obviously on the worn surface of the samples from 10 to 20 Hz, caused by severe sliding between the worn track surface and the grinding ball. Meanwhile, the films of the 10 Hz and 15 Hz samples showed traces of peeling and were accompanied by a small amount of fine abrasive debris. The film is beneficial to reducing abrasion, so the wear rate decreases compared to that tested at the frequency of 5 Hz. In combination with the 3D profile, it can be seen that the surface of the worn tracks is quite rough. The wear mechanism comprises abrasive wear and adhesive wear. Instead, they remain as unbroken films with a relatively flat surface and fine scratches along the friction direction. The large films play a significant role in lubricating and protecting the worn tracks, as evidenced by the extremely low wear rate at 20 Hz.

It is possible that the generation of films may be due to the oxidative wear caused by thermal effects in the worn tracks. To compare and analyze the distribution of oxygen elements on the surface of the worn tracks, EDS mapping of O elements was conducted. It can be seen that the oxygen elements are mainly detected on the worn tracks and are less distributed in the surrounding areas without fretting wear. It was concluded that oxidative wear occurred on the worn track during fretting wear [25]. The third-body film, an oxide with a protective effect against wear, only substantially reduced the wear rate in the case of oxidative wear and adhesive wear.

To further characterize the oxide, XPS analysis was conducted on the surface of the worn track that was tested at the frequency of 20 Hz. For the Cu2p3/2 signal, three small peaks can be analyzed as (932.6±0.2) eV, (933.8±0.2) eV, and (935.2±0.2) eV [29, 30]. The two peaks (953.8±02) eV and (954.6±02) eV were observed in the Cu2p1/2 signal. Among them, the peaks (932.6±0.2) eV and (953.8±02) eV [29, 31] are typical peaks of Cu2O. It can be concluded that Cu2O is contained in the worn tracks. The main peak fitted by the remaining two peaks in the Cu2p3/2 signal and the peak of (954.6±02) eV in Cu2p1/2 are typical peaks of CuO, while the difference between them is nearly 20 eV [32]. Two satellite peaks also existed in Cu2p, which are signatures of Cu^{2+} and are not observed in Cu and Cu^+. The presence of the satellite peak indicates that Cu^{2+} (CuO) must be present in the worn tracks. This also suggests that both CuO and Cu2O are present in the worn tracks. According to the XPS results, it can be deduced that oxidative wear occurs on the surface of the worn tracks during fretting wear. Metal Cu in the fine abrasive debris was transformed into Cu^{2+} and Cu^+, and oxidation generated an oxidized friction film containing CuO and Cu2O, which played a protective and lubricating role and thus reduced the wear rate.

The wear process and mechanism of the aluminum coating under the test condition mentioned above are given. At stage I, with pressure on the steel ball, a small displacement movement occurs on the coating surface. Under low-frequency conditions, abrasive wear and delamination are predominant within the worn tracks. The material of the coating surface was continuously destroyed by shearing force and squeezing pressure and then abrasive debris formed, which resulted in a two-body contact with the counterpart. Subsequently, a significant number of particles peeled off from the coating surface, resulting in deeper wear pits with a few cracks. As the frequency increases, it is inferred that the overall temperature rises due to
the increase in the times of friction per unit time on the contact surface between the counterpart and coatings. Softening occurs on the surface material [33], and the softened fine abrasive debris forms a laminated third body under the repeated squeeze of the counterpart. In this way, the abrasion is transformed into adhesive wear within the worn tracks. The abrasive debris generated in the previous stage is squeezed to form films, which partly detach from the surface of the worn tracks, resulting in a larger area and depth of wear pits. The worn track contains films and a small number of abrasive debris. This is caused by the adhesion phenomenon between the counterpart and the laminated third body formed by the abrasive debris adhering to the coating surface. Meanwhile, frequency caused an increased in the temperature of the contact surface between the counterpart and the coating [34, 35], as well as a decrease in the hardness and an increase in the plasticity of the worn surface. The adhesion effect increased between the counterpart and the coating, resulting in a higher coefficient of friction. It was also proved by the fluctuating friction coefficient and the highest average friction coefficient at the frequency of 15 Hz. The abrasive debris was no longer observed in the marks; only extensive films with some extended cracks were detected. The combination of the environmental temperature and the frictional heat generation in the area of the worn tracks caused the abrasive debris in the repeated friction and squeezing to form a film of oxide [21, 36]. The composition of the oxide film is primarily CuO and Cu2O, both playing a role in lubrication and friction reduction in the late stage of friction. The wear mechanism at this stage is predominantly adhesive wear and oxidative wear.

4. CONCLUSIONS

The aluminum bronze coating was fabricated successfully via HVOF, which exhibited a great resistance performance to fretting wear even at a high frequency. Under the condition of 200 °C and keeping other parameters constant, the coefficient of friction of the aluminum bronze coating increased from 0.653 to 0.929 with the increase of frequency from 5 Hz to 15 Hz. It then decreased to 0.890 when the frequency increased to 20 Hz. The maximum coefficient of friction was 0.929 monitored at the frequency of 15 Hz. The wear rate decreased from 24.08 to 0.3 (×10^{-9} mm^3·n^{-1}·m^{-1}) with the increase in frequency from 5 Hz to 20 Hz. The wear mechanism was dominated by abrasive wear with delamination at low frequencies (5 Hz and 10 Hz). When the frequency increased to 15 Hz and 20 Hz, adhesive wear became dominant, while oxidation wear became gradually more intense. Under the condition of the frequency of 20 Hz, it was revealed that the oxide film consists of CuO and Cu2O, which have the effect of protection and lubrication and lead to reduced wear rates.

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Proceedings 27 (2020) 2191