Effect of Pulse Frequency on Phase Composition and Properties of Amorphous Zirconium Alloy Micro-arc Oxidation Coating

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Abstract. The micro-arc oxidation coating was prepared on the surface of the amorphous zirconium sheet, and the influence of frequency on the micro-arc oxidation coating of the Zr-based amorphous alloy was studied. The results show that the change of the frequency of the electrical parameters of the micro-arc oxidation in the silicate micro-arc oxidation bath will promote the transformation of the t-ZrO₂ phase to the m-ZrO₂ phase in the coating; the frequency affects the gap, uniformity and thickness of the coating. When the frequency is 400 Hz, the coating surface has small voids and no cracks, and the thickness reaches a maximum of 15 μm. With the increase of frequency, the weight loss of the amorphous zirconium micro-arc oxidation coating first decreases and then increases. The wear resistance can be improved.

1. Introduction
In the amorphous alloy system, due to the glass forming ability of the zirconium-based amorphous alloy[1]. The large supercooled liquid region, and the excellent mechanical properties[2], it has attracted the attention of the materials staff [3-6]. At present, the research of amorphous alloys has become a research hotspot in the field of materials science. Zr-based amorphous alloys have been successfully applied, such as golf club heads, aerospace machinery, solar wind collectors, other electronic components and other large-scale forming processes. Zr₆₈Nb₄.₅Cu₁₂Ni₁₁Al₄Y₀.₅ amorphous alloy is mainly used for shaft parts in the consumer electronics industry to replace the commonly used 40Gr and 45 steel quenched and tempered materials. The use of amorphous zirconium instead of medium carbon alloy steel is the development direction. However, in the service process of amorphous zirconium, friction and wear will occur in the relative movement of Zr-based amorphous alloy components, and the wear resistance needs to be improved to meet the requirements of electronic, mechanical parts and special environments for material applications. Therefore, in order to improve the wear resistance of amorphous zirconium alloys while still maintaining the good properties of the material itself, surface engineering technology has become the best choice for solving the wear resistance of amorphous zirconium alloys.

In this paper, ultrasonic micro-arc oxidation surface modification technology is used to form an autogenous ceramic coating on the surface of the amorphous alloy Zr₆₈Nb₄.₅Cu₁₂Ni₁₁Al₄Y₀.₅ to improve the wear resistance of the zirconium-based amorphous alloy. Frequency is one of the main influencing factors of micro-arc oxidation technology. Zhang Ruifeng et al.[7] studied the influence of frequency on magnesium alloy micro-arc oxidation coatings. With the increase in frequency, the porosity of the coatings is reduced and the density is better. The electrochemical corrosion resistance...
is significantly improved. Sun Changfei et al.[8] studied the influence of frequency on the ceramic layer of aluminum alloy micro-arc oxidation thermal barrier. When the frequency is lower than 800 Hz, the thickness of the ceramic layer has an approximate linear and inverse relationship with the power frequency. If the frequency is higher than 800 Hz, the frequency has an effect on the ceramic layer. The thickness effect is not obvious. This paper studies the effect of frequency on the surface morphology, phase composition, bonding force, friction coefficient and weight loss of amorphous Zr micro-arc oxidation coatings, and provides a theoretical basis for practical applications in production.

2. Experimental materials and methods

The micro-arc oxidation method was used to prepare the self-generating ceramic coating on the surface of Zr68Nb45Cu12Ni11Al4Y0.5 amorphous alloy. The size of Zr68Nb45Cu12Ni11Al4Y0.5 amorphous alloy is 10 mm×10 mm×2 mm, and the chemical composition of amorphous zirconium is shown in Table 1. Before the micro-arc oxidation of the zirconium-based amorphous alloy flakes, the sample was polished with 800, 1000, and 1500 mesh sandpaper, and then placed in distilled water for ultrasonic cleaning. Then put the prepared sample in acid solution (1HF:10HNO₃:9H₂O) for pickling for 20 seconds. After pickling, rinse with clean water several times to remove the residual acid on the surface, and dry it for later use. The plating solution for micro-arc oxidation is a silicate plating solution. The plating solution is composed of KOH(20g), Na₂SiO₃(10g), KF(10g), Na₄P₂O₇(10g), NaAlO₂(40g). The micro-arc oxidation voltage is 400 V, the time is 10 min, and the pulse width is 50 μs. The experiment is divided into three groups with frequencies of 300 Hz, 400 Hz and 500 Hz. The above process was used to prepare coatings under different frequency conditions, and the surface morphology of the samples was observed by JSM-6360LV SEM. A microhardness tester was used to detect the hardness of the coating. The model of the hardness tester was HXD-1000TMC, the loading force was 100g, and the time was 15 seconds. SFT-2M pin-disc friction and wear tester was used to study the friction performance of the coating.

| Element | Zr | Nb | Cu | Ni | Al | Y |
|---------|----|----|----|----|----|---|
| Content | 68 | 45 | 12 | 11 | 4  | 0.5 |

3. Experimental results and analysis

3.1 Coating surface morphology

Figure 1 shows the SEM morphology of the coating surface at different frequencies. It can be seen from Figure 1(a) that when the frequency is 300 Hz, the pores on the surface of the zirconium alloy micro-arc oxidation coating are evenly distributed, larger pores locally and microcracks. With the increase in frequency, when it reaches 400 Hz, the surface pores are uniformly distributed and the pores are significantly reduced, as shown in Figure 1(b). When the frequency increases to 500 Hz, it can be seen from Figure 1(c) that the surface pores are unevenly distributed and obvious cracks are observed. As the frequency increases, the number of pores on the coating surface is inversely proportional to the frequency. The reason is that the number of discharges per unit time increases, the time of a single discharge is shortened, and the energy released by a single discharge is reduced, so the number of breakdowns of the film decreases. The pores are reduced. However, when the frequency is low, the single discharge time is long, the energy released by a single discharge increases, and the pores become more numerous.
3.2 Coating section morphology

Figure 2 shows the SEM morphology of the coating section under different frequency conditions. It can be seen from Figure 2(a) that when the frequency is 300 Hz, the thickness of the cross-section coating is about 10 μm, the surface is uneven, and the middle of the coating is relatively loose. When the frequency increases by 400 Hz, the coating thickness increases, and the cross-section coating thickness is about 15 μm. There are micro-pores in the cross-section morphology that gather to form layered pores, as shown in Figure 2(b). With the further increase in frequency, when the frequency reaches 500 Hz, the coating thickness does not increase, and the cross-section coating thickness is still 15 μm, and the surface is relatively flat without obvious pores, as shown in Figure 2(c). The increase in frequency leads to an increase in the number of discharges per unit time, shortens the time of a single discharge, and reduces the energy released by a single discharge, so the number of breakdowns in the film is reduced, and the coating cannot even be broken down, and the porosity of the cross-section of the coating is reduced.

3.3 Phase composition of the coating

Figure 3 shows the XRD patterns of the coating under different frequency conditions. Figure 3(a) shows the matrix peak. Figure 3(b) XRD when the working frequency of the micro-arc oxidation power supply is 300Hz, the 2θ is 31°, 36°, 52°, 60°, and sharp t-ZrO₂ diffraction peaks appear. Figure 3(c) is the XRD diffraction pattern at a frequency of 400 Hz, which is the same as the diffraction peak position of Figure 3(b), but new m-ZrO₂ appears when the diffraction angle 2θ is 29°. Figure 3(d) shows the XRD diffraction pattern of the coating at a frequency of 500 Hz. The coating contains both m-ZrO₂ and t-ZrO₂. The increase in frequency promotes the transition from t-ZrO₂ to m-ZrO₂. However, the increase in frequency has no effect on the formation of Al₀.₀₈Zr₀.₉₂O₁.₉₆ phase.
3.4 Abrasion resistance

Figure 4 shows the bonding strength of the coating at different frequencies. It can be seen from Figure 4(a) that when the frequency is 300 Hz, the bonding force of the coating is 4N. When the frequency increases to 400 Hz, the bonding force of the coating increases, and the bonding force is about 12.5 N. When the bonding force is greater than 12.5 N, a trend change occurs, and then a stable state is formed. It can be seen from Figure 4(c) that when the frequency is increased to 500 Hz, the coating has the best adhesion.

Figure 5 shows the microhardness of zirconium alloy micro-arc oxidation coatings at different frequencies. It can be seen from the figure 5 that the hardness of the zirconium alloy matrix is 480 HV. When the frequency is 300 Hz, the microhardness of the coating is 531 HV; as the frequency increases, when the frequency is 400 Hz, the microhardness of the coating increases to 640 HV. As the frequency
increases, when the frequency is 500 Hz, the microhardness of the coating decreases significantly. Hardness can be used as an important indicator of wear resistance. Without considering the influence of other factors, the higher the hardness, the better the wear resistance. Therefore, it can be inferred that when the frequency is 400 Hz, the zirconium alloy micro-arc oxidation coating has the best wear resistance.

Figure 5 shows the hardness of micro-arc oxidation coating. From Figure 5, it can be seen that the hardness of the coating increases with increasing frequency. The hardness of the coating at 300 Hz is the highest, followed by 400 Hz, and then 500 Hz. The hardness at 300 Hz is significantly higher than that at 400 Hz and 500 Hz.

Figure 6 shows the amount of wear of the coating under different frequency conditions. It can be seen from Figure 6 that when the micro-arc oxidation technology is used and the frequency is 300 Hz, the coating wear loss weight change is small, still being 0.0005 g. When the frequency is further increased to 400 Hz, the coating weight loss reduced to 0.0003 g; when the frequency is further increased to 500 Hz, the coating weight loss significantly increased to 0.0007 g.
4. Conclusion
Based on the results and discussions presented above, the conclusions are obtained as below:

(1) Micro-arc oxidation surface modification technology improves the surface wear resistance, bonding force and friction and wear coefficient of amorphous zirconium. The results show that in the silicate micro-arc oxidation bath, the zirconium alloy micro-arc oxidation coating is composed of m-ZrO2 and t-ZrO2 phases.

(2) With the increase of the frequency of micro-arc oxidation, when the frequency is 400 Hz, the pores on the surface of the coating are small, uniform, and no cracks. The thickness of the coating is the thickest and the largest, about 15 μm, and the thickness of the coating does not increase when the frequency increases again;

(3) When the frequency is 400 Hz, the coating bonding strength reaches the maximum 12.5 N, the friction coefficient is the smallest, the wear loss is the least, and the abrasion resistance of the amorphous zirconium treated by micro-arc oxidation is improved.

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