Review on the Application of Additives in Micro-arc Oxidation of Titanium Alloy

ABSTRACT

Micro-arc oxidation technology of titanium alloy is an efficient, economical and environmentally friendly surface treatment method to improve the properties of titanium alloy. Various additives have been widely used in the industry to improve the properties of micro-arc oxidation film. However, in the process of micro-arc oxidation, due to spark discharge, gas evolution, rapid cooling of molten substances and other factors, a large number of micropores and micro-cracks will be generated in the film. These defects will form a loose layer with poor bonding force on the film surface, which will easily peel off under external force and cause serious abrasive wear on the film surface, which will lead to the failure of the film. A large number of studies show that adding additives into electrolyte can achieve the effect of filling micropores and microcracks, thus improving the corrosion resistance and wear resistance of micro-arc oxidation film. The film obtained by adding additives to the micro-arc oxidation electrolyte not only has excellent metallurgical bonding force, but also can significantly improve the hardness, wear resistance and corrosion resistance of its surface. In this paper, the research status of various additives in micro-arc oxidation of titanium alloy is introduced from three categories: soluble salt additives, nano-particle additives and organic additives, and their action mechanisms are discussed.

Keywords: titanium alloy; Microarc oxidation; Additives.

1. INTRODUCTION

Today, with the rapid development of society, as high-quality light metals, titanium and titanium alloys have attracted extensive attention. The density of titanium is 4.5g/cm3, and its melting point is 1668℃, which is similar to that of magnesium and aluminum. The surface of titanium and its alloy exposed to oxygen will react with oxygen to form an oxide film mainly composed of TiO_2, which can reduce the corrosion of corrosive media to a certain extent and make it have better corrosion resistance. In addition, titanium and its alloy also have a series of excellent properties, such as high specific strength, good mechanical properties and strong biocompatibility. Titanium has two isomorphic isomers. When the temperature is lower than 882℃, the interior of titanium is arranged in a close-packed hexagonal structure, which is called α titanium. When the temperature is higher than 882℃, the interior of titanium is arranged in the form of body-centered cubic structure, which is called β titanium. By adding different alloying elements into these two kinds of titanium, titanium alloys with different characteristics can be obtained by changing the temperature and phase composition. According to the internal structure, the interior of α titanium alloy is composed of α phase solid solution, which is expressed by TA. α titanium alloy has good microstructure stability and oxidation resistance, and can maintain good creep resistance even at high temperature, but it has the disadvantage of low room temperature strength and cannot be heat treated. The interior of β titanium alloy is composed of β phase solid solution, which is generally expressed as TB. β titanium alloy can show good stability at low temperature and room temperature, and can be further strengthened after heat treatment, but its thermal stability at high temperature is poor. (α+β) titanium alloy contains both α phase and β phase, expressed as TC. (α+β) titanium alloy has good microstructure and mechanical properties, and good thermal stability. After heat treatment, its strength can be effectively improved, and its comprehensive properties are excellent. It is also the most widely used titanium alloy.

With the recognition of various excellent physical and chemical properties, the application of titanium alloys in various fields has been far-reaching, mainly in aerospace, automobile industry, marine engineering, biomedical and other high-tech industries.

Compared with ordinary anodic oxidation, micro-arc oxidation has the advantages of economy, high efficiency and environmental protection, and can grow ceramic oxide layer on the surface of light metals such as Al, Mg and Ti in situ [1-3]. In the process of micro-arc oxidation treatment, the anode substrate is introduced into the high-voltage discharge area, and with the instantaneous high temperature and high pressure generated by arc discharge, the molten substance on the substrate surface can interact with the electrolyte solution components to form a ceramic coating mainly composed of substrate metal oxides [4-6]. However, in the process of micro-arc oxidation, due to spark discharge, gas evolution, rapid cooling of molten substances and other factors, a large number of micropores and microcracks will be generated in the film [7-9], and these defects will form a loose layer with poor bonding force on the film surface, which will easily peel off under external force and cause serious abrasive wear on the film surface, which will lead to the failure of the film. A large number of studies show that adding additives into electrolyte can achieve the effect of filling micropores and microcracks, thus improving the corrosion resistance and wear resistance of micro-arc oxidation film [10-13]. In recent years, the research on additives has become a hot direction in the field of micro-arc oxidation.

2. FILM FORMATION MECHANISM OF MICRO-ARC OXIDATION ON TITANIUM ALLOY

The film formation and growth process of micro-arc oxidation is a complex process in which chemical reaction, electrochemical reaction and plasma chemistry occur at the same time, and it involves high-voltage electric field, plasma field and other fields. The film formation is completed in an instant and the mechanism is very complicated [14]. Generally speaking, the process of micro-arc oxidation can be divided into four stages: anodic oxidation, breakdown discharge, micro-arc oxidation and arc discharge [15]. According to the time and voltage curve of micro-arc oxidation, it can be divided as shown in Figure 1 [16].

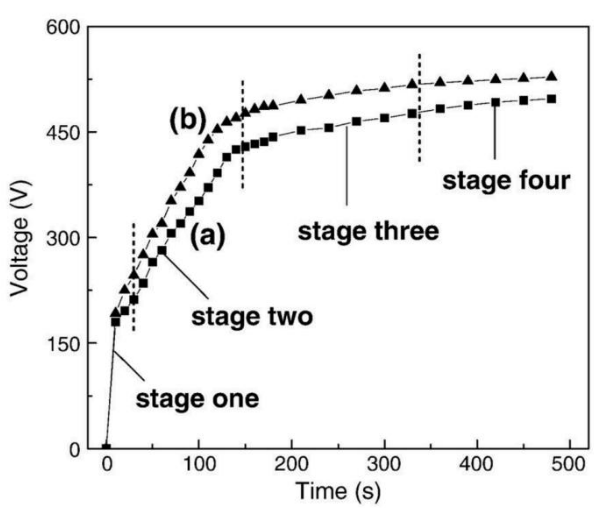


Figure 1 Voltage–time curves of MAO processes

At the initial stage of micro-arc oxidation, the growth mode of the film is consistent with the traditional anodic oxidation, and the main reaction is electrochemical oxidation on the surface of the substrate, and the voltage and current follow ohm's law. At this time, the film has a certain impedance [17-18], but the thickness of the micro-arc oxidation film is small, so it is necessary to continue oxidation to increase the thickness of the film to improve the wear and corrosion resistance of the film. At this stage, similar to the traditional anodic oxidation process, the voltage increases linearly from 0, and the reaction at this time is mainly electrochemical reaction, and the luster of the metal surface gradually becomes dim, forming a passive film. Due to the formation of gas on the surface of anode sample, fine bubbles begin to appear. With the increase of voltage, bubbles will become larger and denser and rise more violently. It will remain at this stage until the voltage reaches the breakdown voltage.

In the stage of breakdown discharge, because the impedance of the film keeps increasing, the voltage keeps rising until the voltage reaches a certain value, and breakdown occurs in the weak part of the micro-arc oxidation film [19]. Apelfeld et al. [20] found that after electrolyte particles enter the oxide film, impurity discharge centers are formed, and a large amount of heat energy is released around the discharge channels. In this area, the oxide film is melted, sintered and cooled on the surface of the substrate to form a ceramic film, and α-Al_2O_3 and γ-Al_2O_3 phases are easily formed inside the ceramic film, while the outer layer of the ceramic film is mainly γ-Al_2O_3 phase. This is because the micro-arc molten Al_2O_3 existing inside and outside the film layer is in different cooling environments, and the cooling rate is different. The direct contact undercooling of molten Al_2O_3 on the outer layer of the oxide film with electrolyte is greater. At this time, the nucleation free energy of γ-Al_2O_3 is smaller than that of α-Al_2O_3 phase, and γ-Al_2O_3 phase is easy to form. When the voltage gradually rises to the breakdown voltage, fine and free discharge sparks begin to appear on the surface of the sample, and the discharge breakdown phenomenon begins to appear on the surface of the film. At this time, the discharge reaction is uneven, and only melting points are formed in local areas, and bubble formation and rupture will be more intense in this process. This stage is also the beginning of the formation of micro-arc oxidation film, but the growth rate is low.

In the micro-arc oxidation stage, according to the micro-bridge discharge model of Nikolaev[21], there are discharge channels in the micro-arc oxidation film. After the weak part of the oxide film is punctured, the released energy leads to the melting and evaporation of oxide, metal and aluminum hydroxide. The molten particles contact the electrolyte through the discharge channel. Because the electrolyte is kept at 30 ~ 40℃ under the action of the cooling system to melt the particles, chilling will occur when contacting the electrolyte, and the generated oxide will solidify around the discharge channel, and the film thickness will increase evenly. With the further increase of voltage, the discharge reaction on the surface of the sample is more intense, forming dazzling discharge spots, and gradually more melting areas appear. The melt covers the surface of the sample under the cooling of electrolyte to form a primary film, and at the same time, with the generation of new melt, the film begins to grow rapidly. At this stage, there will be a violent explosion sound, which is also one of the signs of entering the micro-arc oxidation stage. A large number of discharge channels and micropores formed by plasma discharge will also appear on the surface of the sample. As time goes on, the speed of voltage rise becomes slow and gradually stabilizes around a certain value.

As the micro-arc oxidation continues, it finally reaches the arc discharge stage, at which time the thickness of ceramic film is also increasing. When the film thickness reaches a certain value, the power supply cannot break through the micro-arc oxidation film, and the micro-arc oxidation process ends. The discharge type in the breakdown discharge stage directly determines the performance of micro-arc oxidation film. At the end of micro-arc oxidation, the voltage stopped rising, and the sparks on the surface of the sample gradually became smaller until they disappeared, and the detonation sound gradually stopped, thus ending the growth of micro-arc oxidation film.

Compared with other surface treatment technologies, micro-arc oxidation technology of titanium alloy has some remarkable advantages: low technological requirements, simple operation, high efficiency, capability of treating large quantities of workpieces at the same time, and environmental friendliness due to the use of alkaline electrolyte in most cases. Even if the shape of the workpiece is complex, a uniform film can be grown on the surface of the workpiece in situ by micro-arc oxidation technology. In addition, because the micro-arc oxidation film is grown under the working environment of high temperature and high pressure, it is formed under complex chemical and electrochemical reactions, and the combination between the film and the substrate is relatively tight. The composition of micro-arc oxidation film is generally matrix metal oxide, which can comprehensively improve the hardness, wear resistance and corrosion resistance of matrix surface.

3.EFFECT AND APPLICATION OF ADDITIVES ON MICRO-ARC OXIDATION OF TITANIUM ALLOY

3.1 Soluble Salt Additive

Soluble salt is the most common additive in the electrolyte of micro-arc oxidation of titanium alloy, which can provide ions to the solution to participate in film formation, or influence the film formation process of micro-arc oxidation through the provided ions, thus changing the appearance, structure, composition and performance of the obtained ceramic layer. Luo [22] added Na_2Mo_4 into Na_3PO_4 electrolyte, and prepared Mo-doped TiO_2 ceramic layer on the surface of pure titanium by micro-arc oxidation. With the increase of Na_2Mo_4 content, the number and size of holes on the surface of ceramic layer increased, the absorption spectrum shifted to long wave direction, and the band gap energy decreased. The addition of Na_2 MoO_4 significantly improved the photocatalytic activity of the film. Faiz Muhaffel [23] added $AgNO_3$ to the micro-arc oxidation electrolyte of titanium alloy, and the color of the ceramic layer changed from blue-gray to red-brown, and the film layer was composed of titanium dioxide layer in the inner layer and HA layer in the outer layer. Silver ions are deposited in the outer layer of the membrane layer as nanoparticles through electrophoretic migration. Although the amount of silver deposition is small, it is very helpful to improve the antibacterial property of the biofilm layer. Gao [24] found that the micro-arc oxidation film with copper pyrophosphate has a porous structure, and Cu is mainly concentrated around micropores. Although the hardness of the film is reduced, the friction coefficient can be effectively reduced due to the selflubricating effect of copper, which greatly improves its wear resistance in simulated seawater. On the whole, the addition of soluble salts plays a certain role in changing the wear resistance and corrosion resistance of titanium alloy micro-arc oxidation ceramic film, but its compatibility with the original basic electrolyte needs to be considered.

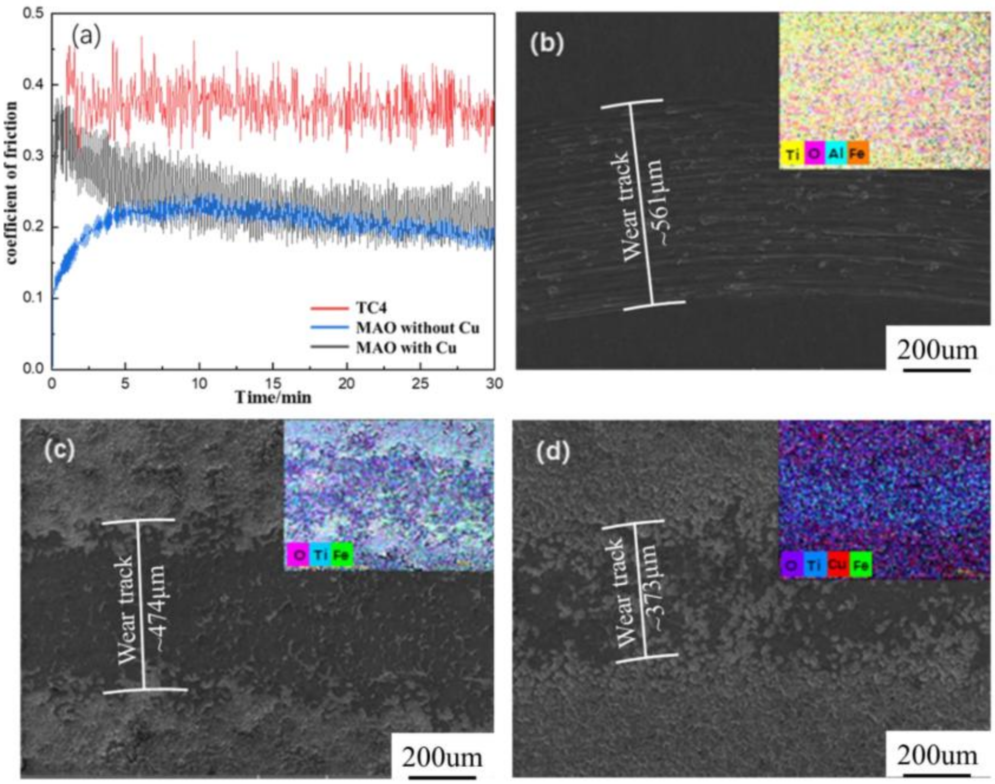
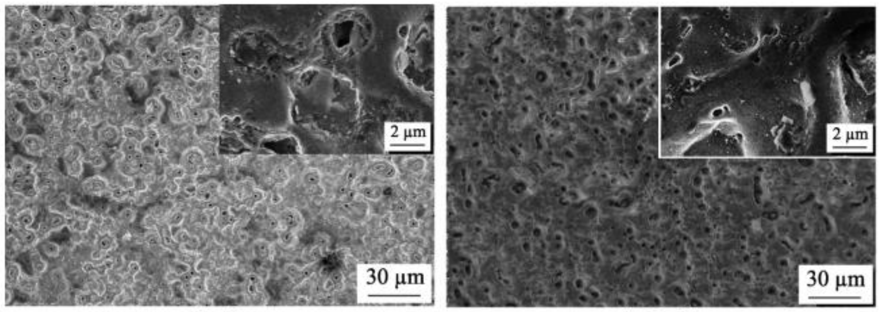


Figure 2 Friction coefficient and wear trace morphology of film prepared by adding copper pyrophosphate[24]

3.2Nano-Particle Additive

When nano-particles are used as additives to participate in micro-arc oxidation reaction, they can reduce the friction coefficient because of their own characteristics of friction reduction and self-repair, and can fill the surface micropores of micro-arc oxidation ceramic coatings, reduce the porosity of the coatings and improve the compactness. Cai [25] added nano-ZrO_2 particles to the electrolyte, and prepared a composite film containing ZrO_2 on the surface of TC4 titanium alloy. Friction and wear experiments show that when the content of ZrO_2 is 9 g/L, its specific wear rate is 3.489× 10-4 mm3/(n m), which is 32.24% of that without adding particles, and the wear resistance of the film is significantly improved. As shown in figure 3. Shokouhfar [26] comprehensively investigated the effect of doping SiC, Al_2O_3 and TiO_2 nanoparticles into aluminate electrolyte on the structure and properties of micro-arc oxidation film. It is found that the film added with TiO_2 nanoparticles shows better corrosion resistance and wear resistance. Aliofkhazraei [27] found that with the addition of CeO_2 nanoparticles, the wear rate of CP-Ti (industrial pure titanium) micro-arc oxidation film also decreased. When CeO_2 nanoparticles were added at 25 g/L, the specific wear rate of the film decreased by 76% compared with that without CeO_2 particles. Wang [28] successfully prepared a micro-arc oxidation film on the surface of TA2 alloy by adding MgO particles into the electrolyte. With the increase of MgO particle concentration, the microhardness and interfacial adhesion of the film were significantly improved, and the comprehensive performance of the film was the best when the MgO particle concentration was 2 g/L. Chen [29] added graphene particles to the electrolyte, and prepared a composite film containing graphene on the surface of TC4 titanium alloy, and studied the corrosion resistance of the film. The results show that when the amount of graphene is 3 g/L, the self-corrosion potential of the composite film is as high as 0.403 V, and the corrosion current density is at least 2.66×10-9 A/cm2, and the corrosion resistance is the best. The above research shows that the hardness and compactness of the film can be significantly improved by adding solid particles, so as to reduce the abrasive wear.



a 0 g/L b 3 g/L

Figure 3 Surface morphology of ceramic film with different ZrO2 concentration

3.3Organic Additive

On the one hand, the addition of organic matter in micro-arc oxidation electrolyte will affect the viscosity of the solution and reduce the conductivity of the solution; On the other hand, organic matter will be adsorbed on the surface of ionic groups in electrolyte, which will change the state and quantity of surface charge and affect its migration in solution, thus affecting the micro-arc oxidation process, film structure and performance. Hyun Lee[30] added ethanol into calcium acetate and calcium glycerophosphate solution, and made Ti6Al4V titanium alloy medical stent by the mixed method of dynamic freeze casting and micro-arc oxidation, and made a ceramic layer with specific and connected surface holes. The compressive strength and elastic modulus of the stent can be controlled by porosity, in which ethanol is mainly used to inhibit the escape of gas in the solution. The research of Shi [31] also shows that CA and EDTA-2Na added into electrolyte can promote the formation of hydroxyapatite in micro-arc oxidation ceramic layer, in which CA reduces the proportion of Al in ceramic layer and EDTA-2Na promotes the formation of $CaTiO_3$. The research of Wang [32] shows that glycerol added to $Ba(OH)_2$ electrolyte can reduce the arc energy and make the arc uniform and fine, thus obtaining a more compact and flat $BaTiO_3$ ceramic film and improving the dielectric properties of the film.

4. SUMMARY AND PROSPECT

(1) Micro-arc oxidation process is a complex process in which chemical reaction, electrochemical reaction and plasma reaction take place at the same time, and it involves high-voltage electric field, plasma field and other fields. The mechanism of instant film formation is very complicated. Researchers in various countries have done in-depth research on its mechanism and put forward many theories, but so far all kinds of theories can not perfectly explain the whole micro-arc oxidation process. It is still of practical significance to explore the mechanism of micro-arc oxidation for guiding engineering practice. It is foreseeable that with the continuous progress of basic science,

(2) There are a lot of defects on the surface of ceramic coating prepared by micro-arc oxidation treatment of titanium alloy, with high porosity and poor compactness. Adding different kinds of additives into micro-arc oxidation electrolyte can greatly improve the film quality and improve the wear and corrosion resistance of aluminum alloy. Different kinds of additives with different concentrations have different effects. Among them, a lot of research mainly focuses on particulate additives, but less on organic matter and soluble salts.

(3) The micro-arc oxidation film prepared on the surface of titanium alloy has the characteristics of high hardness and high wear resistance, which is the best choice for surface treatment of titanium alloy. In recent years, workpieces treated by micro-arc oxidation have emerged frequently, with high value-added products such as automobile body and mobile phone back shell as representatives, showing great market potential and good business prospects.

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