The research progress on micro-arc oxidation of aluminum alloy

Dong Yuting, Liu Zhiyang, Ma Guofeng
Liaoning Province Key Laboratory for Advanced Materials Preparation Technology, Shenyang University, Shenyang 110044

Abstract. The micro-arc oxidation of aluminum alloy is a kind of surface treatment technology for in-situ growth of a hard ceramic film with Al2O3 as the main effect of instantaneous high temperature and high pressure generated by arc discharge on the surface of aluminum alloy. This technology can significantly improve the wear resistance, corrosion resistance, hardness and other properties of the aluminum alloy matrix. This paper introduces the characteristics, influencing factors, research status of domestic and foreign micro-arc oxidation technology, and prospects for future research directions.

1. Introduction
Micro arc oxidation (MAO), also known as plasma electrolytic oxidation (PEO), micro plasma oxidation (MPO). It produces instantaneous high temperature and high pressure on the surface of aluminum and its alloys, through the combination of electrolyte and corresponding electrical parameters and arc discharge. And the ceramic film layer mainly composed of the base metal oxide is grown in situ. The micro-arc oxidation technology of aluminum alloy is mature and easy to operate. After a series of reactions, a dense oxide film with Al2O3 as the main component is formed. The reaction equation is as follows:

Cathodic reaction:
\[ \text{H}_2^+ + 2\text{e}^- \rightarrow \text{H}_2 \]  (1)

Anode reaction:
\[ 4\text{OH}^- - 4\text{e}^- \rightarrow 2\text{H}_2\text{O} + 2\text{O}_2 \]  (2)
\[ \text{Al} - 3\text{e}^- \rightarrow \text{Al}^3+ \]  (3)
\[ \text{Al}^3+ + 3\text{OH}^- \rightarrow \text{Al}(	ext{OH})_3 \]  (4)
\[ 2\text{Al}(	ext{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \]  (5)
\[ 2\text{Al}^3+ + 3\text{SiO}_3^{2-} \rightarrow 3\text{SiO}_2 + \text{Al}_2\text{O}_3 \]  (6)
\[ 4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3 \]  (7)
\[ \gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3 \]  (9)

The oxide film formed by the micro-arc oxidation process has good wear resistance, high hardness, strong corrosion resistance, less defects on the surface of the film layer, and the structure tends to be dense.

2. Principle of micro-arc oxidation technology
The principle of micro-arc oxidation technology is as follows [1]: the metal such as aluminum, magnesium, titanium or its alloy is placed in the electrolyte under the electric field environment as the
anode, the electrolytic cell is the cathode, and the voltage is applied (up to 1000V) and larger current, as shown in Fig. 1.

![Fig 1. Schematic diagram of principle of MAO technology](image)

Immediately after energization, a thin metal oxide insulating film is formed on the metal surface. The formation of a complete insulating film is a necessary condition for micro-arc oxidation treatment. On this basis, the applied voltage of the workpiece rises steadily. When a certain critical value is reached, some weak links on the insulating film are broken first. It will occur in the micro-area arc discharge phenomenon, and instantly form an ultra-high temperature region ($10^3$-$10^4$K) [2]. This causes the oxide and the base metal to be melted or even vaporized. After the molten material is in contact with the electrolytic solution, a ceramic film layer is formed by chilling. Since the breakdown always occurs at a relatively weak portion of the oxide film, and a new oxide film is formed in the original portion after the breakdown. The breakdown point then shifts to other relatively weak areas. Repeatedly, a uniform oxide film is formed on the metal surface.

3. Development of micro-arc oxidation technology

The development of micro-arc oxidation technology can be traced back to the early 1930s. German scientists Gunterschulze and Betz first reported that the metal immersed in the solution will have spark discharge on the surface under the action of high-voltage electric field [3]. Through further observation and research, it was found that the ceramic oxide film can be successfully prepared on the metal surface by using this spark discharge phenomenon. Due to the protective effect of the oxide film, the magnesium alloy anticorrosion was originally applied by this technology [4]. So far, magnesium alloy spark discharge technology is still under study. In the 1970s, the United States, Germany, the Soviet Union and other countries saw the application potential of micro-arc oxidation technology, and joined the research of this technology. The University of Illinois, Karl Marx University of Germany and other units used DC or single-phase pulsed power supply mode to comprehensively analyze aluminum, titanium and other valve metal spark discharge deposition layers, and named them as anode spark deposition [5-6] and spark discharge anodization [7-8]. Compared with the traditional anodizing technology, the biggest advancement of this technology is that the microplasma generated on the surface of the metal during oxidation can be sintered into a crystalline state in a high temperature and high pressure region. The film layer prepared on the aluminum alloy, $\alpha$-$\text{Al}_2\text{O}_3$ and $\gamma$-$\text{Al}_2\text{O}_3$ occupy its main film component [9-10]. In 1977, the institute of inorganic chemistry of the Soviet Union began research on this technology. They used an alternating voltage mode and obtained a similar film layer, in which $\alpha$-$\text{Al}_2\text{O}_3$ and $\gamma$-$\text{Al}_2\text{O}_3$ still occupy the main components of the oxide film. This
technique is named micro-arc oxidation. So far, the micro-arc oxidation technology has been greatly developed [11].

At present, the countries that are engaged in the research of micro-arc oxidation technology in the world mainly include Russia, the United States, Germany, Japan, etc.. Among them, Russia is more advanced. Russia has proposed a relatively complete theory in the research of micro-arc oxidation mechanism, and successfully applied to aviation, petroleum, textile and other industrial fields [12]. Since the 1990s, China has begun to pay attention to the technology of micro-arc oxidation. At present, it has begun to take the form of wear-resistant, corrosion-resistant and decorative film layers, but it is still in its infancy. Generally speaking, the research level of micro-arc oxidation technology abroad is slightly ahead of the domestic. But at present, domestic and foreign countries have not entered the stage of large-scale industrial application. Therefore, in order to understand and master the technology in depth, it is still necessary to carry out a large number of research experiments to prepare a ceramic film layer with better performance, so that it can be practically applied in more fields.

4. Factors Affecting Microarc Oxidation of Aluminum Alloy

4.1. Operating Voltage
The arcing voltage at the beginning of the micro-arc oxidation reaction is closely related to the composition of the electrolyte and the composition of the aluminum alloy. When the working voltage is too low, the micro-arc oxidation reaction is slow and the quality of the oxide film is not good. Ablation occurs when the operating voltage is too high. Moreover, the operating voltage can also determine the thickness of the final oxide film. Therefore, the working voltage has a very important influence on the micro-arc oxidation of aluminum alloy.

4.2. Current density
The current density has an important influence on the growth process, microstructure, element composition, phase composition and corrosion resistance of the aluminum alloy micro-arc oxidation film. As the current density increases, the thickness of the film layer increases and becomes more dense. However, when the current density is too large, the micro-arc oxidation reaction becomes severe, causing the film layer to become rough or even crack.

4.3. Electrolyte composition
The electrolyte used in micro-arc oxidation technology is generally divided into two categories: acidic electrolyte and alkaline electrolyte. However, due to the environmental pollution caused by acidic electrolyte, most of the micro-arc oxidation technology used is alkaline electrolyte. Because the alkaline electrolyte has a dissolution effect on the aluminum alloy, the alkaline concentration of the electrolyte cannot be too high, and sodium hydroxide or potassium hydroxide is usually used to adjust the pH of the electrolyte. Studies have shown that anions in the electrolyte composition participate in the formation of an oxide film, thereby changing the composition, structure, phase structure and properties of the micro-arc oxidation coating. The ceramic layer is selective for the adsorption of particles in the electrolyte, and the order of adsorption from strong to weak is SiO32-, PO43-, VO43-, MoO42-, WO42-, B4O72-, CrO42-[13]. The electrolytes commonly used in micro-arc oxidation are formulated with acid salt systems, phosphate systems, aluminate systems, etc. In addition, complex salts are used in many studies [14].

4.4. Additive
Zhang Xinyu et al [15] found that the addition of DTA and SDBS in the electrolyte can improve the stability and film formation rate of the electrolyte, but has little effect on the hardness and corrosion resistance of the film. Luo Haihe et al [16] studied the effect of adding different concentrations of (NaPO3)6 on the properties of magnesium alloy micro-arc oxidation ceramic coatings. They found that adding appropriate concentration of (NaPO3)6 can effectively increase the thickness of the
coating. It can also improve the chemical composition and structure of ceramic coatings to improve their corrosion resistance.

4.5. Temperature
When the temperature is low, the film grows faster because the large amount of heat released during the reaction at a lower temperature is easily lost, so that the sintering is denser and the performance is better. On the contrary, it will accelerate the loss of active ingredients in the solution, resulting in the failure of the electrolytic solution [17].

5. Application of Microarc Oxidation of Aluminum Alloy
The micro-arc oxidation technology is environmentally friendly and highly efficient. The ceramic coating prepared has the advantages of high strength, wear resistance and corrosion resistance, and is widely used in various fields such as aerospace and petrochemical industries. By using this technology, a porous ceramic film layer having excellent heat resistance, wear resistance and corrosion resistance is grown in situ on a metal surface such as an aluminum alloy, thereby changing the defects of the metal itself. It has a better development space in the military field such as aerospace and has expanded the application range of aluminum alloy.

6. Development trend of micro-arc oxidation
6.1. Development of process database system
The parameters involved in the micro-arc oxidation process are complex and variable, which is not conducive to automated operation. To solve this problem, a process database can be established for the device. The process database contains all the parameters that need to be set for the micro-arc oxidation process. When you use it, you only need to call a micro-arc oxidation process to specify the set value for each parameter of the process, which will greatly improve the efficiency of use.

6.2. Development of low energy micro-arc oxidation process
The conventional micro-arc oxidation process processes ultra-large complex light metal components with high equipment requirements, long working hours and high energy consumption. By designing a scanning mobile cathode and controlling the micro-arc oxidation process, energy consumption can be effectively reduced. In addition, according to Chinalco.com, Beiteng (Shanghai) Technology Co., Ltd. has successfully developed low-voltage micro-arc oxidation technology. Compared with traditional micro-arc oxidation technology and anodizing technology, it not only has the advantages of low voltage, low energy consumption, low processing cost, high efficiency, high environmental protection, and recyclability, but also does not cause any damage to the surface of the base metal.

7. Conclusion
This paper introduces the principle and development of aluminum alloy micro-arc oxidation technology. The factors affecting the micro-arc oxidation technology of aluminum alloy are Operating voltage, current density, electrolyte composition, additives and temperature. We can control these influencing factors to produce a better quality ceramic film. The aluminum alloy adopts micro-arc oxidation technology to change its own defects and expand the application field. There are still some shortcomings in micro-arc oxidation technology. I think that in the future, we should focus on developing process database systems and low-energy micro-arc oxidation processes.

Acknowledgements
The authors gratefully acknowledge the China Postdoctoral Science Foundation (No. 2016M601333), Liaoning Provincial Natural Science Foundation of China (No.2019-MS-236), the Shenyang Science and Technology Project (No. 2018-013-0-14).
References

[1] ZUO H B, KONG Q S, SHANG J Q. Plasma enhanced chemical surface ceramic transformation technology [J]. Materials Protection, 1995, 28(7): 117-120.

[2] XUE W, WANG C, LI Y. Effect of micro-arc discharge surface treatment on the tensile properties of Al-Cu-Mg alloy [J]. Materials Letters, 2002, 56: 737-743.

[3] GUNTHERSCHULZE A, BETZ H. Neue untersuchungen über die elektrolytische ventilwirkung: II die oxydschicht von Sb, Bi, W, Zr, Al, Zn, Mg[J]. Zeitschrift Für Physik, 1932, 78(3/4):196-210.

[4] GÜNTHERSCHULZE A, BETZ H. Die elektronenstromung in isolatoren bei extremen feldstarken[J]. Zeitschrift Für Physik, 1934, 91(1/2): 70-96.

[5] VAN T B, WIRTY G P, BROWN S D. Anodic spark deposited coatings[J]. America Ceramic Society Bulletin, 1976, 55(4): 412.

[6] WIRTZ G P, BROWN S D, KRIVEN W M. Ceramics coatings by anodic spark deposition[J]. Materials and Manufacturing Processes, 1991, 6(1): 87-115.

[7] KRYSENSMANN W, KURZE P, DITTRICK H K, et al. Process characteristics and parameters of anodic oxidation by spark discharge (ANOF) [J]. Crystal Research and Technology, 1984, 19(7): 973-979.

[8] KURZE P, KRYSENSMANN W, SCHREKENBACH J, et al. Colored ANOF layers on aluminum[J]. Crystal Research and Technology, 1987, 22(1): 53-58.

[9] VAN T B, BROWN S D, WIRTZ G P. Mechanism of anodic spark deposition[J]. American Ceramic Society Bulletin, 1997, 56: 105-107.

[10] DITTRICK H K, GLEOAZD L. Micro-arc oxidation of aluminum alloy components [J]. Crystal Research & Technology, 1984, 19(1): 93-96.

[11] LI S H, YIN Y J, CHENG J S. Technology of microarc oxidation and ceramics of material surface[J]. Special Casting & Nonferrous Alloys, 2001, 35(1): 35-36.

[12] ZHANG W H, HU Z Q, MA J. The development of research on microarc oxidation technology in Russia[J]. Light Alloy Fabrication Technology, 2004, 32(1): 25-29.

[13] LI H X, LI W J, SONG R G, et al. Effects of different current densities on properties of MAO coatings embedded with and without α-Al2O3 nano additives [J]. Materials Science and Technology, 2013, 28(5): 565-568.

[14] WHEELER J M, CURRAN J A, SHRESTHA S, et al. Microstructure and multi-scale mechanical behavior of hard anodized and plasma electrolytic oxidation(PEO) coatings on aluminum alloy 5052[J]. Surface and Coatings Technology, 2012, 207: 480-488.

[15] ZHANG X Y, SHI Y L. Technique of plasma microarc oxidation and its application[J]. Journal of Qingdao Institute of Chemical Technology, 2002, 23(1): 69-73.

[16] LUO H H, CAI Q Z, WEI B K, et al. Effects of additive concentration on microstructure and corrosion resistance of ceramic coatings formed by micro-arc oxidation on AZ91D Mg alloy[J]. The Chinese Journal of Nonferrous Metals, 2008, 18(6): 1082-1088.

[17] Curran J A, Clyne T W. The thermal conductivity of plasma electrolytic oxide coatings on aluminium and magnesium[J]. Surface Coating Technology, 2005, 199: 177-183.