Study on the surface ceramization of aluminum alloy

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Abstract. Aluminum alloy has been widely used as a metal material. However, it is usually vulnerable to corrosion, so the protection of aluminum alloy surface is particularly important. At present, the commonly used methods of surface protection of aluminum alloys are anodic oxidation, plasma micro-arc oxidation, chemical oxidation and so on. In this experiment, chemical protective coatings were prepared by chemical oxidation of Aluminium 1100 and 6063 treated with H₂O₂ or KMnO₄ solution. The results showed that the oxidation capacity of H₂O₂ solution from 3% concentration to 15% concentration to Al1100 was successively enhanced. Moreover, the ceramic coating produced when the concentration of H₂O₂ is 12%-15% has a better effect, and the structures are cauliflower, concave and convex, and hydrophobic. It is expected that the surface has lotus leaf effect.

1. Introduction

Aluminum element is the most abundant metal element in the crust, accounting for about 7.73 percent of the total, and widely distributed, aluminum material in production and life in the application range after steel, is the second largest application material. At present, pure aluminum is rarely used in the production of practical structural materials, but the alloy formed by the combination of pure aluminum and other elements is a very good composite material [1]. With the progress and development of the economy, aluminum alloy materials play a very important role in various fields, and its surface decorative [2] and other performance requirements are increasingly high. Aluminum alloy materials have the characteristics of small relative density, light mass, non-magnetic, high specific strength, stable structure, good conductivity, and no pollution to the environment [3], which are widely used in many industrial sectors. However, the surface hardness of aluminum alloy is soft and easy to be worn, and it is easy to be corroded in the atmospheric environment, damaging the surface gloss and various surface properties, and it is difficult to meet the requirements of higher-level products in various fields [4]. Although the aluminum alloy itself will generate a layer of oxide film covering the surface, which has some protective effect on the alloy itself, the natural oxide film of aluminum alloy can only provide limited protection to the matrix, and the moisture and salt in the air will accelerate the corrosion of the aluminum matrix. Preparation of a protective coating on the surface of aluminum alloy can improve its surface hardness, corrosion resistance, high temperature resistance, hydrophobicity and other properties [5]. Aluminum alloy surface is usually treated by electroplating, chemical conversion, anodic oxidation and micro-arc oxidation [6]. Recently, the surface ceramization technology of aluminum alloy has attracted more and more attention in various fields, and it is the main research method of surface modification technology of aluminum alloy. This method is that...
aluminum alloy is the matrix material, and a layer of ceramic film is prepared on the surface of the matrix, so that the surface of the matrix can have the properties of ceramic material, and can combine and cooperate with each other. Ceramic coating hardness, resistance to high temperature, wear and corrosion resistance and cheap manufacturing cost, has some excellent properties of ceramics. The excellent properties of the metal material and combined the excellent properties of ceramic materials, ceramic coating adhesive on the metal material surface does not affect the performance of metal materials, and the composite materials with special performance of metal materials and ceramic materials, superior comprehensive performance [7], aluminum matrix ceramic coating in the shuttle, electrical energy, the machine is widely applied in aspects of chemistry, is suitable for the single metal or ceramic materials can apply environment, so is the current solution is not stable, easy to corrode metal material surface an important technology, such as the defects by attention and concern. Among the preparation technologies of ceramic coating on aluminum alloy surface, several technologies are widely used: anodic oxidation, plasma micro-arc oxidation, chemical oxidation, laser cladding and sol-gel [8-10].

Anodic oxidation technology on the surface of the metal material: put metal materials as anode materials in electrolyte solution, then the cathode material is a kind of corrosion resistance of the conductive material, pass into the current in the current under the action of the anode materials generated on the surface of a layer of good wear-resisting caustic resistance, corrosion resistance and other functional or decorative ceramic layers of coating process [11].Anodic oxidation mainly deals with some light metal materials, especially aluminum and aluminum alloy, magnesium alloy, titanium and titanium alloy. The coating prepared by anodic oxidation technology is thicker, stronger and has good density, hardness, abrasion resistance, corrosion resistance, absorption and insulation [12]. The anodic oxidation coating thickness of aluminum alloy can be large or small, and it has a special honeycomb structure. The porosity of the film layer is also affected by the different abilities of electrolyte and the generation speed of coating [13]. The type of electrolyte, process design and pretreatment will affect the structure and performance of the film. However, anodic oxidation also has some disadvantages, such as the substrate surface needs to have a better quality, flat and clean. Therefore, before the preparation of the membrane, a series of complicated pre-treatment procedures must be carried out first, which is time-consuming and time-consuming. Moreover, the equipment required in the preparation of anodic oxidation film is more expensive, the technology is more complex, the energy consumption is more, and the quality of the film layer is not easy to control, especially for the coating of large parts, the operation is more difficult [14].

Micro-arc oxidation is a new technology of material surface modification. In this technology, aluminum, magnesium, titanium, zirconium, niobium, tantalum and other metals are immersed in the corresponding electrolyte, and a higher voltage is applied on the surface of the material to generate local instantaneous high-temperature and high-pressure oxidation of the material and generate a ceramic coating mainly composed of the matrix material oxide and containing the elements contained in the electrolyte [15]. Micro-arc oxidation technology is simple to operate, green environmental protection, low production cost, wide range of applications. Micro-arc oxidation technology can greatly enhance the hardness, wear resistance and damage resistance of the surface of materials. Its micro hardness is equivalent to that of cemented carbide. The coating prepared by anodic oxidation technology has better corrosion resistance. It can make many metal materials in the application process to enhance the corrosion resistance of the material itself, so that in the actual application of the material selection has more consideration. The film has a good heat resistance, short time to withstand the high temperature of about 1000°C and the film is not destroyed. Compared with anodic oxidation, chemical oxidation is easier to operate, does not require expensive and complex equipment, and the production process is relatively clean. The ceramic coating prepared by chemical oxidation method can enhance the adsorption and wet ability of the material and ceramic layer, and has the advantages of uncomplicated preparation process, simple operation, cheap production price, excellent and stable coating structure, etc. In this paper, ceramic coating on aluminum alloy surface by chemical oxidation is studied.
Chemical oxidation method is to put the metal material in the corresponding solution with the same temperature, make the metal material react with the solution, make the metal ions and oxygen in the oxidation solution combine with each other, and create a protective oxide film layer on the surface of the metal material. Chemical oxidation can also be used to prepare a ceramic coating on the surface of aluminum alloy as a protective layer to protect the substrate. This ceramic coating can protect the surface of the substrate and can also be used as the bottom layer of paint to enhance the adsorption. The chemical oxide ceramic layer endows the aluminum alloy with some properties that it does not have and effectively broadens the applicable range of aluminum alloy. Chemical oxidation method is used to prepare ceramic layer on the surface of aluminum alloy. In addition to the fact that the existence of the film layer does not affect the original properties of aluminum alloy, the ceramic layer has dense structure, strong wear and corrosion resistance, bright appearance, and tight combination, which does not affect the properties of the substrate itself. Compared with other preparation methods, chemical oxidation method can be used for coating some work piece with uneven, uneven and irregular surface morphology, and the combination is better. Although chemical oxidation is more environmentally friendly than anodic oxidation, there are still some pollutants discharged, causing damage to our living environment. The chemical oxidation process in the paper may solve these problems.

2. Experimental

2.1. Reagents and instruments

Hydrogen peroxide 30% (AR pure, Tianjin komeo chemical reagent co., LTD.), potassium permanganate (AR pure, Sinopharmaceutical group chemical reagent Beijing Co., LTD.); 1100 aluminum plate, 6063 aluminum bar.

SU-5000 Field emission scanning electron microscope (Hitachi, Japan), MX-6RT type optical metallographic microscope (Ningbo shun-yu instrument Co., LTD.), X8-600 hand-held alloy analyzer (Condensing technology Co., LTD.).

2.2. Experimental process

2.2.1. H2O2 oxidation 1100 aluminum sheet

The hand-held alloy analyzer was used to test the aluminum sheet in the package shell and the purchased aluminum bar, to determine the alloy components, and to cut a number of small pieces with a length of about 2mm². With 30% H₂O₂ solution, 10ml of H₂O₂ solution with concentration of 3%, 6%, 9%, 12% and 15% were prepared. The samples of equal mass were put into the beaker of H₂O₂ solution with the above concentration, soaked for 24 hours, taken out and dried, and then the surface morphology of the samples was observed by SEM.

2.2.2. KMnO4 oxidation 6063 aluminum rod

Using a 10cm diameter aluminum strip, cut the sample with a growth of about 15cm. Use metallographic sandpaper to smooth the surface. The composition of the sample aluminum bar was determined as 6063 aluminum alloy by the hand-held alloy analyzer. Solid KMnO₄ was taken and KMnO₄ solution with concentration of 6%, 9%, 12% and 15% was prepared. The prepared samples were immersed in different concentrations of KMnO₄ solution for 24 hours, then taken out and dried.
3. Results and discussion

3.1. Alloy analyzer analysis results

Table 1. Chemical Constituents of Aluminum Sheets for Pharmaceutical Packaging

| composition | content% | +/-[%2]  |
|-------------|----------|----------|
| Al          | 98.658   | 0.859    |
| Fe          | 0.650    | 0.047    |
| Si          | 0.600    | 0.066    |
| Co          | 0.0041   | 0.032    |

Table 2. Chemical Constituents of Aluminum Alloy Bars Used in the Experiment

| composition | %       | +/-[%2]  |
|-------------|---------|----------|
| Al          | 98.424  | 0.914    |
| Mg          | 0.749   | 0.225    |
| Si          | 0.596   | 0.063    |
| Fe          | 0.103   | 0.023    |

According to the analysis of the alloy composition of the aluminum sheet of the handheld alloy analyzer, Table 1 shows that the content of Al accounts for 98.658% and contains a small amount of Fe, Si and other impurities. It can be determined from table 1 that the aluminum sheet is Al1100. According to the analysis of the alloy composition of the aluminum bar by the hand-held alloy analyzer, table 2 shows that the content of Al accounts for 98.424%, and contains a small amount of Mg, Si, Fe and other impurities. It can be determined from table 2 that the aluminum bar is 6063 aluminum alloy.

3.2. SEM analysis

Figure 1. SEM images of aluminium sheets treated with 3% H2O2 solution
(a) 600 times amplification  (b) 2000 times amplification

It can be seen from figure 1 that when the concentration of H2O2 solution is 3%, the oxidized part on the surface of the sample is sparse and distributed in small spots, with uneven distribution.

Figure 2. SEM images of aluminium sheets treated with 6% H2O2 solution
(a) 450 times amplification  (b) 900 times amplification  (c) 2500 times amplification
It can be seen from figure 2 that when the concentration of H$_2$O$_2$ solution is 6%, the oxidized part on the surface of the sample presents a linear distribution, but the coverage is relatively small, and many places are still in the state of no coating.

![Figure 2](image1)

Figure 3. SEM images of aluminium sheets treated with 9% H$_2$O$_2$ solution
(a) 500-times amplification  (b) 1300-times amplification

It can be seen from figure 3 that when the concentration of H$_2$O$_2$ solution is 9%, there are obvious and dense oxide layers on the sample surface. But it still doesn't completely cover the surface of the sample.

![Figure 3](image2)

Figure 4. SEM images of aluminium sheets treated with 12% H$_2$O$_2$ solution
(a) 2200 times amplification  (b) 4000 times amplification

It can be seen from figure 4 that when the concentration of H$_2$O$_2$ solution is 12%, there is a layer of oxidation products on the surface of the sample, and the surface organization of the oxidation products is dense, concave and convex, which is in the shape of cauliflower.

![Figure 4](image3)

Figure 5. SEM images of aluminium sheets treated with 15% H$_2$O$_2$ solution
(a) 1800 times amplification  (b) 10000 times amplification  (c) 10000 times amplification

It can be seen from figure 5 that when the concentration of H$_2$O$_2$ solution is 15%, there is a layer of dense oxidation products on the surface of the sample, and the oxidation products are evenly distributed, with good organizational structure and concave and convex surface, in the shape of cauliflower.
3.3. Metallographic analysis

Figure 6. Metallographic micrograph of aluminum bar treated without KMnO4 solution (1000 times amplification)

Figure 7. Metallographic micrograph of aluminum bar treated with different concentrations of KMnO4 solution (1000 times amplification)

Concentration is (a): 6%, (b): 9%, (c): 12%, (d): 15%

After looking at the metallographic photographs in FIG. 6 (a), FIG. 6 (b), FIG. 7 (a), FIG. 7 (b), FIG. 7 (c) and FIG. 7 (d), it was found that the surface of the sample was loose and not dense, and some special structures on the surface were difficult to be seen. After treating the sample with KMnO4 solution, the product may be manganese dioxide, potassium manganate, etc. And potassium permanganate solution itself has color, compared to H2O2 is not easy to observe the resolution. Therefore, it is difficult to tell whether the ceramic coating was formed after the sample was treated with KMnO4 solution.

4. Conclusion

Compared with the experimental process and result analysis of sample treatment with H2O2 solution and sample treatment with KMnO4 solution, it shows that the use effect and preparation effect of H2O2 solution are better than that of KMnO4 solution, so the preparation technology of ceramic coating with H2O2 solution is superior. From 3% concentration to 15% concentration, the oxidation capacity of H2O2 solution to Al1100 was successively enhanced, moreover, the ceramic coating produced when the concentration of H2O2 is 12%-15% has a better effect, and the structures are cauliflower, concave and convex, and hydrophobic. It is expected that the surface has lotus leaf effect.

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References

[1] Smitha V S, Syamili S S, Peer Mohamed A. 2018, New J. Chem., 42, 10337-10347.
[2] Yan G J, Chen G D, Sun K. 2014. RSC Advances.4.6840-6844.
[3] WuYH, ZhaoW J, WangW R. 2016. RSC Advances.6.5100-5110.
[4] Zhuang J L, 2018. Study on Technology of Aluminium Alloy/Ceramic Gradient Material by Laser Deposition. Shenyang Aerospace University Thesis for Masters Degree.

[5] He X, 2013, Ordnance Material Science and Engineering. 36(1):39-42.

[6] Wang M, Dong X P, Yang F, Zheng X Y, 2015, Special Casting & Nonferrous Alloys. 35(04):427-429.

[7] Wang M, 2015, Study on Preparation Processes of Ceramic Coating on Aluminum Surface. Huazhong University of Science and Technology.

[8] Wu Y H, Zhao W J, Wang W R. 2016, RSC Advances. 6, 94074-94084.

[9] Gao J H, Li F H, Gong Y L, Ren S, 2018, Plating & Finishing. 40, 18-23.

[10] Qian J C, Zou H Q, Fang M, Xu B, 2019, Equipment Environmental Engineering, 16(3):58-62.

[11] Wang Y M, Zou Y C, Wang S Q, Chen G L, Ou Y J H, Wei D Q, Jia D C, Zhou Y, 2018, China Surface Engineering, 31(4):20-45.

[12] Ling H, 2015. Effect of Anodic Oxidation Film on Formation of Micro-arc Oxidation Ceramic Coatings on Aluminum Alloy. Xihua University.

[13] Wu H W, 2015. The Study of technology on cast aluminum alloy micro arc oxidation coating and its wear resistance. Harbin Institute of Technology.

[14] Tian L, Song Q L, Wang A R, 2013, Plating & Finishing, 35(11):5-8.

[15] Tian Y, Zhao Y G, Liu C W, Wang Y L, 2014, Aeronautical Science & Technology, 25(1):51-53.