Analysis for anodized film blackening of aluminum alloy components

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Abstract
Sulfuric acid anodic oxidation is an important means to improve the corrosion resistance of aluminum alloy components. The blackening phenomenon of aluminum alloy components after sulfuric acid anodizing is analyzed by chemical composition test, mechanical property test, process parameters analysis, metallographic examination and other tests. The analysis results are compared with normal color components after anodized. The result shows that the unsufficient solid solution heat treatment is the main reason for anodized film blackening of the aluminum alloy components, which result in the abnormal microstructures. At last, the measure of secondary heat treatment is taken to solve this problem effectively.

1. Induction
The method of sulfuric acid anodic oxidation of aluminum alloy has been widely used in aerospace and other fields due to its advantages such as low cost and simple composition of anodizing liquid, convenient operation and maintenance, good coloring, strong adsorption, good corrosion resistance, weather resistance and wear resistance\textsuperscript{[1]}. A batch of aluminum alloy connecting components was purchased by a company in Shanghai. These components were formed by aluminum alloy forgings with the brand material of 7A09, which were anodized by sulfuric acid and sealed by chromic acid after the process of machining and heat treatment. The oxide films on the surface of some components were found to be dark black when the components were inspected at the company, as shown in Fig.1.

7A09 aluminum alloy belongs to Al-Zn-Mg-Cu material which can be heat treated to strengthen the multiple aging alloy. It is developed on the basis of the Al-Zn-Mg ternary material. 7A09 aluminum alloy has the advantages of high strength, low density, good thermal performance, and so on. It is the main structural material in the aerospace field and is also one of the hot spots in the development of structural materials in the world at present\textsuperscript{[2]}. 7A09 aluminum alloy is a kind of high strength aluminum, and its corrosion resistance is poor. Therefore, sulfuric acid anodic oxidation treatment was usually adopted when the high requirement against corrosion of the components are necessary. The process is that the thin films of dense yellowish oxide layer are formed at the anode aluminum alloy surface after electrolysis reaction under the specific conditions and applied current in a certain concentration of sulfuric acid solution when the aluminum alloy components are worked as anode and the lead plates as cathode. In the sulfuric acid electrolyte, the formation of anodic oxide film is the comprehensive result...
of the electrochemical process of oxidation reaction generated Al₂O₃ and the chemical dissolving process of the generated oxide film by sulfuric acid in electrolyte at the same time. Only when the generated rate of the electrochemical oxidation film is greater than the chemical dissolution rate, the oxide film will be able to generate and grow to the design thickness[3]. Then the generated oxide film is usually sealed by dichromate, which can improve the corrosion resistance of aluminum alloy components.

In order to analyze the causes of the abnormal dark black color of the oxide films after sulfuric acid anodic oxidation of these aluminum alloy components and the influence on the product performance, chemical composition test, mechanical property test, process parameters analysis, metallographic examination, energy spectrum analysis and other tests are used to analyze the color difference of the oxide films.

![Fig.1 Abnormal blackening morphology of a component after sulfuric acid anodic oxidation](image1)

2. Test and analysis

2.1 Morphology analysis

A component was taken as 1# sample for morphological observation from this batch of aluminum alloy components with abnormal oxide film, and another component was taken as 2# sample from this batch of aluminum alloy components with normal oxide film, as shown in Fig.2. Most areas of the inner and outer surfaces of 1# sample are blackened, but there is no mechanical damage or metal matrix exposure on the black area. Some corner surfaces of 1# sample is yellow-green, which is the normal color of the oxide film after sulfuric acid anodic oxidation. There are continuous and dense anodized layers on the surface of both the abnormal area and the normal area. No material peeling was observed by hand wiping or adhesive tape. There was no difference between the black abnormal area of 1# sample and 2# sample when touched by hand. There was only the difference in color of the black area of 1# sample and 2# sample by using a magnifying glass.

![Fig.2 the samples of aluminum alloy components](image2)

2.2 Chemical composition analysis

The chemical composition, microstructure and metal phase uniformity of the aluminum alloys will affect the formation and properties of oxide films. For example, the local segregation of silicon content in aluminum alloys may result in abnormal phenomena such as local area without oxide film or black stripe, or local selective dissolution and holes[4]. The chemical composition of 1# and 2# samples were analyzed by the direct reading spectroscopic instrument, as shown in Tab.1.
Tab.1 Chemical composition of the samples %

| Elements | Sample No. | Mg   | Mn  | Cu   | Zn  | Cr  | Fe  | Si  | Al  |
|----------|------------|------|-----|------|-----|-----|-----|-----|-----|
| Standard specified value | 2.0~3.0 | ≥0.15 | 1.2~2.0 | 5.1~6.1 | 0.16~0.30 | ≤0.50 | ≤0.50 | margin |
| 1# sample       | 2.72       | 0.10 | 1.56 | 5.70 | 0.23 | 0.42 | 0.40 | 88.66 |
| 2# sample       | 2.70       | 0.11 | 1.55 | 5.70 | 0.22 | 0.42 | 0.37 | 88.93 |

The chemical composition of 1# sample listed in Tab.1 could satisfy the standard requirements, which was as same as that of 2# samples, and also conformed to the material quality certificate of the same furnace.

2.3 Mechanical property test
After 1# and 2# samples machined, the tensile properties and surface hardness were tested. The test results were shown in Tab.2.

Tab.2 Mechanical properties of the samples

| Items | Sample No. | Tensile strength σb (MPa) | Hardness (HB) |
|-------|------------|---------------------------|---------------|
| Standard specified value | ≥509.6 | ≥125 |
| 1# sample | 393.0, 395.2 | 99, 105, 103 |
| 2# sample | 515.5, 522.1 | 129, 129, 130 |

According to the test results, the mechanical properties of 1# sample cannot satisfy the requirements of the material standard GBN 223-1984 ‘Aluminum Alloy Forgings’, while 2# sample can satisfy the requirements. Compared with 2# sample, the strength and surface hardness of 1# sample decreased greatly. The raw material forgings of 1# and 2# samples belonged to different heat treatment batches, and other blackened components were in the same batch as 1# sample. Therefore, it can be inferred that the processing and manufacturing of the raw material forgings of the black components did not satisfy the design requirements.

2.4. Technological process and parameters analysis
The raw material of this batch of components was 7A09 aluminum alloy forging, and the technological process was as follows: smelted casting, homogenizing annealing, sawing, heating and hot forging. The forged materials had been subjected to multiple batches of solid solution plus aging state heat treatment. Then the process of sulfuric acid anodic oxidation is carried out. The anodic oxidation procedure by sulfuric acid was as follows: forging processing and forming → mounting → chemical oil removal → light out → alkali corrosion → light out → anodic oxidation by sulfuric acid → cleaning → sealing by dichromate → blow-dry → drying[5]. The solution composition and parameters of sulfuric acid anodizing process and dichromate sealing process are shown in Tab.3.

Tab.3 Solution composition and parameters of anodized film procedure

| Anodic oxidation process | Solution composition | Procedure parameters |
|-------------------------|----------------------|----------------------|
|                        | Sulfuric acid (AR) g/L | Pure water (A grade) | Temp. °C | Density of electric current A/dm² | Voltage V | Time min |
|                        | 180~200 margin        | 15                   | 1~1.5     | 15                               | 40       |

| Sealing process | Solution composition | Procedure parameters |
|-----------------|----------------------|----------------------|
|                 | Kalium dichromicum (CP) g/L | Pure water (A grade) | Temp. °C | Time min |
|                 | 50~60 margin          | 90                   | 15       |

After documents checking and inquiry of relevant operators and inspectors, the surfaces of aluminum alloy components before the process of sulfuric acid anodic oxidation were clean. The composition of anodic oxidation solution and dichromate sealing solution were reverified, and the content of suspended
impurities, dusts, and copper or iron metal impurity ions satisfied the procedure design. The operation process and parameters of anodic oxidation were accord with the general technical regulations, and no abnormal phenomenon was found in the operation process.

2.5. Metallographic examination

The microstructures of 1# sample and 2# sample were observed by Scanning Electron Microscopy (SEM). The observation result shows that there were continuous and dense anodized films on the surface of both 1# and 2# samples. The thicknesses of the coatings were about 8μm, which satisfy the design thickness (7~10μm), as shown in Fig.3. The number of micropores on the anodized film of 2# sample is less than that of 1# sample, and the average grain size of 2# sample is also smaller than that of 1# sample. There was no significant difference in the microstructures of the anodized films after further amplification.

![Fig. 3 Thicknesses of the samples film](a) 1# sample (b) 2# sample

According to the test results of energy spectrum analyzer, there is no difference in the anodized films composition of 1# and 2# samples, which mainly contain elements of O, Al and a small amount of S, Cr and Zn, as shown in Fig.4.

![Fig. 4 Surface energy spectrum of the samples anodized films](a) 1# sample (b) 2# sample

After the anodized films on the surface of 1# and 2# samples were polished, the metallographic structures of the base metal materials were observed. The microstructures of the base metal were all solid solution structures of aluminum alloy. It was characterized by many small black strengthening phases and massive precipitates distributed on the fibrous tissue. The strip and block precipitates were distributed both at grain boundaries and inside grains. However, the strip and block precipitates and strengthening phases of 1# sample were more and larger than those of 2# sample, and more inclusions are precipitated on grain boundaries, as shown in Fig.5.
The strip and block precipitates at the grain boundary of 1# sample were analyzed by energy spectrum analyzer. The main components were Mg (0.9%~0.8%), Al (58.3%~65.2%), Fe (13.4%~31.2%), Cu (7.8%~16.5%), Mn (0.45%~1.6%), S (5.9%~6.8%), Zn (3.9%~4.1%), etc. It can be inferred that the black precipitates were the residual strengthening phases such as CuMgAl₂, MgZn₂, Al₂Mg₂Zn₃ and insoluble inclusion phases of (Mn, Fe) Al₆ distributed at the grain boundary.

3. Analysis summary and conclusions

According to the above tests of the aluminum alloy samples, the conclusion is that the difference of metallographic structure is the main reason for the films blackening of aluminum alloy components after anodizing, which is caused by the unqualified heat treatment process applied to a heat treatment batch of the components.

The 7A09 material used in the aluminum alloy components is belongs to Al-Zn-Mg-Cu alloy, which can be strengthened by heat treatment, and the strength of the alloy can be improved by aging after solution. Cu, Zn and Mg are the main strengthening elements formed the main strengthening phases of CuMgAl₂, MgZn₂, Al₂Mg₂Zn₃ and other phases, which dissolve in the solid solution and form supersaturated solid solution after heat preservation and cooling. In the subsequent aging treatment, the strengthening phases are gradually desolved, which increases the hardness and strength of the material. Therefore, the most important process is whether supersaturated solid solution can be fully formed during solid solution[6].

The factors affecting the solution process include solution temperature, holding time, cooling rate and transfer time of the quenching procedure. After checking the documents, the components with abnormal films were made from small workblanks cut from the large forgings. The nominal thickness of large forgings was 250 mm, and heat treatment of this large thickness forgings can easily lead to inconsistent cooling rates at the center and surface. The cooling rate requirements of solid solution heat treatment of aluminum alloy is very strict. When the cooling rate of solid solution heat treatment is slow, the strengthening phases of CuMgAl₂, MgZn₂, Al₂Mg₂Zn₃ precipitate from the intracrystalline
completely, which will reduce the strength and corrosion resistance after aging. In addition, the transfer speed is slow during quenching process because of the large forging weight, and the unstable supersaturated solid solution decomposes into the strengthening phase during the transfer process. The precipitation of the strengthening phase not only leads to the decrease of material mechanical properties, but also leads to the decreased corrosion resistance and the increased anodizing corrosion speed. Then the soluble dispersive precipitated phase is preferably dissolved and the oxide film holes are generated. The inclusions phase is left to form the oxide film inclusions, which result in the blackening and darkening phenomenon of the oxide film.

![Fig.6 The aluminum alloy component after secondary heat treatment](image)

4. Treatment measures
According to the above test analysis, the unsufficient solution heat treatment of the batch aluminum alloy components and the short holding time is the main reason for blackening. Therefore, the blackened components must be taken treatments of solid solution and aging after deoxidizing the films. The heat treatment type and procedure should be not changed. At this time, the cooling speed of each part is uniform and the cooling transfer speed is fast, because the effective thickness of the components is only about 4mm. After the heat treated components are anodized, their surface film color completely returns to normal, as shown in Fig.6.

For small aluminum alloy components by sulfuric acid anodic oxidation, it is not recommended the method of small components cut from the large forgings with a very big thickness. If the conditions do not allow, the workblanks should be cut off for secondary heat treatment and the solid solution treatment should be sufficient to prevent the blackening phenomenon. After adopting the above improvement measures, the blackening phenomenon on the anodized films of aluminum alloy components by sulfuric acid anodic oxidation is not appear again in the past one year.

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