Measurement research for pitting potential of aluminium alloy with chromate passivation layers

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Abstract. This paper describes common technology for measuring corrosion resistant properties of aluminium alloy with chromate passivation layers. It gives a resolution to characterize corrosion resistant properties of pitting potential. The method, including sample preparation, measuring polarization and the determining of pitting corrosion potential, was proposed. Tests of repeatability and reproducibility can meet the demand of measurement precision. In addition, comparison of the positional relationships between polarization curves and nominal pitting corrosion potential was provided to judge products.

1. Introduction

Aluminium alloy is identified by its low specific gravity, good thermal conductivity and electrical conductivity as well as its reflectivity, processability and low cost. Aluminum has also been widely applied in aviation, space, transportation, light industry, building materials and other fields [1-3]. Chromate passivation can greatly improve corrosion resistance, expand the application range and prolong the service life of aluminium alloy. However, in order to meet the requirements of the European Union environmental standards (European Union RoHS directive and WEEE), relevant environmental laws and regulations of China some technologies are being phased out. In China, the hexavalent chromium electroplating technology has been gradually eliminated and environmental trivalent chromium electroplating technology or chromium-free electroplating technology are used instead [4-7]. A gap in the corrosion resistance between trivalent chromium passivation or chromium-free passivation products and hexavalent chromium passivation products can be ascertained via practical test but the quality cannot be easily controlled through this method [8-9]. Further research is necessary in order to standardize aluminum alloy passivation markets as well as guarantee their development. This will also reduce the corrosion waste, expand application of surface treatment technique of aluminium alloy, and enhance the service performance, especially the anti-corrosion capacity. It is also necessary to conduct further research the anti-corrosion capacity of aluminium alloy with chromate passivation layers. This forms the corresponding detection methods which play an important supervising function in the quality control of aluminium alloy with chromate passivation layers.

The current internationally recognized test for corrosion is the “Corrosion Tests in Artificial Atmospheres: Salt Spray Test”. This conventional test evaluates the anti-corrosion properties of material surfaces. After hydrochloric acid corrosion, evaluating anti-corrosion properties by assessing
weight loss or the degree of corrosion on surface spots. However, simulating a practical environment to assess passivation layers' properties can be time-consuming, costly and fuzzy [10]. Consequently, electrochemical etching, characterised to be sensitive, fast and accurate, is receiving increased attention. The energy of pitting potentials indicates corrosion resistant properties of passivation layers. Pitting corrosion potentials were measured by means of potentiodynamic polarization measurements. This method has received extensive attention in corrosion theory, while in the field of measurement engineering, rare detection methods adopt potentiodynamic polarization measurements with the exception of pitting potential measurement for stainless steels. There is no evaluation criterion in pitting corrosion potential for evaluating corrosion resistant properties so far. This paper aims to seek out such a standard criterion.

2. Experiments

2.1. Sample preparation

Stainless steel has a different sample preparation than that of preparing aluminium with chromate passivation layers for pitting potential. During the process of sample preparation it is necessary to avoid damage to the detecting surface, therefore, this paper excogitated a suit of specific sample preparation methods.

Preparation: a small block with an area equal to 1 cm² was cut by linear cutting machine from the chromium passivation aluminum sheet; Polypropylene (PPR) pipe was sectioned into several pieces with each piece being approximately 20 mm long; 0.5 mm² conducting wire was cut into several pieces, each approximately 100 mm long; approximately 10 mm of coating was stripped from the two ends of wire. The non-detection surface was cleaned with alcohol or sand paper. One end of the conducting wire was adhered on the non-detection surface with a double face adhesive tape to ensure conductivity between the wire and sample after the stick. The sample was attached with conducting wire on the flat table and with double face tape, then inset into PPR pipe and fixed on the same table. AB glue was mixed in a ratio of 1:1 quickly until smooth, then poured into PPR pipe within three minutes of mixing and along conducting wire. Non-detection surfaces and bare wires should be surrounded and covered completely. Setting of the AB glue started after sealing and ended after approximately six hours. Finally, double face tape was peeled from the table and sample. After the sample was prepared, the surface was delaminated, cleaned and dried using alcohol.

2.2. Polarization detection

Electrochemical workstation type Reference 600, supplied by American Gamry, was introduced and a three-electrode system was used during testing. Electrodes and reference electrodes were platinum pieces and saturated calomel electrode, respectively. According to GB/T 1266, 35g sodium chloride were dissolved into 965ml distilled water of deionized water to obtain sodium chloride with 3.5% concentration. The solution was injected into an electrolysis bath, the ration between solution volume and sample area was over 200mL/cm². The solution was then heated to approximately 30±1 degree and held there. Nitrogen with a purity of not less than 99% was bubbled through the solution for over 30 minutes until deaerated and aeration rates equalled 0.5L/min approximately. The sample was immersed in electrolysis bath after being washed and dried, which was below the surface of liquid within 1 cm and after approximately 10 minutes of immersion, the open circuit potential $U_0$ was measured. Polarized scanned from ($U_0$-0.1) V to ($U_0$+0.3) V at a scanning rate of 1mV/s.

3. Results and discussion

3.1. The determined method of pitting potential

GB/T 17899-1999 “The Measurement for Pitting Potential of Stainless Steel” is equivalent to JIS G 0577-1981 and the pitting potential is represented by the most positive, potential value. This corresponds with the 10 μA/cm² or 100 μA/cm² of the current density on the anodic polarization curve,
because there is a continuous self-passivation phenomenon on the surface of stainless steel in the anodic polarization process. Pitting potential is represented by only the most positive potential value when analysed by the current standards, as such, the polarization current shows an increase with this fluctuation.

Stainless steel has a different, obvious curve when compare to the anodic polarization curves of aluminium allows with chromate passivation layers. Figure 1 illustrates a series of curves which are based on the logarithm of aluminium polarization potential and polarization current where a clear inflection point can be identified. Before inflecting, the current is increased slowly then a sharp increase of current is applied. The results show that aluminium alloy chromate passivation layers suffer from pitting corrosion at the inflection point corresponding to the pitting potential. Although there are minute differences between open circuit potential, the potential corresponding to the inflection point are close, therefore, it is more reasonable to use pitting potential to judge corrosion resistance of aluminium alloy with chromate passivation layers.

![Figure 1. The potentiodynamic polarization curves.](image)

In order for the pitting potential to correspond with the inflection point it is necessary to export dates corresponding to the anodic polarization curves and analyse them independently. By researching several potentiodynamic polarization curves and their corresponding curve date, it can be found that when sample occurred pitting corrosion, every increased 1 mv of voltage, the corresponding current increment will be increased. Based on the results, a method for measuring the pitting corrosion potential is developed. Polarization potential increases by 1mv during the process of potentiodynamic polarization while polarization current increases by over 1μA.

3.2. Repeatability and reproducibility of analytical methods

The ability of these analytical methods to be reproduced or repeated is essential to determine accuracy of the analytical methods themselves. When it comes to the acceptability of R & R standards for measuring system, the system share common rules. As a result, a value of %R&R was less than 10 % which represents high accuracy, satisfactory testing and a reliable result. Accuracy is mainly effected by testing and analysis methods as well as an influence of repeatability that is larger than that of reproducibility. It has been shown that in the proposed method, reproducibility is within 5%, can ensure the requirements for accuracy in test and analysis methods.

Repeatability can be characterized with relative standard deviation (RSD), standard deviation divided by average value is RSD. Group A and Group B were chosen with each group comprised of 40 samples. At the same time, all samples were consistent. The proposed method were performed to execute the repeatability test with the results listed in Table 1. As can be seen from the table, repeatability of two groups of samples are lower than 5%. Consequently, this method can meet the demand of repeatability and reproducibility.
Table 1. The repeatability of test and analysis methods.

| Sample | Pitting Potential / mV | Average Value / mV | Standard Deviation / mV | RSD (%) |
|--------|------------------------|--------------------|-------------------------|---------|
| A      | 634 599 637 645 619 620 649 647 636 637 | 628.8 | 14.5 | 2.31 |
|        | 619 646 634 627 647 629 628 636 596 624 | 614 630 646 643 627 625 620 639 632 | 635.4 | 14.9 | 2.35 |
| B      | 627 649 634 600 628 637 636 628 628 615 | 618 628 627 630 622 645 639 618 613 630 | 635.4 | 14.9 | 2.35 |

3.3. Criterion for quality

A determination method of pitting potential has direct significance to the research for pitting potential of aluminium alloy with chromate passivation layers, but also demands to analyse the polarisation curves which is relatively sophisticated. A new and simple method for determining pitting potential is required in order to maintain quality control during analytical testing.

Figure 2. The judgement of product quality.

Based on pitting corrosion potential in a graph showing polarization potentiodynamic measurements, a line called pitting corrosion potential was drawn. The products’ quality of chromate passivation layers determine the position of this nominal straight line. When the affecting point of polarization curves is located at the left side of the line, we conclude that the quality does not meet quality control or performance requirements. When the affecting point of polarization curves is located at the right side of the nominal pitting corrosion potential, we conclude that the quality does not meet quality control or performance requirements. When two point nearly coincide, we can tell the relationship by doubling tests. Only if all tests tell relationship between inflection point and the line considerably, can we judge them as qualified products. A criterion for quality is represented in Figure 2.

4. Conclusion

There are negatives associated with conducting salt-mist corrosion tests including the time involved, the high cost and the indeterminate results. A kind of evaluation of pitting potential of aluminium alloy with chromate passivation layers was proposed through a great deal of experimentation. This analytical method introduced the preparation process of the polarization corrosion sample and testing process of the dynamic potential polarization corrosion in detail. A new method for measuring the putting potential was developed through analysis and processing of this large data set resulting in the.
following conclusions. During the process of potentiodynamic polarization, while polarization potential increases by 1 mv, polarization current increases by over 1 μA, it is confirmed that the polarization potential is pitting corrosion potential. Repeatability and reproducibility of this analytical methods is helpful in determining how accurately the method is. This method can meet the demand of repeatability and reproducibility. In order to simplify the process of the criterion, comparison of the positional relationship between polarization curves and nominal pitting corrosion potential were put forward.

References
[1] Teng S L, Yin Y S, Du J B, Cheng S and Yan L N 2007 Research Progress of Rare Earth Passivation on Metal Surface Shandong Metallurgy 29 7-9
[2] Yu H C, Chen B Z, Shi X C, Li B and Wu H Y 2008 Preparation and Electrochemical Properties of Trivalent Chromium Coating on 6063 Aluminium Alloy Acta Phys Chim Sin 24(8) 1465-1470
[3] Kang K, Huang S H, Feng Y, Dong L Q and Zhu L A Y 2008 Fabrication of Colloidal Photonic Crystals by a Micro-cell Based on AL Thin Film Acta Chimica Sinica 66(14) 1615-1619
[4] Peng J D, Deng C Y, Shi Y and Xiong Y 2011 Nature Color Passivation Process of Trivalent Chromium for Aluminum Alloy Castings Foundry 60(2) 147-149
[5] Zhao Y C 2010 Trivalent Chromium Passivation of Aluminum Alloy Electroplating & Pollution Control 30(2) 47
[6] Feng Y, Mceguire G, Shenderova O, Ke H and Burkett S 2016 Fabrication of Copper/Carbon Nanotube Composite Thin Films by Periodic Pulse Reverse Electroplating Using Nanodiamond as a Dispersing Agent Thin Solid Films 615 116-121
[7] Jordan M, Feng Y and Burkett S 2015 Development of Seed Layer for Electrodeposition of Copper on Carbon Nanotube Bundles Journal of Vacuum Science & Technology B 33(2) 021202
[8] Li J, Sun J and An C Q 2008 Research Development of Aluminium Alloy with Chromate-free Passivation Surface Technology 137(4) 60-62
[9] Fang Z 2009 Development Trends of Chemical Conversion Films Electroplating & Finishing 28(9) 30-34
[10] Ge S S, Yang Y X and Shao Q 2006 Morphology and Anticorrosion Property of A Black Conversion Film with Non-chromate on Casting Aluminum Alloy Corrosion Science and Protection Technology 18(3) 228-230