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Corrosion of AlSi18Cu3CrMn Aluminum Alloy in a Chloride-Containing Medium

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Abstract. This paper presents the results from a study of the corrosion behavior of AlSi18Cu3CrMn aluminum alloy in 1M NaCl.The corrosion resistance of the alloy for different types of its chemical composition has been determined by a gravimetric method.The corrosion rate has been calculated for the media under consideration, and it has been established that for the modified AlSi18Cu3CrMn alloys this rate is lower compared to the one for unmodified alloys. The gravimetric analysis has confirmed that during the period of study the weight loss decreases.

INTRODUCTION

Aluminum alloys 3003, 5754, 5083, 5086, 6060, and 6061 are widely used for the manufacturing vessels and equipment for the food and canning industry, operating in media, containing sodium chloride [1]. Due to the fact that the aluminum-silicon alloys contain chemical elements that impair the corrosion resistance of aluminum (Si, Cu, Fe), the corrosion behavior of these alloys is a subject of scientific interest. Paper [2] considers the corrosion behavior of a two-component hypereutectic aluminum-silicon alloy AlSi18, both unmodified and modified by different types of modifiers. Interfused aluminum-silicon alloys are commonly used in industry and therefore it is important to study the corrosion resistance of the complexly interfused AlSi18Cu3CrMn alloy in sodium chloride.

The corrosion behavior of aluminum and its alloys is largely determined by the chemical resistance of the protective oxide layer on their surface [3]. This natural oxide layer consists of three very different elements – an anodal porous element, a cathode barrier and a neutral element. Therefore, any chemical or mechanical impact, leading to either removal or disintegration of this layer, changes the potential of aluminum and increases the degree of its corrosion [1].

The present study monitors the corrosion rate and corrosion potential of unmodified, phosphorus-modified and complexly-modified alloys. The influence of the heat treatment mode parameters on the corrosion behavior of the alloys has been discussed.

The aim of the present study is to determine the degree of corrosion of unmodified, phosphorus-modified and complexly-modified AlSi18Cu3CrMn alloys in media, containing chloride ions, by determining the corrosion rate, the electrode potentials in 1M AlCl₃, and the corrosion potentials in 1M NaCl.

EXPERIMENTAL STUDY

Determination of the Electrode and Corrosion Potentials of AlSi18 Cu3CrMn Aluminum Alloys

The experimental measurements were performed using five samples, made of the following types of AlSi18Cu3CrMn alloy: unmodified AlSi18 Cu3CrMn; AlSi18Cu3CrMn, modified with 0.04 % P; complexly modified AlSi18Cu3CrMn with 0.04 % P, 0.2 % Ti, 0.04 % B, 0.007 % Be; AlSi18Cu3CrMn alloy, modified with 0.04 % P and heat treated by T6 (ageing at 250 °C for 12 h) and AlSi18Cu3CrMn alloy, modified with 0.04 % P and heat treated by T6 (ageing at 330 °C for 8 h). The total surface area of each of the tested samples is 4.70 cm². The used experimental samples were preliminarily placed in ethyl alcohol for 5 minutes, then washed with distilled water and dried. The EMF values of the tested types of AlSi18Cu3CrMn alloys were experimentally determined for 1M AlCl₃ and the corrosion potential – for 1M NaCl. The measurements were reduced to determining the electromotive force (EMF) of a galvanic cell [4], composed of two half-cells - a saturated calomel electrode and an electrode, made of AlSi18Cu3CrMn aluminum alloy. The potential of the saturated calomel electrode is constant $E_{SCE} = + 0.242$ V [5]. The sought potential is calculated by the formula (1):

$$EMF = E_C - E_A (1),$$

where E_C is the electrode potential of the cathode, V; E_A is the electrode potential of the anode, V.

All laboratory tests were performed at a temperature of 293 K using a MAS830 digital multimeter with an accuracy class of 1.5. The measured electrode potential is used to assess the corrosion risk for the alloys, considering that the electrodes are mixed-type for aqueous solutions because of more than one conjugated electrode reactions proceeding at the same time.

The calculated corrosion potential of the alloys (Ecorr, V) is used to determine the active (passive) behavior of the alloy under the given conditions [6].

Immersion Tests

The aluminium alloy test samples had the composition, given in Table 1.

TABLE 1. Composition of the AlSi18Cu3CrMn aluminium alloy samples

Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Al
18,5	0,25	3,1	0,71	0,01	0,9	0,01	0,13	rest

Five types of samples, made of AlSi18Cu3CrMn, were used to perform the corrosion tests: unmodified AlSi18Cu3CrMn; AlSi18Cu3CrMn, modified with 0.04 % P; complexly modified AlSi18Cu3CrMn with 0.04 % P, 0.2 % Ti, 0.04 % B, 0.007 % Be; AlSi18Cu3CrMn alloy, modified with 0.04 % P and heat treated by T6 (ageing at 250 °C for 12 h) and AlSi18Cu3CrMn alloy, modified with 0.04 % P and heat treated by T6 (ageing at 330 °C for 8 h). The total area of each of the samples was 4.70 cm². The samples were exposed for 360 hours to 1M NaCl solutions in 50 ml. A mixture of 50 vol.% ethanol/50 vol.% water was used to clean the samples before the immersion tests. Afterwards the samples were dried and weighed. Then they were immersed in a test tube with 1M NaCl. The system was slightly covered with a parafilm.

First time the weight loss of each sample was determined after 72 h and then – at every 144 h of exposure. The maximum period of exposure was 360 h. After the immersion period the samples were cleaned by brushing them under running water, using a fiber-bristle brush to remove the corrosion products. Then they were rinsed with tap water, dried under a stream of air, and weighed.

For each of the immersion periods the corrosion rate (CR) of the alloy was determined using the following equation (2):

$$CR = \frac{(m_1 - m_2)}{S.t}$$
(2),

where m_1 is the weight of the sample, g; m_2 is the weight of the sample after the corrosion test, g; S is the area of the sample, m², and t is the exposure time, h.

RESULTS AND DISCUSSION

Electrode and Corrosion Potentials of AlSi18Cu3CrMn Alloy Samples

Table 2 presents the experimentally measured electrode potentials of the samples, made of the studied AlSi18Cu3CrMn alloy and immersed in 1M AlCl₃. The measured values are more positive than the standard electrode potential of aluminum (-1.66 V), which shows that the activity of the tested samples is greatly reduced, most likely due to the formation of a passive layer of Al₂O₃. Of the five types of the alloy under study, the unmodified AlSi18Cu3CrMn one, as well as the one, modified with 0.04 % P, are with the most positive potentials. The most negative potentials have the samples, made of the alloy, subjected to heat treatment, which implies a higher risk of corrosion compared to the other types of samples.

The corrosion potentials of the electrodes from the studied AlSi18Cu3CrMn alloy, measured for the case of immersion in 1M NaCl (Table 2), are more negative than the experimentally determined values of EMF for 1M AlCl₃, i.e. the activity of these alloys is increased by the active chloride ions present in the corrosive medium. These ions are adsorbed on the protective Al_2O_3 layer of the alloys and displace the oxygen ions. Thus the metal surface remains unprotected and corrosion accelerates in these areas.

AlS18Cu3CrMn	EMF V, vs. KCl	E _{corr} V, vs. KCl	
	1M AlCl ₃	1M NaCl	
AlSi18Cu3CrMn unmodified	-0,382	-0,500	
AlSi18Cu3CrMn+ 0.04 % P	-0,375	-0,493	
AlSi18Cu3CrMn + 0.04 % P, 0.2 % Ti, 0.04 %			
B, 0.007 % Be	-0,460	-0,512	
AlSi18Cu3CrMn + 0.04 % P + T6			
(ageing at 250 °C/12 h)	-0,467	-0,528	
AlSi18Cu3CrMn + 0.04 % P + T6			
(ageing at 330 °C/8 h)	-0,425	-0,516	

TABLE 2. Electrode potentials (EMF in 1M AlCl₃) and corrosion potentials (Ecorr in 1M
NaCl) of AlSi18Cu3CrMn aluminum alloy

The values of the corrosion potential of the heat-treated AlSi18Cu3CrMn alloy are again more negative compared to the values of E_{corr} of the other tested samples. This is probably due to the fact that the corrosion potential of the aluminum alloys depends on their heat treatment [1].

Immersion Tests

The alloy destruction when immersed in chloride-containing media is measured by the weight loss. For each of the studied periods of immersion in 1M NaCl, the corrosion rate (CR) was calculated. The summarized CR data, concerning the different types of AlSi18Cu3CrMn samples, are presented in Table 3. The data analysis shows that at the beginning of the tests the corrosion rate increases and then gradually decreases. 72 hours after the immersion in 1M NaCl, the highest CR value of 0.0048 $g/m^2.h$ was observed for the unmodified AlSi18Cu3CrMn alloy, followed by the same alloy, modified with 0.04 % P, whose CR was 0.0038 $g/m^2.h$. The hardened AlSi18Cu3CrMn alloy, which was subjected to artificial ageing at a temperature of 250°C for 12h, had the lowest CR value of 0.0026 $g/m^2.h$.

TABLE 3. Corrosion rate of AlSi18Cu3CrMn aluminum alloys in 1M NaCl

AlSi18Cu3CrMn	72 h	216 h	360 h
	CR, $g/m^2.h$	CR, $g/m^2.h$	CR, $g/m^2.h$
AlSi18Cu3CrMn unmodified	0.0048	0.0030	0.0018
AlSi18Cu3CrMn + 0.04 % P	0.0038	0.0024	0.0016
AlSi18Cu3CrMn + 0.04 % P, 0.2 % Ti,			
0.04 % B, 0.007 % Be	0.0028	0.0020	0.0014
AIS118Cu3CrMn + $0.04 \% P + 16$ (ageing at 250 °C/12 h)	0.0026	0.0015	0.0014
AlSi18Cu3CrMn + 0.04% P + T6	0.0020	0.0012	0.0011
(ageing at 330 °C/8 h)	0.0031	0.0018	0.0014





FIGURE 1. Comparison of corrosion rate vs. exposure time graphs for the five AlSi18 Cu3CrMn alloys immersed in 1M NaCl

In spite of the fact that the samples, made of the phosphorus-modified AlSi18Cu3CrMn alloy, subjected to hardening and artificial ageing (at different operating parameters) have a high value of their corrosion potential, implying increased activity, relatively low mass loss and low corrosion rate are observed with them.

CONCLUSION

- Over time, under the conditions, specified in the present work, the corrosion rate of the studied AlSi18Cu3CrMn alloy in 1M NaCl decreases. In the considered corrosive medium, the unmodified AlSi18Cu3CrMn alloy is most easily destroyed, and the highest degree of corrosion resistance is shown by the alloy type, subjected to hardening and subsequent artificial ageing at 250 °C for 12 hours.
- The obtained results show that the corrosion potential of the studied AlSi18Cu3CrMn alloy is influenced by the parameters of the performed heat treatment. Of particular importance are the operating parameters of the artificial ageing, conducted after the hardening. Under the same conditions of hardening, when the artificial ageing is performed at lower temperatures and at longer exposure time, the studied alloy has the best mechanical properties and corrosion resistance due to the structure it obtains.
- The complexly modified AlSi18Cu3CrMn alloy before heat treatment is with better corrosion resistance than the alloy, modified with phosphorus; and with comparable corrosion resistance to the corrosion resistance of the hardened alloy, subjected to artificial ageing at 330 °C for 8 h. This shows that the proposed combination of modifiers can be successfully used to modify interfused hypereutectic aluminum-silicon alloys and study their influence on the structure, mechanical and operational properties of these alloys before and after heat treatment.

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