The Evaluation of the Corrosion Resistance of the Al-Si Alloys Antimony Alloyed

J. Svobodova*, J. Cais, V. Weiss
Department of Technology and Material Engineering, J.E. Purkyně University in Ústí nad Labem, Pasteurova 7, 400 01 Ústí nad Labem, Czech Republic
*Corresponding author. E-mail address: svobodova@fvtm.ujep.cz

Received 04.03.2014; accepted in revised form 30.03.2014

Abstract

This paper deals with the evaluation of the corrosion resistance of the Al-Si alloys alloyed with the different amount of antimony. Specifically it goes about the alloy AlSi7Mg0.3 which is antimony alloyed in the concentrations 0; 0.001; 0.005; 0.01 a 0.05 wt. % of antimony. The introduction of the paper is dedicated to the theory of the aluminium alloys corrosion resistance, testing and evaluation of the corrosion resistance. The influence of the antimony to the Al-Si alloys properties is described further in the introduction. The experimental part describes the experimental samples which were prepared for the experiment and further they were exposed to the loading in the atmospheric conditions for a period of the 3 months. The experimental samples were evaluated macroscopically and microscopically. The results of the experiment were documented and the conclusions in terms of the antimony impact to the corrosion resistance of the Al-Si alloy were concluded. There was compared the corrosion resistance of the Al-Si alloy antimony alloyed (with the different antimony content) with the results of the Al-Si alloy without the alloying after the corrosion load in the atmospheric conditions in the experiment.

Keywords: Surface treatment, Metallography, Corrosion resistance, Aluminium alloys, Corrosion testing

1. Introduction

The aluminium materials have besides the low density, good electrical and heat conductivity the high corrosion resistance too. This material resists good especially in the atmospheric environment. One of the factors which have the influence to the corrosion resistance of the aluminium alloys is the chemical composition of the alloy. The highest corrosion resistance has the pure aluminium. The content of Mn has favourable influence to the corrosion resistance of the Al alloys because the next alloying elements for example Na, Cu, Co, Pt, Ag, Th, V, Sn Cd etc. are to aluminium cathode. The influence of the aluminium alloying elements to the corrosion resistance is depend on the environment where is the alloy situated and on the structure of the material too, thus if the impurities are excluded in the form of the heterogeneous particles or they are presented in the solid solution. Dangerous are the phases excluded in the grain boundaries. These phases are nobler that the metallic base, dissolved in the electrolyte and leads to the anodic dissolution of the base metal [1, 2, 3].

The content of the Cu is decisive for the Al alloys corrosion resistance. The alloys without the copper content have almost the same corrosion resistance like the pure aluminium. The alloys for example based on AlM, AlMg, AlZnMg etc. belongs to the group of the aluminium alloys without Cu content. The corrosion resistance of these types of the alloys can be reduced at the causing of the elevated temperatures. The alloys with the Cu content have the low corrosion resistance. These are the alloys of the AlCuMg, AlMgCuSi, AlZnMgCu content etc. If there is the requirement for the improvement of the corrosion resistance of these alloys we use for example the plating technology with the pure aluminium or the plating with the Al-Zn alloy [2, 4, 5].
Although the regularities of the corrosion processes are known and we can predict the behaviour of the given material in the given environment it is needed experimentally check the corrosion behaviour of the materials. The reason is the complexity of the corrosion process and the possibility of the influencing and the occurrence of the random factors which acts on the material during its lifetime. The testing methods of the aluminium alloys are of course supported by the standards (for example ČSN ISO 11845). The material testing can perform using the exposure methods while the tests are based on the exposure of the samples or the whole product to the different corrosion environments. The exposure methods are mainly the long-term atmospheric tests. The corrosion and condensation chamber test are performed then in the laboratory conditions [1, 6]. The different criteria can be used in the evaluating the corrosion resistance. We can observe the visual changes, dimensional changes and weight changes in the evaluation – macroscopic analysis. The microscopic evaluation is performed for the evaluation of the changes inside the material – metallographic evaluation [8]. We'll evaluate the samples this way in our experiment.

The influence of the antimony alloying on the AlSi7Mg0,3 alloy

How the previous research at the Faculty of Production Technology and Management, University of J.E. Purkyně in Ústí nad Labem (FPTM, UJEP) shows the antimony has the modification effect on the AlSi7Mg0,3 alloy which is its secondary effect. The antimony in the Al-Si alloy makes intermetallic phases AlSb (primary effect) which has, how it was experimentally checked, positive influence on the ductility of the alloy.

The modification ability of the antimony is manifested by the rounding off the needles of the eutectic silicon and by the reducing of the dimensions of these particles in the microstructure of the material. The positive influence of the antimony on the alloy microstructure is visible to the content of 0.1 wt. % and after exceeding of this limit it has completely the opposite trend. The content of the antimony more than 0.1 wt. % leads to coarsening of the silicon needles. We can conclude that the supplement of the antimony to the alloy has the similar influence like in the modification with the strontium [1, 4, 5].

The samples were prepared after the casting of the alloy and these samples were subjected to the static tensile test. The results obtained in the static tensile test correspond with the state of the microstructure of the material. To the content of the 0.1 wt. % Sb in comparison with the primary alloy the ductility increases to the 51.98% and the yield strength to 12.92 % which is due to the formation of the new intermetallic phases AlSb and due to the significant change of the morphology (coarsening) of the eutectic silicon needles. The ductility and yield strength values are opposite to the primary alloy lower after the crossing the limit 0.1 wt. % Sb what is due to the change of the silicon needles morphology (rouglier and bigger needles) caused by the over modification of the alloy with the antimony [5].

2. Experimental part

The description of the experimental samples and its chemical composition is described in the experimental part. Further it is here described the marking of the experimental samples and the conditions of the atmospheric corrosion test.

2.1. Experimental samples

The evaluation of the corrosion resistance of the aluminium alloy of the Al-Si type was performed in the experiment. Concretely the alloy AlSi7Mg0,3 antimony alloyed in the amount 0; 0.001; 0.005; 0.01 a 0.05 wt. % of antimony was tested. These alloys were exposed to the corrosion test in the atmospheric conditions. The samples in the form of rods with the designation 0 – 0 hm % Sb, 1 – 0.001 hm. % Sb, 2 – 0.005 hm. % Sb, 3 – 0.01 hm. % Sb, 4 – 0.05 hm. % Sb were prepared for the experiment. The samples were further processed after the casting. The half of the each sample was left with the surface after the casting and the second half of the sample was lathed. The evaluation of the surface treatment on the corrosion resistance of the alloy AlSi7Mg0,3 was performed in the conclusion. The experimental samples before the exposure are shown at the fig. 1. The dimensions of the samples – sample height is 60 mm and the diameter Ø 20 mm. The chemical composition of the samples is shown in the table 1.

![Fig. 1. The samples of the alloy AlSi7Mg0,3 before the exposition](image)

Table 1.

| Alloy | Al | Si  | Mg  | Fe  | Cu  | Mn  | Zn  | Ti  | Sb  |
|-------|----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0     | 93.37 | 6.188 | 0.176 | 0.08 | 0.0028 | <0.002 | 0.0065 | 0.106 | <0.007 |
| 1     | 94.13 | 5.548 | 0.147 | 0.095 | 0.01 | <0.002 | 0.0027 | 0.0042 | <0.007 |
| 2     | 94.28 | 5.466 | 0.118 | 0.069 | 0.0037 | <0.002 | 0.0033 | 0.0045 | <0.007 |
| 3     | 94.91 | 4.842 | 0.112 | 0.069 | 0.0012 | <0.002 | 0.0034 | 0.0055 | 0.0086 |
| 4     | 95.2 | 4.505 | 0.091 | 0.092 | 0.001 | <0.002 | 0.0039 | 0.0067 | 0.049 |

Note: A spectrometer which is part of the faculty equipment does not have standards with the antimony content less than 0.007 wt.%. Therefore samples with antimony 0.001 and 0.005 wt.% the device was not able to determine the exact content of antimony but we know only that it is less than 0.007 wt.% Sb.
2.2. Atmospheric corrosion test

The prepared experimental samples were loaded in the atmospheric conditions. The corrosion loading time was in the case of these experimental samples set at 3 months. According to this time it goes about the short time atmospheric test. The samples were exposed to the atmosphere acting in the period from 12.12.2012 to 12.3.2013. The highest aggressiveness of the environment was waited in this period (changing of the temperatures, humidity). The test was performed in Ústí nad Labem. The city and its neighbourhood are one of the most polluted areas in Czech Republic mainly due to the operation of the coal mining, coal-fired power plants and chemical industry. The average conditions of the loading in the period shown above are: temperature – 1,2°C and the average rainfall 51,5 mm. The marking of the experimental samples is shown in the table 2. The samples were marked due to the corrosion loading time 1. month – A, 2. month – B, 3. month – C.

| Alloy | Content of Sb [wt. %] | Marking of the sample |
|-------|-----------------------|-----------------------|
| 0     | 0                     | primary               |
| 1     | 0,001                 | 1A                    |
|       |                       | 1B                    |
| 2     | 0,005                 | 2A                    |
|       |                       | 2B                    |
| 3     | 0,01                  | 3A                    |
|       |                       | 3B                    |
| 4     | 0,05                  | 4A                    |
|       |                       | 4B                    |

3. Experimental part

The evaluation of the corrosion attack from the macroscopic and microscopic point of view was performed after exposure of the samples in the atmospheric conditions.

3.1. Macrocscopic analysis

The matte layer created on the sample surface after the 1. month exposure when we macroscopically evaluate the samples. The brown corrosion products occur on the casting part by the samples with the content of antimony. The areas of the occurrence of the corrosion products are labelled on the fig. 2.

The corrosion products occur by the all samples antimony alloyed on the casting surface where it is possible to observe the impurities pushed into the sample surface after casting. With the increasing content of antimony the corrosion attack get worst. The lathed part of the experimental samples is in this part of the experiment without the bigger change. This is due to the removing of the impurities by the machining which acts like the centre for the corrosion attack on the casting part. We can conclude that the lathed surface has better corrosion resistance that the casting surface. The impurities on the material surface (oxides, impurities) are therefore the most serious problem from the corrosion resistance point of view than the influences act on the state of the material after machining (influence of internal stresses, surface roughness).

The corrosion products occur by the all samples antimony alloyed on the casting surface where it is possible to observe the impurities pushed into the sample surface after casting. With the increasing content of antimony the corrosion attack get worst. The lathed part of the experimental samples is in this part of the experiment without the bigger change. This is due to the removing of the impurities by the machining which acts like the centre for the corrosion attack on the casting part. We can conclude that the lathed surface has better corrosion resistance that the casting surface. The impurities on the material surface (oxides, impurities) are therefore the most serious problem from the corrosion resistance point of view than the influences act on the state of the material after machining (influence of internal stresses, surface roughness).

The samples after 2 months exposure in the atmospheric conditions are shown in the fig. 3. We can observe even more pronounced loss of gloss on the lathed sample part by these samples. No significant change of the appearance occurs by the primary alloy. The corrosion damage was slightly extended on the casting part of the antimony alloyed samples.

The macroscopic analysis result is finding that the influence of the antimony to the alloy corrosion resistance AlSi7Mg0,3 is
negative. We can conclude in this phase of the experiment that with the increasing amount of the antimony the corrosion attack of the experimental samples grows.

3.2. Microscopic analysis

The microscopic analysis was performed on the confocal laser microscope Olympus LEXT OLS 3100. The samples after corrosion load are documented (after 3 months) on the fig. 4-13.
The microscopic analysis of the samples 0 – 4C on the casting part is documented on the pictures 4, 5, 6, 8 and 8. The corrosion attack and the interdendritic porosity were observed by these samples. The best results occurs the primary alloy after corrosion load. The primary alloy is without the corrosion attack. The corrosion was observed mainly on the sample 1C with 0,001 wt. % of antimony, fig. 5. We performed the corrosion attack depth measurement. The maximum measured depth of the corrosion attack is 89μm by the sample 1C. The next sample on which it was seen the corrosion attack from the surface is 4C with the content 0,05 wt. % of antimony, fig. 8. The depth of the corrosion attack was measured from the sample surface to the depth of 95μm by this sample. The corrosion attack by the samples 1C and 4C spreads around the material dendritic cells. The samples 2C and 3C are without the significant corrosion attack on the material surface part after casting. The microscopic analysis of the samples on the casting part is influenced by the formation of the interdendritic porosity. This porosity is more significant factor for the corrosion formation than the antimony content in the alloy itself by this part of the samples (the part after casting).

Microscopic analysis on the sample part after turning is shown on the fig. 9, 10, 11, 12 and 13. There is observed no corrosion attack by the samples 0 – 4C on the lathed part. Only by the sample 4C appeared corrosion on the material surface on the lathed part in the depth of max. 13μm. We can conclude from the microscopic analysis of the samples on the lathed part that the highest content of antimony has adverse influence on the samples corrosion resistance which confirms the results from the macroscopic evaluation. This trend is not uniform by the samples on the casting part because the material tends to the corrosion due to its microstructure (porosity).
4. Conclusions

This paper presents only part of the extensive research performed at FPTM UJEP. The aim of the research is to provide the better mechanical and chemical properties by the new prepared material antimony alloyed. The aim of this paper was the evaluation of the corrosion resistance of the AlSi7Mg0,3 alloy alloyed by the different content of antimony. The samples with the content of antimony 0 – 0 wt. % Sb, 1 – 0,001 wt. % Sb, 2 – 0,005 hm. % Sb, 3 – 0,01 hm. % Sb, 4 – 0,05 hm. % Sb are corrosion loaded in atmospheric conditions in the experiment. Except the antimony content was evaluated the influence of the material surface treatment on the corrosion resistance of the alloy as the next. The samples are divided into two parts namely the part after casting when the part of the sample is left untreated after the removal from the casting mold and the part after the turning when the second half of the sample was machined and thus deprived of impurities and mistakes of the surface after casting. All the samples were exposed to the atmospheric environment for the 3 months.

The macroscopic and microscopic analysis was performed after the exposure of the experimental samples after the corrosion load.

From the results of the macroscopic analysis is apparent that with the increasing content of the antimony it leads to increased corrosion attack of experimental samples.

The microscopic analysis results are not unequivocal. The significant difference is by the sample without Sb and alloyed Sb. The sample without Sb (primary alloy) has the better corrosion resistance. Therefore we can conclude that the antimony influence on the corrosion resistance of the AlSi7Mg0,3 alloy is rather negative. We can conclude about the surface treatment that the machined surface of the material has better results after the corrosion loading that the part of the material after casting. We have been influenced by the presence of the interdendritic porosity in the research of corrosion resistance of the AlSi7Mg0,3 alloys as documents the microscopic analysis. The other factors which should influence on the evaluation were the defects on the surface and mainly the material surface impurities which occurred on the surface of the sample due to the used technology of the samples (gravity casting) and these defects becomes the nucleus of the corrosion attack on the casting part of the sample. The interdendritic porosity of the material causes the worst alloy resistance against corrosion.

For the further research in this area we recommend to use higher differences of wt. % for the alloy Al-Si alloys with antimony (for example 0; 0,005; 0,05; 0,1 and 0,2 hm. % Sb). The results of the antimony influence on the corrosion resistance of the Al-Si alloys would be probably clearer.

References

[1] Michna, Š., Lukáč, I., Očenášek, V., Kořený, R., Drápala, J., Schneider, H., Miššufová, A. a kol. (2005). Aluminium Materials and Technologies from A to Z. 1. vyd. Adin s.r.o. Prešov. ISBN 80-89041-88-4.
[2] Bolibruchová, D., Tillová, E. (2005). Foundry Alloys Al-Si. EDIS Žilina. ISBN 80-8070-485-6.
[3] Pietrowski, S., Szymczak, T., Siemińska-Jankowska B., Jankowski A. (2010). Selected characteristic of silumins with additives of Ni, Cu, Cr, Mo, W and V. Archives of Foundry Engineering. Volume 10 (Issue 2/2010), 107-126. ISSN 1897-3310.
[4] Medlen, D., Bolibruchova, D. (2011). Influence of antimony on the mechanical properties and gas content of alloy AlSi6Cu4. Archives of Foundry Engineering. Volume 11 (Issue 1/2011), 73-78. ISSN 1897-3310.
[5] Cais, J. (2012). The Influencing of the Structure and Properties of the Al-Si Alloys Using Antimony. Diploma thesis, University of J.E. Purkyně in Ústí nad Labem, Czech Republic.
[6] Kreibich, V., Hoch, K. (1991). Corrosion and Technology of Surface Treatment. ČVUT v Praze.
[7] Kuśmierczak, S., Michna, Š. (2011) Analysis of the Corrosion Damage of the Aluminium Materials surface by the long-term Storage. Strojírenská technologie, Vol. 4, No. 4, 32-36.
[8] Michna, Š., Kuśmierczak, S. (2009). Defects on the Anodized Surface and Anodizing Ability of the Aluminium Alloys. Strojírenská technologie, Vol 14, No 2, 21-27.