INFLUENCE OF TiN AND TiCN NANOSIZED MODIFYING COMPOSITIONS ON THE CORROSION BEHAVIOUR OF AlSi7Mg ALLOY

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Abstract. The nanomodification of aluminum alloys is usually applied in order to improve the mechanical properties of alloys but it influences their corrosion behavior also. The influence of TiN and TiCN nanosized modifying compositions on the corrosion resistance of AlSi7Mg alloy is investigated in this paper. Accelerated corrosion tests are carried out to compare the resistance to uniform, intergranular and pitting corrosion of the non-modified and modified AlSi7Mg alloys. The uniform corrosion test is performed by continuous immersion of specimens in a 3%NaCl+0.1%H₂O₂ environment for 360 hours at 25 °C and at 50 °C. The Intergranular (IGC) and pitting corrosion tests are performed in 3%NaCl+1%HCl solution at 25 °C under full immersion conditions. Data on the corrosion rate change of modified alloys (1.6 to 3.6 times reduction) depending on the modifying composition type and the test temperature are obtained. It was found that uniform corrosion in all investigated alloys occurred 2 to 5 times faster at 25 °C than at 50 °C.

Keywords: nanomodification, AlSi7Mg, nanosized TiCN and TiN, corrosion.

1. INTRODUCTION

In recent decades, aluminum alloys have been widely used in the automotive and aerospace industries because they combine the characteristics of high-strength materials with a relatively low weight. The maximum strength of forged aluminum alloys is in the range of 550 to 600 MPa, but at elevated temperatures the strength significantly decreases [1, 2]. To increase the

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strength of aluminum alloys at elevated temperatures, new modifications of the already known brands are needed.

The materials for low weight constructions in automotive equipment must meet complex requirements. It is essential to combine good formability with high strength, excellent corrosion resistance and weldability [1]. AlSiMg alloys usually meet these requirements and are increasingly used in the automotive and power transmission industries.

One of the advanced techniques to improve the mechanical properties of metallic materials during the last decades is the modification of aluminum alloys with Ti, TiN, TiCN, SiC nanosized particles. The introduction of nanoparticles into the molten metal results in the formation of a self-organizing dispersion system where the solid particles serve as crystallization nuclei for the solid phase formation. However, nanoparticles demonstrate nucleation properties only if they are plated with an activated transition layer. The layer provides good wetting of particles by the melt and creates favorable conditions for the solid phase growth on their surface, even after moderate overcooling. The transition layer can be produced by mechanical or chemical processing of nanoparticles in a planetary mill [3] or by other methods of depositing metal coatings [4]. Experimental studies have shown that aluminum alloys modified with nanoparticles have a refined grain structure, better mechanical properties (strength and hardness) and improved wear resistance [5, 6].

Investigations have been performed to study the influence on corrosion processes of various elements introduced in small quantities [7] as well as of nanosized modifiers added in iron and aluminum alloys [8–11]. Data about the impact of Ti, TiN, TiCN nanosized modifiers on the corrosion resistance of AlSi7Mg are missing [12].

This study is aimed to investigate how the modifiers TiN and TiCN, which are basically introduced in AlSi7Mg alloy in order to increase the mechanical properties, influence its corrosion behavior also. The nanomodifiers TiN, SiC and TiN+Cr are introduced in the coating of welding electrode E300 and the corrosion resistance of the overlay weld metal is investigated. It was found that the introduction of TiN+Cr nanomodifier showed better results compared to TiN nanomodification.

2. EXPERIMENTAL

2.1. Tested materials and test specimens

The base material BA1 is cast alloy AlSi7Mg with chemical composition: 6.65wt% Si; 0.49wt% Fe; 0.05 wt% Cu; 0.28 wt% Mg; 0.07wt% Zn. It is modi-

fied with Nanocomposition (NC) based on Nanopowders (NP) TiN and TiCN to produce modified alloys AlN1 and AlN2, respectively. For better wetting and absorption and hence higher efficiency, the nanopowders are plated with Cu and Ti in a planetary mill. The nanocompositions are introduced into the furnace crucible and the mixture homogenization is carried out by means of a vane. The samples are cast in thin-walled steel containers [13]. The designation of the obtained modified AlSi7Mg alloys and the type of modifying compositions are given in *Table 1*. The amount of nanosized modifier is recalculated in weight percent and given in the table also.

TABLE 1

Type alloy AlSi7Mg	Modifying composition designation	Modifier content in wt%
BAI		
AlN1	1TiN:1.5Cu	0.05wt%TiN
AlN2	1TiCN:2Ti	0.04wt% TiCN

Four plates about 3 mm thick and with average area of about 20 cm² are cut from the non-modified alloy BAI and from the modified alloys AlN1 and AlN2. The plates are prepared as specimens for the corrosion tests. Prior to testing each specimen is consecutively washed with acetone, treated with 5%NaOH, 30%HNO₃ and washed with hot water.

2.2. Test methods

Three methods are applied to determine the influence of nanomodification on the corrosion behavior of the AlSi7Mg alloy: uniform corrosion, Intergranular (IGC) and pitting corrosion. The amount of corrosive medium for each method is determined according to the rule: at least 10 ml per cm² of the specimen area.

2.2.1. Uniform corrosion test

The uniform corrosion test is carried out by means of gravimetric method by continuous immersion of the samples in a medium of 3%NaCl+0.1%H₂O₂ for 15 days (360 hours) at two temperatures: 25 °C and 50 °C. Two specimens from each tested material: non-modified alloy BAI and modified alloys AlN1 and AlN2 are tested at both temperatures. The test is conducted in a thermostat to provide a constant temperature of the corrosive medium. The index pH of the solution is controlled in the range of 5.0 to 5.2. At the test completion the corrosion products are removed with 30%HNO₃ in an ultrasonic

bath. The specimens are weighed before and after the test with an accuracy of 0.00001 g.

The gravimetric method is chosen because of the formation of numerous pits scattered on the studied aluminum surface in corrosion environments leaving large areas of metal between them unaffected. In this case, it is better to calculate the velocity of corrosion K [g/m²h] using the mass loss indicator Δm [g].

2.2.2. Intergranular and pitting corrosion test

The intergranular and pitting corrosion tests are performed in a solution of 3%NaCl+1%HCl at 25 °C and full immersion conditions. The depth of IGC is determined 48 hours after the test completion on metallographic specimens, prepared normally to the examined surface by standard procedure of grinding and polishing with diamond paste.

In order to identify better local corrosion changes, the development of pitting corrosion is determined after the second hour of immersion in the corrosion solution.

3. RESULTS AND DISCUSSION

3.1. General corrosion test results

The results of the uniform corrosion tests are given in *Table 2* and shown in *Fig. 1*. The mass loss index Δm is determined by weighing the samples before test and after removal of the corrosion products. Corrosion rate K is calculated for each of the tested alloys at temperatures of 25 °C and 50 °C. The obtained data are the mean values of the two samples tested at each temperature. K_1 indicates the corrosion rate at 25 °C and K_2 at 50 °C.

The corrosion rate gradient is determined by the parameters X and Y . The parameter $X = K_1/K_2$ shows the decreasing of the corrosion rate K_1 relative to the corrosion rate K_2 for each of the tested alloys. The parameters $Y_1 = K_{1BA1}/K_{1A1N}$ and $Y_2 = K_{2BA1}/K_{2A1N}$ indicate decreasing the corrosion

TABLE 2

Type alloy AlSi7Mg	K_1 [g/m ² h]	K_2 [g/m ² h]	X	Y_1	Y_2
BA1	0.275	0.088	3.1	–	–
AlN1	0.172	0.030	5.7	1.6	2.9
AlN2	0.077	0.033	2.3	3.6	2.7

Fig. 1. Change of the corrosion rate of the tested specimens with the temperature

rate of the modified alloys relative to non-modified alloy at 25 °C and 50 °C, respectively.

The obtained data show that the presence of nanomodificators significantly reduces the corrosion rate of the investigated AlSi7Mg alloy. At the solution temperature of 25 °C the corrosion rate of modified specimens decreases 1.6 times for AIN1, modified with TiN and 3.6 times for AIN2, modified with TiCN compared to the original non-modified specimen. At a solution temperature of 50 °C, the effect of the two modifying compositions is almost equal and the corrosion rate reduction is within the range of 2.9÷2.7 times.

The corrosion of aluminum alloys develops over the time as a function of the pH, solution temperature, and chlorine ion concentration in the solution. The main corrosion product is aluminum hydroxide $\text{Al}(\text{OH})_3$ – gray-white substance, deposited on the specimens surface. Aluminum hydroxide adheres well to the metal surface, forms a passivating film and acts as a corrosion inhibitor at temperature of the corrosion solution of 50 °C. At a solution temperature of 25 °C, a part of $\text{Al}(\text{OH})_3$ is separated in the solution, near the metal surface. It is known that the corrosion behavior of aluminum is different at different temperatures. When the temperature increases, the oxygen solubility decreases and its diffusion ability increases. It has been proven that the temperatures between 40 °C and 50 °C are optimal for aluminum to maintain a balance be-

tween the amount of oxygen and the integrity of the passive film. At lower or higher temperature the passive film is destroyed and the corrosion rate starts increasing [14–17]. This explains why the corrosion rate of the alloys obtained in our tests at 50 °C is 2 to 5 times lower than at 25 °C.

Similar data were obtained earlier in our study of the impact of nanosized TiCN, SiC and TiN modifiers on the corrosion resistance of the weld metal obtained with the modified standard welding electrode E300 [12].

3.2. Results of intergranular corrosion test

The results of the intergranular corrosion test are estimated by observation of metallographic samples prepared normally to the corroded surface at a distance of more than 5 mm from the edge of the test specimen. The results are shown in *Fig. 2*.

Fig. 2. Intergranular corrosion

The depth of corrosion penetration in the non-modified BAl specimens reaches $500\div 600\text{ }\mu\text{m}$; in AlN1 modified with TiN – up to $1000\div 1100\text{ }\mu\text{m}$; in AlN2 modified with TiCN – up to $1000\div 1200\text{ }\mu\text{m}$. Microscopic observation shows that the penetration of corrosion occurs in places along the borders of primary silicon crystals or silicon euthetics plates.

A stoichiometric second phase Mg_2Si is formed in aluminum alloys in the presence of Mg and Si. Aluminum alloys with high content of Cu and Si show a tendency to localized corrosion. It is known that intergranular corrosion in AlSiMg alloys is caused by the dissolution of the intermetallic compound Mg_2Si or by the presence of Si-depleted layer at grain boundaries [18]. In this study, we found some negative effect of nanomodifiers on the development of intergranular corrosion. The depth of corrosion penetration in non-modified specimen is almost two times less than the penetration depth in the TiN and TiCN modified specimens.

3.3. Results of pitting corrosion test

Pitting corrosion was detected after the second hour of testing. Surfaces of the specimens affected by pitting corrosion are shown in *Fig. 3*.

Fig. 3. Pitting corrosion

Pitting corrosion development is due to the presence of aggressive chlorine ions in the solution. Many metal cations exhibit high solubility in chloride-containing media. Chlorine ions have strong electronic affinity and high diffusion, which makes them very harmful for the passive film formed on the metal surface. It is believed that the chlorine ions destroy the passive film by replacing the oxygen anions in it. In addition, chloride ions tend to migrate to the bottom of the pitting to maintain charge neutrality [14–17].

4. CONCLUSION

- The effect of nanosized modifying compositions 1TiN:1.5Cu (0.05wt% TiN) and 1TiCN+2Ti (0.04wt% TiCN) on the uniform corrosion of AlSi7Mg alloy at 25 °C and 50 °C in 3%NaCl + 0.1%H₂O₂ is investigated.
- It was found that the corrosion rate of both non-modified and modified specimens at 50 °C was 2 to 5 times lower than at 25 °C.
- The corrosion rate of the TiN modified specimens at a solution temperature of 25 °C is 1.6 times lower and the corrosion rate of the TiCN-modified specimens 3.6 times lower compared to the corrosion rate of the non-modified specimens. At a solution temperature of 50 °C the effect of the two modifying compositions is similar: reduction of the corrosion rate in the range of 2.9 to 2.7 times.
- No positive impact of nanosized modifiers on intercrystalline corrosion is found in the tested alloys. The penetration depth of intergranular corrosion in the non-modified specimen is almost two times smaller than the penetration depth of in the TiN and TiCN modified specimens.
- No positive impact of nanomodifiers on the pitting corrosion is found. The number of pittings on a unit surface area of the non-modified specimen is less than that of the modified specimens.

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ВЛИЯНИЕ НА НАНОРАЗМЕРНИ МОДИФИЦИРАЩИ КОМПОЗИЦИИ С TiN И TiCN ВЪРХУ КОРОЗИОННОТО ПОВЕДЕНИЕ НА СПЛАВ AlSi7Mg

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Резюме. Наномодифицирането на алуминиеви сплави обикновено се извършва с цел подобряване на техните механични характеристики, но то оказва влияние и на тяхната корозионна устойчивост. Влиянието на наномодифицирането е изследвано върху алуминиева сплав AlSi7Mg, след въвеждане на стопилки на нанокomпозиции 1TiN:1,5Cu и 1TiCN:2Ti. Проведени са ускорени корозионни изпитвания за определяне на устойчивостта на изходната и модифицираните сплави на обща, интеркристална и питингова корозия. Изследването на обща корозия е извършено по гравиметричен метод чрез непрекъснато потапяне на образците в среда на 3%NaCl +0,1%H₂O₂ в продължение на 360 часа при температури 25 °C и 50 °C. Изследването на интеркристална и питингова корозия е извършено в смесен разтвор на 3%NaCl+1%HCl при температура 25 °C, в условията на пълно потапяне. Получени са данни за понижаването на скоростта на корозия на модифицираните сплави спрямо изходната от 1,6 до 3,6 пъти в зависимост от вида на модифициращата композиция и температурата на изпитването. Установено е, че общата корозия във всички изследвани сплави протича от 2 до 5 пъти по-бързо при 25 °C отколкото при 50 °C.

Ключови думи: наномодифициране, AlSi7Mg, наноразмерни TiCN и TiN, корозия.

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