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THE INFLUENCE OF THE CHEMICAL COMPOSITION ON THE CORROSION PERFORMANCES OF A MEDIUM STRENGTH Al-Mg-Si (6XXX) TYPE ALLOYS

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Abstract

The effect of the chemical composition, i.e. content of silicone (Si) and other alloying elements (Zr, Mn, etc) on the corrosion behaviour and mechanical properties of Al-Mg-Si (6xxx) type alloys was investigated in this paper. Open circuit corrosion potential (OCP) measurements, linear polarization and potentiodynamic anodic/cathodic polarization were employed in order to determine the corrosion behaviour of artificially aged Al-Mg-Si samples in the chloride ions containing aqueous corrosion solutions. The difference in OCPs for the tested 6xxx type alloys in relation to the standard AA1020 alloy was observed to be between 1-4%, except for the AlMg0.65Si0.76Zr0.1 alloy when the difference was 14% (about 100 mV). The presence of zirconium and manganese in AlMgSi0.7 base alloy, that contains small excess of Si, shifts the OCPs to more negative values for -15 mV (~2%) and -88 mV (~11%) in natural water and 0,51 mol NaCl, respectively. All the tested 6xxx type alloys, except AlMg0.7Si1.2Mn0.8, show almost the same corrosion rates and other corrosion characteristics in chloride solution, with mass loss per year between 2.3-3 g/m^2.

Key words: AA6xxx, Extrusion, Corrosion rate, Linear and Potentiodynamic Polarization

Introduction

The 6xxx series of aluminum alloys are very attractive for the application in transportation industry because of their high specific strength to weight ratio. These alloys contain silicon and magnesium approximately in the proportions required to form magnesium silicide (Mg_2Si) phase. The formation of (Mg,Si)-particles can be facilitated when the Mg and Si contents are at the high level. The proper ratio for Mg_2Si is

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Mg/Si=1.73, which is almost impossible to achieve with common operating tolerances and most Al-Mg-Si alloys contain either magnesium or silicon in excess. Magnesium excess leads to better corrosion resistance but lower strength and formability; silicon excess produces higher strength without loss of formability and weldability, but there is some tendency to intergranular corrosion [1-2]. The corrosion resistance of aluminum is attributed to the formation of an exceptionally stable oxide film on its surface. This oxide film is resistant to water and oxygen attack in a wide range of temperatures and pH levels, thus making aluminum alloys protected and useful for the application in a variety of corrosive environments [3]. However, the presence of aggressive ions, like Cl^- ions, may create an extensive localized attack [4]. In addition, it is well known that the corrosion behavior of aluminum alloys can be significantly affected by the presence of second phase particles in the matrix. Particles that contain Al, Cu and Mg tend to be anodic relative to the alloy matrix, while those that contain Al, Cu, Fe and Mn tend to be cathodic relative to the matrix [5-6]. 6xxx series of Al-alloys are generally considered to be corrosion resistant although they can be susceptible to intergranular corrosion (IGC), which is supposed to be caused by Si concentration in excess of the Mg_2Si ratio, precipitation of elemental Si or Cu-containing phases [7], or due to the anodic dissolution of the Mg_2Si particles along grain boundaries [8]. The ageing precipitates and grain boundaries are considered as the most preferable initiation sites for corrosion processes in Al-Mg-Si alloys, and the most of present precipitates enhance the corrosion rate due to their cathodic activity [9−11]. There have been many research activities concerning the preparation and processing of the AlMgSi alloys which contain Mg_2Si particles [12]. Some of the latest results show that Si particles are always cathodic to the alloy matrix, while Mg_2Si particles are anodic related to the Al-matrix and corrosion occurs on its surface at the beginning [13]. However, during its preferential dissolution the enrichment of Si occurs which makes Mg_2Si particles transformation to cathodic, thus leading to the corrosion of the Al-matrix in its neighboring area at a later stage. With an extension of the corrosion time, Si particle dissolution leads to the severe corrosion propagation [13].

The aim of the present paper was to investigate the corrosion behaviour and mechanical properties of five AlMgSi0.5, AlMgSi0.7 and AlMgSi1 alloys, in relation with their chemical composition and different content of silicone (Si), and some other alloying elements (Zr, Mn, etc). Open circuit corrosion potential (OCP) measurements, recorded as a function of time for 60 minutes, linear polarization and measuring the polarization resistance (R_{pol}), corrosion current (i_{corr}), corrosion rate (Corr rate) and equilibrium potential ($E_{(i=0)}$), as well as potentiodynamic anodic and cathodic polarization were employed in order to determine the corrosion behavior of artificially aged Al-Mg-Si samples.

Experimental Procedure

The Al-Mg-Si alloys used in this study were produced industrially from the semi-continuous cast billets and supplied in the form of extruded profiles. The chemical compositions of the tested alloys are listed in Table 1. The first one is typical AlMgSi0.5 alloy with the smallest excess of silicone. The other two are generally AlMgSi0.7 which differ in a small addition of Mn and Zr, and the last two are typical AlMgSi1 alloys, with differences in Mg_2Si ratios, as well as the Mn and free Si content.

All investigated alloys belong to the 6xxx series of Al-Mg-Si alloys with excess of silicon.

Table 1. Chemical composition of the tested Al-Mg-Si alloys (% wt)

N°	**Alloy**	**Mg**	**Si**	**Mn**	**Fe**	**Zr**	**Zn**	**Cu**	**Mg_2Si**	**Excess* Si**
1	AlMg0.44Si0.54	0.44	0.54	0.006	0.46		0.120	0.028	0.69	0.17
2	AlMg0.63Si0.71	0.63	0.71	0.07	0.23		0.043	0.007	0.99	0.29
3	AlMg0.65Si0.76Zr0.1	0.65	0.76	0.12	0.21	0.1	0.054	0.004	1.03	0.33
4	AlMg1Si0.91Mn0.47	1.03	0.92	0.47	0.21		0.067	0.005	1.63	0.27
5	AlMg0.7Si1.2Mn0.8	0.7	1.22	0.81	0.23		0.040	0.037	1.10	0.76

* Excess Si=(wt.% Si in the Alloy)−[(wt.% Mg in Alloy)/1.73+0.25×(wt.% Fe in the alloy)].

Cast billets with 7 m in length and a diameter of 0.2 m were homogenized for 12 hours at 570 °C, subsequently cut to the length of 0.62 m and extruded through the hydraulic press with direct metal flow into the rectangular tube, through the single-hole bridge die, with extrusion ratio of 74. Extruded profiles were quenched directly on the press with blown air (except the alloy N° 5 which was quenched with water spray), cooled to room temperature, stretched and subsequently artificially aged under laboratory conditions. The temperatures of the press container and pre-heated billets were 420 °C and 520 °C, respectively, for all investigated alloys. After the extrusion all the specimens were subjected to the ageing treatment at 170 °C for 6 hours in the laboratory furnace.

The PAR-352 system of potentiostat-galvanostat (mod 273), with MK-047 cell and software PAR SOFTCORR 352 II was employed to investigate the corrosion behavior of tested alloys in two aqueous corrosion ambiences: 1) natural water containing 8 mg/dm^{3}of Cl$^-$, and 2) 0.51 mol sodium chloride solution, as a simulation of sea water conditions. Three different testing techniques were used in order to evaluate corrosion behavior of the tested Al-Mg-Si alloys:

1. Open circuit corrosion potential (OCP) measurements, recorded as a function of time for 60 minutes,
2. Linear polarization and measuring the polarization resistance (R_{pol}), corrosion current (i_{corr}), corrosion rate (Corr rate) and equilibrium potential ($E_{(i=0)}$)
3. Potentiodynamic anodic and cathodic polarization, and measuring the corrosion current (i_{corr}), corrosion rate (Corr rate) and equilibrium potential ($E_{(i=0)}$)

For the purpose of comparison of corrosion characteristics, the testing of annealed AA1020 alloy sheet sample was also performed. The mechanical properties (tensile strength, yield stress and total elongation) of heat-treated profiles were determined according to the standard methodology, using the tensile testing "Instron" equipment.

Results and discussion

The Al-Mg-Si system of alloys offers a wide range of tensile properties. Chemical compositions of the tested alloys are within the limit prescribed in the standards causing a wide variation of the microstructure, while mechanical properties and corrosion characteristics can be achieved depending on manufacturing process, including both mechanical and heat treatments. The tensile properties of investigated alloys in final tempers are listed in Table 2, and illustrated in Figure 1.

Table 2.Tensile properties of aged profiles, extruded at T_{Billet}=520°C, quenched directly on the press, andsubsequently artificially aged under the laboratory conditions at 170 °C for 6 hours

N°	Alloy	Quenching type before ageing, directly on the press	$R_{p0,2}$, MPa	R_m, MPa	A, %
1	AlMg0.44Si0.54	Blown air	244	266	12
2	AlMg0.63Si0.71	Blown air	233	272	12
3	AlMg0.65Si0.76Zr0.1	Blown air	282	311	7
4	AlMg1Si0.91Mn0.47	Blown air	249	266	11
5	AlMg0.7Si1.2Mn0.8	Sprayed water	314	338	14

The alloys AlMg0.44Si0.54, AlMg0.63Si0.71 and AlMg1Si0.91Mn0.47 show similar tensile properties in the T5 condition, after processing under the selected thermo-mechanical scheme for the extrusion and its heat treatment. Small addition of Zr (0.1%) and Mn (0.12%) to AlMgSi0.7 base alloy containing small excess of Si, resulted in a significant increase of strength of profiles in T5 temper, as the value of 280 MPa of yield stress and 311 MPa of tensile strength were achieved. Compared to the tensile properties of basic AlMgSi0.7 alloy, this represents an increase of 21% in the yield stress and almost 15% in tensile strength.

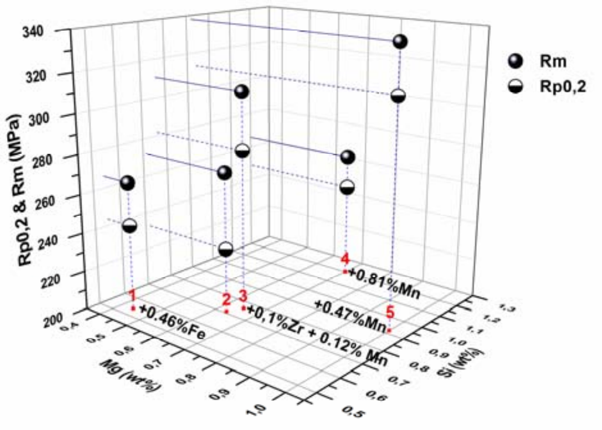


Fig. 1. Tensile properties of investigated 6000 alloys after the artificial ageing, as a function of the content of alloying elements.

The AlMg1Si0.91Mn0.47 alloy shows the lowest strength in relation to other tested 6000 alloys. This is due to small quenching effects connected with the relatively slow cooling rates for air quenching, compared to the water spray quenching, which is recommended for the given combination of main alloying elements. The profiles of AlMg0.7Si1.2Mn0.8 alloy, aged effectively for 6 hours at 170°C in laboratory conditions, exhibited the best properties in terms of the tensile strength and yield stress that significantly exceed the 300 MPa.

Corrosion behavior of the Al-Mg-Si alloys has been investigated in natural water and in synthetic seawater, using three accelerated methods of testing. The evolution of corrosion potential for tested alloys, immersed in natural water and in 0.51 mol NaCl solutions during one hour, is presented in Figure 2.

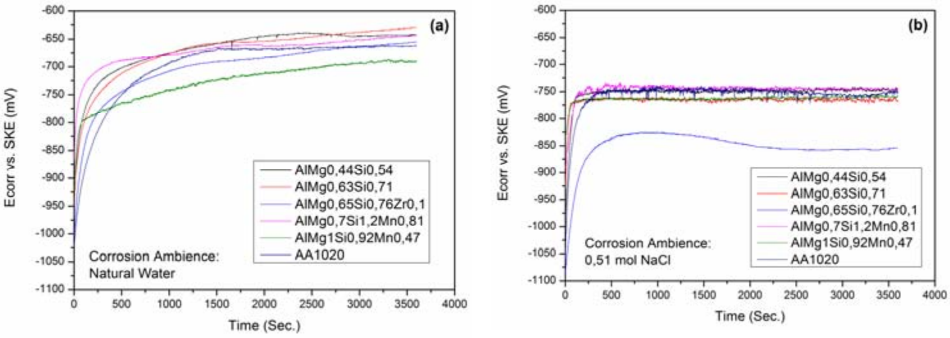


Fig. 2. Open circuit potential vs. time graphs of tested 6000 samples in (a) natural water and (b) 0.51 mol NaCl solutions, open to air at room temperature

The shapes of the curves that represent the evolution of E_{corr} for different alloys were similar for the both corrosion ambiences. In Fig. 2 it can be observed that the onsets of the open circuit corrosion potentials (OCP) for all alloys are shifted in the direction of more electropositive values. Rise in potential in the electropositive direction is usually observed for the samples that exhibit passivity in given corrosion ambience.

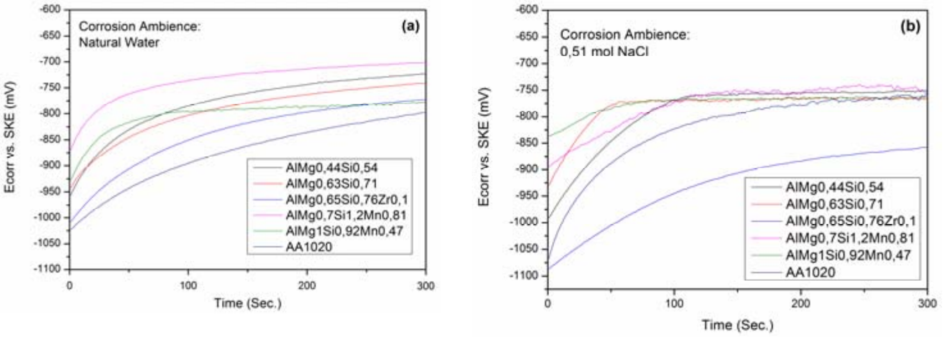


Fig. 3. Open circuit potential vs. time graphs of tested 6000 samples in (a) natural water and (b) 0.51 mol NaCl solutions, open to air at room temperature during the first 300 seconds

The open circuit corrosion potentials of all alloys increase quickly during the first 200 seconds, showing a significant rate of passivation (Fig. 3). The highest rate of passivation in 0.51 mol NaCl solution is indicated for AlMg0.63Si0.72 alloy. This sample reaches a stable value of the open circuit corrosion potential in the first 50 seconds of the immersion (Figure 3.b). Final values of the corrosion potential, after 60 minutes, are listed in Table 3. Final open circuit corrosion potentials of all alloys were in the range between -630mV and -692 mV in natural water, and between -746 mV and -854 mV in 0.51 mol NaCl solution.

Table 3. The final value of corrosion potential, after 60 minutes

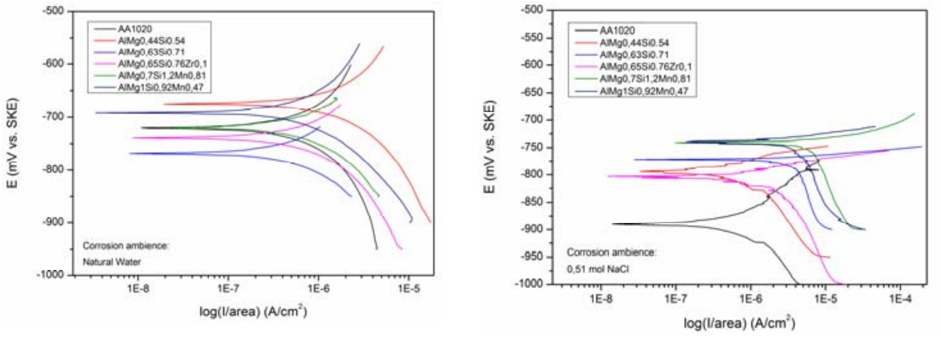
Alloy	**E_{corr}, mV vs. SKE, (in natural water)**	**E_{corr}, mV vs. SKE, (in 0,51 mol NaCl)**
AA1020	-662	-750
AlMg0.44Si0.54	-642	-747
AlMg0.63Si0.71	-630	-766
AlMg0.65Si0.76Zr0.1	-655	-854
AlMg1Si0.91Mn0.47	-690	-759
AlMg0.7Si1.2Mn0.8	-644	-746

Open circuit corrosion potentials of tested 6000 alloys are quite close and comparable with the OCPs of annealed AA1020 sheet sample, especially in 0.51 mol NaCl solution. Differences in OCPs of 6000 alloys in relation to AA1020 were between 1-4 %, except for the AlMg0.65Si0.76Zr0.1 alloy in chloride solution where the difference is 14 % (about 100 mV). Comparison of OCPs of AlMg0.63Si0.71 and AlMg0.65Si0.76Zr0.1 alloys, indicate that the addition of Zr and Mn to AlMgSi0.7 base alloy containing small excess of Si, shifts the OCP to more negative values, for -15 mV (~2%) and -88 mV (~11%) in natural water and 0.51 mol NaCl, respectively.

Potentiodynamic scanning curves and the corresponding corrosion parameters of tested alloys are presented in Figure 4 and Table 4. Similarities in the shapes of the anodic and cathodic parts of the potentiodynamic scanning curves are evident for all samples, in both corrosion ambiences.

Table 4. Corrosion parameters calculated in potentiodynamic testing conditions of 6000 Al alloys

	In natural water			**In 0,51 mol NaCl solution**		
Alloy	**I_{corr}, $\mu A/cm^2$**	**Corr rate µm/year**	**$E_{(I=0)}$, mV vs. SKE**	**I_{corr}, $\mu A/cm^2$**	**Corr rate µm/year**	**$E_{(I=0)}$, mV vs. SKE**
AA1020			-720.0	1.304	0.531	-890.0
AlMg0.44Si0.54	0.428	0.219	-674.4	0.867	0.353	-793.5
AlMg0.63Si0.71	0.537	0.219	-767.1	3.068	1.251	-776.3
AlMg0.65Si0.76Zr0.1	1.615	0.658	-738.4	2.941	1.199	-805.3
AlMg1Si0.91Mn0.47	1.126	0.459	-718.8	5.022	2.045	-745.7
AlMg0.7Si1.2Mn0.8	2.728	1.113	-891.5	3.037	1.2390	-739.1



(a) *(b)*

Fig. 4. Potentiodynamic polarization diagrams for investigated 6000 alloys' samples immersed in (a) natural water and (b) 0.51 mol NaCl solutions, at room temperature.

Values of the potentials E(I=0) under potentiodynamic scanning conditions of all tested 6000 type alloys were in the range between of -674 mV and -891 mV, in natural water, and between -739 mV and -805 mV in 0.51 mol NaCl solution. It is clear that AlMg0.63Si0.71 alloy in natural water and AlMg0.65Si0.76Zr0.1 in 0.51 mol NaCl solution exhibit the most negative potentials. The potentiodynamic scanning curve of AlMg0.7Si1.2Mn0.81 alloy, containing a maximum amount of alloying elements has the maximum tensile strength, and are almost in the same positions of potentials as the AA1020 sample in natural water, noting that the slope of the anodic part of the curve is in favour of the A1020 alloy, in terms of corrosion rate.

Both, AlMg0.7Si1.2Mn0.81 and AlMg1Si0.91Mn0.47 alloys, whose potentiodynamic curves almost overlap and are located in so-called "more noble" areas of less negative potentials compared to other tested alloys, show similar behaviour in chloride solution (Figure 4.b).

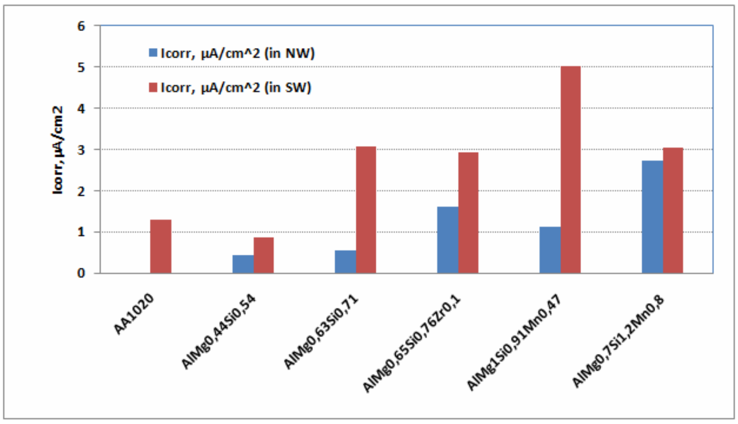


Fig. 5. I_{corr} *of artificially aged samples of tested alloys under potentiodynamic conditions in both corrosion ambiences.*

Figure 5 has the values of corrosion current as a function of the type of alloy for potentiodynamic conditions in both corrosion ambiences. Values of the corrosion currents generally increase with increasing content of alloying elements in alloys, and the corrosion rate is proportional to the corrosion current in both solutions. The corrosion current, and corrosion rates of tested typical AlMgSi0.5 and AlMgSi0.7 alloys in potentiodynamic corrosion test conditions in natural water are approximately the same.

The results obtained by the linear polarization testing are given in Table 5 and shown in Figure 6. The alloys AlMg0.44Si0.54 and AlMg0.63Si0.71 show similar values of polarization resistance, corrosion current and, subsequently, the corrosion rates in natural water. In Table 5, it can also be observed that the values of these corrosion parameters for the other three tested alloys are almost at the same levels. Small addition of Zr and Mn to AlMgSi0.7 base alloy, containing small excess of Si, resulted in significant decrease of Rpol and increase of the corrosion rates of these profiles, noting that these properties are at the same levels as for the alloys containing much more of major alloying elements. Although this is change in corrosion parameters is nearly 50 %, it should be noted that mass loss per year, due to corrosion, is only about 2.2 g/m^2 in natural water.

Table 5. Corrosion parameters calculated in linear polarization testing conditions of 6000 Al-alloys

	In natural water				**In 0,51 mol NaCl solution**			
Alloy	**R_{pol}, kΩ**	**I_{corr}, µA/cm^2**	**$E_{(I=0)}$, mV**	**Corr rate µm/year**	**R_{pol}, kΩ**	**I_{corr}, µA/cm^2**	**$E_{(I=0)}$, mV**	**Corr rate µm/year**
AA1020	32.56	0.667	-779.3	0.272	11.24	1.931	-864.5	0.787
AlMg0.44Si0.54	20.48	1.061	-759.2	0.432	8.016	2.709	-766.6	1.105
AlMg0.63Si0.71	20.22	1.074	-735	0.438	9.981	2.176	-800.2	0.887
AlMg0.65Si0.76Zr0.1	11.24	1.933	-903	0.788	8.581	2.53	-959.3	1.032
AlMg1Si0.91Mn0.47	12.13	1.79	-847.2	0.730	8.376	2.593	-860.9	1.057
AlMg0.7Si1.2Mn0.8	11.48	1.894	-720.8	0.772	3.789	5.731	-749.5	2.33

Corrosion behaviour of these alloys in chloride solution assessed using linear polarization is somewhat different. All investigated 6000 type alloys, except AlMg0.7Si1.2Mn0.8, show almost the same corrosion rates and other corrosion characteristics, with mass loss per year between 2.3-3.0 g/m^2. Addition of Zr and Mn into the base AlMgSi0.7 alloy slightly deteriorates its corrosion characteristics by changing the properties for about 16 %. An AlMg0.7Si1.2Mn0.8 alloy showing the highest strength, but also the highest percentage of "free" silicone (0.76 %) exhibits the highest corrosion rate, in terms of mass loss per year being almost 7 g/m^2.

Conclusion

Corrosion behavior and mechanical properties of Al-Mg-Si type alloys (6xxx series) were investigated in relation with different chemical composition.

The results of the corrosion testing showed similar shapes of the curves that represent the evolution of E_{corr} of different alloys, as well as the shapes of the anodic and cathodic parts of the potentiodynamic scanning curves, in both tested corrosion solutions. Final open circuit corrosion potentials (OCPs) of all alloys were more negative in Cl^-containing solution than in natural water. The presence of Zr and Mn to AlMgSi0.7 base alloy, containing small excess of Si, shifts the OCPs to more negative values, for -15 mV (~2 %) and -88 mV (~11 %) in natural water and 0.51 mol NaCl, respectively. On the other hand, these elements significantly increase the strength of the alloy in T5 temper, approaching more than 280 MPa of yield stress and 311 MPa of tensile strength. Compared to the basic AlMgSi0.7 alloy, this represents an increase of 21 % in the yield stress and almost 15 % in tensile strength.

Values of the corrosion currents generally increase with the increasing amount of alloying elements. Small additions of Zr and Mn to AlMgSi0.7 base alloy, resulted in a significant decrease of R_{pol} and an increase of the corrosion rates of these profiles.. Although this change of corrosion parameters is almost 50 %, it should be noted that mass loss per year is, due to corrosion, only about 2.2 g/m^2 in natural water. All investigated 6000 type alloys, except AlMg0.7Si1.2Mn0.8, show almost the same corrosion rates and other corrosion characteristics in Cl^- containing solution, with mass loss per year of 2.3-3 g/m^2. Addition of Zr and Mn into the base AlMgSi0.7 alloy slightly deteriorates its corrosion behavior by changing the properties by about 16 %. An AlMg0.7Si1.2Mn0.8 alloy aged effectively for 6 hours at 170°C in laboratory conditions achieved the best strength level that exceeds 300 MPa, while it also exhibits the highest corrosion rate, which, in terms of mass loss per year, is almost 7 g/m^2 in chloride solution.

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