Experimental researches and statistical analysis of the corrosion behavior of rolled and heat treated 2xxx Al alloys

ILEANA NICOLETA POPESCU, VASILE BRATU, MARIA CRISTIANA ENESCU
Department Faculty of Materials Engineering, Mechatronics and Robotics
University Valahia of Targoviste
Address Bd. Carol I, no. 2, 130024, Targoviste, Dambovita
COUNTRY ROMANIA
rectorat@valahia.ro, pinicoleta24@yahoo.com, http://www.valahia.ro

Abstract: The material for experiments was an aluminum alloys series 2xxx obtained by thermo-mechanical processing using different parameters of artificial aging. The slab of Al alloys was rolled at 450-400oC for 7-8 hours , solution treated at 500 ± 5o C, maintaining time 40 minutes, quenched in water and artificial aging at 100-220o C during respectively 10-240 minutes. After rolling and heat treatment the obtained alloys was corroded in solution of NaCl with 7.33-8.33 pH at room temperature and analyzed the evolution of potential of electrode depending on time in correlation of structural modification. In addition was studied the electrochemical corrosion behaviour in sodium thiosulphate solution 0.5M using a potentiostatic device. The corrosion characteristics of rolled and heat treated 2xxx Al alloys were predicted through statistical analysis of the measured pitting potential and pitting time at different parameters of aging.

Key-Words: Aluminum alloys**,** Artificial aging, Pitting, Electrochemical corrosion, Statistical analysis.

1 Introduction

The aluminium alloys are attractive for their lightweight (three times lighter than cast iron) properties, higher thermal conductivity, specific heat, superior mechanical properties, good resistance to uniform corrosion and higher wear resistance over cast iron. For this reason their can be utilized in a wide range of application including the electric and electronic engineering. By application of hard-aging treatments on the aluminium alloys we obtain an improvement of mechanical properties. These thermal treatments can provoke susceptibility to the alloy at different types of localized attack (pitting, intergranular, cracking, etc) in HCl, HS , 98% HNO_3 and in majority of bases.

Pitting corrosion in aluminum alloys is recognized as a significant aspect of one of degradation mechanisms that affects the long-term reliability, durability and integrity materials in aggressive medium. It is widely known that the inhomogeneous distribution of Cu in 2XXX series alloy, especially in Al–Cu–Mg-(Mn) system (tendency to separate of intermetallic compounds to the grain boundary) is a major cause for low resistance to pitting corrosion, [1, 2, 3, 4 and 5]. In Al–Cu–Mg-(Mn) system, the intermetallic compound particles Al2CuMg (S phase) are attributed to the pitting corrosion [6]. Micro-flaws in the oxide film exist at the heterogeneity sites and potential differences exist between the intermetallic particles and the Al matrix. These micro-flaws and the galvanic couples would result in localized attack and enhance the susceptibility of Al alloys with Cu and Mg alloying elements to pitting corrosion when the alloy is exposed to solutions containing chloride ions.

2 Problem Formulation

For understanding one or more aspects of the complex phenomena which appears at corrosion of 2xxx Al alloys mechanical and thermal treated under different aging parameters it is necessary to investigate the corrosion behavior of these alloys in aggressive medium in correlation with hardness and structural aspects of corrosion. To optimize the aging parameters, the programming experiment was performed by statistical analysis. The material selected for investigations in this study was 2xxx series aluminium alloys, supplied from ALRO S.A. Romania. The slab of Al alloys was rolled at 450-400oC for 7-8 hours. The rolled Al alloy was cut in rolling directions, in pieces 100 specimens with following sizes: 25 x 50 x 2 mm. The heat treatment consisted in solution treated at 500±5^o C for 40 minutes, quenched in water and then artificial aging at different temperatures (100, 130, 160, 180, 220^o C) and different times (10, respectively 60, 120, 180, 240 minutes). Solution treatment was made into laboratory room furnace and the artificial aging was made into furnace

The chemical composition and the physical properties of aluminium alloys were determined according to ASTM standard methods.

Heat treated samples was tested for hardness, microstructural and corrosion resistance point of view.

The hardness tests were made on Rockwell installations with 100 Kg applied load and 1/16'' sphere. For microstructural analysing after heat treatment the samples were grinded on metallographic paper up to 600 grit, polished with slurry of Al2O3 (1 µm granulation) and etching with Keller's agent.

The corrosion was made in solution of NaCl with 7.33-8.33 pH at room temperature by studying the graphics potential of electrode in function of time. The corrosion tests were made on pH/mV-meter type "pH OM-4" with automatically recording (from 2 and 2 min) of pH and potential of electrode. The electrochemical corrosion behaviour was made in sodium thiosulphate solution 0.5M using a potentiostatic device with saturated calomel electrode as reference electrode and platinum counter electrode. The working electrode area was 1 cm2.

3 Problem Solution

3.1. Materials and Experimental Procedure

The chemical composition is presented in Table 1.

Table 1 The experimental values of chemical composition of the Al alloy used in the present study

Element	**Cu**	**Mg**	**Mn**	**Si**	**Fe**
(wt %)	3.9	1.56	0.42	0.17	0.29
Element	**Cr**	**Zn**	**Ni**	**P**	**Al**
(wt %)	0.004	0.007	0.04	0.01	Balance

The physical properties of aluminum alloys in rolled state (as sheet) at room temperatures are: specific weight 2.7 g/cm3, thermal conductivity-159.331 W/m grd, electrical resistivity-2.63 10 -8 Ωm.

The dependence of hardness on different condition of aging (temperature and times) are shown in Fig 1.

The aspects of pitting corrosion of rolled and heat treated materials in different conditions are presented in Fig 2.

The dependence of electrode potential's variation ε_p [mV] on time for the heat treated samples at 500^o C /40 minutes solution treatments, artificial aging at 100, 130, 160, 180, 220^o C and different times of artificial aging were presented respectively in Fig 3.

According with figure 1 and 3e) the maximum values of hardness and maximum susceptibility of corrosion we obtain at 220^{o}C/60 respectively 120minutes, more rapidly then the maximum values of hardness at temperature below 130^{o}C.

ITM 50 with automatically adjustment of temperatures

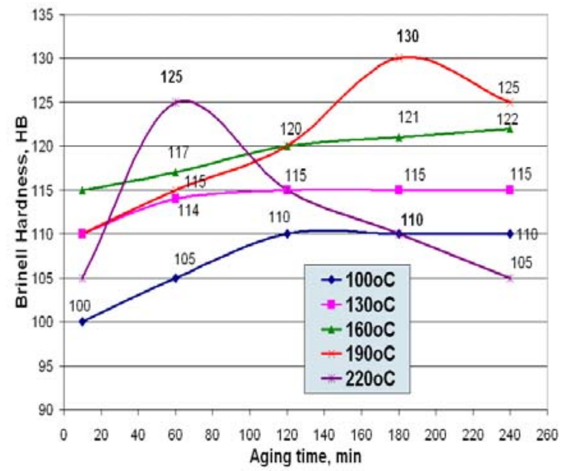

Fig 1 - The Brinell Hardness on different temperatures (100-220^{o}C) and times (10-240 min) of aging.

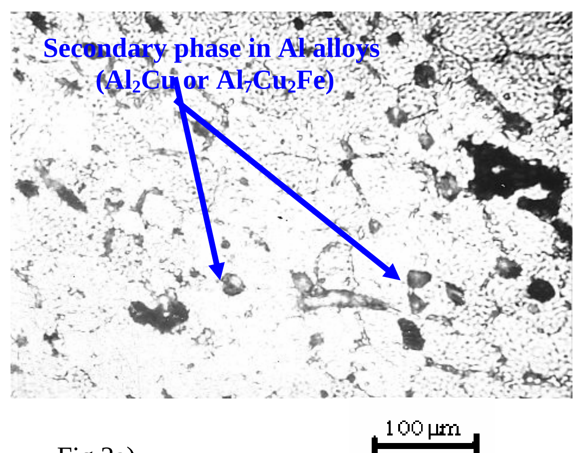

Fig 2a)

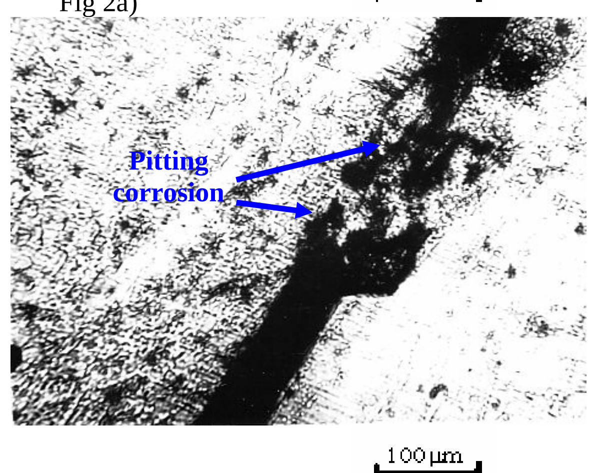

Fig 2b)

Fig 2 -The structural aspects of samples a) heat treated only - solution treated at 500 ± 5^o C /40 minutes/water, aging at190^{o}C/ 180′

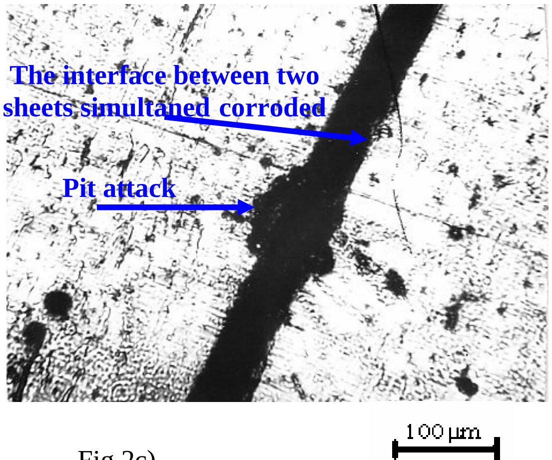

Fig 2c)

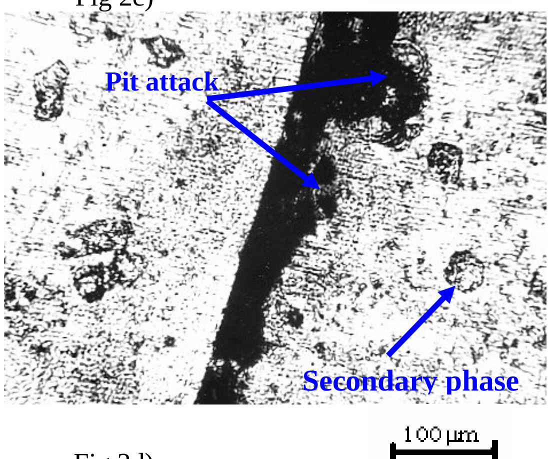

Fig 2d)

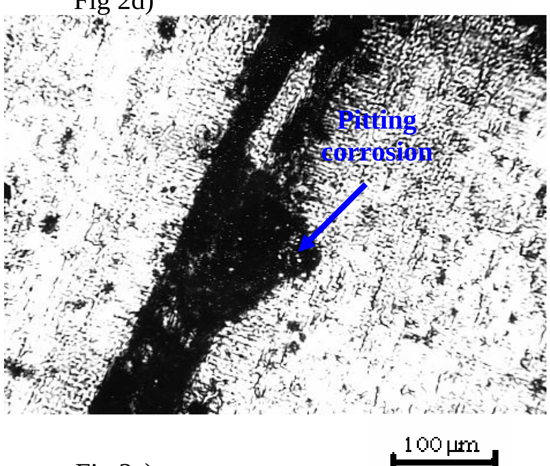

Fig 2e)

Fig 2 b-e) The aspect of head treated and corroded sheet aluminium alloys in NaCl solution with 7.33-8.33 pH at room temperature in different conditions: b) aging at 220°C / 60 ′; c aging at 220°C /120′, d) aging at 160°C / 120′ e) aging at 220°C / 180 minutes ; f) the magnification aspect of pitting corrosion at artificial aging at 190°C / 180 minutes.

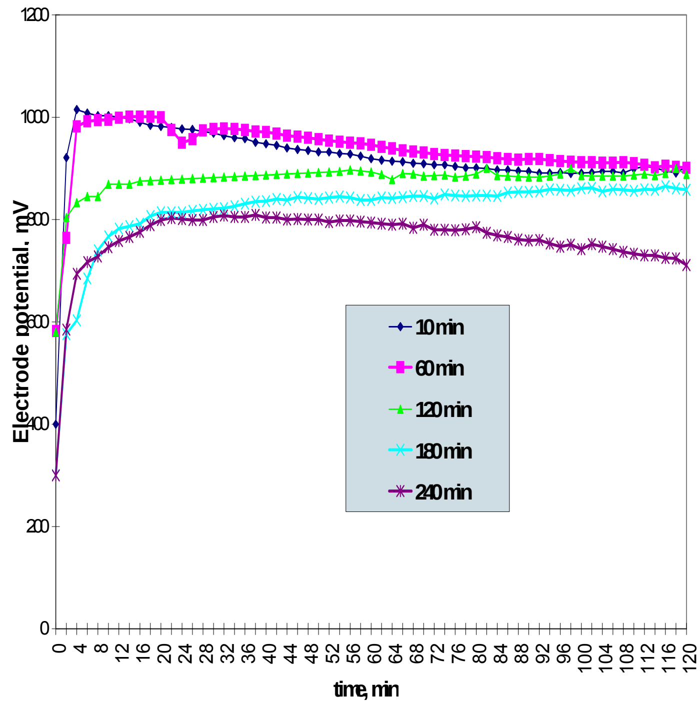

Fig 3 a)

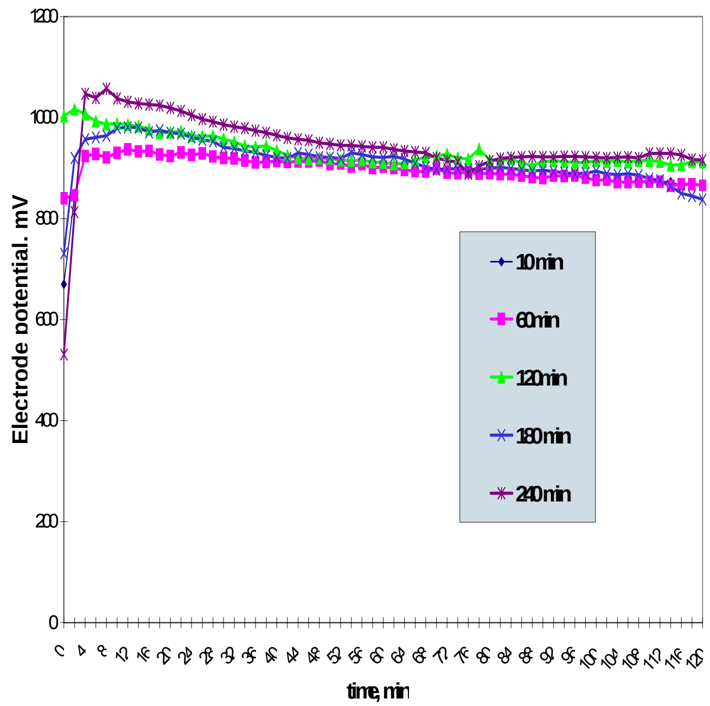

Fig 3b)

Fig 3 - The dependence of electrode potential's variation on time for the heat treated samples at 500 C / 40′ solution treatments, artificial aging at 10-240 min, and at different aging temperatures : a) 100° C; b) 130 ° C;

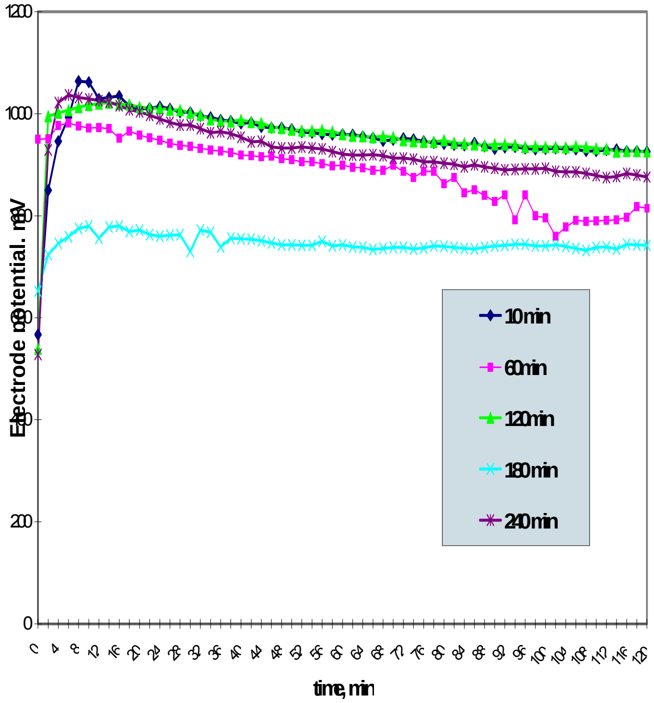

Fig. 3c)

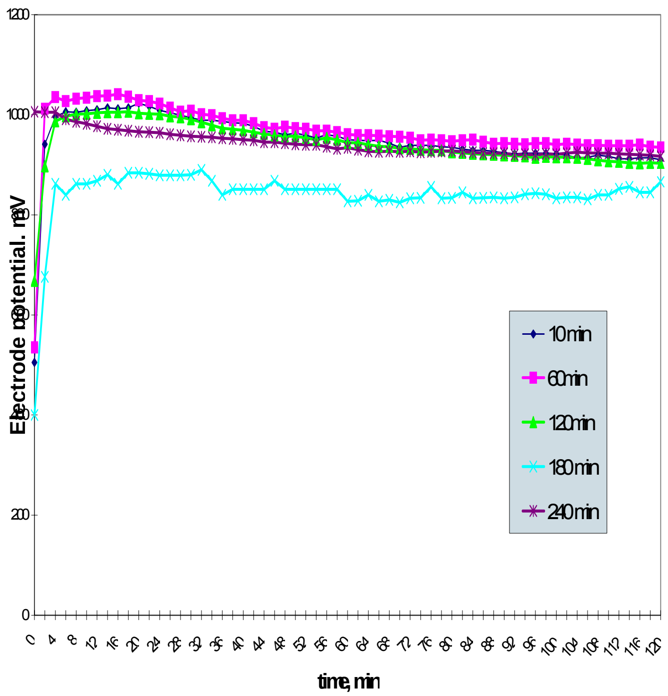

Fig 3d)

At 190oC, the condition of appearance of pitting starts at 60 minutes and the susceptibility of pitting is maintaining higher during the time. For 100oC the electropotential is higher for the first hours of corrosion and than decrease.

In Table 2 and 3 are presented the current density (in

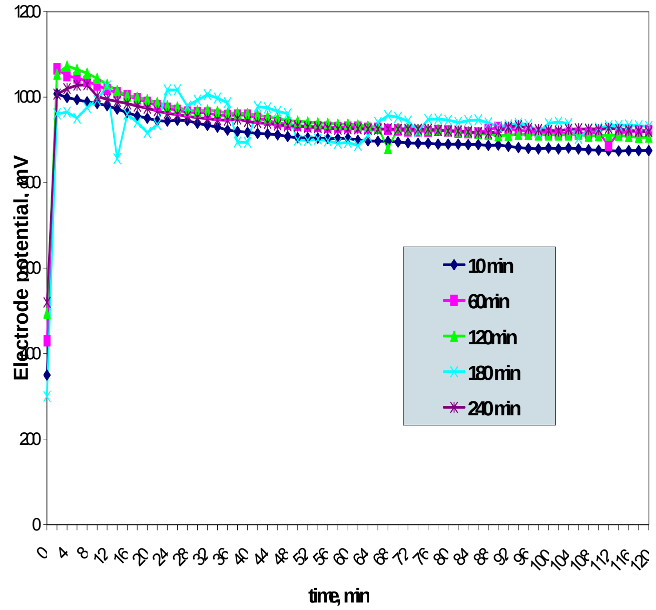

Fig. 3e)

Fig 3 **-**The dependence of electrode potential's variation on time for the heat treated samples at 500 C / 40′ solution treatments, artificial aging at 10-240 min, and at different aging temperatures: c) 160° C; d) 190 ° C; e) 220 ° C;

Table 2

Current density / E , V	160°C/1h		190°C/3h		190°C/4h	
	I, mA	logI	I, mA	logI	I, mA	logI
-0,8	-	-	0.14	-0.854	0.06	-1.222
-0,7	0.02	-1.699	0.2	-0.699	0.08	-1.097
-0,6	0.1	-1	2.6	0.415	3.6	0.556
-0,5	0.5	-0.301	7	0.845	8	0.903
-0,4	2	0.301	12	1.079	12	1.079
-0,3	2.2	0.342	15	1.176	16	1.204
-0,2	2.7	0.431	18	1.255	21	1.322
-0,1	5.6	0.748	23	1.362	25	1.398
0	11	1.041	27	1.431	30	1.477
0,1	16	1.204	31	1.491	34	1.531
0,2	18	1.255	35	1.544	38	1.580
0,3	21	1.322	39	1.591	42	1.623
0,4	25	1.398	43	1.633	46	1.663
0,5	27	1.431	47	1.672	50	1.699
0,6	31	1.491	50	1.699	60	1.778
0,7	35	1.544	52	1.716	60	1.778
0,8	38	1.580	-	-	-	-
0,9	40	1.602	-	-	-	-

net and logarithm form), as a function of potential for aluminium alloys solution treated at 500±5° C for 40 minutes, quenched in water and artificial aging at : 160°C for 1h and 190°C for 3h respectively 4h (in Table2) and at 220°C for 1h , 3h respectively 4h (Table 3).

Table 3

Current density / E , V	220°C/1h		220°C/3h		220°C/4h	
	I, mA	logI	I, mA	logI	I, mA	logI
-0,8	0.02	-1.699	0.02	-1.699	0.02	-1.699
-0,7	0.05	-1.301	0.12	-0.921	0.04	-1.398
-0,6	0.06	-1.222	3	0.477	4	0.602
-0,5	0.063	-1.2	6.8	0.833	9	0.954
-0,4	0.07	-1.16	11	1.041	14	1.146
-0,3	0.079	-1.1	15	1.176	25	1.398
-0,2	0.08	-1.097	18	1.255	35	1.544
-0,1	0.4	-0.398	26	1.415	42	1.623
0	0.8	-0.097	27	1.431	47	1.672
0,1	2	0.301	32	1.505	54	1.732
0,2	2.4	0.380	36	1.556	60	1.778
0,3	3.6	0.556	39	1.591	64	1.806
0,4	4	0.602	44	1.643	70	1.845
0,5	6.4	0.806	-	-	74	1.869
0,6	10.2	1.009	-	-	80	1.903
0,7	10.5	1.021	-	-	98	1.991
0,8	-	-	-	-	99	1.996
0,9	-	-	-	-	99	1.996

The polarization curves are presented in the next figures:

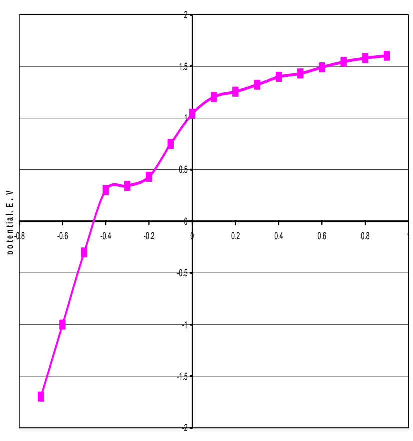

Fig. 4a) 160°C /1h

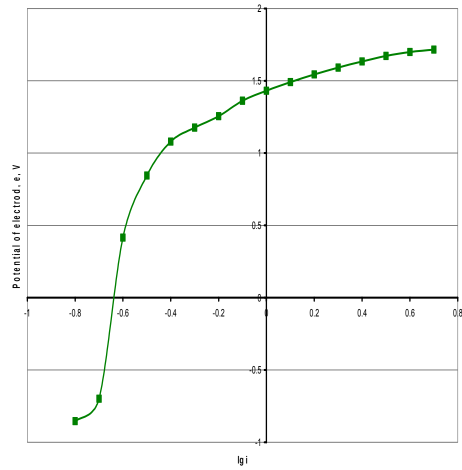

Fig 4b) 190°C /3h

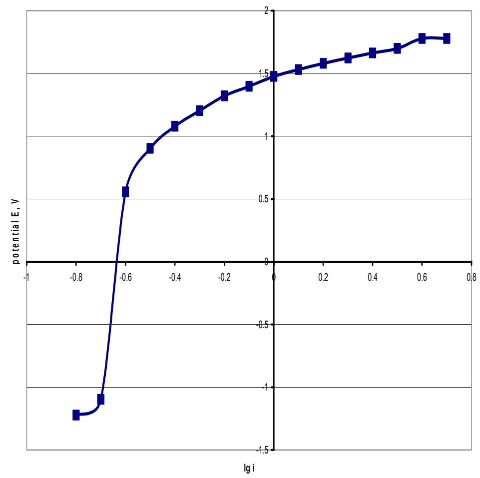

Fig 4c) 190°C /4h

Fig 4 - Polarization curves for Al-4Cu-1,5 Mg –Mn solution treated at 500 ± 5° C for 40 minutes, quenched in water and artificial aging at 160°C for 1h (a) and 190°C for 3h respectively 4h (b, c)

At temperature of 190°C at 3 respectively 4 hours of electrochemical corrosion we didn′t notice the substantial modification of shape of polarization curves, and also the values of Brinell Hardness are very close one over the other; the maximum hardness was obtained at 190°C /3h (130HB) and susceptibility at corrosion pitting. As we know, the alloys of Al-Cu-Mg-Mn alloys (the duralumin type) are hardened by precipitation and there is a strong correlation between the existence of secondary phase precipitated in structure and mechanical resistance and corrosion susceptibility.

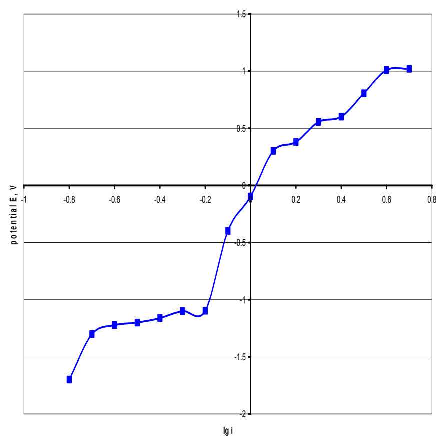

Fig. 5a) 220^{o}C/1h

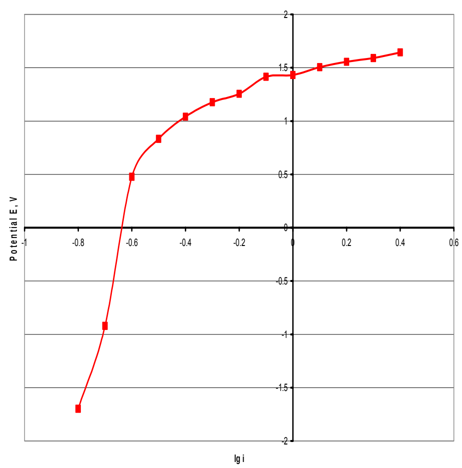

Fig 5b) 220^{o}C 3h

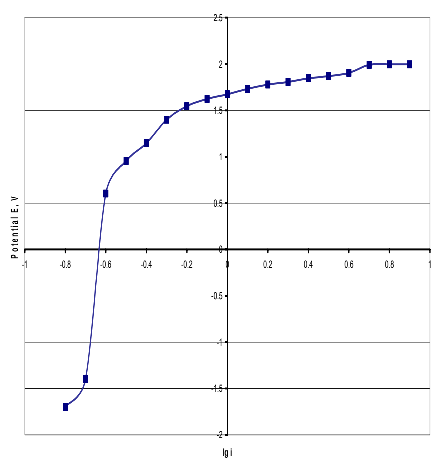

Fig. 5c) 220^{o}C/4h

Fig. 5 – Polarization curves for Al-4Cu-1,5 Mg –Mn solution treated at 500±5^o C for 40 minutes, quenched in water and artificial aging at 220^{o}C for 1h (a) , 3h (b) respectively 4h (c)

From equilibrium diagram we know that the maximum solubility of Cu in solid solution α is 5.7 %, at eutectic temperature (548 ^{o}C). The solubility of Cu in aluminum at low temperature is low, which allow, at the equilibrium condition to form the secondary phase $CuAl_2$ (θ phase). By heating above the solubility curve the alloys is brought in a single phase state (it is in solid state solution), and then is quenched rapidly in water for avoid the separation of secondary phase (we formed the supra-saturated alloys). At reheating at moderate temperature (aging treatment) the meta-stabile alloys are formed, and, in the first stages of aging, appears the pre-precipitate, the clusters of Cu (zones Guiner-Preston) which increasing the strengthening of materials (as we see in Fig. 1 at Al alloys aged at 100-130^{o}C at 10-60 min). We obtained the maximum of hardness in concordance with formation of intermediaries precipitate θ′ . The maximum hardness in Fig. 1 appears at 190^{o}C /180′ and 220^{o}C/60′(Fig 1 and Fig. 3). But the material factors above mentioned are correlated with the medium aggressive where the materials are used in many applications. For that reasons, is necessary to predicted through statistical analysis the correlation between potential pitting and pitting time at different parameters of aging.

3.2. Factorial design

For study the influence of two factors x1 (aging temperature) and x2 (aging time), the response variable of process Y (represented by pitting potential and time of pitting) is necessary to build a factorial design of experiment the type $P^n = 2^2$, which means that the minimum number of trial experiments to be conducted for each material is four. The "*n*" corresponds to the number of factors, n=2 (i.e. temperature and time of aging) and "*P*" represent the number of levels, which in this case are two *P*=2 (i.e. upper and lower level of each variable). In Table 4 are represented the levels of each factors and their coded values. The interval of variation Δ*i* of Z_1 is 30 and for Z_2 is 1.

Table 4 - Levels of each factor and their coded values

No.		Variables	
	Factor levels	Z_1 - Aging temperat. (^{o}C)	Z_2 - Aging time (hours)
	Coded values	x_1	x_2
1.	Upper level (+1)	220	4
2.	Base level (0)	190	3
3.	Lower level (-1)	160	2

Thus, if pitting potential is represented by Y_1 and time of pitting is represented by Y_2, the linear regression equation for these experiments could be written as:

$Y_i = bi_0 + bi_1 x1 + bi_2 x2 + bi_3 x1x2$ (1) ;

Where bi0 is the response variable of pitting potential and time of pitting respectively at the base level; bi1, bi2 are coefficients associated with each variable of aging temperatures and aging times and bi3 is interaction coefficient between x1 and x2, within the selected levels of each of the variables.

Experiment planning matrix (the values of individual variables with their pitting potential in each trial tested for 2xxx Al alloy rolled and heat treated) for Y1 and Y2 are presented in Table 5 :

Table 5 - The values of individual variables with their pitting potential in each trial tested for 2xxx Al alloy rolled and heat treated

Trial no.		Aging temperature (^oC)	Aging time (hours),		Pitting potential	Pitting time
	x_0	x_1	x_2	$x_1\,x_2$	y_1	Y_2
1	(+1)	220 (+1)	4 (+1)	(+1)	1029	18
2	(+1)	160 (-1)	4 (+1)	(-1)	1040	2
3	(+1)	220 (+1)	2 (-1)	(-1)	982	8
4	(+1)	160 (-1)	2 (-1)	(+1)	1073	4

The calculation of dispersal reproducibility for y_1 - pitting potential was made in cases in which the values of x1x2 have the base level. The four parallel experiences are presented in the Table 6:

Table 6 - The 4 parallel experiences for variable response (y1 - pitting potential)

No.	$\overline{y'_u}$	$\Delta y'_u = y_{exp}\,\overline{y'_u}$	$(\Delta y'_u)^2$	ν_2
1	1031	6	36	3
2	1000	-25	625	3
3	1040	15	15	3
4	1029	4	4	3

Where u=no. of experience; n - number of parallel experiments (4)

$\overline{y'_u}$ = arithmetic average of the obtained results; ν^2 = n -1.

The calculation of reproducibility dispersion is based on the relationship (2):

$$S_0^2 = \frac{\sum_{u=1}^{n} \Delta \overline{y'_u}}{n-1}$$ (2); Resulted that S_0^2 =300.66

The coefficients were determinate statistically using the Student criterion and the accordance degree of the regression equations was verified with the Fischer criterion, thus:

The coefficients of each variable from Eq. (1) were calculated with Eq. (3 and 4).

$$b_i = \frac{\sum_{u=1}^{n} x_{iu} \cdot y_u}{(x_{iu})^2}$$ (3) for linear effects and

$$b_{ij} = \frac{\sum_{u=1}^{n} x_{iu} \cdot x_{ju} \cdot y_u}{(x_{iu} \cdot x_{ju})^2}$$ (4) for interaction effects

By introducing the calculated coefficients in Eq. 3 result:

$$Y_1 = 1031 - 25.5x_1 + 3.5x_2 + 20x_1x_2 \quad (5)$$

The dispersion in determination of coefficients is:

$$S_{bi}^2 = \frac{S_0^2}{\sum_{j=1} x_{ij}}$$ (6) and $S_{bi} = \sqrt{S_{bi}^2}$ =8.67

The Student criterion $t_{0.05;4}$ =2.776 and $\Delta b_i = 2.776 \cdot S_{bi}$; $\Delta b_i = 24.07$

But $|b_0|$, $|b_1| > |\Delta b_i|$ (b_0 =1031 ; b_1 = 25)

The calculated liniar model of the process will be: Y1=1031-25.5 x1 where $x_i = \frac{z_i - z_{i0}}{\Delta i}$ (7) where z_{i0} represent the real value of independent parameter, at the base level.

The calcul of dispersion produced by the liniar equation of regression is S_{conc}^2 is presented in table 7:

Table 7

No.	y_{exp}	$\overline{y}$	Δy_u	$(\Delta y_u)^2$	ν_1 = N-k
1	029	005,5	3.5	52.25	1
2	040	056.5	16.5	72.25	1
3	982	005.5	3.5	52.25	1
4	1075	056.5	16.5	72.5	1

Where $\Delta y_u = |y_{\exp} - \overline{y}|$,

$$S_{conc}^{2} = \frac{\sum_{u=1}^{n} (\Delta y_u)^2}{\nu_1}$$ (8) $\Rightarrow$ The calculated Fischer criterion is $F_c = S_{conc}^2 / S_0^2$ (9)

F_c= 0.1823. From anexes [7] resulted $F_{\alpha}, \nu_1, \nu_2 = F_{0,05}, 1, 3$ = 10.13

Because $F_c < F_{0,05}, 1, 3$ $\Rightarrow$ The linear model is in concordance with analysed process.

In the same way was calculated the 4 parallel experiences for variable response (y2 - pitting time).

Table 8- The four parallel experiences for variable response (y2 - pitting time).

No.	$\overline{y''_u}$	$\Delta y''_u$ =yexp- $\overline{y''_u}$	$(\Delta y'')^2$	ν_2
1	7	0	0	3
2	5	-2	4	3
3	10	3	9	3
4	6	-1	1	3

In this case, according with rel. (2) S_0^2 =4.66. The coefficients calculated with Eq. (3) and (4) and introduced in (1) are:

$Y_2 = 8 + 5x_1 + 4x_2 + 3x_1x_2$ (10)

The dispersion in determination of coefficients is calculated with Eq.(6) resulting:

$S_{bi} = \sqrt{S_{bi}^2}$ =1.08

The Student criterion $t_{0.05;4}$ =2.776 and $\Delta b_i = 2.776 \cdot S_{bi}$; Δb_i =2.998

But $|b_0|$, $|b_1|$, $|b_2|$, $|b_{12}| > |\Delta b_i| > |\Delta b_i| > |\Delta b_i|$. The linear model of process for variable response (y2 - pitting time) is the same with Eq. (10):

$Y_2 = 8 + 5x_1 + 4x_2 + 3x_1x_2$

The calculation of dispersion produced by the linear equation of regression is S_{conc}^2 is presented in Table 9:

Applying Rel. (8)$\Rightarrow$ The calculated Fischer criterion Eq. (9) is F_c= 3.43 From anexes [7] resulted $F_{\alpha}, \nu_1, \nu_2 = F_{0,05}, 1, 3$ = 10.13. Because $F_c < F_{0,05}, 1, 3$ $\Rightarrow$ The liniar model is in concordance with analysed process.

Table 9

No.	y_{exp}	$\overline{y}$	Δy_u	$(\Delta y_u)^2$	$\nu_1 = N - k$
1	18	20	-2	4	1
2	2	4	-2	4	1
3	8	6	2	4	1
4	4	2	2	4	1

Conclusion

We observed (in Fig. 1) that the maximum value of hardness (peak hardness) exhibited at 190^{o}C temperature of aging after 180 minutes of aging. For aging made at lower temperatures, the maximum exhibited after long periods of aging , but for aging made at higher temperatures (for example 220 ^{o} C) the maximum are obtained after shortest periods of aging, after that the hardness decrease. The variation of hardness is in correlation with structural modifications (fig. 3) and with mechanical characteristics, which have been appear at the aging periods. The peak hardness corresponded with intense precipitation, and the decreasing of hardness was explained by coalescence phenomena.

According with figures 2-5 where we analyzed the corrosion behaviour in different conditions of aging, we've observed that intensive precipitation correspond of peak hardness and higher pitting sensitivity. For the domain where appear coalescence phenomena, the pitting sensitivity was lower. The experimental results obtained at different parameters of aging was correlated with the experimental factorial and It has been demonstrated that the increasing of pitting potential is inverse proportional with aging temperature and the pitting time is direct proportional with pitting potential and pitting time and interaction between them.

References:

[1] S.Zamfir, R.Vidu, V. Branzoi *The Corrosion of Metallic Materials*, Bucharest, 1994

[2] T. Suter and R.C. Alkire, *J. Electrochem. Soc.* 148 (2001), pp. B36

[3] H.M. Obispo, L.E. Murr, R.M. Arrowood and E.A. Trillo, *J. Mater. Sci.* 35 (2000), pp. 479

[4] C.M. Liao and R.P. Wei, *Electrochim. Acta* 45 (1999), pp. 881

[5] R.G. Buchheit, R.P. Grant, P.F. Hlava, B. Mckenzie, *J. Electrochem. Soc.* 144 (1997), p. 2621.

[6] R.G. Buchheit *J. Electrochem. Soc.* 142 (1995), p. 3994.

[7] D. Taloi, E. Florian, C. Bratu, E. Berceanu, *The Optimisation of Metallurgical Processes*,Bucharest, 1983