Contributions Regarding the Corrosion Behaviour of Some Al-Cu-Mg Superalloys

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The paper presents a comparative study, using gravimetric method, on corrosion behaviour of some aluminum superalloys used in aeronautical field. The corrosion rate and penetration index were respectively determined by mass loss measurements, immersing the aluminum alloys (DURAL and 2090 –type alloys) with different metallurgical processing states (extruded, quenched and aged) in an aqueous NaCl 50 g/L solution. The corrosion behaviour settle of the analyzed aluminum alloys was made by framing into classification of corrosion stability and corrosion resistance degree, respectively. The study demonstrates that the quenched aluminum alloy of 2090-type has the best corrosion behaviour, with the smallest corrosion penetration index in the metallic matrix. It was evidenced that all aluminum superalloys tested on corrosion in a NaCl solution are stable or very stable on corrosion, with the degree of corrosion resistance between 2 and 5. The study also demonstrates that the gravimetric method is an efficient method for appreciation of the corrosion behaviour of aluminum superalloys, allowing a selection of the adequate metallurgical processing state for obtaining a higher corrosion resistance.

Keywords: aluminum superalloys, processing state, extruded, quenched, aged, corrosion, gravimetric method, NaCl solution

Although aluminum is a thermodynamic reactive metal, it presents an excellent corrosion resistance due to the presence on its surface of an oxide film, that suddenly remakes if it is damaged, irrespective of the environment in which the metal is. This is the reason for which aluminum is the most frequently used. Even by exposing in dry atmosphere an oxide film of 1 nm thickness is formed, on a fresh polished surface protecting successfully aluminum against corrosion. Usually, the oxide layers grown in thickness much more than 1nm are composed from two layers. The internal oxide layer in contact with metal bulk is an amorphous and compact layer with variable thickness depending by temperature only ; at a certain temperature the same thickness is obtained irrespective of environment: oxygen, dried air, humid air. Over this layer is forming an external oxide layer, thinner and more permeable. In most cases, the interpretation of corrosion behaviour is developed on the basis on chemical properties of these oxide layers, namely on dynamic equilibrium between opposite tendencies, those to form a compact layer and those to destroy the layer. In the case of dried air, the destructive force is absent and the layer will be faster formed. If the destructive forces prevail, the oxide will be faster hydrated than is formed, so that a less significant layer will be obtained. When the opposite tendencies are in reasonable balance, the relative thickness of formed oxide layer is 20-200 nm [1].

According to Pourbaix diagram [2], the conditions of dynamic stability are in *p*H domain between 4 and 8.5 where the aluminum is passive, being protected by oxide layer. The limits of this interval of *p*H vary with temperature, as well as with the presence of corrosion products that can form soluble or insoluble complex salts with aluminum. As an example, the relative stability in passive domain was sustained by the results of weight losses obtained for 3004-H14 aluminum alloy samples exposed both in water and in salt solutions at different *p*H values [3].

Outside of the passive domain, aluminum is corroded in aqueous solutions mainly because the aluminum oxide is soluble in most acids and bases. However, there are situations when corrosion does not appear, for instance if the layer is not soluble or is stable maintained due to oxidizing nature of solution.

In the previous study [4] the corrosion behavior of classical aluminum alloys of DURAL type, which is an Al-Cu-Mn-Mg alloy was studied. The aim of the present paper is to investigate comparatively the corrosion behaviour of new aluminum alloys, so called the ‘super lights alloys’ (Al-Li-Cu-Mg-Zr-Ti alloys), in different metallurgical processing states (extruded, quenched and aged).

Experimental part

Corrosion tests were carried out using samples from Al-Li-Cu-Mg-Zr alloys with/without Ti content (2090-type superalloys) and Al-Cu-Mn-Mg alloys (2024-type alloys, DURAL) in different metallurgical processing conditions [4]. Both 2024-type and 2090-type without Ti alloys were elaborated and semi-continuously casted to Institute of Non-ferrous and Rare Metals, IMNR Bucharest, whereas Al-Li-Cu-Mg-Zr-Ti alloys (2090-type with Ti content) were elaborated and casted to Department of Science of Materials and Physical Metallurgy from University Politehnica Bucharest. The chemical composition and processing state are presented in tables 1 and 2.

In experiments the gravimetric method based on determination of the corrosion gravimetric index [5] was used. Measurements of the mass losses by immersing in a corrosive solution at different time intervals were performed using an analytical balance (Sartorius, SUA). The electrolyte was a NaCl 50g/L aqueous solution and the temperature was maintained at 25°C.

The dimensions of samples tested on corrosion, of plate or cylindrical shape, are presented in table 3.

The gravimetric index of the corrosion rate (V_{corr}) was computed with the following equation [5]:

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Table 1
CHEMICAL COMPOSITION OF THE INVESTIGATED ALLOYS FOR THE CORROSION BEHAVIOUR

Alloy type	Symbol	Chemical composition, wt.%								
		Li	Cu	Mg	Si	Fe	Zr	Ti	Mn	Al
Al-Li-Cu-Mg-Zr	2090	2.5	2.8	0.29	0.14	0.15	0.14	-	-	rest
Al-Li-Cu-Mg-Zr-0.15%Ti	2090	1.65	2.67	0.14	0.12	0.15	0.08	0.15	-	rest
Al-Li-Cu-Mg-Zr-0.45%Ti	2090	1.64	2.51	0.14	0.12	0.15	0.07	0.45	-	rest
Al-Cu-Mn-Mg (DURAL)	2024	-	4.1	1.51	0.22	-	-	0.07	0.46	rest

Table 2
EXPERIMENTAL ALLOYS SUBMITTED TO THE CORROSION TEST

Sample no.	Alloy type	Symbol	Processing state
1	Al-Li-Cu-Mg-Zr	2090	Extruded
2	Al-Li-Cu-Mg-Zr	2090	Extruded + Quenched 490°C/120 h /water
3	Al-Li-Cu-Mg-Zr	2090	Extruded + Quenched 490°C/120 h / water + Aged 180°C/48 h /air
4	Al-Li-Cu-Mg-Zr-0.15%Ti	2090	Cast + Quenched 490°C/120 h / water + Natural Aged 90 days
5	Al-Li-Cu-Mg-Zr-0.45%Ti	2090	Cast + Quenched 490°C/120 h / water + Natural Aged 90 days
6	Al-Cu-Mn-Mg (DURAL)	2024	Extruded
7	Al-Cu-Mn-Mg (DURAL)	2024	Extruded + Quenched 493°C/4 h / water
8	Al-Cu-Mn-Mg (DURAL)	2024	Extruded + Quenched 493°C/4 h / water + Aged 160°C/19 h /air

$$V_{corr} = \frac{\Delta m}{S \times t} \quad \text{(usually, } V_{corr} \text{ in g m}^{-2}\text{h}^{-1}\text{)} \qquad (1)$$

where:

only Δm is the mass variation of sample during the corrosion process;

S - the surface area;

t - the exposing time to corrosion.

For all alloy samples submitted to corrosion tests in NaCl solution the penetration index in metallic mass was also determined using the following expression [5]:

$$P = \frac{V_{corr}}{\rho} \times 8.76 \qquad (2)$$

where V_{corr} is expressed in g $m^{-2}h^{-1}$ and ρ is the density of alloy, g/cm^3; it was taken into account that one year has 8760 h.

For the appreciation of the stability group of the alloys tested on corrosion the classification shown in table 4 [5] was used.

Results and discussion

In table 5, the results of mass loss (Δ m) during corrosion tests and gravimetric index (V_{corr}) computed for the experimental samples are presented.

The curves corresponding to the variation in time of the gravimetric index for each of eight samples corrosion tested are presented in figures 1 (a-h).

In the interpretation of diagrams representing the gravimetric index variation, we take into account that a negative value of gravimetric index means the existence of a film onto the surface with adherent-protective character, leading to a passivation of the material and a positive value of index indicates a corrosion process with destroying the film and an attack of metal bulk.

The following aspects may be evidenced:

The Al-Li-Cu-Mg-Zr alloy without Ti content (a kind of 2090-type alloy), in any metallurgical processing state presents in the first 4-6 days of immersion in NaCl solution an oxide film which has an adherent-protective character and, therefore, protects against corrosion by passivation of the material. After this time period the protecting film is destroyed and the material corrosion starts to be carried out. The greatest value of the corrosion resistance was obtained in the case of quenched sample (no.2 in fig.1.b), with a corrosion beginning after 6-7 days of immersion. It was noticed that for the extruded sample (no.1 in fig.1.a) as well as the aged sample (no.3 in fig.1.c), the corrosion process starts early (after 4 days). Moreover, the maximum of the gravimetric index of the quenched sample is smaller than in cases of extruded and aged alloys of this type.

By comparing the behavior of Al-Li-Cu-Mg-Zr-Ti alloys (2090-type with Ti content alloys) the sample with 0.45%Ti presents a greater corrosion resistance (no.5 in fig.1.e) than the sample with 0.15%Ti (no.4 in fig.1.d). Thus, the positive gravimetric index for sample 5 in entire domain of immersion time may be explained by the presence of a relatively stable oxide film, with adherent-protective

Table 3
THE DIMENSIONS OF SUPERALLOYS SAMPLES SUBMITTED TO THE CORROSION TEST

Sample no.	Dimensions				Surface area
	H [mm]	L [mm]	l [mm]	ϕ [mm]	[mm^2]
1	10	23.6	17.7	-	1661.44
2	10	23	15.5	-	1483
3	9.8	23	15	-	1434.8
4	3.7	-	-	23	1098.3
5	4.2	-	-	22.8	1117.4
6	9.5	-	-	20	1225.22
7	9.5	-	-	20	1225.22
8	9	-	-	20	1193.8

Table 4
THE CLASIFICATION OF CORROSION BEHAVIOUR OF METALLIC MATERIALS ACCORDING TO STABILITY CLASS AND CORROSION RESISTANCE DEGREE

P, [mm/year]	Stability class	Corrosion resistance degree
< 0.001	I - Perfectly stable	1
0.001-0.005	II - Very stable	2
0.005-0.01		3
0.01-0.05		4
0.05-0.1	III - Stable	5
0.1-0.5	IV - Relative stable	6
0.5-1.0		7
1.0-5.0	V - Low stability	8

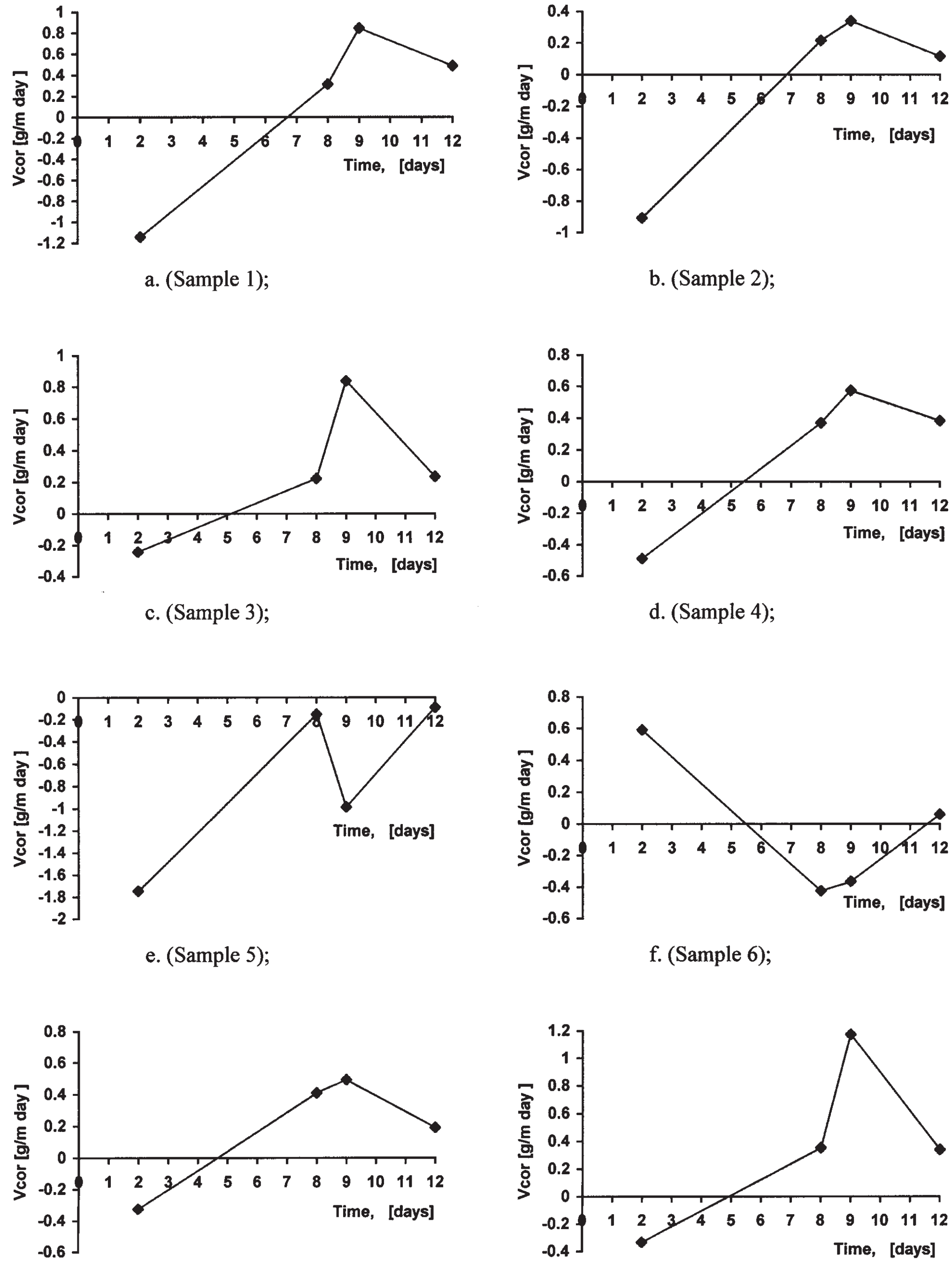
Table 5
VALUES OF MASS LOSSES (Δm) AND GRAVIMETRIC INDEX (V_{cor}) FOR THE INVESTIGATED SAMPLES

Sample no.	Immersion time in NaCl 50 g/L solution							
	2 days		8 days		9 days		12 days	
	Δm, g	V_{corr}, g/(m^{2}day)	Δm, g	V_{corr}, g/(m^{2}day)	Δm, g	V_{corr}, g/(m^{2}day)	Δm, g	V_{corr}, g/(m^{2}day)
1	-0.0038	-1.1435	0.0031	0.3109	0.0014	0.8426	0.0024	0.4815
2	-0.0027	-0.9103	0.0019	0.2135	0.0005	0.3371	0.0005	0.1123
3	-0.0007	-0.2439	0.0019	0.2207	0.0012	0.8363	0.0010	0.2323
4	0.0013	0.5918	-0.0028	-0.4248	-0.0004	-0.3641	0.0002	0.0606
5	-0.0039	-1.7451	-0.001	-0.1491	-0.0011	-0.9844	-0.0003	-0.0894
6	-0.0012	-0.4897	0.0027	0.3672	0.0007	0.5713	0.0014	0.3808
7	-0.0008	-0.3264	0.0030	0.4080	0.0006	0.4897	0.0007	0.1904
8	-0.0008	-0.3350	0.0025	0.3490	0.0014	1.1727	0.0012	0.3350

character and also the formation of insoluble corrosion products that provide a passivation even after 12 days in contact with aggressive solution. We consider that the sample 4 maintains a covered state with an oxide film that is broken after 5 days of immersion and the corrosion products seem to be more soluble, recording a beginning of sample corrosion.

Regarding the behavior of DURAL alloys (Al-Cu-Mn-Mg, 2024-type alloy) we noticed a similar corrosion behavior with 2090 alloy without Ti for quenched (no.7 in fig.1.g) and aged (no.8 in fig.1.h) alloys. Thus, in the first 3-5 days both samples 7 and 8 show a negative gravimetric index, indicating presence of an initial oxide film with adherent-protective character and after this time period the protective film is broken and the corrosion starts. The higher corrosion resistance was obtained in case of quenched sample (no.7) that has an initial incubation of corrosion of 5 days of immersion; moreover, this alloy presents a plateau for positive gravimetric index and after 9-12 days a very diminished gravimetric index. The extruded sample (no.6 in fig.1.f) has a quite opposite behavior comparing to the other ones, with an initial corrosion period; the formation of insoluble products provides a temporary protection (time interval between 8th and 12th day of immersion).

In table 6 is presented the total mass variation for each sample tested after a time period of 12 days; using these data there are also given the values for corresponding gravimetric index (V_{corr}) and corrosion penetration index (P, computed with relation (2) in which the density is approximated as having value of 2.6 g/cm^3).



a. (Sample 1); b. (Sample 2);

c. (Sample 3); d. (Sample 4);

e. (Sample 5); f. (Sample 6);

g. (Sample 7); h. (Sample 8).

Fig. 1. The variation in time of gravimetric index for investigated aluminum alloys (see also Table 2) immersed in 50 g/L NaCl aqueous solution at 25 ºC: a. Al-Li-Cu-Mg-Zr extruded alloy (sample 1); b. Al-Li-Cu-Mg-Zr alloy extruded + quenched 490°C/120h/water (sample 2); c. Al-Li-Cu-Mg-Zr alloy extruded + quenched 490°C/120h/water + aged 180°C/48h/air (sample 3); d. Al-Li-Cu-Mg-Zr-Ti alloy with 0,15%Ti (sample 4); e. Al-Li-Cu-Mg-Zr-Ti alloy with 0,45%Ti (sample 5); f. Al-Cu-Mg (DURAL) alloy extruded (sample 6); g. Al-Cu-Mg (DURAL) alloy extruded + quenched 493°C/4h/water (sample 7); h. Al-Cu-Mg (DURAL) alloy extruded + quenched 493°C/4h/water + aged 160C/19h/air (sample 8)

Table 6
VALUES OF CORROSION PENETRATION INDEX COMPUTED AFTER MEASUREMENTS IN 12 DAYS OF IMMERSION IN NaCl SOLUTION

Sample no.	Δm, g	V_{corr}, g/(m^{2}day)	P, mm/year
1	0.0031	0.1554	0.0203
2	0.0002	0.0112	0.0015
3	0.0034	0.1974	0.0279
4	0.0017	0.1289	0.0182
5	0.0063	0.4698	0.0645
6	0.0066	0.4488	0.0630
7	0.0035	0.2380	0.0334
8	0.0043	0.3001	0.0421

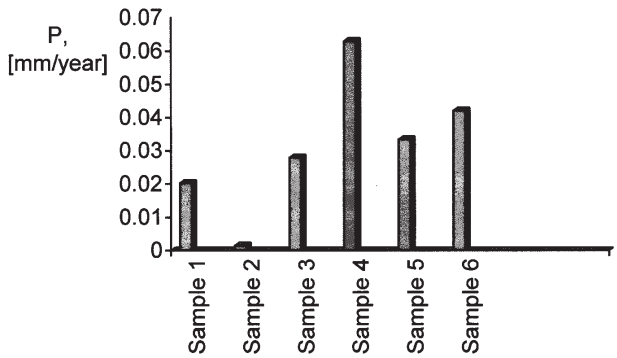


Fig. 2. The histogram showing a comparison of penetration index for investigated aluminum alloys.

Table 7
THE FRAMING IN CLASSIFICATION ABOUT CORROSION BEHAVIOUR OF INVESTIGATED ALLOYS

Sample no.	P, [mm/year]	Stability class	Corrosion resistance degree
1	0.0203	III - Stable	4
2	0.0015	II - Very stable	2
3	0.0279	III - Stable	4
4	0.0182	III - Stable	4
5	0.0645	III - Stable	5
6	0.0630	III - Stable	5
7	0.0334	III - Stable	4
8	0.0421	III - Stable	4

Both table 6 and histogram of penetration index (fig. 2) for all types of investigated alloys with various states of metallurgical processing show clearly the extremes regarding the corrosion behavior; thus, the quenched sample no.2 (Al-Li-Cu-Mg-Zr quenched alloy without Ti content) has the best corrosion resistance, with the lower corrosion penetration index in the metallic matrix, whereas the sample no.4 (Al-Li-Cu-Mg-Zr-Ti alloy with 0.15 % Ti) has the lowest corrosion resistance.

The results about framing of alloys considering their behavior in NaCl solution, are presented in table 7.

In general, we appreciate that all alloys tested in NaCl solution are stable or very stable from corrosion protection point of view, for these alloys the corrosion resistance degree being between 2 (sample 2) and 5 (samples 5 and 6). Obviously, the behaviour of quenched sample 2 is remarkable.

The high corrosion resistance of this quenched alloy is explained by the occurrence of elemental cooper in structure of extruded and aged alloys, as particles of secondary phases which present a more electropositive character than the matrix (α-Al solid solution), producing local galvanic microcells between those phases and matrix.

Conclusions

Using the gravimetric method in a comparative study of corrosion behavior of some aluminum alloys of 2090-type (with/without Ti content) and DURAL allloys, in different metallurgical processing states (extruded, quenched and aged), we demonstrated the best corrosion resistance for 2090-without Ti type, in a form of quenched sample (sample 2). This alloy with the lowest corrosion penetration index, belonging to class II (very stable) of materials stability and also having the highest degree of corrosion resistance (2nd class). The study, also pointed out that all aluminum superalloys, tested for corrosion in NaCl solution, may be stable (class III) at least, or even very stable (class II) in aggressive media, the corrosion resistance degree being between 2 and 5.

Comparative analysis of the corrosion behaviour for alloys in aged state indicates that DURAL (Al-Cu-Mn-Mg) aged alloy (sample 8) has the highest corrosion resistance from all aged alloys; introducing Ti additions, from 0.15% Ti (sample 4) to 0.45% Ti (sample 5), in the 2090 alloy (sample 3) an increasing of the corrosion resistance is produced, to values comparable with those of the DURAL alloy (sample 8).

On the basis of comparative analysis of the obtained results we found out that the studied superalloys present a higher corrosion resistance in quenched state; on contrary, a lower corrosion resistance is for alloys in aged or extruded state. The explanation consists in the occurrence of elemental Cu particles as secondary phases in these last forms, which present a more electropositive electrode potential comparing to the matrix (α-Al solid solution), forming local galvanic microcells.

The study demonstrates that the gravimetric method is a simple and efficient method to establish the corrosion behaviour of the aluminum superalloys, allowing also to select the suitable metallurgical processing state to obtain the highest corrosion resistance.

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