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Pretreatment effects on the electrochemical responses for aluminium–magnesium alloy AA5083 corrosion behaviour

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Abstract Electrochemical investigations on aluminium alloy corrosion in a sodium chloride solution have been performed by potentiostatic and potentiodynamic (electrochemical impedance spectroscopy) methods. Measurements have been obtained after mechanical polishing or electrochemical stripping in deaerated or not solution. All the results are strongly depending on the pretreatments that are undergone in the laboratory before the experimental measurements. Mechanical polishing induces huge effects on the surface of the analysed samples and a long time is necessary to avoid the effects of this treatment; instead, an electrochemical cleaning does not modify the surface and results can be regarded more rapidly as significant of the surface with higher reproducibility.

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Introduction

Due to their properties, such as low density or good extrudability, the aluminium alloys have a wide range of uses and therefore they are the subject of a very large number of experimental studies on their mechanical and chemical properties and particularly on their corrosion behaviour [1–7]. Among these alloys, those with magnesium (5000 series) are still useable in transportation in which the use of low thickness plates is advantageous for reducing weight [1]. To obtain such plates, thermomechanical treatments are undertaken as rolling with or without annealing. During these treatments, phase transitions occur and some intermetallic particles can grow that can be responsible for faster pitting or localised corrosion process that appears when aggressive ions as chloride, break protection locally or attack the passive film [2, 4, 5, 8–17]. This topic has been the purpose of very numerous reports and varied experimental techniques have been implemented. Among them, the electrochemical impedance spectroscopy (EIS) has been tested extensively and results have been analysed to determine the corrosion mechanism or to compare the resistivity of the aluminium alloys according to the medium in which they were immersed or according to the treatment they have undergone [1, 5, 9, 12, 15, 18–21]. Obviously, the alloys used in these studies come from industrial samples. Accordingly, they have been previously thermomechanically treated or not, or they are in a state of cleanliness that requires preparation prior to an electrochemical study. These pretreatments affect the surface and therefore the electrochemical response should be modified. Aballe et al. [14] have reported the influence of the degree of polishing on the behaviour against localised alkaline corrosion for alloy AA 5083 by loss of weight measures and anodic polarisation curve recordings.

Table 1 Chemical composition of aluminium alloy AA5083

Element	Mg	Fe	Si	Mn	Cr	Zn	Ti	Cu	Other
Concentration %	4–4.9	0.4	0.4	0.3–1	0.25–0.5	0.25	0.15	0.1	0.15

They have concluded that the corrosion behaviour of the alloy was depending on the number of cathodic intermetallic particles exposed on the surfaces that was increasing from 80 to 1,200 grit. Up to now, to our knowledge, there has been no study on the EIS responses according to pretreatment despite numerous studies. Our goal is to make a first attempt to answer this question before undertaking a more detailed study of the influence of industrial processes as rolling and annealing. Our experiments have been undertaken with aluminium–magnesium alloy AA5083-H321 which is used for its behaviour against the atmospheric corrosion.

Experimental techniques and methods

The aluminium alloy AA5083-H321 plates used in this study have a chemical composition described in Table 1 in which the elements are given. The samples have been prepared from the same sheet that has undergone during the industrial manufacturing process a cold rolling followed by an industrial stabilisation (in such industrial process the annealing temperature is maintained between 50 and 200 °C). Finally, the samples have undergone an annealing at 420 °C that has been performed during 1.5 h in a salt bath followed by a quiet air cooling. The sheet thickness was equal to 12.7 mm.

The electrochemical measurements have been undertaken with 1-cm^2 samples immersed in a sodium chloride solution (3% weight) at room temperature. For some experiments, the solution was deoxygenated by nitrogen flow during 1 h before the beginning and during the whole measurement time. A classic three-electrode method has been used. The reference electrode was a saturated calomel electrode (SCE); the auxiliary electrode was a platinum foil.

Rest potential and current–potential curves has been obtained by means of a radiometer potentiostat (PGP 201) controlled by Voltamaster 4 software.
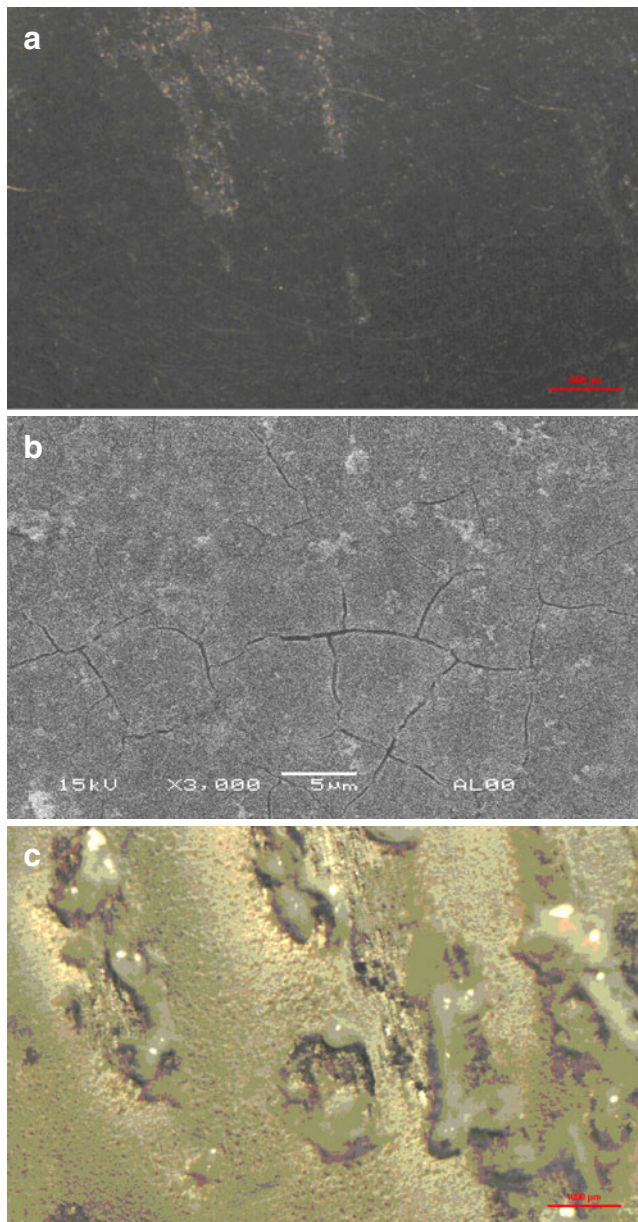

Fig. 1 Images of samples after 1 month of immersion in aerated NaCl 3% solution. **a** and **b** initial rolled and annealed surface, **c** after cold rolling (96% rate) without final annealing. All the samples have been mechanically polished. Magnifications: **a** and **c** ×10; **b** ×2,000
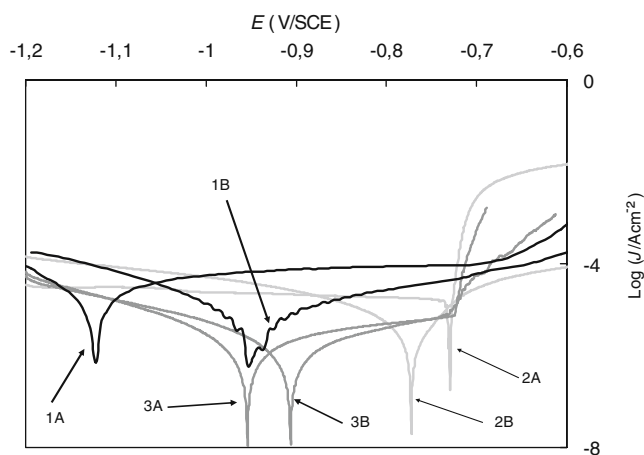

Fig. 2 Current potential curves for samples in NaCl 3% solution. *A* 1 h after immersion, *B* 2 weeks after immersion. *1* electrochemical stripping and oxygenated solution. *2* mechanical polishing and oxygenated solution. *3* mechanical polishing and oxygen-free solution
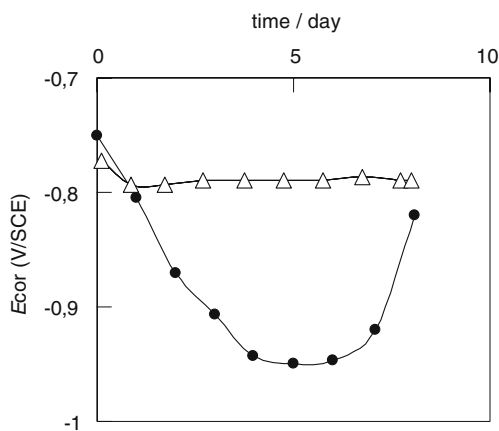
Fig. 3 Corrosion potential versus time for mechanically polishing in NaCl 3% solution. Rolled face (*empty upright triangle*), perpendicular face to the rolled face (*filled circle*)

Fig. 4 Electrochemical Impedance Nyquist plot of a mechanically polished rolled surface in NaCl 3% solution. Immersion time at the beginning of EIS measurement: *empty square* 3 h; *empty upright triangle* 171 h; *filled circle* 195 h

Measurements of potentiodynamic polarisation tests have been conducted with a scanning rate equal to 60 mV/min from an initial value equal to 700 mV below the rest potential.

The electrochemical impedance spectroscopy measurements were carried out by means of a frequency response analyser Solartron 1250, in a frequency range from 20 kHz down to 1 mHz and a 20 mV peak to peak potential modulation amplitude. To obtain accurate values of the electrochemical impedance, integration has been performed for ten cycles.

Scanning electronic microscopy microphotographies have been performed by means of a JEOL JSM 6460LA SEM.

Some samples have been mechanically polished using emery papers from 240 to 4,000 grit, others have been electrochemically stripped by a cathodic sweeping from the rest potential to −2.2 V/SCE with a scanning rate equal to 10 mV/s. At last, all samples have been cleaned with alcohol then water and cool-dried before each experiment.

Results and discussion

SEM and optical microphotographies of mechanically polished sample have been made after several days of immersion in the chloride solution; an example is given
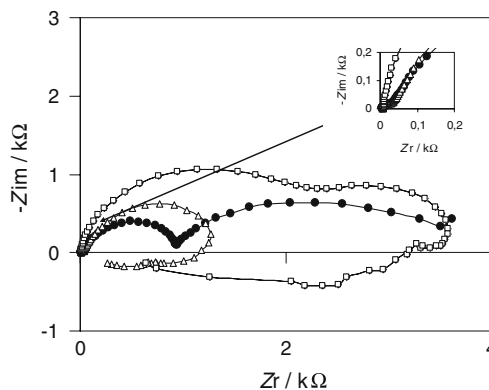
Fig. 1a for a sample immerged during 1 month in an aerated solution. In this case, no localised attack could be observed even with a higher magnification (Fig. 1b). Obviously, the corrosion seems uniform unlike for the same sample after hardening by cold rolling (Fig. 1c) where more common localised alkaline corrosion can be assumed as generally mentioned in literature. This fact could be explained by the high homogeneity of our thick (12.7 mm thickness) sample that has been homogenised by the final annealing at 420 °C.

The current–potential curves that have been obtained for samples immersed in aerated sodium chloride solution for 1 h and 2 weeks show two different behaviours depending on the pretreatment. For an electrochemical strip, the corrosion potential increases in a large amount (Fig. 2 curves 1A and 1B) while a mechanically polished sheet has a slightly decreasing corrosion potential (Fig. 2 curves 2A and 2B). The two potentials seem to converge to the same value as the corrosion potential of a mechanically polished sheet in a deoxygenated solution (Fig. 2 curves 3A and 3B). This unique value corresponds to a long-time corroded sample when the passive film is in a steady state, therefore to the potential corrosion of all samples whatever the pretreatment or the surface that has been exposed to the corrosion process. For example, Fig. 3 exhibits the corrosion potential of two mechanically

Table 2 Polarisation resistance R_p corresponding to the current potential curves in Fig. 2 for sample area equal to 1 cm^2

Type of pretreatment	Electrochemical stripping and aerated solution	Mechanical polishing and aerated solution	Mechanical polishing and oxygen-free solution.
R_p/kΩ (After immersion. curves A in Fig. 2)	1.2	0.16	22
R_p/kΩ (After 15 days immersion. Curves B in Fig. 2)	5.0	0.25	17

polished faces of the same sample versus time: the rolled face and the face perpendicular to the rolled face. If the rest potentials have quite the same values at the beginning of the corrosion process and after 1 week of immersion in the aerated chloride solution, it is obvious that the passive film growth kinetics is not similar. Here, the phenomenon is different from those reported by Aballe et al. [14] due to the fact that the initial value of the corrosion potential has the same value in both cases. Moreover, significant differences have to be noticed between the polarisation resistance values obtained at the corrosion potential, they are depending on the pretreatment of the sample before immersion in the chloride solution (Table 2) and highlight a decrease of the corrosion current densities that is more rapid for and electrochemical pretreatment in aerated solution.

To have deeper insights on corrosion kinetics, some electrochemical impedance spectroscopy measurements have been performed on different samples. After a few hours, the low evolution of the electrode surface allows performing some measurements during a long time and therefore to get some low-frequency impedances with high accuracy due to the long integration time that has been used; this low-frequency measurement can be carried out during several days as the passivating layer is not too thick and provokes a scattering of experimental points as it can be observed for the lowest frequency points of the electrochemical impedance diagrams that have been measured for the longest immersion times. It is obvious that significant differences can be highlighted depending on the pretreatment the samples have undergone. For the mechanically polished sample, some very-well-defined inductive loops at low frequencies are observed for the rolled surface during the first days of immersion; these loops disappear
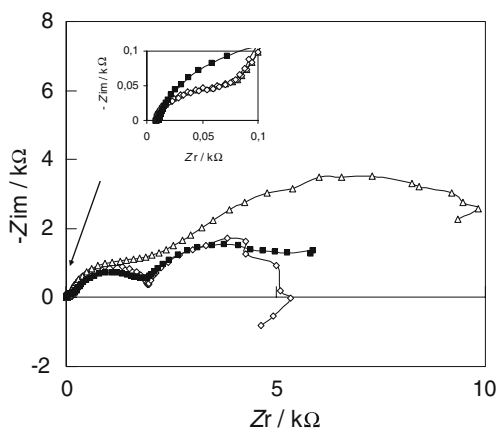

Fig. 6 Electrochemical Impedance Nyquist plot of an electrochemically stripped rolled surface in NaCl 3% solution. Immersion time at the beginning of EIS measurement: *empty diamond* 3 h; *empty upright triangle* 171 h; *filled square* 195 h

after few days (Fig. 4). Such inductive response is not observed during the beginning of the corrosion process for a surface perpendicular to the rolled face which has been pretreated with the same experimental setup (Fig. 5). Now, if we analyse the electrochemical impedances of an electrochemically cleaned sample, only a weak inductive behaviour can be detected for early immersion time (curve for 3 h in Fig. 6) but disappears very quickly and is no longer detectable after a few hours. The very large inductive responses for the mechanical polishing have to be carefully noticed because very often the experimental frequency domain is limited to higher frequencies than in our experiments and therefore, it is not possible to detect this inductive loop, this fact can induce a wrong determination of the polarisation resistance because the impedance limit value at zero frequency is poorly estimated by the impedance measurements; it is often the case when the

Fig. 5 Electrochemical impedance Nyquist plot of a mechanically polished surface perpendicular to the rolled one in NaCl 3% solution. Immersion time at the beginning of EIS measurement: *filled square* 27 h; *empty upright triangle* 171 h; *empty diamond* 243 h
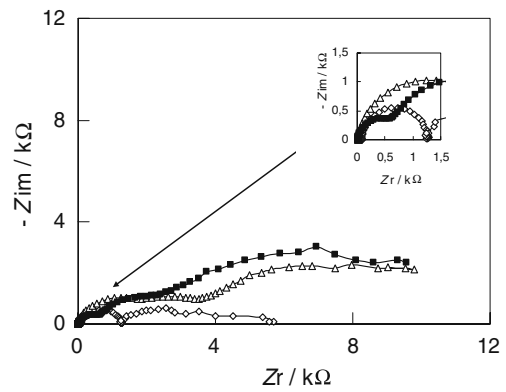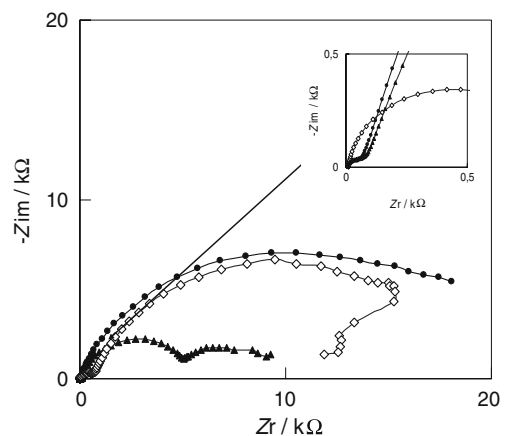

Fig. 7 Electrochemical Impedance Nyquist plot of a mechanically polished rolled surface in deaerated NaCl 3% solution. Immersion time at the beginning of EIS measurement: *empty diamond* 3 h; *empty upright triangle* 171 h; *filled circle* 195 h
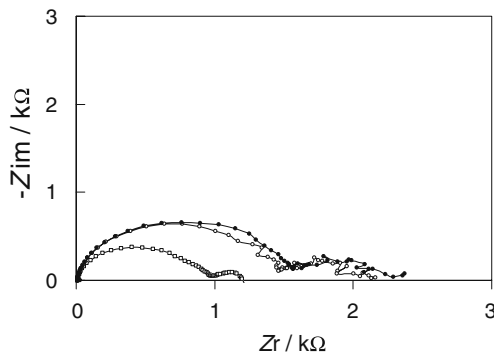
Fig. 8 Electrochemical Impedance Nyquist plot of an electrochemically stripped rolled surface in deaerated NaCl 3% solution. Immersion time at the beginning of EIS measurement: *empty square* 27 h; *empty circle* 171 h; *filled circle* 195 h

corrosion process is evolving as it is, for example, for the 3-h immersion experiment (Fig. 7) where the lowest frequency points could not be considered as significant for a 3-h immersed sample but show an evolutionary process or when the passivating film can induce some scattered points as it can be observed for the 243-h immersion sample in Fig. 5.

Some experiments have been undertaken with free oxygen solutions. In this case, both for electrochemically cleaned and for mechanically polished samples, no inductive loop exists. The Nyquist diagrams exhibit three capacitive loops for the mechanically polished case during

the first days (Fig. 7) while only two well-defined capacitive loops are present for the electrochemically cleaned alloy (Fig. 8). If we only consider the rolled face with a mechanical polishing, the lack of inductive behaviour in a free oxygen solution could be considered as a piece of evidence that the oxygen is responsible for the inductive response of the aluminium alloy corrosion process when a mechanical pretreatment is realised before immersion

An analysis of the high-frequency loop allows determining the double-layer capacitance and transfer resistance values. For a specific set of the experimental conditions, the double-layer capacitance is quite constant during the corrosion process except for the very first moments (3-h experiments) where the surface evolves quickly and for very long times when a thick oxide layer has been formed (Tables 3 and 4). If we disregard these initial periods and long time durations, an average value of about 20 μF cm^2 is obtained for all the samples except for the mechanically polished rolled surface for which the double-layer capacitance value is quite lower (8 μF cm^2). The fact that this double-layer capacitance value did not

Table 3 Transfer resistance R_t and double-layer capacitance C_d of the electrochemical stripped rolled face sample versus time of immersion for sample area equal to 1 cm^2

	Time	R_t/kΩ	C_d/μF
With oxygen	3 h	1.2	50.5
	27 h	4.3	22.4
	2 days	4.5	21.4
	3 days	4.4	21.9
	4 days	4.8	20.1
	5 days	5	19.3
	6 days	4.7	16.4
	7 days	2.7	22.6
	8 days	1.3	18.7
Without oxygen	3 h	0.8	30.2
	27 h	1	15.2
	2 days	1.1	17.5
	3 days	1.2	19.9
	4 days	1.3	18.7
	5 days	1.4	16.8
	6 days	1.5	16.2
	7 days	1.6	15.7
	8 days	1.6	18.5

Table 4 Transfer resistance R_t and double-layer capacitance C_d of the mechanically polished sample versus time of immersion for sample area equal to 1 cm^2

	Time (days)	R_t/Ω	C_d/μF
With oxygen, rolled face	3 h	2,600	3.9
	7 days	36	11.0
	8 days	40	7.9
	14 days	240	0.8
	29 days	5,000	200
With oxygen, perpendicular face	3 h	410	8.0
	27 h	240	16.1
	2 days	210	18.3
	3 days	180	21.
	4 days	114	21.3
	5 days	104	23.4
	6 days	74	20.7
	7 days	100	19.3
	8 days	114	16.9
	9 days	96	15.9
Without oxygen, rolled face	3 h	820	6.1
	27 h	480	5.2
	2 days	160	7.9
	3 days	94	6.7
	4 days	128	7.8
	5 days	124	10.2
	6 days	120	10.5
	7 days	114	11.1
	8 days	106	7.4

change during the immersion, can be regarded as a piece of evidence that the structure of the sample surface has not been modified significantly during the intermediate corrosion evolution, the aluminium oxide layer which still existed, did not evolve as it happens during a pitting corrosion process or during a large increase of the oxide layer thickness. The difference that exists between the mean values of the two double-layer capacitances as quoted above must be assumed as non-significant.

On the other hand, and if we do not consider the first moments and the very long durations as before, the transfer resistance kept a quite constant value of about few hundred ohms per square centimetre for a mechanical pretreatment and about few ohms per square centimetre for an electrochemical one whatever the other conditions (oxygen present in the solution or not and regardless of the surface). The higher mean value of the transfer resistance that is determined with an electrochemical cleaning can be explained by a passive layer thickness; more important of which still exists even for the first moments of immersion, but which has been removed by the more efficient mechanical treatment. This hypothesis is supported by the larger value (about 5 kΩ/cm^2) of this transfer resistance after a long time (29 days) of immersion for the mechanically polished sample (Table 4) when the pretreatment has no more efficiency.

If we consider all the reported EIS diagrams and the first analytical values we have determined, some main conclusions can be stated, the first one, which is well known, concerns the effect of the oxygen in the solution that is responsible for the inductive behaviour of the impedance response but is not involved in the rapid transfer process. The second one which must be more emphasised is the large effect of the mechanical polishing on the electrochemical measurements. It has been mentioned before by Aballe et al. [14] that the degree of polishing was determining on the corrosion behaviour of an aluminium alloy, but in the case they studied, they claimed that the amount of cathodic intermetallic compounds exposed to the corrosive solution was responsible for the rest potential and weight loss differences and that the different degree of polishing only revealed and highlighted this amount modification. In our case, we can conclude that the mechanical polishing induces a huge modification of the surface because the existing passive layer that has been formed during the industrial treatments can be largely removed. That is not the case with simple electrochemical and chemical cleanings which are less harsh and do not affect so much the surface state of the sample, therefore, they allow to reach a steady state more rapidly as it can be highlighted by comparison of the impedance diagrams in Figs. 3, 4, 5, 6, and 7. But the most remarkable results concern the differences during the corrosion process

between rolled (deformation due to an elongation) and non-rolled (deformation due to compression) surfaces; this fact has to be deeply analysed and correlated to the modifications that have been induced by the thermo-mechanical treatments.

Conclusion

We have investigated the electrochemical corrosion of an aluminium–magnesium alloy by rest potential measurements and electrochemical impedance spectroscopy method. The behaviour of the alloy in a sodium chloride solution is strongly depending on the pretreatments that have been undergone before the experimental measurements. Two aspects have to be considered: the thermo-mechanical history of the samples and the pretreatment that is carried out in the laboratory before electrochemical experiments. For a sample, the corrosion process can be different for two surfaces if they have undergone different mechanical strains even after an annealing up to 420 °C. Before the electrochemical experiments, a mechanical polishing induces large modification of the surface state and long measurement time is needed to get responses which are not so much induced by the mechanical pretreatment and which can be regarded as typical of the sample. Electrochemical and chemical cleanings give results that are more representative of the material surface.

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