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Influence of the cathodic intermetallics distribution on the reproducibility of the electrochemical measurements on AA5083 alloy in NaCl solutions

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Abstract

The corrosion behavior of alloy AA5083 in solutions of NaCl at 3.5% is controlled by the density of the cathodic precipitates of Al(Mn,Fe,Cr) present in the alloy. These precipitates are not distributed homogeneously over the surface of the alloy. Further, their presence conditions the electrochemical response of the alloy. For these reasons, in order to guarantee the reproducibility of electrochemical tests on this alloy, it is necessary to determine the minimum surface area exposed to the medium which represents the average behavior of the system. In the present study, a systematic analysis has been conducted on the degree of reproducibility of electrochemical tests as a function of the area of surface exposed, for the alloy AA5083 in solutions of NaCl at 3.5%. A high dependence between the dispersion of the electrochemical data and the exposed area has been established. This behavior contrast with those of other alloys, like AA1050, which is not conditioned by the values of exposed area. This has been related to the much lower cathodic precipitates density in this alloy.

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Keywords: Corrosion; Aluminum alloys; Electrochemical techniques; Reproducibility; NaCl

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1. Introduction: Corrosion of alloy AA5083 in NaCl solutions

Localized corrosion of aluminum alloys is usually related to the presence of heterogeneities either in the metal or medium or in the exposure conditions [1]. In relation to the properties of the alloy, its surface can contain some physical inhomogeneities which can cause a permanent distribution of cathodic and anodic zones that can promote different forms of localized corrosion [1–5]. These inhomogeneities are frequently intermetallic compounds or inclusions distributed throughout the metallic matrix, either from intentional development to improve mechanical properties or present as impurities. Thus, anodic intermetallic particles have been found to be common sites for pits nucleation [5–7]. By a different process, cathodic intermetallic particles provoke alkaline localized corrosion in the metallic matrix surrounding the precipitates [2,6,8]. Additionally, the existence of heterogeneities can either promote failures in the protective film of oxide [9,10] or form the initiation sites of cracks in both stress corrosion cracking and corrosion fatigue processes [11,12].

From the point of view of its corrosion behavior in solutions of NaCl at 3.5%, aluminum alloy AA5083 can be characterized as undergoing two clearly differentiated processes [8,13]. From the first moments of its exposure, the alloy is affected by localized attacks basically in the zones surrounding particular types of intermetallic compounds, Fig. 1. This type of attack leads to the formation of large numbers of hemispherical pits, which extend to cover a large proportion of the exposed surface area, over prolonged periods of exposure. This effect can be clearly observed in the scanning electron microscopy (SEM) image reproduced as Fig. 2(a).

As reported in [14], this process is associated with the cathodic character of the precipitates of Al(Mn,Fe,Cr) in proximity to which this type of attack is produced. According to [8,13–16], the cathodic character of these precipitates in respect of the matrix causes the reaction of O₂ reduction to take place on top of these precipitates, with the consequent formation of OH⁻ groups. This in turn produces a local increase in pH, which gives rise to the dissolution of the layer of oxide in the area surrounding the precipitate. Once this layer of oxide has been dissolved, the local alkalization causes an intense attack on the interface between the matrix and the precipitate. This effect of corrosion of the matrix in the zone surrounding the precipitates of Al(Mn,Fe,Cr) can be clearly appreciated in the image of Fig. 2(a). The cavities that can be seen in this image are associated with the detachment of the precipitates as a consequence of the loss of contact between them and the matrix.

In parallel to this, a second type of corrosion process takes place in the matrix which, under the conditions of exposure studied, gives rise to the growth of a layer of alumina which ends by covering almost completely the entire surface of the sample, Fig. 2(b).

As commented previously, the process of localized alkaline corrosion is the one that takes place with greater intensity. Therefore, as this type of process is related to the existence of Al(Mn,Fe,Cr) precipitates, the surface distribution of this type of compound could become a determining factor in the behavior of alloy AA5083 in solutions of NaCl.

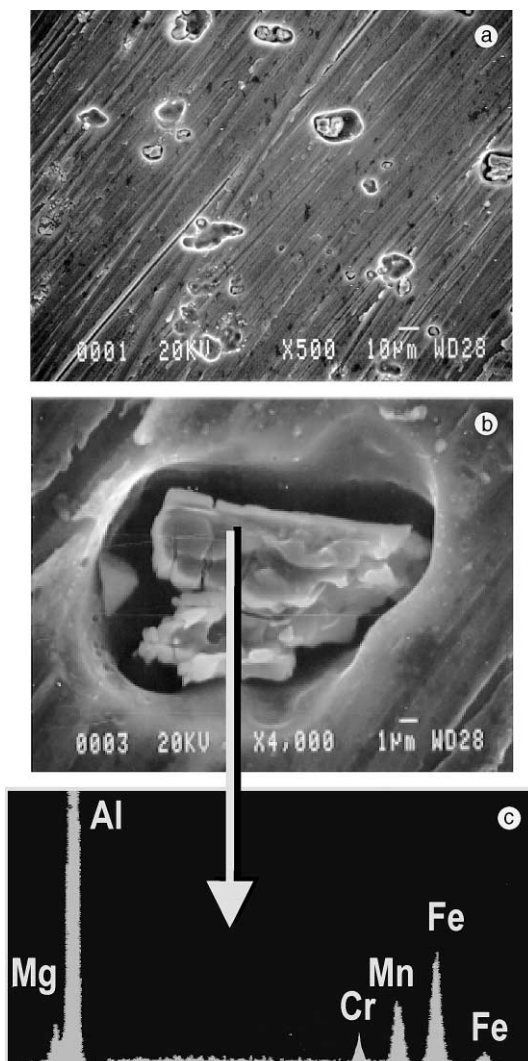


Fig. 1. (a) SEM image obtained on a sample of AA5083 alloy after 6 h of immersion in an aerated solution of NaCl at 3.5%. (b) Details of the area corroded by local alkalization. (c) EDS spectrum acquired on the precipitate Al(Mn,Fe,Cr).

Alloy AA5083 is classified as one of those designated as wrought alloys [17]. These are used without the application of any type of heat treatment. For this reason, one of the microstructural characteristics of this type of alloy is that the surface distribution of intermetallic precipitates is not very homogeneous. In other words, on the surface of the same sample there may co-exist zones with very different densities of these precipitates. In Fig. 3, the metallographic images corresponding to two

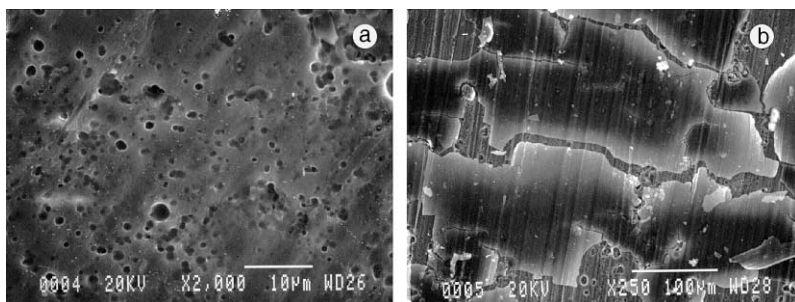


Fig. 2. SEM images obtained on a sample of AA5083 alloy after 15 days of immersion in an aerated solution of NaCl at 3.5%: (a) micropits in descaled sample and (b) oxide layer in sample without being descaled.

adjacent zones of the same sample of alloy AA5083 are shown. As can be seen, the distribution and density of precipitates in each zone varies considerably.

As commented previously, when measurements of characterization are taken in reduced areas of sample surface, the lack of homogeneity in the surface distribution of the precipitates may produce a high degree of dispersion in the results, giving rise to a low level of reproducibility of results. This would be the case when carrying out electrochemical measurements, which are commonly utilized in the study of corrosion behavior.

This paper describes a study conducted of the dispersion obtained in the measurement of various electrochemical parameters when the alloy AA5083 is corroded in solutions of NaCl. The variable allowing the modification of the surface density of the precipitates in the samples is the size of surface area of the sample exposed. From the statistical analysis of the results obtained, the objective has been to establish the experimental conditions that would guarantee the reproducibility of results.

2. Experimental

A study has been conducted of samples of the aluminum–magnesium alloy AA5083, the composition of which as determined by ICP, is given in Table 1.

To perform the various tests, samples of 5 mm thickness of this alloy were used, each with different sizes of surface area exposed to the medium. These samples were prepared using a mechanical process of wet sanding with SiC papers of 220 and 500 grits. Before the tests, the samples were carefully degreased with ethanol of 99% purity and rinsed with abundant distilled water.

As the aggressive medium, an aerated solution of NaCl at 3.5% and pH of 5.5 was used. Initially, the electrochemical measurements were taken with a K235 flat cell supplied by Parc EG&G, coupled to a SI 1287 potentiostat. In this cell, the area of exposure of the sample is 1 cm². As commented previously, the experimental variable is the size of the area of exposure of the samples. With the objective of being able to modify this area, a three electrodes cell was designed, as shown in the diagram

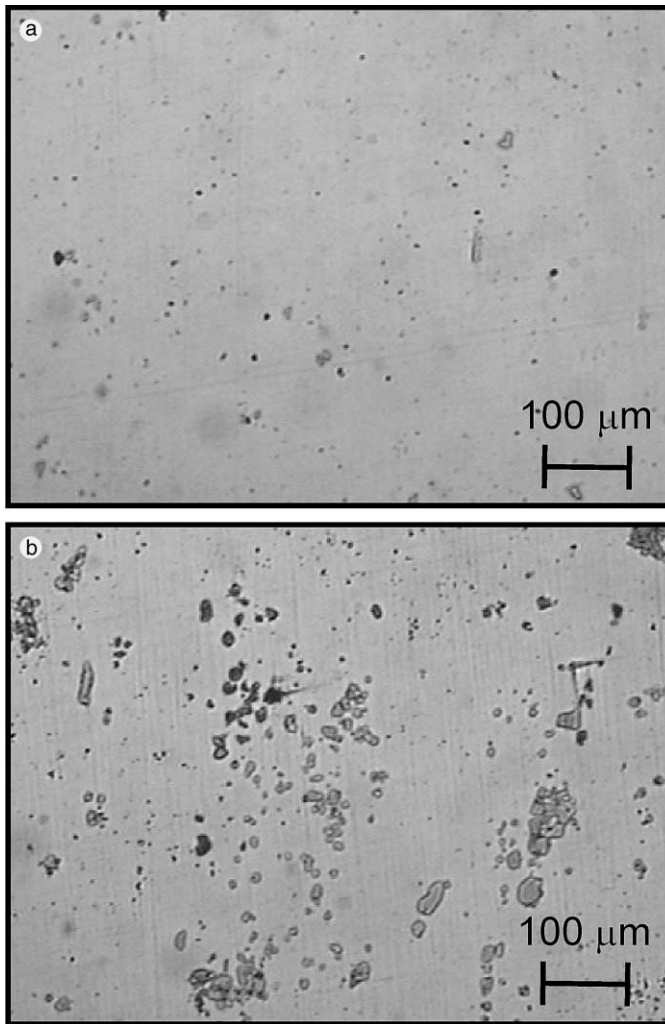


Fig. 3. Optical microscope images obtained from a sample of alloy AA5083 polished to mirror quality. Zones with different superficial density of precipitates.

Table 1
Weight percent compositions of AA5083 and AA1050 alloys

	Mg	Mn	Si	Fe	Ti	Cu	Cr	Al
AA5083	4.9	0.5	0.13	0.3	0.03	0.08	0.13	Rest
AA1050	0.05	0.05	0.25	0.40	0.03	0.05	Other 0.13	Rest

presented as Fig. 4, which would enable the surface area of the sample to be varied. In both types of cell, a Crison Ag/AgCl electrode, model 52-40, was employed as

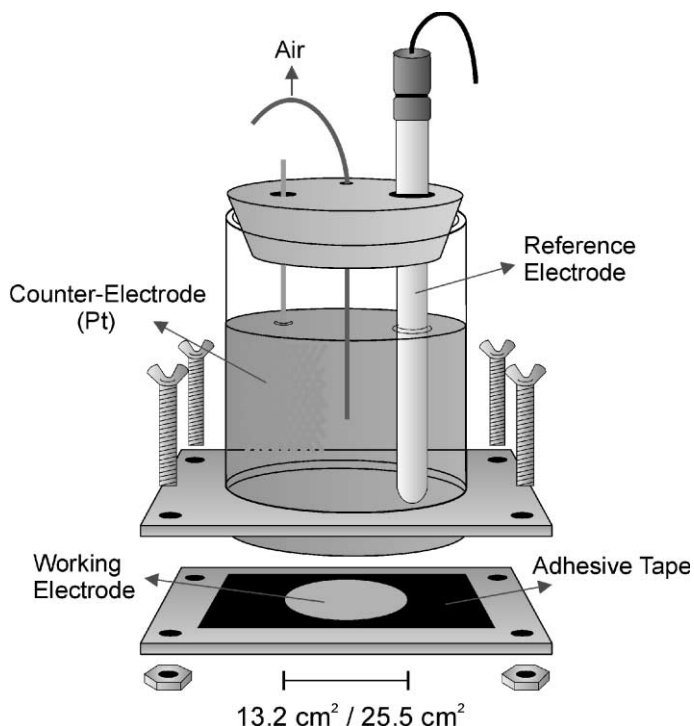


Fig. 4. Three electrodes cell with variable exposition area.

reference electrode; the potential of this, in respect of the NHE, is 0.207 V. All the experimental potential data presented in this paper are referred to this Ag/AgCl reference electrode. The studies of the evolution in function of time of the open circuit potential (OCP) were performed acquiring 5 points per second. For the measurements of linear polarisation and R_p , sweeps of potential at a speed of 10 mV/min were made.

The studies by SEM were carried out with a JEOL 820-SM scanning microscope fitted with an AN-10 000 LINK dispersive energy analyzer.

Additionally, in order to determine the influence of the cathodic particles density on the reproducibility of the electrochemical response of the AA5083 alloy, a comparative study has been performed using samples of AA1050 (99.5% Al) alloy. The composition of this alloy as determined by ICP, is also given in Table 1.

3. Results and discussion

One of the techniques used to monitor the corrosion behavior of alloy AA5083 was the recording of the potential of corrosion in function of time. Initially, samples with the same level of surface finish (500 grits), with an exposure area of 1 cm², were

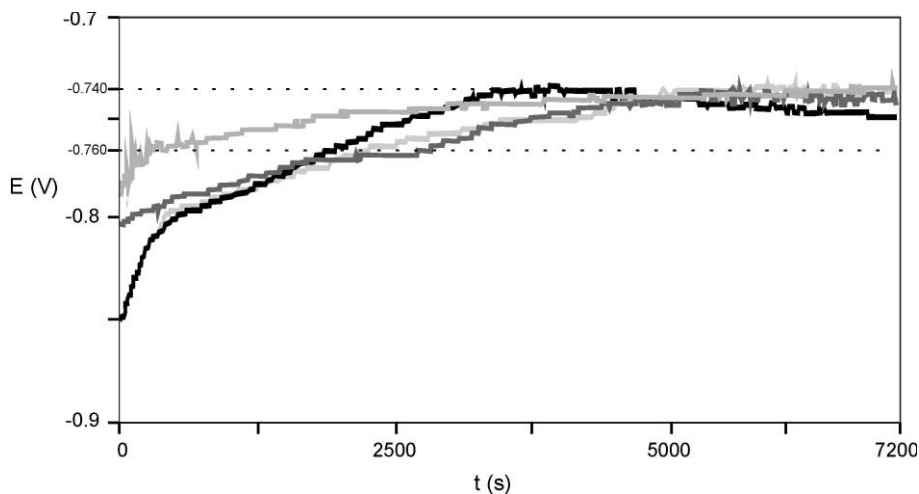


Fig. 5. $E_{\text{corr}}-t$ plots obtained on a sample from alloy AA5083 after 2 h in solution of NaCl at 3.5%. Exposed area: 1 cm^2 .

tested. The recordings obtained are shown in Fig. 5. As can be appreciated from this figure, the measurements taken present a high degree of dispersion in the values of the potential of corrosion, both in respect of the initial potential and of its evolution over time. Moreover, it can be observed that the widest differences are in the measurements taken after relatively short exposure times, whereas for prolonged periods of exposure, all the curves tend to converge. In line with the comments made in the preceding section and with the data reported in [8,18], the initial polarisation and, therefore, the potential of corrosion that the samples acquire during the first moments of their immersion in the medium, is determined by the demand for current imposed by the cathodic process. It follows from this that the differences observed in the potential of corrosion must be related to differences in the number of cathodic precipitates present on the surface of the various samples studied in Fig. 5.

These differences could be due to the fact that, as already mentioned, the production process of alloy AA5083 does not involve the application of heat treatment for homogenization. This lack of heat treatment causes the distribution of the precipitates to be more heterogeneous. Hence, when experiments are conducted such as those included in Fig. 5, in which samples of 1 cm^2 surface area are employed, there are likely to be considerable differences in the number of intermetallics exposed in each experiment. Consequently, the data included in Fig. 5 seem to indicate that when working with exposure surfaces of 1 cm^2 , a response that is representative of the behavior of the system will not be obtained.

Analogous results have been found in recording curves of linear polarisation of the same system at 5 min after the immersion of the sample, Fig. 6. Table 2 gives the values of the initial potential of corrosion (E_{corr}^0), the potential of pitting nucleation (E_{pit}) and resistance of polarisation (R_p) obtained from the recording of a total of 15

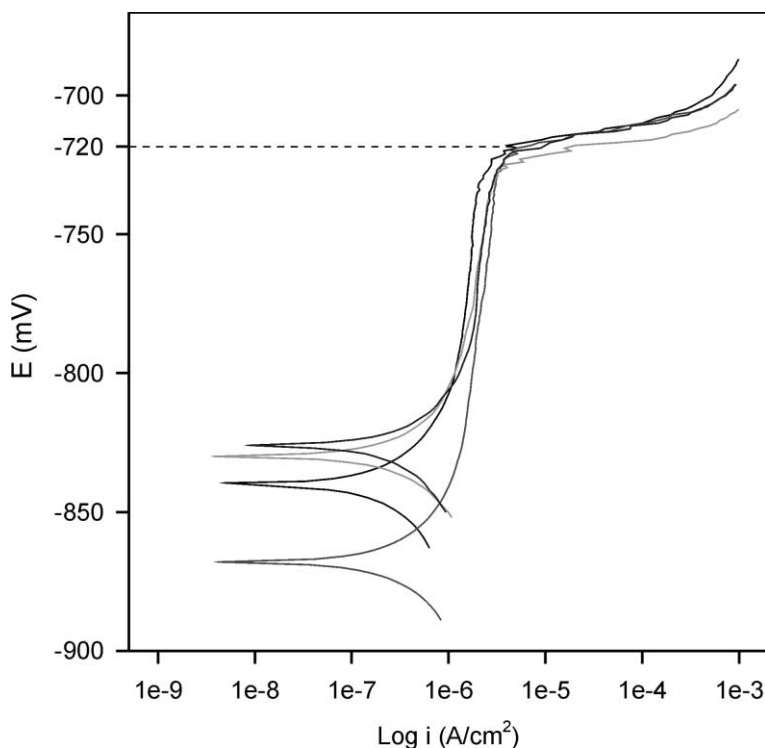


Fig. 6. Polarisation plots obtained on a sample from alloy AA5083 after 2 h in solution of NaCl at 3.5%. Exposed area: 1 cm².

curves. It can be observed in this table that, in line with the results obtained from recording $E_{\text{corr}}-t$ curves, a high degree of dispersion exists in the values of the potential of corrosion. This same dispersion is observed in the values calculated for R_p . To quantify the dispersion found in the experimental data, a simple statistical analysis can be conducted based on the study of the values of the standard deviation and the error.

The values of the standard deviations of E_{corr}^0 and R_p have been obtained from the data included in Table 2; these are:

$$\sigma(E_{\text{corr}}^0) = 33.747 \quad \sigma(R_p) = 13.3271$$

In turn, the corresponding standard errors obtained were:

$$\varepsilon(E_{\text{corr}}^0) = 8.713 \quad \varepsilon(R_p) = 3.4410$$

On comparing the values of $\sigma(E_{\text{corr}}^0)$ and $\sigma(R_p)$ with the corresponding mean values, $\langle E_{\text{corr}}^0 \rangle$ and $\langle R_p \rangle$ included in Table 2, the high degree of dispersion present in the experimental data can be observed; this leads to a high degree of uncertainty in the measurement, as shown by the values of the standard errors. As previously

Table 2
Electrochemical parameters of AA5083 alloy obtained from anodic polarisation tests

E_{corr}^0 (mV)	E_{pit} (mV)	R_p (k Ω)
–858	–722	52.44
–806	–722	37.97
–840	–717	32.32
–868	–719	24.89
–760	–724	20.88
–797	–723	41.14
–826	–720	22.46
–859	–722	21.86
–830	–722	47.73
–879	–719	60.20
–882	–720	56.66
–878	–723	49.94
–880	–717	45.21
–881	–722	30.10
–888	–721	29.23
<i>Average</i>		
–850	–721	38.2

Sample area: 1 cm².

commented, the initial potential of corrosion, E_{corr}^0 , and the resistance of polarisation, R_p , are closely related to the density of cathodic precipitates present on the surface of the alloy. Therefore it is logical to conclude that the high degree of dispersion obtained is originated by the differences in density of the precipitates present on the surface of the various samples. As previously stated, these differences are caused by the lack of homogeneity in the surface distribution of the precipitates in the alloy studied. In consequence, the density of intermetallic particles can vary notably from one area of 1 cm² to another in the same sample of alloy. This implies that the results of the electrochemical measurements may be very different depending on the zone where the measurements are taken. In accordance with these results, it would not seem adequate to use a surface area of only 1 cm² to reproduce the mean behavior of the system, at least not in terms of the two electrochemical parameters referred to.

In contrast to that observed for the values of E_{corr}^0 and R_p , the data given in Table 2 demonstrate a good reproducibility in the values of the potential of pitting nucleation, which is situated around –720 mV. The values calculated for the standard deviation and error E_{pit} are, respectively:

$$\sigma(E_{\text{pit}}) = 2.133 \quad \varepsilon(E_{\text{pit}}) = 0.551$$

The low dispersion obtained in the values of E_{pit} may be associated with the fact that this potential is related to the characteristics of the matrix and not with the distribution of the precipitates [18,19]. Thus, when studying samples of 1 cm² surface area, a reproducible measurement of E_{pit} is obtained, which can be considered representative of the behavior of the matrix.

As previously commented, with the aim of avoiding the dispersion of data produced when working with samples of 1 cm², experiments of $E_{\text{corr}}-t$ and of linear polarisation were conducted employing a cell with three electrodes in which it is possible to modify the area of surface exposed, Fig. 4.

In Fig. 7(a)–(c) are given the values of E_{corr} , R_p and E_{pit} for each of the three different surface areas tested. As can be observed, the dispersion of the values of E_{corr} and R_p decrease as the area of surface exposed increases, Fig. 7(a) and (b). This result is reflected in the corresponding values of the standard deviation and error:

$$\sigma_{13.2}(E_{\text{corr}}^0) = 8.74 \quad \sigma_{25.5}(E_{\text{corr}}^0) = 5.47$$

$$\varepsilon_{13.2}(E_{\text{corr}}^0) = 2.26 \quad \varepsilon_{25.5}(E_{\text{corr}}^0) = 1.41$$

$$\sigma_{13.2}(R_p) = 8.66 \quad \sigma_{25.5}(R_p) = 2.25$$

$$\varepsilon_{13.2}(R_p) = 2.24 \quad \varepsilon_{25.5}(R_p) = 0.58$$

With the increase in the area of the samples, the probability of there is existing a similar density of precipitates increases in the different samples. The lower dispersion observed in the values of E_{corr} and R_p strengthens the conclusion that a relationship should exist between the value of the two parameters and the surface density of the cathodic precipitates.

With reference to the potential of pitting nucleation, E_{pit} , the values given in Fig. 7(c) demonstrate that its dispersion is similar for all three areas studied. This finding strengthens the hypothesis that the process of corrosion by pitting is not directly related to the surface density of the intermetallic compounds.

The values of the deviation the error only provide information on the degree of dispersion presented by a series of data, but from these values it is not possible to determine the degree of symmetry of the distribution around the mean value. This degree of symmetry would allow us to accept or reject the mean value of the electrochemical parameters as that representing the behavior of the system. In any series of data, this degree of symmetry cited can be determined by studying the frequencies. To do this, for each series of data analyzed, a different width interval has been taken in function of the maximum and minimum values recorded, Tables 2–4.

Fig. 8 shows the frequency distribution of E_{corr} for the three areas studied. Superimposed in this figure are the lines, which, in each case, represent the function of density of probability associated with each of the distributions. The first finding to be noted is the lack of symmetry existing when working with an area of surface exposure of 1 cm², as a certain bias to the left can be seen and no well-defined mode is observed. The wide range of potentials found causes the high degree of dispersion in the values observed. This fact, taken together with the asymmetric character of the distribution, obliges us to reject the values $\langle E_{\text{corr}}^0 \rangle$ and $\langle R_p \rangle$ as representative of the electrochemical response of the system. From the statistical point of view, a possible solution would be to increase the number of tests. However this would only provide us with more centralized, but not less dispersed measurements, and would also be rejected as a solution on practical grounds.

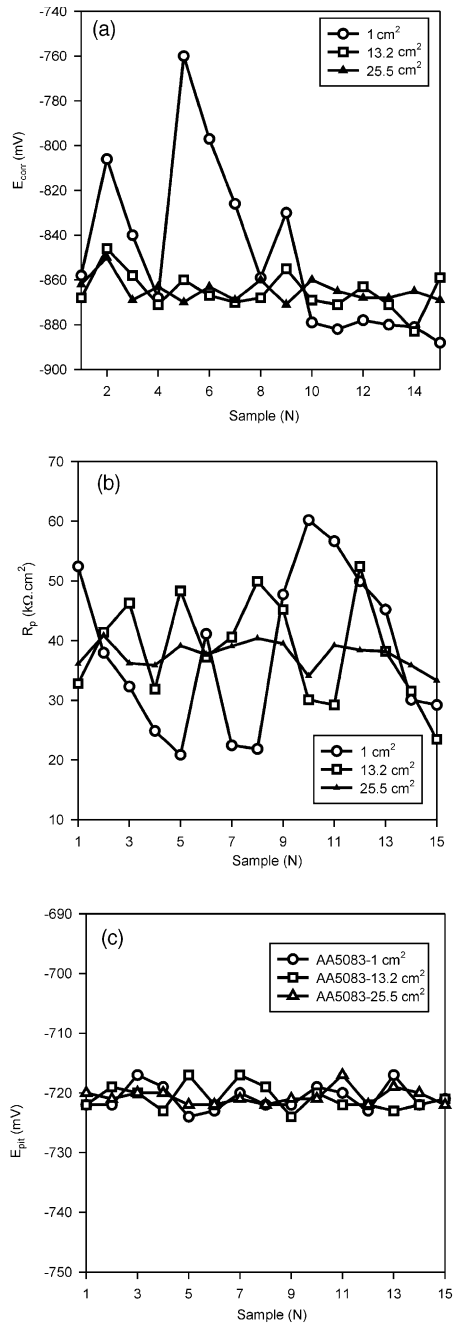


Fig. 7. Electrochemical parameters obtained after exposing samples with different areas: (a) corrosion potential, (b) polarisation resistance and (c) pitting nucleation potential. Samples from alloy AA5083. Medium: NaCl at 3.5%.

Table 3

Electrochemical parameters of AA5083 alloy obtained from anodic polarisation tests

E_{corr}^0 (mV)	E_{pit} (mV)	R_p (k Ω)
-868	-722	32.81
-846	-719	41.41
-858	-720	46.29
-871	-723	31.86
-860	-717	48.33
-867	-722	37.22
-870	-717	40.60
-868	-719	49.94
-855	-724	45.21
-869	-720	30.10
-871	-722	29.23
-863	-722	52.44
-871	-723	38.20
-883	-722	31.56
-859	-721	23.45
<i>Average</i>		
-865	-721	38.6

Sample area: 13.2 cm².

Table 4

Electrochemical parameters of AA5083 alloy obtained from anodic polarisation tests

E_{corr}^0 (mV)	E_{pit} (mV)	R_p (k Ω)
-862	-720	36.10
-850	-721	40.89
-869	-720	36.21
-863	-720	35.88
-870	-722	39.13
-863	-722	37.67
-869	-721	39.06
-860	-722	40.40
-871	-721	39.52
-860	-721	34.10
-865	-717	39.23
-868	-722	38.41
-868	-719	38.20
-865	-720	35.86
-869	-722	33.33
<i>Average</i>		
-865	-721	38

Sample area: 25.5 cm².

Furthermore, as can be appreciated in Fig. 8, by increasing the area of exposure, an increase is achieved in the degree of symmetry of the distribution and a narrowing of the range of potentials obtained. As can be observed, for areas of exposure of both 13.2 and 25.5 cm², the resulting mode is well-defined and coincided with the mean

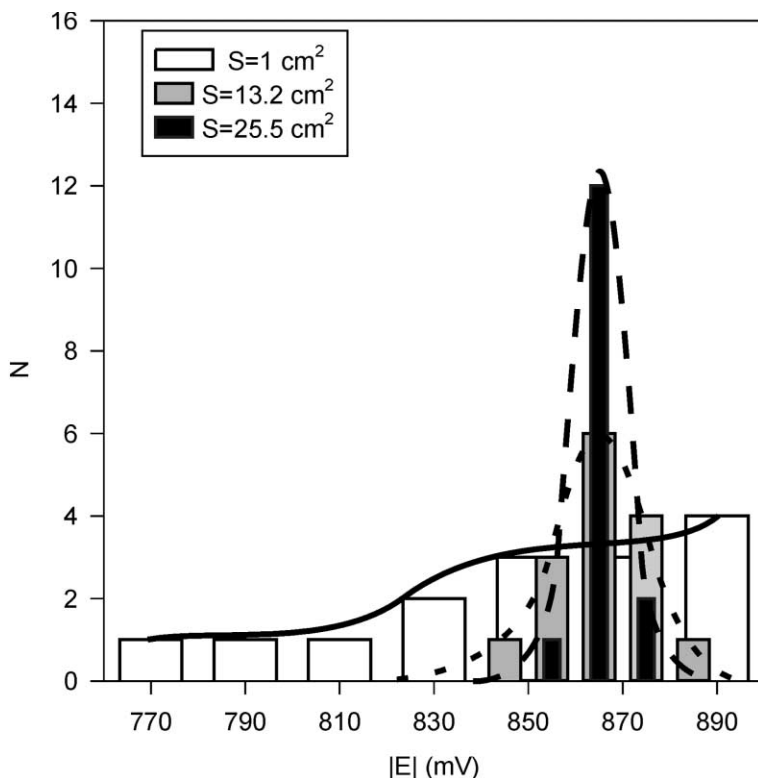


Fig. 8. Frequency distribution and probability density function of the corrosion potential for the three areas studied. Samples from alloy AA5083. Medium: NaCl at 3.5%.

value. This allows us to consider it as a Gaussian distribution, with parameters $\langle E_{\text{corr}} \rangle$ and $\sigma_{E_{\text{corr}}}$. Therefore, the increase in the surface area of the sample not only decreases the degree of dispersion of the measurements but also increase the degree of symmetry of the distribution, which thus allows us to accept the values of $\langle E_{\text{corr}}^0 \rangle$ and $\langle R_p \rangle$ as representative of the behavior of the system.

The aforementioned comments with regard to E_{corr} are equally applicable to R_p , Fig. 9. However, even if the exposed area is 13.2 cm², the R_p values do not show a Gaussian distribution. Consequently, even though the potentials distribution suggests using an area of 13.2 cm² to perform the tests, in order to evaluate the average activity of the system, it is recommendable to employ an area of 25.5 cm².

3.1. On the influence of the density of cathodic precipitates

In order to reinforce the hypothesis proposed, different tests have been carried out in a system where the density of cathodic precipitates dispersed on the surface of the

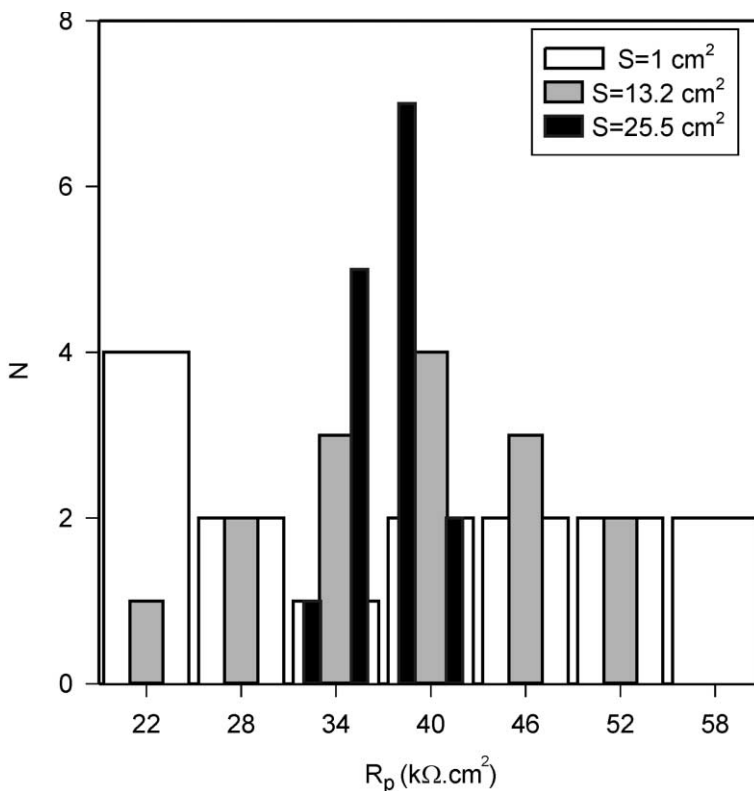


Fig. 9. Frequency distribution of the polarisation resistance for the three areas studied. Samples from alloy AA5083. Medium: NaCl at 3.5%.

alloy is considerably lower. Thus, a 99.5% purity aluminum alloy has been tested in NaCl at 3.5% solution.

Fig. 10 shows a SEM image of a sample of AA1050 (99.5%) alloy. As it can be observed, the number of cathodic intermetallics in this alloy is much lower than the observed in AA5083 alloy, Fig. 1. Two kinds of precipitates have been distinguished through EDS, Fig. 10. These precipitates have been identified as (Al,Fe) and (Al,Fe,Si), which, according to [17,20] would correspond to $\text{Al}_{12}\text{Fe}_3\text{Si}_2$, Al_6Fe or Al_3Fe . These intermetallics present a cathodic behavior respect the metallic matrix in NaCl solutions [21]. Therefore, when a sample of AA1050 alloy is exposed to a NaCl at 3.5% solution, its behavior and its electrochemical response must be comparable to that shown by the AA5083 alloy.

Fig. 11 shows SEM images corresponding to a sample after being full immersed in the NaCl solution during 30 days. These images reveal a similar behavior between this alloy and AA5083, Fig. 1. Thus the corrosion is localized in the matrix surrounding the cathodic intermetallics. However, the intensity of the attack is clearly lower in the AA1050 alloy since the cathodic particles density is much lower.

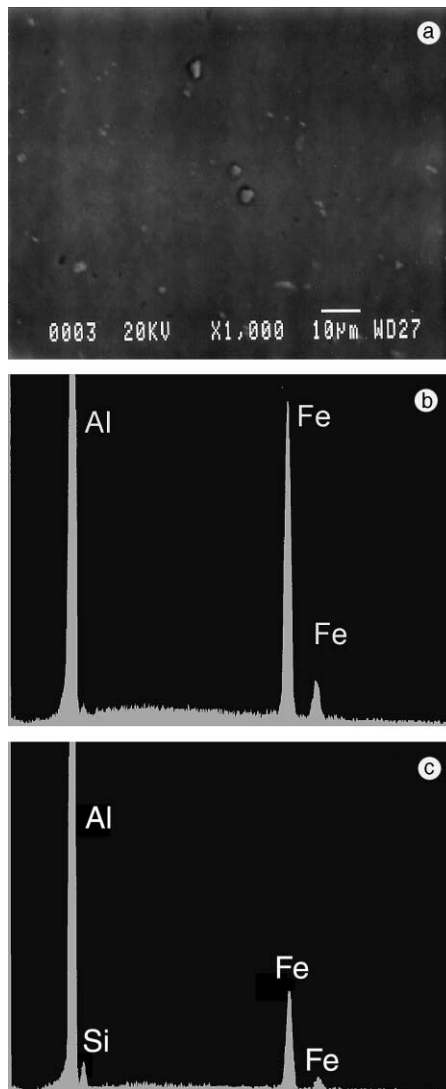


Fig. 10. (a) SEM image obtained on a sample of AA1050 alloy. (b) and (c) EDS spectrum acquired on the intermetallic compounds.

Fig. 12 plots the OCP diagram recorded in NaCl on 1 cm² of a sample of AA1050 alloy during 30 days. As a reference, Fig. 12 includes a diagram corresponding to a sample of AA5083 alloy. Note that the initial value of E_{corr} for AA1050 alloy is lower than that for AA5083 alloy. Moreover, the time to reach the stabilization potential is higher. Both findings are also reflected in the corresponding linear polarisation curves, Fig. 13, and they can be related with the lower cathodic precipitates density present in the AA1050 alloy.

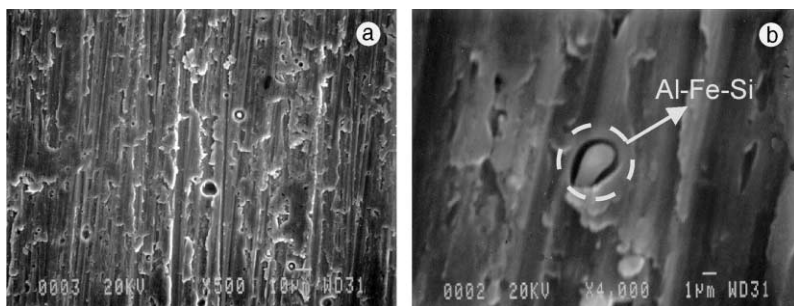


Fig. 11. (a) SEM image obtained on a sample of AA5083 alloy after 30 days of immersion in an aerated solution of NaCl at 3.5%. (b) Details of the area corroded by local alkalization.

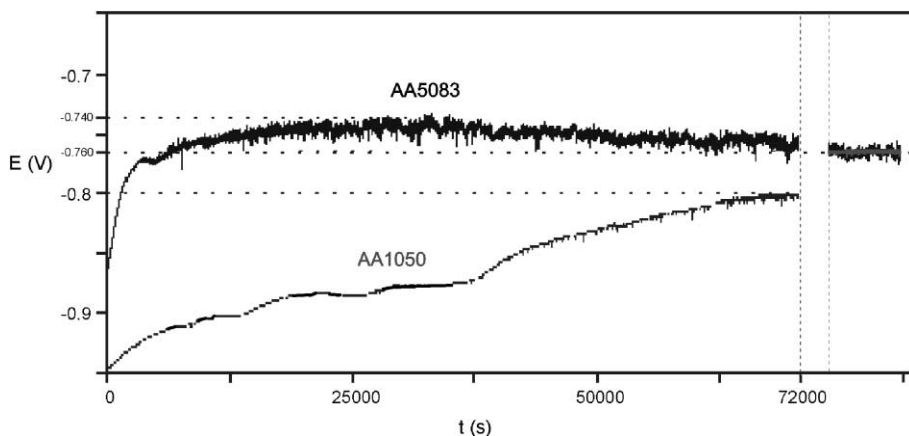


Fig. 12. $E_{\text{corr}}-t$ plots obtained on samples from alloys AA5083 and AA1050 after 2 h in solution of NaCl at 3.5%. Exposed area: 1 cm^2 .

As regards the hypothesis proposed, this lower density should be also reflected in a higher reproducibility of the electrochemical measurements. Table 5 contains the electrochemical parameters calculated from 15 linear polarisation curves recorded on 1 cm^2 samples of AA1050 alloy after 5 min of full immersion in NaCl at 3.5% solution. A high degree of reproducibility of the curves can be observed in these values and in the values of the standard error and the standard deviation:

$$\sigma(E_{\text{corr}}^0) = 4.04 \quad \sigma(R_p) = 2.46$$

$$\varepsilon(E_{\text{corr}}^0) = 1.04 \quad \varepsilon(R_p) = 0.63$$

Note that these values are even lower than those obtained for AA5083 alloy when samples of 25.5 cm^2 of area were exposed to the solution. The higher concentration

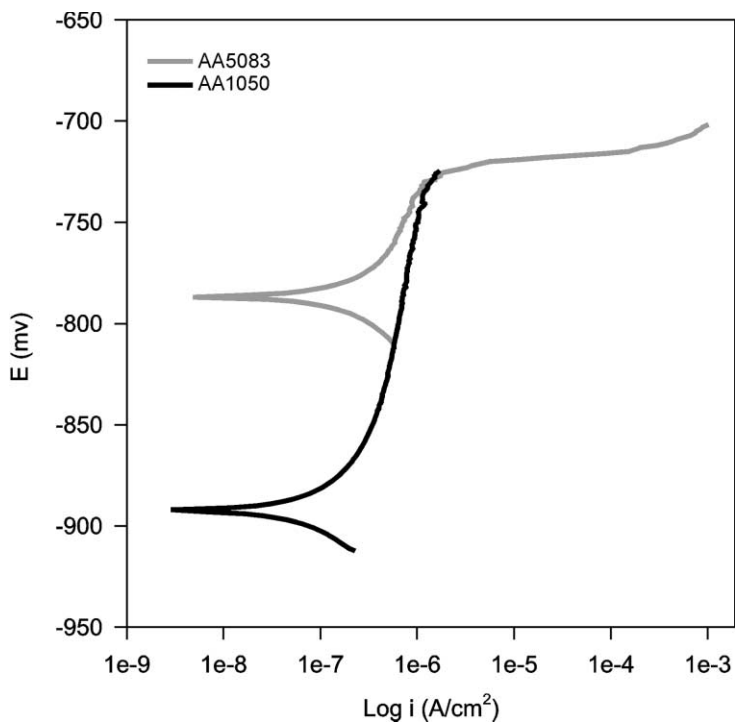


Fig. 13. Linear polarisation curves obtained on samples from alloys AA5083 and AA1050 after 2 h in solution of NaCl at 3.5%. Exposed area: 1 cm².

Table 5
Electrochemical parameters of AA1050 alloy obtained from anodic polarisation tests

E_{corr}^0 (mV)	E_{pit} (mV)	R_p (k Ω)
-891	-722	60.10
-898	-724	60.45
-892	-723	66.41
-890	-720	65.81
-890	-722	59.13
-895	-717	60.37
-893	-719	61.06
-890	-722	60.00
-893	-717	59.45
-889	-722	61.10
-888	-721	59.23
-899	-722	58.41
-889	-719	64.20
-898	-720	60.86
-885	-723	63.33
<i>Average</i>		
-893	-721	61.33

Sample area: 1 cm².

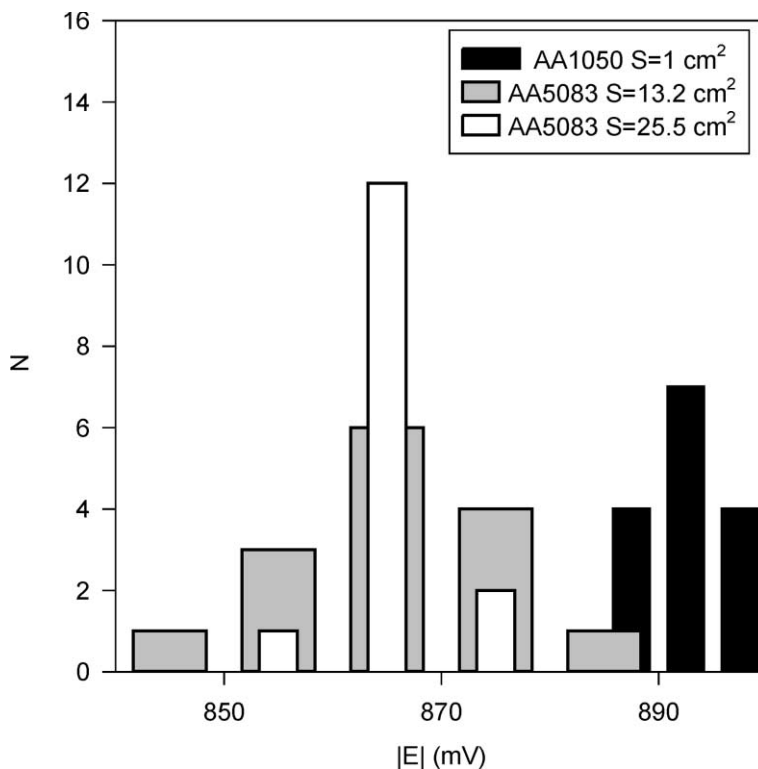


Fig. 14. Frequency distribution of the corrosion potential for 13.2 and 25.5 cm² samples from alloy AA5083 and 1 cm² samples from alloy AA1050. Medium: NaCl at 3.5%.

of the values of both parameters and the higher symmetry of their distribution can be observed in Figs. 14 and 15.

These results reinforce the hypothesis that the data dispersion obtained for the AA5083 alloy is related to the lack of homogeneity in the cathodic particles surface distribution.

4. Conclusions

The corrosion behavior of aluminum alloy AA5083 is mainly related with its surface distribution of Al(Mn,Fe,Cr) precipitates. When characterization measurements are taken on small areas of sample surface, the lack of homogeneity in the surface distribution of the precipitates produces a high degree of dispersion in the results, giving rise to a low level of results reproducibility.

The results obtained through electrochemical tests show that the dispersion of the data is considerably reduced when the exposed area is increased. Thus, the lowest reproducibility of the results corresponds to a exposed area of 1 cm². This finding could be related to the heterogeneity of the intermetallic particle distribution. In this

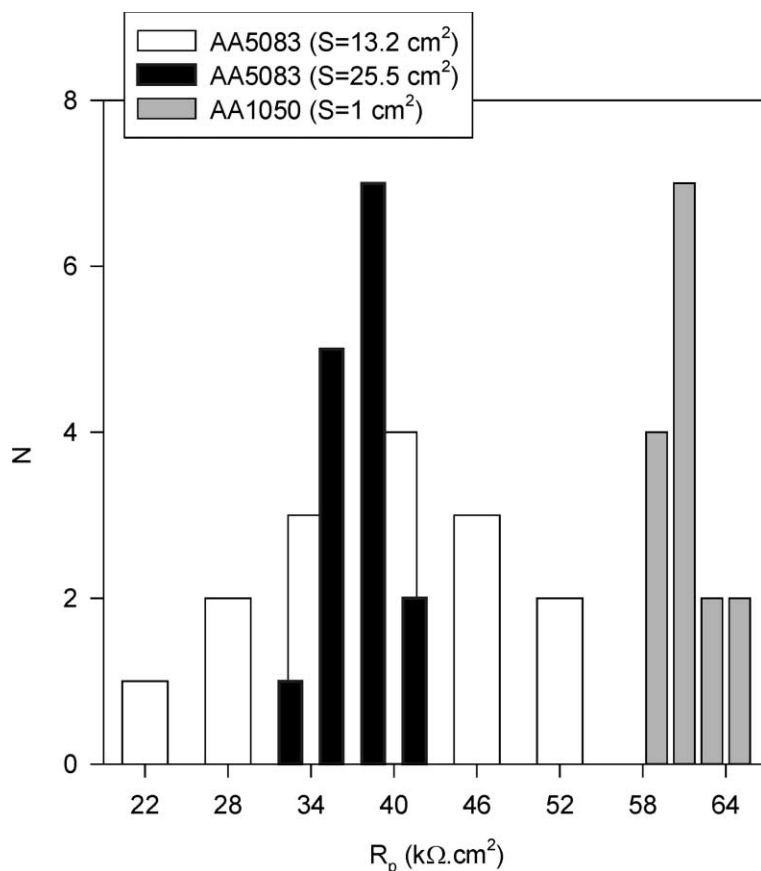


Fig. 15. Frequency distribution of the polarisation resistance for 13.2 and 25.5 cm² samples from alloy AA5083 and 1 cm² samples from alloy AA1050. Medium: NaCl at 3.5%.

sense, both corrosion potential and polarisation resistance are clearly affected by the heterogeneity of the surface. In contrast, pitting nucleation potential values show an almost null dispersion since this parameter is related to the metallic matrix properties but not to the number of cathodic particles.

This hypothesis has been confirmed through the study of the electrochemical response of the alloy AA1050. In this alloy, the number of cathodic particles is much lower. Thereby, E_{corr} and R_p values are not so affected by the value of the exposed area.

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