Studies of Corrosion Resistance of Passive Layers on Al–Ni Alloys in the Presence of Chloride Ions

B. Perić[*], *Z. Grubač and* L. Sablić

*Laboratory of General and Inorganic Chemistry, Faculty of Technology,
University of Split, 58000 Split, Croatia*

The corrosion resistance of passive layers was studied on cast Al–Ni alloys with an ever-increasing mass content of nickel (w(Ni) = 0.54 – 4.30%). The method of potentiodynamic polarization, measuring to 10 V, the method of measuring the changes of the current at a constant potential of 0 V, and the method of determining the critical concentrations of chloride ion gave identical dependence of the corrosive resistance of the passive layers on the mass content of nickel in the alloy.

The method of potentiodynamic polarization at low potentials to 1 V was applied to obtain the dependence of insulating properties of the passive layers on the mass content of nickel in alloy.

INTRODUCTION

Frequent application of aluminium and its alloys in various branches of industry and in different corrosion media is made possible by the fact that aluminium is a typical valve metal, which, in contact with air or water, is coated with a layer of aluminium oxide. When exposed to air, a 3–5 nm thick layer develops spontaneously, protecting it from further oxidation.[1] The oxide layer thickness, as well as its protective properties, can be increased by anodic oxidation. The composition and concetration of the electrolyte, temperature, and anodizing conditions cause a different structure, composition and properties of anodic oxides.

The anodic oxide films developed on aluminium are classified into two general types: barrier films and porous films. Barrier films develop in almost neutral solutions of borates, citrates, tartarates, phosphates, *etc.*, in which aluminium oxide is insoluble. In contrast, porous films develop by anodic oxidation in acid solutions promoting oxide dissolution (sulfuric, oxalic, phosphoric).[2-4] Porous oxide growth comprises, at the initial stage, formation of a barrier oxide. This barrier film is maintained dur-

---

[*] Author to whom correspondence should be addressed

ing further oxide growth as a semispherical oxide layer at pore bottoms.[19] The characteristic of aluminium-oxide is that it is covalent, soluble in strong alkalic and strong inoxidable acids. The presence of the halogenide ion, the chloride ion in particular, causes a local corrosion attack (pitting corrosion).[5,6]

Continuing our studies of corrosive resistance of the passive layers on binary Al–alloys,[14–17] in this work we studied the passive layers on Al–Ni alloys.

It is known from literature[7,8] that aluminium and nickel form the intermetallic Al_3Ni phase which is very cathodic to aluminium and has an adverse influence upon resistance to corrosion.

Five Al–Ni alloys with an ever-increasing mass content of nickel were studied. The mass content of other elements present was practically constant. The passive layers on the alloys were strengthened by anodic oxidation.

The object of these studies was to determine and compare the corrosive resistance of the passive layers on Al–Ni alloys. For comparison, the passsive layer on pure aluminium ($w(Al) = 99.7\%$) of which the alloys were prepared (sample no. 6) was also studied.

The chemical composition of the alloys was determined by the quantimeter and presented in Table I.

TABLE I

Invesitgated samples

Sample number	Mass content, $w / \%$				
	Ni	Cu	Si	Ti	Fe
1	0.54	0.01	0.06	0.03	0.12
2	0.90	0.01	0.05	0.02	0.15
3	1.41	0.01	0.06	0.03	0.12
4	3.10	0.01	0.06	0.02	0.15
5	4.30	0.01	0.06	0.02	0.14
6	–	0.01	0.07	0.03	0.12

EXPERIMENTAL

Ring-shaped samples were protected with teflon in the way known from literature.[9] The exposed surface of the sample (lateral area) was 1.5 cm². Porous anodic films were formed by anodizing samples individually at a constant current density, $j = 15$ mA cm^{-2}, and about 10 V potential in sulfuric acid, $c(H_2SO_4) = 3$ mol dm^{-3}, until the stationary state (30 minutes) was achieved. Prior to and after passivation, the samples were treated according to the treatments from literature.[10]

All the studies were carried out at a constant temperature (298 K) by:

I – Potentiodynamic polarization:[11–13]

    a) In the potential region to 1 V,

    b) In the potential region to 10 V.

II – Measuring the current changes at a constant potential.[13]

III – Determining the critical concentrations of chloride ion in the passivating solution.[14–17]

The studies under II and III were carried out in the presence of chloride ions.

Using the potentiodynamic polarization method, the passivated sample was dipped into boric acid and sodium borate solution, $c(H_3BO_3) = 0.5$ *mol dm^{-3}*, $c(Na_2B_4O_5(OH)_4) = 0.05$ mol dm^{-3}, pH = 7.1.

The platinum electrode was used as counter electrode and the saturated calomel electrode (SCE) as referent electrode. Potentiometric curves were taken by the Wenking potentiostat, model 70 HC3 with the Linear sweeper, model SMP72 and the Houston recorder 2000. At all measurements, the sweep rate of the potential was 0.6 V min^{-1}. In order to insrease the sensitivity of the potentiostat and to make it possible to take the polarization curves on aluminium and its alloys in the potential range to 1 V, the picoammeter was connected to the measuring system.[11–13] The picoammeter of the Keithley Instruments, Model 414 A, was applied for this purpose.

The solution NaCl, $c(NaCl) = 1$ mol dm^{-3} with pH = 4.3 was used as electrolyte for measurement at a constant potential. The passivated samples were kept at a constant potential of 0 V *vs.* SCE and the current change with time was measured on the *x-t* recorder.[13]

The critical chloride ion concentration in the passivating solution was determined by the presence of the chloride ion in the sulfuric acid solution in which passivation was accomplished. Passivation was carried out successively with ever increasing chloride ion concentrations until the concentration that prevented formation of the passive layer was achieved. The chloride ion concentration was increased by adding the sodium chloride solution, concentration $c(NaCl) = 1$ mol dm^{-3}, into sulfuric acid, $c(H_2SO_4) = 3$ mol dm^{-3}. The total volume of thus obtained solution was always 100 cm^3.

RESULTS AND DISCUSSION

Interpretation of the role of Cl$^-$ ion in the breakdown process of the oxide layer is not the subject of this paper, only the effect of alloying and impurities of aluminium are discussed here.

Polarization curves of aluminium and Al–Ni alloys in the boric acid and sodium borate solution are shown in Figures 1 and 2. Figure 1 shows the current density dependence on the potential to 1 V and Figure 2 the current density dependence on the potential to 10 V.

When measuring the polarization curves in the potential region to 1 V, very low currents occur, 10^{-8}–10^{-7} A order of magnitude. As the surface of studied sample is almost 1 cm^2, the current densities are also of the same order of magnitude.

In neutral solutions, in the absence of Cl$^-$ ions, by charging the passive layer with low potentials, this layer acts as an insulator, that is, it obstructs the passing of the current. However, since deffects that weaken insulation occur in the passive layers on the alloys due to impurities, alloying components and changes in the structure of the layer by increasing the potential even for small values (to 1 V), the current, proportional to the number of defects, passes through the layer. By increasing the potential to 10 V, a certain threshold is reached at which a sharp increase of the current occurs (order of magnitude 10^{-6}–10^{-5} A). Therefore, S. Sato *et al.*[13] think that, at such potentials ($\leq$ 10 V), the current consists of three components:

a) The charging current I_c, from which the barrier layer capacitance can be determined,

b) The leakage current I_R, from which the resistance of the barrier layer can be determined,

c) The formation current, I_f, of the passive layer arising from the Faradaic reactions in that layer.
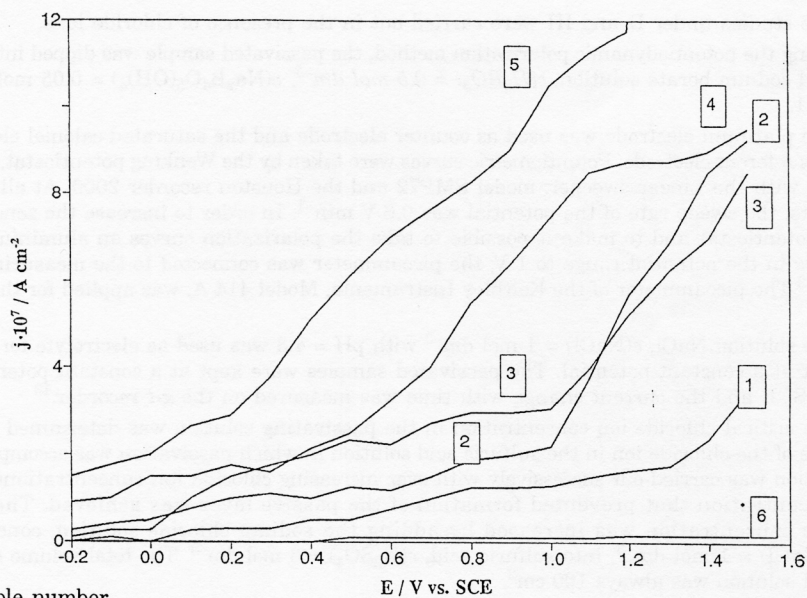
* Sample number

Figure 1. Curves of current density dependence, j/A cm^{-2}, upon the passivated sample potential (*vs.* SCE), E/V, (region of potential change to 1 V).
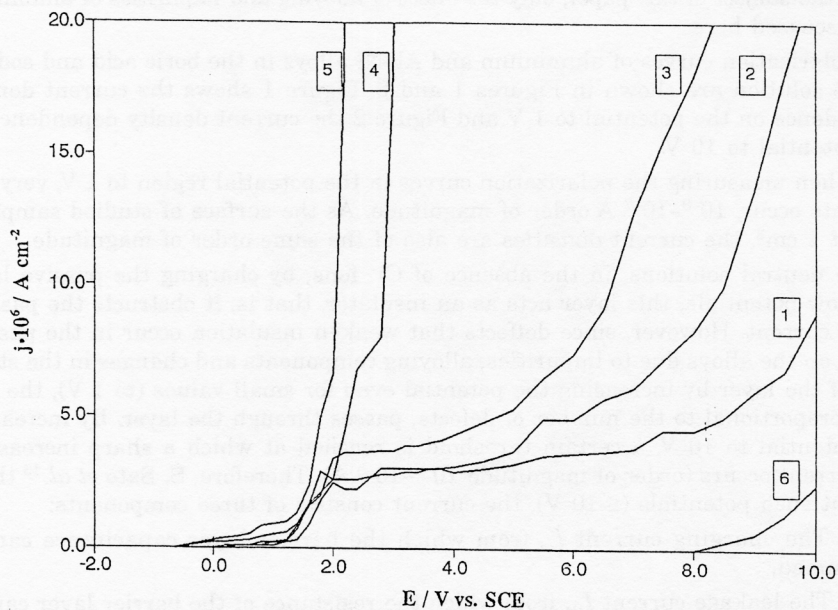
* Sample number

Figure 2. Curves of current density dependence, j/A cm^{-2}, upon the passivated sample potential (*vs.* SCE), E/V, (region of potential change to 10 V).

For alloys, this current may be not only due to the film formation, but also to the O_2-evolution on electron-conductivity parts of the oxide layers (Ni-oxide, incorporated into the Al-oxide).

When measuring at low potentials (≤ 1 V) the measured current consists predominantly of I_c and I_R. It is known[13] that the method of measuring very low currents (10^{-9}–10^{-8} A) at low potentials (≤ 1 V) cannot be applied successfully on aluminium aloys because their structure and corrosion are irregular. In this work, as well as in Ref. 17, it is believed that it could be useful to apply measuring of very low currents at a low potential (here the insulating resistance of the passive layers is measured) for the following reasons:

1. A series of Al–Ni alloys with approximately the same content of the other elements was tested.

2. All the alloys were melted and cast to avoid the influence of structural changes. Though certain irregularities between samples 2 and 3 are visible in Figure 1, it is obvious that an increase of the current ($I_c + I_R$) occurs with the increase of the potential, first in sample 5 and then in samples 4, 3, 2, 1, in that order, and finally in sample 6. This agrees with the observation that, with an increase of the mass content of nickel in alloy, the number of defects in the passive layer on these alloys also increases.

Figure 2 shows measurements at higher potentials (≤ 10 V) in boric acid and sodium borate solution, at which the potential threshold is clearly discernible. Here, considerably greater currents (I_f), almost two orders of magnitude higher than at the potential up to 1 V, occur. The sharp increase of the current at the lowest potential is seen in sample 5, which has the largest mass content of nickel. After that, the sharp increase of current gradually approaches the higher potentials as mass content of nickel in the alloy decreases. This means that the resistance of the passive layers on the samples increases with a decrease of the mass content of nickel in the alloy.

The results obtained by the current change method at constant potential are shown in Figure 3.

If Al and Al-alloys are dipped into a relatively neutral or weakly acid solution of sodium chloride, intensive local corrosion of aluminium (pitting corosion) occurs. The possible mechanisms of attacks by chloride ions are described in literature.[18,19] The samples were dipped into the sodium chloride solution with pH = 4.3. The current density depending on time was measured. Measurements were carried out at a constant potential of 0 V, which is considerably more positive than the pitting corrosion potential for aluminium.[13,20,21] In this way it was possible to determine the corrosive resistance of the passive layers on Al–Ni alloys by measuring the time up to a sharp increase of current as a result of pitting. A short period of time to the appearance of high current densities suggests weak resistance of the passive layer while a long (longer) period of time to a sharp increase of the current density points to the existence of a resisting passive layer.[13]

A sharp increase of the current density, as seen from Figure 3, appears first in sample 5, and than in samples 4, 3, 2 and 1, in that order. In sample 6 ($w(Al) = 99.7\%$) a sharp increase of current density appears only after 280 minutes. These results show that the time needed for a sharp increase of current density rises with a decrease of the mass content of nickel in the alloy.
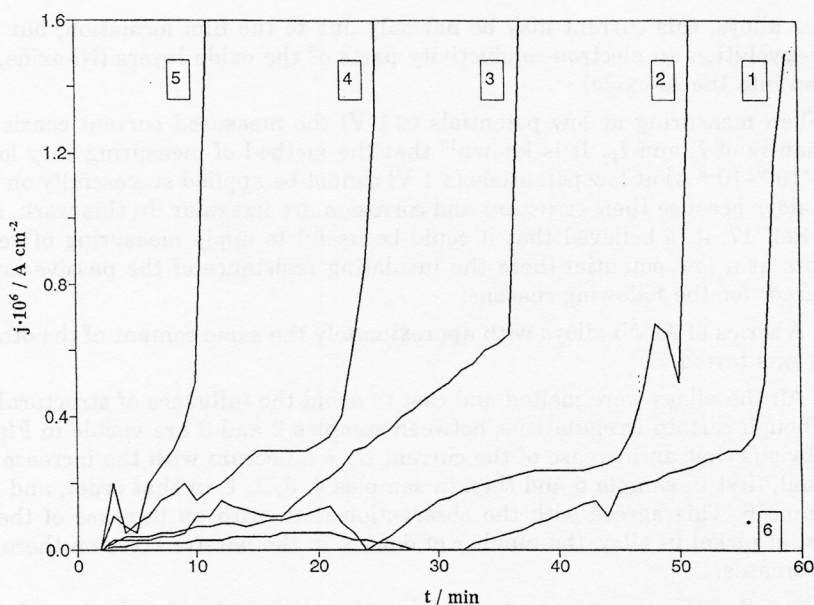
Figure 3. Anodic polarization curves for Al and Al–Ni alloys constant potential at 0 V (*vs.* SCE).

Table II shows the results of determining critical concentration of chloride ions. It can be seen from that table that the critical concentration of the chloride ion is the lowest in sample 5, and than increases in samples 4, 3, 2, 1 and 6.

This shows that, under the conditions of our study, the resistance to the presence of the chloride ion in the solution for passivation grows with a decrease of the mass content of nickel in the alloy.

TABLE II

Possibility of passivating samples in the presence of the chloride ion in the passivating solution

Sample number	w(Ni)/%	V(NaCl)/cm^3, c(NaCl) = 1 mol dm^{-3}	V(H$_2$SO$_4$))/cm^3, c(H$_2$SO$_4$) = 3 mol dm^{-3}	*c(NaCl) $\cdot$ 10^2 mol dm^{-3}	c(H$_2$SO$_4$) mol dm^{-3}
1	0.54	4.0	96.0	4.0	2.880
2	0.90	3.5	96.5	3.5	2.895
3	1.41	2.5	97.5	2.5	2.925
4	3.10	2.2	97.8	2.2	2.934
5	4.30	1.5	98.5	1.5	2.955
6	–	7.5	92.5	7.5	2.775

* Critical concentration of the chloride ion in the passivating solution, *i.e.* maximum concentration at which passivation is still possible.

CONCLUSIONS

The tree methods applied (potentiodynamic polarization, measuring the current changes at a constant potential, determination of the critical concentration of chloride ions) gave identical results.

The measurement results point to the dependence of corrosive resistance of the passive layers on Al–Ni alloys on the mass content of nickel in the alloy. By increasing the mass content of nickel, the resistance of the passive layers on Al–Ni alloys decreases.

The potentiodynamic polarization measurements in the potential region to 1 V show that the insulating properties of the passive layers on Al–Ni alloys weaken with an increase of the mass content of nickel in the alloy.

These conclusions refer to the studied region of the mass content of nickel in the alloy.

REFERENCES

1. J. Gruberger and E. Gileadi, *Electrochim. Acta* **31** (1986) 1531.
2. G. E. Thompson and G. C. Wood, in: *Treatise on Materials Science and Technology*, J. C. Scully (Ed.), Academic Press, New York, Vol. 23, 1983, p. 205.
3. I. A. Ammar, S. Darwish, and P. Khalil, *Z. Werkstoffetechn.* **12** (1981) 421.
4. T. Fukushima, Y. Fukuda, G. Ito, and A. Shimizu, *J. Met. Finish. Soc. Jap.* **25** (1974) 542.
5. H. H. Strehblow, *Werkst. Korros.* **29** (1978) 654.
6. F. Quary, L. Tomcsanyi, and T. Turmezey, *Electrochim. Acta* **33** (1988). 323.
7. F. L. La Que and H. R. Copson, *Corrosion Resistance of Metals and Alloys*, Reinhold Publishing Corporation, New York, 1963.
8. W. Hufnagel, *Aluminium Tachenbuch*, Aluminium Verlag, Düsseldorf, 1988, p. 31.
9. H. G. Feller and J. Osterwald, *J. Electrochem. Soc.* **111** (1964) 119.
10. O. Korelić, Dissertation, University of Zagreb, 1970.
11. M. S. Hunter and P. Fowle, *J. Electrochem. Soc.* **101** (1954) 481.
12. M. S. Hunter and P. Fowle, *J. Electrochem. Soc.* **103** (1956) 482.
13. S. Sato, Y. Itoi, and A. Hasumi, *Electrochim. Acta* **26** (1981) 1303.
14. S. Lipanović, L. Sablić, and B. Perić, *Kem. Ind.* **31** (1982) 397.
15. L. Sablić, B. Perić, and S. Lipanović, *Kem. Ind.* **33** (1984) 493.
16. B. Perić, S. Lipanović, and L. Sablić, *Kem. Ind.* **34** (1985) 615.
17. S. Lipanović, L. Sablić B. Perić, and Z. Grubač, *Kem. Ind.* **36** (1987) 389.
18. H. H. Strehblow, *Werkst. Korros.* **35** (1984) 437.
19. A. Despić and V. P. Parkhutik, *Electrochemistry of Aluminium in Aqueous Solutions and Physics of Its Anodic Oxide,* in: *Modern Aspects of Electrochemistry*, J. O'M. Bockris, R. E. White, and B. E. Conway (Eds.), Plenum Press, New York, Vol. 20, 1989, p. 410, 439.
20. K. Sugimoto, *Corrosion Engng.* **20** (1971) 443.
21. Z. A. Foroulis and M. J. Thubrikar, *J. Electrochem. Soc.* **122** (1975) 1296.

B. PERIĆ *AT AL.*

SAŽETAK

Ispitivanje korozijske otpornosti pasivnih slojeva na Al–Ni legurama uz prisutnost kloridnih iona

B. Perić, Z. Grubač i L. Sablić

Proučavana je korozijska otpornost pasivnih slojeva na lijevanim Al–Ni legurama s rastućim masenim udjelom nikla (w(Ni) = 0.54–4.30%). Metoda potenciodinamičke polarizacije (mjerenje do 10 V), metoda mjerenja promjene struje pri konstantnom potencijalu od 0 V i metoda određivanja kritične koncentracije klorid-iona dale su podudarnu ovisnost korozijske otpornosti pasivnih slojeva o masenom udjelu nikla u leguri.

Metodom potenciodinamičke polarizacije pri malim potencijalima do 1 V dobivena je ovisnost izolacijskih svojstava pasivnih slojeva o masenom udjelu nikla u leguri.