

INFLUENCE OF PH AND CHLORIDE CONCENTRATION ON THE CORROSION BEHAVIOR OF AL-6061 ALLOY

J. Dutta, C. Bhattacharya, D. Sarkar

B. E. College, Howrah

S. Bandyopadhyay

School of Materials Science & Engineering, University of New South Wales, Sydney, Australia

ABSTRACT

The present paper deals with the evaluation of corrosion properties of Al-6061 alloy exposed to aqueous solutions of 0%, 0.05%, 1% and 3% NaCl within the range of acidic to alkaline pH at room temperature. Studies were conducted using techniques like potentiodynamic polarization at sufficiently low scan rates and immersion tests. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to study the morphology of the corroded surfaces and to identify the corrosion products.

INTRODUCTION

6xxx Al alloys have applications in space craft, electronic, marine and automotive industries¹⁻³ due to their good strength at high temperature, structural rigidity, dimensional stability and light weight. Although extensive studies⁴ have been made on the mechanical properties, corrosion behavior of these materials remained unexplored.^{5,6,7} The objective of this work is to investigate inter-granular and other localized corrosion behavior of 6061 matrix alloy in presence of different levels of chloride at different pH in aerated conditions through electrochemical techniques and immersion studies. The corrosion parameters like corrosion potentials (E_{corr}) in mV, corrosion current density (I_{corr}) in A/cm² and corrosion rates in mm/year were evaluated through Tafel analysis⁸ and some of the typical data of weight loss have been derived from immersion studies in 1% NaCl solution at different pH. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) have been employed for characterization of the surfaces. The results have been compared with the results of differential scanning calorimetry (DSC) and transmission electron microscopy (TEM).^{9,10}

EXPERIMENTAL TECHNIQUES

Electrochemical Corrosion and Immersion Studies

The material for this study was obtained from Comalco Research Centre of Thomastown, Victoria, Australia. Solutions of 0%, 0.05%, 1% and 3% NaCl, (AR, E-Merch) at pH 2, 7 and 12 were prepared with triple distilled water. Potentiodynamic polarization studies (linear sweep voltammetry)¹¹ were conducted at a scan rate of 1 m V/s within the potential range of -2000 mV to 1000 mV in a cell of three electrode assembly consisting of working electrode (the material form of coupon with exposed area of 0.2 cm²), counter electrode (Pt foil of area 2 cm²) and saturated calomel electrode (SCE) (reference electrode), employing computerised potentiostat - galvanostat AUTOLAB 30 (Netherlands). Weight loss during immersion tests in 1% NaCl solution at pH 2, 7 and 12 for 48 hours were obtained from the difference between weight of the samples before and after immersion.

SURFACE CHARACTERISATION

During polarization and immersion studies some of the test samples were found to be covered with white precipitates, possibly of aluminium compounds. The corroded samples after usual pretreatment¹² were subjected to SEM JEOL 840, EDS - JEOL 5200 SEM analysis.

RESULTS AND DISCUSSION

Figure 1 and 2 represent typical polarization curves for the alloy. The evaluated electrochemical corrosion parameters are given in Table 1. For a particular pH the I_{corr} values increase with increasing chloride ion concentration. For a particular chloride ion concentration, the order of I_{corr} and corrosion rate is pH 12 > pH 2 > pH 7. Although broad passive regions were discernible at pH12 (vide Figure 3), the E_{corr} values are highly negative compared to those at pH 2 & pH7. Notably chloride ions are known to be specifically absorbed on the oxide film on Al or its alloys and the amount absorbed is directly proportional to the bulk ion concentration. These Cl ions react with the metallic phase underneath the oxide layer with the breakdown of passivity¹³. In acidic pH solubility of Al^{3+} facilitates the the dissolution of the matrix and further accelerate the chloride attack. However, the mechanism of corrosion of the matrix in neutral and alkaline medium is associated with formation of $Al(OH)_3$ and its subsequent dissolution in purely alkaline medium (pH12). In fact the Al-Si-Mg containing second phase particles (identified in SEM studies with 6xxx series alloy as reported earlier¹⁴) is found to be strongly reactive in chloride medium. Moreover the stable and metastable precipitation sequences for this monolithic alloy were reported^{9, 10} through DSC and TEM studies. Possibly the inter-metallic compound in this alloy namely Mg_2Si becomes highly reactive towards chloride and hydroxyl ions and it appears that pit initiation is accelerated at pH12 by the formation of MgO and SiO_2 leading to intergranular corrosion as well.

Figure 4 shows the extent of weight loss per unit area during the immersion studies in 1% NaCl solution at different pH and the order is found to be pH12 >> pH2 > pH7 which also corroborates the observations of potentiodynamic polarization studies.

The scanning electron micrographs (Figure 5-10) of the corroded surfaces of the samples after polarization and immersion tests strongly support the above features. Localised pitting is found to occur on the surface of the materials under exposure in chloride media at almost all pH but to different extent. Figure 5, of the material polarised in 1% NaCl at pH2, reveals that pits and cracks have grown throughout the exposed surface. Solution containing 1% NaCl at neutral pH seems to be less aggressive to the material showing less number of pits as shown in Figure 6. However the material is found to be prone to corrosion at pH12 even in absence of chloride ions. When polarised in 0% NaCl at pH12 moderate corrosion attack is exhibited on the surface as shown in Figure 7. At higher levels of chloride (3%) the material clearly shows extensive corrosion attack, with elongation of pits and cracks accompanied by uplifting and flaking of surfaces as revealed in Figure 8. Figure 9 shows a pit which has been located on the surface of the material during immersion in 1% NaCl solution at pH7 at higher magnification (X450). At pH12 with same level of chloride, cracks appear on the surface and the surface is found to be covered with precipitates possibly of metal oxide in forms of large and tiny spheres as shown in Figure 10. Figure 11 represents the EDS analysis of the same sample indicative of the presence of Na, Al, Cl and Si on the surface.

CONCLUSION

Al 6061 alloy is found to be degradable under drastic conditions of pH and at higher levels of chloride ions. Throughout the range of acidic to alkaline pH the material is susceptible to pitting due to chloride attack to varied extent. Notable corrosion resistance of the material is exhibited at neutral pH.

REFERENCES

1. R. J. H. Wanhill, I. Sehra, W. G. J. Hant in L. Arnberg et al. (Eds.), Proceedings, The 3rd International Conference in Aluminium Alloys, Norway, 1992, p. 357.
2. C. H. William, in: R. J. Arsenault, R. K. Everett (Eds.), Metals Matrix Composites: Processing and Interfaces, Academic Press, New York, 1991.
3. F. Boey et al. Fiber reinforced MMC by a high deformation consolidation approach. Mater. Manufacture, Proceedings, Vol. 12 (2), 1997, p. 229.
4. C. T. Kuniohi in K.A. Khor, T.S. Srivatsan and J.J. Moore(Eds.) Processing and fabrication of Advanced Materials VI, The Institute of Materials, 1998, p. 1173.
5. J. Datta, P. S. Bannerjee, P.J. RoyChoudhury, in Corrosion its Mitigation and Preventive Maintenance, CORCON-2000, Proceedings 2000, pub NACE, India.
6. J. Datta, S. Datta, M.K. Bannerjee and S. Bandopadhyay, Proceedings of ACUN IV International Composites Conference - 2002, p 295.
7. J. Datta, S. Datta, M.K. Banerjee and S. Bandopadhyay, Proceedings of International Conference on "Advances in Materials and Materials Processing" ICAMMP-2002, IIT Kharagpur, India, p 162.
8. J.O'M. Bockris and A.K.N. Reddy, Modern Electrochemistry, Plenum Press, New York, 1998 Vol. 2B, chapter 12.
9. T. Das, S. Bandyopadhyay, S. Blairs, L. Materials Science 29 (1994) 5680.
10. T. Das, P. R. Munroe, S. Bandopadhyay, J. Materials Science 31 (1996) p 5351.
11. M.G. Fontana, Corrosion Engineering, McGraw-Hill Inc., Singapore, 1987 p 33-152.
12. K. sotoudeh, T.H. Nguyen, R.T.Foley and B.F. Brown, Corrosion 37(6) (1981) 358-362.
13. Szklarska- Smialowska - Z, Corr. Sci. 33 (1992) 1193.
14. T.D. Burleigh, E. Ludwiczak, R. A. Petri, Corrosion, 51 (1995) 50.

Table 1 : Electrochemical corrosion parameters in different NaCl solutions at various pH.

Corrosion Parameters	0%	0.05%	1%	3%
pH2				
$E_{corr}(mV)$	-734	-586	-650	-680
$I_{corr} (A/cm^2) \times 10^5$	4.41	11.60	13.00	24.00
Corr. Rate (mm/yr)	0.46	1.22	1.36	2.35
pH7				
$E_{corr}(mV)$	-623	-561	-632	-689
$I_{corr} (A/cm^2) \times 10^5$	0.33	1.05	1.53	2.15
Corr. Rate (mm/yr)	0.03	0.11	0.16	0.22
pH12				
$E_{corr}(mV)$	-1433	-1454	-1371	-1399
$I_{corr} (A/cm^2) \times 10^5$	2.05	2.33	2.77	3.20
Corr. Rate (mm/yr)	2.17	2.35	2.92	3.35

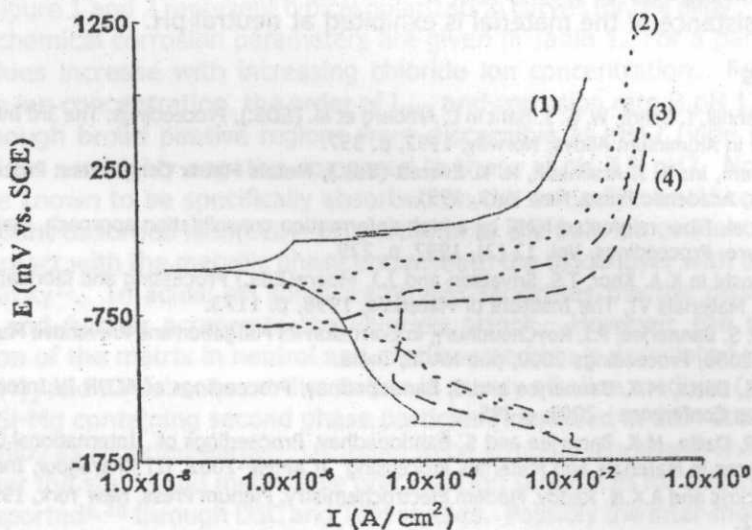


Fig. 1 : Potentiodynamic polarization curves at pH7 in different NaCl solutions. [(1) — 0% NaCl; (2);0.05% NaCl; -.-.-1% NaCl and (4) -----3% NaCl]

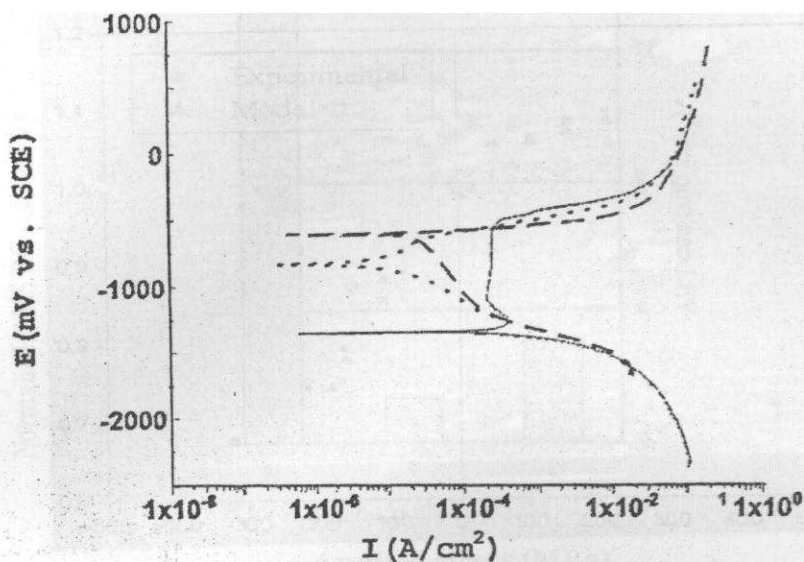


Fig. 2 : Potentiodynamic polarization curves at different pH in 1% NaCl solution. [.....pH7; -----pH2 and ———pH12]

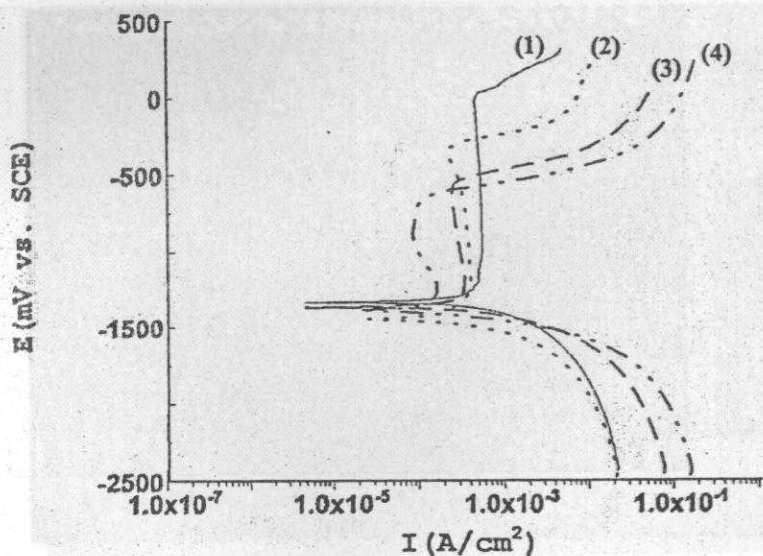


Fig. 3 : Potentiodynamic polarization curves at pH7 in different NaCl solutions. [(1) ———0% NaCl; (2);0.05% NaCl; -.-.-1% NaCl and (4) -----3% NaCl]

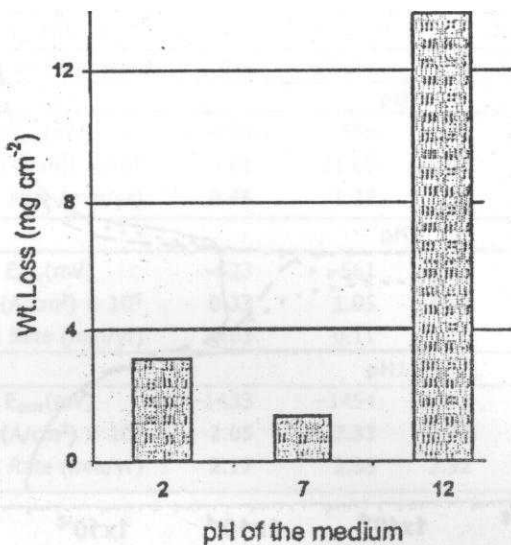


Fig. 4 : Plot of weight loss with pH of the medium

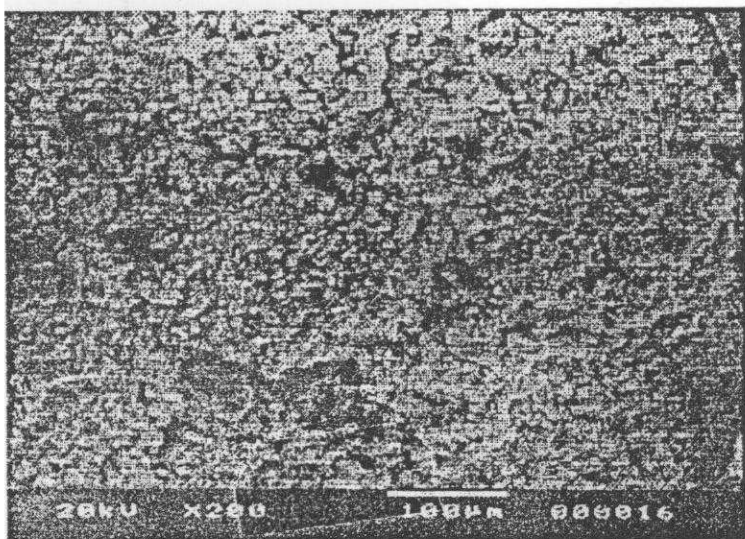


Fig. 5 : SEM of the sample polarized in 1% NaCl solution at pH2

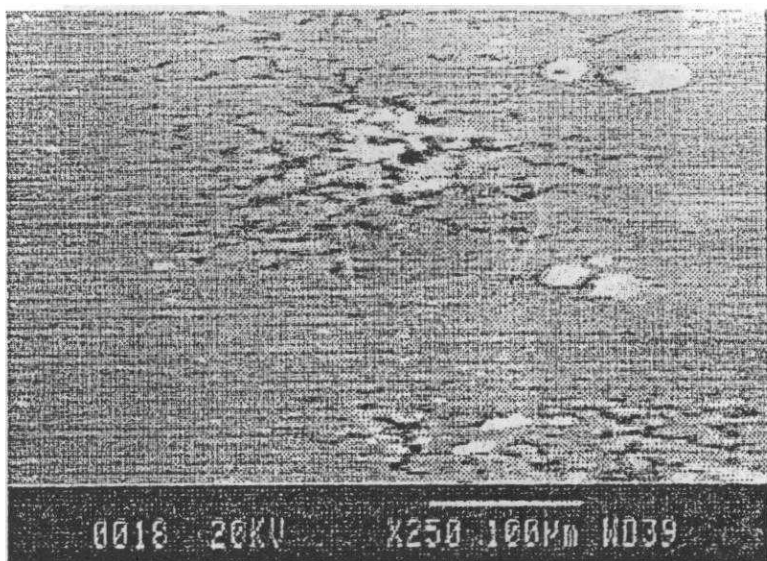


Fig. 6 : SEM of the sample polarized in 1% NaCl solution at pH7

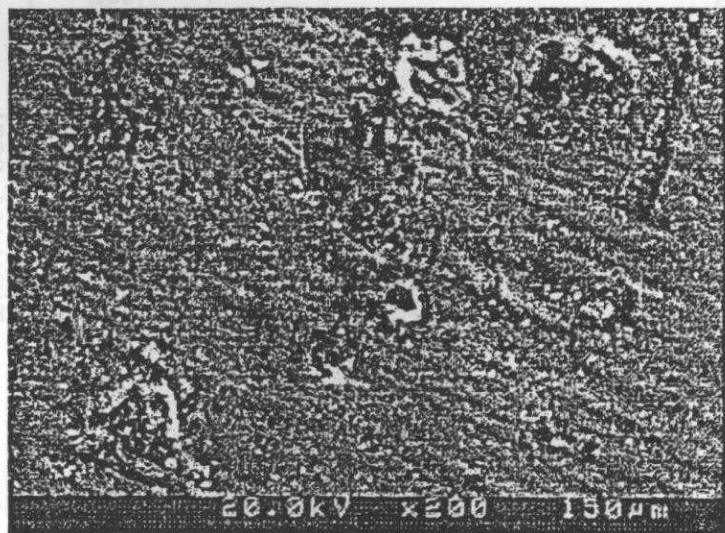


Fig. 7 : SEM of the sample polarized in 1% NaCl solution at pH12



Fig. 8 : SEM of the sample polarized in 3% NaCl solution at pH12



Fig. 9 : SEM of the sample immersed in 1% NaCl solution at pH7 for 48 hours

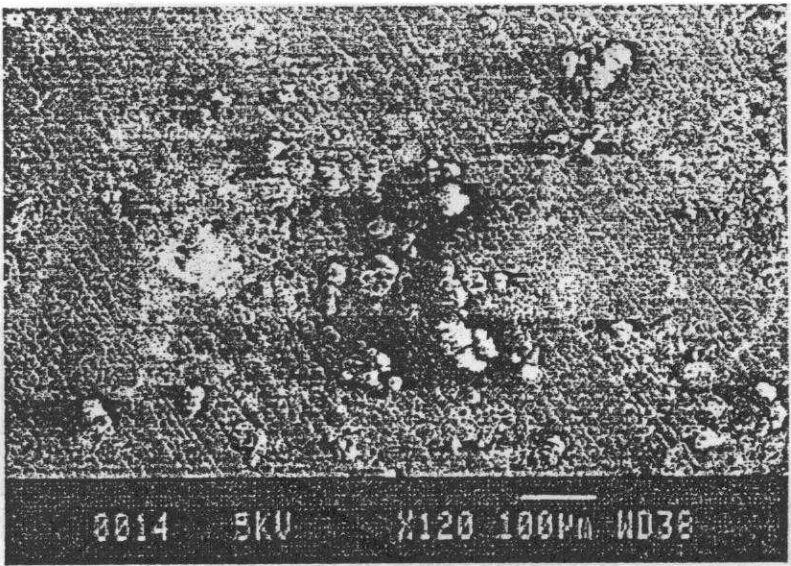


Fig. 10 : SEM of the sample immersed in 1% NaCl solution at pH12 for 48 hours

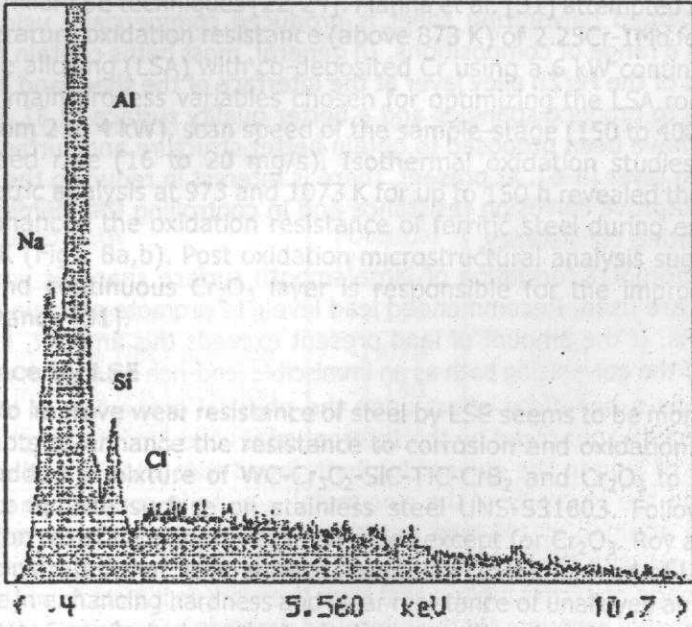


Fig. 11 : EDS of the sample immersed in pH12 at 1% NaCl solution for 48 hours.