

Corrosion Behaviour of Al₂O_{3p} Reinforced Al-Zn-Mg-Cu-Ni-Co Alloy Fabricated via PM

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Abstract: In this research, comparative study of corrosion resistance of PM Al-Zn-Mg-Cu-1%Ni-1%Co alloy (I) and PM Al-Zn-Mg-Cu-1%Ni-1%Co-5%Al₂O₃ alloy (II) produced using mechanical alloying process has been investigated. PM milled alloy (I) and alloy composite (II) specimens were sintered after compaction then homogenized, aged then retrogressed and reaged. PM Al-alloys were subjected to corrosive media (acidic: 1.0M HCl) and using weight loss method to evaluate their corrosion resistance. The findings of this study indicated that the PM Al₂O_{3p} reinforced Al-Zn-Mg-Cu-Ni-Co matrix composite exhibited superior corrosion resistance in comparison to the PM unreinforced of Al-alloy A samples in HCl solution after undergoing to the similar heat treatment conditions. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to show the corroded surfaces.

Keywords: Al-Zn-Mg-Cu-Ni PM alloy; Alumina additives; Milling alloying; Corrosion behaviour

1. Introduction

In aeronautical industries due to their attractive comprehensive properties, such as low density, high strength, ductility, toughness and resistance to fatigue, Al-Zn-Mg-Cu alloys have been widely used as structural materials [1, 2]. However, Al-Zn-Mg-Cu alloys are susceptible to local corrosion, such pitting, inter-granular corrosion (IGC), exfoliation corrosion (EXCO) and stress corrosion cracking (SCC) [3-5]. A major corrosion issue with Aluminum and its alloys is the localized breakdown of the passive film, which lead to the induction and growing of corrosion cavities in chloride containing environments. New heat treatments for Al-Zn-Mg-Cu systems can be improved resistance of corrosion with the optimum of mechanical properties [6, 7]. Recently, the interest of researchers for reducing the susceptibility of corrosion by controlling of grain sizes using manufacturing by means of severe plastic deformation such surface mechanical attrition and equal channel angular processing [8, 9] or by modification of chemical composition of Al-alloys using adding rare earth elements, Bobby et al [10] and Fang et al [11] found that the resistance to SCC or EXCO of the Al-Zn-Mg-Cu alloy can be substantially improved by conquering recrystallization through Sc or Cr, Yb and Zr additions, respectively.

Naeem et al [12] investigated that addition of nickel into Al-Zn-Mg-Cu produced by casting technique led to improve the corrosion resistance in Al-alloys containing 0.5% nickel after series of heat treatments. However, up to now, there is not research which had paid attention to investigate of additions of nickel affecting on corrosion behavior of Al-Zn-Mg-Cu alloys producing using powder metallurgy method. Therefore, research aims to study synergistic effects of Alumina particulates, the aging at T6 and the retrogression and reaging on resistance of Al-Zn-Mg-Cu-Ni-Co PM produced by mechanical milling alloying.

2. Experimental Procedures

Elemental powder precursors of Al, Zn, Mg, Cu, Cr, Fe, Ni, Co, Al₂O₃ were used as starting materials to produce two Al

based Alloys; **I** (Al-5.5%Zn-2.5%Mg-1.5%Cu-0.4%Fe-0.2%Cr-1%Ni-1%Co) and **II**(Al-5.5%Zn-2.5%Mg-1.5%Cu-0.4%Fe-0.2%Cr-1%Ni-1%Co-5%Al₂O_{3p}) compositions. All compositions are expressed in weight percentages (wt. %).

Table 1: Specification of materials

Powder	Description	Particle sizes (µm)	Purity (%)
Al	Flake	51	98.00
Zn	Rounded	18	96.00
Mg	Rounded	115	98.00
Cu	Irregular	39	99.50
Fe	Rounded	200	99.50
Cr	Irregular	160	99.50
Ni	Rounded	11	99.50
Co	Rounded	17	99.50
Al ₂ O ₃	Rounded	4	99.50

All Al-Zn-Mg-Cu-Cr-Fe-1%Ni-1%Co PM and Al-Zn-Mg-Cu-Cr-Fe-1%Ni-1%Co-5%Al₂O₃ PM Alloys were produced using the ball milling alloying process then compacted and sintered under a certain conditions as reported in our research [13]. After producing of the sintered alloy **I** and alloy composite **II**; PM Al-alloy specimens are homogenized then followed by quenching in cold water immediately after each step. Thereafter the ageing at T6 temper then the retrogression and re-aging (RRA) process were conducted on PM alloys according to [14-15]. To preparation of specimens for the corrosion tests, the specimen surfaces were ground with 1200 grit silicon carbide paper and then polished using 3µm diamond paste to obtain a good surface finish. The coupons were then washed in distilled water, followed by acetone, and then allowed to dry thoroughly.

The corrosion tests were static immersion tests conducted at room temperature using the conventional weight loss method to an accuracy of 0.1 mg. Each specimen was first weighed before being immersed in 250 ml open beakers containing 200 ml of 1 M HCl solution and later taken out after 24, 48 and 72 hours, respectively. HCl acid solution was chosen as the corrodent for accelerated consequences. After each corrosion test, the specimen was immersed in Nitric acid for 1 min and gently cleaned with a soft brush to remove

adhered scales. After drying thoroughly, the specimens were weighed again. The weight loss was measured and converted into corrosion rate expressed in millimeters per year (mm/y) as according to Eq. 1., [12].

$$\text{Corrosion rate (C.R)} = \frac{K \times W}{A \times T \times D} \quad (1)$$

Where,

$W = \text{weight loss in mg} = W_0 - W_f$

$W_0 = \text{original weight of the sample,}$

$W_f = \text{final weight of the sample after immersion}$

$D = \text{Density of the sample in } \frac{g}{cm^3}$

$A = \text{Total surface area of sample in } cm^2$

$T = \text{exposure time in hours}$

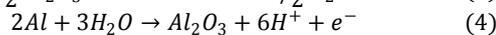
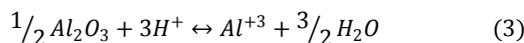
The corroded surfaces were analyzed using scanning electron microscopy (SEM) coupled with the energy dispersive X-ray spectroscopy (EDS) was used.

3. Results and Discussions

Generally, Aluminum has reacted with Oxygen within the protective layer of Al as assumed:

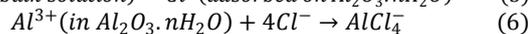
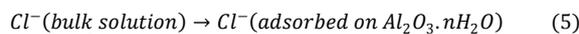


From the solution, the oxide formed and acted as a static barrier that isolated the metal. However, acid solutions may bear upon its properties. On the characteristics of the medium, disintegration of the protective layer or repassivation of the metal may be come according to [16].



The reformation of oxide layer under the conditions used in this study, which did not appear to come due to an increased dissolution of Aluminum, is observed in all cases.

Aluminum dissolution in chloride solutions has been largely investigated and its chemical mechanism almost clearly understood. It is agreed that several staircase are involved in the chemical mechanism of Al dissolution including of the adsorption of chloride ions at the oxide surface, penetration of the oxide film by chloride ions, dissolution which come about beneath the oxide film at the metallic element oxide at the metal/oxide interface and Cl⁻aided. This can be represented as following [17]:



This process lead to the oxide film thinning [18] thus the corroded of metal was started.

Table 2 shows the results of corrosion rates for the PM alloy I included: as sintered **I-milled**, as well as the aged in T6#**I-milled** and RRA#**I-milled** samples in 1 M HCl solution for interval time included 24 h, 48 h and 72 h.

Table 2: Corrosion rate of **PM alloy I** samples for different procedures in HCL solution

Alloys	Types of procedures	Corrosion rate * 10E-01(mm/y)		
		After 24h exposure	After 48h exposure	After 72h exposure
PM Milled I	As sintered I-milled	35.00	25.453	23.374
	T6# I-milled	24.126	20.147	18.132
	RRA# I-milled	21.105	17.326	16.205

It can be observed that the decrease in corrosion rates of the RRA#**I-milled** and the T6#**I-milled** 40% and 31%, during 24 hours, respectively, as compared to the as sintered **I-milled**.

These enhancements of corrosion resistance of samples of alloy **I** underwent the aging at T6 and RRA attributed to the having of precipitations phases as well as intermetallic Ni/Co-rich compounds that contributed to increasing mechanical strength of Al-Zn-Mg-Cu matrix thus to improve corrosion resistance as have stated by [7, 13,15, 19].

Table 3 presents the findings of corrosion rates for alloy composite as sintered **II-milled**, the T6#**II-milled** and RRA#**II-milled** samples in 1 M HCl solution for interval time included 24 h, 48 h and 72 h.

Table 3: Corrosion rates of **alloy composite II** samples for different procedures in HCL solution.

Alloys	Types of procedures	Corrosion rate* 10E-01 (mm/y)		
		After 24h exposure	After 48h exposure	After 72h exposure
PM composite Milled II	As sintered II-milled	27.456	19.486	16.832
	T6# II-milled	19.358	13.012	10.468
	RRA# II-milled	18.764	12.143	10.012

It can be observed that the increased corrosion resistance of RRA#**I-milled** and T6#**I-milled** 33% and 28%, during 24 hours, respectively, as compared to the as sintered **II-milled**.

Clearly, it can be seen from corrosion rates values in Table 2 and 3 for both of PM unreinforced (alloy I) and PM reinforced by Al₂O₃ particulates underwent different heat treatments, that samples of PM alloy II composite have higher corrosion resistance than PM alloy I.

Enhancement of corrosion resistance of PM alloy II composite attributed to Al₂O₃ particles besides hard intermetallic compounds with precipitates of MgZn thus led to superior corrosion behaviour.

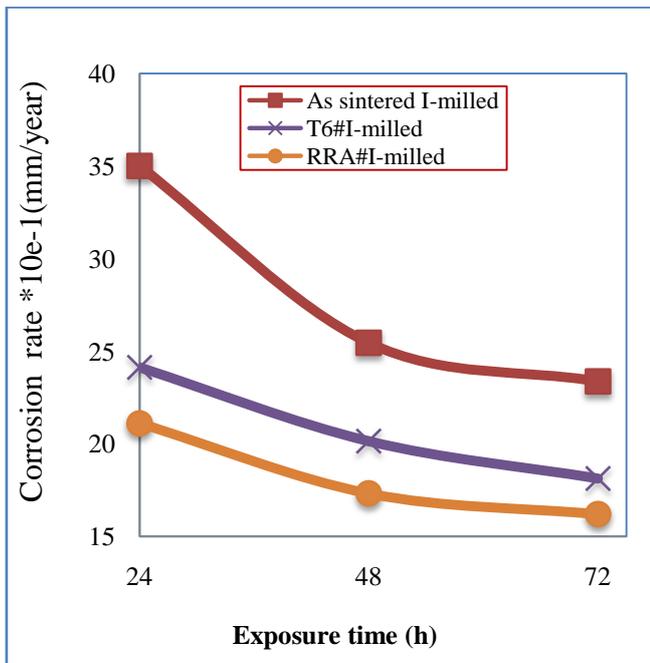


Figure 1: Graphs of corrosion rates of PM alloy I for several of heat treatments and extrusion process vs. exposure time in 1 M HCl solution.

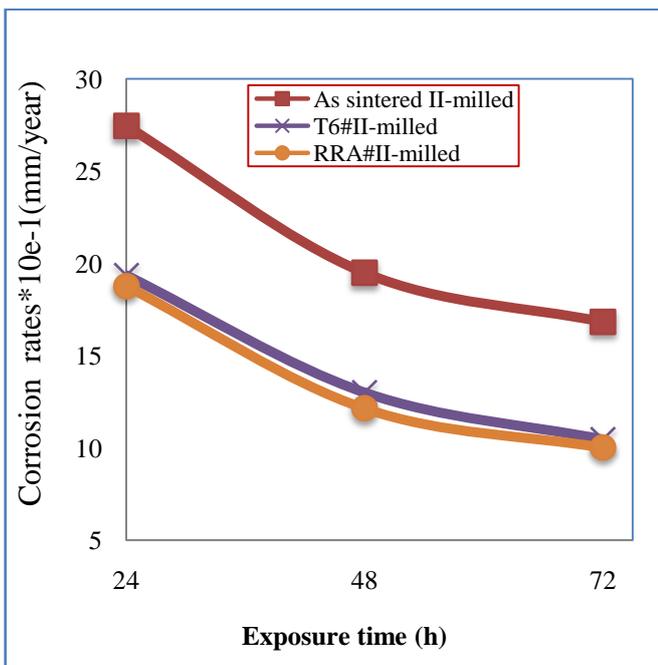


Figure 2: Graphs of corrosion rates of alloy composite II underwent different treatments vs. exposure time in 1 M HCl solution.

Mohammed et al [21] found that PM Al-Zn-Mg-Cu-1Ni produced milling alloying have superior corrosion resistance undergoing heat treatments. Alaneme et al [22] stated that additions of Al₂O₃ in Al6063 composite exhibited excellent corrosion resistance in NaCl media.

Moreover, it can be seen that in each case as in Figures 1 and 2, there is a decrease in corrosion rate with increase in duration of exposure to the corrodent, implying that the corrosion resistance of the materials tested increases as the exposure time is increased.

Visible inspection showed that there were no hydrogen bubbles clinging onto the surface of the test specimens. The phenomenon of monotonically decreasing corrosion rate with respect to time indicates some passivation of the matrix alloy. Garcia et al [23] observed in the suit of localized corrosion in HCl solution, the surfaces of aluminum alloys are passive and back up a relatively thick alumina film that does not allow hydrogen to evolve.

Ma et al [24] believe that the black film formed on the surface consists of an Al hydrated oxide compound which protects the bulk stuff from further corrosion in the acid medium.

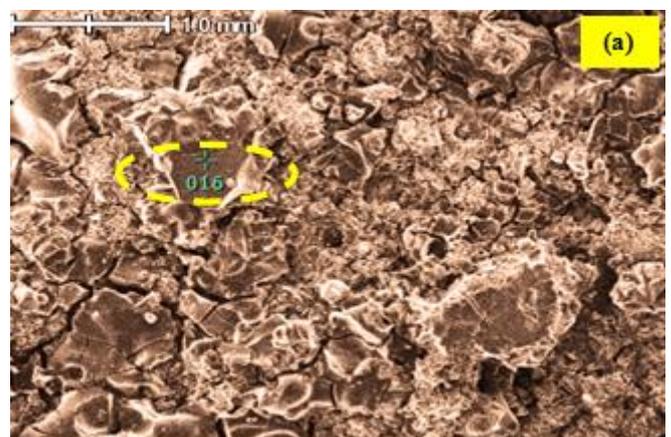
The SEM micrograph of debris of PM Al-alloy I sample after T6 as shown in Figure 3a reveals corroded surface of aluminum matrix. The α -Al with existent major alloying elements of Zn, Mg, Cu and Nickel which are evident as presented in Figure 3b. Further, the presence high percentage of chloride ions due to reactions taken place in the base alloy during the immersed in acidic medium as mentioned former (Eq. 5 and 6). The SEM image for the debris of PM Al-alloy composite II underwent corrosion testing of in Figure 4a. Figure 4b reveals the EDS spectrum the having of nickel and cobalt remain as well as Al₂O₃ is high peaked as.

4. Conclusions

The results for this study reveals that corrosion rate is decreased of PM milled Al-alloy I samples after applying the aging; retrogression and reaging. On the other hand, regard to PM milled alloys underwent to the aging at T6 and RRA possesses corrosion resistance higher than as sintered samples, due to the precipitation phases of alloying elements are occurred. Furthermore, Corrosion resistance of PM milled Al-alloy II composite is enhanced more than alloy I due to the additions of Al₂O₃ particulates with having of dispersion intermetallics as well the precipitations particles.

5. Acknowledgements

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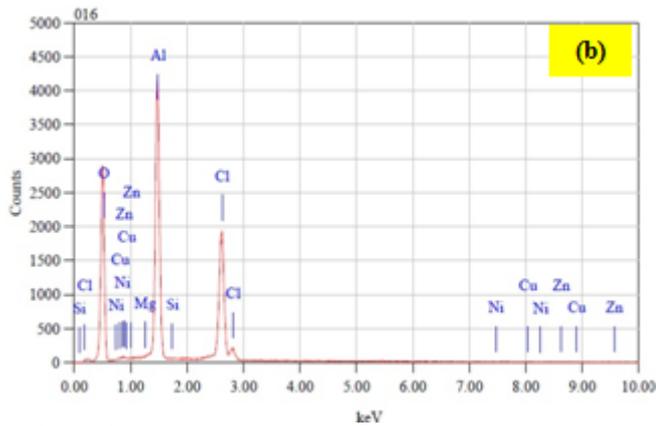


Figure 3: a) SEM micrograph of corroded surface of PM milled Al-alloy I in 1 M HCl solution after 72 hours; and b) Corresponding EDS analysis of debris of the attacked surface and chemical composition of corroded surface.

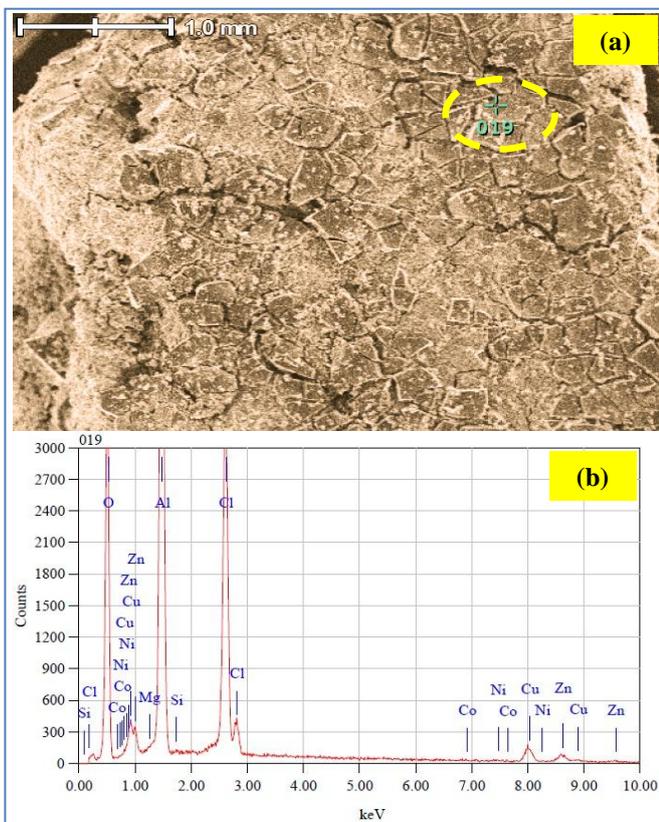


Figure 4: a) SEM micrograph of corroded surface of alloy II, in 1 M HCl solution after 72 hours; and b) EDS analysis.

References

- [1] [1] A. Heinz, A. Haszler, C. Keidel, S. Moldenhauer, R. Benedictus, and W. Miller, "Recent development in aluminium alloys for aerospace applications," *Materials Science and Engineering: A*, vol. 280, pp. 102-107, 2000.
- [2] [2] J. C. Williams and E. A. Starke Jr, "Progress in structural materials for aerospace systems," *Acta Materialia*, vol. 51, pp. 5775-5799, 2003.
- [3] [3] F. Wall and G. Stoner, "The evaluation of the critical electrochemical potentials influencing environmentally assisted cracking of Al-Li-Cu alloys in selected environments," *Corrosion science*, vol. 39, pp. 835-853, 1997.
- [4] [4] A. Conde, B. Fernandez, and J. De Damborenea, "Characterization of the SCC behaviour of 8090 Al-Li alloy by means of the slow-strain-rate technique," *Corrosion science*, vol. 40, pp. 91-102, 1998.
- [5] [5] D. Najjar, T. Magnin, and T. Warner, "Influence of critical surface defects and localized competition between anodic dissolution and hydrogen effects during stress corrosion cracking of a 7050 aluminium alloy," *Materials Science and Engineering: A*, vol. 238, pp. 293-302, 1997.
- [6] [6] F. Andreatta, H. Terryn, and J. De Wit, "Corrosion behaviour of different tempers of AA7075 aluminium alloy," *Electrochimica Acta*, vol. 49, pp. 2851-2862, 2004.
- [7] [7] L. Huang, K. Chen, S. Li, and M. Song, "Influence of high-temperature pre-precipitation on local corrosion behaviors of Al-Zn-Mg alloy," *Scripta Materialia*, vol. 56, pp. 305-308, 2007.
- [8] [8] J. Brunner, J. May, H. Höppel, M. Göken, and S. Virtanen, "Localized corrosion of ultrafine-grained Al-Mg model alloys," *Electrochimica Acta*, vol. 55, pp. 1966-1970, 2010.
- [9] [9] M.-K. Chung, Y.-S. Choi, J.-G. Kim, Y.-M. Kim, and J.-C. Lee, "Effect of the number of ECAP pass time on the electrochemical properties of 1050 Al alloys," *Materials Science and Engineering: A*, vol. 366, pp. 282-291, 2004.
- [10] [10] M. Bobby Kannan and V. Raja, "Enhancing stress corrosion cracking resistance in Al-Zn-Mg-Cu-Zr alloy through inhibiting recrystallization," *Engineering Fracture Mechanics*, vol. 77, pp. 249-256, 2010.
- [11] [11] H. Fang, K. Chen, X. Chen, H. Chao, and G. Peng, "Effect of Cr, Yb and Zr additions on localized corrosion of Al-Zn-Mg-Cu alloy," *Corrosion Science*, vol. 51, pp. 2872-2877, 2009.
- [12] [12] H. T. Naeem, K. S. Mohammed, R. Khairrel, and A. Rahmat, "EFFECTIVENESS OF ALUMINA DISPERSOIDS PARTICLES WITHIN (7XXX SERIES) ALUMINUM ALLOY UNDER THE RETROGRESSION AND REAGING TREATMENTS", *Digest Journal of Nanomaterials and Biostructures* Vol. 9, No. 1, January - March 2014, p. 295 - 304
- [13] [13] H. T. Naeem, K. S. Mohammed, R. Khairrel, and A. Rahmat, "Characteristics of Al-Zn-Mg-Cu Alloys with Nickel Additives Synthesized via Mechanical Alloying, Cold Compaction, and Heat Treatment", *Arabian Journal for Science and Engineering*, Vol. 39, No. 11, 07 November 2014, p. 295 - 304
- [14] [14] H. T. Naeem, K. S. Mohammed, R. Khairrel, and A. Rahmat, "The role of direct chilling, retrogression and reaging treatment on mechanical properties of high strength aluminum alloy," *Advanced Materials Research*, vol. 795, pp. 211-218, 2013.
- [15] [15] Haider T. Naeem, Kahtan S. Mohammed, Khairrel R. Ahmad, Azmi Rahmat, "A comparative study an aditives of nickel, cobalt, tin affecting the microstructures and mechanical properties of Al-Zn-Mg-Cu alloys," *Pensee Journal*, vol. Vol 76, Mar 2014.
- [16] [16] A. Santos, L. Vojkuvka, J. Pallarés, J. Ferré-Borrull, and L. Marsal, "In situ electrochemical dissolution of the oxide barrier layer of porous anodic alumina fabricated by hard anodization," *Journal of*

- Electroanalytical Chemistry, vol. 632, pp. 139-142, 2009.
- [17][17] F. M. Al-Kharafi and W. A. Badawy, "Corrosion and passivation of Al and Al-Si alloys in nitric acid solutions II—Effect of chloride ions," *Electrochimica acta*, vol. 40, pp. 1811-1817, 1995.
- [18][18] R. Foley, "Localized corrosion of aluminum alloys—a review," *Corrosion*, vol. 42, pp. 277-288, 1986.
- [19][19] Y.-P. Xiao, Q.-L. Pan, W.-B. Li, X.-Y. Liu, and Y.-B. He, "Influence of retrogression and re-aging treatment on corrosion behaviour of an Al–Zn–Mg–Cu alloy," *Materials & Design*, vol. 32, pp. 2149-2156, 2011.
- [20][20] X. Fan, D. Jiang, L. Zhong, T. Wang, and S. Ren, "Influence of microstructure on the crack propagation and corrosion resistance of Al–Zn–Mg–Cu alloy 7150," *Materials characterization*, vol. 58, pp. 24-28, 2007.
- [21][21] Kahtan S. Mohammed, Haider T. Naeem, raid T. Hadi, Effect of Nickel on Corrosion resistance of Al-Zn-Mg-Cu PM alloy Produced by Mechanical alloying, *IJSR*, Vol.3, Dec.2014.
- [22][22] K.K. Alaneme, M.O.Bodunrin, Corrosion Behaviour of Alumina Reinforced Aluminum 6063 Metal Matrix Composites, *Journal of Minerals & Materials Characterization & Engineering*, Vol. 10, No.12, pp.1153-1165, 2011
- [23][23] F. Garcia-Garcia, P. Skeldon, G. Thompson, and G. Smith, "The effect of nickel on alloy microstructure and electrochemical behaviour of AA1050 aluminium alloy in acid and alkaline solutions," *Electrochimica Acta*, vol. 75, pp. 229-238, 2012.
- [24][24] J. Ma, J. Wen, Q. Li, and Q. Zhang, "Effects of acidity and alkalinity on corrosion behaviour of Al–Zn–Mg based anode alloy," *Journal of Power Sources*, vol. 226, pp. 156-161, 2013.