Investigating Corrosion Behaviour of Aluminium and Aluminium–Copper Alloy in H_2SO_4 as Anodizing Solution

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Abstract

The present research work investigated the corrosion behaviour of casted pure aluminium metal and aluminium–copper alloy after running weight loss tests in different concentration ratios of H_2SO_4 media at RT and 50 °C, respectively. Corrosion penetration rate was determined within interval immersion periods of 5 hours. At RT, it was observed that pure aluminium samples have low corrosion resistance in concentrations 10% and 15% of H_2SO_4 solutions. Moreover, corrosion rate increases slightly with increasing concentration of H_2SO_4 media and the attack was more significant at 50 °C. Al–Cu alloy show decreasing of weight loss and more corrosion resistance in both ratios. The corrosion penetration rate of Al samples increases in the order Al–Cu < Al as a result of the formation of thin protective aluminium–copper oxide films. The visual observations shown that there is a streaking and grooves of both samples correlated directly with the increased exposure period in the acidic medium but in case of Al–Cu alloy there are a several horizontal fine darkened pits grew along the surface.

Keywords: Corrosion Penetration; Aluminium; Aluminium Alloys

Introduction

The increased attention for studying the performance and corrosion forms of aluminum metal and its alloys is due to their excellent characteristics such as low weight "its density one-third that of steel", nontoxicity, high reflectivity, high conductivity, availability and widespread usage. In particular, aluminium alloys play a role in automobiles, aviation, household appliances, containers and electronic devices [1-5].

In usual, Al used as a part of an alloy rather than as a pure metal because pure aluminium metal isn't strong enough for large scale. High strength Al alloys can be obtained by addition of appropriate alloying elements, such as Cu, Mg, Si and Zn. Generally, the alloying elements and other raw materials can influence the morphology and corrosion resistance of aluminum by forming different oxides that have compatible structures [6,7]. Many Al alloys such as Al-Si alloys have been increasingly employed in the automotive industry, owing to their good cast, low thermal expansion coefficient and excellent mechanical properties [8,9]. Aluminum die casting alloys are also lightweight, offer good corrosion resistance, ease of casting, good mechanical properties and dimensional stability. The various applications of aluminum metals and alloys are often possible because of the natural tendency of aluminium to form surface oxide film which can be deteriorated in aggressive media. The protection of aluminum and its oxide films against the corrosive action of chloride ions have been extensively discussed [10-14].

The corrosion property of pure Al metal and its alloys like Al-Cu and Al-Si alloys was investigated in aqueous solutions in the absence and presence of common salts [15]. Many researchers and detailed publications studied for several decades the pitting corrosion of aluminum alloys [16-17]. Owing to the corrosion is fundamental process which plays an important role in economics and safety. Apparently, corrosion cannot be avoided, but its severity can be reduced to a lower magnitude.

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A large variety of researches and test methods were employed to study in details the corrosion resistance of aluminium and its alloys using different aqueous media of acids and salts [18-25]. Different acidic media has been used for pickling, chemical and electrochemical etching of Al and its alloys. As well, different grades of corrosion inhibitors are used to inhibit its corrosion in the acid media [26-30].

The present research was investigated the corrosion of pure Al metal and Al-Cu alloy in 10% and 15% of H_2SO_4 environments. The influence of alloying elements in corrosion behavior of aluminium was studied under specific conditions.

Experimental Procedures
Materials

Aluminium metals and alloys used for this research work were produced locally via casting methods in ultrapure quality by Bahrain Alloys Manufacturing Company (BAMCO), Bahrain, as shown in Figure 1. Aluminium metals and alloys were produced locally via casting methods. The percentage of alloying of copper (15%) is added to achieve final aluminium alloys specification. The typical chemical composition (in wt. %) of pure aluminium metal is ($\approx$ 99.9%) and aluminium-copper alloy is (85% : 15%), respectively.

Methods

Preparation of Specimen (surface)

In this laboratory scale study, the aluminium metals and alloys were machined and cut into test specimens (50 x10 x 5 mm coupons). The samples surfaces were treated by abrading them through successive grades of finer emery papers. They were rinsed in distilled water and then in acetone before drying. The prepared samples were stored in desiccators until the start of the experiment.

Preparation of Immersion Media

The environments prepared for the evaluation of its corrosion behaviour were H_2SO_4 and Na_2CO_3 media solutions. The environment ranges from a percent of 10% and 15% H_2SO_4 which were prepared following standard procedures.

Corrosion Penetration Evaluation

Aluminium samples were immersed in the prepared environments for time intervals 1 to 5 hours and different temperatures. The samples were removed from the corrosion environment with the aid of tong, cleaned in distilled water and dried with cotton wool and dried. The dried samples were weighed with digital chemical weighing balance and recorded at different immersion periods for weight loss analysis. Corrosion penetration (CP) values were calculated in cm were obtained from weight loss analysis using the Equation (2) [31].

$$Corrosion\ Penetration\ (CP) = \frac{W}{A \cdot D}\quad (cm)\qquad (2)$$

Where W is the weight loss in g;

  D is the density of the specimen in g/cm^3;

  A is the total exposed surface area of the specimen in cm^2;

Corrosion Reaction Kinetics

From the corrosion penetration results obtained for all aluminium samples, the corrosion reaction kinetics also determined in media of 10% and 15% H_2SO_4, respectively, using the parabolic rate law, as shown in Equation (3), even with increasing the temperature to 50 °C.

$$X = K\ t^{1/2}\qquad (3)$$

Where X is the measure of corrosion extent in cm (i.e. CP);

  t is the immersion time of the specimen in hr;

  K is the parabolic rate constant in $cm/h^{1/2}$.

Visual Morphology

The pure Al and Al–Cu alloy surfaces were tested using an imaging digital scanner (HP Deskjet 1050 J410 series) which displayed a real-time image.
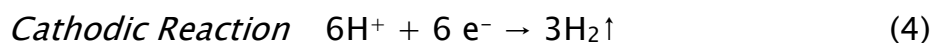
RESULTS AND DISCUSSION

Weight Loss Measurements

As a first step of this work, the weight loss was employed against exposure time of pure Al and Al–Cu (%85–%15) alloy samples immersed in 10% and 15% H_2SO_4 media, respectively, as shown in Table 1. Results were observed from Figure 2a show that the weight losses of all pure Al samples increase by increasing immersion time, concentration even at elevated temperature (Figure 2b) in all media. Clear observations can be noted between both media. In general, pure Al was found to have high weight loss values in 15% H_2SO_4 media compared to other two media. Moreover, the weight loss values exhibited a characteristic decreasing in 10% H_2SO_4 environment under the same conditions. As a comparison study, Figure 3a shown that the weight loss values of Al–Cu alloys slightly increased by increasing immersion time and media concentration but less than pure Al samples in all media. At 50 ℃ there is a clear excess of weight loss values with the same trend as shown in Figure 3b. This corrosion resistance may attribute to the oxidative surface of Al–Cu alloy rather than in case of pure Al metal.

These changes were found to be as a result of the alloying elements which can influence the corrosion resistance of aluminum metals and its alloys by forming protective aluminium oxide layers. In a wet environment, different aluminium–copper oxides can be obtained when an aluminium alloy is placed in corrosive medium rather than aluminium [6,7].

Corrosion Penetration Evaluations

The obtained results of static corrosion tests for Al and Al–Cu samples in the base solutions (10% and 15% H_2SO_4) are shown in Figs. 4 and 5 as a plot of the corrosion penetration vs. the square root of time. The corrosion penetration (CP) is calculated using Eq. 2 [31]. As observed from Table 2, the CP is low in the first hour of immersion and it is increased with increasing the time. As well, the corrosion penetration is accelerated with increasing temperature. Fig. 4a shows that, the straight line drawn indicates that the corrosion reaction kinetics in 10% and 15% H_2SO_4 follows the parabolic rate law, as in Eq. 3, even with increasing the temperature to 50 °C as in Fig. 4b. The parabolic rate constant (*k*) values were increased with increasing temperature. This observation might be attributed to a rapidly formed surface oxide film at lower temperature, but at high temperature this oxide film will be unstable [32]. As stated the dissolution rate of aluminum is increased in presence of H_2SO_4, especially, with increasing its concentration as enhancing factor. Therefore, temperature could be another factor to enhance the Al–alloy dissolution. The deleterious effects of acid with increasing temperature could be attributed to activating the cathodic reaction (proton reduction as in Eq. 4), which has faster kinetics than oxygen reduction [33], and enhancing the Al–dissolution (anodic reaction as in Eq. 5). As well, acidic medium could activate the originally passive alloy surface as in the case of iron surface [34].

$$\textit{Cathodic Reaction} \quad 6H^+ + 6\ e^- \rightarrow 3H_2\uparrow \qquad\qquad (4)$$

$$\textit{Anodic Reaction} \quad 2Al \rightarrow 2Al^{3+} + 6\ e^- \qquad\qquad (5)$$

As shown in Fig. 5a, the increasing of Cu concentration leads a significant decrease in the corrosion penetration (CP), at room temperature. The maximum decrease of CP was obtained in presence 15% Cu at room

temperature. Of a particular interest to notice that in the first hour of immersion the CP is reduced by 25 % (in case of Al–Cu alloy), but after five hours of immersion, the CP was reduced by 40 % comparing to the CP in case of pure Al at such time. The reaction kinetics still follows a parabolic law (Eq. 2). Moreover, As shown in Fig. 4a, CP of pure Al increases with increasing the acidic percentage. The decreasing of the CP was obtained of using 10% H_2SO_4 and the corrosion was dramatically decreased. As proposed the Cu element has a good resistance effect, especially at high ratio. In the case of decreasing the CP, Cu element may play a role in increasing oxide film passivation on metal surface, as mentioned, to form a protective conversion coating and a more resistant oxide film on the surface may be achieved [35–38]. This film is unstable if the immersion is extended to 5 hours. This observation could be rationalized on the basis that the presence of ions (SO_4^{-2}) could increase the aluminum dissolution (Eq. 5).

In case of H_2SO_4, the increasing of its concentration will lead to increase the sulfate ions in solution, which help in accelerating the CP as seen when the concentration is increased to 15%. CP is accelerated with increasing temperature to 50 °C as shown in Fig. 5b. This behavior could be explained on the basis that the increasing of temperature could de-stabilize the Al–oxide interaction and activate the corrosion reactions (Eqs. 4 and 5) [33,34]. This de-stabilization arises because of the SO_4^{-2} penetration into the oxide lattice, followed by substitution for O^{2-}. Supplying heat, which is essential to complete this reaction, could enhance this substitution. It is stated that Al has a greater chemical reactivity at moderate temperatures and it combines with most of non-metallic elements [39]. The variation of the CP of Al and Al–Cu in presence of the tested media, especially after immersing intervals for 5 hours is important to be noticed. As presented in Table (2), the CP increases as the following order: 15% H_2SO_4 > 10% H_2SO_4 at RT and 50 °C.

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Visual Morphology

This part employs a visual investigations to study changes taking place on surfaces and describes changes that happened. The surface morphology of pure aluminum metals and aluminium alloys in aggressive media has attracted considerable attentions due to its importance in corrosion [40–43]. Cu containing aluminum alloys also show a surface morphology in sulfuric acid solutions but for these alloys the surface sensitivity results from pitting process. In general, the surface attack takes place preferentially along grooves producing streaks. Both sets of the alloys show a significant changes. The rate of attack growth is dependent mainly on the chemical composition of the material, the microstructure of the material, temperature, duration of attack, local solution conditions, and the state of stress [44]. Furthermore, pitting corrosion in conjunction with externally applied mechanical stresses, for example, cyclic stresses, has been shown to severely affect the integrity of the oxide film as well as the fatigue life of a metal alloy [45,46].

Figure (6) show the visual investigations of pure Al surfaces. It clearly seen the attack forms on the surface of pure Al substrates exposure to 15% H_2SO_4 solutions for 5 hours. The abrasion marks on the surface are 45° and the streaking corrosion of the surface appeared. The changes during the exposure were difficult to define both in real time and on reviewing recorded images. However, the different images shows that many streaks, seen as thin lines that had grown in the 5 hours period predominantly along a single abrasion groove. Fig. 6b is a magnified area of Fig. 6a. The arrow points to the site where some streaks initiated and grew in both directions and others terminated. In addition, unlike pitting corrosion for Al–Cu alloy samples which ran within an individual grooves, the attack was predominantly in bands incorporating many adjacent abrasion grooves. The pitting showed a propagating trend on the exposed area with some penetrations as shown in the magnified area (Fig. 7b). A different sample images (Fig. 7a), show this surface attack during a 5 hours exposure period.

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Conclusions

This study presets the investigating corrosion behaviour of pure Al and Al–Cu alloy samples in H_2SO_4 media at RT and 50 °C. The weight loss and corrosion penetration values of pure Al was increased with increasing H_2SO_4 concentration more than in case of Al–Cu. This observation might be attributed to difference in Al–Cu surface oxide layes. The corrosion reaction of Al and Al–Cu in the tested solutions follows the parabolic rate law. The visual morphology of both samples affected in presence of the tested solution. The attack of the surface is increased in presence of the concentrations, which accelerate the corrosion penetration, but the concentrations, which decrease the corrosion penetration reduces the surface attack. The streaking and grooves of both samples correlated directly with the increased attack period in the acidic medium in which Al–Cu alloys surface shown a clear horizontal darkened pitts.

Acknowledgements

References

[1] C. Vargel, Corrosion of Aluminium., Oxford, Elsevier, (2004) Pp.13–15.

[2] M. Abdulwahab, I.A. Madugu, S. A. Yaro, A. P. I. Popoola, (2012) *Silicon*, **4,** 2, Pp.137.

[3] O. O. Ajayi, O. A. Omotosho, K. O. Ajanaku and B. O. Olawore, (2011) *Env. Res. J.*, **5**, 4, Pp.163.

[4] R. Rosliza, W. B. W. Nik, (2010), *Current Applied Physics,* 10, Pp. 221.

[5] B. Davó, J.J. Damborenea., (2004), *Electrochim. Acta.,* 49, Pp. 4957.

[6] H. Cordier, Ch. Dumont, W. Gruhl., (1979), *Aluminum*, 55, Pp. 777.

[7] D. Talbot, J. Talbot., (2007), *Corrosion Science and Technology: Taylor & Francis Gp*.

[8] L. Kyuhong, N.K. Yong., (2008), *J. Alloys Compd*. 461, Pp.532.

[9] L. Lasa, J.M. Rodriguez-lbabe., (2002), *Scripta Mater.*, 46, Pp.477.

[10]   L. Vrsalovic, M. Kliskic and S. Gudic, (2009), *Int. J. Electrochem. Sci.,* 4, Pp.1568.

[11]   M.A. Amin, H. H. Hassan, O. A. Hazzazi, M. M. Qhatani, (2008), *J Appl Electrochem.*, 38, Pp.1589.

[12]   W.A. Badawy, F.M. Al-Kharafi, A.S. El-Azab. (1999), *Corros. Sci.*, 41, Pp.709.

[13]   Z. Grubac, R. Babic, M. Metikoš-Hukovic. (2002), *J. Appl. Electrochem.*, 32, Pp.431.

[14]   G.Y. Elewady, I.A. El-Said and A.S. Fouda. (2008), *Int. J. Electrochem. Sci.*, **3**, 177, Pp.644.

[15]   S. S. Abdel Rehim, H.H. Hassan, M.A. Amin, (2002), *J. Appl. Surf. Sci.,* 187, Pp.279.

[16]   J.-D. Kim, S.-I. Pyun., (1995), *Electrochim. Acta.*, 40, Pp.1863.

[17]   F.M. Al-Kharafi, W.A. Badawy., (1998), *Corrosion.*, 54, Pp.377.

[18]   S. A. Umoren, I. B. Obot, E. E. Ebenso, P. C. Okafor, O. Ogbode, E. E. Oguzie, (2006), *Anti-Corrosion Methods and Materials,* 53, Pp.277.

[19]   J. Halambek, K. Berkovic, J. Vorkapic-Furac, (2010), *Corrosion Science,* 52 , Pp.3978.

[20]   D. B. Hmamou, R. Salghi, A. Zarrouk, B. Hammouti, S. S. Al-Deyab, Lh. Bazzi, H. Zarrok, A. Chakir, L. Bammou, (2012), *Int. J. Electrochem. Sci.*, 7, Pp.2361.

[21]   A. P. I. Popoola, O. S. I. Fayomi, M. Abdulwahab*,* (2012), *Int. J. Electrochem. Sci.,* 7, Pp.5817.

[22]   A. A. Ghoneim , M. A. Ameer and A.M. Fekry, (2012), *Int. J. Electrochem. Sci.,* 7, Pp.10851.

[23]   B. J. Babalola, M. O. Bodunrin, J. O. Borode and K. K. Alaneme, (2013), *J. Miner. Mater. Characteriz. Eng.,* 1, Pp.245.

[24]   W. B. Wan Nik, O. Sulaiman, A. Fadhli and R. Rosliza, (2010), *Proceedings of MARTEC, Int. Conf. Marine Techno.,* Pp.175.

[25]   J.R. Davis, (1999), „*Corrosion of Aluminum and Aluminum Alloys",* ASM International.

[26]   L. Wing, G. L. Evarts and D. M. Tramontana, (1992), *J. Mat. Eng,*Pp. 26.

[27]   R. J. Lash, (1993), *Proc. of the 6th Automotive Corrosion and Prevention Conf.*, *Society of Automotive Engineers, Warrendale, PA*, Pp.153.

[28]   N. Hackerman and H. Kaesche, (1958), *J. Electrochem. Soc.*, 105, Pp.191.

[29]   N. Mora, E. Cano, J. L. Polo, J. M. Punete and J. M. Bastidas, (2004), *Corros.Sci.*, 46, Pp.563.

[30]   B. R. W. Hinton, (1991), *Met. Finish*, 89, Pp.55.

[31]   A. B. Brown, (1987), *J. Electrochem. Soc.*, **134**, 10, Pp.2506.

[32]   V. Branzoi, F. Golgovici, and F, Branzoi, (2002), *Materials Chemistry and Physics*, 78,Pp.12

[33]   L. A. Pawlick and R. G. Kelly, (1995), *J Corros. Sci. and Engineering*, November, Pp.1.

[34]   C. S. Brossia, E. Gileadi and R. G. Kelly, (1995), *Corros. Sci.*, **37**, 9, Pp.1455.

[35]   A. J. Davenport, H. S., Isaacs and M. W. Kending, (1991), *Corros. Sci.*, 32, Pp.653.

[36]   B. R. W. Hinton, D. R. Anott and N. E. Ryan, (1986), *Mater. Forum*, 9, Pp.162.

[37]   A. E. Hughes, R.J. Taylor, B.R.W.Hinton and L.Wilson, (1995), *Surf. InterfaceAnal.*, 23,Pp.540.

[38]   S. Szklarska–Smialowska, (1992), *Corros. Sci.*, 33, Pp.1193.

[39]   T. H. Nguyen and R. T. Foley, (1980), *J. Electrochem. Soc.*, 127, Pp.2563.

[40]   J. T. Gundrsen, A. Aytec, S.Ono, H. H. Nordhien, K. Nisancioglu, (2004), *Corros.Sci.*, 46, Pp.265

[41]   P. J. E. Forsyth, (1998), *Mat. Sci. Technol.*, 14, Pp.151.

[42]   H. S. Isaacs, G. Adzic, C. S. Jeffcoate, (2000), *Corrosion*, 56, Pp.971.

[43]   Q. J. Meng, G. S. Frankel, (2004), *J. Electrochem. Soc.*, 151, Pp.B271.

[44]   S. Maitra, G. C. English, (1981), *Metall. Trans. A.*, 12, Pp.535.

[45]   H. Leth–Olson, A. Afseth, K. Nisancioglu, (1998), *Corros. Sci.*, 40, Pp.1195.

[46]   E. Akiyama, G. S. Frankel, (1999), *J. Electrochem. Soc.*, 146, Pp.4095.

Table (1): Weight loss measurements of Al and Al–Cu samples under specific conditions of immersion time, media and temperature.

Aluminum Samples	Immersion Time (Hours)	Weight loss (mg/Cm^2)			
		Room Temperature		50 ℃	
		10 % H_2SO_4	15 % H_2SO_4	10 % H_2SO_4	15 % H_2SO_4
Pure Al	1	0.06	0.08	0.13	0.20
	2	0.12	0.16	0.16	0.24
	3	0.13	0.21	0.18	0.28
	4	0.14	0.24	0.28	0.30
	5	0.18	0.36	0.36	0.59
Al 85% Cu 15%	1	0.05	0.07	0.11	0.11
	2	0.09	0.15	0.11	0.21
	3	0.10	0.18	0.17	0.26
	4	0.11	0.25	0.24	0.35
	5	0.15	0.30	0.32	0.43

Table (2): Effect of immersion time on the corrosion penetration of aluminium samples at different media and temperature.

Aluminum Samples	Time ($h^{1/2}$)	Corrosion Penetration (CP) X 10^{-5} (cm)				Parabolic Rate Constant (K) X 10^{-5} (cm/$h^{1/2}$)			
		RT		50 ℃		RT		50 ℃	
		10 % H_2SO_4	15 % H_2SO_4	10 % H_2SO_4	15 % H_2SO_4	10 % H_2SO_4	15 % H_2SO_4	10 % H_2SO_4	15 % H_2SO_4
Pure Al	1.00	2.2	2.9	4.8	7.4	2.2	2.9	4.8	7.4
	1.41	4.4	5.9	5.9	8.9	3.1	4.2	4.2	6.3
	1.73	4.8	7.8	6.7	10.2	2.8	4.5	3.8	5.9
	2.00	5.2	8.9	10.4	11.3	2.6	4.4	5.2	5.6
	2.24	6.7	13.3	13.2	21.9	3.0	6.0	5.9	9.8
Al 85% Cu 15%	1.00	1.5	1.9	3.0	3.0	1.5	1.9	3.0	3.0
	1.41	2.5	4.1	3.0	5.8	1.8	2.9	2.1	4.1
	1.73	2.8	5.0	4.7	7.2	1.6	2.9	2.7	4.1
	2.00	3.0	6.9	6.6	9.6	1.5	3.4	3.3	4.8
	2.24	4.1	8.3	8.8	11.8	1.8	3.7	3.9	5.3

Legends for figure

1. Aluminuium metal and alloy specimens produced via sand casting method.
2. Weight loss analysis of pure Al in different environments at room and 50°C temperature.
3. Weight loss of Al–Cu alloy in different environments at room and 50°C temperature.
4. Corrosion penetration of pure Al in different environments at room and 50°C temperature.
5. Corrosion penetration of Al–Cu alloy in different environments at room and 50°C temperature.
6. A real images of pure Al immersed in 15% H_2SO_4 aquoeus solution for 5 hours
7. A real images of Al–Cu alloys immersed in 15% H_2SO_4 aquoeus solution for 5 hours
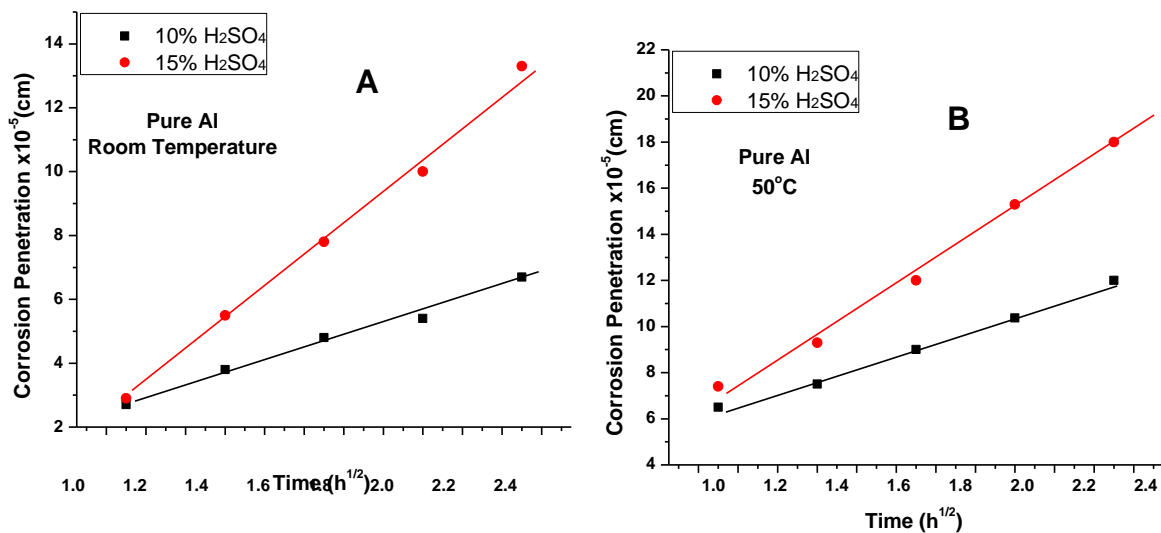

Pure Al   Al–Cu

Fig. 1

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Fig. 2

Fig. 3

Fig. 4

Fig. 5

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Fig. 6

Fig. 7

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