

Corrosion Behaviour of Al-Si Cast Alloy Reinforced with Titanium diboride (TiB₂) and Scandium (Sc)

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Abstract: The aluminium-silicon (Al-Si) based on Metal Matrix Composites (MMCs) is widely used in light-weight constructions and transport applications requiring a combination of high strength and ductility. A grain refinement plays a crucial role in improving characteristics and properties of Al alloys. In this investigation, titanium diboride (TiB₂) and scandium (Sc) inoculants were added to the Al-Si alloys for grain refinement of an alloy. In this investigation, the corrosion resistance rate of Al-Si cast alloy reinforced by TiB₂ and Sc were measured by potentiostat (AUTOLAB) instrument. The aim of this research is to investigate the corrosion rate for Al-Si-TiB₂-Sc composites that immersed in different concentration of acidic solutions. Besides, the immersion time of acidic solutions also was investigated. All the samples were prepared accordingly for ASTM standard by the composition of 6.0 wt% TiB₂ and 0.6wt% Sc. All the samples undergo cold mounting technique for easy handling on corrosion tests. Then the samples were immersed in two different concentrations acidic medium solutions, which were 0.1 and 1.0 M hydrochloric acids (HCl). The corrosion rate also was investigated for immersion samples of 1.0 M HCl for 21 days. From the results obtained, added TiB₂ and Sc onto Al-Si alloy gave the better properties in corrosion resistance. Corrosion rates to reduce when the samples were immersed in a lower concentration of acidic medium, 0.1 HCl. However, there are some significant on the result but it still following the corrosion rates trend. Thus, improvements to reinforcement content need to be done in further research to cover the lack of this corrosion rates trend.

Key words: *Al-Si alloy, metal matrix composites, titanium diboride, scandium, corrosion rate*

INTRODUCTION

Aluminum alloys have been tremendous applicable in automobile and aerospace industries. It has variety superior properties such as high specific strength, chemically inert and good performances at low temperature. This types MMCs however, it has the main weaknesses which are low resistance to wear [1]. Miscellaneous of aluminum alloys have been fabricated to create the desired properties while adding the variety of reinforcement including ceramic and organic compound. The recent generation of aluminum alloys is known as aluminum hybrid composites (AMCs). The performances of these materials depending on the selecting foreign compound as it reinforced particles [2].

Aluminium matrix composites (AMCs) are used in various application due to their good physical and mechanical properties. The addition of reinforcements into a metallic matrix to improves the stiffness, specific strength, wear, creep and fatigue properties [3]. One of the main reasons for using MMCs is the addition of the reinforcement on MMCs corrosion resistance. That is important in aluminium alloy based composites where the protective oxide film imparts corrosion resistance. The corrosion resistance of aluminium and Al alloys can be attributed to natural protective oxide layer that forms on the surface. Accelerated MMCs corrosion starts from electrochemical and chemical interaction [4].

According to Terence, [5], corrosion is a breakdown of metal due to reactions within its area. It is the loss of water and air molecules. Corrosion also

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occurs when an acidic or basic material touches another material. The addition of the reinforcing fibers and particles can cause accelerated corrosion of metal matrix compared to corrosion of unreinforced matrix alloy.

Ibrahim et al. [6] had studied morphology and mechanical properties of Al-Si reinforced with different TiB_2 contents. It showed that the eutectic silicon microstructure in Al-Si alloy changed from needles-look or acicular to fine grain size or globular when the added of TiB_2 . The mechanical studies showed that the ductility of Al-Si alloy was much lower in the absence of grain refiner, TiB_2 . The tensile strength of unrefined Al-Si and Al-Si with 6 wt.% TiB_2 as grain refinement were recorded 275 and 312 MPa respectively. The hardness value for the unrefined Al-Si alloy also shows less compared with Al-Si with grain refiner, 6 wt.% TiB_2 , which are 74 and 78 MPa. This showed the results were significant improvements in mechanical properties have been obtained with the use of TiB_2 as grain refiner to Al-Si alloy.

The addition of TiB_2 will increase the hardness of Al-based alloy. The increase in hardness will decrease the TiB_2 particle grain size. When TiB_2 content is added to an alloy, the corrosion potential and corrosion current are decreased. Therefore the addition of TiB_2 has positive factors to the corrosion resistance in Al. This behavior leads to positive factors of TiB_2 addition on the grain size refinement [6].

Rosmamuhamadani et. al. [7] used Gamry-Electrode Potentiometer for measuring the corrosion rate of Al-Cu alloys. From their experiment, anodic and cathodic polarization curves were plotted with the presence of the reference sample and Al-Cu alloys in 0.1 M HCl solution in current density range from 2 to 6 mA/cm². The result from anodic and cathodic polarization curves shows that corrosion potential decreases with increasing the TiB_2 content in the alloys. While the corrosion current decreased when increasing the TiB_2 content. The advantage of the Linear Polarization Technique (LPR) is that the measurement of corrosion rate is made instantaneously. But LPR can only be successfully performed in relatively clean aqueous electrolytic environments. LPR will not work in gases or water where contaminate of the electrodes will prevent measurements being made.

The corrosion properties of Al-Cu cast alloy reinforced with TiB_2 by salts spray fog test also was studied [8]. The samples were exposed to the salt environment for the duration of 1 month in cabinet test in 5 %NaCl solutions. The results obtained Al-6 wt.%Cu alloy with 3 wt.% TiB_2 gave the lowest value in weight loss compared to Al-6 wt.%Cu with 6

wt.% TiB_2 and as cast Al-6 wt.%Cu alloy. Al-6 wt.%Cu alloy with 3 wt.% TiB_2 exhibited high corrosion resistant, resulting from its ability to form naturally corrosion oxide film on the surface, and the corrosion resistance improved due to stable oxide layer formation due to the behavior of the surface during corrosion test. From the data obtained, they found that is a variation of the corrosion rates with different TiB_2 particles contents. The result shows that Al-6 wt.%Cu with 3 wt.% TiB_2 exhibit the good corrosion property of alloy compared than other compositions in Al-6 wt.%Cu alloy. The corrosion rate gave the lowest value for Al-6 wt.%Cu with 6 wt.% TiB_2 composite following Al-6 wt.%Cu alloy in 5 %NaCl solutions. By increasing the TiB_2 contents particles to Al-6 wt.%Cu alloy, the results show that the corrosion rates decreased proportionally especially for the composition of 3 wt.% TiB_2 content within 720 hours [8].

Abdel Rehim et. [9] investigated the Cu addition on the mechanical properties and corrosion resistance of commercially pure Al. Three different Al-Cu alloys of 3, 6 and 9 wt.% Cu content was prepared and experimentally tested both mechanically and chemically. The results show the addition of Cu resulted in a linear increase of the hardness, and substantial reduction in the grain size, slight reduction the impact energy, a substantial increase in the flow stress at 0.2 strains, and improve in the mechanical properties. The potentiostatic measurements showed that the susceptibility of the samples towards corrosion decreases in the order: Al>Al-3 wt% Cu>Al-9 wt% Cu>Al-6 wt% Cu. The corrosion rates of the 3, 6 and 9 wt% Cu alloys in HCl were found to be 0.29, 0.13 and 0.21 nm/s, respectively. The different properties, i.e. impact energy, flow stress at 0.2 strain, mechanical characteristics and corrosion resistance, showed that the 6 wt. % Cu is an optimal composition.

Svobodova et. al. [10] studied the evaluation of the corrosion resistance of the Al-Si alloys alloyed with the different amount of antimony. Specifically it goes about the alloy Al-Si-7Mg 0,3 which is antimony alloyed in the concentrations 0, 0,001, 0,005, 0,01 a 0,05 wt. % of antimony. The experimental part describes the experimental samples which were prepared for the experiment and further they were exposed to the loading in the atmospheric conditions for a period of the 3 months. The experimental samples were evaluated macroscopically and microscopically. From the results of the macroscopic analysis is apparent that with the increasing content of the antimony it leads to increased corrosion attack of experimental samples. The microscopic analysis results are not unequivocal. The significant difference is the sample without Sb and alloyed Sb. The sample without Sb (primary alloy) has the better corrosion resistance.

Therefore they concluded that the antimony influence on the corrosion resistance of the AlSi7Mg0,3 alloy is rather negative. The surface treatment that the machined surface of the material has better results after the corrosion loading that the part of the material after casting. It has been influenced by the presence of the interdendritic porosity in the research of corrosion resistance of the AlSi7Mg0,3 alloys as documents the microscopic analysis. For the further research in this area, they also recommended using use higher differences of wt. % for the alloy Al-Si alloys with antimony (for example 0; 0,005; 0,05; 0,1 and 0,2 hm. % Sb). The results of the antimony influence on the corrosion resistance of the Al-Si alloys would be probably clearer.

Polarization is said to be either anodic or cathodic for displacement of an electrode potential from its equilibrium value. Anodic polarization caused by a slow anodic reaction called oxidation while cathodic polarization caused by a slow cathodic reduction. Corrosion of Al-Si, Al-Si/TiB₂ and Al-Si/TiB₂/Sc in two different concentrations of HCl was studied. To measure corrosion rates, the method must follow its standards requirement and procedure.

EXPERIMENTS

Composite Fabrication

Firstly, Al-7wt% Si was melted at 780°C in an induction furnace. After that two types of reinforcement were added to the molten Al-7wt% Si in the atomic ratio in accordance with TiB₂ and Sc by stirring method. The stirrer that uses in the stirring method is mild steel stirrer that was coated with zirconia. To avoid contamination of the molten metal with iron, the latter coating was applied to the mild steel stirrer. The steps are repeated to reinforced the alloy with other composition, 0.6 wt.% and TiB₂ and 0.6%wt Sc.

Permanent mold made of stainless steel was involved in a casting process. Permanent mold casting is commonly used to produce complex parts. Permanent mold casting also is preferred because it produced in tight dimensional tolerances with high surface quality. The permanent mold casting that user is able to produce three samples at one pouring.

An electrical furnace that heat is applied by induction heating of metal known as induction furnace. The advantages of the induction furnace are clean, energy-efficient and well-controllable melting process. The induction furnace is more efficient than other means of metal melting. The furnace is a channel type induction furnace and contains shell lined with refractory material. Feed material, an alloy containing

ore and carbon reluctance that charged through a hole at the side of the furnace. The material then was heated by combustion of different gases that formed after heated the carbon reluctance and ore mixture under certain conditions and additional fuel combustion. The temperature controller was used to monitor the furnace temperature was maintained at 700-780 °C. Then molten metal was poured into the mold cavity and leave it cool down for a few minutes. The metal was removed after 20 minutes holding time.

Sample preparation

The samples Al-Si, Al-Si/TiB₂, and Al-Si/TiB₂/Sc alloy were cut by using the linear precision saw (Buehler IsoMet@5000). The speed used is 500 rpm. The sizes of the samples were 4cm². Then the nichrome wire that was inserted into glass tubing rod were soldered to the samples. The wire content of the soldering method was Sn and Pb with ratio 60:40. The soldering technique was careful handled to attach the nichrome wire to the sample. Figure 1 and 2 shows the glass tubing rod with nichrome wire and soldering the nichrome wire to the sample.

Cold mounting was used to cast the sample. The process required are mixing the epoxy and hardener with a ratio of 10:1. The mixture was poured into a mold for 24 hours. It formed a solid sample and makes it easy to handle during grinding and polishing process. Figure 3 shows the cold mounting sample made up from mixed of epoxy and hardener.



Figure 1 Glass tubing rod with nichrome wire



Figure 2 Soldering the nichrome wire to the sample

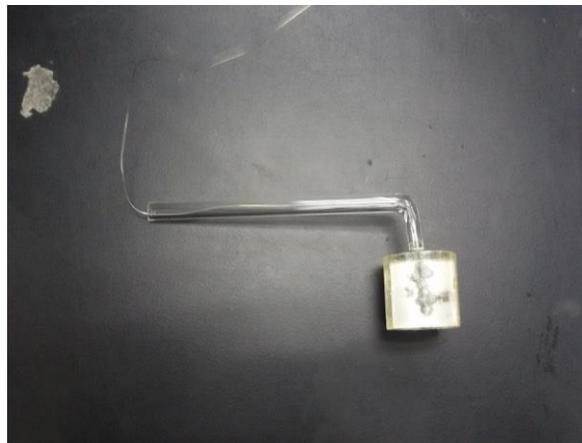


Figure 3 Cold mounting sample

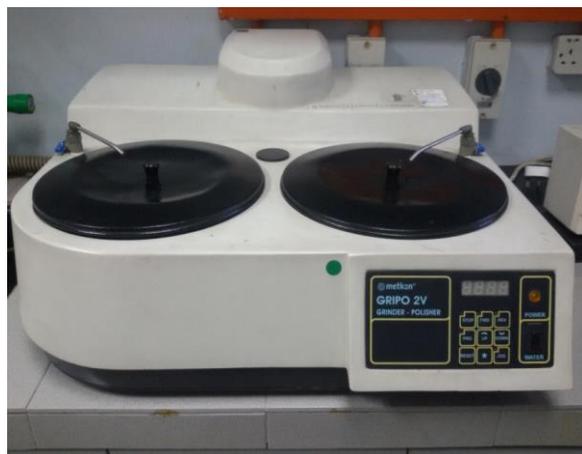


Figure 4 Grinding and polishing machine

1 μ m silica paste. Figure 4, shows the grinding and polishing machine, while Figure 5 shows the alloy specimen mounted in a mould.

Corrosion testing

Corrosion test was carried out on each alloy in the as-cast conditions. Potentiostatic polarization measurements were carried out using a Radiometer Analytical model PGZ 100 Potentiostat/Galvanostat with VoltaLab software. The working electrodes employed were the graphite and Al-Cu bars. Anodic and cathodic polarization curves were plotted. Figure 6 below shows the Potentiostat (AUTOLAB) machine used for corrosion test



Figure 5 Sample surface for corrosion test



Figure 6 Potentiostat (AUTOLAB) for corrosion test

The samples surface were ground with sandpaper with starting grit of 120 then followed by 320, 600, 800 and 1000. The sandpaper that has a small number of grit shows that abrasive paper is roughness while a large number of grit shows the fine roughness. The function of sandpaper grind is to ensure that the surfaces of samples are clean, flat and smooth. Then the sample was polished using the polishing cloth and

The investigated electrodes were cut as cylindrical rods, welded with Cu-wire for electrical connection to contact the test solution. The experiments were performed in a 250 ml volume Pyrex glass cell using Pt wire and a saturated calomel electrode as auxiliary and reference electrodes, respectively. All potentials given in this research are referred to this reference electrode. The experiments

were carried out in 0.1 and 1.0 M HCl solution. The HCl solution was freshly prepared from analytical grade using doubly distilled water. For each run, a freshly prepared solution as well as a cleaned set of electrodes was used.

Besides, the test also was carried out in immersed the specimens in 1.0 HCl within 21 days. The data were taken for every week to determine the corrosion rate of Al-Si-TiB₂-Sc composites. The experiment was performed in a 250ml volume of beaker using nichrome wire and titanium as auxiliary and Ag/AgCl as reference electrodes. The set-up is shown as in figure 7.

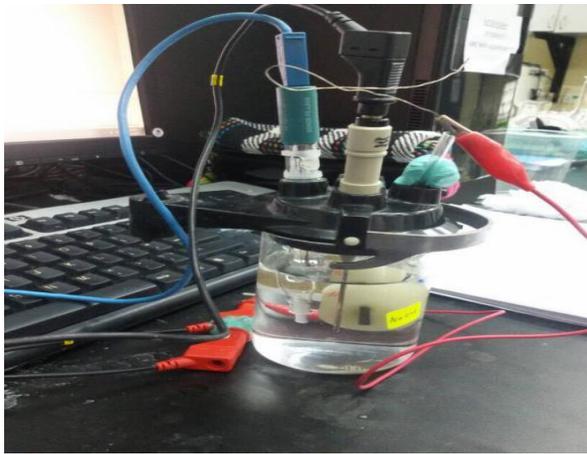


Figure 7 The set-up connection to the data reader

RESULTS AND DISCUSSION

Corrosion rate was measured by Polarization Resistance (LPR) method. This method potentiostat AUTOLAB instrument was used to obtain the data needed. There is corrosion potential (E_{corr}), corrosion current (I_{corr}) and corrosion rates. Based on Table 1, it was found that corrosion potential (E_{corr}) and corrosion rates (CR) is decreasing when all the reinforcement mixed with Al-Si cast alloy.

Nevertheless, there was some increment of corrosion rate at Sc reinforcement. The best corrosion resistance was present when the Al-Si reinforced with TiB₂ and Sc. While, the Table 2 showed that the reinforced metal matrix with TiB₂ gives the higher value of corrosion rates when immersed in a higher concentration of HCl solution. The amounts of corrosion rate are 53.36 mm/year. The corrosion current and corrosion rates showed the minimal value when all the reinforcement mixed together with Al-Si

metal matrix. The amount of corrosion rate was 5.0×10^{-4} mm/year.

The addition of Sc can improve the ductility, fracture, impact properties and formation into grain refinement that help to reduce corrosion rate. The small amount of Sc was good enough to modify the Al-Si properties. In this research, the Sc content used was 0.5wt% and it's good enough to reduce the corrosion rates. The reason was proved by the percent decrement of corrosion rate that was 98.9% with the minimal amount of corrosion rate.

Table 1 Electrochemical parameters for Al-Si reinforcement immersed in 0.1M

Reinforcement	E_{corr}	I_{corr}	CR (mm/year)
Al-Si	-635.25	17.4×10^{-6}	0.58
Al-Si-TiB ₂	-644.92	2.53×10^{-6}	0.16
Al-Si-TiB ₂ -Sc	-246.63	5.56×10^{-9}	3.13×10^{-4}

Table 2 Electrochemical parameters for Al-Si reinforcement immersed in 1M HCl solution

Reinforcement	E_{corr}	I_{corr}	CR (mm/year)
Al-Si	-727.91	73.26×10^{-6}	2.34
Al-Si-TiB ₂	-155.72	10.01×10^{-6}	0.56
Al-Si-TiB ₂ -Sc	-506.04	9.46×10^{-9}	5.0×10^{-4}

The bar chart in Figure 8 showed the variation of corrosion rates values when the sample immersed in 0.1M HCl acid solution. Summarize it as a whole, it showed that corrosion rates were reduced when all the reinforcement of TiB₂ and Sc was mixed together with Al-Si metal matrix. Based on this bar chart, it can be clearly seen that the reinforcement with Sc is not significant in value. The corrosion rate continues to reduce when metal matrix mixed with Sc. The trend of corrosion rates was proved that Sc can reduce the corrosion rates.

While Figure 9 showed that the corrosion rates when sample immersed in a higher concentration of HCl acid solution. The corrosion rates showed that there was an increased value than corrosion rates values in immersion into a lower concentration of HCl acid solution. The bar chart showed the reinforcement of metal matrix with TiB₂ gives significant value. Nevertheless, the corrosion resistance is good when all the reinforcements are mixed together

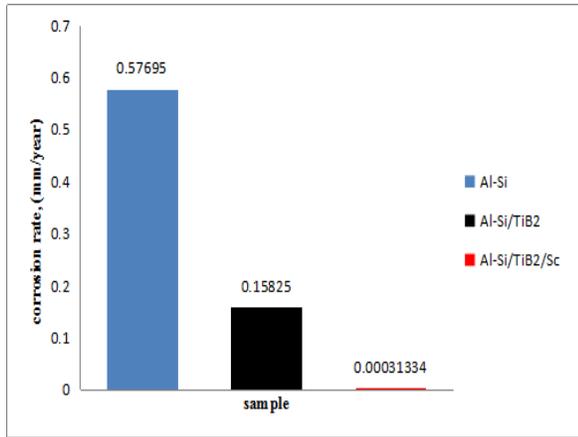


Figure 8 Corrosion rates in 0.1M HCl acid solution

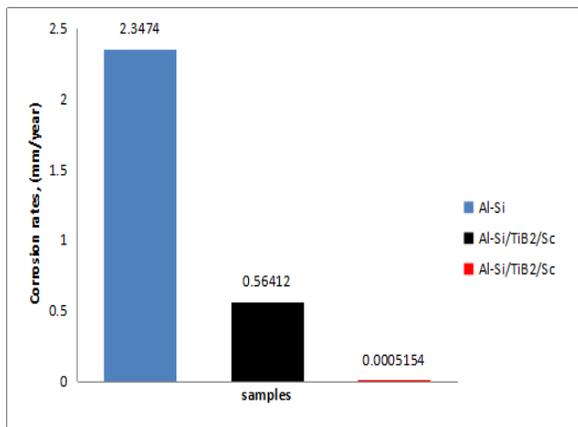


Figure 9 Corrosion rates in 1.0M HCl acid solution

Figure 10 shows typical polarization curves for Al-Si reinforcement in chloride media. It shows the anodic polarization curve of Al-Si reinforcement. The curves showed a monotonic increase of current with potential until the current reached the maximum value. After this maximum current density value, the current density declined rapidly with potential increased. As the result obtained, Sc gives smallest value of corrosion rates, 3.13×10^{-4} mm/year. I_{corr} value obtained also the smallest value, 5.55780 nA. Reinforcement with TiB₂ also gives better corrosion resistance and polarization curve shows the decreasing in I_{corr} value that was 2.526µA.

Figure 11 showed the polarization curve of sample when immersed in higher concentration of HCl solution. From the curve obtained, it is suggested that Sc curve gives better corrosion resistance when the polarization curve shows the minimal value of I_{corr} . However the corrosion rates are higher than the corrosion rates of Sc that immersed in lower concentration of HCl solution. The value obtained was 5.15×10^{-4} mm/year that smallest value obtained from

other reinforcement and I_{corr} value obtained is 9.46210nA.

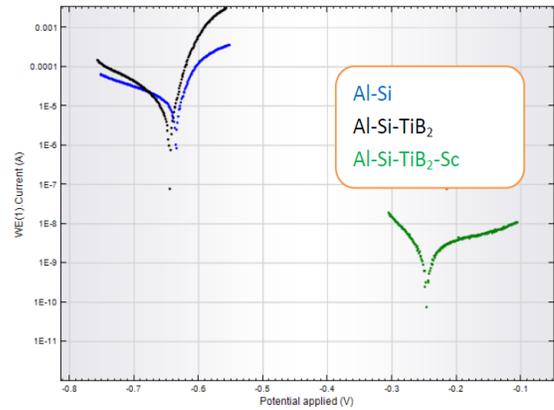


Figure 10 Polarization curve of samples immersed in 0.1M HCl acid solution

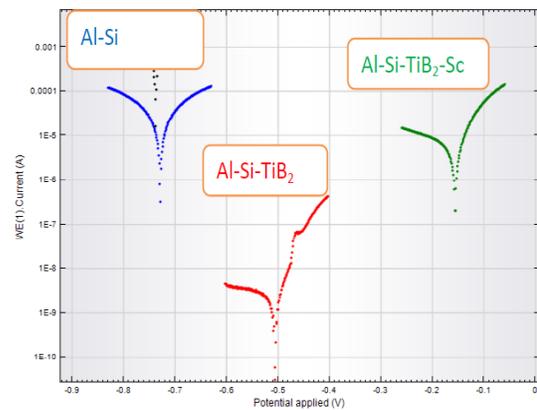


Figure 11 Polarization curve of samples immersed in 1.0 M HCl acid solution

Effect of immersion time

Al-Si without any reinforcement shows the highest corrosion rate compared to the others which was 1027.8 (mm/year). In addition to another compound which is TiB₂, the corrosion rate showed slightly reduced for 7.7% compared to Al-Si cast alloy. Table 3 shows the summarized of corrosion rate when Al-Si cast alloy was reinforced by TiB₂ and Sc. It showed a corresponding result to the previous research and was supported by Kumar et. al. [11]. They stated the corrosion rate of aluminium based MMCs increase with increasing in TiB₂ content in the cast and forged. Al-Si-TiB₂-Sc composite shows the lowest in corrosion rate which was 0.00379. In short, the corrosion rate increased directly proportional to the addition of reinforcements used.

Table 3 Corrosion rate of Al-Si cast alloy and their composites immersed in 1.0 HCl for 21 days

Type of alloys	1 st week	2 nd week	3 rd week
Al-Si	1027.8	590.9	391.5
Al-Si-TiB ₂	862.7	411.5	495.5
Al-Si-TiB ₂ -Sc	0.0038	0.0041	0.0068

For the immersion in 14 days (2nd week), there were a presence certain uncertainties results that affected the corrosion rate of the alloys. Referring to Table 3, the value of corrosion rate of Al-Si shows dramatically increased to 590.97 mm/year compared to the 7 days. However, it shows that Al-Si-TiB₂-Sc composite possessed excellent in corrosion resistance than others. The result of Al-Si-TiB₂-Sc composite quite excellent which is 0.0040 mm/year and gave 59% better than Al-Si cast alloy itself. Conventionally, the addition of scandium element might enhance the physical characteristic such as strength refine grains and inhibit recrystallization [12].

For the days of 21 (3rd week) immersed in HCl, the corrosion rate was 3915mm/year for Al-Si cast alloy, while for Al-Si-TiB₂, and Al-Si-TiB₂-Sc composites, the value were 0.0068 and 0.0036 respectively. From the days 7, Sc element made the composite having a high value in corrosion resistance. However, the trend in corrosion rate of these alloys was very slowly when increased by exposure time. Figure 12 shows the corrosion rate was obtained from Autolab-potentiostat for 21 days) and were summarized in the histogram. Based the corrosion potential, the rate for hydrogen to evolve is equal to the rate of metal dissolution and expressed as current density displayed in the anodic-cathodic graph in figure 13.

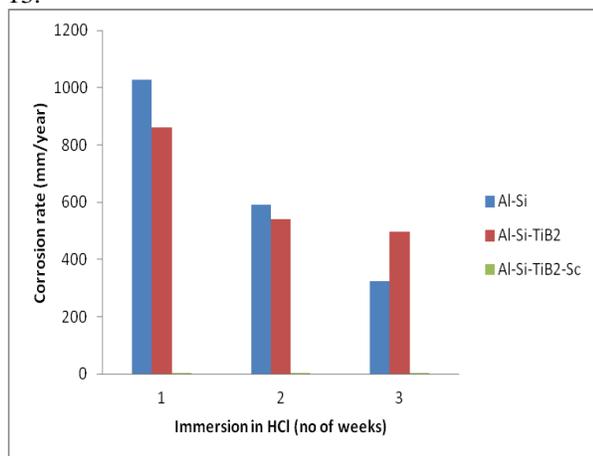


Figure 12 The corrosion rate of Al-Si cast alloy and their composites from Autolab-potentiostat for 21 days

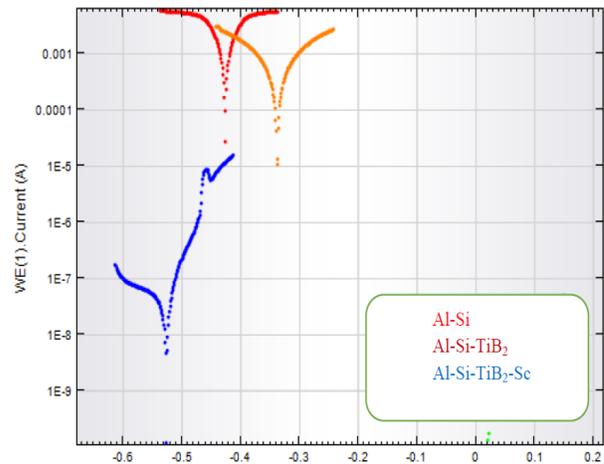


Figure 13 The relationship between current (A) and potential applied (V) on different samples of alloy.

CONCLUSIONS

From the study, it can be concluded that the corrosion rates reduced when TiB₂ and Sc were added to Al-Si cast alloy. These content to gave better corrosion resistance when immersed in two different concentrations of HCl solutions. It found that the composite of Al-7wt% Si -6wt% TiB₂-0.6wt% Sc that immersed in lower concentration acid solution. 0.1 M gave better corrosion rates. The results also show that the corrosion resistance of Al-Si-TiB₂-Sc composite gave the lower value compared to Al-Si-TiB₂ and Al-Si cast alloy itself. The values were lower in the days of 7, 14 and 21 days when immersed for 21 days in HCl solution.

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