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Corrosion Resistance of Aluminium–Silicon Hypereutectic Alloy from Scrap Metal

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Abstract

This study was carried out to investigate the corrosion resistance of Al–Si hypereutectic alloy in 5.0% NaCl solution using BMW 5 series piston head. The corrosion behaviours were investigated through immersion and electrochemical corrosion tests. The immersion test was carried out for 7–28 days, whereas for electrochemical test the exposure time was only about 15 min. Hardness test and microstructure study were carried out on samples before and after corrosion test. It was found that the dark phase is silicon and the white area is aluminium. The silicon dispersed in aluminium alloy. It was also found that corrosion rate of the Al–Si hypereutectic alloys decreases as exposure time increases in immersion corrosion test. This was due to the formation of thin and protective corrosion product on the metal surface that acted as barrier between the metal and the environment. The corrosion rates of immersion test were more than electrochemical test due to high concentration of oxygen ions in the solution. SEM/EDS analysis confirmed that all metals suffer from uniform and localized corrosion, namely pitting. The localized corrosion is mainly due to breaking of oxide layer. The hardness was also confirmed to decrease as the time immersion increased.

Keywords Al–Si hypereutectic alloys · BMW 5 series piston head · Immersion test · Electrochemical test · Corrosion · Pitting

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1 Introduction

Due to their lightweight, low cost, good amenability to casting and high detailed strength, Al–Si alloys are widely used as components in many applications such as automotive and aerospace industries and construction establishment [1, 2]. But, increase in mechanical properties had triggered decrease in the corrosion resistance owned to the formation of the precipitates in adding alloying elements. Silicon plays many significant roles in manufacturing the Al–Si alloys, it aids the flow tendency of liquid aluminium, the size contraction is reduced during the process of solidification, the thermal expansion coefficient and porosity are lowered, and it enhances weldability [1–3]. The Al–Si alloys that contained 11–13% silicon are regarded as eutectic alloy, and the one with < 11% silicon is termed hypoeutectic, while those with more than 13% silicon are known to be hypereutectic Al–Si alloys [1].

It improves aluminium alloy properties in many other ways: reduction in specific mass, wear and tear between the contact surfaces and smothering the contact surfaces and

similar thermal expansion to other engine aluminium parts [2]. Consequently, the noise would be reduced, the machining of dissimilar materials would be eliminated, and recycling properties would be improved [3]. Also, silicon is also useful in many other alloys; it makes magnesium alloys heat treatable, increases the mechanical strength of copper alloys and reduces the internal contraction during their solidification, thereby making machining easier [4]. Al–Si alloys are chosen material for piston head which retained good wear properties [1, 2, 5]. This study was necessary to determine the mechanical properties and examine the corrosion type and rate of aluminium–silicon hypereutectic alloy which could limit its quality in aerospace and automotive applications during metallic reaction with other composites.

2 Materials and Methods

The BMW 5 series piston head was obtained from a car workshop. The material was cut into rectangular specimens with $25 \times 15 \times 4$ mm dimension. The specimens were mechanically ground up to 1000 grid using grinding paper with water as lubricant. The specimens were washed in acetone and water [6, 7], dried for 24 h and weighted before subjected to test. The microstructure of the specimen was examined using Nikon optical microscope, scanning electron microscope and energy dispersive spectroscopy.

The immersion test of the specimens with known initial weight was conducted at a room temperature of 27°C to determine their corrosion rate using weight loss method according to [8], and the surface area of the samples was exposed to the corrosive environment of 5.0% NaCl solution inside a 12 cm^2 container for 7, 14, 21 and 28 days in accordance with [9]. The specimens were freely suspended with nylon string at the centre of the container. The tank was kept closed to avoid foreign particle. At the end of the test, the corrosion product of specimens was removed by immersing it in nitric acid for 30 s, washed, dried for 24 h and weighted again. SEM was used to observe the morphology and evolution of the corrosion layers that formed on the material surface. EDX was used to identify elemental composition.

Micro-hardness tests were carried out before and after immersion test using a Vickers indenter at a load of 9.807 N, employing Shimadzu HMV-2 series micro-hardness tester in accordance with [10]. Prior to the indentation, the specimens were ground and polished to a final polishing of $1\text{-}\mu\text{m}$ diamond paste and the micro-indentation tests were conducted with the indenter perpendicular to the specimen surface.

The electrochemical test was then conducted to evaluate corrosion resistance of Al–Si hypereutectic alloy. This test was performed using square specimens with dimension 1×1 cm ground until 2000 grid paper followed by polishing. The experimental setup consisted a conventional

three-electrode cell comprising the working electrode, saturated calomel electrode as a reference electrode and a standard platinum electrode as a counter electrode in 5.0% NaCl solution as an electrolyte. The changes in the free corrosion potential (E_{ocp}) was monitored as a function of time under open circuit conditions for approximately 60 min [11]. After a stabilization period of 1 h in the solution, the potentiodynamic polarization tests for Al–Si hypereutectic alloy at $37 \pm 1^\circ\text{C}$ were carried out at a scan rate of 1 mV/s to determine the corrosion potentials (E_{corr}) and the corrosion current densities (i_{corr}) [12].

3 Results and Discussion

3.1 Optical Analysis

The optical images of the material revealed the casting microstructure with hypereutectic Al–Si Alloy (LM30) as presented in Fig. 1 with low and high magnification. It is clearly observed that the hypereutectic Al–Si consists of aluminium (bright phase) and silicon structure (dark phase). The corresponding EDS pattern is presented in Fig. 2.

3.2 Immersion Test

Figure 3 presents the sample of LM 30 aluminium alloy before immersion test. By visual inspection, corrosion occurred on entire surface of the sample. An attempt was made to remove this corrosion product, but the grey layer of corrosion product remained yet, and it was hard to be detached. Four samples were immersed, each one for 7 days, 14 days, 21 days and 28 days. After immersion of LM 30 aluminium alloy for sometimes, the samples were inspected visually for any changes on the appearance. They appeared to corrode uniformly, and the surfaces were covered by grey colour corrosion products. This corrosion product layer was formed due to the dissolved salts which also accelerate the rate of corrosion. In addition, the corrosion product layer formed on the hypereutectic Al–Si Alloy became thicker successively from 7 to 28 days of immersion time. Increase in immersion period led to more change in appearance as shown in Table 1. As more corrosion product formed on the surface of the samples, corrosion rate reduced through the deposit which acts as a barrier between the metal and the environment (Table 2).

3.3 Weight loss measurement after immersion test

This allows an accurate determination of the mass loss of the metal or alloy that occurred during exposure to the corrosive environment. Each sample was weighed before and after the immersion for 7–28 days. The data of the

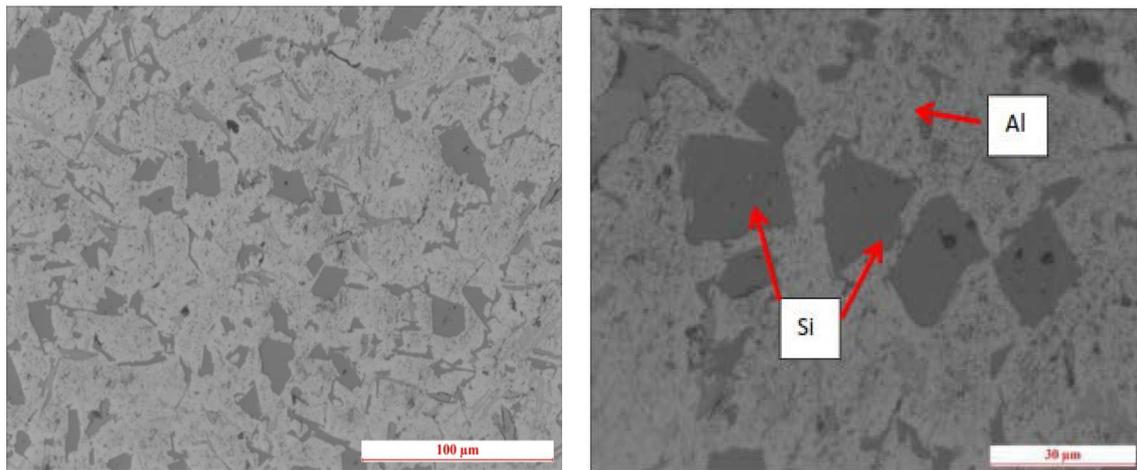


Fig. 1 Microstructural image of LM 30 with low and high magnification

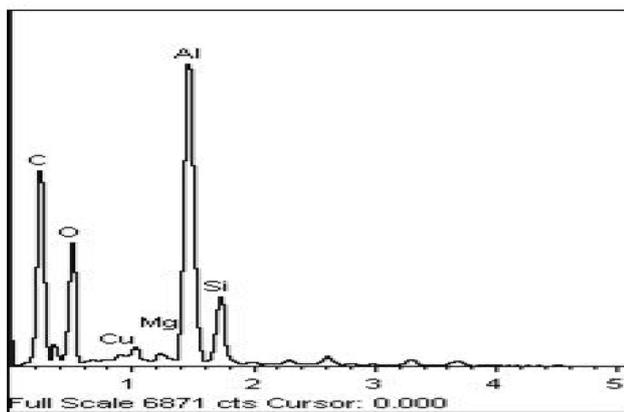


Fig. 2 EDX spectrum of the sample

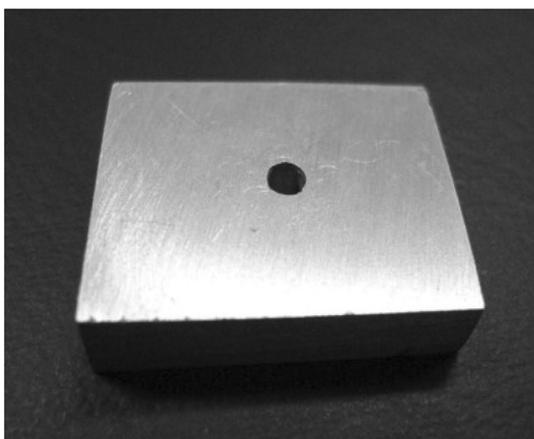


Fig. 3 Sample of LM 30 aluminium alloy before immersion test

weight loss were calculated and plotted in graph as presented in Fig. 4. It is clearly shown that the weight loss

of immersed samples in 5.0% NaCl solution for 7 to 28 days increased dramatically. The weight loss ranges from 0.008 to 0.027 g.

3.4 Corrosion Rate Measurement

All the specimens were immersed in 5.0% NaCl at different immersion times. After the immersion, the corrosion rates of the samples were evaluated using the weight loss method as the standard practice for evaluating the corrosion rates [8] described in Eq. (1), where the constant K is 8.76×10^4 millimetre per year (mm/year) and the density of LM 30 is 2.8 g/cm^3 . The corrosion rates for all samples are given in Table 3 and plotted in Fig. 4.

$$\text{Corrosion rates} = \frac{KW}{ATD}, \quad (1)$$

where K is the corrosion rate constant, T is the time of exposure (h), A is the exposed surface area (cm^2), W is the mass loss (g) and D is density (g/cm^3).

Figure 5 shows increase in corrosion rate from initial day up to 7 days of immersion time. The increase in corrosion rate was due to the initial corrosion attached on the surface and, as a result, corrosion products were formed. As immersion time increased from 7 to 14 days, the corrosion rate started to decrease. This was because the corrosion product formed on the surface became thicker, hard and very protective from corrosion. Thus, there were less formed ions and electron migrating between anode and cathodic areas. The corrosion rate slightly increased from 14 to 21 days. The corrosion rate became almost constant after 21–28 days of immersion. In other words, the protective of oxide layer increased linearly with time and, as a result, the corrosion rate was reduced.

Table 1 Immersion of LM 30 samples in 5.0% NaCl solution for 7–28 days before and after remove corrosion product

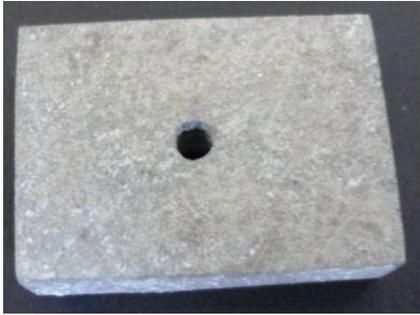
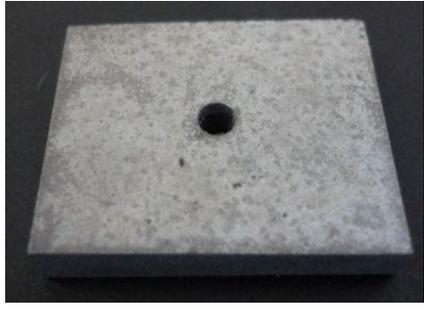
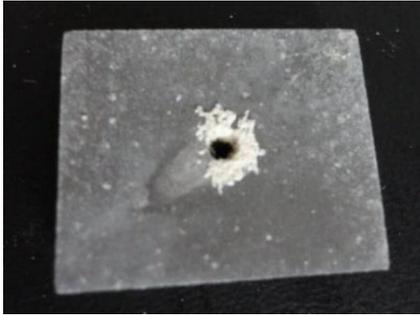
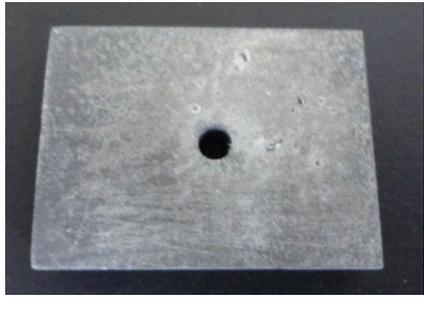
| Immersion time (days) | Before remove corrosion product | After remove corrosion product |
|-----------------------|---|---|
| 7 |  |  |
| 14 |  |  |
| 21 |  |  |
| 28 |  |  |

Table 2 Weight loss measurement and corrosion rates for 7–28 days in 5.0% NaCl solution

| Immersion time (days) | Area (cm ²) | Mass before immersion (g) | Mass after immersion (g) | Mass loss (mg) | Corrosion rate (mm/y) |
|-----------------------|-------------------------|---------------------------|--------------------------|----------------|-----------------------|
| 7 | 11.914 | 4.623 | 4.615 | 8 | 0.1173 |
| 14 | 12.3441 | 4.900 | 4.888 | 12 | 0.0849 |
| 21 | 12.5201 | 4.816 | 4.795 | 21 | 0.0977 |
| 28 | 12.5013 | 4.765 | 4.738 | 27 | 0.0943 |

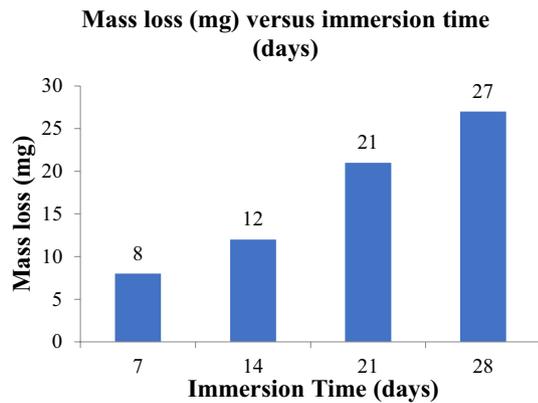


Fig. 4 Weight loss versus immersion time for 7 to 28 days in 5.0% NaCl solution

Table 3 Result of electrochemical testing in aerated 5.0% NaCl solution

| Specimen | E_{corr} (mV) | i_{corr} (A/cm ²) | CR (mm/year) |
|----------|------------------------|--|-----------------------|
| LM 30 | - 680 | 6.28 | 3.93×10^{-2} |

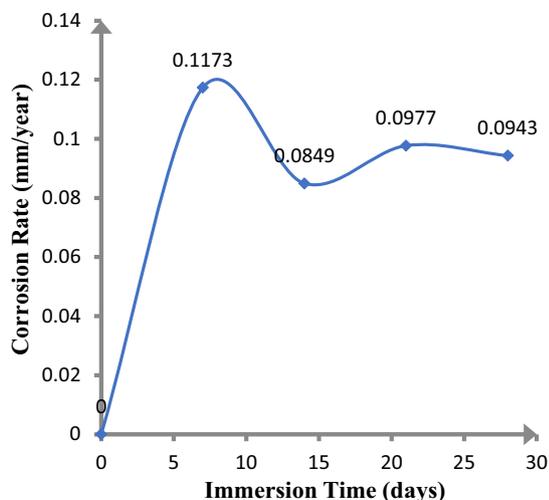


Fig. 5 Corrosion rates (mm/year) of LM30 sample for 7–28 days of immersion in 5.0% NaCl solution

3.5 SEM analysis after immersion test

Figure 6a shows typical small pit observed on the surface area of LM30. The higher magnification SEM image reveals details of the pit area as shown in Fig. 6b, c. The corresponding EDX result at the pitting adjacent of silicon (c1) shows the area contained Al, C, O, Si and Cu as presented in Fig. 5d. The mechanism of pitting corrosion occurred because NaCl acts as catalyst to corrosion. The area was not

consumed in the process but helps to break down the oxide passive layer and allow the corrosion process to continue. The pitting observed occurs at site of oxide film layer failure. Several factors that might cause this failure include casting defect due to solidification or hydrogen liberation and phase particles or other precipitants. However, once pitting initiated, corrosion proceeded at high rate due to crevice effect. The preference site of pitting was intermetallic–Al interface [13].

Surface examination of sample revealed several stages of corrosion attack. Initially, pitting on the sample occurred preferentially around the base metal surrounding the hypereutectic Si [14]. The cathodic side was hypereutectic Si and/or the intermetallic precipitate [13]. At side where uniform corrosion was evident, the hypereutectic Si was seen to protrude slightly from the surrounding Al. Some pitting was seen to occur at the side of hypereutectic Si.

3.6 Electrochemical test

Figure 7 shows the graph of electrochemical test. The results of electrochemical test in aerated 5.0% NaCl solution with the corrosion potentials (E_{corr}) of - 680 mV, corrosion current (i_{corr}) of 6.28 A/cm² and the corrosion rate (CR) of 3.93×10^{-2} mm/year are presented in Table 3. Corrosion rate measured in electrochemical test was lower than immersion test. These results were expected because of the lesser concentration of oxygen ions in the solution. Thus, measure corrosion rate from the immersion test was taken after 4 weeks and the corrosion rate from electrochemical testing is only for the period of the electrochemical test.

3.7 Hardness test

Hardness measurement was taken before and after immersion corrosion test. The sample preparation and hardness measurement were carried out in accordance with [10]. Figure 8 presents the hardness of LM30 immersed in 5% NaCl. The hardness of LM30 decreased as immersion time increased. This was due to the change in microstructure of the material and pitting that occurred in the surface of specimen.

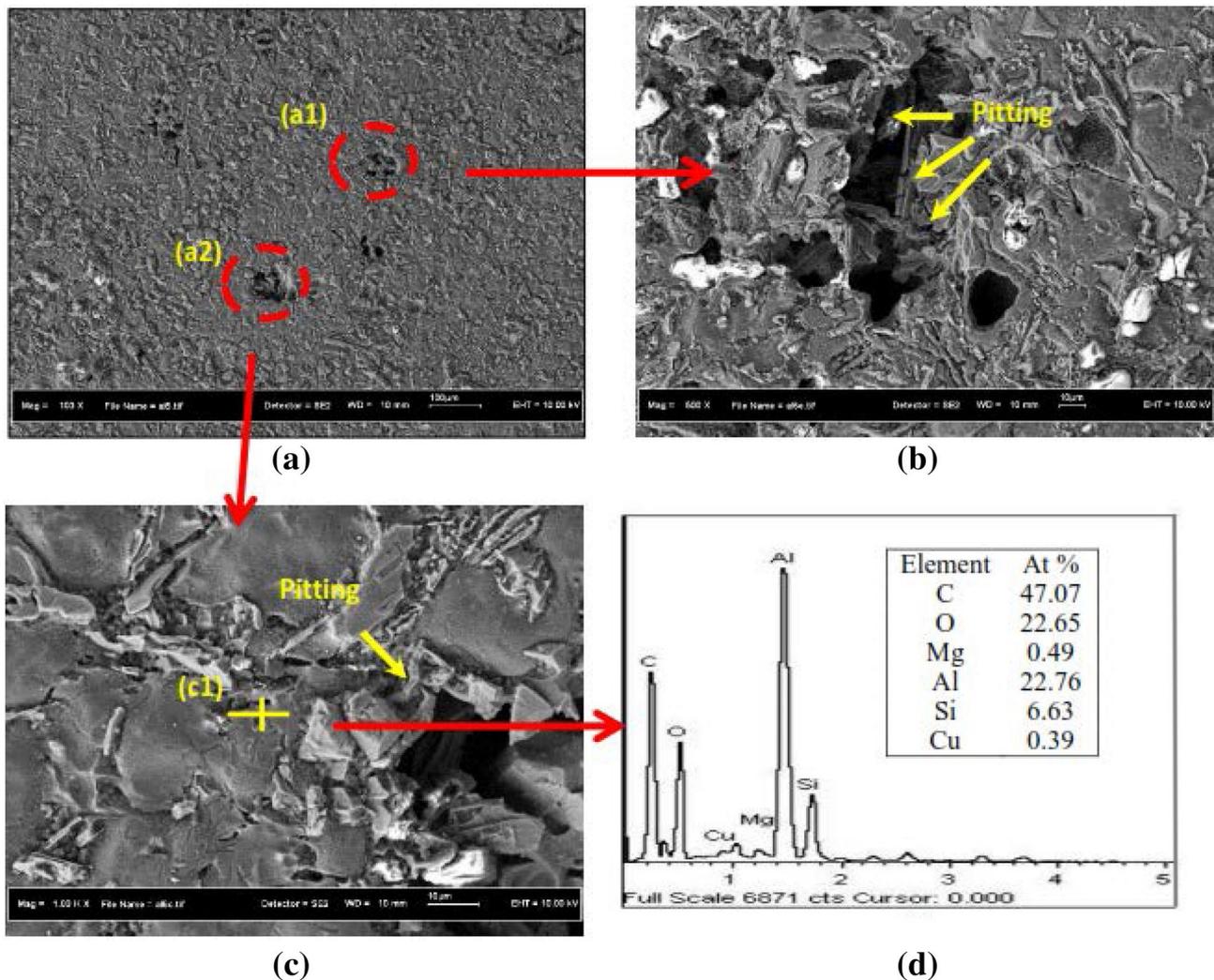


Fig. 6 SEM micrographs of LM30 after immersion test in 5.0% NaCl solution for 21 days; **a** with low magnification; **b** area of a1 with high magnification; **c** area of a2 with higher magnification; **d** EDX spectrum of area c1

4 Conclusion

This scrap metal of BMW 5 series piston head was confirmed as LM30 (Al-Si₁₇Cu₄Mg) cast aluminium alloy with hypereutectic Silicon. The corrosion rate of LM30 showed increase for a period of time and then decrease as exposure time increases for immersion corrosion test. From SEM/EDX studies, it was found that the metal corrodes uniformly and suffers from localized attack, namely pitting. The hardness of LM30 showed decreases as expose time increases for immersion corrosion test. The corrosion rate of immersion test was higher than electrochemical test for interval time.

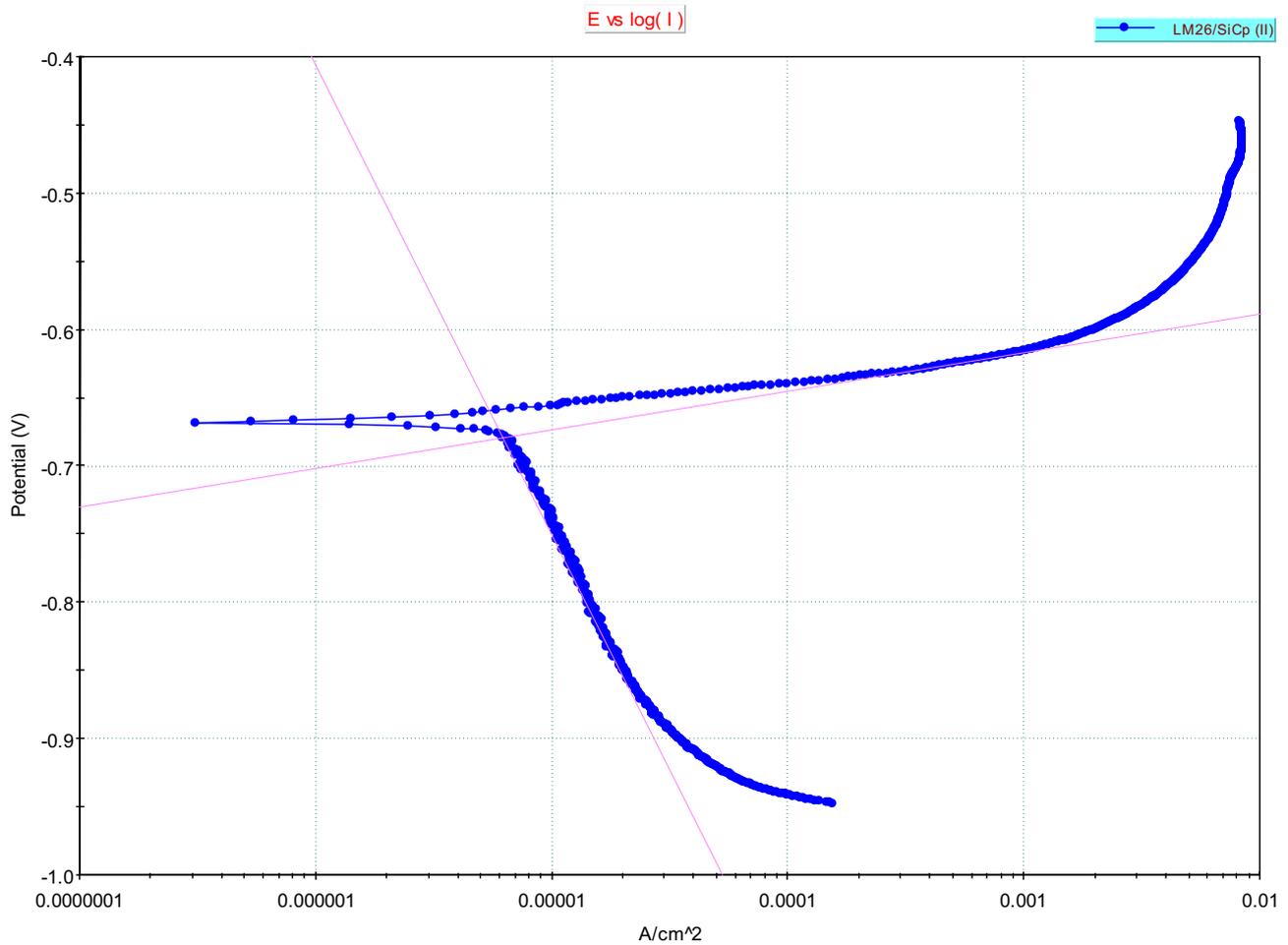


Fig. 7 Electrochemical behaviour of LM30 5% aerated NaCl solution

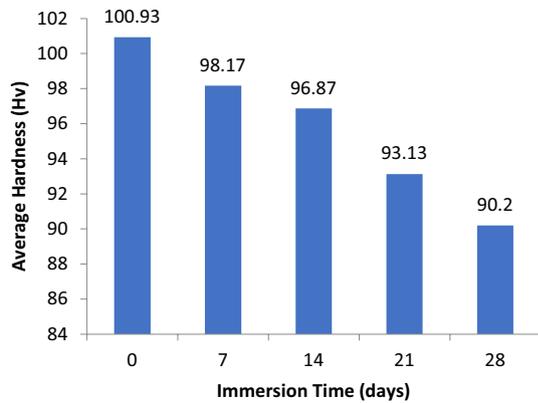


Fig. 8 Average hardness (Hv) of LM30 before and after immersion corrosion test in 5.0% NaCl solution from 0 to 28 days

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Compliance with Ethical Standards

Conflict of interest On behalf of all authors, I state that there is no conflict of interest.

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