Corrosion Characterisation of Al-Cu Reinforced In-Situ TiB$_2$

R. *Rosmamuhamadani*[1,*], S. *Sulaiman*[2] , M.A. *Azmah Hanim*[3] , M.I.S. *Ismail*[4] , M.K. *Talari*[5], and *Sabrina* M. Yahaya[6]

[1,2,3,4]Mechanical and Manufacturing Department, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.

[5]Materials Technology Programme, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia.

[6]Applied Chemistry Programme, Faculty of Applied Sciences, Universiti Teknologi MARA, 40150, Shah Alam, Selangor, Malaysia

Abstract. Aluminium (Al) based in-situ metal matrix composites (MMCs) have better properties and performance compared to ex-situ MMCs. In this research, aluminium-copper (Al-Cu) alloy was reinforced with 3 and 6wt.% titanium diboride (TiB$_2$). Al-MMCs has been fabricated with salt route reaction process at 800 °C via potassium hexafluorotitanate (K$_2$TiF$_6$) and potassium tetrafluoroborate (KBF$_4$) salts. Hardness vickers tester and Gamry-Electrod Potentiometer were used to characterize the hardness properties and to determine the corrosion rate of Al-Cu alloys. From results obtained, increased TiB$_2$ contents will increase the hardness of Al-Cu alloys. Increased of TiB$_2$ contents also will increase the corrosion rate of Al-Cu alloys. Al-Cu with 3wt.%TiB$_2$ gave the good properties of corrosion when the wear rate recorded the lowest value compare to Al-Cu alloy itself and 6 wt.% TiB$_2$. The corrosion rate of Al-Cu with 3wt.TiB$_2$ was 16.15, while Al-Cu and Al-Cu-6wt%TiB$_2$ were 22.5 and 58.7 mm/y respectively.

1 Introduction

Al is the most popular matrix for MMCs. Al-MMCs has a wide application in the fields of aerospace, automobile and so on, because of their high specific strength, rigidity, wear resistance and good dimensional stability [1].

Recently, *in-situ* techniques have been developed to fabricate Al-based MMCs, which can lead to better adhesion at the interface and hence better mechanical properties. These *in-situ* routes provide many advantages such as the *in-situ* formed reinforcement phases are thermodynamically stable, disperse more uniformly in matrix, free of surface contamination and leading to stronger particle matrix bonding [2].

All metals and alloys undergo corrosion, which is defined as the destructive attack of a metal by the environment, by chemicals, or electrochemical processes [3]. The driving force is the free energy of reaction of the metal to form, generally, a metal oxide. Since

---

[*] Corresponding author: rosma614@salam.uitm.edu.my

corrosion reactions generally occur on the metal surface, they are called interfacial processes. The corrosion process takes place at the metal medium phase boundary and therefore is a heterogeneous reaction in which the structure and condition of the metal surface have a significant role. The corrosive medium must be transported to the surface and the corrosion products removed. Therefore, material transport phenomena, including free convection and diffusion into adjacent surface layers, must also be taken into account. Metallurgical factors that can affect corrosion in an alloy include: crystallography, grain size and shape, grain heterogeneity, impurity inclusions, and residual stress due to cold work.

The influence of nitric acid (HNO3-) on corrosion of the Al-Cu alloys, containing 1.3-30 at.% Cu have been studied [3]. They found the corrosion rates of the Al-1.3 at.% Cu and Al-2.7 at.% Cu alloys in HNO3- were be ~5 and 10 nm min−1 respectively. The corrosion of an Al-30 at.% Cu alloys was less uniform, with a local rate to ~13 nm s−1. Meanwhile [4] have studied the pitting corrosion of ClO4- on pure Al, Al-2.5 wt% Cu and Al-7 wt% Cu alloys in 1.0 M Na2SO4 solution at 25 °C. The susceptibility of the three Al samples towards pitting corrosion decreases in the order: Al>Al-2.5 wt% Cu>Al-7 wt% Cu.

Potentiostatic measurements showed that the rate of pitting initiation increases with increasing ClO4- ion concentration and applied step anodic potential, while it decreases with increasing Cu content. The corrosion behavior of pure Al, Al-6% Cu and Al-6% Si alloys in Na2SO4 solutions in the absence and presence of NaCl, NaBr and NaI were studied [5]. The corrosion resistance increases in the order Al<Al-6%Cu<Al-6%Si. The chloride ion showed the highest aggressiveness. The purpose of their work is to investigate the influence of Cu addition on the mechanical properties and corrosion resistance of commercially pure aluminum.

Cu addition on the mechanical properties and corrosion resistance of commercially pure Al have been investigated [6]. They studied the influence of Cu addition to commercially pure aluminum on microstructure, microhardness, grain size, impact energy, flow stress at 0.2 strain, mechanical behavior and corrosion resistance. Three different Al-Cu alloys of 3,6 and 9 wt.% Cu content were 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, 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.

2 Methodology

2.1 Composite Fabrication

Al-6wt.% Cu was respectively melted at 720 °C in an induction furnace. The melts were homogenized for 15 minutes before added the salts which were K_2TiF_6 and KBF_4. These salts then were pre-heated to 250 °C for 1 hour. After melting of the base metals, the two salts were slowly added into the molten Al-6wt.% Cu in an atomic ratio in accordance with TiB_2 by using the stirring method.

2.2 Heat Treatment

The aging behaviour of the composites was studied by solutionising the samples at 540 °C for 2 hours followed by quenching in cold water and aging at 170 °C for different intervals. The composites subjected to age were tested their hardness properties within 48 hours regarding to [7] specifications.

2.3 Hardness Test

Vickers hardness is one of a method to measure the hardness of a material. Vickers test procedure as per [7] standard specifies making indentation with a range of loads using a diamond indenter which is then measured and converted to a hardness value.

2.4 Corrosion Characterization

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. 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 0.5 M NaCl solution. The NaCl 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.

3 Results and Discussion

3.1 Hardness Properties

Hardness is one of the most important properties, which is commonly used to give a general indication of the strength and resistance to wear and scratching of a material. It can be defined as the ability of a material to resist permanent indentation or deformation when it is in contact with an indenter under load.

Table-1. Vickers hardness properties of un-aged and aged Al-Cu with different TiB_2 contents

Materials	Vickers Hardness Al-Cu alloy (Hv)		
	Un-aged	Aged (540 °C, 2h)	Aged (150 °C, 48h)
Al-Cu	125	136	174
Al-Cu-3wt.% TiB_2	134	142	175
Al-Cu -6wt.%TiB_2	141	152	150

For Vickers hardness, as references, the initial hardness of un-aged Al-Cu was 113 Hv for 5 N load. Similar trend can be shown in aged Al-Cu which was 136 Hv. Both of un-aged and aged-Al-Cu alloys, the value of hardness increased when TiB_2 contents increased.

The hardness of un-aged Al-Cu-6wt.%TiB$_2$ were recorded 125 with 5 N load, while aged Al-Cu-6wt.%TiB$_2$ were 152 Hv. The addition of TiB$_2$ resulted in an increased of the hardness of Al-Cu alloy. The increase in hardness of the composites can be attributed to the decrease in the grain size to TiB$_2$ particles. It is evident that addition of TiB$_2$ leads to significant increment in the hardening by the precipitates, which can be attributed to additional strengthening due to coherency strains and misfit dislocations formed by the precipitation on TiB$_2$ particles. These results then are illustrated graphically in Table 1 and Figure 1 below.

The properties of a metal are strongly influenced by the grain size and the well-known Hall–Petch equation. It predicts an increase in yield strength with a decrease in grain size (d). This equation has been shown to be applicable to a wide variety of metals.

$$\sigma_y = \sigma_0 + kd^{-1/2}$$

(1)

Where σy, σo, and k is yield strength, friction stress and a constant respectively. In the as-cast condition, the hardening of the Al–Cu–TiB$_2$ composites can be attributed to the fine TiB$_2$ particles and reduction in grain size (due to grain refinement by TiB$_2$). In the case of solutionised composites, the hardness is governed by solid solution strengthening, in addition to Hall-Petch hardening and hardening from TiB$_2$ particles. The increase in the hardness of the solutionised composite with increase in fraction of TiB$_2$ particles clearly gives the contribution of TiB$_2$ particles to the hardness of the composites.
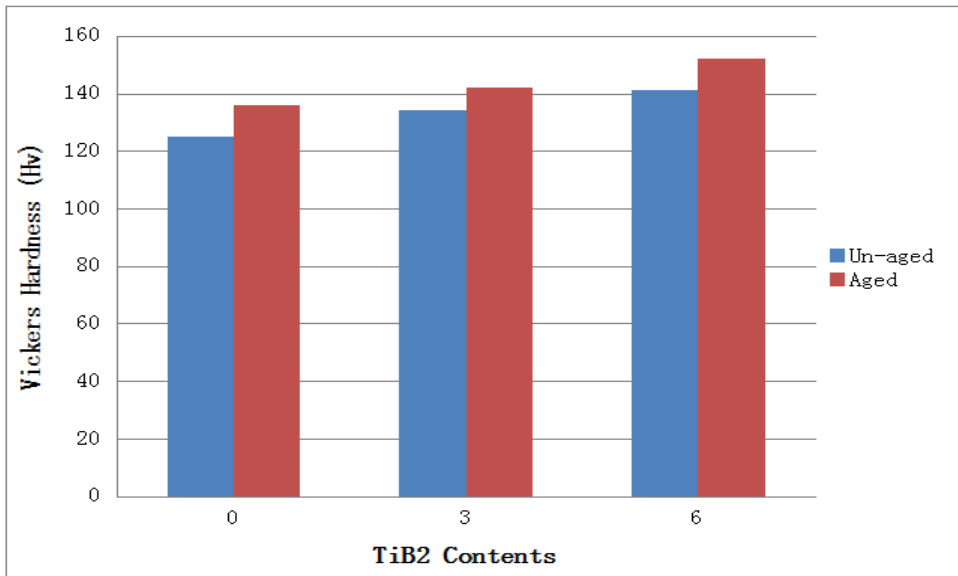

Fig. 1. Vickers hardness (Hv) of Al-Cu with different TiB$_2$ contents with 5N loads

3.2 Effect of ageing

Thus, the presence of higher amount of TiB_2 particles enhances the aging kinetics of Al–Cu alloy. The increase in aging kinetics in presence of TiB_2 particles could be attributed to the possible nucleation of the precipitates of Al2Cu on the basal planes of the TiB_2 particles. In addition, the difference in the coefficient of thermal expansion between Al (23.5×10^{-6} K−1) and TiB2 (7×10^{-6} K−1) causes the development of strain field at the interface between the reinforced particle and the matrix, which leads to an increase in the dislocation density. These dislocations can also act as nucleating sites during precipitation. From the research, tensile strength and Vickers hardness gave highest value compare alloy without aged.
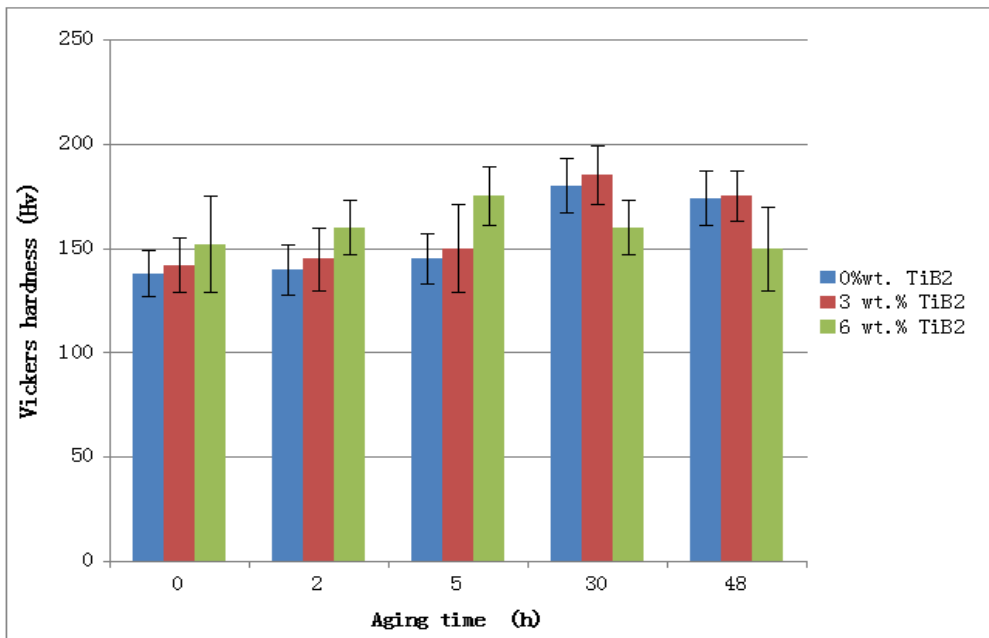

Fig. 2. Hardness of Al-Cu with different TiB_2 contents after aged for 48 hours

Fig. 2 above shows the age hardening response of the base Al-6Cu alloy and its composites. It is clearly evident from the figure that the peak hardness for Al-6Cu, Al-6Cu-3wt.%TiB2 and Al-6Cu-6wt.%TiB_2 were reached at 30, 30 and 5 hours, respectively. The figure also shows that the peak hardness increases with increasing reinforcement TiB_2 content (wt.%). The hardness of Al-6Cu alloy increases from 170 Hv in the base alloy to 188 Hv for the 6TiB_2 composite at optimum peak. Thus, the TiB_2 particles not only increase the hardness but also enhance the aging kinetics of Al-6Cu alloy.

3.3 Corrosion Characterization

Polarization is the displacement of an electrode potential from its equilibrium value and the magnitude of this displacement is the overvoltage which is expressed in terms of plus or minus volts (or mV) relative to the equilibrium potential. Potentiostatic polarization can be used to calculate the electrochemical parameters. Anodic and cathodic polarized potentials were measured to a reference sample and Al-Cu alloys in 0.1 M HCl solution in current density range of 2 to 6 mA/cm2 as shown in Figure 3. The electrochemical parameters;

corrosion potential (Ecorr), corrosion current (Icorr) and corrosion current density (in nm/s) were calculated from Figure 3 and summarized in Table 2. Corrosion potential decreases with increasing the TiB2 content in the alloys. The corrosion current decreases with increasing the TiB2 content reaching a minimum at 3 wt. %TiB$_2$ and then begin to increase with increasing the TiB2 content.

Table 2. Electrochemical parameters for Al-Cu with different TiB$_2$ alloys in 0.1 M HCl solution

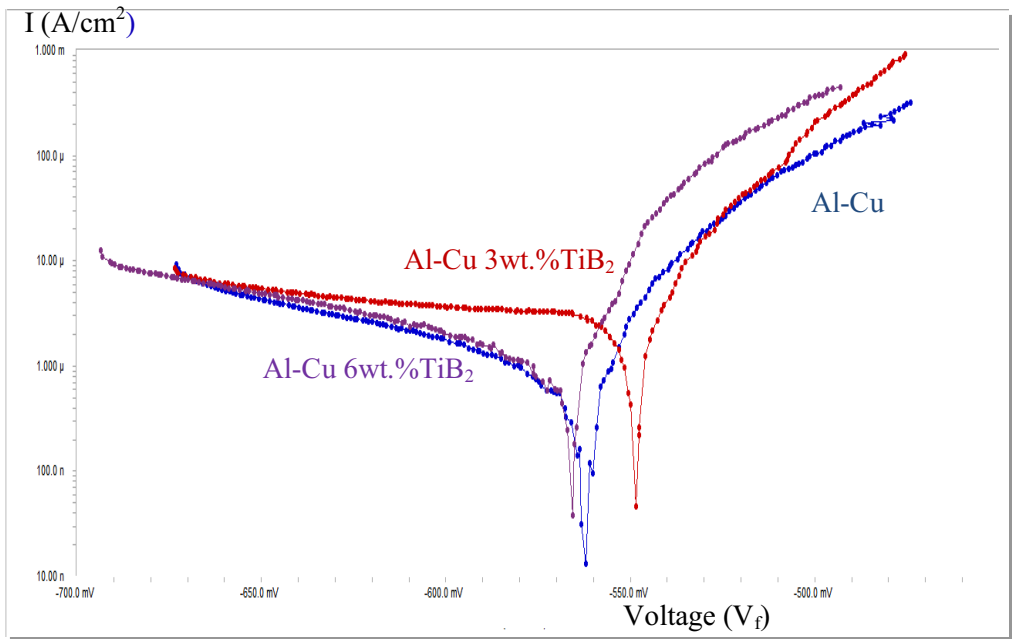| TiB$_2$ [%]	E$_{corr}$ [mV] (10^{-6})	I$_{corr}$ [mA/cm²] (10^{-3})	CR [mm/y]
0	-568.0	1.942	22.50
3	-566.0	1.39	16.15
6	-574.9	5.06	58.7

Fig. 3. Anodic and cathodic polarized curves of Al-6wt.%Cu alloys and Al-6wt.%Cu-TiB$_2$ in 0.5 M NaCl solution

The corrosion current and corrosion rate show an optimal value at 3 wt. %TiB$_2$. Addition of TiB$_2$ has a positive influence on the corrosion resistance in Al. This behavior can be attributed to the positive influence of TiB$_2$ addition on the grain size refinement. The fine grained materials have a more advantageous behavior with respect to corrosion and oxidation have been approved [8].

From Figure 3 above, Al-6wt.%Cu alloy with 3wt.%TiB_2 showed the best corrosion resistance compare to other composition of TiB2. The value of corrosion rate at 3 wt.% TiB2 was 16.15 x 10^{-3} mm/y, then decrease to 58.8 x 10^{-3} mm/y for Al-Cu with 6wt.%TiB2. The susceptibility of the Al-Cu alloys towards corrosion decreases in the order of:

$$Al\text{-}Cu\text{-}3wt.\%TiB_2 > Al\text{-}Cu > Al\text{-}Cu\text{-}6\ wt\%TiB_2 \qquad (2)$$

The lowest value of corrosion rate exhibit the alloy has a good property to withstand the corrosion.

4 Conclusions

From the research, we can conclude several conclusions which are;

i. *In-situ* Al-Cu alloy composites containing different weight fractions of particles of TiB_2 phase were synthesized successfully by the salt-metal reaction method and the particles were distributed evenly in the matrix of the composites.

ii. The susceptibility of the Al-Cu alloys towards corrosion decreases in the order of: Al-Cu-3wt.%TiB_2> Al-Cu> Al-Cu-6 wt%TiB_2.

iii. The composition of 3wt.%TiB_2 gave the best corrosion rate compare to cast Al-Cu alloy which were 16.15 and 22.50 x 10^{-3} mm/y.

References

1. S. Kumar, M. Chakraborty, V.S. Subramanya, B.S. Murty, Wear, **265**, 134 (2008)
2. H. Wang, L. Guirong, Z. Yutao, C. Gang, Mater. Sci. Eng., A **527,** 2881 (2010)
3. Y. Liu, M.A. Arenas, A. de Frutos, J. de Damborenea, A. Conde, P. Skeldon, G.E. Thompson, P. Bailey, T.C.Q. Noakes, Electrochim. Acta, **53**, 4454 (2008)
4. M.A. Amin, S.S. Abd. El-Rehim, S.O. Moussa, A.S. Ellithy, Electrochim. Acta, **53,** 5644 (2008)
5. S.S. Abdel Rehim, H.H. Hassan, M.A. Amin, Appl. Surf. Sci., **187**, 279 (2002)
6. A.E. Al-Rawajfeh, S.M.A. Al-Qawabah, Emirates Journal for Engineering Research*,* **14**, 47 (2009)
7. *Standard Test Method for Vickers Hardness of Metallic Materials*, **82** (ASTM E92, 2003)
8. K.T. Kashyap, T. Chandrashekar, Bull. Mater. Sci., 2**4**, 345 (2001)