Electrochemical corrosion behavior of $Al_{18}B_4O_{33}$w/Al composite

J. HU
School of Materials Science and Engineering, Harbin Institute of Technology, P.O. BOX 433 Harbin 150001, People's Republic of China; Department of Materials Physics, University of Science and Technology, Beijing, Beijing 100083, People's Republic of China
E-mail: mzhu@hope.hit.edu.cn

K. TIAN
School of Materials Science and Engineering, Harbin Institute of Technology, P.O. BOX 433 Harbin 150001, People's Republic of China

W. Y. CHU
Department of Materials Physics, University of Science and Technology, Beijing, Beijing 100083, People's Republic of China

The effects of the volume fraction of alumina borate ($Al_{18}B_4O_{33}$) whisker and the scan rate of potentiodynamic technique on the localized corrosion behaviors of $Al_{18}B_4O_{33}$w/Al composite were investigated. Potentiodynamic polarizations and cyclic polarizations were performed to examine the electrochemical corrosion behavior of the composites. The surface morphologies of the as-cast composite were observed by optics microscopy and the surface morphologies of the composite after corrosion tests were observed by scanning electronic microscopy (SEM). The results of electrochemical measurement indicated that the anodic passive region reduced with the increasing in the volume fraction of $Al_{18}B_4O_{33}$ whisker in the composites (at the same scan rate), and the anodic passive region reduced with the decreasing in the scan rate of potentiodynamic technique (in the same volume fraction of whisker). The results of cyclic polarization indicated that increase in the volume fraction of $Al_{18}B_4O_{33}$ whisker in the composites results in a significant decrease of protection potential and an increase of the area of cyclic hysteresis loop.

1. Introduction

With the recent focus on high properties and low cost metal matrix composites (MMCs), the emphasis has shifted towards short fiber reinforcements [1]. MMCs fabricated with lightweight aluminum and high modulus reinforcements offer excellent structural properties. However, addition of reinforcements to aluminum will change the corrosion behavior significantly [2]. Therefore, the attention given to its corrosion behavior has gradually increased in recent years.

Pitting represents one of the most common forms of corrosion for aluminum matrix composites, particularly in solutions containing chloride ions. Several corrosion studies on MMCs have been reported in the literature [3–5] and it is generally regarded that the reinforcement additions are detrimental to corrosion resistance. In electrochemical tests performed on AA6061 and SiCw/AA6061 by Aylor and Moran [6], they observed similarities of open-circuit potentials (E_{corr}) between the composite and the matrix alloy, which suggested that E_{corr} was not affected by the presence of SiC whisker in the composite. They suggested that the presence of SiC did not increase the susceptibility of the aluminum oxide film to breakdown. Other studied also revealed that the increasing in the size or volume fraction of reinforcement did not alter E_{corr} or pitting potentials (E_{pit}) very much for some composites [7]. In accelerated immersion tests in a sodium chloride-hydrogen peroxide environment Metzger [8] reported that pitting corrosion occurred around the reinforcement/matrix interface in Al_2O_3w reinforced Al-2 wt%Mg MMCs; whereas the unreinforced materials was relatively unaffected. This was attributed both to the formation of a magnesium-aluminum intermetallic, Mg_5Al_8, which suffered rapid corrosion even below the pitting potential (E_{pit}) of the matrix, and the enhance magnesium concentration of the local solid solution, which lowered the corrosion potential of the matrix.

Aylor and Moran found SiCp/AA6061 and SiCw/AA6061 immersed in sea water exhibited pitting concentrated around SiC [6]. McIntyre *et al.* [9] and Aylor and Kain [10] found that crevices formatted at the SiC/Al matrix interfaces by metallographic analysis. They considered that theses represented preferential sites for attack. But other investigations had reported that the SiC/Al interface did not act

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as a preference sites for attack [3, 11, 12]. Some studies reported that pitting has been observed in the Al matrix, at the SiC/Al matrix interface. These investigations also revealed that the pit concentration was higher and more uniformly distributed over MMC samples, presumably because of the greater number of active sites. It can only be assumed that differences in the materials and fabrication are responsible for the discrepancies observed in the different investigations.

Although research has been carried out on the corrosion behaviors of composites, limited information is available regarding the pitting behavior of $Al_{18}B_4O_{33}$w/Al composite in sodium chloride solution.

2. Experimental

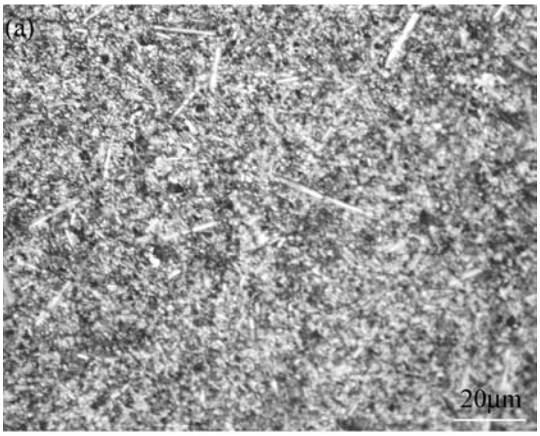
The composite used in this study was fabricated by squeeze casting. The matrix is pure aluminum. The reinforcement is $Al_{18}B_4O_{33}$ whisker with a diameter of 0.5–1 μm and length of 10–30 μm; the volume fraction of the whisker is about 15, 25 and 35%, respectively. The preheating temperature of the mode and perform was about 500°C, and the melting pure aluminum was 750–800°C, die pressure was about 100 MPa.

Potentiodynamic polarization tests were carried out on cylindrical specimens (15 mm diameter and 5 mm height) and wet-ground with silicon carbide (SiC) paper up to 1000 grit and cleaned with acetone in an ultrasonic bath. A potentiostat and the ASTM standard cell with a saturated calomel reference electrode (SCE) and a graphite counter electrode were used. Tests were performed at room temperature in 3.5%NaCl solution. Polarization curves were obtained potentiodynamically, the potential was swept at various scan rate such as 10, 20 and 30 mVmin^{-1} from -1400 to -500 mV (SEC). The electrochemical behavior was examined using cyclic polarization technique in the same corrosion condition. The polarization behavior was examined for the potential range -1400 to -500 mV(SEC) and then the scanning was reversed in the cathodic direction. At least three separate samples were tested for each measurement.

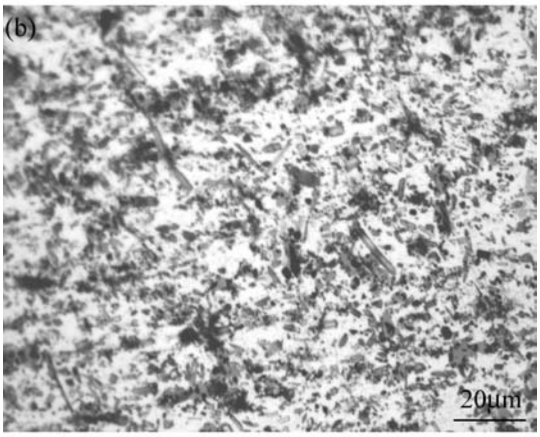
3. Results and discussions

3.1. Microscopic observation

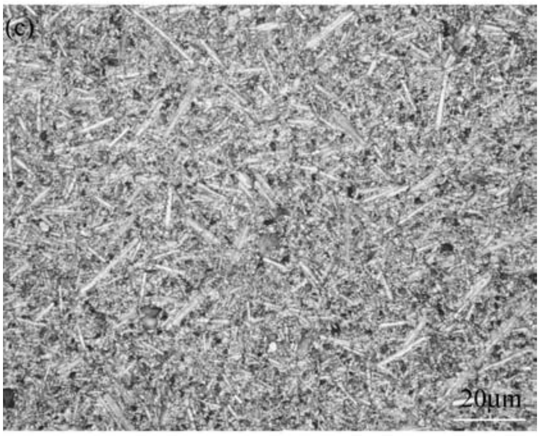
The composite microstructures are shown in Fig. 1. It can be seen that the whisker is uniformly distributed in the composite for all composites studied. As at increasing reinforcement volume fraction some hole can be found in the composite (as shown in Fig. 1b and Fig. 1c) that some porosity occurred.



(a) $Al_{18}B_4O_{33}$w/Al composite (V_f = 15%)



(b) $Al_{18}B_4O_{33}$w/Al composite (V_f =25%)

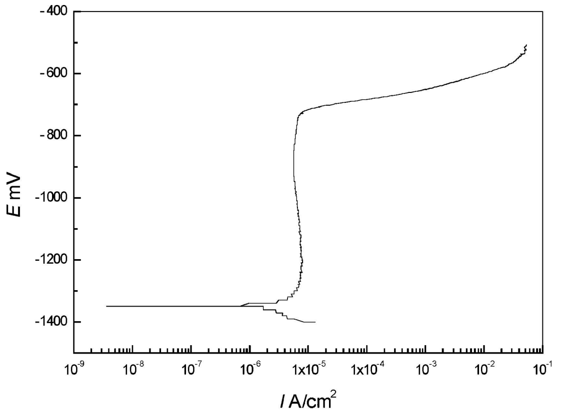


(c) $Al_{18}B_4O_{33}$w/Al composite (V_f = 35%)

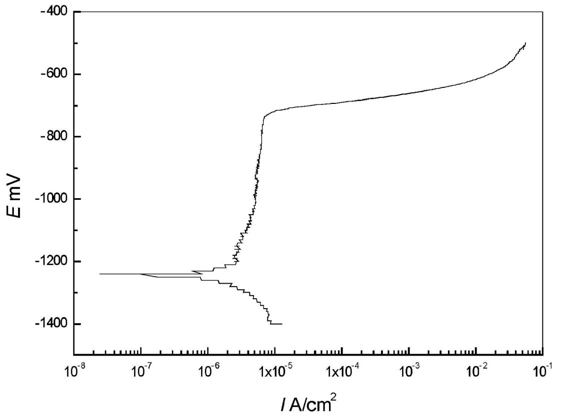
Figure 1 Microstructures of as-cast composites.

3.2. Polarization experimental

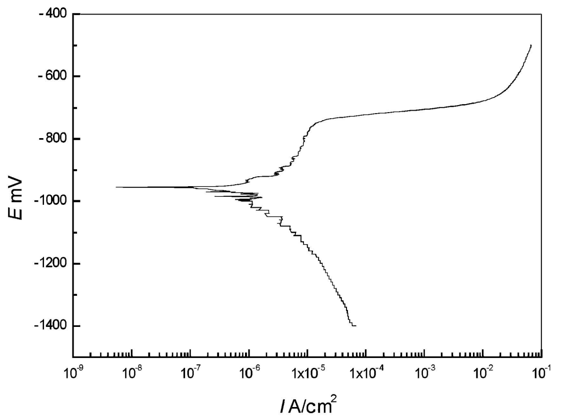
Typical polarization curves with various volume fractions of the whisker in the composites are shown in Fig. 2. These curves show that the pitting potential is independent of the amount of $Al_{18}B_4O_{33}$ whisker. All curves had the similar form for the composites with lower volume fraction of the whisker (such as 15 and 25%) that an obvious passive region exists in the anodic polarization curve of the composites when various scan rates was applied. However, the limited passive region exists in the anodic polarization curve of the composite with 35% reinforcement volume fraction, and the passive region almost disappears with increasing in scan rate. The values of E_{corr}, E_{pit} along with $E_{pit} - E_{corr}$ at various scan rates was shown in Table I. Effects of the volume fraction of $Al_{18}B_4O_{33}$ whisker (V_f) and the scan rates of potentiodynamic technique on the electrochemical behaviors were demonstrated. The parameter $E_{pit} - E_{corr}$ is a measure of the extent of the passive region on the polarization curve and provides an indication of the susceptibility to pitting. From Table I, it



(a) $Al_{18}B_4O_{33}$w/Al composite (V_f= 15%)



(b) $Al_{18}B_4O_{33}$w/Al composite (V_f= 25%)



(c) $Al_{18}B_4O_{33}$w/Al composite (V_f= 35%)

Figure 2 Potentiodynamic polarization curves for the $Al_{18}B_4O_{33}$w/Al composites.

can be found that the extent of the passive region has been reduced from 630 to 330 mV for 15% composite, from 490 to 230 mV for 25% composite and from 160 to 0 mV for 35% composite with increasing in scan rate. The extent of passive region has also been reduced with increasing in volume fraction of the whisker at same scan rate. It suggested that volume fraction of the whisker and scan rate have an important influence on the susceptibility to pitting for $Al_{18}B_4O_{33}$w/Al composite.

Some pits can be seen by SEM observation on all three corrosion surfaces. At higher magnifications, large number of whiskers had been found in the pits for all specimens studied. Fig. 3 is the microstructures of the corrosion surface of the composite with 15% reinforcement volume fraction.

3.3. Cyclic polarization experimental

Fig. 4 compares the polarization behavior of the composites with various volume fraction of the whisker. An obvious change has occurred in protection potential, E_{rp}, the value increase with decreasing in volume fraction of the whisker. Reversal of the scan from potentials above E_{pit} cause the current to fall back to the level of the passive current (on the forward scan) at E_{rp}, and then decrease further as the corrosion potential was approached. But the E_{rp} value is lower than E_{corr} for 35% composite. From Fig. 4, it can be found that a very narrow hysteresis loop exists in the polarization curve of 15% composite, as the whisker volume fraction increase, a large loop was obtained. The area of the hysteresis loop is related to the amount of pit propagation that occurs during the potential sweep. The more the area of hysteresis loop, the more the susceptibility to location corrosion; the higher the protection potential, the better the capacity of passive film to repair by itself.

4. Discussion

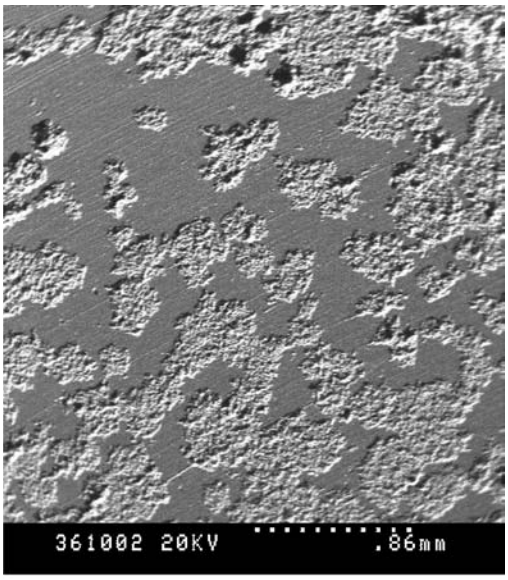
The experiments showed that addition of $Al_{18}B_4O_{33}$ whisker to pure aluminum significantly affected the corrosion behavior of the composite. The trend was in agreement with some researcher's report, that aluminum matrix composite showed a greater susceptibility to pit initiation than unreinforced aluminum alloy [8, 13].

It is generally accepted that no corrosion occurred in NaCl solution for pure aluminum due to a compact oxide film covered the surface of pure aluminum. The corrosion characteristics of $Al_{18}B_4O_{33}$ w/Al composites can be considered from the effect of the interface between whisker and matrix and its microstructure.

Anodic dissolution should occur at the place where the energy densities and the chemical potential were high, such as the dislocation tangle, the point of

TABLE I Summary of polarization tests

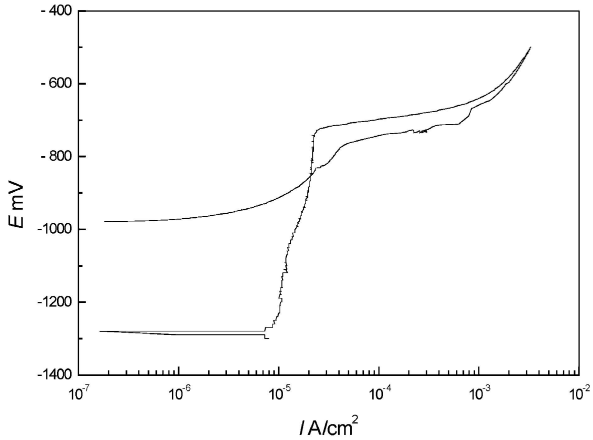
	E_{corr} (mV) Scan rate (mVmin^{-1})			E_{pit} (mV) Scan rate (mVmin^{-1})			$E_{pit} - E_{corr}$ (mV) Scan rate (mVmin^{-1})		
$Al_{18}B_4O_{33}$ V_f (%)	30	20	10	30	20	10	30	20	10
15	−1350	−1150	−1100	−720	−770	−770	630	380	330
25	−1210	−1090	−990	−720	−760	−760	490	330	230
35	−910	−880	−770	−750	−810	−770	160	70	0



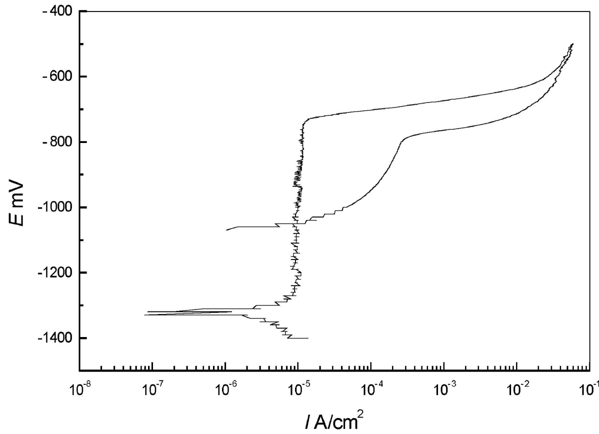
(a) pits in the composite

(b) higher magnification graph of pit

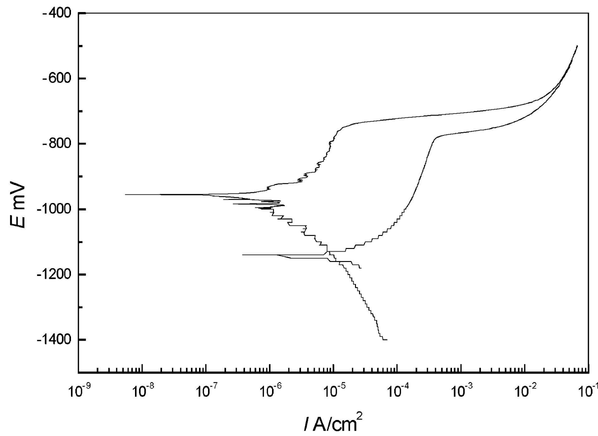
Figure 3 Microstructures of corrosion surface for the composite (V_f = 15%).



(a) $Al_{18}B_4O_{33}$w/Al composite (V_f = 15%)



(b) $Al_{18}B_4O_{33}$w/Al composite (V_f = 25%)



(c) $Al_{18}B_4O_{33}$w/Al composite (V_f = 35%)

Figure 4 Cyclic polarization curves for the $Al_{18}B_4O_{33}$w/Al composites.

emergence of dislocation. Due to the large difference of the thermal expansion coefficient (TEC) between $Al_{18}B_4O_{33}$ whisker and aluminum matrix, as the composite cool down from high temperature, the great difference of TEC will result in a high density of dislocation at the $Al_{18}B_4O_{33}$–Al interface. The interface can act as an active center as the composites are immersed in NaCl solution. In addition, the $Al_{18}B_4O_{33}$w-Al interface in the composite will provide numerous micro crevice sites owing to the poor interface bonding; all of these sites are potential locations for the development of location attacks. The more the volume fraction of $Al_{18}B_4O_{33}$ whisker, the more the interface in the composite, the higher the density of dislocation and the more the number of the micro-cells in the composite, the susceptibility to pit attack of the composite increase continuously with volume fraction of whisker.

The presence of whisker led to the oxide film might be nonuniform. The location oxide film, which is weak, will be thinned by dissolution. In addition, the interface in the composite may be provided numerous micro-crevice sites. The micro-crevice may arise either as a result of poor bonding at the whisker-Al interface or from the presence of cracked whisker. These sites are potential locations for the development of location attacks. Pits preferred nucleation at interface owing to the difference of chemical potential or the formation of crevices.

When the volume fraction of whisker is lower, the defective passive film on the surface of the composite was little; once the films of surface break they can be repair as soon as. The E_{rp} is higher and the area of hysteresis loop is smaller, the density of pits on the surface is low.

The active sites increase with volume fraction of the whisker, the breakdown of the oxide film is easy, the stability of passive film of surface decreased. The electrochemical reaction between composite and corrosion solution resulted in the increasing of the density of pits, the number of pits on the surface of the composite was more. Thus, the susceptibility to pitting increased gradually with the volume fraction of whisker. When the volume fraction of the whisker is 35%, the surface of the composite was corroded badly, which means that the process may be slow to repassivate. Once the passive film breaks, they do not repair themselves easily, so its E_{rp} is the lowest and the area of hysteresis loop is the largest.

The increase in scan rate will reduce the interactional time between the composites and the corrosion medium, so relative corrosion degree on the surfaces of the samples decreases, the sensibility of location corrosion decreases. Moreover the increase in scan rate will reduce the corrosion test time and further weaken the affect of crevice corrosion at the interface between whisker and aluminum on the measurement of pitting. Therefore, it has been found that the composite in same volume fraction of the whisker show increased susceptibility to pitting attack with decrease in scan rate.

5. Conclusions

1. The addition of $Al_{18}B_4O_{33}$ whisker reinforcement to pure aluminum showed increased susceptibility to pitting attack compared with unreinforced aluminum in 3.5%NaCl solution.

2. The passive region reduced and the stability of passive film of surface decreased and the number of active sites increased as the volume fraction of whisker increased. Increased in the whisker volume fraction resulted in a significant decreased in E_{rp} and a significant increased in the area of hysteresis loop led to the susceptibility of $Al_{18}B_4O_{33}$w/Al composite to pitting increased.

3. In same whisker volume fraction, the susceptibility to pitting attack increased with scan rate decreased for $Al_{18}B_4O_{33}$ whisker reinforced pure aluminum composite.

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