Corrosion susceptibilities of Al-Cu/TiC MMCs fabricated by conventional hot pressing

Mehmet Gavgali
Burak Dikici & Fevzi Bedir

aDepartment of Mechanical Engineering, Ataturk University, 25240 Erzurum, Turkey
bErcis Technical Vocational School of High Education, Yuzuncu Yil University, 65400 Ercis-Van, Turkey
cDepartment of Mechanical Engineering, Suleyman Demirel University, 32260 Isparta, Turkey

Received 21 August 2006; accepted 23 May 2007

The effect of TiC particle volume fraction on the electrochemical behaviours of metal matrix composites (MMCs), which is Al-Cu based reinforced with TiC, has been investigated in both aerated and deaerated 1.0 N H₂SO₄ aqueous solutions. Composites reinforced with TiC particles at volume fractions of 20, 30 and 40% have been produced by conventional hot pressing method and then, artificially aged (T6). The corrosion susceptibilities of the composites have been analyzed by using the cyclic potentiodynamic polarization technique. The surface morphology of the composites has been determined by scanning electron microscopy (SEM). The results show that the corrosion susceptibilities of the composites increase with increased TiC particle content but decreases with T6 heat treatment performed on the composites.

IPC Code: C22F, C22C 47/00

Aluminum alloys and aluminum based metal matrix composites (AMMCs) are important materials to use in many applications, such as automobiles, aviation, household appliances, containers, and electronic devices, owing to their many favorable characteristics including their high electrical and thermal conductivities, low density and high ductility. Nowadays, the production and potential applications of particle reinforced aluminum-based metal matrix composites (AMMCs) have greatly increased with technological developments. However, researchers have focused on producing high volume-low cost MMCs. TiC particle is particularly useful as a component for MMCs because of their hardness, good wear resistance, the high strength/density ratio and high temperature stability. As well known, the corrosion resistance of aluminum is provided with oxide film formed by anodization on metal surface in acidic solutions. Protectiveness can be altered according to (i) morphology of oxide film, (ii) electrical conductivity of reinforcement and (iii) heat treatment type performed on composites. Therefore, the addition of a reinforcing phase in matrix causes discontinuities or defects in surface oxide film, and hence increases the regions for pitting initiation.

Further, when an alloy element such as Cu is added to this matrix, intermetallic phase (Al₂Cu) is formed by aging affects, and then negatively oxidation resistance and porosity of oxide occur. Some research groups reported that the corrosion inhibition of aluminum alloys is provided by SO₄²⁻ anions in H₂SO₄ solutions because this compound can be adsorbed on the aluminum surface and can block the active pits. Thus, the corrosion rate decreases. The main problem of these composites is the low adhesion energy of TiC when compared with other Al/ceramic systems above the melting point of the matrix alloy. These results may be important for corrosion science because low wettability causes voids in the matrix/TiC interfaces. In addition, Wood et al. have shown that pitting on both aluminum and stainless steel initiates from flaws in the oxide film and propagates by the ion transport mechanism.

In the literature, the corrosion behaviours of AMMCs are generally determined in the NaCl aqueous solutions. Therefore, the initial purpose of this study was to investigate the corrosion behaviour of hot pressed Al-Cu/TiCp MMCs in acidic media because critical potentials of these composites can be shifted to more noble values due to aggressive anions in acid pH range. However, it was seen that the composites exhibited a peak in the passive areas of potentiodynamic polarization curves differently.

*For correspondence (E-mail: mgavgali@atauni.edu.tr)
conventional behaviour of the matrix alloy. Thus, it was decided to determine the nature and cause of this phenomenon in this study.

Experimental Procedure

The composites reinforced with TiC particles at volume fractions of 20-40% were produced by conventional hot pressing method and then artificially aged (T6). The matrix alloy used in this work was aluminum-based alloy containing 5 wt% Cu. The details of the production method and aging process were given elsewhere.[32]

The electrochemical behaviour of Al/TiC-T6 composites were investigated by potentiodynamic polarization technique. All electrochemical measurements were carried out in accordance with ASTM standard G5-94.[33] The electrochemical behaviour of the composites has been analyzed in aerated 1.0 N H₂SO₄ aqueous solutions at room temperature in a Pyrex glass cell. In the second stage of the study, these tests were also repeated in the deaerated solutions. The potentiodynamic polarization curves were obtained by using an AgCl/Ag reference electrode and a Pt counter-electrode. The exposed area of the samples was about 1 cm². The corrosion tests were performed by using a Wenking PGS95 potentiostat (BANK). The corroded surfaces were examined by using Jeol 6400 scanning electron microscope (SEM).

Results and Discussion

In order to determine the overall porosity content, density measurements were conducted on composites reinforced with different TiCₚ volume ratios. The results are given in Table 1. The difference between the calculated density (Dₛ), which was obtained by using chemical composition of the composites, and experimental density (Dₑ) is due to the existence of porosity in the structure. Calculated density (Dₛ) was derived from Halpin-Tsai equation, while the experimental density (Dₑ) was determined using the Archimedean method. The experimental readings were taken five times to obtain the average values of Dₑ.

\[
\rho_c = \rho_m V_m + \rho_p V_p \quad \ldots (1)
\]

where \(\rho_c\) is the density of the composite, \(\rho_m\) is the density of the matrix alloy, \(\rho_p\) is the density of the reinforcing particle, \(V_m\) is the volume fraction of the matrix alloy and \(V_p\) is the volume fraction of the reinforcing particle.

As seen from Table 1, porosity values in hot pressed condition for all type of composites are in the range of ~0.99 to 1.32%.

The electrochemical behaviour of the specimens was observed both in aerated and deaerated 1.0 N H₂SO₄ aqueous solutions but the results between the two groups were very similar. Therefore, polarization results obtained under the aerated conditions were presented in this study. Typical polarization curves of unaged composites were given in Fig. 1, which shows the effect of reinforced volume fraction on the corrosion resistance of the composites reinforced with 20, 30 and 40% volume fraction TiC particles. In addition, the open circuit \((E_{ocp})\), corrosion \((E_{cor})\), pitting \((E_{pit})\), pitting inhibition \((E_i)\) potentials and corrosion current density \((i_{cor})\) values calculated from these curves were tabulated in Table 2. Interestingly, each of the polarization curves presented a peak in the passive area. As seen from Fig. 1 and Table 2, increasing the TiCₚ content reduces the \(E_{pit}\) and \(E_i\) values but increases the \(i_{cor}\) value from 30 to 65 \(\mu\text{A/cm}^2\).

<table>
<thead>
<tr>
<th>Materials</th>
<th>(E_{ocp}) (mV)</th>
<th>(E_{cor}) (mV)</th>
<th>(E_{pit}) (mV)</th>
<th>(E_i) (mV)</th>
<th>(i_{pas}) (µA/cm²)</th>
<th>(i_{cor}) (µA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-20% TiCₚ</td>
<td>-424</td>
<td>-426</td>
<td>794</td>
<td>1006</td>
<td>210</td>
<td>30</td>
</tr>
<tr>
<td>Al-30% TiCₚ</td>
<td>-453</td>
<td>-460</td>
<td>742</td>
<td>984</td>
<td>300</td>
<td>40</td>
</tr>
<tr>
<td>Al-40% TiCₚ</td>
<td>-415</td>
<td>-407</td>
<td>733</td>
<td>965</td>
<td>500</td>
<td>65</td>
</tr>
</tbody>
</table>

Fig. 1—Potential versus current density curves of unaging composites in the aerated 1.0 N H₂SO₄ solution
In the aging conditions, potentiodynamic polarization curves of the composites are given in Fig. 2. In addition, the $E_{ocp}$, $E_{cor}$, $E_{pit}$, $E_i$ potentials and $i_{cor}$ values calculated from these curves are given in Table 3. The results indicate a decrease in the $E_{pit}$ values with the increased TiC content for the composite. The points of pitting and its inhibition are seen clearly likewise in unaging. Table 3 also demonstrates that, the current density values for all type of materials are very close to each other and approximately 40 µA/cm$^2$ in the aging condition.

Corroded surfaces of the Al-20% and 40% volume fraction TiC composites are shown in Fig. 3. In addition, Fig. 4 shows Cu distribution in the aged conditions for Al-20% and Al-40% volume fraction TiC$_p$ composite. The results of X-ray maps of the

<table>
<thead>
<tr>
<th>Materials</th>
<th>$E_{ocp}$ (mV)</th>
<th>$E_{cor}$ (mV)</th>
<th>$E_{pit}$ (mV)</th>
<th>$E_i$ (mV)</th>
<th>$i_{pas}$ ($\mu$A/cm$^2$)</th>
<th>$i_{cor}$ ($\mu$A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al─20% TiC$_p$</td>
<td>-489</td>
<td>-427</td>
<td>780</td>
<td>974</td>
<td>600</td>
<td>41</td>
</tr>
<tr>
<td>Al─30% TiC$_p$</td>
<td>-481</td>
<td>-478</td>
<td>755</td>
<td>986</td>
<td>400</td>
<td>38</td>
</tr>
<tr>
<td>Al─40% TiC$_p$</td>
<td>-392</td>
<td>-406</td>
<td>750</td>
<td>995</td>
<td>300</td>
<td>40</td>
</tr>
</tbody>
</table>

Fig. 2—Potential versus current density curves of aging composites in the aerated 1.0 N H$_2$SO$_4$ solution

Fig. 3—SEM morphology (a) of 20% vol. TiC$_p$ composite, (b) of 40% vol. TiC$_p$ composite after corrosion test

Fig. 4—X-ray maps of Cu for (a) 20% vol. TiC$_p$, (b) 40% vol. TiC$_p$ composite at T6 condition.

Fig. 5—Preferentially corrosion formed at the around of gas voids.
composites show that the Cu concentration is relatively high around TiC_p.

Figure 5 indicates preferentially corrosion formed around gas void in the composite. The pit cells occurred on the composites, as shown in Fig. 6. Pit cell sizes developed were measured in the range of 15-20 µm, 10-15 µm and 5-10 µm for 20%, 30% and 40% vol. TiC_p composites, respectively.

In Figs 1 and 2, the E-I curves show anodic current peaks which are the regions of active metal dissolution. The pitting potential can be defined, as the potential (E_pit point in Fig. 1) below which the metal surface remains passive and above which pitting corrosion starts to grow on the metal surface, as shown in these potentiodynamic polarization curves in Fig. 1. In addition, the potential above pitting corrosion is described as pitting inhibition potential (E_i point in Fig. 1) by some researchers.

In the unaging conditions (Fig. 1 and Table 2), several reasons can be stated for fluctuations in E_ocp and E_cor values such as the size and the volume fraction of TiC, voids at the TiC/Al interface, reactions between the Al alloy matrix and TiC particles, segregation of alloy elements to TiC/Al interface, high dislocation densities and residual stresses formed in the vicinity of TiC particles, because corrosion resistance of AMMCs may be greatly affected by these factors. Therefore, the current density value is directly related to the electrode potential, and it can provide more realistic results related to electrochemical behaviour of the composites. As seen from Table 2, both the corrosion current density (i_cor) and the passive current density (i_pass) of the composites increase with increasing the TiC_p volume fraction before the aging process. On the other hand, the oxide film resistance of the surface decreases with increasing the TiC_p volume fraction. These results are in accordance with composite theory because it is well known that the addition of reinforcement in the matrix alloy may cause cracks and discontinuity on the surface oxide layer that increase with increasing the reinforcement volume fraction. Moreover, TiC_p has higher surface energy than aluminum (1.665 J/m² for TiC and 0.948 J/m² for aluminum). Therefore, low wettability occurs in the Al/TiC interface relative to the other Al matrix-ceramic composite systems. Consequently, when the potential exceeds the E_pit value, these interfaces become corrosion-starting points. In Fig. 3, the pitting corrosion occurred principally at the Al/TiC interfaces because the surface oxide film in these areas is defective. X-ray mapping analyses indicate that the Cu content is relatively high at the Al/TiC_p interfaces (Fig. 4). White points in the left hand of the side images of Fig. 4 are Cu elements. Differentiations both in the Cu

Fig. 6—Pit morphologies of (a) 20% vol.; (b) 30% vol. and (c) 40% vol. TiC_p composites.
alloy segregation and the surface energy of the Al/TiC interface may reduce $E_{\text{pit}}$ potentials of the composites. The copper seriously diminishes the corrosion resistance of the Al alloys. However, it is an essential component to produce aged high strength alloys\cite{42,43}. Cu forms $p$-type oxide on the surface which its electrical conductivity increases with the oxygen pressure, whereas Al forms $n$-type oxide on the surface, whose electrical conductivity decreases with the oxygen pressure\cite{44}. In our previous study\cite{45}, forming of Al$\text{}_2$Cu phases in Al matrix has already been observed with microstructural analysis after ageing process In the ageing conditions, free-Cu amount in the matrix decreases due to the formation of Al$\text{}_2$Cu intermetallic phase. Thus, $p$-type oxide quantity in the protective film decreases and the protective layers contain less pores in this state. Consequently, the $i_{\text{cor}}$ values of the composites did not alter due to the formation of this more stable and coherent layer in spite of increasing TiC$_p$ content in the aged conditions (Table 3). In addition, the layer is less complex when compared with unaging conditions. The aging mechanism for Al-Cu alloys is developed by controlled decomposition of unstable supersaturated solid solution\cite{42}. During the aging process, Cu atoms depart from the Al lattice to form the Al$\text{}_2$Cu phase. Thus, strains in the Al lattice relax. Therefore, Al lattice distortion decreases relative to the unaging state. Another reason of the decrease in the value of $i_{\text{cor}}$ may be the relaxation of these strains. When the potential reaches the $E_{\text{i}}$, the active sites on the aluminum surface are blocked and the surface oxide film has mended itself by corrosion products. Thus, the specimen becomes passive again. Interestingly, as seen from Table 3, $E_{\text{i}}$ potentials increase while the $E_{\text{pit}}$ values decreases with increasing TiC$_p$ volume fraction. This can be seen as a contradiction. However, the practical use of the $E_{\text{i}}$ value is limited, because susceptibility of crevice corrosion can be observed at the potentials above the $E_{\text{i}}$ value\cite{35}. Therefore, $(E_{\text{i}}-E_{\text{pit}})$ parameter must be used to determine the tendency of the active metal dissolution in the media. (ii) From the potentiodynamic polarization curves, when the potential has reached the $E_{\text{it}}$, the active sites on the aluminum surface are blocked and the surface oxide film was has mended itself by corrosion products. (iv) The SEM images show preferentially corrosion formed around the gas voids in the composites (Fig. 5.). (v) Differentiations both in the potential of CuAl$_2$ phase and the surface energy of Al/TiC interface may reduce $i_{\text{pas}}$ current densities of the composites in the aging conditions.

Conclusions
The following conclusions can be drawn from this study:

(i) The results show that the TiC$_p$ and its volume fraction have a great effect on the electrochemical behaviors of the composites in 1.0 N H$_2$SO$_4$ solution.

(ii) $(E_{\text{i}}-E_{\text{pit}})$ parameter must be used to determine the tendency of the active metal dissolution in the media.

(iii) From the potentiodynamic polarization curves, when the potential has reached the $E_{\text{it}}$, the active sites on the aluminum surface are blocked and the surface oxide film has mended itself by corrosion products.

(iv) The SEM images show preferentially corrosion formed around the gas voids in the composites (Fig. 5.).

(v) Differentiations both in the potential of CuAl$_2$ phase and the surface energy of Al/TiC interface may reduce $i_{\text{pas}}$ current densities of the composites in the aging conditions.

Acknowledgements
This work was financially supported by TUBITAK (The Scientific & Technological Research Council of Turkey, MAG 106M156) and Ataturk University (BAP No: 2005/14).

References