GALVANIC CORROSION OF AL ALLOYS—III.
THE EFFECT OF AREA RATIO*

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Abstract—The Al alloys 2024 and 7075 have been electrically coupled to Cu, stainless steel 304L, 4130 steel, Ti-6Al-4V, Cd or Zn in 3·5%NaCl. Galvanic current and weight loss data have been obtained for area ratios $A^c/A^a = 0·1, 1$ and 10 in 24 h tests. Experimental results confirm theoretical calculations based on mixed potential theory, according to which the galvanic c.d. $i^g$ with respect to the anode is directly proportional to the area ratio: $i^g = k_1 A^c/A^a$, while the dissolution rate $r^a$ of the anode is related to the area ratio by: $r^a = k_2 (1 + A^c/A^a)$. The galvanic current $I_g$ is independent of anode area $A^a$ and directly proportional to the cathode area $A^c$: $I_g = k_3 A^c$. The galvanic c.d. $i^g$ can be converted into dissolution rates $r^a$ according to:

$$r^a = k_2 i^g (1 + A^c/A^a).$$

INTRODUCTION

In a systematic study of galvanic corrosion of Al alloys coupled to a variety of dissimilar metals, the effect of the nature of the dissimilar metal and the nature of the solution composition have been investigated earlier. Results of a study of the effect of area ratio of anode to cathode on the rate of galvanic corrosion are reported in this publication.

When the Al alloys 1100, 2024, 2219, 6061 and 7075 were coupled to a variety of dissimilar metals and alloys in 3·5%NaCl, the rate of galvanic corrosion of the Al alloys decreased in the order $Ag > Cu > 4130$ steel $>)$ stainless steels $\approx Ni >$ Inconel 718 $>)$ Ti-6Al-4V $\approx$ Haynes 188 $> Sn > Cd$. A comparison of galvanic current data in 3·5%NaCl, Thousand Oaks, CA tapwater, and distilled water showed that dissolution rates of Al alloys coupled to a dissimilar metal were higher in 3·5%NaCl than in tapwater and distilled water, where they were found to be comparable. While in 3·5% NaCl the ranking of dissimilar metals was $Cu > 4130$ steel $>$ SS304L $> Ti-6Al-4V$, results in tapwater and distilled water led to a ranking of $Cu > SS304L \approx Ti-6Al-4V > 4130$ steel.

The studies described above were carried out for an area ratio of $A^c/A^a = 1$ (equal areas of anode ($A^a$) and cathode ($A^c$)). In practice, the area ratio $A^c/A^a$ of cathode to anode is usually different from one, a large area ratio being especially damaging to the anode. In the present study, galvanic currents have been measured in 3·5%NaCl for area ratios $A^c/A^a = 0·1$ and 10. These data have been compared with earlier results for $A^c/A^a = 1$.1

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EXPERIMENTAL

(A) Materials and test solution
Al alloys 2024–T851 and 7075–T76 (for chemical composition, see Ref. 1) were coupled to Cu (OFHC), stainless steel 304L, 4130 steel, Ti–6Al–4V, Cd (99.97%) or Zn (99.9%) in air-saturated, but unstirred 3.5% NaCl at 22 ± 1°C.

(B) Test method
Flat test specimens were prepared so that an area of about 2 or 20 cm² was exposed to the electrolyte. After degreasing, cleaning and weighing (for details), the two test specimens were immersed in 3.5% NaCl and the corrosion potentials measured for 15 min. The two metals were then connected to the zero impedance ammeter described by Lauer and Mansfeld and galvanic current $I_g$ and galvanic potential $\phi_g$ of the couple continuously recorded for 24 h on a strip chart recorder. From the galvanic current $I_g$–time trace the average galvanic current density (c.d.) $i_g = I_g/A$ was calculated, where $A$ is the geometric area of anode ($A^a$) or cathode ($A^c$) in the galvanic couple. Note that for $A^a \neq A^c$ the galvanic c.d. with respect to anode or cathode will have different values ($I_g/A^a \neq I_g/A^c$).

Weight loss data for the materials in a given galvanic couple in the 24 h test were used to calculate dissolution rates of anode and cathode.

RESULTS

Figure 1 shows galvanic current $I_g$–time traces recorded for the Al 2024–Cu couple for area ratios $A^c/A^a = 0.1$, 1 or 10. For area ratios of $A^Al/A^Cu = 0.1$ or 1 the area of the Cu electrode was kept constant at about 20 cm², while for $A^Al/A^Cu = 10$ the area of Cu was about 2 cm². Figure 1 shows that under these conditions the galvanic current is independent of area ratio for $A^Al/A^Cu = 0.1$ or 1, but decreases by about a factor of 10 for $A^Al/A^Cu = 10$.

![Fig. 1. Galvanic current $I_g$ as a function of time and area ratio for Al 2024/Cu in 3.5% NaCl.](image-url)
When the galvanic current data are replotted as galvanic c.d. $i_g$ vs time, different behavior is observed for the galvanic c.d. $i_{\text{Al}}^g = I_{\text{Al}}/A_{\text{Al}}$ and $i_{\text{Cu}}^g = I_{\text{Cu}}/A_{\text{Cu}}$. Figure 2 shows that the galvanic c.d. $i_{\text{Al}}^g$ with respect to the Al alloy (the anode) decreases by about a factor of 10 when the area ratio $A_{\text{Al}}/A_{\text{Cu}}$ is increased by a factor of 10. The galvanic c.d. $i_{\text{Cu}}^g$ with respect to Cu (the cathode) seems to be independent of area ratio (Fig. 3); $i_{\text{Cu}}^g$ is negative, since Cu is the cathode in the Al 2024–Cu couple.

Similar results were obtained for the other galvanic couples studied. Table 1 shows the results (average galvanic c.d. over 24 h) obtained for three different area ratios. Results for $A_{\text{Cu}}/A_{\text{Al}} = 1$ are from Ref. 1. For the couples Al 2024/Zn, Al 2024/Cd and Al 7075/Zn, the Al alloys were the cathode in the galvanic couple. Consequently, the galvanic c.d. $i_{\text{Al}}^g$ is negative. The area ratio used for these couples was $A_{\text{Cu}}/A_{\text{Al}} = A_{\text{Al}}/A_X$, where $X$ refers to the more active material (Zn or Cd).

In Table 2 dissolution rates $r_A$ calculated from weight loss data for Al alloys are listed in a manner similar to Table 1. For all galvanic couples in which the Al alloys were the anodes, the galvanic c.d. $i_{\text{Al}}^g$ and the dissolution rate $r_A$ calculated from weight loss data increase with increasing area ratio $A_{\text{Cu}}/A_{\text{Al}}$.

For the couples Al 2024/Cd, Al 2024/Zn and Al 7075/Zn, in which the Al alloy was the cathode, no systematic changes with area ratio were observed for galvanic current or weight loss data. As observed earlier,\textsuperscript{1,2} coupling to Zn does not result in cathodic protection of Al 2024 or 7075, but leads to accelerated corrosion as can be
FIG. 3. Galvanic current density $i_{\text{g}}^\alpha$ with respect to Cu as a function of time and area ratio for Al 2024/Cu in 3.5% NaCl.

TABLE 1. GALVANIC CURRENT DATA IN 3.5% NaCl AS A FUNCTION OF AREA RATIO $A^\alpha/A^\text{Cu}$ ($i_{\text{g}}^\alpha$ IN $\mu$A/cm$^2$)

<table>
<thead>
<tr>
<th>Dissimilar metal</th>
<th>$A^\alpha/A^\text{Cu}$</th>
<th>$A^\alpha/A^\text{Cu}$</th>
<th>$i_{\text{g}}^\alpha$</th>
<th>$A^\alpha/A^\text{Cu}$</th>
<th>$i_{\text{g}}^\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Al 2024</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.09</td>
<td>2.34</td>
<td>1.01</td>
<td>41.0</td>
<td>11.7</td>
</tr>
<tr>
<td>SS304L</td>
<td>0.10</td>
<td>2.04</td>
<td>1.03</td>
<td>12.8</td>
<td>11.8</td>
</tr>
<tr>
<td>Ti-6-4</td>
<td>0.08</td>
<td>1.83</td>
<td>0.98</td>
<td>5.3</td>
<td>11.9</td>
</tr>
<tr>
<td>4130</td>
<td>0.10</td>
<td>2.18</td>
<td>1.04</td>
<td>24.5</td>
<td>12.3</td>
</tr>
<tr>
<td>Cd</td>
<td>0.09</td>
<td>-2.52</td>
<td>0.88</td>
<td>-1.54</td>
<td>11.7</td>
</tr>
<tr>
<td>Zn</td>
<td>0.08</td>
<td>-12.1</td>
<td>1.02</td>
<td>-6.8</td>
<td>11.8</td>
</tr>
<tr>
<td>(B) Al 7075</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.08</td>
<td>2.28</td>
<td>0.95</td>
<td>45.0</td>
<td>10.5</td>
</tr>
<tr>
<td>SS304L</td>
<td>0.08</td>
<td>2.59</td>
<td>0.97</td>
<td>17.0</td>
<td>10.2</td>
</tr>
<tr>
<td>Ti-6-4</td>
<td>0.08</td>
<td>1.73</td>
<td>0.90</td>
<td>8.3</td>
<td>9.9</td>
</tr>
<tr>
<td>4130</td>
<td>0.09</td>
<td>2.74</td>
<td>0.98</td>
<td>25.0</td>
<td>10.5</td>
</tr>
<tr>
<td>Cd</td>
<td>0.07</td>
<td>0.94</td>
<td>0.91</td>
<td>5.9</td>
<td>10.1</td>
</tr>
<tr>
<td>Zn</td>
<td>0.10</td>
<td>-2.05</td>
<td>1.06</td>
<td>-3.4</td>
<td>12.4</td>
</tr>
</tbody>
</table>

seen from a comparison of the measured dissolution rates $r_A$ with the corrosion rates of uncoupled Al alloys $r_e$. 
Table 2. Dissolution rates $r_A$ from weight loss data as a function of area ratio $A^C/A^A$ ($r_A$ in mdd)

<table>
<thead>
<tr>
<th>Dissimilar metal</th>
<th>$A^C/A^A$</th>
<th>$r_A$</th>
<th>$A^C/A^A$</th>
<th>$r_A$</th>
<th>$A^C/A^A$</th>
<th>$r_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A) Al 2024 ($r_o = 5.25$ mdd$^4$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.09</td>
<td>16.4</td>
<td>1.01</td>
<td>63.1</td>
<td>11.7</td>
<td>433</td>
</tr>
<tr>
<td>SS304L</td>
<td>0.10</td>
<td>18.1</td>
<td>1.03</td>
<td>26.5</td>
<td>11.8</td>
<td>181</td>
</tr>
<tr>
<td>Ti-6-4</td>
<td>0.08</td>
<td>18.0</td>
<td>0.98</td>
<td>17.2</td>
<td>11.9</td>
<td>128</td>
</tr>
<tr>
<td>4130</td>
<td>0.10</td>
<td>20.4</td>
<td>1.04</td>
<td>38.1</td>
<td>12.3</td>
<td>323</td>
</tr>
<tr>
<td>Cd</td>
<td>0.09</td>
<td>26.5</td>
<td>0.88</td>
<td>5.9</td>
<td>11.7</td>
<td>13.2</td>
</tr>
<tr>
<td>Zn</td>
<td>0.08</td>
<td>57.6</td>
<td>1.02</td>
<td>19.3</td>
<td>11.8</td>
<td>28.0</td>
</tr>
<tr>
<td></td>
<td>(B) Al 7075 ($r_o = 0.95$ mdd$^4$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.08</td>
<td>5.6</td>
<td>0.95</td>
<td>58.8</td>
<td>10.5</td>
<td>483</td>
</tr>
<tr>
<td>SS304L</td>
<td>0.08</td>
<td>6.6</td>
<td>0.97</td>
<td>16.2</td>
<td>10.2</td>
<td>167</td>
</tr>
<tr>
<td>Ti-6-4</td>
<td>0.08</td>
<td>5.4</td>
<td>0.90</td>
<td>8.5</td>
<td>9.9</td>
<td>152</td>
</tr>
<tr>
<td>4130</td>
<td>0.09</td>
<td>9.6</td>
<td>0.98</td>
<td>26.0</td>
<td>10.5</td>
<td>344</td>
</tr>
<tr>
<td>Cd</td>
<td>0.07</td>
<td>6.6</td>
<td>0.91</td>
<td>5.9</td>
<td>10.1</td>
<td>103</td>
</tr>
<tr>
<td>Zn</td>
<td>0.10</td>
<td>19.0</td>
<td>1.06</td>
<td>4.0</td>
<td>12.4</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Discussion

A. Theoretical considerations

A general discussion of area ratio relationships in galvanic corrosion has been given earlier for the cases of charge transfer and diffusion control. A more detailed analysis is necessary to interpret the experimental results of this study.

It has been shown earlier for the case of diffusion control of the cathodic reaction that the dissolution c.d. $i_a^d$ of the anode in a galvanic couple is proportional to the area ratio $A^C/A^A$:

$$i_a^d = i_{O_2}^L \left( 1 + \frac{A^C}{A^A} \right)$$  \hspace{1cm} (1)

where $i_{O_2}^L$ is the limiting c.d. for diffusion of oxygen. Equation (1) is the so-called "catchment principle".

The galvanic current $I_g$ is equal to the difference between the anodic and cathodic currents for the anode at the potential of the couple $\varphi_g$ and equal to the cathodic current for the cathode at $\varphi_g$:

$$I_g = I_a^A(\varphi_g) - | I_c^A(\varphi_g) | = | I_c^C(\varphi_g) |.$$  \hspace{1cm} (2)

Equation (2) can be written in terms of current densities and areas:

$$i_g^A A^A = i_a^A A^A - i_c^A A^A = i_c^C A^C.$$  \hspace{1cm} (3)

Due to diffusion control:

$$i_c^A = i_c^C = i_{O_2}^L$$  \hspace{1cm} (4)
which leads to:

\[ i^A_g = i^A_a - i^L_{O_2} = i^L_{O_2} \frac{A^C}{A^A}. \]  

(5)

Equation (5) shows that the galvanic c.d. \( i^A_g \) is directly proportional to the area ratio \( A^C/A^A \).

From equation (5) relationships between the dissolution c.d. \( i^A_a \) of the anode and the galvanic c.d. \( i^A_g \) with respect to the anode can be found in the form:

\[ i^A_a = i^A_g + i^L_{O_2} = i^A_g + i^A_{corr}, \]  

(6)

since for diffusion control:

\[ i^L_{O_2} = i^A_{corr} \]  

(7)

and in the form:

\[ i^A_a = i^A_g \left(1 + \frac{A^A}{A^C}\right), \]  

(8)

since \( i^L_{O_2} = i^A_a \frac{A^A}{A^C} \) (equation 5). According to equation (5) the galvanic c.d. \( i^A_g \) is a measure of the "galvanic effect", which is the increase of the dissolution rate of the anode due to galvanic coupling to a cathode.\(^5\) Equation (8) shows that the values of \( i^A_a \) and \( i^A_g \) will become comparable for large area ratios \( A^C/A^A \). Equation (31) in Ref. 4 is not correct and should have been written as:

\[ \frac{i^A_{a}}{i^A_{g}} = 1 + \frac{A^A}{A^C} \]  

(9a)

\[ \frac{i^A_{d}}{i^A_{g}} = 1 + \frac{A^C}{A^A} \]  

(Ref. 4).

B. Correlation between galvanic current data and area ratio

According to equation (2), the galvanic current \( I_g \) is equal to the cathodic current for the cathode:*

\[ I_g = I^C_{c} (\varphi_g) = i^L_{O_2} A^C. \]  

(2a)

Equation (2a) explains the results in Fig. 1, where for \( A^Al/A^Cu = 0.1 \) and 1 the galvanic current \( I_g \) was independent of area ratio. For these two area ratios the area of Cu \( (A^C) \) had been held constant. To obtain an area ratio \( A^Al/A^Cu = 10 \), the area of Cu was reduced by a factor of 10 and consequently the galvanic current was lower by about a factor of 10. Equation (2a) can also be used to explain earlier data by Pryor and Keir\(^7\) for Al-mild steel couples in 1N NaCl, who found that current flow

* Anodic (dissolution) reactions occurring on the cathode at \( \varphi_g \) are neglected.
and weight loss of Al were proportional to $A^C$ and much less dependent on $A^A$. Similar observations were already made by Tödt in 1928 for a variety of galvanic couples in HCl and acetate buffer.

According to equation (5) the galvanic c.d. $i^A_g$ with respect to the anode is directly proportional to the area ratio $A^C/A^A$. This is qualitatively confirmed by the data in Fig. 2 which show an increase of $i^A_g$ with $A^C/A^A$. Similar results can be seen in Table 1.

The galvanic c.d. $i^C_g$ with respect to the cathode should be independent of area ratio since according to equation (2a):

$$\frac{i^C_g}{A^C} = \frac{i^C}{A^C} = i^C_{\text{th}} = \text{const.} \tag{2b}$$

The data of Fig. 3 confirms equation (2b).

When the $i^A_g$ data in Table 1 are plotted vs area ratio $A^C/A^A$ according to equation (5) in a log–log plot, a best straight line can be drawn with a slope of one for both Al 2024 (Fig. 4) and Al 7075 (Fig. 5). The data for Al 2024/Cd, Al 2024/Zn and Al 7075/Zn have been omitted since in these couples the Al alloys were the cathodes. The different values of $i^A_g$ at a constant value of $A^C/A^A$, which have also been observed in earlier studies, result from the fact that contrary to the normal assumption, that the limiting diffusion c.d. $i^A_{\text{th}}$ is independent of cathode material, experimental values of $i^A_{\text{th}}$ are found to be dependent on the nature of the cathode. Mansfeld and Parry have shown, based on potentiostatic polarization curves, that in 3.5% NaCl $i^A_{\text{th}}$ is larger for SS304 than for Ti–6Al–4V. Similar conclusions have been reached by Fink et al. for stain-

![Graph](image)

**Fig. 4.** Dependence of galvanic c.d. $i^A_g$ on area ratio $A^C/A^A$ for Al 2024 (data of Table 1).
related to a corresponding decrease of \(i_{O_2}^A\). Based on experimental evidence, equation (4) is not exactly fulfilled and equation (5) has to be rewritten as:

\[
i_g^A = i_{O_2}^C \frac{A^C}{A^A}
\]  

(5a)

where \(i_{O_2}^A\) is material-dependent. This material dependence might result from the poor electronic conductivity of the passive film on Ti as compared to stainless steel or the presence of corrosion products through which oxygen has to diffuse before it can be reduced at the metal surface.

C. Correlation between weight loss data and area ratio

The dissolution rates calculated from the weight loss of the Al alloys in galvanic couples have been plotted vs. \(1 + A^C/A^A\) in log-log plots in Figs. 6 and 7. The approximately straight line relationship with a slope of one confirms equation 1 since the dissolution c.d. \(i_a^A\) is related to the dissolution rate \(r_A\) by Faraday's law. The dependence of dissolution rates on cathode material at a constant area ratio can be explained as above. For material-dependent limiting c.d. the catchment principle has to be expressed as:

\[
i_a^A = i_{O_2}^{A^C} + i_2^{L^C} \frac{A^C}{A^A}
\]  

(1a)

For very small area ratios the dissolution rate \(r_A\) should approach the corrosion rate \(r_0\) for uncoupled Al alloys (\(r_0 = 5.25\) mdd for Al 2024, \(r_0 = 0.95\) mdd for Al 7075
Dependence of dissolution rate $r_d$ on area ratio for Al 2024 (data of Table 2). (Ref. 1)). The Al alloy will in this case not be polarized to its pitting potential, while for area ratios of 1 : 1 as in Fig. 7 this is still the case. The deviation in Fig. 7 (Al 7075) from the straight line with a slope of one might be due to this situation. Since $r_o$ is higher for Al 2024, the deviation in Fig. 6 is not as pronounced. Studies with small area ratios could further clarify this point.

D. Calculation of dissolution rates from galvanic current data

The measured values of the galvanic c.d. $i_g^A$ represent the "galvanic effect" which is the increase of dissolution rates due to galvanic coupling (see equation 5) provided that equation (7) is valid. In certain cases it might be desirable to calculate the total dissolution c.d. $i_d^A$ of the anode from galvanic current data. This can be done using equation (8):

$$i_d^A = i_g^A \left(1 + \frac{A_A}{A_C}\right).$$

Using the measured values of $i_g^A$ for the three area ratios studied (Table 1), values of $i_d^A$ have been calculated and converted into dissolution rates $r_g$ using Faraday's law (1 $\mu$A/cm$^2$ = 0.81 mdd). These data have been plotted in Fig. 8 against the dissolution rates $r_d$ calculated from weight loss data (Table 2). Most data points are close to the theoretical line with a slope of one, the largest deviations are found for Al 7075 at area
Fig. 7. Dependence of dissolution rate $r_d$ on area ratio for Al 7075 (data of Table 2).

Fig. 8. Correlation between weight loss data ($r_d$) and galvanic current data ($r_g$).
ratios of 0.1 and 1. The reason for these deviations might be that the dissolution rates $r_A$ for Al 7075 are much lower than for Al 2024, while the galvanic c.d. $i_g^A$ are comparable. In Fig. 7, the dissolution rates $r_A$ seem to decrease faster with decreasing area ratio than indicated by the theoretical line with a slope of one. A further reason for the observed deviation lies in the fact that equation (8) can only be derived in the form used to plot Fig. 8 under the assumption of equation (4). Experimental data show, however, that the cathodic c.d. $i_c^C$, $i_c^A$ and $i_{O_2}^C$ are not equal in most cases. Finally, some of the deviations, especially at low dissolution rates, might be due to experimental difficulties in determining small weight loss data.

CONCLUSION

The observed increase with area ratio $A^C/A^A$ of dissolution rates $r_A$ and galvanic c.d. $i_g^A$ of the Al alloys 2024 and 7075 coupled to more noble metal and alloys in 3.5% NaCl can be expressed as:

$$r_A = k_2 \left(1 + \frac{A^C}{A^A}\right)$$

and

$$i_g^A = k_1 \frac{A^C}{A^A}.$$

These relationships have been derived using mixed potential theory for galvanic couples in the case of diffusion control of the cathodic reaction. In this treatment one would assume that $k_1 = i_{O_2}^C$, where $i_{O_2}^C$ is the material independent limiting diffusion c.d. for oxygen reduction. The experimental data show, however, that $k_1$ is material-dependent due to different activity for oxygen reduction for the materials studied.

Based on the simple assumption of diffusion control for the cathodic process one arrives at a correlation between dissolution rates of the anode $r_A$ and galvanic current data $i_g^A$:

$$r_A = k_3 i_g^A \left(1 + \frac{A^C}{A^A}\right) = r_g,$$

where $k_3$ is the Faraday constant for Al. Relatively good agreement is obtained between dissolution rates $r_A$ calculated from weight loss data and $r_g$ calculated from galvanic current data except for some deviations at lower area ratios for Al 7075.

REFERENCES

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