ANALYSIS OF TWO KINDS OF CORROSION TROUBLES IN WELDED TITANIUM MATERIALS IN CHEMICAL PLANTS

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Introduction

It is generally recognized that the effect of welding on corrosion of titanium is less compared with most of other metallic materials such as aluminum alloys and stainless steels (1). However, strictly speaking, the corrosion resistance of welded zone of titanium is less than that of base materials (2), (3).

The present authors have come across two kinds of corrosion phenomena for welded titanium used in chemical plants. One is general corrosion of welded zone and another is pitting corrosion of base material although the welded zone is immune. These phenomena suggest that the corrosion resistance of welded zone and base material will reverse by difference of corrosion environment.

The present study was conducted to clarify the effect of iron and oxygen content increased by welding on the corrosion resistance of commercially pure (c.p.) titanium.

Experimental Procedures

1. Analysis of corrosion phenomena of titanium-made reactors

The visual inspection was carried out. Corrosion loss and microstructure were also observed. The contents of iron and oxygen of titanium were analyzed.

2. Laboratory test

The welded specimens of c.p. titanium having various kinds of iron contents were prepared using iron wire-wound titanium welding rod as shown in Fig.1. The iron and oxygen contents and microstructures of the specimens were shown in Table 1 and Fig.2 respectively.

Furthermore, c.p. titanium plates having various kinds of oxygen content were also used for the electrochemical tests.

The specimens for immersion tests were prepared by cutting a 20×25mm plate as shown in Fig.3. The electrode was prepared by welding a titanium lead wire to the immersion specimen and then coated with resin except for measuring area of 10×10mm.

The immersion tests were conducted using H₂SO₄ solutions at 80°C and general corrosion rate was obtained from the corrosion weight loss. A boiling 5% H₂SO₄ solution and a 0.1% Br⁻ solution (NaBr) at 210°C were used for the electrochemical tests.
Results and Discussion

1. Analysis of corrosion phenomena of chemical equipment

(1) Heat exchanger for industrial waste treatment (General corrosion in H$_2$SO$_4$ solutions)

The surface appearance of titanium-made heat exchanger handling a 0.5% H$_2$SO$_4$ solution at 250°C for 700 hours was shown in Fig.4. Both titanium tubes and tube plate were subject to slight general corrosion. Therefore, the general corrosion rate calculated from the thickness loss was obtained and iron and oxygen contents were also analyzed as shown in Table 2. Table 2 revealed that iron and oxygen contents and corrosion rate of welded zone were higher than those of parent metal.

Consequently, it was confirmed that the general corrosion of c.p. titanium was accelerated by welding.

(2) Reactor for synthesis of organic compounds. (Pitting corrosion in Br$^-$ solutions)

The reactor was made of steel lined with three grades of c.p. titanium. The corrosive environment was an acetic acid solution containing a small amount of bromide at about 250°C under high oxygen pressure.

As mentioned elsewhere 4), only parent material of ASTM G1, in which the content of iron and oxygen was small compared with G2 and G3 suffered from pitting corrosion after a few months' operation.
Table 2 Corrosion rates and contents of iron and oxygen of titanium used for the heat exchanger.

<table>
<thead>
<tr>
<th></th>
<th>Fe (%)</th>
<th>O (%)</th>
<th>Corrosion rate (mm/yr)</th>
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</thead>
<tbody>
<tr>
<td>Parent</td>
<td>0.08</td>
<td>0.105</td>
<td>0.15 - 0.18</td>
</tr>
<tr>
<td>Weld</td>
<td>0.13</td>
<td>0.181</td>
<td>0.28 - 0.31</td>
</tr>
<tr>
<td></td>
<td>1.80</td>
<td>0.160</td>
<td>0.36 - 0.42</td>
</tr>
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</table>

Surface appearance of the attacked shown in Fig. 5 revealed that the corrosion products grew in concentric rings but the products were not recognized at welded zone. Table 3 shows the contents of iron and oxygen. It was apparent that the oxygen content of welded zone was higher than that of parent material.

These results suggest that the welding accelerates the general corrosion but suppresses the pitting corrosion of titanium.

2. Effect of welding on the corrosion resistance of c.p. titanium

(1) General corrosion

Fig. 6 shows the effect of iron content on the general corrosion rate of welded and non-welded titanium in boiling H_2SO_4 solutions. The corrosion rate of welded specimen was higher than that of non-welded one and this tendency became noteworthy with increasing of iron content.

Therefore, it is considered that the welded zone is attacked more severely compared with non-welded zone (parent material) when the welded titanium is subject to general corrosion.

(2) Pitting corrosion

The passivation phenomena for the non-welded and welded titanium with various contents of iron have been investigated because pitting corrosion is one of the break down phenomena of the passive film. Fig. 7 shows the potential decay curves after potentiostatic...
Table 3 Contents of iron and oxygen of titanium used for the reactor.

<table>
<thead>
<tr>
<th></th>
<th>Fe (%)</th>
<th>O (%)</th>
<th>Pitting occur.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent</td>
<td>0.058</td>
<td>0.052</td>
<td>Yes</td>
</tr>
<tr>
<td>Weld</td>
<td>0.060</td>
<td>0.081</td>
<td>No</td>
</tr>
</tbody>
</table>

Fig. 5 Surface appearance of titanium-made reactor after operation for 10 months. (Br⁻ solution, 250°C)

Fig. 6 Relationship between corrosion rate and iron content of titanium.

electrolysis at +0.2 V vs Ag/AgCl reference electrode for 10 minutes for the various specimens in a boiling 5% H₂SO₄ solution.

In Fig.5, the Flade potentials and the corrosion potentials for all specimens were approximately same but the time to reactivation, ta (time to reach the corrosion potential) varied. Consequently, the ta for the welded specimen with the iron content of 0.07% (A) was 12min. From this result, the relationship between ta and iron content was obtained as shown in Fig.8. The ta for the welded specimens decreased with increasing of iron content but the ta for the welded specimens with iron content less than 1% showed longer value compared with the non-welded specimen.

Subsequently, the relationships between depassivation pH, pHd and depassivation temperature, Td and iron content of titanium were shown in Fig.9 and 10 respectively. First, Fig.9 revealed that the welded specimens with iron content under 0.3% showed lower pHd than the non-welded specimen (parent metal: Fe = 0.07%). Next, it was made
clear from Fig.10 that Td for the welded specimens with lower iron content was higher than that of parent metal and this tendency became more distinguished in a 1% H$_2$SO$_4$ solution. It is considered that these phenomena are attributable to the higher oxygen content in the welded specimen compared with the non-welded specimen (parent metal).

The present authors have already reported that titanium passive film becomes more stable with increasing of oxygen content and therefore the resistance against pitting corrosion is improved by addition of oxygen to titanium.

Fig.11 shows the relationship between the pitting corrosion, Epit of titanium in a 0.1% Br$^-$ solution at 210$^\circ$C and oxygen content. It is obvious that the Epit becomes more noble with increasing of oxygen content.

From these results, it was considered that the pitting corrosion shown in Fig.5 was suppressed at the welded zone because oxygen content of the welded zone was high.
Conclusion

Based on the experience of two kinds of corrosion phenomena of welded titanium used in chemical plants, the effect of welding on the corrosion resistance of titanium was investigated. The results obtained are summarized as follows;

(1) In case of a $\text{H}_2\text{SO}_4$ solution, the welded titanium shows higher general corrosion rate compared with non-welded titanium. In particular, this tendency becomes more clear with increasing of the content of iron.

(2) In case of a bromide solution, the welded titanium is more immune against pitting corrosion compared with non-welded titanium. This phenomenon is attributable that the oxygen content of titanium is increased by welding.

Consequently, it is concluded that the welding improved the stability of the titanium passive films but accelerates the corrosion rate if the passive film is broken down.

References

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