1. Introduction

Commercial pure titanium forms a very stable passive film on its surface, and therefore exhibits better corrosion resistance than stainless steel and Ni-based alloys in neutral chloride and oxidizing acid environments. Pure titanium is widely used in chemical plants, for condensers in thermal and nuclear power plants, and for heat exchangers where seawater is used as a coolant. However, ever since corrosion was experienced in tube-tube plate crevices in a seawater desalination plant,\(^1\) it is clear that pure titanium has a risk of crevice corrosion in a high temperature chloride solution. Furthermore, overall corrosion takes place in non-oxidizing acid solutions (HCl, H\(_2\)SO\(_4\) and the like) when the pH value is low. One way to improve corrosion resistance is to add alloying elements. Effectively used corrosion resistant titanium alloys include ASTM Grade 7 (JIS H 4600 (TP 340 Pd H/C)), Ti-0.12 - 0.25% Pd, (hereinafter “Gr.7”), and ASTM Grade 12 (Ti-0.8% Ni-0.3% Mo, hereinafter “Gr.12”). A although crevice corrosion resistance and uniform corrosion resistance of the Gr.7 titanium alloy to non-oxidizing acids have been greatly improved, compared to those of pure titanium, the material is costly because of the addition of about 0.15% Pd within the platinum group of elements. On the other hand, although Gr.12 titanium alloy material is superior to Gr.7 titanium alloy material with respect to its low cost, its application where workability is required (e.g., heat exchangers) is limited. This is due to insufficient corrosion resistance and workability due to precipitation of ductility-deteriorating intermetallic compounds like Ti\(_2\)Ni produced by the addition of Ni and Mo.

This explains the search for a corrosion resistant titanium alloy equipped with high corrosion resistance, low cost, and high workability.

Nippon Steel & Sumitomo Metal Corporation has developed ASTM Grade 17 (Ti-0.05% Pd alloy, SMIACE\textsuperscript{TM}, hereinafter “Gr.17”) and ASTM Gr.30 (Ti-0.05% Pd-0.3% Co alloy SMIACE\textsuperscript{TM}, hereinafter “Gr.30”), where the addition of Pd within the

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platinum group of elements has been significantly minimized. Also commercialized has been ASTM Grade 13 (Ti-0.5% Ni-0.05% Ru alloy TICOREX, hereinafter “Gr.13”), where economical Ru in the platinum group of elements is added and, to compensate corrosion resistance, elements of the iron family are added to the extent that workability does not greatly deteriorate. This report presents the mechanism for improving corrosion resistance of these alloys, and states their characteristics and some of their applications.

2. Corrosion Resistant Alloys SMIACE™ and TICOREX

2.1 Characteristics of SMIACE™ and TICOREX

Typical chemical compositions of the corrosion resistant titanium alloys Gr.17, Gr.30 (SMIACE™) and Gr.13 (TICOREX) produced by Nippon Steel & Sumitomo Metal are shown in Table 1.

Through the use of X-ray diffraction, the precipitates were identified as Ti$_2$Ni and Ti$_2$Co phases, respectively.

Table 2 shows the tensile properties of various corrosion resistant titanium alloy sheets. The test specimen shape was of JIS 13 B (JIS Z 2241). The test piece was sampled in the transverse direction to the direction of rolling. Gr.17 titanium alloy with a sole platinum group element exhibited elongation exceeding 45%. Also, in the Erichsen cupping test that is designed to represent press formability, the alloy exhibited an Erichsen cupping test value higher than that of Gr.2 pure titanium. Gr.17 titanium alloy is equipped with sufficient ductility for use in formed members, which require high formability. On the other hand, Gr.13 and Gr.30 titanium alloy materials with an added iron family element compound exhibit strength and elongation equivalent to those of Gr.2 pure titanium, and ductility (elongation) higher than those of Gr.7 and Gr.12 titanium alloys. It is considered that the difference in ductility between the titanium alloy material with an added platinum group element and the titanium alloy material with an added platinum group element-iron family element compound is due to the existence or non-existence of fine compound (Ti$_2$Ni and Ti$_2$Co) precipitates.

The existence or non-existence of finely precipitated compounds affects not only the mechanical properties but also the mechanism of corrosion resistance. Effects attributed to corrosion resistance are described in the following chapter.

2.2 Mechanism of corrosion resistance

Titanium can maintain corrosion resistance as it forms a stable passive film on its surface. Pitting corrosion is not developed even in an environment where a solution contains chloride ions. This is attributed to the fact that titanium has a strong affinity for oxygen, and the fact that the passive film formed on the surface of titanium is very stable. However, there are cases where it does not exhibit sufficient corrosion resistance, as in the non-oxidizing acids hydro-

<table>
<thead>
<tr>
<th>ASTM B265</th>
<th>Chemical compositions (mass%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gr.7</td>
<td>N 0.008 C 0.006 H 0.0018 Fe 0.07 O 0.109 Ru 0.14 Pd – Ni – Co – Mo Bal. – Ti 0.71</td>
<td></td>
</tr>
<tr>
<td>Gr.12</td>
<td>N 0.016 C 0.008 H 0.0044 Fe 0.11 O 0.145 Ru – Pd – Ni 0.71 Co 0.29 Mo Bal. –</td>
<td></td>
</tr>
<tr>
<td>Gr.13</td>
<td>N 0.003 C 0.004 H 0.0010 Fe 0.03 O 0.040 Ru 0.054 Pd – Ni 0.52 Co – Mo Bal. – Ti 0.43</td>
<td>TICOREX</td>
</tr>
<tr>
<td>Gr.17</td>
<td>N 0.006 C 0.005 H 0.0013 Fe 0.03 O 0.033 Ru – Pd 0.06 Ni – Co – Mo Bal. – Ti 0.27</td>
<td>SMIACE™</td>
</tr>
<tr>
<td>Gr.30</td>
<td>N 0.007 C 0.006 H 0.0065 Fe 0.05 O 0.087 Ru – Pd 0.05 Ni – Co 0.27 Mo Bal. – Ti 0.27</td>
<td>SMIACE™</td>
</tr>
</tbody>
</table>

Photo 1 Typical microstructures of platinum group metals added and platinum group metals-iron family elements compound added titanium alloys (typical microstructures of SMIACE™ and TICOREX)
chloric acid and sulfuric acid. Furthermore, even in a neutral chloride solution environment, susceptibility to crevice corrosion is high when the temperature and concentration are high.

As for the mechanism of crevice corrosion, a state of oxygen shortage is developed inside. This is due to oxygen consumption inside, the delay of oxygen supply from the outside, and an oxygen concentration cell produced between the inside and outside of the crevice. Although titanium initially maintains a passive film, Ti<sup>3+</sup> dissolved in the crevice acting as an anode produces H<sup>+</sup> through hydroylisis. This reaction lowers the pH in the crevice; and at the same time, in order to maintain electrical neutrality, Cl<sup>-</sup> ion electrophoresis takes place from the outside into the crevice. As pH decreases and reaches the value where depassivation starts (pH values as low as 0.5 to about 1.0 have been confirmed by actual observation), active dissolution starts, triggering crevice corrosion.

**Figure 1** shows the polarization behaviors of high corrosion resistant titanium alloys in a boiling acidic chloride solution of 4.27mol/l-NaCl with a pH of 0.5. Pure titanium (Gr.2) shows a less noble corrosion potential of −0.8 V vs. SCE, and an active dissolution peak current of anodic polarization curve in the vicinity of −0.6 V vs. SCE. Gr.7, Gr.13, Gr.17 and Gr.30 containing a platinum group metal show a corrosion potential in the vicinity of −0.2 V vs. SCE, which is substantially nobler than that of Gr.2, and no active dissolution current peak because of passivation. The corrosion potential of Gr.7 alloy is the noblest among them because of its largest Pd content, while no noticeable difference is observed among those of Gr.13, Gr.17 and Gr.30 alloys.

As Photo 1 shows, the microstructures of corrosion resistant titanium alloys are classified in two categories: one is a material that exhibits α phase-like single phase structure, as seen in Gr.17 with the addition of a platinum group element alone; the other is a material that exhibits fine compound precipitation through the addition of Ni and Co, such as Gr.13 and Gr.30 alloys with an added platinum group-iron-family element compound. **Figure 2** shows temporal changes of the corrosion potential in a highly concentrated brine of pH 0.5 at 80˚C, which simulates a crevice environment. Gr.17 alloy, the typical material of the former category, and Gr.13 alloy, the typical material of the latter category, are shown for comparison with that of pure titanium (Gr.2).

Pure titanium (Gr.2) is not passivated and maintains its less noble potential, which is apparent in the active dissolution state. This means that Gr.2 continues to corrode in the crevice environment. On the other hand, fine precipitates of Ti<sub>2</sub>Ni are exposed on the surface of Gr.13 alloys, exhibiting noble potential from the initial stage of immersion. The potential grows nobler as time elapses. Taki et al. analyzed Ti<sub>2</sub>Ni precipitated in Gr.13 alloys, and discovered that Ru partly substituted Ni. The Ru concentration detected in Ti<sub>2</sub>Ni is 20 times higher than the amount added, being concentrated to the level 1.2%. In other words, the precipitate in Gr.13 alloys is considered to be Ti<sub>2</sub>(Ni<sub>x</sub>Ru<sub>y</sub>) containing Ru. Ru is a metal with low overpotential in a hydrogen anode reaction. As a result, by lowering the hydrogen overpotential in the Ti<sub>2</sub>(Ni<sub>x</sub>Ru<sub>y</sub>) compound, corrosion potentials of the alloys become nobler, as shown in Fig. 2. Above the noble potential of −0.3 V vs. SCE, titanium is passivated.

In contrast, corrosion potentials in Gr.17 alloys exhibit a less no-
ble potential, indicating an active state at the initial stage of immersion; however, the corrosion potential becomes nobler after a short period of time. It is believed that, similar to pure titanium, as the surface of Gr.17 alloys at the initial stage is in single phase of the α phase, it shows a less noble potential. The phenomenon of the temporal change in nobleness of corrosion potential is considered to exhibit a change process in surface conditions by active dissolution.

The corrosion rate in a boiling hydrochloride solution was investigated. A temporal change in the state of crevice corrosion was displayed, as shown in Fig. 3. Unlike pure titanium (Gr.2), which exhibits a constant high corrosion rate independent of immersion time, Gr.17 alloys wherein Pd is solid-soluted show decreasing corrosion rates over time. It is believed that the change in the corrosion rate is due to temporal changes in the surface condition.

Figure 3 shows the test for a Gr.17 alloy immersed in a boiling hydrochloric acid solution for 96 h. Pd concentration in the depth direction from the surface was measured with Glow Discharge-Optical Emission Spectroscopy (GDOES). The respective results are shown in Fig. 4. Compared to the material not immersed in the boiling hydrochloric acid solution, concentration of Pd near the surface is high, reaching about 9% at the surface, and the highest concentration of Pd was confirmed to be within 10 nanometers below the surface.

Figure 5 shows the results of FE-SEM observations and element mapping developed by AES analysis from the surface where Pd is concentrated by immersion in the boiling hydrochloric solution. It is known that very fine Pd particles less than a micron in size precipitate in a scattered manner on surfaces. In the Gr.17 alloy matrix, Pd exists as a solid solution in the α phase. Therefore, in the strong acidic environment in the crevice, Pd is simultaneously dissolved into the solution when the matrix is dissolved. However, since Pd is a metal of the platinum group, which exhibits highly noble oxidation-reduction potential, Pd ions near the surface are reduced and electrolytically deposited (electrolytically replaced) as metallic particles. The results are displayed in Figs. 4 and 5.

Platinum group metals, including Pd, have low overpotentials in hydrogen electrode reactions. It is believed that Pd electrolytically deposited on surfaces lowers the hydrogen overpotential and therefore, the corrosion potentials of the alloys are nobler and passivate the alloy surfaces, as shown in Fig. 1. Since active dissolution takes place primarily where the passivation film is weak and Pd is deposited primarily in the actively dissolving areas, dissolution → deposition is suspended when the surface reaches the passivation potential. As a result, Pd is considered to be distributed in a scattered manner without covering the overall surface.

Figure 6 is a schematic illustration of the high corrosion resistance mechanism of Gr.13 where fine precipitates of Ti₂(Ni₁₋ₓRx) are exposed above the surface. In Gr.17 alloys, these fine precipitates are exposed where solid-soluted Pd exists in the α phase. It is believed that, in the Gr.13 alloy, Ti₂(Ni₁₋ₓRx) penetrates through...
the passive film and is exposed in advance, exhibiting noble corrosion potential. It is also believed that in Gr.17 alloys, as passive film on the surface is destroyed first, and Pd is then deposited on the surface; therefore, the potential grows nobler as time elapses, as shown in Fig. 2.

2.3 Corrosion resistance in various environments

2.3.1 Corrosion resistance in chloride environments

(1) Hydrochloric acid resistance

Figure 7 shows the corrosion rates of various titanium alloys in a boiling hydrochloric acid solution. As compared to the corrosion rate of pure titanium material (Gr.2), the corrosion rates of Gr.13, Gr.17 and Gr.30 alloys are smaller by two-digit numbers under the same concentration, exhibiting excellent hydrochloric acid resistance. Furthermore, as opposed to Gr.12 alloys, which exhibit rapid deterioration in corrosion resistance in a hydrochloric acid solution with concentrations of 2% or higher, Gr.13, Gr.17 and Gr.30 alloys, do not exhibit any recognizable rapid increase in corrosion rate. This is similar to Gr.7 alloys.

(2) Crevice corrosion resistance

Kitayama et al. report that a qualitative correlation between the crevice corrosion resistance of titanium alloys and their acid resistance in a boiling hydrochloric acid solution with concentration of 3% has almost been established.7 A study was conducted to compare crevice corrosion resistance of Gr.13, Gr.17 and Gr.30, which exhibited corrosion rates in a boiling hydrochloric solution of 3% concentration that were lower than those of pure titanium (Gr.2) and Gr.12 alloys. Figure 8 shows the shape of the test specimen for studying crevice corrosion resistance, and the configuration of the fixture set. As crevice corrosion is influenced by the material forming the crevice,8 a polytetrafluoroethylene (PTFE) sheet was inserted between the two test pieces, and the crevice was formed by tightening all test pieces to a common torque. Table 3 shows the test results. Even with the heterogeneous chloride material, Gr.13, Gr.17 and Gr.30 alloys exhibited an excellent crevice corrosion resistance equivalent to that of Gr.7. On the other hand, in pure titanium Gr.2 and Gr.12 alloys, severe crevice corrosion was recognized in all environments.

2.3.2 Corrosion resistance in a sulfuric acid environment

Figure 9 shows the corrosion resistance in a sulfuric acid environment. Sulfuric acid is a typical non-oxidizing acid equivalent to hydrochloric acid. When compared, the corrosion rates of Gr.13 and Gr.30 alloys are smaller than that of pure titanium (Gr.2), by one to two digit numbers. These corrosion resistant alloys exhibit excellent corrosion resistance in a sulfuric acid solution as well.
### 2.3.3 Sodium hydroxide resistance

Figure 10 shows corrosion rates in a sodium hydroxide solution, a typical alkaline solution environment. At a temperature of approximately 100°C, pure titanium has excellent sodium hydroxide resistance. Not all corrosion resistant titanium alloy materials are superior to pure titanium. One characteristic is that the corrosion rate of Gr.13 alloy is smaller than that of pure titanium (Gr.2) by about half. Gr.13 alloy is the only alloy among the aforementioned corrosion resistant alloys that contains Ni. Ni is an element with high sodium hydroxide resistance. It is presumed that Ti\(_2\)\((\text{Ni}_{1-x}\text{Ru}_x)\) containing finely precipitated Ni in the Gr.13 alloy enhances sodium hydroxide resistance.

### 3. Examples of Application

The mechanical properties and corrosion resistance in various environments have been discussed with respect to the following alloys: Gr.13 (TICOREX), Gr.17 and Gr.13 (SMIACE™). These alloys exhibit excellent corrosion resistance in high concentration chloride solution at high temperatures. Applications of these alloys vary depending on the configuration of the applied members and the required economic benefit. Gr.17 alloy is often used in complex press-forming configurations because it is very ductile and can handle intense formability. Furthermore, for use where economic benefits are required, Gr.13 alloy with added Ru is often used. Ru is the cheapest metal among the platinum group elements.

Specific examples of application are introduced hereunder.

#### 3.1 Seawater heat exchangers for gas cooling

Air fin seawater heat exchangers are used to liquefy gas exiting the top of oil-refining toppers. They use sheets and welded pipes of Gr.13 and Gr.30 alloys with excellent chloride resistance and crevice corrosion resistance. (see Photo 2)

#### 3.2 Autoclaves in nickel refining plants

Materials capable of corrosion resistance under high temperatures and high pressures (about 200°C and 3.9MPa) are required for autoclaves in plants that produce intermediate products, such as sulfide mixed with nickel and cobalt. Furthermore, they need to withstand highly concentrated sulfuric acid that contains ions of various metals originating in low grade ores. As a material appropriate for such environments, the sulfuric acid resistance of Gr.17 alloys is acceptable and Gr.17 has been used as an inner wall material for autoclaves. (see Photo 3)

#### 3.3 Salt production plants

Rock salt is generally used for the production of salt; however, since rock salt resources are scarce in Japan, domestic salt producers often produce salt from seawater. This process includes condensing seawater by heating and evaporation. Conventionally, for this purpose a copper alloy material has been used for shell and tube type heat exchangers. However, periodical replacement of heat exchangers has been necessary due to the development of overall corrosion, inside corrosion of tubes, and crevice corrosion of tube plates. In order to eliminate these issues, a heat exchanger made of Gr.13 or
3.4 Salt electrolyzing plant

Salt electrolyzing plants produce sodium hydroxide (NaOH), chlorine and hydrogen gases by electrolyzing saltwater solutions. Conventionally, soda electrolyzing has been conducted through a mercury or diaphragm process; however, in order to prevent public nuisances arising from the use of mercury and asbestos, the ion-exchange membrane process is becoming globally employed. The process uses a diaphragm cell composed of filter-pressed 100 cells in series, with each cell composed of an anode and cathode chamber, sandwiching an ion exchange membrane. In the anode chamber, titanium is used not only for the meshed electrode that generates the electrochemical reaction, but also for the material of the frame that holds the electrolytic solution in the anode side.

Figure 11 shows the schematic structure of the anode element composition. When a gasket is installed between the ion exchange membrane and the anode element made of titanium, a crevice is formed between the gasket surface and the titanium flange surface. In the electrolytic soda process, the anode element made of titanium is exposed to high temperatures in a highly condensed chloride solution environment. In an element made purely of titanium, severe crevice corrosion takes place. To avoid the occurrence of crevice corrosion, Gr.13 and Gr.17 alloys are used for the part which comes in contact with the gasket. Recently, in order to enhance electrolyzing efficiency, anodes with complicated configurations are required. To achieve such configuration in press forming, titanium alloys having good formability have been sought. Gr.17 alloy is used as the corrosion resistant titanium that satisfies such a requirement.

4. Conclusion

The material requirements used in advanced equipment at various chemical plants are becoming more critical with harsher operating environments. Prolonging service life, performance sophistication and reliability in corrosion resistance are becoming indispensable. In a growing number of cases, higher corrosion resistance is required for members where pure titanium properties are now deemed insufficient.

Under such circumstances, there is a need for highly cost-effective corrosion resistant alloys having corrosion resistance equivalent to that of Gr.7 alloy and high formability equivalent to that of pure titanium.

Nippon Steel & Sumitomo Metal is marketing the following titanium alloys: SMIACE™ (Ti-0.06Pd), in which the addition of the platinum group element Pd is reduced to the minimum level, and corrosion resistance and excellent formability compatibly exist; and TICOREX (Ti-0.5Ni-0.05Ru), in which corrosion resistance and low cost are both achieved through use of the cheap platinum group element Ru, and by adding, to the extent that they do not deteriorate formability, iron family elements to obtain corrosion resistance. We are fully convinced that promotion of the appropriate corrosion-resistant titanium alloys will not only satisfy customers’ needs, but will result in more applications for these alloys.

References

5) Kitayama, S., Shida, Y.: Tetsu-to-Hagané. 77 (9), 1495 (1991)