Corrosion behavior of C-22, Ti-0.2Pd and Ti-32Mo alloys in the aqueous solution of hydrochloric acid and sodium chlorate

Mingyue Zhang¹, Bingqing Ma, Jian Xu, Huangwei Zhou, Yi Liu, Zhibing Chen, Ziwei Xu, Jia Chen and Jiafan Ye
Chengdu Industry and Trade College, Chengdu Technician College, Chengdu, Sichuan, P.R. China

¹Email: zhangmyanhb@126.com

Abstract. Corrosion behavior of Hastelloy C-22, Ti-0.2Pd and Ti-32Mo alloys in the aqueous solution of hydrochloric acid and sodium chlorate was investigated. The C-22 alloy was pitted because the intergranular carbides rich in Cr and Mo would lead to the lack of corrosion-resistant elements in the adjacent area. The Ti-0.2Pd alloy was pitted because the passivation trend decreased in reducing solution and Cl⁻ broke through the passivation film. The weight loss rate and corrosion depth of Ti-0.2Pd alloy increased sharply after pitting corrosion, which was due to the rapid corrosion of the materials exposed inside by the corrosion medium. The Ti-32Mo alloy was pitted due to the transpassivation of Mo caused by NaClO₃. In the process of corrosion, the products of reaction between Mo and Cl⁻ formed an insoluble and dense protective film, which slowed down the corrosion rate of Ti-32Mo, that is why the weight loss rate and corrosion depth increased slowly even if pitting corrosion happened.

1. Introduction
Hastelloy alloy C-22, titanium alloys Ti-0.2Pd and Ti-32Mo are corrosion resistant materials which may be applied in mechanical engineering and chemical apparatus construction [1] [2] [3]. In C-22 alloy, the alloying element Cr is used for corrosion resistance in oxidizing environment and Mo for reducing environment [4]. Therefore, C-22 alloy has good corrosion resistance in both oxidizing and reducing solutions. However, in order to ensure the good corrosion resistance in the environment containing Cl⁻, the content of Cr, Mo and W in the C-22 alloy should reach the required value [5]. For Ti-0.2Pd alloy, the addition of Pd increases the exchange current density of Ti and therefore, facilitates passivation in many systems [6]. However, the pitting sensitivity of Ti-0.2Pd increases with the increase of chloride concentration [7]. Ti-32Mo alloy has excellent corrosion resistance in strong reducing medium. However, the anode potential will increase with the addition of strong oxidant, which will lead to transpassivation and corrosion of the alloy[8].

A new type of disinfectant for tap water containing high concentration hydrochloric acid and sodium chlorate has been widely used in recent years. A company once used C-22 alloy as the storage tank material of this disinfectant, while the tank was severely corroded after a period of time. Therefore, it is necessary to find a more suitable corrosion-resistant material in order to store the disinfectant safely.

In this work, the corrosion behavior of C-22, Ti-0.2Pd and Ti-32Mo in hydrochloric acid and sodium chlorate solution was investigated. After a period of corrosion, the weigh loss rate and corrosion depth were measured. Moreover, the macro and micro morphologies of the specimens after
corrosion were observed, and the corrosion mechanism was analyzed. This work can provide a reference for the selection of materials used in the environment containing both oxidizing and reducing media.

2. Experimental procedure
Commercially Hastelloy alloy C-22, Ti-0.2Pd and Ti-32Mo alloys were prepared with 25 mm in diameter and 10 mm in length. Compositions of these alloys are listed in Table 1.

The surfaces of all the specimens were ground using 2000# emery paper and ultrasonically cleaned with ethanol for 15 min. Then the specimens were immersed in corrosive solution, which is composed of NaClO₃ solution (the mass ratio of NaClO₃ to H₂O is 1:2.5) and HCl with the volume ratio of 1:2. After immersed for 2, 4, 6, 8 months, the specimens were taken out for corrosion resistance study.

Table 1. Chemical compositions of C-22, Ti-0.2Pd and Ti-32Mo alloys (wt.%).

| Alloy | C-22 | Ti-0.2Pd | Ti-32Mo |
|-------|------|----------|---------|
| Pd    | --   | 0.2      | --      |
| Mo    | 13   | --       | 32      |
| Fe    | 3    | 0.05*    | 0.3*    |
| O     | --   | 0.15*    | 0.015*  |
| N     | --   | 0.007*   | 0.015*  |
| H     | --   | 0.01*    | 0.015*  |
| C     | 0.015* | 0.08*    | 0.1*    |
| Ti    | --   | Bal.     | Bal.    |
| Cr    | 22   | --       | --      |
| W     | 3    | --       | --      |
| Co    | 2.5* | --       | --      |
| V     | 0.35* | --       | --      |
| S     | 0.02* | --       | --      |
| Si    | 0.08* | --       | 0.15*   |
| Ni    | Bal. | --       | --      |

*Maximum

In order to study the weigh loss rate, the specimens before and after corrosion were weighed by a precision electronic balance (FA 3204). The macroscopic morphology of the specimens was photographed by a camera (D3300, Nikon). The surface micromorphology and corrosion depth of the specimens were characterized by a color three-dimensional (3D) laser scanning microscope (VK-9710K).

3. Results and discussion

3.1. Weigh loss rate
Figure 1 shows the weigh loss rate of different alloys as a function of corrosion time. The weigh loss rate of all specimens increases with the increase of corrosion time, but the speed of increase was different. After corrosion for two months, the weigh loss rate of Ti-0.2Pd is the lowest, and that of C-22 and Ti-32Mo alloy is close to each other. After corrosion for 4 or 6 months, the weight loss rate was Ti-0.2Pd, Ti-32Mo and C-22 from low to high. After corrosion for 8 months, the weigh loss rate...
of Ti-0.2Pd increases sharply and becomes much higher than the other two alloys. These phenomena will be analyzed in detail later.

![Figure 1. Weigh loss rate of specimens after different corrosion time.](image)

3.2. Macroscopic morphology and corrosion depth

The macro-morphologies and 3D micro-morphologies of specimens after corrosion are shown in Figure 2-4. The corrosion depths are shown in Figure 5. For all of the alloys, the corrosion depth increases with the increase of corrosion time and pitting corrosion occurs after a certain time.

For C-22 alloy, a rough surface and patina is presented after corrosion for 2 months. Pits with a maximum depth of 298.4 μm are observed after corrosion for 4 months. Then locally connected corrosion pits with a maximum depth of 366.4 μm occur after corrosion for 6 months. Finally, a corrosion pit with a diameter of about 5000 μm and a depth of 3000 μm appears and small corrosion pits are scattered around.

For Ti-0.2Pd alloy, it shows uniform corrosion when the corrosion time is less than 4 months, and the corrosion depth after 2 and 4 months is 163.2 μm and 208.3 μm respectively. Scattered pits with a maximum depth of 254.4 μm appear after corrosion for 6 months. Then several large and deep pits with the maximum diameter of about 3000 μm and the depth of 2500 μm occur and small corrosion pits are scattered after corrosion for 8 months.

For Ti-32Mo alloy, it shows uniform corrosion when the corrosion time is less than 4 months, and the corrosion depth after 2 and 4 months is 208.3 μm and 230.3 μm respectively. There are scattered or even flaky corrosion pits with a maximum depth of 400.4 μm after corrosion for 6 months. Then more small pits can be observed and local spalling occurs, and the maximum corrosion depth is 558.8 μm after corrosion for 8 months.

It can be seen from Figure 5 that after the pitting corrosion, the pit depth of C-22 alloy increases slowly at first, and then increases sharply after corrosion for 6 months; the pit depth of Ti-0.2Pd increases sharply, while that of Ti-32Mo increases slowly in the experimental time.
Figure 2. Macro-morphologies and 3D micro-morphologies of C-22 alloy after corrosion for different time: (A, a) -2 months, (B, b) - 4 months, (C, c) - 6 months and d-8 months.

Figure 3. Macro-morphologies and 3D micro-morphologies of Ti-0.2Pd alloy after corrosion for different time: (A, a) -2 months, (B, b) - 4 months, (C, c) - 6 months and d-8 months.

Figure 4. Macro-morphologies and 3D micro-morphologies of Ti-32Mo alloy after corrosion for different time: (A, a) -2 months, (B, b) - 4 months, (C, c) - 6 months and (D, d)-8 months.
3.3. Corrosion mechanism

Typical micrographs of specimens after corrosion are listed in Figure 6. It can be seen that corrosion occurs both at the grain boundary and inside the grain. After corrosion for two months, the grain boundaries appear to be marked and attack in depth is found inside the grain. The grain size of Ti-0.2Pd alloy is the largest, so the area of the grain boundary contacting with the corrosion solution is the least, resulting in the smallest weigh loss rate in the initial period when the grain boundary corrosion dominates.

In the C-22 alloy, elementals Cr, Mo and W are added into the matrix Ni. Cr is needed for corrosion resistance in oxidizing environment, Mo and W are needed for their protection against attack by reducing environments [2] [5] [9]. However, some carbides that form principally at the grain boundaries are generally richer in Cr and Mo than in the matrix; therefore, the matrix immediately adjacent to these carbides are depleted in these elements causing a localized decrease in the corrosion resistance of the alloy. A depletion of Mo causes an increase in the corrosion rate in HCl and a depletion in Cr causes an increase in the corrosion rate in the NaClO₃ solution [1]. A thin layer of nickel halide formed by the reaction of Ni with halogen, which is insoluble and has good protective performance, can slow down the corrosion rate [9]. Therefore, pitting corrosion occurs and the weigh loss rate increases slowly in C-22 alloy.

In the Ti-0.2Pd alloy, the addition of Pd increases the exchange current density of Ti and therefore, facilitates passivation in many systems [3]. In oxidizing acid, Ti-0.2Pd alloy is easier to passivate, and the passivation film is hard to break down. However, in reducing solution, the passivation trend decreases and Cl⁻ will break through the passivation film. The thickness of passivation film is only a few nanometers, so the exposed bulk material [3] inside will be corroded rapidly after contacting with corrosive solution, which is the reason why the weigh loss rate and corrosion depth of Ti-0.2Pd alloy increase sharply after pitting corrosion.

In the Ti-32Mo alloy, Mo can improve the corrosion resistance of Ti in reducing medium due to its high thermodynamic stability, high corrosion potential, and stable bluntness in HCl solution. However, strong oxidants, such as NaClO₃, can increase the anode potential, which leads to transpassivation and corrosion of Mo [8]. In the process of corrosion, the products of reaction between Mo and Cl⁻ form a insoluble and dense protective film [10], which slows down the corrosion rate, that is why the weigh loss rate and corrosion depth increase slowly even if pitting corrosion happens.
Figure 6. Typical micrographs of specimens after corrosion: a, c and e are micrographs of C-22, Ti-0.2Pd and Ti-32Mo after corrosion for 2 months, respectively; b, d and f are micrographs of C-22, Ti-0.2Pd and Ti-32Mo after corrosion for 8 months, respectively.

4. Conclusions
Corrosion behavior of C-22, Ti-0.2Pd and Ti-32Mo alloys in the aqueous solution of hydrochloric acid and sodium chlorate was investigated. The main conclusions are the followings:

(1) After corrosion for six months, all the alloys were pitted, and the corrosion rate of Ti-0.2Pd increased dramatically after pitting corrosion.

(2) In order to improve the corrosion resistance in the aqueous solution of hydrochloric acid and sodium chlorate, the content of Cr, Mo and W in C-22 alloy should be adjusted. At the same time, intergranular carbides rich in Cr and Mo need to be suppressed as much as possible.

(3) The passivation state of Ti-0.2Pd alloy in reducing medium is easy to be destroyed. Cl\textsuperscript- will destroy the passivation film, and then corrodes the exposed bulk material inside. Therefore, the Ti-0.2Pd alloy was pitted dramatically when it contacts with strong reducing medium for a long time.

(4) The corrosion rate of Ti-32Mo alloy was the lowest even if pitting occurred. This is because the products of reaction between Mo and Cl\textsuperscript- form an insoluble and dense protective film.

(5) In order to improve the corrosion resistance in the environment where strong oxidant and reductant coexist, it is necessary to pay attention to the titanium alloy with both Pd and Mo added in.
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