Erosion corrosion of Ti and Zr in acidic metastannic acid synthesis

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Abstract

In synthesis of metastannic acid, erosion corrosion caused by strong acid and abrasion triggered by stannum granular both create a complex circumstance for reactor. Titanium and zirconium, as the major choices for fabricating the reactor, sustained the combined impact of corrosion and abrasion in the circumstance. While there are very few researches, focusing on the erosion corrosion of the reactor, in the synthesis of metastannic acid. The erosion corrosion behaviors of commercial reactor materials Ti (TA2) and Zr (Zr-1) were investigated in the acidic conditions (20 vol\% H\textsubscript{2}SO\textsubscript{4} or 20 vol\% HNO\textsubscript{3} solutions) according to the complex circumstance. Therefore the wear and corrosion properties were tested by weight loss method and electrochemical method separately, the corrosion situation, such as open circuit potential (OCP) and Tafel plot, of Ti and Zr were tested, the mass loss caused by corrosion and wear were quantitatively, and the surface morphology was observed by scanning electron microscope (SEM). Moreover the corrosion abrasion situation, OCP, Tafel plot, mass loss and surface morphology, had been investigated using self-made corrosion abrasion testing device too. The results showed that in the solution of 20 vol\% HNO\textsubscript{3}, the corrosion rate of Zr increased by 120 times when the solution was heated to 200 °C under corrosion condition, and the corrosion rate of Ti increased by 8 times, indicating that the corrosion resistance of Zr is easier affected by temperature, the corrosion resistance of Zr is better than Ti. Under abrasion condition, using abrasion quartz sand particles as abrasion material, the mass loss rate of Ti and Zr was 159.23 mg/(m\textsuperscript{2}·h) and 252.23 mg/(m\textsuperscript{2}·h). Under erosion corrosion condition, the synergistic effect of erosion corrosion of Ti and Zr exacerbated the mass loss, their mass loss rate respectively was 788.05 mg/(m\textsuperscript{2}·h) and 225.4 mg/(m\textsuperscript{2}·h) especially in Ti-H\textsubscript{2}SO\textsubscript{4} and Zr-HNO\textsubscript{3} systems. A dense oxide layer detected on the surface of Ti and Zr, could improve the corrosion resistance, but it was easy to fatigue and peel off when there was abrasion material in the solution. A erosion corrosion model of Ti and Zr were established for serve life prediction, which could provide theoretical guidance for the design of reaction in production of metastannic acid.

1. Introduction

Erosion corrosion behavior, which is the material loss caused by mechanical wear, is associated with chemical or electrochemical corrosion. Because of the significant harm to materials, erosion corrosion behavior has garnered the interest of researchers, and some research has been conducted on corrosion and wear behavior [1–3]. Bateni studied the wear and erosion corrosion behavior of 304 stainless steel in 3.5 wt.% NaCl solution [4]. Dong studied the tribological properties of Al\textsubscript{2}O\textsubscript{3} ceramic/1Cr18Ni9Ti stainless steel friction pair in pure water and different concentrations of H\textsubscript{2}O\textsubscript{2} solutions [5]. Li found that the wear rate of Mg-Zn-Ca alloy in SBF is higher than that under dry friction [6]. The interaction between corrosion and wear is the key point in the study
of material wear behavior. The test of friction components mainly includes cathodic protection, pure water replacement, the addition of corrosion inhibitors, and air replacement [7]. Ding [8] used a pure water replacement method to measure the friction component in the research on the corrosion and wear performance of titanium alloys [9]. The corrosion component can also be obtained by measuring the corrosion rate of metals. The main categories are weightless methods, electrochemical methods (polarization curve [10], potentiostat [11], and electrochemical impedance [12]), and gas measurement methods. Iwabuchi used the pulse potential method to simulate the corrosion characteristics of the fresh surface formed after the passivation film was destroyed [13]. The study of the erosion corrosion mechanism is significantly important in reducing the loss of the material, proper use of metals and alloys, and control of the erosion corrosion rate.

As an industrial product prepared by the reaction of refined tin and nitric acid, H2SnO3 is widely used in chemical fibers and textiles, plastic products, paints, coatings, and flame retardants in epoxy resin sealing materials. To fully induce the reaction in the production process, the tin particles must be continuously stirred in the nitric acid solution, which unavoidably brings the tin particles into contact with the inner wall of the reaction kettle, leading to a certain degree of wear. In an erosion corrosion environment, material failure is usually accelerated owing to the synergy between the mechanical action of wear/rubbing and the corrosion reaction occurring on the inner wall of the reactor [14, 15]. Owing to the effect of corrosion and abrasion, not only will the service life of the reactor be affected, but the purity of H2SnO3 will also be affected by the corrosion/wear products. Ti and Zr metals exhibit excellent corrosion resistance in strong corrosive environments such as acids, alkalis, salts, and organic solutions [16, 17]. Their chemical properties are stable at normal temperatures. Under heating conditions, the oxide film formed due to oxidation on the metal surface will enhance the corrosion resistance of the material; therefore, it is the most commonly used reactor material when fixed on the inner wall of the kettle by welding [18–21]. So far, there is a notable lack of research focusing specifically on the corrosion and wear behavior of Ti and Zr metals under high wear and strong corrosion environments.

In this study, the operating environment of the reaction kettle was simulated in order to conduct a corrosion and wear test for common reactor materials. The wear behavior of pure Ti and pure Zr metals in a corrosive environment was studied, and the erosion corrosion mechanism was clarified. The corrosive wear models of TA2 and Zr-1 were established for lifetime evaluation, which might provide theoretical guidance for the design of a metastannic acid producing reactor.

2. Material and methods

In this study, commercially available TA2 (GB/T3620.1-2016) and Zr-1 (GB/T21183-2007) were used as samples. The x-ray diffraction pattern of Ti and Zr is shown in figure 1. The curved surfaces of each sample were used as the abraded or corroded surface. Prior to the corrosion and abrasion test, samples were washed with acetone and coated with resin so that only the curved surface was exposed to the medium. Microhardness studies were performed using a VH-5 digital microhardness tester with a Vickers indenter. A constant load of 500 g was applied for 10 s each time to generate indentations in all deposits, and the average hardness value was obtained from five identical measurements. The x-ray diffraction (XRD) patterns of the samples were obtained using a Rigaku-Ultima x-ray diffractometer. After the corrosion and abrasion of the sample, the microscopic morphology of the sample surface was obtained using a ZEISS EVO18 scanning electron microscope.
The corrosion products were analyzed using a laser micro Raman spectrometer model XperRam200 NANOBAES with an excitation wavelength of 532 nm. Electrochemical corrosion tests of all samples were performed using a CHI760C electrochemical analyzer (Shanghai, China) in 20 vol% HNO₃/H₂SO₄ solution. The corrosion behaviors were evaluated by immersing Ti/Zr samples vertically in a 20 vol% HNO₃/H₂SO₄ solution for 21 d at room temperature or under heating conditions. The degree of corrosion was determined by the solute content measured by ICP after immersion, which is expressed in μg/ml. This research involves two kinds of samples. The first one is used for static corrosion, abrasion and corrosion abrasion. In order to maintain the morphology of the inner wall of the reactor, the sample design is shown in figure 2(a). The dimension of sample is 5 × 3 × 10 × 7.85 mm, due to the actual use of the reactor’s internal diameter is 200 mm, of which 7.85 mm is the arc length of the inner wall. The second type is used for electrochemical corrosion, with a sample size of 10 × 10 × 5 mm. Alloys had a fixed exposed area of 7.85 × 10⁻⁵ m² which was protected with insulating glue of 50 μm thickness. Corrosion test and erosion corrosion test was completed in strict accordance with the GB/T 19746-2005 and GB/T 31205-2014, respectively. According to the uniform corrosion standard, the capacity of the corrosion solution for a single sample during static corrosion is 100 ml. The specific experimental parameters are shown in table 1.

All experiments were performed at 25 °C and 80 °C by using a conventional three-electrode electrochemical cell in a 100-ml reactor containing a corrosive medium solution. Each specimen was connected to a copper wire and mounted in epoxy resin in such a way that a surface area of 1 cm² of the sample would be exposed to the testing solution. The polarization curves of the specimens were measured by using a commercial corrosion

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### Table 1. Experimental parameters.

| No. | Sample | Corrosive medium | Temperature (°C) |
|-----|--------|------------------|------------------|
| 1#  | Ti     | 20 vol%HNO₃     | 25 ± 2           |
| 2#  | Ti     | 20 vol%HNO₃     | 200 ± 2          |
| 3#  | Ti     | 20 vol%H₂SO₄    | 25 ± 2           |
| 4#  | Zr     | 20 vol%HNO₃     | 25 ± 2           |
| 5#  | Zr     | 20 vol%HNO₃     | 200 ± 2          |
| 6#  | Zr     | 20 vol%H₂SO₄    | 25 ± 2           |
| 7#  | Zr     | 20 vol%H₂SO₄    | 200 ± 2          |

The corrosion products were analyzed using a laser micro Raman spectrometer model XperRam200 NANOBAES with an excitation wavelength of 532 nm. Electrochemical corrosion tests of all samples were performed using a CHI760C electrochemical analyzer (Shanghai, China) in 20 vol% HNO₃/H₂SO₄ solution. The corrosion behaviors were evaluated by immersing Ti/Zr samples vertically in a 20 vol% HNO₃/H₂SO₄ solution for 21 d at room temperature or under heating conditions. The degree of corrosion was determined by the solute content measured by ICP after immersion, which is expressed in μg/ml. This research involves two kinds of samples. The first one is used for static corrosion, abrasion and corrosion abrasion. In order to maintain the morphology of the inner wall of the reactor, the sample design is shown in figure 2(a). The dimension of sample is 5 × 3 × 10 × 7.85 mm, due to the actual use of the reactor’s internal diameter is 200 mm, of which 7.85 mm is the arc length of the inner wall. The second type is used for electrochemical corrosion, with a sample size of 10 × 10 × 5 mm. Alloys had a fixed exposed area of 7.85 × 10⁻⁵ m² which was protected with insulating glue of 50 μm thickness. Corrosion test and erosion corrosion test was completed in strict accordance with the GB/T 19746-2005 and GB/T 31205-2014, respectively. According to the uniform corrosion standard, the capacity of the corrosion solution for a single sample during static corrosion is 100 ml. The specific experimental parameters are shown in table 1.

All experiments were performed at 25 °C and 80 °C by using a conventional three-electrode electrochemical cell in a 100-ml reactor containing a corrosive medium solution. Each specimen was connected to a copper wire and mounted in epoxy resin in such a way that a surface area of 1 cm² of the sample would be exposed to the testing solution. The polarization curves of the specimens were measured by using a commercial corrosion
measurement system at a scan rate of 0.002 V s\(^{-1}\). The saturated calomel electrode (SCE) was used as the reference electrode. A platinum electrode with a purity of 99.99% is used as an auxiliary electrode.

A schematic diagram of the modified magnetic stirrer used in the corrosive wear test is shown in figure 2. The samples were fixed on the inner wall of the magnetic stirrer, then 20 g of abrasive was poured into the magnetic stirrer, and 500 ml of corrosion solution or deionized water was added to simulate the wear environment. The magnetic stirrer operated at a speed of 100 r min\(^{-1}\), and the wear time was uniformly controlled at 48 h. It was weighed with a high-precision electronic balance (Sartorius, BT125D) with an accuracy of 0.01 mg every 8 h. Considering that the change in the abrasive particle size and the change in the pH value may affect the wear behavior of the materials, the abrasive and corrosive solution was changed every 8 h. The study on the wear behavior of the samples without corrosion in deionized water, and the corrosion and wear behavior of the samples in a corrosive solution were conducted. In order to shorten the experimental period, quartz sands were used as abrasives instead of tin particles, the particle size of tin particles is 622 \(\mu\)m, and quartz sand is 752.6 \(\mu\)m.

Figure 3. The relationship between dissolved amount and time in static corrosion at room temperature: (a) Ti; (b) Zr.

Figure 4. Corrosion shape of the samples in static corrosion at room temperature (red areas are pitting pits): (a) 1\#; (b) 3\#; (c) 4\#; (d) 6\#.
By testing the wear rate of the two abrasives, it was found that the reaction rate increased by 3.1-fold when using quartz sand. The shape of the abrasive is shown in figure 2.

3. Results and discussion

3.1. Corrosion resistance

As shown in table 1, static corrosion experiments were performed on the 7 groups of samples listed. Samples 1#, 3#, 4#, and 6# were used to study the static corrosion behavior at room temperature, and the rest of the samples were used to study the static corrosion behavior in the heating condition. TA2 reacts with sulfuric acid, and the corrosion rate is 10,145-fold that of Zr-1; therefore, TA2 is not a suitable option for sulfuric acid reaction solution.

The relationship between the dissolved amount of the sample and the time in static corrosion at room temperature is shown in figure 3. It can be seen that the dissolved amount of 1#(Ti-HNO₃), 4#(Zr-HNO₃), and 6#(Zr-H₂SO₄) first increased to a certain value, and then remained constant. However, the times taken to reach the peak were not the same. The time taken for 1# and 4# is relatively short. The dissolved amount of 3#(Ti-H₂SO₄) increased with time, and no peak appeared. Comparing the four groups of data, it can be seen that the relationship of the dissolved amount is 4#<6#<1#<3#, and the amount of dissolved in the 20 vol% HNO₃ solution was observed to be lower than that in the 20 vol% H₂SO₄ solution. This indicates that the sample
has stronger corrosion resistance in HNO₃ solution. Moreover, it can be seen that the amount of dissolved Zr is lower than that of Ti under the same corrosive environment.

The corrosion shapes of the samples during static corrosion at room temperature are shown in figure 4. It can be seen that pitting pits with different degrees of corrosion appeared on the surface of the samples. Among them, the pitting pits of 1#, 4#, and 6# are smaller, while the pitting pits of 3# are very obvious, which is consistent with the results shown in figure 3. The corrosion of 1#, 4#, and 6# was weak, and that of 3# was subject to strong corrosion.

The relationship between the dissolved amount and time in high-temperature static corrosion is shown in figure 5. The dissolved amounts of 2# (Ti-HNO₃), 5# (Zr-HNO₃), and 7# (Zr-H₂SO₄) reached their peak values at different times, respectively. Compared with the amount of static corrosion dissolved at room temperature, the dissolved amount of 1# attains peak value after 7 d (0.39 μg/ml) and the dissolved amount of 2# reaches its peak value after 48 h (9.0 μg/ml). It can be seen that the reaction speed increased 8-fold due to the effect of high temperature. Similarly, the reaction speed of 5# is increased by 120-fold compared to that of 4#, and the reaction speed of 7# increased by 620-fold compared to that of 6#, indicating that the corrosion resistance of Zr is more susceptible to temperature.

The laser microscopic Raman spectrum of the sample after high-temperature static corrosion is shown in figure 6, and the excitation wavelength is 532 nm. By comparing the positions of the characteristic peaks, it can be determined that Ti will generate TiO₂ on the surface when it is subjected to high-temperature static corrosion in a 20 vol% HNO₃ solution. The dense TiO₂ isolates the samples from the corrosive medium and protects the internal tissues from the effects of corrosion. Similarly, a dense layer of ZrO₂ is formed on the surface when Zr is subject to high-temperature corrosion, also playing a role in protecting internal tissues. It can be seen that Zr produces the same products in different corrosive media, which indicates that Zr will not undergo chemical reactions in these two media and will only be oxidized. By comparing the characteristic peak intensity, it can be
seen that the characteristic peak intensity of Ti in 20 vol% HNO₃ solution is higher than that in 20 vol% H₂SO₄ solution, owing to the stronger oxidation effect in the 20 vol% HNO₃ solution, which is consistent with the static corrosion results (figures 2 and 4). According to the analysis of micro Raman spectroscopy results, the sample will undergo a passivation reaction under heating conditions, and a layer of passivation film will be generated on the surface of the samples. The passivation process is shown in figure 7.

3.2. Electrochemical tests

Figure 8 shows the evolution of the open circuit potential (OCP) of the experimental materials in different corrosion environments. It can be seen that with an increase in the reaction time, OCP increases by varying degrees. A stable value was reached at 200 s, indicating that the material was passivated. In fact, the thermodynamic instability of the unoxidized Ti and Zr samples in the corrosive solution leads to the formation of a layer of oxide film that insulates the material from the medium.

Table 2 lists the stable open circuit potential of Ti and Zr samples after the 200 s tests in the corrosion solution. A high OCP generally indicates a lower corrosion tendency. The higher the open circuit potential is, the lower the corrosiveness of the materials.

Table 3. Electrochemical parameters obtained from Tafel method extrapolation on samples in various corrosive environments.

| Sample | Corrosive Environment | Ti     | Zr     |
|--------|-----------------------|--------|--------|
| HNO₃   | 20 °C                 | 0.32   | 0.63   |
|        | 80 °C                 | 0.34   | 0.73   |
| H₂SO₄  | 20 °C                 | –0.38  | –0.12  |
|        | 80 °C                 | –0.62  | 0.0027 |

Table 2. Stable open circuit potential value under different corrosion systems.

| Corrosive Environment | OCP (V) |
|-----------------------|---------|
|                        | Ti      | Zr      |
| HNO₃                  | 0.3     | 0.5     |
| 20 °C                 |         |         |
| 80 °C                 | 0.34    | 0.72    |
| H₂SO₄                 | −0.45   | −0.2    |
| 20 °C                 |         |         |
| 80 °C                 | −0.63   | −0.36   |

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3.2. Electrochemical tests

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Table 2 lists the stable open circuit potential of Ti and Zr samples after the 200 s tests in the corrosion solution. A high OCP generally indicates a lower corrosion tendency. The higher the open circuit potential is, the lower the corrosiveness of the materials [22, 23]. In the corrosion solution, the potential value of the same sample in the 20 vol% HNO₃ solution is higher than that in the 20 vol% H₂SO₄ solution. This indicates that both
Ti and Zr have stronger corrosion resistance in 20 vol% HNO₃ solution, which is related to HNO₃ being a strong oxidizing acid. As shown in the Raman spectrum analysis (figure 6), a dense oxide film is formed on the surface of the sample under the effect of oxidation. Heating is also conducive to the generation of the oxide film. In the 20 vol% H₂SO₄ solution, the minimum potential value of the sample Ti under heating environment is −0.63 V, which is consistent with the result of static corrosion, and the corrosion resistance of Ti was the worst in this corrosion environment. The potential value of Zr is higher than that of Ti under the same conditions, indicating that the corrosion resistance of Zr is stronger than that of Ti.

Figure 9 shows the Tafel curves of Ti and Zr under different corrosion environments, and the potential corresponding to the curve tip is the OCP. By comparing the corrosion current density in table 3, results consistent with OCP can be obtained. The corrosion current density of Zr is higher than that of Ti under the same conditions, indicating that the corrosion resistance of Zr is more potent than that of Ti in the same environment. The corrosion current density of the samples shows a regular change with the increase in temperature. The corrosion current density $I_{corr}$ of the Ti sample in the 20 vol% H₂SO₄ solution was the largest, and as the temperature increased, the value of $E_{corr}$ decreased and the value of $I_{corr}$ increased. The results show that the corrosion resistance of Ti in H₂SO₄ solution decreases with increasing temperature, which is related to the rate of chemical reaction of Ti in H₂SO₄ solution exceeding the rate of oxide film formation. The corrosion current densities of the Ti-HNO₃, Zr- HNO₃, and Ti-H₂SO₄ systems all decrease with increasing temperature. This is because the oxide film of the samples is more easily formed with increased temperature, and the sample does not easily react with the corrosion solution.

### Table 4. Wear rate of the sample in deionized water.

| Sample | Ti   | Zr   |
|--------|------|------|
| Hardness (HV₀.₅) | 131  | 211  |
| Wear rate (mg/(m²·h)) | 159.23 | 252.23 |

### Table 5. The erosion corrosion rate of the specimen in different corrosive environments.

| Sample | 1# | 3#  | 4#  | 6#  |
|--------|----|-----|-----|-----|
| $V_{corr}$ (mg/(m²·h)) | 185.77 | 1961.78 | 477.7 | 277.7 |
3.3. Wear behavior

3.3.1. Wear rates

The micro-hardness test on Ti and Zr samples was conducted, and the test results are shown in Table 4. It can be seen that the hardness of Ti is 131 HV0.5, the hardness of Zr is higher than that of Ti, and the value of which is 211 HV0.5. The wear rate of the material was calculated by the weight loss method, and the area of the wear surface of the sample was $7.85 \times 10^{-5}$ m$^2$. Ding used a pure water substitution method to measure the wear component when studying the corrosion and wear properties of titanium alloys. The abrasion rate of the sample after 48 h abrasion in deionized water is shown in Table 4. It can be seen from the table that the wear rate of Ti is lower than that of Zr because of the formation of a more fatigue-peeling structure after a long period of abrasive wear due to the poor toughness of Zr.

Corrosion and wear tests for 1#, 3#, 4#, and 6# were conducted. The corrosion and wear rates were calculated using the weight-loss method. The data are collected in Table 5. The corrosion and wear rate of 1# is the smallest, indicating that the greatest corrosion resistance among the samples. By analyzing the composition of the corroded surface (Figure 6), it can be concluded that Ti will produce a layer of TiO$_2$ on the surface in the corrosion solution, and Zr will produce a layer of ZrO$_2$ in the corrosion solution. It is known that the Mohs hardness of TiO$_2$ and ZrO$_2$ are 6 and 8.5, respectively. After a long period of wear, the higher the hardness value and the more easily tissue fatigue stripping occurs, which is also why the corrosion and wear rates of 4# and 6# are higher than those of 1#.

The SEM images of the corrosion and wear morphology of the samples are shown in Figure 10. It can be seen that the erosion corrosion surface is mainly divided into a furrow wear zone, fatigue stripping zone, and localized corrosion zone. The furrow wear zone is generated owing to the contact between the abrasive and the sample surface during the wear process, which is the standard abrasive wear characteristic [24]. The pitting pits appearing on the surface of the samples are localized corrosion zones, which are caused by the corrosive effect of the corrosive media on the materials. After a long period of wear, a part of the structure of the specimen produced fatigue stripping, which is shown as the fatigue stripping zone in the figure.

In Figures 10(a) and (b), it can be seen that there are more pitting pits in the furrow. The corrosion resistance of 1# and 3# is weak, which is consistent with the relationship between the dissolved amount and time under static corrosion at room temperature (Figure 3). In Figures 10(c) and (d), the peeling marks and small pitting pits are obvious, which is due to the peeling off of the ZrO$_2$ because of its brittleness.

3.3.2. Quantitative estimation of the synergy effect

As previous research has highlighted, the corrosive wear of materials is not a simple combined effect of the two events of corrosion and wear. Synergies can control the behavior of materials in corrosive environments. The weight loss rate of Ti and Zr metals in the erosion corrosion behavior can be expressed as follows [25]:

$$V_{\text{total}} = V_c + V_w + \Delta V$$  \hspace{1cm} (1)

Among them, $V_{\text{total}}$ is the total wear rate in corrosive wear, $V_w$ is the pure wear rate (no corrosion in solution), $V_c$ is the pure corrosion rate, and $\Delta V$ is the synergistic effect of wear and corrosion. So
Table 6. Synergistic effect of samples in different corrosion environments.

| Sample | $V_{\text{total}}$ (mg/(m²·h)) | $V_{w}$ (mg/(m²·h)) | $V_{c}$ (mg/(m²·h)) | $\Delta V$ (mg/(m²·h)) | $\Delta V/V_{\text{total}}$ (%) | $V_{w}/V_{\text{total}}$ (%) | $V_{c}/V_{\text{total}}$ (%) |
|--------|--------------------------------|----------------------|----------------------|-------------------------|-------------------------------|-----------------------------|-----------------------------|
| 1#     | 185.77                         | 159.23               | 1.86                 | 24.86                   | 13.4                          | 85.6                        | 1                          |
| 3#     | 1961.78                        | 159.23               | 1014.5               | 788.05                  | 40.2                          | 8                           | 51.8                        |
| 4#     | 477.7                          | 252.23               | 0.0265               | 225.4                   | 47.2                          | 52.8                        | <0.01                       |
| 6#     | 277.7                          | 252.23               | 0.1                  | 25.37                   | 9.2                           | 90.8                        | <0.01                       |
The synergistic effect of the erosion corrosion behavior of 1#, 3#, 4#, and 6# was calculated according to equation (2). The results are shown in figure 11 and table 6.

In a corrosive solution, a synergistic effect of wear and corrosion was observed. According to table 6, the total wear rate and pure wear rate of 1# are lower than those of samples 4# and 6#, which is due to the fatigue and shedding of tissues of 4# and 6# during prolonged wear. \( V_c \) is two orders of magnitude lower than \( V_{total} \) and \( V_w \) in 1#, 4#, and 6#, which means that mechanical wear dominates the total erosion corrosion [26]. The synergistic effect of 1# is significantly lower than those of 4# and 6#. 3# has the highest synergistic effect because 3# has the worst corrosion resistance. The \( V_w/V_{total} \) ratios of 1#, 4#, and 6# were 85.6%, 52.8%, and 90.8%, respectively, and the ratios of \( \Delta V/V_{total} \) of 1#, 4#, and 6# were 13.4%, 47.2%, and 9.2%, respectively. 4# easily produces an oxide film, which is the reason for the high value of \( \Delta V/V_{total} \). It can be concluded from the above discussion that in the process of corrosion and wear, although the oxide layer will be generated on the surface of Ti and Zr to improve their corrosion resistance, the oxide layer easily produces a fatigue structure and falls off in the case of long-term wear, thus increasing the material loss.

A synergistic attack of corrosion and wear can result in a higher rate of material removal. During corrosive wear, plastic deformation makes the target surface more anodic and thus accelerates material dissolution.

According to the previous analysis, a dense oxide layer is formed on the surface of Ti and Zr in the case of long-term wear, which improves the corrosion resistance of the sample. However, since the oxide layer is worn by an abrasive for a long time, the oxide layer easily falls off. When the surface oxide layer falls off, the material matrix is exposed, which will cause abrasive wear, in turn aggravating mechanical damage. Furthermore, the exposed matrix is corroded by the corrosive solution and forms pitting corrosion. After the matrix loses the

\[ \Delta V = V_{total} - V_c - V_w \] (2)

Figure 12. Corrosion and wear mechanism of Ti and Zr.
protection of the oxide film, it loses electrons and reacts with the anode \([27]\). The anode reaction formula is as follows:

\[
\text{Ti} \rightarrow \text{Ti}^{4+} \, + \, 4e^{-}
\]

\[
\text{Zr} \rightarrow \text{Zr}^{4+} \, + \, 4e^{-}
\]

In the process of corrosion, there must be a coupling of the cathode reaction and anode reaction to produce corrosion. In this study, erosion corrosion occurs in an acidic environment, and because of the experimental conditions of strong stirring, the cathode reaction is as follows:

\[
2\text{H}^{+} \, + \, 2e^{-} \rightarrow \, \text{H}_{2} \, \text{and} \, \text{O}_{2} \, + \, 4\text{H}^{+} \, + \, 4e^{-} \rightarrow \, 2\text{H}_{2}\text{O}
\]

As shown in figure 12, the interaction mechanism of Ti and Zr corrosion and wear can be summarized as follows: abrasive wear continuously removes the oxide film on the sample surface, exposes the new active surface to the corrosive medium, and promotes the corrosion process. At the same time, corrosion will produce pitting on the surface of the material, reduce its anti-abrasive wear performance, and promote wear.

Usually, the weight loss is caused by the combined effect of corrosion and wear. When a passive metal or alloy is subjected to sliding wear in a corrosive environment, the total material wear rate is different from that predicted by simply adding the wear rate measured in the absence of corrosion and the corrosion rate observed in the absence of wear. The experimental observations of the mechanical and chemical synergistic effects of erosion corrosion of materials are well reviewed. Synergy effects play a significant role in damaging many industrial facilities when exposed to a corrosive environment. With respect to Ti and Zr, abrasive wear in a corrosive environment also follows the same general rules of corrosion–wear behavior, which is the higher hardness of materials results in a lower synergy effect and a larger resistance to mechanical plowing when abrasive wear occurs in a corrosive environment. However, the oxide layer produced on the sample surface and the substrate undergo a sudden change in hardness. During long-term wear, the TiO\(_2\) and ZrO\(_2\) oxide layer and the matrix with a higher hardness are prone to fatigue and falling off owing to the sudden change in mechanical properties. Solving the mechanical mutation of the oxide layer and matrix structure will enhance the corrosion resistance–wear resistance of the reactor.

According to the above research on static corrosion and erosion corrosion in the case of using quartz sand as an abrasive, the rule of corrosion wear rate with temperature in the actual working conditions of the tin chemical industry is obtained:

\[
V_{\text{total}} = aT^b + \frac{10}{31}(cT + V_w)
\]

In the formula, \(a\), \(b\), and \(c\) are constant, and \(V_w\) is the wear amount of pure wear at room temperature. The values of \(a\), \(b\), \(c\), and \(V_w\) of the three systems are shown in table 7.

### 4. Conclusions

1. Under corrosive wear conditions with nitric acid solution, the wear resistance of Ti is higher than that of Zr. Although they exhibit similar abrasive behavior, the corrosive wear rate of Zr is lower than that of Ti; moreover, the corrosion resistance of Zr is more negatively susceptible to temperature.

2. Ti and Zr metals show abrasive wear in deionized water and show pitting corrosion, tissue fatigue stripping, and abrasive wear in corrosive medium. Abrasive wear plays a leading role in the total corrosion wear. Synergy plays an essential role in Ti- \(\text{H}_2\text{SO}_4\) and Zr- \(\text{HNO}_3\), and seems less important in Ti-\(\text{HNO}_3\) and Zr- \(\text{H}_2\text{SO}_4\).

3. The interaction mechanism of corrosion and wear can be summarized as abrasive wear continuously removes the oxide film on the surface of the sample, thereby exposing the new active surface to the corrosive

| Table 7. The constant value of different corrosion wear systems. |
|-------------------|--------|--------|--------|--------|
| Corrosive wear environment | \(a\)  | \(b\)  | \(c\)  | \(V_w\) |
| Ti-\(\text{HNO}_3\) | 0.00284 | 2.16   | 1.25   | 159.23 |
| Zr-\(\text{HNO}_3\) | 1.626 \times 10^{-5} | 2.46885 | 11.27  | 252.23 |
| Zr-\(\text{H}_2\text{SO}_4\) | 1.8724 \times 10^{-5} | 2.865  | 1.27   | 252.23 |
medium and facilitating corrosion. At the same time, corrosion produces pitting on the surface of the material, reduces its anti-abrasive wear performance, and encourages wear.

(4) The corrosive wear models of TA2 and Zr-1 were established for lifetime evaluation, which might provide theoretical guidance for the reactor design of metastannic acid production.

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