

Tribocorrosion behaviors of Ti–6Al–4V and Monel K500 alloys sliding against 316 stainless steel in artificial seawater

CHEN Jun^{1,2}, YAN Feng-yuan¹

1. State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China;
2. Graduate School of Chinese Academy of Sciences, Beijing 100864, China

Received 22 July 2011; accepted 20 September 2011

Abstract: The tribocorrosion behaviors of Ti–6Al–4V and Monel K500 alloys sliding against 316 stainless steel were investigated using a ring-on-block test rig in both artificial seawater and distilled water. It is found that friction coefficients are in general larger in distilled water compared with seawater. The wear losses of Ti–6Al–4V and Monel K500 alloys are larger in seawater compared with distilled water. The mechanical action can destroy the passive film and increase the corrosion rate. The synergism effect between corrosion and wear occurs. The synergism action between corrosion and wear is related to the corrosion rate and with the increase of corrosion rate, the synergism becomes more important. 316 stainless steel suffers severe wear sliding against Monel K500 alloy compared with sliding against Ti–6Al–4V alloy in both distilled water and seawater.

Key words: Ti–6Al–4V alloy; Monel K500 alloy; seawater; tribocorrosion; synergism effect

1 Introduction

Tribocorrosion is a material degradation resulting from simultaneous action of wear and corrosion[1]. Passive metals are particularly susceptible to tribocorrosion because rubbing can easily destroy the protective properties of the passive film and lead to a high corrosion rate before the surface repassivates. The synergism between wear and corrosion may lead to an acceleration of the degradation of metals. Therefore, it is important to identify the contribution of corrosion and wear to material removal in tribocorrosion process in order to minimize the material degradation [2,3]. Many factors determine the interaction between wear and corrosion. For example, the mechanical abrasion of the passive film usually leads to wear-accelerated corrosion due to high chemical reactivity of the bare metal surface exposed to the corrosive environment. On the other hand, the passive films seem to decisively influence the surface mechanical response of metals as well as the third body behavior. Many previous studies have performed to evaluate the friction behavior and the synergy action

between wear and corrosion in a corrosive environment. STEMP et al [1] and STOJADINOVIC et al [4] have done many studies on the tribocorrosion, including the wear mechanism of passive film and the mechanistic models. Many researches were also made on the tribocorrosion of different alloys including stainless steels, Co-based alloys and Ni-based alloys and so on [5–7]. DING et al [8] evaluated the corrosion wear behaviors of aluminum alloy.

With the rise of exploiting ocean all over the world, attention has been increasingly paid to the application performance of various metallic materials in ocean environment [9]. Seawater hydraulic drive is a key technology in ocean exploitation and widely used in deep-sea submergence vehicle, underwater robot, submarine oil production system, etc. This system requires high-performance frictional pair materials [10,11]. Metals may performance poor because of the synergism between wear and corrosion in seawater. The salt concentration, which plays an important role in physical and chemical processes, can affect the tribocorrosion.

Many scientists focused on studying the

tribocorrosion behavior of passive metals sliding against alumina or zirconia, which was considered to act as an inert antagonist in the tribocorrosion systems. However, the ceramic materials have a poor plasticity and low machinability performance, making it unsuitable for application in bearing system, precision instruments and orthopaedic implants. Therefore, passive metal frictional pairs are widely used compared with metal-alumina frictional pairs. Moreover, the tribocorrosion properties of passive metals sliding each other in corrosion mediums have not yet been investigated in detail. Therefore, it is of primary importance to study the tribocorrosion behavior of passive metals in seawater. Titanium and its alloys, nickel and its alloy and stainless steels possess an excellent corrosion resistance in seawater and are widely used in marine [1,7,12,13]. The tribocorrosion behaviors of Ti-6Al-4V and Monel K500 alloys sliding against 316 stainless steel in artificial seawater and distilled water are performed in this work.

2 Experimental

2.1 Material and solution

The chemical compositions of the three alloys are shown in Table 1, and their mechanical properties are listed in Table 2. The solutions used in this study were distilled water and artificial seawater. The seawater was prepared according to ASTM D1141—98 standard. Table 3 shows the compositions of the artificial seawater, where the gross concentration employed in the standard is an average of many reliable individual analyses. The concentration of the seawater was 3.5%. To evaluate the effect of salt concentration, 0.5%, 1%, 2%, 3% and 4% seawater were prepared by adjusting all the compounds in accordance with the mass fraction shown in Table 3. The pH values of all the seawater solutions were adjusted to 8.2 using 0.1 mol/L NaOH solution. The concentration of dissolved oxygen in seawater with different salinities was measured using JPSJ-605 dissolved oxygen meter.

Table 1 Chemical composition of three alloys

Alloy	Composition/%
Ti-6Al-4V	6.25Al, 4.21V, 0.0073H, 0.19O, 0.22Fe, Balance Ti
Monel K500	30Cu, 3Al, 0.6Ti, 1Fe, 0.1C, Balance Ni
316 stainless steel	17.2Cr, 10.2Ni, 2.1Mo, 0.04C, ≤0.03S, ≤1Si, ≤2Mn, Balance Fe

Table 2 Mechanical properties of three alloys

Alloy	Elastic modulus/ GPa	Hardness (HV)	Yield strength/ MPa	Tensile strength/ MPa	Poisson ratio
Ti-6Al-4V	126	363	830	910	0.34
Monel K500	210	220	790	1125	0.308
316 stainless steel	200	200	310	620	0.3

Table 3 Chemical composition of 3.5% seawater

Compound	Concentration/(g·L ⁻¹)
NaCl	24.53
MgCl ₂	5.20
Na ₂ SO ₄	4.09
CaCl ₂	1.16
KCl	0.695
NaHCO ₃	0.201
KBr	0.101
H ₃ BO ₃	0.027
SrCl ₂	0.025
NaF	0.003

2.2 Polarisation curves

Potentiodynamic polarisation curves were measured at room temperature of (25±1) °C using a CHI760C electrochemical test system with a three-electrode cell. The active area of the Ti-6Al-4V and Monel K500 electrode was 0.2 cm². Prior to experiments, the electrode was polished using grade 1200 silicon carbide paper. A platinum plate and saturated calomel electrode (SCE, 0.244 V with respect to the standard hydrogen electrode) were used as the counter and reference electrodes, respectively. Before starting the polarisation curve, a cathodic pre-polarisation of 5 min at -1 V was performed. The potential was swept from -1 to +1 V at a sweep rate of 10 mV/s. The potentiodynamic polarization curves were automatically acquired.

2.3 Tribocorrosion tests

The schematic contact diagram of the frictional couple is shown in Fig. 1. The friction and wear behavior was evaluated using an MRH-03 type ring-on-block test rig. The upper block with dimensions of 19 mm×12 mm×12 mm was made of Ti-6Al-4V or Monel K500 alloy. Lower ring with dimensions of $\varnothing 49.22$ mm×13.06 mm was made of 316 stainless steel. Friction and wear tests were carried out at a linear velocity of 0.5 m/s, load of 100 N, and duration of 60 min. Before each test, the stainless steel ring was abraded to reach a surface roughness of about 0.10 μ m. Then, the ring and block were ultrasonically cleaned with acetone. The aqueous

medium lubrication between the sliding surfaces was realized by continuously dropping the medium onto the sliding surface at a rate of 900–950 mL/h. The wear volume loss of the blocks is calculated as:

$$\Delta V = \frac{m_0 - m_1}{\rho} \quad (1)$$

where ΔV is the wear volume loss (mm^3); m_0 is the mass of materials before corrosion wear (mg); m_1 stands for the mass of specimen after corrosion wear (mg); ρ is the density. Each experiment was repeated at least twice to check for reproducibility.

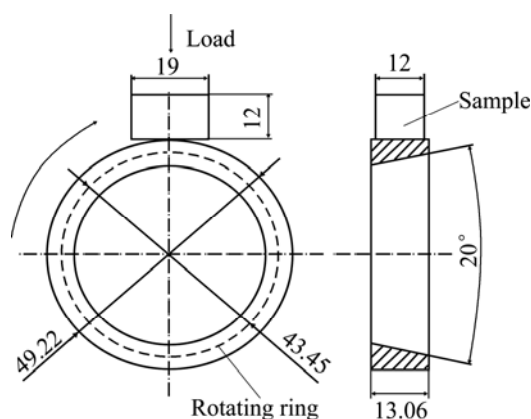


Fig. 1 Contact schematic diagram for frictional couple (unit: mm)

2.4 Characterization

After completion of the sliding, the metal specimens were ultrasonically cleaned in acetone. The morphologies of the worn surfaces were examined using a JEM-5600LV scanning electron microscope (SEM). The chemical composition of the wear scar was investigated with a PHI-5702 multi-functional X-ray photoelectron spectroscope (XPS) having Al K_{α} radiation as the excitation source and the binding energy of contaminated carbon (C_{1s} at 284.8 eV) as the reference.

3 Results

3.1 Polarisation curves

Figure 2 shows the typical potentiodynamic polarization curves of the three alloys in 3.5% seawater. The polarization curves show four potential domains. The cathodic domain includes potentials below the corrosion potential where the corrosion current is determined by the reduction of water and, partially, of dissolved oxygen. The narrow domain characterized by the transition from cathodic to anodic current appears at the vicinity of corrosion potential. Then a large passive zone is found, where the current density remains approximately constant [14,15]. Moreover, Ti-6Al-4V alloy exhibits the most wide passive region and excellent

corrosion resistance in the three alloys[14].

The corrosion current densities (J_{corr}) of Ti-6Al-4V alloy and Monel K500 alloy in seawater with different salinities are summarized in Table 4. It can be seen that both alloys have the maximum corrosion rate with the increase of salinity. The concentration of dissolved oxygen in seawater with different salinities is shown in Fig. 3. It can be seen that the salt concentration increases with the decrease of dissolved oxygen in seawater. The

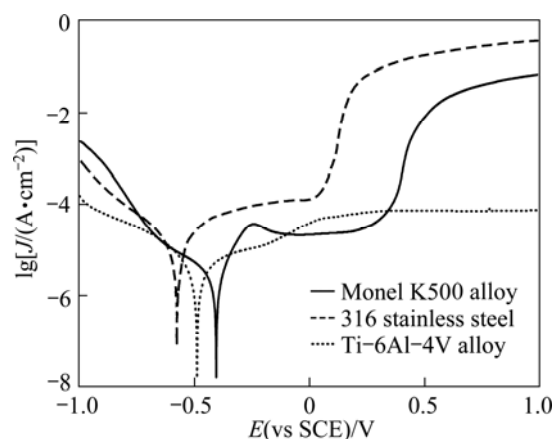


Fig. 2 Typical potentiodynamic polarization curves of three alloys in 3.5% seawater

Table 4 Corrosion current density of Ti-6Al-4V and Monel K500 alloys by Tafel plot analyses

Solution	Current density/ ($\mu\text{A}\cdot\text{cm}^{-2}$)	
	Ti6-Al-4V alloy	Monel K500 alloy
0.5% seawater	0.251±0.053	6.52±0.67
1% seawater	0.268±0.087	8.97±0.85
2% seawater	0.313±0.062	11.34±0.58
3% seawater	0.329±0.046	10.89±0.39
3.5% seawater	0.344±0.067	10.69±0.37
4% seawater	0.342±0.059	10.41±0.49

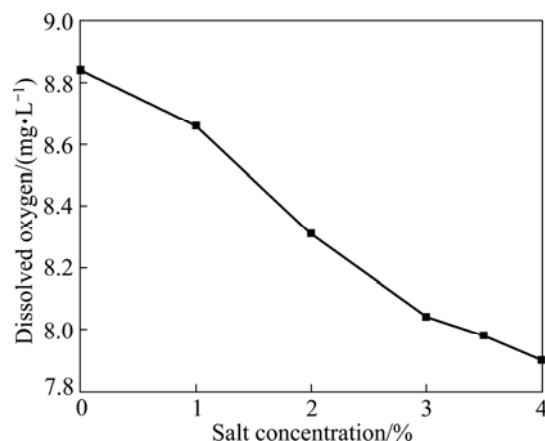


Fig. 3 Dissolved oxygen in seawater with different salinities

dissolved oxygen in pure water is 8.84 mg/L. However, it is only 7.89 mg/L in 4% seawater. Seawater has good conductivity, which can enhance the activity of metals and improve the corrosion rate. However, the decrease of the oxygen concentration will slow down the cathodic reaction (oxygen reduction) and decrease the corrosion rate [16]. The maximum corrosion rate is due to the synergism of salt concentration and dissolved oxygen in seawater.

3.2 Friction and wear

The typical evolution of friction coefficient with sliding time in distilled water and 3.5% seawater is shown in Fig. 4. The frictional coefficient rapidly reaches a steady state, exhibiting some peaks at fairly regular time intervals. Such fluctuations are attributed to the formation and ejection of wear debris [17,18]. Friction coefficients are larger in distilled water compared with seawater for both friction pairs. Less fluctuation is observed in seawater. The remarkable antifriction effect of the seawater is of particular note. The friction coefficient is reduced due to corrosion.

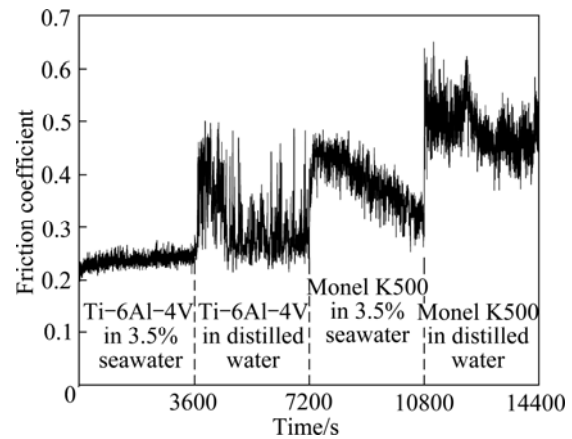


Fig. 4 Evolution of friction coefficient in different media

Moreover, the Monel K500 alloy exhibits larger friction coefficient compared with Ti-6Al-4V alloy.

The wear volumes are determined by the mass decrease of metal samples. The obtained values are plotted in Fig. 5 for Ti-6Al-4V alloy sliding against 316 stainless steel and in Fig. 6 for Monel K500 alloy sliding

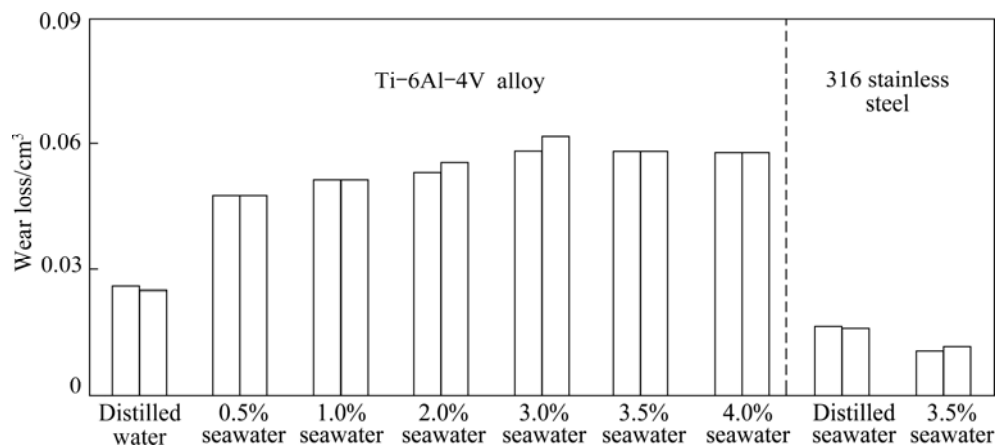


Fig. 5 Wear volumes for Ti-6Al-4V alloy sliding against 316 steel in different media (Each bar corresponds to an independent experiment)

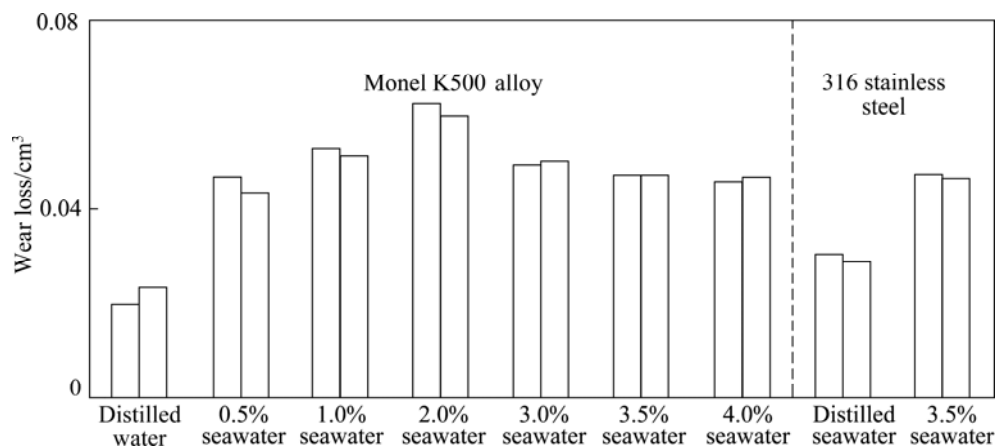


Fig. 6 Wear volumes for Monel K500 alloy sliding against 316 stainless steel in different media (Each bar corresponds to an independent experiment)

against 316 stainless steel. The wear volume is significantly smaller in distilled water compared with seawater for Ti-6Al-4V and Monel K500 alloys. This indicates that corrosion could reduce the wear resistance. The salinity of seawater affects the wear volume also. For Ti-6Al-4V alloy, wear loss increases rapidly from distilled water to 0.5% seawater and slightly reaches a maximum value in 3% seawater. For Monel K500 alloy, wear loss increases to a maximum value in 2% seawater and then sharply decreases to a steady value in 3% seawater. However, for the 316 counterpart metals, the wear loss exhibits different trends when sliding against different alloys. The wear loss of 316 stainless steel is larger in seawater compared with distilled water when sliding against Monel K500 alloy. The wear loss is accelerated due to the corrosion. The wear loss is a little small in seawater compared with distilled water when sliding against Ti-6Al-4V alloy. Interestingly, the effect of corrosion on wear of 316 stainless steel exhibits different trends when sliding against different alloys. 316 stainless steel suffers severe wear sliding against Monel K500 alloy compared with sliding against Ti-6Al-4V alloy in both distilled water and seawater.

3.3 Surface analysis

The SEM images of wear worn surfaces for Ti-6Al-4V and 316 stainless steel pairs in distilled water and 3.5% seawater after cleaning are given in Fig. 7. The surfaces for 316 stainless steel show mainly flat regions

interrupted by a few fine grooves parallel to the sliding direction. The surfaces of Ti-6Al-4V alloy exhibit severe grooves compared with 316 stainless steel. Ti-6Al-4V alloy suffered severe wear in this friction pairs. Wear debris and cracks are found around the wear scars sliding in the seawater for Ti-6Al-4V alloy. And the surface of 316 stainless steel suffered minor corrosion sliding in seawater. The SEM images of wear worn surfaces for Monel K500 and 316 stainless steel pairs in distilled water and 3.5% seawater after cleaning are given in Fig. 8. It can be seen that both alloys exhibit severe plastic deformation. Cracks and thin flake are found for both alloys. A lot of wear debris are found around the wear scars sliding in the seawater for Monel K500 alloy. And the surface of 316 stainless steel suffered severe corrosion.

The XPS analysis shows the presence of carbon, calcium, magnesium, iron and oxygen for both Ti-6Al-4V and Monel K500 alloys. Titanium and nickel are shown in Ti-6Al-4V alloy and Monel K500 alloy, respectively. Typical spectra of the relevant elements are given in Fig. 9. The Ti $2p_{3/2}$ peak locates at approximately 459 eV corresponding to TiO_2 . The Ni $2p_{3/2}$ peak position (853 eV) indicates that nickel is present corresponding to NiO. The peak energy of Fe $2p_{3/2}$ (711 eV) is of trivalent iron corresponding to Fe_2O_3 . These results indicate that the metal particles due to the passive film removal by mechanical action mainly consist of TiO_2 , Fe_2O_3 on Ti-6Al-4V alloy and NiO,

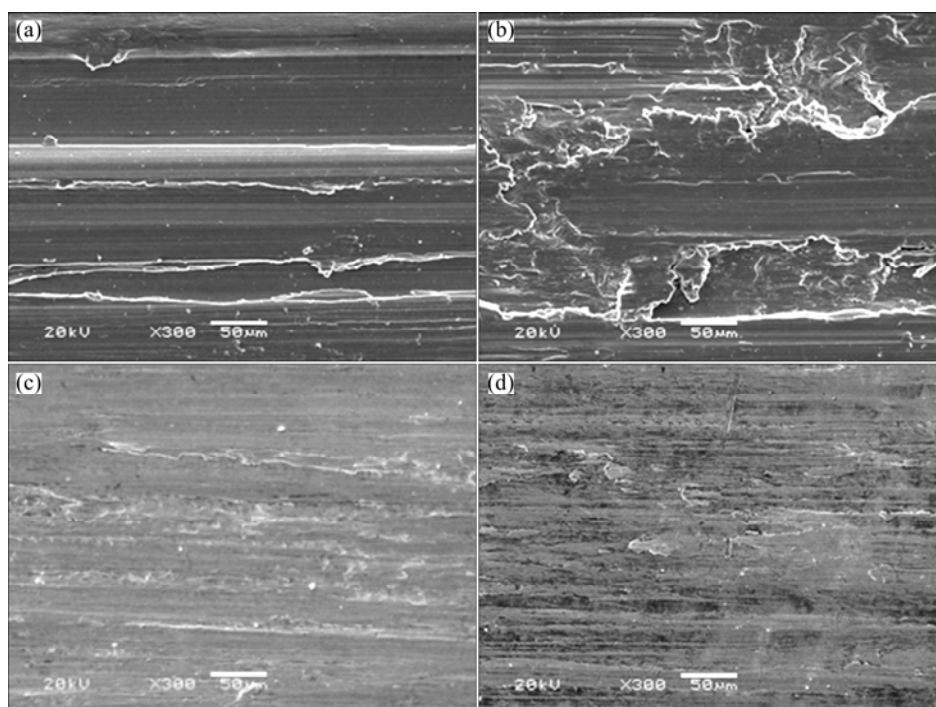


Fig. 7 SEM images of wear worn surfaces for Ti-6Al-4V and 316 stainless steel pairs in distilled water and 3.5% seawater: (a) Ti-6Al-4V alloy in distilled water; (b) 316 steel in distilled water; (c) Ti-6Al-4V alloy in 3.5% seawater; (d) 316 steel in 3.5% seawater

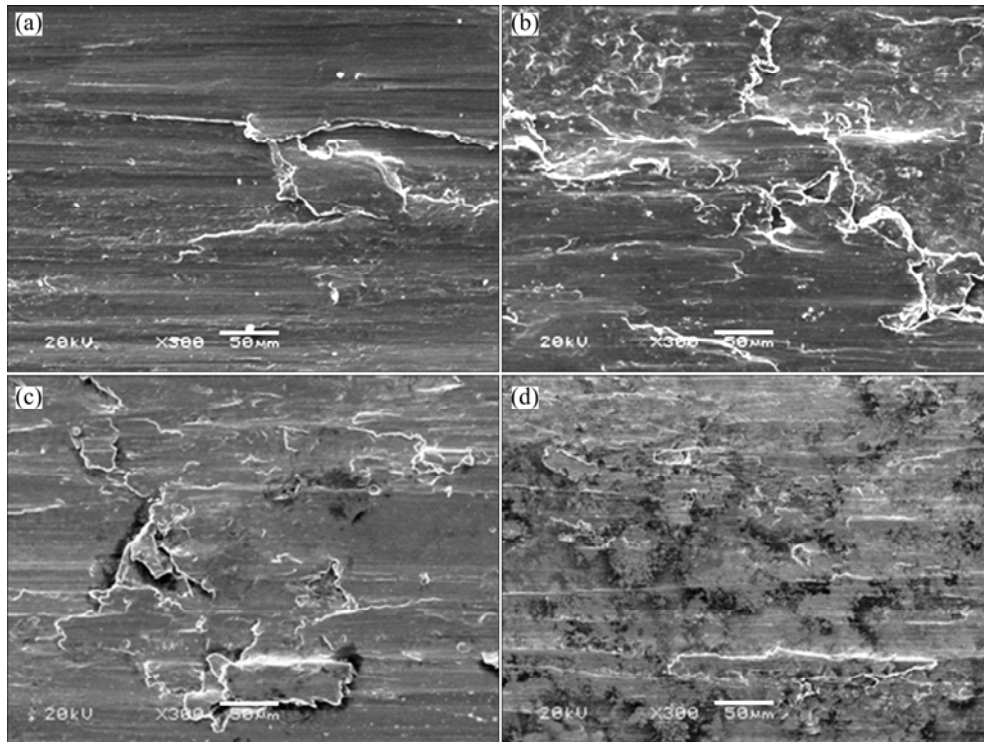


Fig. 8 SEM images of wear worn surfaces for Monel K500 and 316 stainless steel pairs in distilled water and 3.5% seawater: (a) Monel K500 alloy in distilled water; (b) 316 steel in distilled water; (c) Monel K500 alloy in 3.5% seawater; (d) 316 steel in 3.5% seawater

Fe_2O_3 on Monel K500 alloy. The Fe_2O_3 passive film of 316 stainless steel is removal and transferred [19,20]. Moreover, calcium and magnesium are observed on the worn surface. The peak of Mg 2s around 88 eV is assigned to $\text{Mg}(\text{OH})_2$ and the peaks of Ca 2p at 347 eV and 351 eV are assigned to $\text{Ca}(\text{OH})_2$. Seawater contains Mg^{2+} and Ca^{2+} . The OH^- is significant due to the cathodic reaction (oxygen reduction), and $\text{Mg}(\text{OH})_2$ and CaCO_3 are deposited on the friction interface, which can low the coefficient of friction [21].

4 Discussion

4.1 Synergistic effect

To investigate the synergism effect between corrosion and wear, the synergism ΔV can be calculated according to the typical corrosion wear model as [2] follows:

$$\Delta V = V - V_c - V_w \quad (2)$$

where V is the total wear loss after sliding in seawater, V_w stands for the pure mechanical wear; V_c stands for the wear loss induced by pure corrosion in the absence of wear, which can be calculated by static J_{corr} , as [22]:

$$V_c = \frac{vSt}{\rho} \quad (3)$$

$$v = 3.73 \times 10^{-4} \frac{M_r J_{\text{cor}}}{n} \quad (4)$$

where v is the corrosion rate; M_r is the relative molecular mass; n is the valence in the process of corrosion; ρ is density; t is the time of friction test and is 60 min here; S is the average contact area. There are many methods to determine the material loss caused by pure mechanical effect. One of them, which is adopted in this study, is to suppose that in pure water there is no electrochemical corrosion and the oxidation effect could be ignored because of its low oxidation rate. Therefore, in this study, V_w can be obtained in pure water with quite low electric conductivity [23,24]. The contribution of V_c , V_w and ΔV to total wear loss, V , of Ti-6Al-4V and Monel K500 alloys in seawater are summarized in Table 5 and Table 6.

It can be seen that all the contributions of V_c are very small, which indicates that pure corrosion in the absence of wear is negligible in seawater. Ti-6Al-4V and Monel K500 alloys have excellent corrosion resistance in seawater. The contributions of V_w/V and $\Delta V/V$ are significant, indicating that wear loss is induced by mechanical abrasion and synergism action between corrosion and wear. The synergism action varies with the different salinities. Interestingly, the synergism action between corrosion and wear is related to the corrosion rate and increases with the increase of corrosion rate, the synergism ΔV becomes more important. The synergism ΔV is controlled by the electrochemical reactions [24].

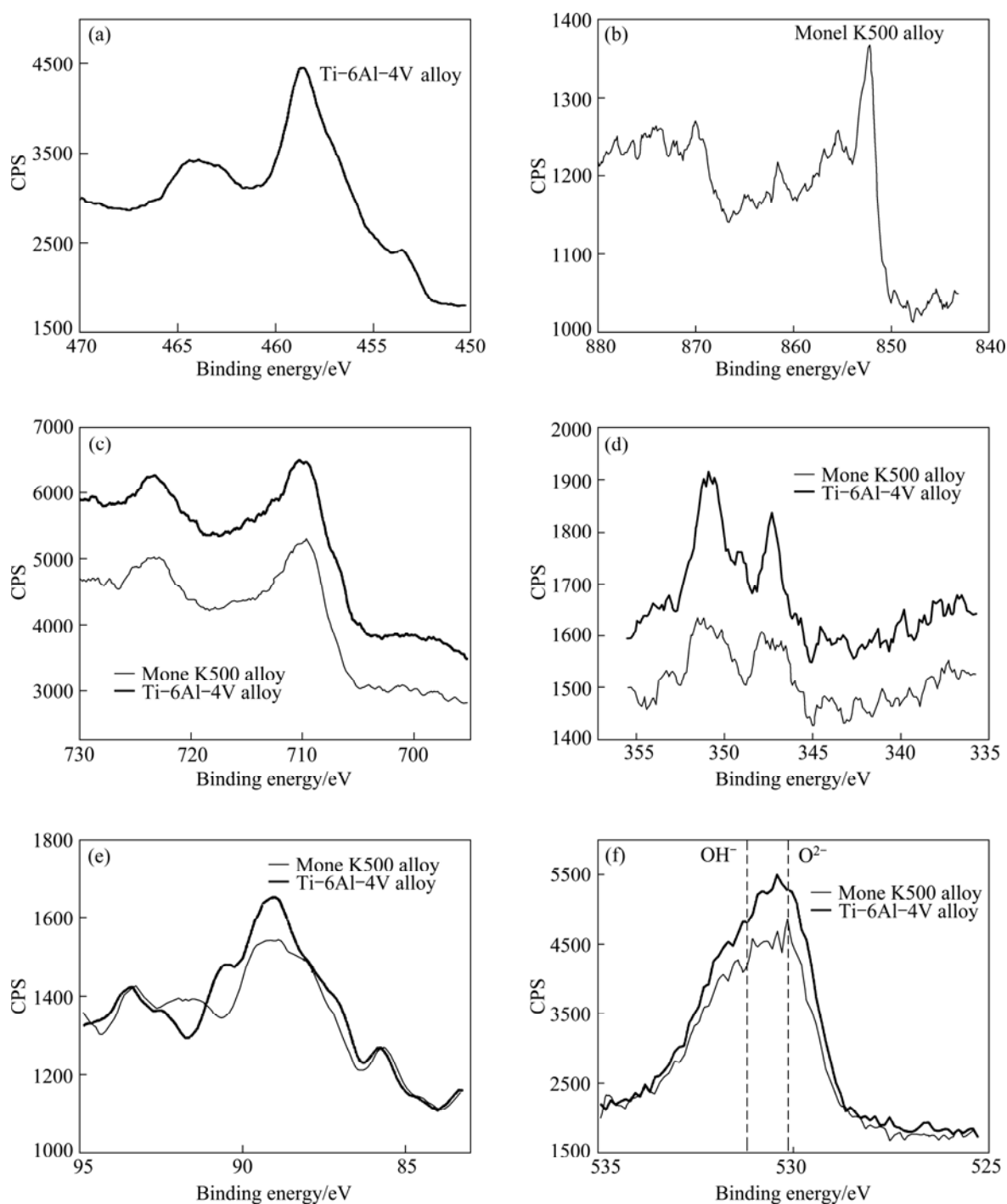


Fig. 9 XPS spectra of binding energy region of Ti 2p (a), Ni 2p (b), Fe 2p (c), Ca 2p (d), Mg 2s (e) and O 2s (f)

Table 5 Contribution of each parameter to wear loss of Ti-6Al-4V alloy

Solution	$(V_c/V)/10^{-6}$	V_w/V	$\Delta V/V$
0.5% seawater	2.351	0.5419	0.4581
1% seawater	2.345	0.4977	0.5023
2% seawater	2.595	0.4716	0.5284
3% seawater	2.566	0.4438	0.5562
3.5% seawater	2.876	0.4375	0.5625
4% seawater	2.656	0.4418	0.5582

Table 6 Contribution of each parameter to wear loss of Monel K500 alloy

Solution	$(V_c/V)/10^{-6}$	V_w/V	$\Delta V/V$
0.5% seawater	6.832	0.5349	0.4651
1% seawater	8.356	0.4664	0.5336
2% seawater	11.23	0.3663	0.6337
3% seawater	13.73	0.4917	0.5083
3.5% seawater	12.83	0.5125	0.4785
4% seawater	12.49	0.5186	0.4814

4.2 Wear mechanism

A simple mechanical model was proposed by Uhlig to describe the material removal caused by wear and corrosion [3]. In this model, material removal results from two distinct mechanisms: mechanical wear and wear-accelerated-corrosion. The former mechanism is due to the metal particles detached by the mechanical action. Meanwhile, the passive film originally formed on surface is destroyed due to wear. Corrosion can be accelerated due to the mechanical removal of a surface film to expose the bare material to the electrolyte, leading to the onset of corrosion of the bare metal [25]. Thus, wear-accelerated-corrosion occurs on the bare metal. Corrosion can decrease the coefficient of friction. When corrosion takes place, an increase in the surface roughness occurs and, consequently a reduction occurs in the contact area. Then friction coefficient is reduced [15].

The third bodies are formed by the accumulation of debris particles detached by wear between the contacting areas [3,26]. The formation of the third bodies can play a critical role in tribocorrosion. Figure 10 schematically illustrates the possible material flows occurring in tribocorrosion contacts in the case of passive metals sliding against each other. The metal particles detached from both passive metals due to mechanical action (flow 1) involves the direct ejection of particles (flow 2) and corrosion ions (flow 7) dissolving out of the metals, as postulated in Uhlig's model. Moreover, some particles act as the third body in the tribo-contact (flow 3). The third body particle can adhere to both the metal surface (flow 4) or can get fragmented in smaller particles (flow 5). The smaller particles may repeat above process (flows 4 and 5). Once they reach a critical size, the small particles can be ejected from the contact (flow 6) due to the ejection action of friction and the cleaning action of seawater. Wear-accelerated corrosion mainly occurs on two fields: on the third body particles during fragmentation (flow 8) and on the both bare metals (flow 7) after particle detachment. Moreover, the metal particles (flow 4) deposited onto the surface can modify friction and thus decrease the coefficients of friction.

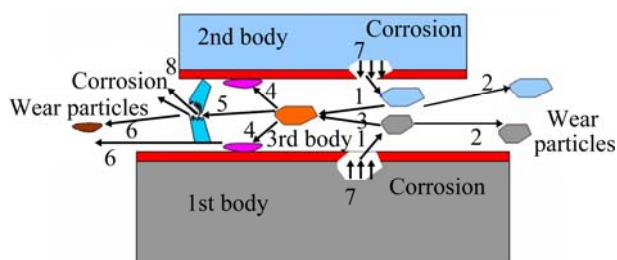


Fig. 10 Schematic illustration of material flows and reactions in tribocorrosion system involving the 1st body, the 2nd body and the third body

Such particles consisting of hard oxides may induce abrasion on the metal surface.

For the 316 stainless steel, the wear loss exhibits different trends when sliding against different alloys. It may be explained by the galvanic corrosion theory. When metals with high standard electrode potential difference contact each other in corrosion environment, galvanic corrosion occurs. This may play a critical role in tribocorrosion when friction pairs are different metals. Whether galvanic corrosion occurs or not, the standard electrode potential difference between metals is the most important criterion. The corrosion of metal with relative negative electrode potential is accelerated, while the relative positive electrode potential will slow down the corrosion of metals. In the tribocorrosion process, the passive film is failure. The bare metal exposes to seawater and the galvanic corrosion may occur. The standard electrode potentials of different bare metals used in this study are shown in Table 7. The standard electrode potential differences of Ti, Fe and Ni, Fe are 1.186 V and 0.192 V, respectively. Galvanic corrosion can play a critical role for Ti–6Al–4V and 316 stainless steel pairs. The schematic diagram is presented in Fig. 11(a). Galvanic corrosion is negligible for Monel K500 and 316 stainless steel pairs, and is schematically represented in Fig. 11(b). Some factors can influence the galvanic corrosion rate. The standard electrode potential difference between Ti and Fe is 1.186 V. This potential difference greatly increases the corrosion of Ti–6Al–4V (anode) and effectively protects the 316 stainless steel (cathode). Seawater has a good conductivity and increases the current transmission. The bare area of 316 stainless steel is much larger compared with Ti–6Al–4V, which can enhance the galvanic corrosion of Ti–6Al–4V.

Table 7 Standard electrode potentials (vs SCE) of different elements (V)

Ti	Al	Fe	Ni	Cr	Cu
−1.628	−1.662	−0.442	−0.250	−0.774	+0.153

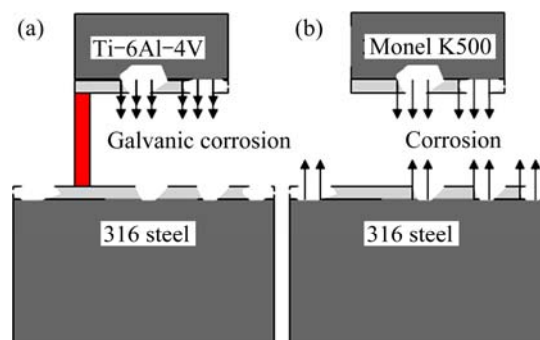


Fig. 11 Galvanic corrosion schematic diagram of different metals contacting Ti–6Al–4V alloy (a) and Monel K500 alloy (b) sliding against 316 stainless steel

Therefore, the galvanic corrosion should be considered if both friction pairs are metals in a corrosive environment [27,28].

5 Conclusions

1) The friction coefficient is in general larger in distilled water compared with seawater. Corrosion leads to an increase in the surface roughness and reduction in the contact area. Then friction coefficient is reduced.

2) The wear loss of Ti–6Al–4V and Monel K500 alloys is larger in seawater compared with distilled water. The mechanical action can destroy passive film and increase the corrosion.

3) The wear loss of 316 stainless steel sliding against Monel K500 alloy is larger in seawater compared with distilled water. However, when sliding against Ti–6Al–4V alloy, the wear loss of 316 stainless steel is larger in distilled water compared with seawater, which is due to the protective effect of galvanic corrosion.

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Ti-6Al-4V 和 Monel K500 合金在海水环境中与 316 不锈钢对磨时的腐蚀磨损性能

陈 君^{1,2}, 阎逢元¹

1. 中国科学院 兰州化学物理研究所, 固体润滑国家重点实验室, 兰州 730000;

2. 中国科学院 研究生院, 北京 100864

摘 要: 研究 Ti-6Al-4V 和 Monel K500 合金在海水和纯水环境下的腐蚀磨损性能, 对偶材料为 316 不锈钢, 实验装置为环-块摩擦磨损试验机。研究结果表明, Ti-6Al-4V 和 Monel K500 合金在海水中的摩擦因数明显小于在纯水中的摩擦因数, 在海水中的磨损量明显大于纯水中的磨损量, 这主要是由于摩擦作用破坏了金属表面的钝化膜, 增加了腐蚀速度。磨损和腐蚀产生交互作用, 交互作用量随着腐蚀速度的加快而增加。当和 Monel K500 配副时, 316 不锈钢的磨损严重, 而和 Ti-6Al-4V 配副时磨损相对较小。

关键词: Ti-6Al-4V 合金; Monel K500 合金; 海水; 腐蚀磨损; 交互作用

(Edited by LI Xiang-qun)