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Investigation on Electrochemical Behaviour and Corrosion Resistance of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru Alloy in Simulated Conditions for Oil and Gas Exploration

Mifeng Zhao¹, Hongtao Liu¹, Qiang Liu^{2,*}, Shafei Zhai³, Juantao Zhang², Ning Li¹, Junfeng Xie¹, Fangting Hu¹, Guangshan Li², Dan-ping Li², Sheng-yin Song², Cheng-xian Yin²

 ¹ Petroleum Engineering Institute, CNPC Tarim Oil field Co, Ltd., Kuerle 841000, Xinjiang, China.
 ² State Key Laboratory for Performance and Structural Safety of Petroleum Tubular Goods and Equipment Materials, CNPC Tubular Goods Research Institute, No.89, Jinye 2nd Road, Xi'an , Shaanxi 710077, China.
 ³ School of stomatology, Xi'an medical university, No.1, Xinwang 1st Road, Xi'an, Shaanxi 710021, China., Xi'an medical university, No.1, Xin-wang 1st Road, Xi'an, Shaanxi 710021, China.
 *E-mail: <u>liuqiang030@cnpc.com.cn</u>

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Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy, which a new high corrosion resistance alloy developed by Tubular Goods Research Institute of China National Petroleum Company, was investigated by electrochemical techniques, such as open-circuit potentials, potentiodynamic polarization and electrochemical impedance spectroscopy under harsh oil & gas exploration conditions in this work, the surface morphology and chemical compositions of passive films on the Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloys were also examined with scanning electron microscopy (SEM) and X-ray photo-electron spectroscopy (XPS). Results indicated that the dense passive film were rapidly formed and stabilized on the surfaces of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy, the passive film resistance were decreased and became thinner with the increase of acidity and temperature, since the passive films were mainly composed of the most stable oxide TiO₂ with a few amount of metallic ruthenium and Nb⁵⁺ existed , which not only effectively increased the stability, repassivation ability and the thickness of the passive film, but also greatly reduced the point defects in the passive film and the electromigration process of titanium ions, the surface potential of the uppermost layer of the passive film was also elevated, resulting in the excellent corrosion resistance of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy for oil & gas exploration application.

Keywords: Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy, Oil & gas exploration, Passive film, Electrochemical behavior, Corrosion resistance, X-ray photoelectron spectroscopy

1. INTRODUCTION

Stem from the high specific strength, low density, low elastic modulus, excellent toughness and corrosion resistance, titanium alloy has become a hot material for oil country tubular goods (OCTG) in rigorous service environment [1-3]. However, the oil and gas exploration environment is much harsh in China [4-7], the requirement of OCTG in China is much higher than that of any other countries[8,9], most commercial titanium alloys are developed for biomedicine, aerospace and marine engineering, there is huge difference in environments of the above mentioned fields and oil & gas exploration conditions, so common titanium alloy are not suitable for the oil and gas exploration environment due to corrosion problems[10,11].

Lots of works have been conducted to promote the corrosion resistance of titanium alloy under oil & gas exploration circumstance. Tomashov [12] studied the corrosion behavior of titanium alloy and found that adding 0.1wt.% of platinum group metals (such as Pt or Pd) to titanium alloys can significantly reduce the corrosion rate of titanium alloys in boiling strong reducing acids (sulfuric acid, hydrochloric acid). Schutz's work[13-16] revealed that additions of Pd, Pt and Ru elements to existing common alpha titanium and alpha-beta alloys were proven to be crevice and stress corrosion resistant to hot, sour, acidic NaCl-rich brines at high temperatures. Tomashov [17] proposed that alloying Pd or Pt to titanium alloy will expanded corrosion resistance in much aggressive HCl and H2SO4 solutions. Sedricks [18] found that the corrosion resistance of Ti-Ru alloy was comparable to Ti-Pd alloys in H₂SO₄. Lingen [19] indicated that titanium-ruthenium alloys compared well with palladium-containing titanium alloys. Taki and Sakuyama [20] found that when 0.01 wt.% to 1wt.% of Ni, Mo and W were added to the titanium alloy, the content of Pd and Ru can be reduced to 0.1 wt.% while maintaining the corrosion resistance. However, there exist much harsher oil and gas exploration environment in China, the requirement of oil country tubular goods in China exceeds that of other countries, therefore, a new high strength and high toughness titanium alloy OCTG, the Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy, was developed by Tubular Goods Research Institute of China National Petroleum Company (CNPC) to meet the requirement of China' s oil and gas exploration.

Unfortunately, the corrosion properties and electrochemical behavior of this new Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy in China' s harsh oil &gas exploration environment are still unclear, the structure and corrosion resistance mechanism of the passive film of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy still need to be studied in depth. The lack of research results will pose a risk in using of this new Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy OCTG for oil & gas exploration application. Therefore, the purpose of this study is to investigate the electrochemical behavior and structure characteristics of passive film on the surface of this new Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy, including open-circuit potentials, potentiodynamic polarization, and electrochemical impedance spectroscopy, corrosion resistance properties of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy in harsh oil & gas exploration environment, with x-ray photoelectron spectroscopy (XPS) and scanning electron microscope(SEM) analyses, the structure characteristics of the passive film on the surface of this new titanium alloy are revealed finally.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

2.1 Materials preparation

The experimental Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru titanium alloy tubular with 88.9mm in diameter and 10mm in thickness was supplied b Tubular Goods Research Institute of CNPC. All samples were cut from the longitudinal tubular with $15\text{mm} \times 15\text{mm} \times 10\text{mm}$ and polished by silicon carbide papers from 400 to 1200 grit, then polished with diamond pastes of 6 µm and 1 µm and ultrasonically cleaned with distilled water and ethanol. The chemical compositions (in wt. %) of alloy was analyzed by Thermo iCAP 6300 plasma emission spectrometer and was listed in Tab. 1, and the microstructures of the alloy were analyzed using MEF3A and MEF4M metallographic microscopes and shown in Fig.1, the metallographic structure are Widmanstatten structure.

Table 1. Chemical composition of titanium alloy sample used in the test (wt. %)

Samples	Al	V	Ru			0	С	Н	Ν	Ti
Tested titanium alloy	5.9 2	4.02	0.05	0.54	0.52	0.08 2	0.009 8	0.006 2	0.00 9	Bal.



Figure 1. Microstructures of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru titanium alloy

2.2 Working electrolytes conditions

The typical oil & gas exploration conditions of a gas field in western China was selected for the electrochemical measurements and corrosion resistance evaluation of this paper, the tested working electrolytes conditions are listed in Tab.2. Considering the change of working environment at different stages in the process of oil & gas exploration, the different pH value and temperature conditions in the simulated medium environment was considered.

Test conditions	рН	Temperature /°C	Total pressure /MPa	H ₂ S partial pressure/MPa	CO2 partial pressure/MPa	Composition /mg·L ⁻¹
Condition A	3	23				HCO ₃ ⁻ /189, Cl ⁻
Condition B	1.5	23	- 12(inlet N ₂)	<1.2 MPa	6MPa	/128000, SO4 ²⁻ /430, Ca ²⁺ /8310
Condition C	1.5	60	12(Infect 1(2)	$\equiv 1.2$ WH a	olvii u	$Mg^{2+/561}$, $K^{+/6620}$,
Condition D	1.5	100				Na ⁺ /76500

Table 2. Test conditions of electrochemical measurements and corrosion resistance evaluation	Table 2.	Test conditions	of electrochemical	l measurements and	corrosion	resistance evaluation
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2.3 Electrochemical measurement

Electrochemical test specimens were cut from the tubular in the form of discs with 15 mm diameter \times 3 mm thickness and sealed with epoxy resin in a special ring, The exposed surface area for all electrochemical tests was1.76 cm², all samples were polished by silicon carbide papers from 240 to 1200 grit and ultrasonically cleaned with distilled water, acetone and ethanol.

The electrolysis procedures were carried out in a conventional water-jacketed three-electrode electrochemical cell with a Pt plate counter electrode and an Ag/AgCl reference electrode, electrochemical measurements were performed with AMETEK 273A electrochemical workstation and potentials in the text refer to the SCE scale. Before the OCP test, all samples were pre-treated by -1.2V_{SEC} for 5min to remove the oxide from the sample surface and immersed in different test solutions in the high-temperature high-pressure autoclave for 72h to stabilize the electrode/solution interface, after immersion, the time-dependent open-circuit potentials (OCP) tests were carried out on all samples for 1 hour to reach the steady-state of passivation. The potentiodynamic polarization (PDP) was performed from -500mV vs. OCP to 1600mV_{SCE} with a scan rate of 0.5mV/s. electrochemical impedance spectroscopy (EIS) measurements were conducted after the OCP test, the scanning frequency range was 10^5 Hz ~0.01Hz at 10 points per decade, the signal amplitude was ±10mV with sine wave form.

2.4 Corrosion simulation test

In the corrosion experiment, the 40 mm×10mm×3 mm samples were cut from the longitudinally pipe by wire cutting method and polished by silicon carbide papers to 1200 grit, the surface roughness was less than 1.6µm. Crevice corrosion specimens were taken from the tube body in the size of square piece with 38 mm x 38 mm x 3 mm, after polishing by1000 grit sand paper, a Φ 10 mm round hole were drilled in the center of the each specimens. A 0.3mm×15mm×15mm PTFE gasket was used to form a gap between two square plates, all the crevice corrosion specimens were connected with titanium alloy bolts of the same material, and a torque wrench of 86cm•kg was applied uniformly to tighten the test piece string to form the crevice corrosion samples according to the same test [21]. Three 115 mm × 15

 $mm \times 5$ mm four-point bending samples were cut in the longitudinal direction of the pipe, after grinding and polishing along the long side of the samples with 1200grit sand papers, the scratches were all parallel to the long side. According to the NACE TM0177-2005 standard, the stress corrosion cracking (SCC) tests was carried out by point bending, the loading stress was 758MPa, the SCC specimens and SCC specimens shown in Fig. 2.



Figure 2. SCC (a) and crevice corrosion (b) specimens of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy used in tests

The simulated solution of working condition prepared according to condition D in Tab. 2 and all corrosion samples were loaded into the 34.4MPa high-temperature high-pressure autoclave manufactured by Cortest Company, All the corrosion tests were conducted for 720 hours, after the corrosion tests, all samples were ultrasonically cleaned in an acetone bath for 15 min and dried with compressed air, the surface morphology were observed. The specimens were all weighted with an analytical balance to calculate corrosion rate.

2.5 XPS analysis and microstructure observation

The surface chemical composition of origin alloy samples and immersed samples were analyzed and compared with XPS using a K-alpha XPS spectrometer with a monochromatic Al K_{α} X-ray source and a take-off angle of 90°, the pass energy was 50eV with an energy step size of 0.1eV for high resolution scan, the area of beam spot was 400µm. Standard binding energy of titanium, oxygen, aluminum, vanadium and ruthenium were determined according to NIST XPS database.

Surface morphology of samples after the corrosion and immersion tests were observed and analyzed by TESCAN VEGA - II scanning electron microscopy (SEM) and the OXFORD - INCA350 energy dispersive spectrometer (EDS).

3. RESULTS AND DISCUSSION

3.1 Open-circuit potential

The variations OCP evolution with immersion time for Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy are shown in Fig. 3, It is revealed that the open-circuit potential of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy increased quickly at the beginning of tests and gradually reached a plateau with the increase of the immersion time, which indicating that the passive films were rapidly formed and stabilized on the surfaces of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy under these harsh oil &gas exploration conditions[22,23]. It can be obviously conducted from the Fig. 3 that the final OCP values of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy stabilized at approximately -268mV_{SCE} at 23°C with pH=3 and the nearsteady state OCP of the tested alloy shifted positively with the increase of pH value at the same temperature 23°C. It was worthy to note that the near-steady open-circuit potential was determined by the electrode kinetics and thermodynamics, and can reflect the passivation behavior of metal in solution, therefore the oxide layer on the surface of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy was more stable under high acidity at the same temperature. Furthermore, when the temperature increased under the same acidic conditions (pH=1.5), near-steady state OCP of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy shifted significantly from -246mV_{SCE} at 23°C to -30mV_{SCE} at 60°C, and slightly decreased to -88mV_{SCE} when the temperature further increased to 100°C, indicating that the stability of passive film have increased with the increase of temperature. Compared with the work of Wang [24], it is revealed that the thermodynamic stability of Ti-6Al-4V-0.11Ru alloy was better than that of Ti-6Al-4V.



Figure 3. OCP evolution with immersion time for Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloys sample under test conditions

3.2 Potentiodynamic polarization analysis

The Fig.4 indicate the potentiodynamic polarization curves of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy under different oil &gas exploration conditions after immersed in solutions for 72h. It is revealed from the figure that the current density remained basically stable when the potential of the anode polarization branch of tested alloy exceeded 0.4 V_{SCE} in all test conditions, indicating that there were obvious passivation zones formed on the surface of Ti-6Al-4V-0.5Ni-0.05Ru alloy under all oil &gas exploration conditions. In these passive region, the electrochemical corrosion reactions were all

controlled by anode reaction, this passivity domain continues at more anodic potential than the corrosion potential. This remark was in agreement with the presence of an oxide layer at the OCP very well.

The electrochemical parameters were determined and summarized in Tab.3, The corrosion potential (E_{corr}) was obtained at the potential of current change from cathodic to anodic. The corrosion current density (I_{corr}) was equal to the passivation current density, I_{PASS}, were obtained at 0.6 V_{SCE} due to the clear passivity domain in anode region. From the Tab.3, it is can be conducted that the corrosion potential of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy shifted negatively with the decreasing of pH value at the same temperature (23°C), while the corrosion current density increased slightly, indicating that acidity has little effect on the corrosion potential of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy, but it has a more obvious effect on the corrosion current density, the corrosion resistance of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy decreased with the increase of acidity at 23°C. Furthermore, when the acidity stayed constant (pH=1.5) and test temperature increased, the corrosion potential of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy increased significantly, and the corrosion current showed a rapid increase, as shown in Fig.4, indicating that the temperature had a great influence on the corrosion resistance of TTi-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy, accorded with the previous study results of Schuzt [25] that the Ti-6Al-4V alloy has a corrosion resistance threshold around 60°C -80°C, while the corrosion resistance of TTi-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy was better than that of Ti-6Al-4V alloy. The Tab.3 also illustrated that Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru titanium alloy generated passive film in all simulation solutions, and the passive film required higher passivation current density to stay stable with the increase of acidity and temperature, as shown in Fig.4.



Figure 4. Potentiodynamic polarization curves for Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloys

Table 3. Electrochemical parameters of different titanium alloys under variation test conditions

Condition	Ecorr/mV	Icorr/Acm ⁻²	Bc/ mVdec ⁻¹	IPASS/Acm ⁻ ₂
Condition A (23°C, pH=3)	-341	1.770×10 ⁻⁷	-146	3.366×10 ⁻⁶
Condition B (23°C, pH=1.5)	-348	3.270×10 ⁻⁷	-85	4.137×10 ⁻⁶
Condition C (60°C, pH=1.5)	-238	1.272×10 ⁻⁶	-84	1.797×10 ⁻⁴
Condition D (90°C, pH=1.5)	-239	2.188×10 ⁻⁶	-53	2.821×10 ⁻⁴

Fig. 5 illustrate the cyclic potentiodynamic polarization test results of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy in condition C, it is revealed that the reverse-going polarization curves of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy intersected with the positive-going polarization curves in the anodic branch region, indicating that tested titanium alloys had good passivation and repassivation ability under the test condition. Cao's work [26] shows that the repair ability of the passive film depends on the thickness of the original passive film, the protection potential E_p , and the pitting potential E_t of material. The higher the protection potential E_p , the stronger the repassivation tendency of the material surface, and the pitting potential E_t is correlated with the repair ability of the surface pitting corrosion. It is can be derived from Fig.5, the protective potential E_p of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy was about 2278mV_{SCE} in condition C, which is higher than the 1890 mV_{SCE} of Ti-6Al-4V alloy[27,28], exhibiting better surface repassivation ability. The pitting potential E_t of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy the similar repair ability of the surface pitting corrosion between other Ti-Al-V titanium alloys [29].



Figure 5. Cyclic polarization curves of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy under test condition C

3.3 Electrochemical impedance spectroscopy

In order to further study the electrochemical and structural characteristics of the passive film on the surface of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy under gas exploration conditions, EIS measurement were performed for Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy. Fig. 6 shows the Bode diagrams and Nyquist plots of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy under different test conditions, it can be conducted that the phase angles of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy had only one wide obvious peak from low frequency to high frequency, indicating that the impedance has only one time constant. The maximum phase angles of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy was above 80 degrees, indicative of typical capacitive characteristics. The frequency range of obtaining high relatively constant phase angle and the phase angle maximum all decreased with the increasing of acidity and temperature. The absolute impedance of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy increased with almost the same slope from high frequency (10^{3} Hz) to low frequency (10^{-2} Hz) and was independent of frequency in the high frequency

regime. In the low frequency regime, the absolute impedance decreased from condition A to condition D, illustrating that test environments have a significant influence on the characteristics of passive films on the alloy surface, because of the predominance of solution resistance, the absolute impedance in the low frequency region was quickly dropped, as shown in Fig. 6(a).



Figure 6. Bode (a) and Nyquist diagrams (b) for Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy samples under variation test



Figure 7. Equivalent electrical circuit model used for impedance spectra analysis of titanium alloy

Fig. 6(b) illustrates the characteristics of a large semicircle capacitive loop with a time constant in Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy, the diameter of the capacitive loop decreased with the increasing of acidity and temperature, indicative of less corrosion resistance, especially at high temperatures. The EIS results of tested titanium alloy are in line with the most used equivalent circuit model of dense passive film, the simplified Randles equivalent circuits was selected to fit the data [30-32], as shown in Fig.7. Where R_p represent the resistance of the compact passivation film, R_s represent the solution resistance, the constant phase element (CPE_p) was selected to instead of pure capacitance due to the non-uniform distribution of current on the surface. The CPE_p can be expressed as [21]:

$$Z_{CPE_P} = \frac{1}{Q(j\omega)^n} \tag{1}$$

Where Q is the capacitance of dense passive film, j is the imaginary unit, ω is the angular frequency and n is the deviation parameter which is related to the constant phase angle[33], When the value of n approaches 1, the phase angle constant CPE_p represents the dielectric layer formed on the surface of the solution and the alloy and behaves as the ideal capacitance Q. Based on the equivalent circuits model in Fig.7, the impedance of electrode and the resistance R_p can be calculated as following,

$$Z_{\omega} = \frac{1}{\frac{1}{R_s} + Q(j\omega)^n}$$

$$R_P = \lim_{\omega \to 0} (Z_{\omega})$$
(2)
(3)

The EIS fitting results are summarized and listed in Tab.4, it can be seen that the deviation parameter n of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru are all close to the number 1, so the phase angle constant CPE_p acts like an ideal parallel-plate capacitor Q_p . The solution resistance R_s of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy are much smaller than passivation film resistance R_p under the same test conditions. However the passivation film resistance R_p of Ti-6Al-4V-0.5Ni-0.05Ru alloy were drastically reduced with the increase of acidity and temperature, which indicates the continuous decline of the corrosion resistance of the passivation film on the surface of Ti-6Al-4V-0.5Ni-0.05Ru alloy.

Items	$R_s/\Omega cm^2$	$R_p/k\Omega cm^2$	Qp/ Fcm ⁻² s ⁿ⁻¹	n
Condition A	2.89±0.06	701.69±8.77	7.09×10 ⁻⁵ ±0.00	0.945±0.00
Condition B	2.62±0.17	278.08 ± 8.92	9.51×10 ⁻⁵ ±0.00	0.944 ± 0.00
Condition C	8.91±0.13	40.47 ± 0.79	$1.40 \times 10^{-4} \pm 0.00$	0.922±0.01
Condition D	11.69±0.24	38.95±0.59	$1.81 \times 10^{-4} \pm 0.05$	0.914 ± 0.01

Table 4. Electrochemical parameters of different titanium alloys under variation test conditions

In order to further study the passivation film behavior of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy under variation tested conditions, with an assumption that the capacitance acted like a parallel-plate capacitor, the thickness of passive film can be calculated according to the research of Xi and Wang [21,24,34]:

$$C = \frac{\varepsilon \varepsilon_0 A}{d} \tag{4}$$

Where *d* is the thickness of passive film, ε represents the relative permittivity and is set to 48 for titanium[35], ε_0 is the permittivity of vacuum and is about 8.85×10^{-14} F•cm⁻¹, A is the effective surface area, usually 3 times the geometric surface, in cm², and C represents the capacitance of the passive film. According to the work of Mark Orazem[36-38], when a normal time-constant distributed through a surface layer, the relationship between CPE_p parameters and effective capacitance requires an assessment of the characteristic time constant corresponding to the impedance of the layer. So the effective capacitance value C can be calculated from the CPE value form the following expression:

$$C = Q_p^{1/n} R_p^{(1-n)/n}$$
 (5)

Thus the film thickness of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy under variation experimental conditions can be calculated and shown in Fig. 10, it is indicated that the passivation film of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy appeared more thinner when temperature increased, however, the average thickness of passivation film on the Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy surface was thicker than that of Ti-6Al-4V alloy[35] in different harsh oil &gas exploration environments, which mean that the Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy has better corrosion resistance in these environments.



Figure 8. Thickness of the passive films for Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy and Ti-6Al-4V alloy under different conditions

3.4 X-ray photoelectron spectroscopy analysis of the surface film

The surface passivation film of Ti-6Al-4V-0.5Ni-0.5Nb-0.0.05Ru alloy before test and after immersion 3d in condition D were selected to detected the surface chemical composition by X-ray photoelectron spectroscopy (XPS) analysis, the deconvoluted Ti_{2p} spectra of the passivation film surface before test and after immersion in condition D are shown in the Fig.9, It is revealed that the tetravalent titanium oxides in the passive film of Ti-6Al-4V-0.5Ni-0.5Nb-0.0.05Ru alloy were prominent with doublets at approximately 458.4eV and 464.2eV under all conditions, combined with deconvoluted O_{1s} spectrum, it can be determined that the passive films of tested alloy was mainly composed of TiO₂ [39]. Before the immersion 3d in condition, the content of tetravalent titanium in the passive film of Ti-6Al-4V-0.5Ni-0.5Nb-0.0.05Ru alloy accounted for 75% of the total ions, meanwhile, there were a moderate amount of trivalent titanium and bivalent titanium existed in the passive films, which represented the metastable oxides of Ti₂O₃ and TiO₂²⁻[40,41]. However, after 72 hours immersion in service conditions D, the content of of trivalent titanium oxides and bivalent titanium oxides decreased significantly in the surface film of Ti-6Al-4V-0.5Ni-0.5Nb-0.0.05Ru alloy, indicating that the oxide film of tested alloy consisted mainly of tetravalent titanium oxides (TiO₂) after immersion.



Figure 9. Deconvoluted Ti_{2p} (a,b) and $O_{1s}(c,d)$ spectra of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy (a,c)before test and (b,d) after immersion in condition D

The research of Zhi [42] shows that Ti^{4+} ions in the passivation film TiO_2 can no longer be oxidized due to the highest valence state, so they are more stable than metastable oxides of titanium. Because Ti^{3+} and Ti^{2+} ions are passivated as a defect in the film, the passivation film is more sensitive to stress and strain, and it is easy to crack under the action of surface stress and destroy the integrity of the passivation film, so the less the content of unstable oxides, the better corrosion resistance.

Fig.10 shows the deconvoluted high-resolution XPS spectra of Ru_{3d} and Ni_{3d} on the surface film of Ti-6Al-4V-0.5Ni-0.5Nb-0.0.05Ru alloy after immersion 72h in condition D, there was no obvious peak of ruthenium element was found before the test. After immersion, the XPS spectrum of Ru_{3d} in the passive film changed significantly, the binding energy of the Ru_{3d} was mainly close to 280.0eV, indicating that the Ru element mainly existed in the passive film on the surface of the alloy with atoms state[43], the metallic ruthenium existed in the passive film will increase the surface potential of the top layer, resulting an increase in passivation ability and a decrease in the content of metastable oxides in the passivation film[44], resulting in the better stability and repair ability of passive film and good corrosion resistance of Ti-6Al-4V-0.5Ni-0.5Nb-0.0.05Ru alloy.

Meanwhile, there were a moderate amount of niobium ions ,mainly in the chemical state of pentavalent, detected in the surface films of tested alloy after immersion, According to the research of Milo^ssev [45], the niobium element mainly forms Nb₂O₅ and a small amount of NbO₂ in the alloy, and

Wu [46,47] found that since the ionic radius of Nb⁵⁺ is very similar to that of Ti⁴⁺, when there is Nb⁵⁺ in the material, a part of Nb⁵⁺ will be doped into the lattice of TiO₂ and replace a part of the position of Ti⁴⁺ without causing a larger lattice distortion. The research of Chen [48] found that when a part of the titanium ions in the lattice of TiO₂ was replaced by Nb⁵⁺, thus the grain growth of TiO₂ will be inhibited duo to the radius of Nb⁵⁺ was slightly larger than that of Ti⁴⁺, resulting in the reduction of the grain diameter of TiO₂, and at the same time reducing the number of oxygen vacancies and titanium interstitials, effectively reducing the diffusion rate of titanium ions.



Figure 10. Deconvoluted XPS spectra of (a)Ru_{3d} and (b) Nb_{3d} for Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy after after immersion 72h in condition D

3.5 Corrosion test in harsh oil &gas exploration conditions

The corrosion tests under simulated conditions were conducted in the high-temperature highpressure autoclave under test condition D, after tests, the surface morphology of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy were observed by SEM, and compared with the results of TC4[49] alloy under the same test conditions, the SEM images are shown in Fig. 11, it is revealed that polish marks can still be observed on the surface of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy and no pitting morphology can be found on the surface, the average corrosion rate from the tests was calculated to be 0.0007mm/a, which are all profited from the strong passivation ability and good corrosion resistance of passive film on the surface of Ti-6Al-4V-0.5Nb-0.05Ru alloy, meanwhile, obvious local corrosion can be observed on the surface of Ti-6Al-4V alloy, there are several deep pitting cavities nearby and the diameter of the pitting cavities is about 10-100µm, indicating much poorer corrosion resistance under the same test conditions.

Fig. 12 illustrated the surface morphology of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy and compared TC4 alloy[49] after crevice corrosion test, it can be seen that no obvious corrosion traces can be seen on the surface of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy, while plenty of corrosion products were produced on the surface of the Ti-6Al-4V alloy, and there are multiple cracks and spalling around the edges of Ti-6Al-4V alloy, EDS results showed that the main corrosion products were alumina and titanium oxide. It seems evident that the failure of the passive film on the surface of Ti-6Al-4V alloy

underwent two main processes: the dissolution of the passive film and the initiation of cracks, which is well accord with the research of Li [Error! Bookmark not defined.].



Figure 11. SEM images of surface morphology for (a) Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy and (b) Ti-6Al-4V alloy [49] after the test



Figure 12. Surface morphologies of samples after crevice corrosion test:(a) Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy and (b)Ti-6Al-4V[49] alloy

After 720 hours of four-point bending SSC test at 783MPa, the surface morphology of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy is shown in Fig.13, it can be disclosed that the sample remains intact and no obvious cracks are found on the surface of the sample, the results illustrate that Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy has excellent resistance to stress corrosion cracking in the oil and gas development environment.





4. CONCLUSIONS

The following conclusions can be drawn from the study on electrochemical behavior and corrosion resistance of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy in harsh oil & gas exploration environment:

(1) The passive films were rapidly formed and stabilized on the surfaces of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy in oil & gas exploration conditions, the temperature had a great influence on the corrosion resistance of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy while the effect of acidity was slightly, the passive film of tested alloy exhibited better surface repassivation ability.

(2) The EIS results indicated that the passivation film resistance of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy were decreased and became thinner with the increase of acidity and temperature, but the average thickness of passivation film on the Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy's surface was still thicker than that of Ti-6Al-4V alloy.

(3) The passive films of Ti-6Al-4V-0.5Ni-0.5Nb-0.05Ru alloy were mainly composed of most stable oxide TiO₂ after immersion, and the content of meta-stable oxides in the passive film of Ti-6Al-4V-0.5Ni- 0.5Nb-0.05Ru alloy was significantly decreased due to the presence of metallic Ru and Nb⁵⁺ in the passive film.

(4) With the addition of Ni-Nb-Ru in Ti-6Al-4V alloy, the surface potential of the uppermost layer of the passive film can be effectively increased and the diffusion rate of titanium ions was reduced, resulting in the better stability ability of passive film and good corrosion resistance of Ti-6Al-4V-0.5Ni-0.5Nb-0.0.05Ru alloy, which were proved by corrosion tests under simulated harsh oil & gas exploration environments.

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