

Electrochemical Corrosion Behavior of Ti35 Alloy in Nitric Acid Containing Fluoride Ions

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Abstract: The open circuit potential (OCP), potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) of Ti35 alloy were tested by an electrochemical test system in 6 mol/L nitric acid solution containing fluoride ions and the effect of the fluoride ion on the corrosion resistance of Ti35 alloy was investigated. The results show that the corrosion resistance of the alloy decreases with the increase of fluoride concentration while the alloy still exhibits good corrosion resistance in general. The critical concentration of fluoride ions affecting the corrosion resistance of the alloy is about 1.25 mmol/L. Furthermore, the mixed potential theory was adopted to explain the undermined mechanism of the changing corrosion resistance of the alloy.

Key words: titanium alloy; fluoride ions; corrosion behavior; electrochemical

Climate change and energy security have become the big concern of this century. As the core of energy, nuclear power has occupied over 11% of the total electricity demand all over the world^[1]. The reprocessing of spent fuel is the most important part of nuclear energy recycling, which is conducted by separating uranium and plutonium from the solution of spent fuel in nitric acid^[2]. Thus, the demand for available structural materials with good corrosion resistance is high. At present, the candidate structural materials for the spent fuel reprocessing equipment in the world mainly include stainless steel, titanium and zirconium alloys^[3-10]. Most studies focused on the corrosion resistance^[3,4,8,10,11] and corrosion mechanism of these alloys^[5,9,12,13] in different concentrations of nitric acid or with oxidative ions. But, the intergranular corrosion of stainless steel in nitric acid medium, especially in oxidative ions medium^[7,10,12] and the stress corrosion of zirconium in nitric acid medium^[3] were rarely reported. Thus, titanium alloy has potential advantages as a candidate material for reprocessing equipment. Recently, a new design conception of the next generation molten salt reactor, using molten fluoride salts as electrolyte for electrochemical separation in the reprocessing, has been put forward. Therefore, it is unavoidable that there will be fluoride ions in the corrosive

environment of the next generation molten salt reactor. Wang et al^[14-16] investigated the effect of fluoride ions on the corrosion behavior of pure titanium in sulfuric acid. Mareci et al^[17] explained the effect of acidic fluoride solution on the corrosion resistance of ZrTi alloys for dental implant application. Stancheva et al^[18] discussed the influence of fluoride content on the barrier layer formation and titanium dissolution in ethylene glycol-water electrolytes.

However, there are few studies on the corrosion resistance of titanium alloys in nitric acid containing fluorine ions. In the present paper, the corrosion resistance of Ti35 alloy in 6 mol/L nitric acid solution containing fluoride ions was studied. The critical value of fluorine ion concentration affecting the corrosion resistance transition of the alloy was also determined. Moreover, the effects of the fluoride ions on the corrosion resistance of the alloy were analyzed and discussed using the mixed potential theory. It provides experimental basis for material selection of reprocessing equipment.

1 Experiment

The Ti35 alloy was used as the research material, and its nominal chemical composition is shown in Table 1. Samples were embedded into epoxy resin with exposed area of 1 cm²

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Table 1 Chemical composition of Ti35 alloy

Ta	Fe	C	N	O	H	Ti
-	0.01	0.009	0.007	0.067	0.002	Bal.

as working electrode for electrochemical experiments in the nitric acid solution containing fluoride ions (0, 0.25, 1.25, 2.5, 5 mmol/L). Prior to the electrochemical experiments, the samples were ground mechanically by SiC papers (150, 400, 1000 up to 2000 grit), ultrasonically cleaned in acetone, and dried after distilled water washing.

The electrochemical measurements were performed on an IM6 Zahner-elektrok GmbH (Zenniom, Germany) workstation. An Ag/AgCl electrode (saturated KCl) and a Pt foil were used as reference electrode and counter electrode, respectively.

Open-circuit potential (OCP) measurement was set for 600 s. Potentiodynamic polarization curves were obtained in a range from -0.5 V to 2.5 V (vs. Ag/AgCl) at a scanning rate of 0.01 V/s. Electrochemical impedance spectroscopy (EIS) tests were performed with a 10 mV amplitude AC voltage signal, a frequency range from 100 mHz to 100 kHz, and a record of 5 points per decade. All the electrochemical measurements were measured thrice for repeatability, and carried out at 25 ± 1 °C using a water bath pot. The equivalent circuits were used to fit the experimental EIS data using ZSimpWin 3.0 software.

2 Results and Discussion

2.1 OCP measurements of Ti35 alloy

Fig.1 presents the variation trends of the OCPs of the Ti35 alloy with time during the immersion in nitric acid solutions containing various contents of fluoride ions for 600 s. The OCPs of the Ti35 alloy decrease with the increment of fluoride ions concentration. When fluoride ions concentration exceeds 1.25 mmol/L, in particular, the OCPs show the remarkable negative shift, down to nearly 500 mV from 600 mV, indicating the state of surface passive film changes and the alloy has a higher corrosion susceptibility^[19].

Besides, the corrosion tendency of materials can be predicted

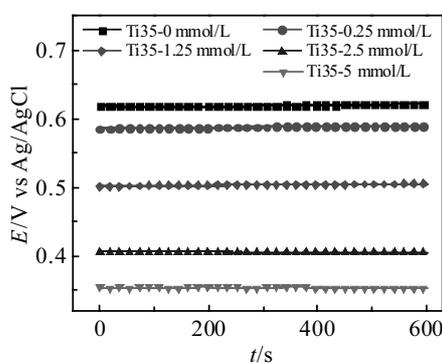


Fig.1 OCPs of Ti35 alloy with the time for 600 s immersion in nitric acid solutions with various contents of fluoride ions

by the OCP value qualitatively, for example, higher OCP stands for more stable materials^[20]. It can be clearly seen from Fig.1 that the OCPs keep nearly constant with increasing time, which means that a quasi-steady-state has been obtained to meet the requirement of the EIS test.

2.2 Potentiodynamic polarization measurements of Ti35 alloy

The potentiodynamic polarization curves of Ti35 alloy in nitric acid solutions containing fluoride ions are shown in Fig.2. It shows that with increasing the fluoride concentration, the electrochemical behavior changes from the spontaneous passive behavior (0, 0.25, 1.25 mmol/L) to the active-passive transition behavior (2.5 and 5 mmol/L). The average corrosion potentials estimated from these curves are 574 , 565 , 535 , 455 and 395 mV (Ag/AgCl), for the 0, 0.25, 1.25, 2.5 and 5 mmol/L, respectively. The critical fluoride ion concentration of Ti35 alloy can be determined as the value about 1.25 mmol/L based on the polarization curves^[15], which is consistent with the result of OCPs measurements (Fig.1).

The variations of the corrosion and passive current density (I_{corr} and I_{pass}) of Ti35 alloy with the fluoride concentration are shown in Fig.3 and Fig.4, respectively. The results of these electrochemical corrosion parameters are determined using Thales software for I/E analysis^[21]. The general corrosion resistance can be usually evaluated by I_{corr} . The I_{corr} increases with the increase of fluoride ion concentration as shown in Fig.3, suggesting deteriorated general corrosion resistance. Similar phenomena were also discovered for the system of Ti alloys in solutions containing fluoride ions^[14,15,22]. The I_{pass} increases with the increase of fluoride ion concentration as shown in Fig.4, which indicates that fluoride ions have a significant influence on the anode process. The details of the effect of fluoride ions on the corrosion process of Ti35 alloy will be further discussed in Section 2.4. However, the cathodic polarization curves are similar for Ti35 alloy in all corrosion mediums, indicating that the same cathodic reactions occur. Besides, a slight dip of current in passive region appears at

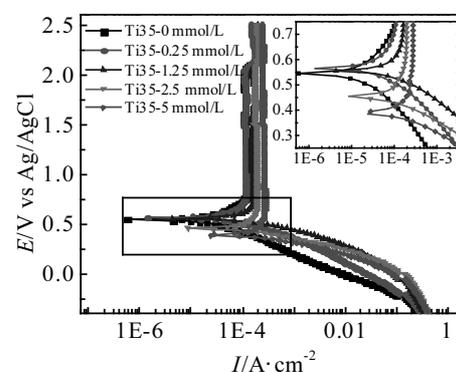


Fig.2 Potentiodynamic polarization curves of Ti35 alloy in nitric acid solutions containing fluoride ions

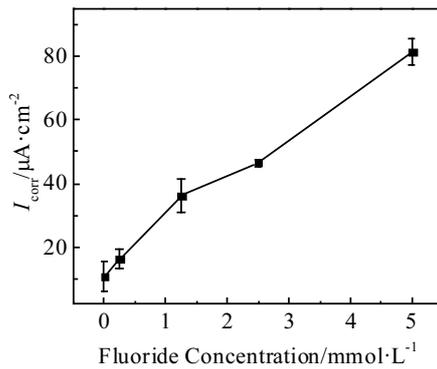


Fig.3 Variation of the corrosion current density (I_{corr}) of Ti35 alloy with the fluoride concentration

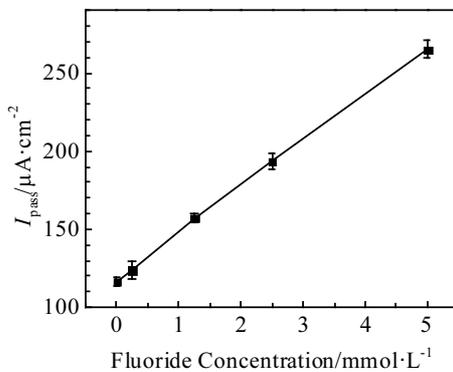


Fig.4 Variation of the passive current density (I_{pass}) of Ti35 alloy with the fluoride concentration

around 1.5 V in all curves, which may be due to the dissolved oxygen in naturally aerated solutions^[16] and the reduction reaction of oxygen occurs at a relatively positive potential^[23].

2.3 EIS measurements of Ti35 alloy

The Nyquist and Bode plots for Ti35 alloy in nitric acid solutions with fluoride ions are shown in Fig.5 and Fig.6, respectively. Fig.5 shows that there is only one single capacitive loop for Ti35 alloy when the fluoride concentration is lower than the critical value, i.e., 0, 0.25, and 1.25 mmol/L, which indicates that there is a time constant in corresponding equivalent circuit. One capacitive loop and one inductance loop appear at higher fluoride concentrations, i.e., 2.5 and 5 mmol/L. This means there are two time constants in the equivalent circuit. Besides, the diameter of the capacitive semicircle gradually decreases with increasing fluoride concentration, which indicates the deterioration of corrosion resistance^[16].

Fig.6 shows that $|Z|$ tends to become relatively constant at high frequencies and the phase angle values fall towards zero or negative values with increasing frequencies. Besides, the phase angles approaching to 90° from the medium to the low

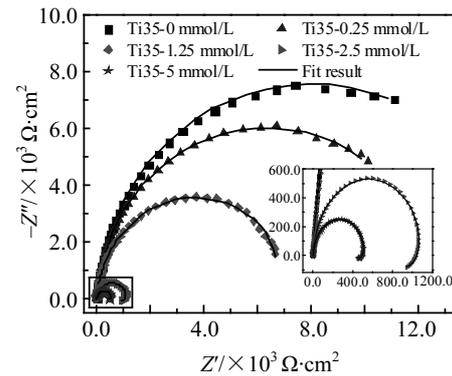


Fig.5 Nyquist plots of Ti35 alloy in 6 mol/L nitric acid with various contents of fluoride ions

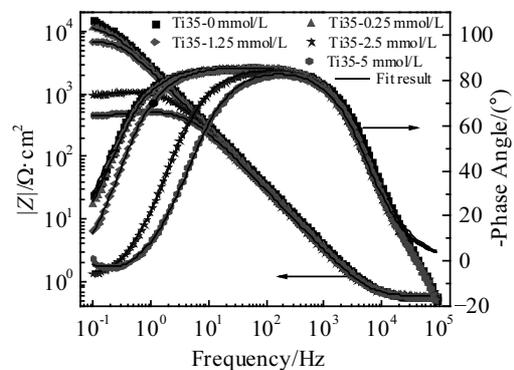


Fig.6 Bode phase angle plots for Ti35 alloy in 6 mol/L nitric acid with various contents of fluoride ions

frequencies can be observed in the cases of fluoride concentrations lower than 1.25 mmol/L, suggesting that highly stable and compact films form under these conditions^[24]. However, when fluoride concentration exceeds 1.25 mmol/L, the width of phase angle is sharply narrowed and the phase angle is close to -20° at high frequency, which indicates the stable and compact films are destroyed and porous films appear on surface of Ti35 alloy^[16].

The EIS spectra were analyzed by the equivalent circuits as shown in Fig.7, and the fitted results show that the chi-squared (χ^2) values are approximately ($10^{-3} \sim 10^{-4}$), indicating satisfactory agreement between the experimental and simulated data. The proposed equivalent circuit is widely used for Ti alloys^[14,16,17,25]. Accordingly, in these two equivalent circuits, R_1 and Q correspond to the resistance and capacitance of the barrier layer, respectively; R_2 and L correspond to the resistance and inductance of the porous layer, respectively; and R_s represents the resistance of the solution. A constant phase element Q was used to replace the capacitance due to the distribution of relaxation times resulting from different

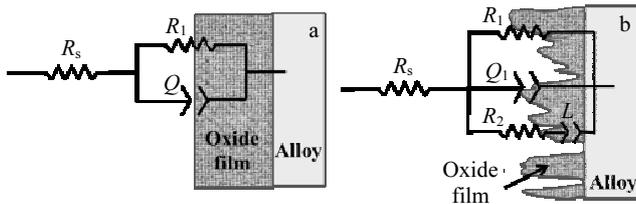


Fig.7 Equivalent circuits used to fit the impedance data for Ti35 alloy in 6 mol/L nitric acid with various contents of fluoride ions: (a) 0, 0.25 and 1.25 mmol/L; (b) 2.5 and 5 mmol/L

degrees of heterogeneities at the electrode surface. The impedance of the Q is given by^[26]:

$$Q = Z_{CPE}(\omega) = [C(j\omega)^n]^{-1} \quad (1)$$

Where, ω is frequency and $-1 \leq n \leq 1$ (for $n=1$, Q represents the capacitance C ; for $n=0$, Q represents the simple resistor)

Generally, the protectiveness of surface film, directly related to the corrosion resistance, can be evaluated by the polarization resistance (R_p), which can be achieved by fitting the EIS spectra using the equivalent circuit^[14]. In the equivalent circuit in Fig.7a, R_1 is equivalent to the polarization resistance, i.e. $R_s=R_1$, while for the equivalent circuit in Fig.7b, the polarization resistance is the parallel connection of R_1 and R_2 , i.e. $R_s=R_1R_2/(R_1+R_2)$. Table 2 shows the values of the electrical parameters obtained from corresponding circuits for Ti35 alloy in all corrosion mediums.

As shown in Table 2, the values of R_s are almost identical, and nearly $0.586 \Omega \cdot \text{cm}^2$, which indirectly indicates the reliability of the equivalent circuit. The R_p values decrease with the increase of fluoride concentration. When the concentration of fluorine ion is higher than 1.25 mmol/L, the values of R_p decrease sharply to $0.85 \text{ k}\Omega \cdot \text{cm}^2$ and $0.44 \text{ k}\Omega \cdot \text{cm}^2$ at 2.5 and 5 mmol/L, respectively. This furtherly indicates that the critical concentration of fluoride ion is about 1.25 mmol/L. Based on the above results, the reasons accounting for this phenomenon may be as follows: the surface passive film is uniform, dense and protective in the solution without fluoride ions. With the addition of fluoride, the local area of the outer

passive film is dissolved, which hardly affects the overall corrosion resistance. Until the concentration of fluorine ion is higher than 1.25 mmol/L, the polarization resistance drops sharply, which shows that most area of the passive film of the alloy surface is dissolved, making the surface passive film become porous. Thus the surface passive film becomes porous and cannot act as a barrier layer against corrosion anymore, which makes the corrosion resistance of alloy deteriorate severely^[16,27,28]. This conclusion is definitely in good agreement with that drawn from the OCPs and potentiodynamic polarization tests.

2.4 Effect of the fluoride ion on anodic process

Based on the above analysis, we can find that with the increase of the concentration of fluorine ions, the OCPs of the alloy decreases and the passivation current density of the dynamic polarization curve increases, which indicates the decrease of corrosion resistance of the alloy. The effect of the fluoride ion on the corrosion resistance of titanium alloy mainly involves the dissolution process of the surface film, which makes the compact passive film of the alloy surface convert into a porous and non-protective film layer. The following reaction would occur in the dissolution process:



According to Eq. (2), it can be speculated that the critical value of the fluoride concentration depends on the dynamic equilibrium between formation and dissolution of the film^[16]. The ideal schematic diagram was proposed to explain the reasons for these results based on mix-potential theory in Fig.8. The curves A1, A2, A3, A4 and A5 represent the ideal anodic polarization curves of Ti35 alloy in the nitric acid solutions with fluoride ions, i.e., 0, 0.25, 1.25, 2.5 and 5 mmol/L, respectively, based on the results shown in Fig.2. Three oblique lines with different colors represent the cathode polarization curve of the initial, the middle and the final state. Different points can be found from the intersections of the oblique cathodic polarization and the anodic polarization curves. The ordinate and abscissa of the intersecting point between anodic curve and cathodic curve correspond to the

Table 2 Electrical parameters obtained for the Ti35 alloy in the fittings using the described circuits for all corrosion mediums

	Fluoride content/ mmol·L ⁻¹	C/ μF·cm ⁻²	n	R _p / kΩ·cm ²	R _s / Ω·cm ²	L/ kH
	0	0.591	0.96	16	0.581	-
Fig.7a	0.25	0.636	0.96	12.6	0.591	-
	1.25	0.686	0.97	7.36	0.588	-
Fig.7b	2.5	0.711	0.96	0.85	0.587	3.73
	5	0.714	0.96	0.44	0.582	1.27

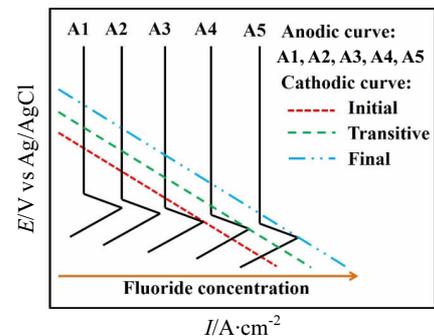


Fig.8 Ideal schematic diagram of the effect of the fluoride ions on anodic process based on mixed-potential theory

corrosion potential and the corrosion current density of the alloy, respectively. It can be evidently seen that the corrosion potential of the alloy decreases and corrosion current density increases with the increase of fluoride concentration, which are consistent with the result of OCPs (Fig.1) and potentiodynamic polarization curves (Fig.2). The intersections points of A1, A2 and cathodic polarization curve are located in the passivation region, indicating that it is spontaneous passivation behavior and fluoride has almost no effect on its corrosion resistance. A3 intersects the initial cathodic polarization curve at two points with one located in the passivation region and the other at the end of the activation region. This means that the dissolution rate of the surface passive film is slightly higher than that of the film formation. Under this condition, the surface passive film is in the unstable state and the corresponding concentration of fluorine ion represents the critical value. The initial cathodic polarization curve intersects A4, A5 producing two points located in activation region. Porosity is formed by dissolving the surface passive film suggesting the sharp decline in corrosion resistance of alloy. However, with the proceeding of redox reaction on the electrode surface, the cathodic polarization curve changes from the initial state to the transitive state and finally to the final stable state. We found that the intersections points between the cathodic polarization curve of the final state and all the anodic polarization curves are located in the passivation region, indicating that the alloy generally has excellent corrosion resistance in nitric acid solutions containing fluoride ions. Therefore, Ti35 alloy can be considered as potential candidate material for nuclear spent fuel processing equipment.

3 Conclusions

1) The corrosion resistance of the Ti35 alloy decreases with the increase of fluoride concentration in the nitric acid solution containing fluoride ions. However, the Ti35 alloy still has good corrosion resistance. It is expected as a candidate material for spent fuel reprocessing equipment.

2) The critical value of fluoride concentration affecting the corrosion resistance of the Ti35 alloy is about 1.25 mmol/L.

3) The effect of fluorine ions on corrosion resistance of the alloy can be explained by the mixed potential theory due to the dissolution process of the surface passive film in the active dissolved area. This process makes the compact passive film on the surface of the alloy convert into porous film.

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Ti35 合金在含氟离子硝酸中电化学腐蚀行为

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摘 要: 采用电化学测试系统测试了 Ti35 合金在含有不同氟离子浓度的 6 mol/L 硝酸溶液中的开路电位 (OCP)、极化曲线、电化学阻抗谱 (EIS), 探讨了氟离子对 Ti35 合金耐蚀性能的影响。结果表明: 随着氟离子浓度的增加, 合金耐蚀性下降, 但总体而言合金仍具有良好的耐蚀性。影响合金耐蚀性转变的氟离子浓度临界值约为 1.25 mmol/L, 进一步应用混合电位理论, 解释合金耐蚀性转变的原因。

关键词: 钛合金; 氟离子; 腐蚀行为; 电化学

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