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Galvanic Corrosion Between Depleted Uranium and 40Cr Steel

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Individual corrosion and galvanic corrosion behaviors of depleted uranium (DU) and 40Cr steel are investigated by electrochemical analyzing technologies in 3.5w.t%NaCl solution, including open circuit potential(OCP) test, linear polarization(LP) test, potentiodynamic polarization(PD) test, galvanic corrosion potential and corrosion current density test. Morphologies and corrosion products are analyzed by Scanning Electron Microscope (SEM) and Energy-dispersive spectroscopy (EDS). The results reveal that the OCP of DU and 40Cr steel are around -790mV and -660mV, respectively. 40Cr has a higher linear polarization resistance than DU in galvanic corrosion. The dynamic processes of galvanic corrosion undergoes a conversion process in the whole test period. DU acts as anode with an accelerated corrosion rate, while the 40Cr steel behaves as cathode during the process of galvanic corrosion for DU/40Cr couple. The galvanic potential and current density of the DU/40Cr couple are around -780mV and 17.5μA/cm^{-2}, respectively. Chloride ions play a vital part in the individual corrosion and galvanic corrosion of specimens.

Keywords: galvanic corrosion; depleted uranium; 40Cr steel

1. INTRODUCTION

Depleted uranium(DU) has many commercial applications in recent years, such as shielding for radioactive waste, ballast for ship, counterweights for aircraft, due to its high density, hardness, self-sharpening properties[1]. As one of the most active metals, however, DU represents a disappointing corrosion resistance in corrosive environments and its performance will be affected seriously when corrosion occurs. The individual corrosion behaviors of DU have been investigated extensively for more than six decades by researchers from countries throughout the world[2-5]. In general, DU reacts with oxygen, moisture or aqueous solution to form products of UO_{2+x} (x is generally accepted as between 0.06 and 0.1 [6,7]), H_2, UH_3 at a relatively low temperature[8,9], and U_3O_8 when temperature up to 260℃[10]. Data on the kinetics of DU and DU alloys corrosion, summarized in [8], were obtained using weight gain(WG) or metal loss(ML) techniques. At room temperature, the oxidation rate of DU in dry air is essentially identical at 4.2×10^{-4}g•cm^{2}•y$^{-1\backslash}$. Whereas, exposure of DU to saturated water vapor at 25℃ increases the corrosion rate by a factor of 400[11]. In H2O, the corrosion rate is 0.07g•cm^{2}•y^{-1}, which increase to 0.4g•cm^{2}•y^{-1} in 3.5w.t%NaCl solution[12].

The increasing interest surrounding the use of DU requires a direct physical or electrical contact with dissimilar metals, which is very prone to occurring galvanic corrosion. Galvanic corrosion is one of the major obstacles during the applications of DU. DU corrosion products can be crumbly, easily spalling and diffusible, taking the form of solids or gases. Buildup of the corrosion products and weight loss may cause an inaccuracy for the counterweight; the ingress of gaseous reaction product of H_2 in the metal will reduce its mechanical properties. These unfavorable effects can be worse when the DU acted as anode in a galvanic corrosion system. In oxidizing conditions, uranium corrodes rapidly[13]. Galvanic corrosion behavior of DU alloys exposed to ASTM or natural seawater are studied for each metal or alloy coupled to remaining test materials as one group(AISI 304 SS, T621, Al, AA 7075-T6, bare AISI 4340 steel etc.)[14,15]. Theoretically, galvanic corrosion can be eliminated by insulating or blocking the direct electrical contact between DU and its coupled metal. However, in most practical utilizing situations, direct contact is required to meet the mechanical joint demands. For example, in a special applicational situation, the DU parts need to be connected with 40Cr steel bolt. Galvanic corrosion for the couple of DU and 40Cr steel may occur when the bolt connected parts is exposed to corrosive atmosphere. However, no report related to galvanic corrosion of DU/40Cr couple is available and the galvanic corrosion data are lack to evaluate the reliability of the bolt connected structure in special atmosphere. Therefore, it is vitally important and valuable to study the galvanic corrosion behaviors of DU/40Cr steel in corrosive mediums.

In this paper work, electrochemical properties of the DU, 40Cr steel and the DU/40Cr couple are measured with an electrochemical measurement system. Several issues are addressed based on the measurements, such as the self-corrosion potential variation with time, the individual linear polarization and potentiodynamic polarization for the individual metal, the galvanic corrosion potential and current density for the DU/40Cr couple. Corrosion morphologies are analyzed by SEM. Corrosion products in local position are identified by EDS, an accessory of SEM. The mechanism of galvanic corrosion for DU/40Cr steel couple is proposed.

2. EXPERIMENTAL

2.1.Sample preparation and corrosion medium.

Samples of DU and 40Cr steel with cylinder shape and size of ϕ16mm×3mm were polished by silicon carbide papers with grades from 320, 500, 800 to 1200 and 1μm-diamond paste, gradually, followed by surface cleaning with acetone, ethanol and distilled water. Each specimen was inserted in a Teflon tube with only a flat work surface with area of 1cm^2 was exposed. A electrolyte of sodium chloride aqueous solution with concentration of 3.5wt.% was used as corrosion medium for all experiments in this study.

2.2. Electrochemical experiment

The main objective of this test was to investigate the relationship between the individual electrochemical properties and the galvanic corrosion behaviors for DU and 40Cr steel system. Electrochemical measurements were performed in a classical three electrodes assembly with the specimen as working electrode (WE), a graphite rod as counter electrode (CE) and a saturated calomel electrode (SCE) as reference electrode (RE).The individual electrochemical properties of DU and 40Cr steel, including linear polarization resistance (LPR) and potentiodynamic polarization, were investigated using a computer controlled PARSTAT$^{\text{TM}}$ 2263 Advanced Electrochemical System. For linear polarization resistance and potentiodynamic polarization tests, data were collected after 1h, 24h and 48h immersion of specimens, respectively. Linear polarization resistance (LPR) measurement was carried out with the potential scanning range from 10mV below to 10mV above the corrosion potential and the scanning rate was 0.167mV/s. Polarization resistance (R_p) was calculated by linear fit of auxiliary software in the measurement system. For potentiodynamic polarization, the potential was increased from 200mV below the corrosion potential to 1000mV in the anodic direction with a scanning rate of 2mV/s. The corrosion current was obtained via Tafel fit based on the data in the strong polarization region.

Open circuit potential (OCP) and galvanic corrosion tests were performed utilizing the zero-resistance ammeter (ZRA) produced by Wuhan Corrtest Instrument CO.LTD. The galvanic current density (I_g) and galvanic potential (E_g) for the DU/40Cr couple was continuously monitored for 48h at room temperature. The exposed area ratio of anode to cathode for all galvanic couples was 1:1.

2.3. SEM and EDS analysis.

Scanning Electron Microscope (SEM) and Energy-dispersive spectroscopy (EDS) investigations were performed on a KYKY-1010B instrument. Morphologies for the specimens of self-corrosion and the galvanic corrosion were compared. The auxiliary EDS was applied to analyze the micro-regional composition of the products after corrosion.

3. RESULTS AND DISCUSSION

3.1. Open circuit potential (OCP) measurement.

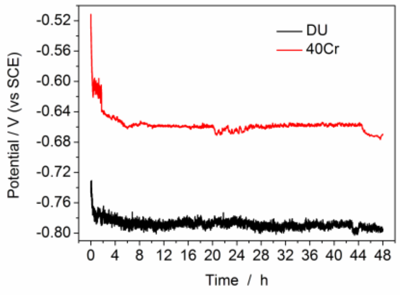


Figure 1. *OCPs* of DU and 40Cr steel vs. time in 3.5wt.%NaCl solution.

The potential difference between the couple metals is the driver of galvanic corrosion for DU/40Cr couple, thus the OCP measurement can supply the galvanic series with data support. Fig.1 presents the potential change of DU and 40Cr steel during 48h immersion in 3.5wt.%NaCl aqueous solution. The OCP of DU fluctuates slightly around -790mV. The OCP of 40Cr steel keeps the value of approximated -660mV(really close to the result in [16]) except that there are two obvious dropping during 48h immersion, one is at about 2h, another is at 44h, which may be the reason of the continuous eroded effect of chloride ions. Because the OCP of 40Cr steel is more positive than that of DU during all the test time, DU shall act as anode while 40Cr steel as cathode for the DU/40Cr galvanic couple in 3.5wt.%NaCl aqueous solution.

3.2. Linear polarization resistance test.

R_p value reflects the ability of corrosion resistance to a limited extent. Table 1 collects the R_p values of DU and 40Cr steel in 3.5wt.% sodium chloride solution after 1h, 24h and 48h immersion, respectively. As can be seen from table 1, the R_p value of 40Cr steel is larger than that of DU during the first corrosion period, which indicates that 40Cr steel shall be more anti-corrosive in 3.5w.t%NaCl solution at this time. In the period immediately following, the R_p value of DU decreases gradually, while the value of 40Cr steel increases a little from 1h to 24h immersion and then decreases sharply from 24h to 48h immersion. The transition of R_p value for 40Cr steel could be explained by taking into account the passivation and adverse effect of chloride ions. Due to the excellent passivation ability of 40Cr steel, a thin layer of passive film is formed, which causes an increase of R_p value at the beginning. Unfortunately, the passive film will undergo a consecutive damage in the chlorions solution. Pitting corrosion occurs explosively, resulting in a rapid decrease of the R_p value.

Table 1. R_p values of DU and 40Cr steel

Specimen	Immersion time, h	R_p, Ω.cm^{-2}
DU	1	2925
	24	2025
	48	1801
	1	3074
40Cr	24	3130
	48	721

3.3. Potentiodynamic polarization test.

Fig.2 illustrates the polarization curves of DU and 40Cr steel in 3.5wt.% NaCl solution at different testing times. After 1h immersion (Fig.2a), the cathodic polarization curves for both DU and 40Cr steel show a typical concentration polarization of oxygen. For the anodic polarization, 40Cr steel exhibits an active behavior with a distinct pitting corrosion characteristics by chloride ions up to a resulting polarization potential of 1V (vs. OCP). Besides, the DU presents a more negative corrosion potential which indicates that DU is preferential to corrosion.

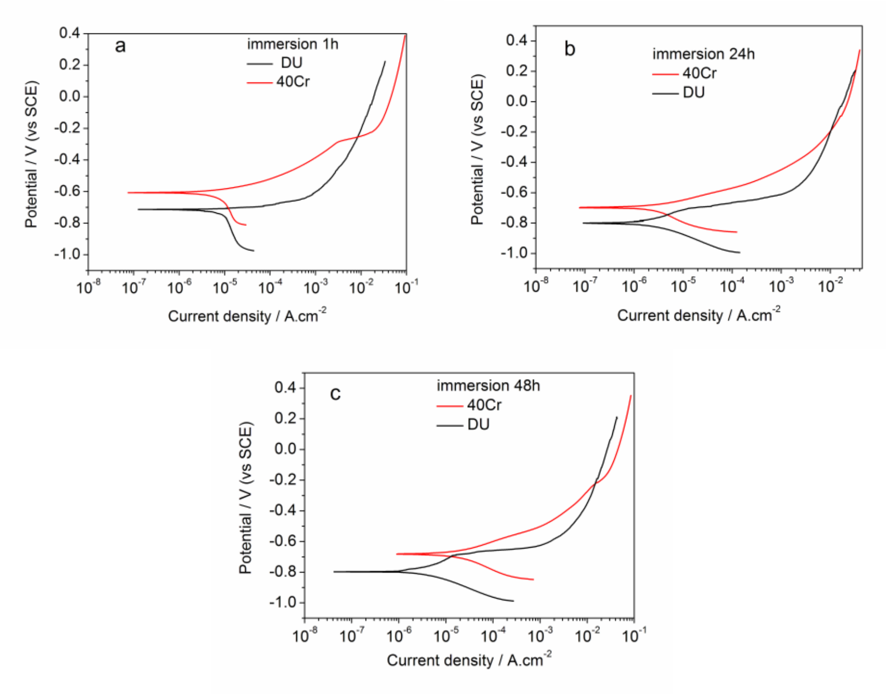


Figure 2. Potentiodynamic polarization curves of DU and 40Cr after: a 1h, b 24h, c 48h immersion in 3.5wt.%NaCl solution.

As can be seen from Fig.2b, after 24h immersion, the potentiodynamic polarization behaviors of DU and 40Cr steel have a significant change compared to that after 1h immersion. The corrosion potentials of both DU and 40Cr steel shift to the more negative direction. Their cathodic polarization curves display an obvious Tafel feature, indicating the disappearance of the oxygen-induced concentration polarization. For the anodic polarization, DU exhibits a pitting corrosion characteristics while the 40Cr steel just displays an active behavior following the Tafel region, mainly as a result of the accelerated corrosion of DU and the build-up of passive oxide film on the surface of 40Cr steel.

After 48h immersion (as seen from Fig.2c), the potentiodynamic polarization curve of DU is similar to that of Fig.2b (after 24h immersion).Whereas, the potentiodynamic polarization curve of 40Cr steel shifts to the right with an obvious increase of the corrosion current density. The damage of the passive film on 40Cr steel and the impact by chloride ions with the corrosion time prolonged may be the reason of this phenomenon.

The corrosion current densities of DU and 40Cr steel calculated from the potentiodynamic polarization curves at Tafel region are listed in Table 2. As can be seen, the corrosion current of DU increases gradually due to the continuous erosion by chloride ions with the immersion time prolonged, while the current density of 40Cr steel decreases at first then increases, corresponding to a stage of the formation of passive film on the sample in the first immersion period, and then the stage of the damage of the oxide film.

Table 2. Tafel fitted dynamic parameters

Specimen	Immersion time, h	Current density, µA.cm^{-2}
DU	1	7.94
	24	9.98
	48	13.22
40Cr	1	7.26
	24	6.94
	48	25.55

3.4. Galvanic corrosion test.

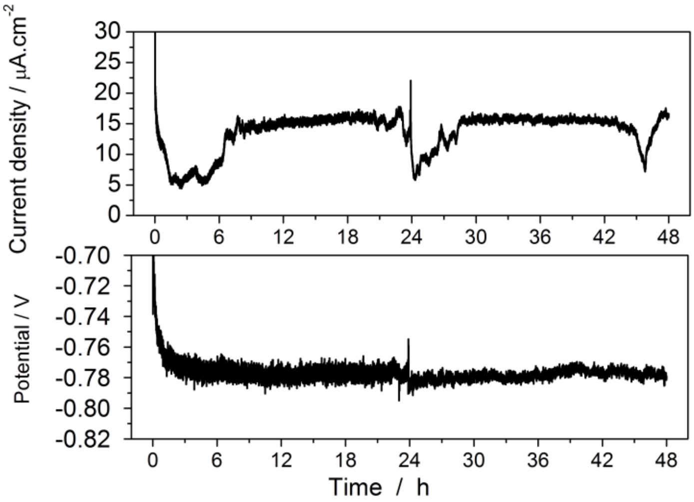


Figure 3. Galvanic potential and current of DU/40Cr couple vs. time in 3.5wt.%NaCl solution.

The steady-state galvanic potential and the current density are measured as function of time as showed in Fig.3. The galvanic potential, E_g, is around -780mV and the galvanic current density, I_g, is about 17.5 µA/cm^{-2} in spite of some fluctuations in 3.5wt.%NaCl solution. Because the cathodic polarization curve for 40Cr steel intersects the anodic polarization curve of DU in the region close to E_g(Figure 2), the galvanic current is not uniquely equal to the corrosion current at the DU anode. According to the concept of mix potential theory[17,18], the dissolution current density of DU resulting from galvanic coupling can be represented as follows:

$$I_g \le I_d \le I_g + I_{corr} \qquad \text{(Eq. 1)}$$

where I_d is the corrosion current density for coupled DU and I_{corr} is the corrosion current density of uncoupled DU. Therefore, 17.5µA/cm^{-2} $\le I_d \le$ 25.5µA/cm^{-2}, the corrosion rate of coupled DU is about 2 to 3 times greater than uncoupled DU. Besides, I_g of DU/40Cr couple is greater than that of DU-0.75Ti/AISI 4340 steel couple ranged between 10～14µA/cm^{-2} in a similar condition[15], which resulted from the more anti-corrosive property of DU when alloyed with Ti.

Fig.4 shows the corrosion morphologies of DU and 40Cr steel analyzed by SEM. As can be seen from Fig.4d and Fig.4f, there is no obvious change in morphologies between the self-corrosion and the galvanic corrosion for DU sample, but the self-corrosion level of 40Cr steel (Fig.4c) is more serious than that of galvanic corrosion (Fig.4e). This indicates that 40Cr steel is protected from corrosion and acts as cathode, while the DU sample acts as anode of DU/40Cr couple with an accelerated corrosion rate. Besides, corrosion products accumulates on the sample surface in appearances of "groups" or "clusters"and full of cracks or "chaps", as showed in Fig.4h.

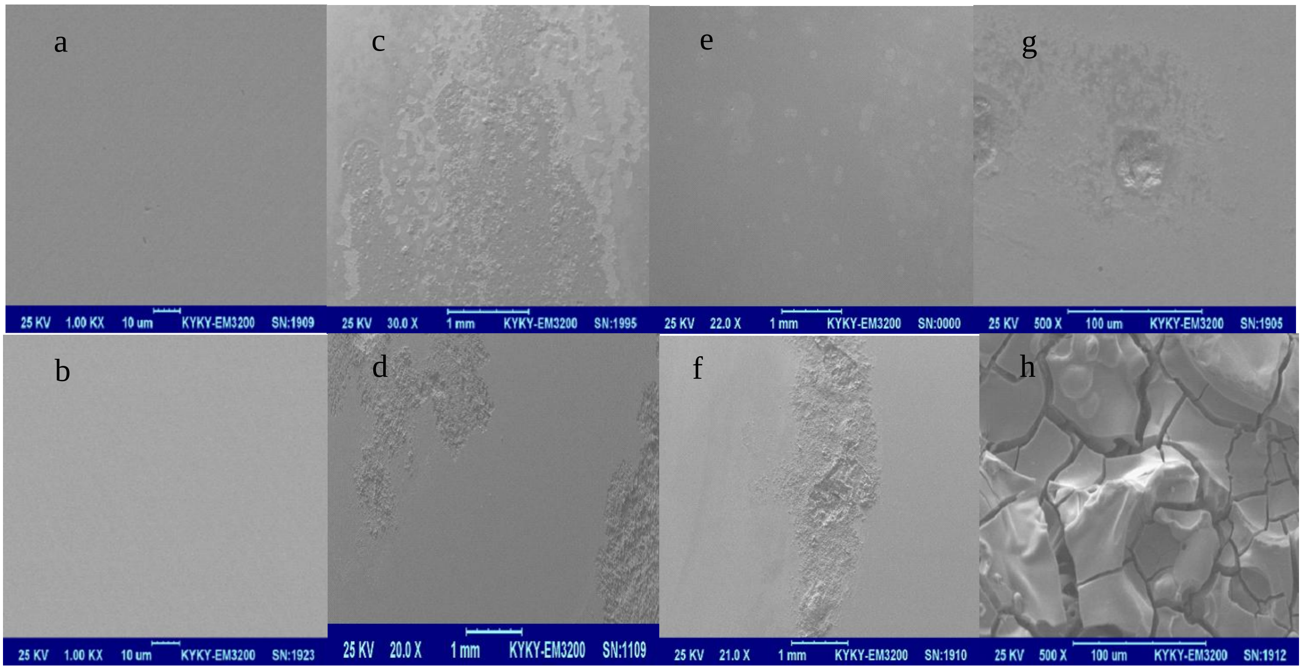
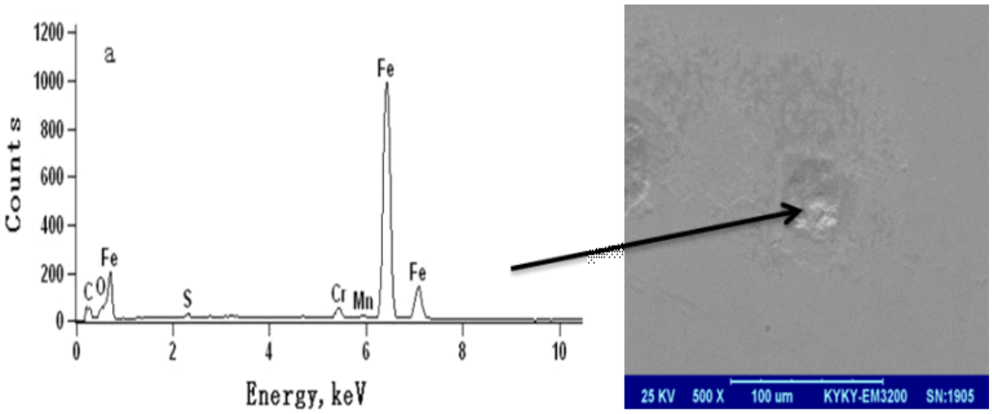


Figure 4. Morphologies of DU and 40Cr sample: a.40Cr before corrosion; b.DU before corrosion; c. Self-corrosion of 40Cr; d. Self-corrosion of DU; e. galvanic corrosion of 40Cr; f. galvanic corrosion of DU; g. micro morphology of 40Cr after galvanic corrosion; h. micro morphology of DU after galvanic corrosion.



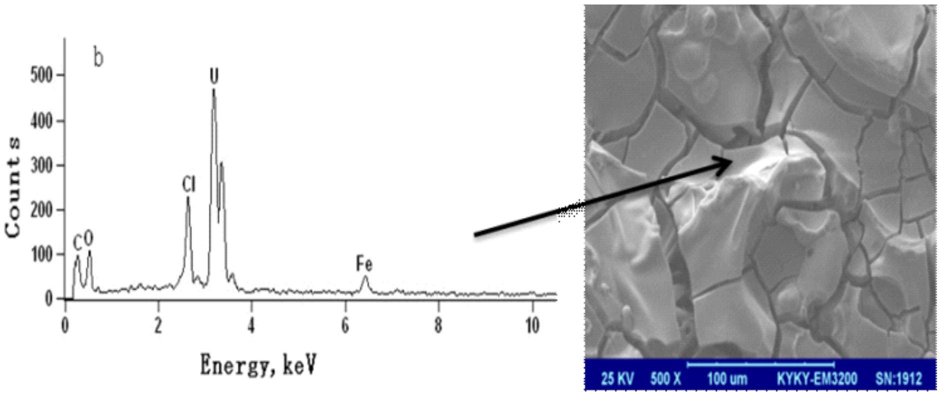


Figure 5. EDS spectra for surface elemental compositions of the galvanic corroded 40Cr steel (A vs. Fig.4g) and DU (B vs.Fig.4h) samples

Fig.5a and Fig.5b are the EDS analysis spectra corresponding to Fig.4g and Fig.4h, respectively. As can be seen from Fig.5a that almost all the peaks presents in the spectra of 40Cr steel come from the compositions (including carbon and oxygen) of the sample itself. The peak from chlorine is observed in the EDS spectra of the galvanic corroded DU sample, which may suggest that its corrosion products are mostly chlorides. Besides, gas products is observed in the process of galvanic corrosion.

3.5. Mechanism of galvanic corrosion.

Analyzing from the difference of OCP (Fig.1) and the corrosion morphologies observed by SEM (Fig.4), it is certain that DU acts as anode with an accelerated corrosion rate, while 40Cr steel acts as cathode during the process of galvanic corrosion for DU/40Cr couple, which is also corroborated by the results of LPR test (Table 1).

The process of galvanic corrosion is complicated. Comparing the galvanic corrosion potential (about -780mV) with the self-corrosion potential (-660mV for 40Cr and -790mV for DU) of uncoupled metals, it can be concluded that the 40Cr steel have been significantly polarized with a polarizing potential, approximately 120mV, below the self-corrosion potential, which let the metal situated in the cathodic protection region (Fig.2a) and ,therefore, is prevented from corrosion. Whereas, the DU would hardly be polarized because of a very small anodic polarizing potential of about 10mV. In addition, a typical concentration polarization of oxygen is observed from the cathodic potentiodynamic polarization curve of 40Cr steel, which indicates that the cathodic process is controlled by the concentration of dissolved oxygen in solution and Eq.2 is the rate-determining step of the cathodic process.

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad \text{(Eq.2)}$$

Meanwhile, the rapid dissolution of DU, as shown in Eq.3 and Eq.4, would happen on anode. Thus the Eq.1 should also be the rate-determining step of the whole galvanic corrosion.

$$U \rightarrow U^{3+} + 3e \qquad \text{(Eq.3)}$$

$$U^{3} \rightarrow U^{4+} + e \qquad \text{(Eq.4)}$$

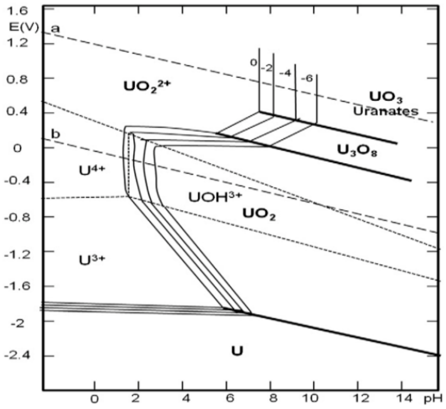


Figure 6. Potential-pH relationship of uranium

After 24h immersion, the concentration polarization effect of oxygen vanishes because of the continuous consumption of the dissolved oxygen in 3.5w.t%NaCl solution on cathode, as shown from the cathodic potentiodynamic polarization curves of 40Cr steel and DU in Fig.2b. This means that an alteration occurs in the cathodic process and Eq.1 is not the major cathodic process any more. From the potential-pH diagram of DU (Fig.6), it is known that the reaction (Eq.4) would occur immediately after reaction (3) and (4).

$$U^{4+} + 2H_2O \rightarrow UO_2 + 4H^{+} \qquad \text{(Eq.5)}$$

Obviously, the cathodic reaction should be reaction (6) referred from the Eq.5,

$$2H^{+} + 2e \rightarrow H_2 \qquad \text{(Eq.6)}$$

Therefore, the reaction (6) should be the main and rate-determining cathodic process in galvanic corrosion during this immersion time. That is the reason why the bubble of H_2 are observed separating out from the surface of cathode during the galvanic corrosion process.

Alteration of the electrode process is also reflected on the change of the galvanic current density as time prolonged, shown in Fig.5. During the first corrosion period, the galvanic corrosion rate is controlled by the concentration polarization of dissolved oxygen, resulting in a relatively lower galvanic current density. Then, with continuous consumption of the dissolved oxygen, the concentration polarization of oxygen disappears and the cathodic process alternates to hydrogen release, .which begins at about 6h immersion in this experimental system, as shown in Fig.5. Consequently, the galvanic corrosion rate, as well as the galvanic current density, increases until the whole corrosion process is controlled by Eq.5 and the galvanic current density reaches a relatively steady value about 17.5μA/cm^{-2}.

Chloride ions have significant effects on the process of galvanic corrosion. In such reaction system, oxide film could be easily formed on the surface of DU sample, especially in the solution containing dissolved oxygen. Unfortunately, chloride ions, as aggressive negative ions, could penetrates into the oxide film and lead to pitting corrosion on the surface to form chlorides by reactions of Eq.7 and Eq.8.

$$U^{3+} + H_2O + Cl^- \rightarrow H^+ + UOHCl^+ \quad \text{(Eq.7)}$$

$$U^{4+} + 2H_2O + 2Cl^- \rightarrow 2H^+ + U(OH)_2Cl^+ \quad \text{(Eq.8)}$$

$$UCl_x + xH_2O \rightarrow U(OH)_x + xHCl \quad \text{(Eq.9)}$$

The total reaction is similar to a hydrolysis reaction (Eq.9), which would lead to a strong acidification of solution inside the pits and an acceleration of the galvanic corrosion of DU.

4. CONCLUSIONS

DU acts as anode with an accelerated corrosion rate, while the 40Cr steel behaves as cathode during the process of galvanic corrosion for DU/40Cr couple in 3.5w.t%NaCl solution. The galvanic potential and current density of the DU/40Cr couple are about -780mV and 17.5μA/cm^{-2}, respectively. The cathodic reaction would alter from oxygen dissolving to hydrogen releasing during the galvanic corrosion process of DU/40Cr couple and the chloride ions have a significant effect on this process.

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