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CORROSION CHARACTERISTICS STUDY ON URANIUM AND ITS ALLOYS (U-Nb, U-Zr, AND U-Zr-Nb)

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ABSTRACT

CORROSION CHARACTERISTICS STUDY ON URANIUM AND ITS ALLOYS (U-Nb, U-Zr, AND U-Zr-Nb). Uranium metal (U) and its alloys, such as U-Zr, U-Nb, and U-Zr-Nb, can be used as fuel in nuclear reactors, especially in research reactors. These fuels have various characteristics, including physical, chemical, mechanical, and corrosion properties. Among these characteristics, fuel corrosion properties play a critical role during the reactor operation, after use, and also during the storage period. Fuel damage due to corrosion is influenced by several factors, such as the concentration of oxidizing agents, the flow rate of corrosive fluids, temperature, and acidity (pH). The corrosion process in uranium metal produces hydrogen gas (H_2), which reacts with uranium to form pyrophoric uranium hydride (UH_3), and uranium oxidation produces UO_2. If the oxidation process continues for an extended period, the uranium metal will be depleted. The corrosion potential (E_{corr}) and corrosion rate (CR) of uranium metal in a passive state do not depend on pH until the pH reaches 7. The corrosion potential increases once the pH exceeds 7 and continues to rise to pH 11. Uranium alloys with low Zr, Nb, or Ru content, when alloyed with Zr and Nb up to 2.5 wt.% and Ru up to 5.0 wt.%, show minimal impact on the corrosion potential (E_{corr}) in the pH range of 4.0–9.0 unless there is a dissolved oxidant. U-Nb alloys with higher Nb content, exhibit greater resistance to corrosion and depleted uranium (without Nb). Under acidic conditions (pH 1.18), U-6Zr-2Nb alloys demonstrate the best corrosion resistance. In demineralized water, U-6Zr-5Nb alloys show the best corrosion resistance, while under basic conditions (pH 11.02), U-6Zr-8Nb alloys exhibit the best corrosion resistance.

Keywords: Corrosion, U metal, U-Zr alloy, U-Nb, U-Zr-Nb.

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INTRODUCTION

Uranium metal and its alloys are used as fuel in nuclear reactors, both for power and research reactors. The use of uranium without alloying with other metals is less practical due to its original inadequate mechanical properties. Therefore, uranium alloys such as UAl_x-Al, U_3O_8-Al, U-ZrH_x, UO_2, and U_3Si_2-Al are commonly used. In addition to these existing alloys, new alloys such as U-Zr-Nb and U-Mo-Ti are also being developed as fuel candidates for future research reactors. The ternary Uranium–Zirconium–Niobium (U−Zr−Nb) alloy is a promising nuclear fuel for research reactors, high-flux reactors (High Flux Isotope Reactors), and fast breeders. This alloy offers many advantageous properties, including higher thermal conductivity and density, ease of fabrication, and good compatibility with fuel cladding [1].

In addition to these properties, corrosion characteristics must be considered as they can impact fuel performance during reactor operation and storage after use. Acidic, neutral, or basic environments can affect fuel performance, not only in terms of physical and mechanical properties but also through corrosion-related degradation. Therefore, studying the corrosion behavior of uranium metal and its alloys, such as U-Zr, U-Nb, and U-Zr-Nb alloys, is crucial.

Zirconium is known for its resistance to corrosion, which is caused by forming a very stable oxide layer on its surface, which acts as a barrier to further corrosion. Niobium also has good corrosion resistance properties, especially against intergranular corrosion at high temperatures. Nb is more stable than uranium at high temperatures and can also improve the mechanical properties of the alloy. Overall, the optimal composition of U-Zr-Nb alloys in terms of corrosion resistance is one with a Zr content of about 5-10% and Nb of about 1-5%, depending on the specific application desired (e.g., high-temperature resistance or mechanical stability).

Corrosion is a material degradation process caused by the influence of the surrounding environment. It is a natural tendency for materials to return to their most thermodynamically stable state. In most metallic materials, corrosion occurs through the formation of oxides, sulfides, or base metal compounds, commonly known as metal ores[2].

Several factors influence the corrosion rate, including the concentration of oxidizing agents, the flow rate of corrosive fluids, temperature, and acidity. As a result, the corrosion rate will be higher in a solution containing dissolved oxygen compared to a deaerated solution or if the dissolved oxygen concentration can be controlled. Several methods have been applied to improve corrosion resistance, including the development of intermetallic alloys, surface coatings, and ion implantation. Intermetallic alloying involves combining two or more metals to form an alloy by melting the metal mixture [3]. The resulting alloy may form a solid solution (single phase) or a mixture of metal phases (two or more solutions), which creates a distinct crystal microstructure in the material. Surface coating is a technique where materials are applied to the surface of a substrate to protect it from environmental influences and extend its service life. This method can be energy-efficient and cost-effective, especially when cheaper materials are used to create the desired surface mechanical structure [4]. Ion implantation is a process carried out at low temperatures, where ions from an element are accelerated toward a solid target, thereby altering the target's physical, chemical, or electrical properties. Typically, ion implantation involves an ion source that produces ions from selected elements using an accelerator. These ions are then accelerated to high energies electrostatically and directed toward the target for implantation.

CORROSION OF URANIUM METAL

Uranium metal has been a primary material used in nuclear reactor fuel, particularly as a metal fuel in certain reactor types, for several decades. Although most power reactors today use oxide fuel, several research reactors, such as Material Test Reactors (MTR), still use fuel in the form of uranium metal or uranium metal alloys. Therefore, it is essential to study the corrosion phenomena of uranium metal, including its behavior throughout the nuclear fuel cycle, whether in reactors, during short-term storage, or in the final disposal process of the fuel [5].

In addition to the reaction rate, there are varying opinions regarding the oxidation mechanism of uranium metal, particularly in its interaction with water. Some researchers argue that oxygen (O_2) diffuses in the corrosion process, while others suggest that hydroxide ions (OH^-) dominate or that both contribute to the process (O_2 and OH^-). Many studies on the corrosion mechanism of uranium metal focus on the formation of uranium hydride (UH_3), which is produced during the corrosion reaction and is considered a key intermediate in the process. However, the formation of this hydride is influenced by various factors, such as temperature, hydrogen pressure, oxidation by water, and the specific reaction mechanisms that affect the corrosion rate [6],[7].

1. Uranium-Water Corrosion System

The corrosion of uranium metal in water is a significant issue due to the formation of hydrogen gas (H_2) as a by-product. The absence of oxygen in water can inhibit H_2 formation [7]. The H_2 gas produced can easily ignite if it reaches a high enough concentration and may react with uranium metal to form uranium hydride (UH_3), which is unstable in air and pyrophoric, meaning it can self-ignite when exposed to large amounts of oxygen [5],[6]. When formed on irradiated uranium, this reaction poses the risk of radionuclide release due to exothermic reactions, which can also release trapped fission products. This creates problems in the handling, transporting, and storing of nuclear waste under wet conditions. The potential for toxicity caused by slow oxidation due to prolonged exposure to water vapor significantly reduces the efficiency and service life of the storage system. Therefore, a comprehensive understanding of the kinetics and mechanisms affecting uranium metal corrosion and the evaluation of the chemical products produced during corrosion reactions is essential for the nuclear industry to predict the behavior and evolution of stored uranium [7].

2. Uranium Oxidation

As with most metal oxidation reactions, uranium (U) metal oxidation is also controlled by a diffusion process. However, the mechanism of oxide formation in uranium is different from that of transition metal oxides. In transition metal oxidation, new oxides form on the outer surface of the existing oxide layer, which is then driven by the diffusion of metal cations from the surface. In contrast, due to the large size of uranium cation ions, diffusion within the uranium oxide crystal lattice is very limited. As a result, new oxides form at the base of the pre-existing oxide layer. Thus, the mechanism and rate of uranium oxidation are highly dependent on environmental conditions (such as temperature and pressure) and the corrosive species present in the system (such as O_2, H_2O, and others) [7]. Factors such as metal pretreatment, fabrication process, and impurity content can also influence the oxidation rate.

Uranium metal is highly electropositive and has a strong affinity for oxygen, which is highly electronegative. Therefore, when exposed to water or oxygen, a clean uranium surface will rapidly oxidize. In the early stages of oxidation, uranium metal exhibits a parabolic corrosion rate. However, once the oxide layer forms, the corrosion rate typically becomes linear or nearly linear, controlled by the diffusion of the oxidizing agent through the formed oxide layer. Uranium oxidation is expected to continue until all the metal is consumed and the available oxidizing agents are depleted. After this, the corrosion rate will approach zero [8].

3. Uranium Reaction with Water ($U+H_2O$)

The reaction between uranium metal and water can be divided into several stages, namely initial oxidation, formation of oxide layer, and kinetics-effects of temperature and pressure.

3.1. Initial Oxidation

Uranium metal has a strong affinity for oxygen, making it easily oxidized in air, even under Ultra High Vacuum (UHV) conditions [8]. During the initial reaction stage, the adsorbed water undergoes full dissociation, with full dissociation being the dominant process [9]. The adsorption process follows the Langmuir chemisorption mechanism [10], forming island-shaped oxides, which marks the beginning of forming a continuous oxide layer. In the initial oxidation stage, oxygen absorption is strong chemically, while hydrogen absorption is weak. Hydrogen atoms are bound to the metal surface. Before forming a complete oxide layer, partial dissociation of oxide absorption begins. Once the surface is fully covered with oxide, water molecules and/or hydroxyl ions undergo strong chemical adsorption on the outer surface, and a hydroxyl double layer may be observed.

3.2. Formation of Oxide Layer

The oxidation of UO_2 by water can be analyzed using various experimental techniques, such as Low Energy Electron Diffraction (LEED), Low Energy Ion Scattering (LEIS), Electron Stimulated Desorption (ESD), X-Ray Photoelectron Spectroscopy (XPS), and Thermal Desorption (TPD) measurements. Experiments using oxide samples with different crystal orientations have been conducted to study whether there is a difference in the reaction rate during the adsorption process. The results of these observations show that water vapor is completely dissociated on the UO_2 surface at a temperature of 300 K, without the formation of OH^- ions. The study of the stoichiometry of UO_2 oxide revealed that most water adsorption processes were reversible, with some water desorbing at the two higher temperature peaks without forming H_2. Furthermore, no hydrogen formation was observed on the annealed UO_2 surface after exposure to water vapor. This finding suggests that H_2O reacts weakly and does not dissociate on the UO_2 surface. However, oxygen defects in the oxide can activate the surface, promoting the dissociation and adsorption of water at these sites. Therefore, in polycrystalline materials, the reaction may occur at oxygen defects on the surface. These defect areas can be repaired by heating (annealing) for a sufficient time or by continuous water spraying. The formation of an oxide layer is very important about the corrosion rate of a material, especially metals. The oxide layer functions as a protector for the metal from the corrosion process caused by chemical reactions with the environment, such as oxygen and water. Some oxide layers that affect the corrosion rate include surface protection, oxide layer stability, metal types and galvanic corrosion, local corrosion, and environmental influence. In general, a good oxide layer can slow the corrosion process, but if this layer is damaged, the corrosion rate can increase rapidly.

In conclusion, it can be stated that water does not dissociate on the surface of pure UO_2, and stoichiometric conditions are not significantly affected by crystal orientation. However, the presence of surface defects, including those caused by radiation damage, can result in the partial or complete dissociation of water molecules at specific locations. Thus, the oxidation of UO_2 is more influenced by surface defects than by other factors.

3.3. Kinetics-Effects of Temperature and Pressure

In oxygen-free conditions, relative humidity (RH) continuously affects the corrosion rate. Colby et al. [29] reported observations on the corrosion of uranium monocarbide in water vapor, showing a consistent increase in the corrosion rate with RH between 1.5% and 95.5% at constant temperature. Similar studies were conducted by other researchers, examining the corrosion of uranium in a closed system at temperatures ranging from 40°C to 100°C and pressures between 0.1 mbar and 667 mbar. Water vapor pressure also plays a significant role, with pressure measurements indicating a linear relationship with the square root of pressure (P0.5) for pressures up to 1013.25 mbar [11], [12]. Various parameters influence the rate and mechanism of corrosion, including the corrosion products formed, their abundance, and the physicochemical properties involved. All of these factors are critical in understanding and controlling uranium corrosion rates. Understanding the characteristics of uranium electrochemical corrosion is particularly important, especially to the formation of uranium hydride (UH_3), which poses challenges for the nuclear industry due to its highly pyrophoric properties, making it very reactive [11],[13].

4. Other Factors Affecting the Rate of Uranium Corrosion

In addition to temperature and pressure, several other factors are also considered to affect the kinetics of uranium oxidation. These include the presence of oxygen, other gases, water pH, pre-heat treatment, metal impurity content, effect of uranium alloying elements, and surface preparation.

4.1. Effect of Oxygen

Oxygen concentration, whether dissolved in water or present in water vapor, can significantly inhibit the rate of uranium corrosion [14]. This oxygen inhibition can reduce the corrosion rate by a factor of 12 to 100, although the results vary depending on experimental conditions, such as the type of sample and whether the experiment is conducted under closed or open conditions. The slowdown in the rate of oxygenated corrosion occurs only within a certain timeframe, depending on the initial oxygen concentration, temperature, and pressure. Oxygen uptake is faster in the uranium-oxygen system and follows a linear pattern [15], while the water vapor pressure remains constant until most of the oxygen has reacted.

Under conditions with sufficient oxygen ($PO_2 > 0.02$ mbar), hydrogen is not produced [16] and a decrease in oxygen pressure does not occur, even if hydrogen is added. Oxygen can inhibit hydrogen uptake in a water vapor or humid environment. At relatively high oxygen pressures ($PO_2 > 0.2$ mbar), the reaction rate becomes independent of both oxygen and water vapor pressures. However, when PO_2 drops below a critical value (0.2–4 mbar), the reaction rate becomes dependent on both PO_2 and $P(H_2O)$. Once oxygen has completely reacted, the reaction rate becomes dependent on the water vapor pressure, and hydrogen begins to evolve. Equilibrium is reached, with a steady reaction rate at a sufficiently high water vapor pressure. Figure 1 shows the generation profiles of H_2O, O_2, and H_2 during the reaction between uranium and water vapor-oxygen [13].

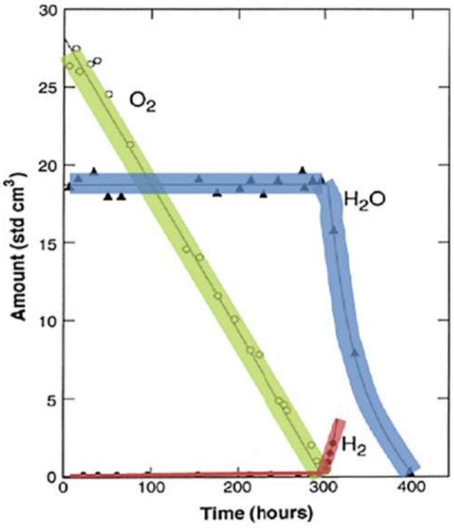

Figure 1. Generation profile of H_2O, O_2 and H_2 gases during the uranium-water [13].

4.2. Effect of Gases Other Than Oxygen

Carbon dioxide (CO_2) can reduce the corrosion rate and hydrogen evolution by approximately 50% at pressures between 0.07 and 2 atm. In an experiment, the volume of CO_2 in the reaction chamber (free volume) remained constant, and no carbon monoxide (CO) was detected during the reaction. This indicates that no adsorption or surface dissociation occurs. Nitrogen gas (N_2) at a pressure of 1 atm and hydrogen up to 6 atm did not significantly affect the reaction rate with water, even though the system was submerged. However, the effects of these gases were observed only in the short term because the experiment was conducted in a closed chamber that was periodically opened for thermogravimetric analysis. Scott et al. [17] exposed a high-carbon uranium sample to water vapor in a pumped system and then exposed the reaction chamber to the atmosphere at very low pressure (~6.67 mbar). The sample was then returned to water vapor, and the results showed that the corrosion rate was reduced. In submerged conditions, the deliberate addition of hydrogen did not affect the corrosion reaction rate. However, the addition of salt, such as sodium carbonate dissolved in water, accelerated the decrease in the corrosion rate.

4.3. Effect of pH Value on Water

The corrosion rate of uranium in water with pH < 2 tends to be slow due to the absence of O_2 or OH^- ions. Between pH 2-3, the corrosion rate increases rapidly and remains stable up to pH 7. At pH 7-13, the corrosion rate decreases due to the reduction of H^+ ions, which inhibit the release of electrons at the uranium-oxide interface. Above pH 10, the corrosion rate increases moderately [13]. A study by Lillard et al. showed an increase in corrosion current between pH 10.7 and 13.6 [13]. At neutral to slightly alkaline pH (pH 7-13), the material will form a passive layer that protects the surface from further damage. This passive layer is often formed due to surface oxidation, which prevents direct contact between the material and the corrosive environment. When the pH increases above 10, the nature of the solution becomes very alkaline, which can affect the previously formed passive layer and cause thinning or damage to the oxide layer that protects the metal surface. For some metals and alloys, this condition can increase corrosion by allowing further reaction between the metal and the alkali solution. So at neutral to slightly alkaline pH, the material can form a protective passive layer, while at very high pH, this layer can be damaged and accelerate corrosion.

At basic pH, especially around pH 10, sodium carbonate (Na_2CO_3) is more effective in inhibiting corrosion than other basic solutions, presumably because the carbonate ion behaves similarly to carbon dioxide. Research by Peretrukhin et al.. showed that in a 0.1 M Cl^- deaerated solution, the corrosion potential was weakly dependent on pH. Still, the corrosion rate increased from pH 6 to 10, as shown in Figure 2 [13].

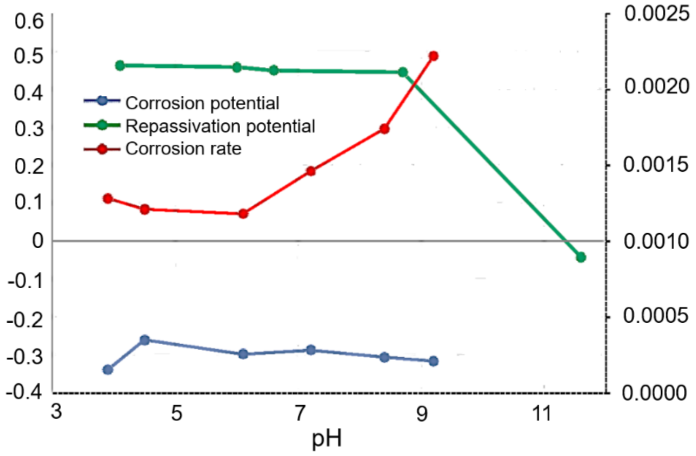

Figure 2. Corrosion potential and rate measured in $NaClO_4$ deaerated solution at different pH [13].

4.4. Effect of Pre-Heat Treatment

Metallurgical processes and heat treatment (annealing) affect the content and distribution of impurities in the metal, and promote the diffusion of light gases, such as H_2, to the surface [18]. Heat treatment of strained samples can alter the early stages of corrosion by inducing strain release, reducing surface defects, and minimizing grain boundaries and twins, thereby decreasing their susceptibility to corrosion [19]. Rapid cooling (quenching) of uranium and its alloys in a vacuum increases corrosion resistance by removing dissolved gases, especially hydrogen [20]. For impure metals, quenching helps to distribute impurities and further increases corrosion resistance. In contrast, powder metallurgy techniques increase porosity, which shortens the corrosion lifespan. Uranium oxidation can be suppressed by a protective oxide layer that blocks water diffusion. Overall, metallurgical and thermal treatments influence the surface characteristics and microstructure of the metal, which in turn alters the mechanism and rate of corrosion. However, for the future process, this quenching technique is not carried out because the work is difficult to do compared to adding alloying elements. However, for the future process, this quenching technique is not carried out because the work is difficult to do compared to adding alloying elements.

4.5. Effect of Metal Impurity Content

The effect of metal impurities on uranium oxidation has been studied by Colmenares et al., who found that low-purity metal (with 97 and 457 ppm impurities) exhibited a 17% higher oxidation rate compared to high-purity metal. Draley et al. [20] also observed that increasing metal purity decreased the corrosion rate of uranium. Carbon, a common impurity in uranium, forms uranium carbides that accumulate and increase the reactivity of the metal, thereby raising the corrosion rate. The interface between uranium and carbides acts as a diffusion path for oxidants, so the higher the carbon content, the more susceptible the metal is to oxidative corrosion.

4.6. Effect of Uranium Alloying Elements

The addition of alloying elements to uranium metal fuel is primarily aimed at stabilizing the γ phase, which shows improved thermal expansion performance compared to pure α-phase uranium. The benefits of alloying include increased resistance to corrosion, which is considered advantageous for the corrosion behavior of spent fuel materials. Elements such as niobium (Nb), molybdenum (Mo), zirconium (Zr), platinum (Pt), tin (Sn), vanadium (V), titanium (Ti), chromium (Cr), columbium, and silicon (Si) have been successfully used as alloying elements in uranium. Uranium samples with high aluminum (Al) and iron (Fe) content that are processed metallurgically show slower corrosion kinetics. The Nb element is added to uranium or uranium alloys in concentrations ranging from 1% to 14.1% (w/o), with the binary Nb-U system demonstrating excellent performance in the range of 8–12%. The Nb_2O_5 layer that forms can slow the corrosion kinetics and physically inhibit the diffusion of OH^- and O_2 into the oxide/metal interface. The addition of 0.26% Sn to a U-Nb 3% alloy increases the resistance of γ-quenched and aged metal fuel to water corrosion. However, increasing the Sn content beyond this point accelerates the corrosion rate. The U-Mo alloy system shows the best corrosion performance at 11.2% Mo by weight. The oxidation resistance of U-Mo alloys is further enhanced by adding (a) copper (Cu), tungsten (W), and zirconium (Zr) in the range of 0.1–1%, (b) chromium (Cr) and titanium (Ti), and (c) platinum (Pt). The addition of these elements significantly reduces hydrogen uptake during the fabrication process. The addition of Ti to uranium (e.g., U-0.75Ti) is used to improve the strength and toughness of the metal [21].

Efforts to reduce the influence of alloying elements on corrosion resistance in U-Zr alloys involve composition control, process control, and microstructural modification that allow the alloy to maintain optimum corrosion resistance while maintaining the required mechanical properties. The addition of alloying elements such as niobium (Nb) must be carefully considered. These elements can improve mechanical properties but sometimes reduce corrosion resistance if present in excessive amounts. Proper melting and mixing processes are essential to ensure an even distribution of alloying elements. The formation of undesirable phases (such as intermetallic phases) between Zr and other elements can worsen corrosion resistance. Therefore, process controls such as induction melting, vacuum melting, or temperature control during alloying can help reduce the formation of less stable phases.

4.7. Effect of Surface Preparation

The corrosion rate can be influenced by the nature of the metal surface and the oxide layer that forms before the reaction [22]. Factors such as surface tension, oxide surface defects, stoichiometry, and oxide thickness can be influenced by the method used for surface preparation. Cleaning with nitric acid (pickling) will accelerate corrosion, compared to samples that are mechanically polished, while the electropolishing process makes part of the metal surface passivated [23].

CORROSION OF U-Zr, U-Nb, AND U-Zr-Nb ALLOYS

1. Corrosion of Uranium Metal with Low Zr, Nb, and Ru Content

Research on the corrosion of uranium metal and its alloys, particularly those containing Zr, Nb, Mo, or Si, has primarily focused on water-cooled nuclear reactors. Although the concentration of small alloying elements (around 0.5%) is often overlooked [23], [24], the corrosion of irradiated uranium can lead to the formation of sludge composed of uranium (IV) and (VI) oxides, uranium peroxide, uranates, and uranium metal particles at the bottom of the cooling bath. The corrosion of uranium in water involves the formation of a passive layer of uranium dioxide (UO_2), which initially forms rapidly and then develops more slowly.

The addition of Niobium (Nb) in uranium-zirconium (U-Zr) alloys can provide benefits in terms of corrosion resistance, but it should be noted that the optimal amount must be by the application objectives, considering the nature of niobium which can affect the microstructure and mechanical properties of the alloy. In general, the addition of Nb aims to increase corrosion resistance in extreme environments, such as in nuclear reactors. Niobium has several properties that are beneficial for corrosion resistance, including: forming a protective layer; reducing damage due to oxidation; and improving the stability of the alloy phase. The addition of niobium (Nb) in U-Zr alloys to increase corrosion resistance should be done in the range of 1-5%. Higher concentrations, although they can provide some advantages in terms of stability at high temperatures, must be considered carefully because they can cause the formation of less stable phases, which can actually reduce the corrosion resistance of the alloy.

The subsequent oxidation process produces unstable compounds, such as uranium hydride (UH_3) and uranium (III). Further oxidation of the passive $UO_2 \cdot nH_2O$ layer can form uranium (VI), particularly relevant under acidic, neutral, or bicarbonate conditions. The deposition of metal oxides, such as ruthenium (Ru) or technetium (Te), on uranium stored underwater is also problematic. Petrukin et al. [25] conducted electrochemical experiments to investigate the effects of Zr, Nb, and Ru on uranium corrosion. The results showed that the corrosion potential (E_corr) and corrosion rate (CR) of uranium metal in 0.1 M $NaClO_4$ solution (pH 4.0–9.0) were only slightly affected by pH, as shown in Table 1. The corrosion rate of uranium alloys with Zr, Nb, and Ru (up to 2.5 wt.% each, and Ru up to 5.0 wt%) increased above pH 7. However, adding these alloying elements did not significantly change the corrosion rate of uranium with a $UO_2 \cdot nH_2O$ passive layer [26].

Table 1. Corrosion potential and rate and Tafel parameters (n is the number of electrons involved in the reaction, α is the transfer coefficient) for uranium metal samples in 0.1 M NaClO4 at different pH [25]

pH	Corrosion potential vs. Ag, AgCl, mV	n	α	Io, μA cm^{-2}	Corrosion rate, mg cm^{-2} h^{-1}
3.94	–294 ± 22	1.02	0.56	0.57 ± 0.06	0.00128
4.54	–216 ± 28	0.98	0.58	0.54 ± 0.07	0.00121
6.08	–253 ± 32	1.00	0.57	0.53 ± 0.04	0.00118
7.17	–242 ± 26	0.89	0.55	0.65 ± 0.04	0.00146
8.37	–261 ± 31	0.88	0.57	0.78 ± 0.03	0.00174
9.16	–271 ± 24	0.87	0.57	1.00 ± 0.08	0.00222

2. Corrosion of Uranium-Niobium (U-Nb) Alloys.

Various methods to improve the corrosion resistance of uranium (U) metal include alloying with other metals, surface coating, and ion implantation. Elements such as titanium (Ti), niobium (Nb), zirconium (Zr), and ruthenium (Ru) are often added to enhance the corrosion resistance of uranium [27], [28].

In addition, coatings made of zinc (Zn), aluminum (Al), titanium (Ti), and chromium (Cr) have also been studied for their potential to strengthen corrosion resistance. Ion implantation techniques are used to form a passivation layer on the uranium surface. Electrochemical methods are commonly employed to assess corrosion behavior, although studies on the morphology of corrosion products on uranium alloys remain limited [29],[30]. To study the effect of niobium (Nb) on corrosion resistance, uranium alloys with Nb contents of 2.5% (U-2.5Nb) and 5.7% (U-5.7Nb) were electro-chemically tested using saturated calomel and graphite electrodes in a chloride solution with pH 7. Linear polarization curves were obtained to analyze the corrosion rate, while SEM and EDX were used to analyze the surface morphology and composition of the corrosion products. Observation of the crystal structure of depleted uranium (DU) after cooling and annealing processes revealed that its crystal structure is orthorhombic. On the other hand, the microstructure of U-Nb alloys depends on the niobium content in the alloy. Figure 3.a [25] shows the morphology of the U-2.5Nb sample observed using an optical microscope, indicating that the alloy has a pearlite structure consisting of α (Nb-depleted) and γ1-2 (Nb-enriched) phases [31]. Meanwhile, in Figure 3.b, the U-5.7Nb alloy shows a single structure, with some Nb patches randomly distributed within the grains and at the grain boundaries, as confirmed by EDX analysis. The distorted single α" martensite structure indicates that the structure is a deformed form of α-U [32], [33]. In the X-ray diffraction (XRD) pattern related to the corrosion of uranium-niobium (U-Nb)[25], there is some important information that can be obtained, especially regarding the phase structure involved, phase changes, and the relationship between corrosion and phase composition.

There is some information that can be obtained from the X-ray diffraction pattern related to the α-U, γ1-2, and α" martensite phases. Overall, the X-ray diffraction pattern can provide a clear picture of how corrosion affects the crystal structure and phases in U-Nb alloys and how these changes can influence the performance of the material. There is some information that can be obtained from the X-ray diffraction pattern related to the α-U, γ1-2, and α" martensite phases. Overall, the X-ray diffraction pattern can provide a clear picture of how corrosion affects the crystal structure and phases in U-Nb alloys and how these changes can influence the performance of the material.

In electrochemical testing, it was found that depleted uranium (DU) and U-Nb alloys immersed in a chloride solution with a concentration of 50 mg/g showed very small potential fluctuations, namely below 2 mV, before reaching the open circuit potential (OCP) value, E_{oc}. The E_{oc} values were obtained from linear polarization measurements. From these data, it can be seen that the E_{oc} value for the U-5.7Nb alloy is higher than that for DU, indicating that the U-5.7Nb alloy has the best corrosion resistance in thermodynamic terms, as reflected in the open circuit potential value [25].

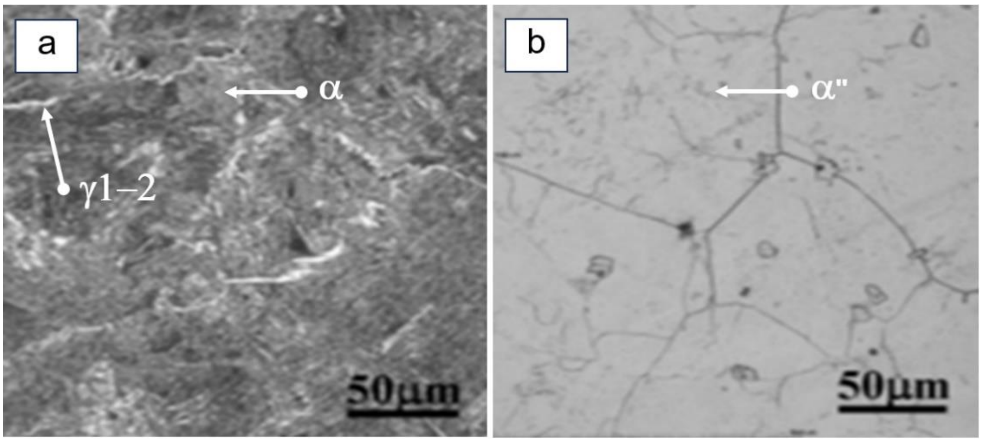

Figure 3. Morphology using an optical microscope from (a) U-2.5Nb, and (b) U-7Nb [25].

To assess the effectiveness of the alloy elements in protecting against corrosion, potentiodynamic polarization measurements were carried out in a chloride solution with a concentration of 50 mg/g [25]. Figure 4 [25] shows the potentiodynamic polarization curves for the DU and U-Nb alloys, indicating that all samples exhibit similar electrochemical behavior in the tested potential range.

The corrosion potential for DU was recorded at approximately 641 mV vs. SCE, while for the U-2.5Nb alloy, the corrosion potential increased by about 120 mV vs. SCE, and the corrosion current density decreased by half. When the Nb content in the alloy increased to 5.7 wt%, the corrosion potential increased by about 200 mV vs. SCE, and the corrosion current density decreased in line with the existing trend. The decrease in corrosion current density is attributed to the addition of Nb, which stabilizes the martensite a" structure (a homogeneous phase without anodic regions that could produce galvanic couples) and increases the thermodynamic stability as well as the corrosion potential of the uranium alloys.

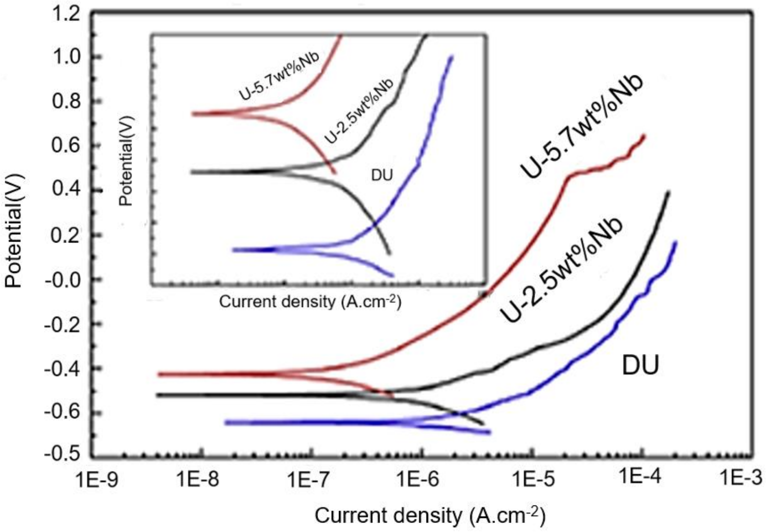

Figure 4. Polarization curves of DU and U-Nb in 50 mg/g Cl

The micrograph of DU after the dynamic potential polarization test, where corrosion pits were observed on the surface of the DU sample [22]. Three types of corrosion morphology were identified: corrosion crevice area (A), corrosion area (B), and bulging area (C). EDX analysis at these points reveals that the elements (U and O) in the corrosion area (B) are similar to those in the matrix. In contrast, the corroded area (A) contains more impurities, such as Al, Si, and O. The bulging area is a collection of corrosion products surrounding the corrosion area, which has a high oxygen content. Impurities can cause surface heterogeneity and induce crevice corrosion features. These impurities affect the corrosion morphology and increase the corrosion rate, which is unrelated to the location of corrosion nucleation.

3. Corrosion of U-Zr-Nb Alloy

Uranium (U) metal has a high density but low mechanical properties and high anisotropy unless alloyed with other elements [36]. The addition of alloying elements such as Nb, Zr, and Mo increases the stability of the γ-U phase, which has better mechanical properties and physical symmetry [34]. U-Zr alloys exhibit good dimensional stability during thermal cycling and maintain the γ-U phase over a wider temperature range. However, U-Zr-Nb alloys are more resistant to swelling than U-Nb or U-Zr alloys [35].

Research on the corrosion of U-Zr-Nb alloys has been conducted by Masrukan and his colleagues [35], who used U-6Zr-xNb alloys (x = 0, 2, 5, 8 wt.%) for corrosion tests using electrochemical techniques. In this study, graphite electrodes were used as auxiliary (counter) electrodes, calomel electrodes as reference electrodes, and the samples as working electrodes. Three solutions with different pH values were used as corrosion testing media: HNO_3 solution with pH 1.18, demi-neralized water with pH 7.53, and NaOH solution with pH 11.02, all of which were not deaerated. The test began with the measurement of corrosion potential (CP), followed by the measurement of polarization resistance (Rp), which was carried out within a potential range of -0.02 to 0.02 V with a scan rate of 0.05 mV/s. The test results using the Tafel extrapolation method are shown in Figures 5.a, 5.b, and 5.c [35]. Figure 5.a shows that the U-6Zr-2Nb alloy has the best corrosion resistance in an HNO_3 acidic environment with pH 1.18, while in an aqueous environment with pH 7.53, the U-6Zr-5Nb alloy demonstrates the best corrosion resistance, as seen in Figure 5.b. On the other hand, Figure 5.c shows that in a basic NaOH environment with pH 11.02, the U-6Zr-8Nb alloy exhibits the highest corrosion resistance. In general, the addition of Nb to the U-6Zr alloy increases corrosion resistance by promoting the formation of the Nb_2O_5 oxide layer on the alloy surface.

Table 2 [35] presents the corrosion rate (CR) values obtained from open circuit potential (OCP) measurements and Tafel extrapolation. The effect of Nb addition on CR in various environments with the range of Nb content from 2% to 5%, the CR values are relatively low, indicating high corrosion resistance [35]. This is due to the interaction between Nb and an oxygen-rich environment, which results in the formation of Nb oxide compounds (Nb_2O_5) and α-martensite. Both of these compounds function as protective layers against corrosion, leading to a lower CR. The Nb_2O_5 compound forms a protective oxide layer, while α-martensite helps homogenize the phase and reduce the galvanic potential difference, ultimately enhancing corrosion resistance. However, at an Nb content of around 2% in a neutral environment, the observed CR value is higher compared to acidic conditions [35]. In a neutral environment, there is insufficient oxygen to react with Nb to form Nb_2O_5, and α-martensite, which aids in phase homogenization, is not formed [36].

Table 2. Ecorr values of U-6Zr-xNb from OCP and Tafel measurements [35]

Sample	*E_{corr}* (V) of OCP			*E_{corr}* (V) of Tafel		
	Acid	Neutral	Base	Acid	Neutral	Base
U-6Zr-2Nb	0.034	−0.718	−0.56	0.052	−0.346	−0.578
U-6Zr-5Nb	0.113	−0.241	−0.182	0.048	−0.263	−0.224
U-6Zr-8Nb	0.022	−0.107	−0.159	−0.026	−0.110	−0.174

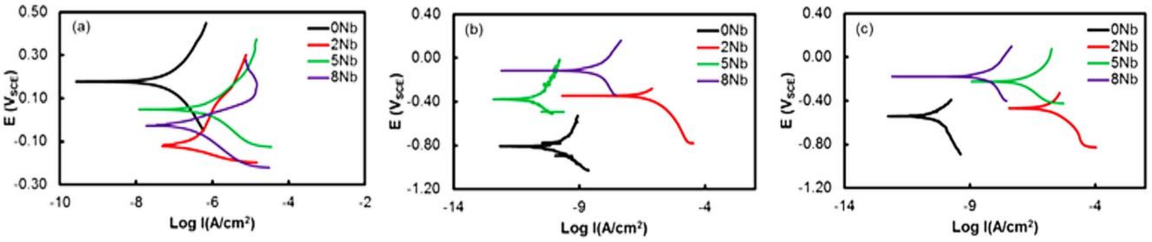

Figure 5. Tafel extrapolation method [35]

CONCLUSIONS

Uranium metal (U) and its alloys (U-Zr, U-Nb, U-Zr-Nb) experience corrosion influenced by environmental conditions. Corrosion of uranium metal produces hydrogen gas (H_2), which can react to form uranium hydride (UH_3), while with oxygen, uranium is oxidized to UO_2. The corrosion potential (E_{corr}) and corrosion rate (CR) of uranium metal do not show significant changes with variations in pH until the pH value reaches 7. However, E_{corr} and CR values increase when the pH exceeds 7, particularly at pH 11. The addition of alloying elements such as Zr, Nb, or Ru in low amounts to uranium alloys does not significantly affect the corrosion potential (E_{corr}) in the pH range of 4.0 to 9.0 unless an oxidizing agent is present. In U-Nb alloys, the higher the Nb content, the better the corrosion resistance. The U-5.7Nb alloy shows better corrosion resistance compared to the U-2.5Nb or depleted uranium (DU) alloys. In an acidic environment (pH 1.18), the U-6Zr-2Nb alloy exhibits the best corrosion resistance, while in neutral conditions (mineral-free water), the U-6Zr-5Nb alloy shows the optimal corrosion resistance. In an alkaline environment (pH 11.02), the U-6Zr-8Nb alloy shows the best corrosion resistance. The addition of Nb to uranium alloys has been shown to improve corrosion resistance, primarily due to the formation of a protective Nb_2O_5 layer on the metal surface.

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