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ELECTROCHEMISTRY OF AQUEOUS
CORROSION—URANIUM AND
ITS ALLOYS

J. S. Bullock
A. D. Brown
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OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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Oak Ridge Y-12 Plant

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ABSTRACT

A capsule summary of the fundamentals of electrochemical studies of corrosion has been compiled, with references. This summary should adequately introduce the main points of such studies to those persons interested in corrosion who do not have an adequate electrochemical background.

A literature review revealed four main points concerning uranium and uranium alloys: (1) their electrochemistry is profoundly dependent on the pH of the environment, due to participation of H^+ in many of the corrosion reactions; (2) chloride (halide) ion lowers their metal/solution potential relative to other ions (operationally, the significance of this fact is that the anodic reaction rate must be increased); (3) hydrogen charging of their surfaces changes the oxide conductivity and lowers their corrosion resistance, while adding good hydrogen recombination catalysts increases their corrosion resistance; (4) the rate of the $H^+ \rightarrow H_2$ and $O_2 \rightarrow H_2O_2$ reduction processes is highly dependent on the state of the surface.

Experimental studies of the alloys of uranium with zirconium, titanium, and niobium have been conducted in a variety of environments. Correlating these studies with literature data allowed several conclusions to be drawn concerning the corrosion of uranium (and its alloys), as well as concerning methods of studying the corrosion.

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SUMMARY

A literature review revealed four main points concerning uranium and uranium alloys: (1) their electrochemistry is profoundly dependent on the pH of the environment, due to participation of H^+ in many of the corrosion reactions; (2) chloride (halide) ion lowers their metal/solution potential relative to other ions (operationally, the significance of this fact is that the anodic reaction rate must be increased); (3) hydrogen charging of their surfaces changes the oxide conductivity and lowers their corrosion resistance, while adding good hydrogen recombination catalysts increases their corrosion resistance; (4) the rate of the $H^+ \rightarrow H_2$ and $O_2 \rightarrow H_2O_2$ reduction processes is highly dependent on the state of the surface.

Experimental work at the Oak Ridge Y-12 Plant^(a) has involved potentiometric and potentiodynamic studies of uranium and its alloys with zirconium, titanium, and niobium, in a variety of environments (although most of the studies were done in a highly alkaline solution). The basic motivation of the studies has been the identification of: (1) the operative electrochemical corrosion mechanisms, and (2) ways to determine the corrosion rate of alloys electrochemically.

From recent experimental work and the information in the literature, several conclusions can be drawn:

1. Uranium alloys behave essentially like uranium in many respects unless enrichment of the alloying element occurs on the alloy surface.
2. The anodic dissolution reaction in oxygenated aqueous environments very possibly has a rate-determining step involving the oxidation of a U(IV) oxide to a U(VI) oxide (which is more soluble).
3. Pure gamma-phase uranium, if it could be prepared, would probably have a lower corrosion rate than pure alpha-phase uranium (exclusive of the alloying elements).
4. The effect of surface treatments of uranium and its alloys can be revealed by a simple polarization technique.
5. Complexity of the variables involved in corrosion dictates the use of statistical methods in planning and analyzing these types of experiments.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

INTRODUCTION

PURPOSE

In the developing field of materials science, corrosion is one of the central areas of concern. In the drive to fabricate objects having closer tolerances, thinner sections, lower masses, and/or more long-term stability with respect to environmental effects, acceptable levels and degrees of corrosion are being continually lowered. Because of these stipulations, it becomes cost effective to bring corrosion studies to bear on the choice and development of alloys used for new and more stringent fabrication requirements. In optimizing the alloy production process, input on the effect of parametric changes (such as major alloying element content, trace element content, physical state of the alloy, material removal methods, and surface treatments) on the corrosion properties of the alloy system under consideration is vital. By making corrosion considerations an integral part of initial decisions concerning choice of materials, satisfactory progress in alloy development is most likely to be achieved.

The question might be raised: Why study corrosion electrochemically? There are several reasons: First, corrosion is, by definition, an electrochemical process. Even high-temperature gaseous corrosion involves the movement of ions and electrons through films on metal surfaces. Processes of this type are not accessible to study by standard electrochemical techniques; but, in principle, the determining processes are still electronation (reduction), deelectronation (oxidation), electron conductance, and ion diffusion. Another reason is that, under the proper conditions, even complex processes of corrosion can be broken down into half-cell reactions with which the electronation and deelectronation processes can be separately studied. The processes can be identified by their relation to the electrode/solution potential and estimates of their rates can be made, based on observed currents. A third reason is that electrochemical methods, if properly developed into specific techniques, are capable of rapid results which can be much more quantitative than nonelectrochemical, accelerated tests.

Corrosion testing by means of electrochemical methods is a subject still very much under development. This report will attempt to summarize a significant part of what is known about the electrochemistry of corrosion of uranium alloys and to suggest profitable avenues for future work.

FUNDAMENTALS OF CORROSION ELECTRODICS

Usually, reports on specific electrochemical subjects will first explain the fundamentals of electrochemistry. This report will be no exception to the usual custom, but the material on the fundamentals is presented in outline form in Appendix A. The outline is organized as a simplified logical construction of the electrochemical approach to studies of corrosion. It is organized under the following headings:

- Definition of the Corrosion Process in Electrochemical Terms

- Variables Usable in Electrochemical Corrosion Studies

- Specific Electrochemical Methods Used to Study Corrosion

If the reader is quite unfamiliar with electrochemical methods, it may be well to consult the available literature for further study.(1 - 36) The following references can be recommended for general reading: Moore(1) for introductory reading; Bockris and Reddy,(3) and West(10) for a more detailed view; Myamlin and Pleskov(37) for the electrochemistry of semiconductors; Tomashov(38) and Uhlig(39) for specifics on applications to corrosion; Delahay(28) for instrumental methods; Hampel's Encyclopedia(40) for a variety of subjects, and Hoar's paper(11) for an overview of corrosion-resistant materials. The book by Hoare(41) on the electrochemistry of oxygen is also highly recommended.

ELECTROCHEMISTRY OF AQUEOUS CORROSION—URANIUM AND ITS ALLOYS

REVIEW OF THE LITERATURE

Introduction

The literature review will briefly touch on uranium chemistry and will describe the interaction between uranium and uranium alloy surfaces with environments, studied and/or promoted by electrochemical methods. Some mention will be made of studies in which electrochemical methods were not used but which contain explicit reference to electrochemical factors. The literature on uranium will be given equal significance with that on uranium alloys for two reasons: first, an understanding of the electrochemistry of the alloys is highly dependent on an understanding of that of the pure metal; and, second, the electrochemistry of uranium is not a widely understood subject. The IUPAC(42) "zinc minus, copper plus" convention will be used for reporting potential values, and the reference electrode used will be specified. Reference electrodes commonly used will be the saturated calomel electrode (SCE), $E = + 0.242$ V vs the normal hydrogen electrode (NHE); the silver-silver chloride electrode (Ag/AgCl), $E = + 0.222$ V vs NHE; and the normal calomel electrode (NCE), $E = + 0.280$ V vs NHE. The NHE, of course, has the arbitrary single electrode value of 0.000.

Uranium Chemistry

Uranium has a valence shell structure of $5f^3 6d^1 7s^2$ and possesses known oxidation states of + 3, + 4, + 5, and + 6.(43) The chemistry of the element was rather completely reviewed by Katz and Rabinowitch,(44) while that of its most technologically important oxide was reviewed by Belle.(45) Further information on uranium chemistry may be found in the books by Cotton and Wilkinson(46) and Chernyaev,(47) and in the proceedings of the ACS Symposium on Lanthanide/Actinide Chemistry.(48) Recent work on the carbonate complexes of U(VI) may be found in the report by Tsymbal,(49) and several papers have appeared recently on the redox properties of certain uranium ions.(50 - 54) The equilibrium relationships of several uranium species as a function of their electrochemical potential and pH is well summarized by deZoubov.(55)

Electrochemical Studies of Uranium

The earliest electrochemical study of uranium reported by Gmelin(56) is that of Muthmann and Fraunberger in 1904,(57) who found that uranium in a 1 N KCl solution would assume an open-circuit potential of - 0.466 V vs NHE. The purge atmosphere was not reported by Gmelin. Other work reported in Gmelin(58) indicated that substantial carbon content in uranium would lead to CO₂ evolution during anodic polarization, and that uranium did not exhibit passivity (an erroneous conclusion).

Anodic electropolishing is a process usually carried out at specimen/solution potentials adequate to bring the process of deelectronation and dissolution of the specimen into a diffusion-limited region,(59) accompanied by loss of passivation.(60) This action results in a brightening of the surface. Electropolishing of uranium has been studied(61 - 63) and, recently, the importance of defining and controlling the process in electrochemical terms

has been noted by Kocik, et al.(64) They reported Tafel equations for intensive anodic dissolution of $\eta = 0.050 + 0.050 \log i$ for the phosphoric/sulfuric/water Mott(63) solution and $\eta = 0.550 + 0.070 \log i$ for a chromic acid/acetic acid solution (referred to a current of 10^{-3} A). Actually, the log coefficients listed are not in agreement with their illustration. Assuming the illustration to be correct, the coefficients should be 0.079 and 0.050 V/decade, respectively. This study showed a limiting current density of 0.085 A/cm² for the Mott solution and an apparent value of about 0.03 to 0.04 A/cm² for the chromic/acetic solution.

Properties of Oxide Films - Katz and Rabinowitch(65) report the work of Pierle' in which the open-circuit potential of platinum electrodes, covered with pastes of UO_2 , U_3O_8 , $\text{UO}_3 \cdot \text{H}_2\text{O}$, and $\text{U}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$, were measured in a 0.027 M $\text{UO}_2 (\text{NO}_3)_2$ solution of unspecified but probably fairly acidic pH. Values reported were: + 0.773 to + 0.787 V for UO_2 and U_3O_8 , + 0.860 V for $\text{UO}_3 \cdot \text{H}_2\text{O}$, and + 0.687 V for $\text{U}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$, all versus the NCE. The significance of these data was not commented on by Katz and Rabinowitch, and it seems from the potential/pH relationships(55) that the only potential-determining process possible in this region is the UO_2/UO_3 and $\text{H}_2\text{O}/\text{O}_2$ mixed potential.

Flint, et al(66) (cited in Young's monograph(67)) produced oxide films of visible-light-interference thickness on uranium by anodization in a concentrated ammonium borate solution at potentials up to 1 - 2 V, in 0.01 N ammonium borate up to 5 V, and in ammonia/ethylene glycol/water up to 100 V. The films were studied by electron diffraction and reported to "contain FCC UO_2 , but to be consistent with any composition between UO_2 and U_3O_8 or even $\text{UO}_3 \cdot \text{H}_2\text{O}$ ". Stebbens and Shreir(68) also produced anodic films in aqueous ammonia at potentials up to 270 V. The refractive index of the films was determined to be $n_1 = 1.93$ to 1.95, and a "growth rate" of 28 angstroms/volt (3.6×10^6 V/cm) was reported. This 3.6×10^6 V/cm field strength is identical to that cited by Vijn(69) as producing an approximate 2×10^{-3} A/cm² anodic film growth rate on uranium, the oxide produced being identified as UO_3 . Vijn correlates the logarithm of the field strength value at this growth rate to the metal/oxygen bond energies of several "valve" metals that include uranium, aluminum, niobium, and titanium, and obtains a linear relationship. It is of interest at this point that Leach and Nehru(34) found a retardation of the oxidation rate of uranium, in water-saturated argon and oxygen, when an external electric field of 1 to 2×10^2 V/cm was applied. The oxidation rate was determined by a method involving the measurement of absorption of reflected light from the growing thin film, the principles of which are well known.(35) The source of the retardation was postulated to lie in the preferred orientation of the water dipoles, with either the partially negative oxygen or the partially positive hydrogen being preferentially adsorbed. Either polarity produced retardation, but positive potentials on the specimen were more effective. The local field strength at the adsorbed layer, which is likely to be higher than the field strength calculated from simple electrode spacing, was not estimated. The rate laws found for the oxidation reactions were: $y^{1.0} = kt$ for wet argon, $y^2 = k't$ for the dry gases, and $y^{1.6} = k''t$ for wet oxygen.

Jouve, et al,(70 - 73) have combined several techniques to study the properties of films anodically formed on uranium as a function of pH. In acid and neutral solutions, the anodic current decreased between - 0.5 and + 0.1 V vs SCE (forming a broad peak); in a basic solution no such current peak was seen, but one was noted around 0 V vs SCE. Electron

diffraction studies of the anodically formed oxide film revealed that: at $\text{pH} \leq 7$, the oxide is UO_2 at all potentials; at $\text{pH} = 13$, for potentials $< -0.05 \text{ V}$ it is UO_2 and for potentials $> -0.05 \text{ V}$ it is $\text{UO}_3 \cdot 2\text{H}_2\text{O}$; at $\text{pH} = 14$, for potentials $< 0.0 \text{ V}$ it is UO_2 and for potentials $> 0.0 \text{ V}$ it is UO_2 plus possibly U_3O_8 . At $\text{pH} = 11.6$, the layer formed was too thin to provide a diffraction pattern; but, after holding the specimen at $+1.2 \text{ V}$ vs SCE, the subsequent open-circuit potential became essentially equal to that of the $\text{UO}_2/\text{UO}_3 \cdot 2\text{H}_2\text{O}$ equilibrium potential (-0.548 V). Coulometric reduction studies revealed a limiting thickness of about 70 angstroms at this potential and pH. The kinetics of the anodic film growth in 0.1 and 1.0 N NaOH have been studied using an interferometric technique with visible light,⁽⁷¹⁾ and were found to depend on the potential and film thickness. Below $+1.2 \text{ V}$ vs SCE, rate laws of the form: $y = kt$ apply, with UO_2 produced below 0 V and $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ above 0 V. Below 0 V, the growth rate increases between -0.2 and -0.1 V vs SCE. The kinetics for growth of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ change above a film thickness of 3000 angstroms. Above a potential of $+1.2 \text{ V}$, the rate law: $y^2 = kt$ applies. The film formed at $\text{pH} = 13$ was studied using an impedance bridge and metal/oxide/metal techniques.⁽⁷²⁾ The $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ was determined to have both ionic and electronic conductivity. Under certain circumstances, a layer of UO_2 can develop between the $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ layer and the metal. This material is summarized in a final report.⁽⁷³⁾

Leach and Nehru,⁽⁷⁴⁾ however, found evidence for the formation of other oxides than UO_2 and $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ on uranium electrodes in an alkaline solution. Electron diffraction showed the presence of U_3O_7 , U_3O_8 , and probably $\text{U}(\text{OH})_4$ on uranium, depending on the potential. It is probable that a variety of oxides could be formed, at least metastably, under the proper conditions.

Leach,⁽⁷⁵⁾ Isaacs and Leach,⁽³³⁾ and Elsayed⁽⁷⁶⁾ report studies of uranium and uranium alloy electrode impedance as a function of potential. They found large increases in electrode capacitance around potentials corresponding to valency changes in the oxide films, notably the $\text{UO}_2/\text{UO}_3 \cdot 2\text{H}_2\text{O}$ potential. This change can be attributed to Faradaic pseudo capacitance associated with the valence changes.

Hydrogen in Oxide Films - Draley and Ruther⁽⁷⁷⁾ observed that the addition of small quantities of nickel (a good hydrogen atom recombination catalyst) ions to water would increase the corrosion lifetime for uranium in the water. Addition of platinum to uranium-(8 to 15) wt % molybdenum alloys had a similar effect.⁽⁷⁸⁾ Baker, et al,⁽⁷⁹⁾ have determined the uranium/water corrosion mechanism to involve, in part, attack by hydrogen atoms to produce a uranium hydride. Hydrogen in uranium electrode surfaces has, therefore, been investigated by electrochemical methods.

Leach⁽⁸⁰⁾ noted that cathodic hydrogen charging did not change the capacity of the oxide film on uranium, but did increase its conductivity by a factor of three. Leach showed⁽⁷⁵⁾ that in solutions of $\text{pH} = 8.4$, a marked increase in conductivity began below potentials of -1.0 V vs NHE (the H_2/H^+ equilibrium at this pH is -0.5 V), although a minor increase was observed at higher potentials. Similar effects were found for a uranium-12 wt % molybdenum (U-12 Mo) alloy by Isaacs⁽⁸¹⁾ who also noted that hydrogen charging changed the kinetics of the hydrogen evolution reaction on the oxide film. Isaacs and Leach subsequently noted⁽⁸²⁾ that changes in the electrode film conductance and changes in the cathodic current during polarization experiments on the molybdenum alloy were linearly related.

Effect of hydrogen in oxide films on electrodes has been discussed by Slaidin'. (83) He offers a mechanism for the increase in conductivity of the films under cathodic polarization and proposes this as an explanation for the rectifying effect of the oxides on valve metals. The proposal is also made that the "hardening" of the passivating oxide retards proton transfer.

Effect of Oxygen - Schroeder, et al, (84) showed that an oxide film formed at 400° C would protect uranium against water corrosion at 100° C for periods of about a day. Baker, et al, (85) demonstrated that gaseous oxygen could inhibit the water oxidation of uranium and postulated a mechanism for the inhibition. Butler and Ison (86) report that, below 90° C, water attack on uranium in the presence of oxygen proceeds by pitting corrosion instead of general corrosion. This behavior is typical of oxidizing inhibitor concentrations lower than necessary for full protection. (87)

Ward and Waber (88) showed that a uranium electrode in 0.1 F(b) KClO₄ saturated with oxygen assumed a potential only 0.002 V more active than the oxygen/peroxide potential—evidence of good passivation. On decreasing the oxygen concentration, the potential only began to strongly deviate from the Nernst potential at partial pressures of oxygen less than about 0.10 atm. In oxygen-free water, a uranium electrode freshly abraded in an inert atmosphere assumed an initial potential, in 0.1 F KClO₄, of - 0.3 V vs SCE. Within three hours, a stable value of - 1.101 V had been reached. Nitrate was indicated to be a better corrosion inhibitor than nitrite (using open-circuit potential measurements), and the oxide formed in the presence of passivating agents gave sharp UO₂ patterns by X-ray diffraction. They also found that an anodic current of 2.2×10^{-6} A/cm² would bring uranium into the passive region in oxygen-free 0.1 F KClO₄.

Jenks (89) found that: films (apparently UO₂) formed above potentials near those for the reaction $\text{UH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{UO} + 5\text{H}^+ + 5\text{e}^-$ ($E_{\text{NHE}}^{\text{O}} = -0.422 - 0.0591 \text{ pH}$), increases in current occurred above potentials near those for the reaction $\text{UO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{UO}_3 + 2\text{H}^+ + 2\text{e}^-$ ($E_{\text{NHE}}^{\text{O}} = 0.415 - 0.0591 \text{ pH}$), and cathodic currents increased rapidly below potentials near those for the reaction $\text{UH}_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2 + 7\text{H}^+ + 7\text{e}^-$ ($E_{\text{NHE}}^{\text{O}} = -0.958 - 0.0591 \text{ pH}$). The exchange current for hydrogen reduction on uranium in 1 N H₂SO₄ was determined to be about 10^{-10} A/cm².

Electrochemical Studies of Uranium Alloys

Leach (75) showed that the hydrogen-free film on U-12 Mo had a conductance in pH 8.4 solutions of less than 10^{-6} mho/cm²; between - 0.3 and - 1.0 V vs NHE, some increase in conductivity was observed; below - 1.0 V, the conductivity increased sharply. Leach suggested that the effects of hydrogen could be reduced by changing the nature of the oxide conductivity, as by forming suitable mixed oxides on the surface. It is worth noting that UO₂ is a p-type semiconductor whose conductivity increases with increasing pressure of oxygen. (90) For hydrogen to increase the conductivity of the oxide film by a mechanism similar to that of oxygen, the hydride ion would have to be formed in the oxide lattice.

(b) Formal—equivalent to molar.

Otherwise, some "disruption" of the oxide structure would have to be postulated. Similar studies by Isaacs(81) have already been mentioned in the section on uranium (Page 9). Leach(75) also found that the Faradaic pseudo capacitance, observed for uranium around valency-change potentials, was found for the U-12 Mo alloy. In studies of a U-10 Zr alloy, Leach and Nehru(74) found, by using a light-absorption method to follow the film thickness, that the corrosion rate could be controlled by varying the potential (specifically, the potential with respect to the hydrogen evolution potential at a given pH). In acidic solution, the corrosion rate increased monotonically as the potential was lowered; in basic solutions the relationships were more complex. The U-10 Zr alloy was found to have a lower corrosion rate than uranium, but similar kinetics. The kinetics changed to a breakaway corrosion at times which depended on the material, the pH, and the potential. In general, the U-10 Zr alloy could tolerate a lower potential for the same breakaway time than could uranium.(91) Activation energy of the aqueous corrosion of unalloyed uranium and of U-5 Zr was determined by Leach and Nehru.(91) Addition of zirconium was found to lower the activation energy noticeably. Also, the activation energy for corrosion in an aqueous solution was found to be lower than that for corrosion in air. The complexity of the corrosion rate/potential relationship in an alkaline solution, which has been already noted, was paralleled by a similar complexity in the activation energy/potential relationship. The work of Isaacs and Leach(82) and Elsayed(76) has already been cited.

Jenks(89) also studied the U-7.5 Nb-2.5 Zr alloy (mulberry). Anodization in K_2SO_4 solution was performed at up to + 5 V vs SCE without apparent decomposition of water. This result was interpreted as evidence of poor electronic conductivity. This film could be dissolved by subsequent anodization in 0.1 N H_2SO_4 . Under hydrogen atmospheres, mulberry cathodically polarized similarly to uranium; but, under oxygen atmospheres, the increase in cathodic current occurred well below the UH_3/UO potential and could be explained in terms of hydrogen rather than UH_3 formation. Jenks reported "transpassive" ($UO_2 \rightarrow UO_3$) behavior for mulberry similar to that found with uranium. Specimens taken into the transpassive region had a lower hydrogen evolution overvoltage than specimens in the unpolarized condition, but specimens anodically treated only to potentials below the UO_2/UO_3 equilibrium (passivated) had hydrogen evolution overvoltages comparable to those of uranium. However, oxygen reduction on the mulberry-passivated surfaces proceeded normally. In general, surfaces of either uranium or mulberry intentionally covered with oxide films were able to reduce oxygen easily, but not able to evolve hydrogen easily.

Jenks also reported the pitting potential(c) in 0.1 M K_2SO_4 /0.01 M KCl to be between 0.0 and - 0.1 V vs SCE. Cathodic polarization of a pitted specimen was reported to raise, subsequently, the measured pitting potentials. The breakthrough potential(d) depended on the chloride concentration and the oxide film condition. A hydrogen atmosphere lowered this value with respect to an air atmosphere. A severely pitted mulberry specimen had a very low hydrogen evolution overvoltage—about - 0.3 V at 10^{-3} A/cm² (this value gives a rather high exchange current density: $\log i = - 5.1$ to - 5.5). Low potentials could protect mulberry from chloride ion attack. At < 0.1 M $[Cl^-]$, unstressed specimens would not be attacked at potentials $< - 0.325$ V vs SCE.

(c) The potential below which a pitted specimen will cease pitting activity.

(d) Potential at which a specimen with an intact film will begin pitting.

Decrease in the hydrogen evolution overvoltage on the mulberry specimens was attributed by Jenks to enrichment in niobium and zirconium oxides on the surface under transpassive conditions. Zehr(92) postulated a similar enrichment for interior surfaces of stress corrosion cracks. These surfaces are exposed, in all probability, to very low pH values during cracking. Zehr also reported that mulberry would not pit in 0.1 N NaCl if driven only by a differential aeration cell (however, in this study, pitting was observed under those conditions in a higher concentration of chloride—~ 1.0 N).

The passive behavior reported for potentials below the UO_2/UO_3 ($-2\text{H}_2\text{O}$?) potential by Jenks(89) and by Jouve(70) is not the only region of passive behavior on the potential field for either uranium or mulberry. Stephenson(93) has shown that there is an active/passive transition for mulberry in 0.5 M NaOH at an $E_{\text{crit}} = +0.209$ V vs NHE and an $i_{\text{crit}} = \text{alog}(-3.43)$. The current in the passive region was essentially independent of potential and was about $i_{\text{pass}} = \text{alog}(-4.37)$. The active/passive behavior was observed for $\text{pH} \geq 12.5$ and not observed for neutral solutions containing chloride (concentration unspecified) or for acidic solutions. Bullock and Condon(14) have also observed active/passive behavior in this region for mulberry in basic solution; however, this action could be observed down to at least a pH of 11.8, even with 0.01 N KCl. However, the i_{crit} was approximately three times greater at chloride concentrations of 0.01 N, at a pH of 13.7.

Macki and Kochen(94) joined α -U, U-4.5 Nb, U-6 Nb, U-8 Nb, mulberry, and U-10 Mo in several galvanic couples in chloride solution and observed their open circuit potentials and corrosion rates. In addition, the single-material open-circuit potentials (for aerated and oxygenated solutions), and their corrosion rates,(95) were reported. Specimens in oxygenated solutions were consistently more positive than those in aerated solutions. The single-material open-circuit potentials and corrosion rates were, however, not well correlated. Bullock and Condon(14) found that U-8.5 Nb alloy specimens were from 0.057 to 0.179 V more positive in oxygenated 0.01 N KCl solution than in an argon-purged solution, depending on the condition of the surface. They also determined that the potentials of uranium and mulberry electrodes were relatively insensitive to the length of time into a 90° C air oxidation if the immersing solution was 1 N KCl, but followed an essentially exponential change to higher values using 1 N K_2SO_4 , KNO_3 , KOH, and saturated KClO_4 solutions. This difference in behavior was interpreted in terms of a penetration of the oxide film by the chloride ion. Such behavior was confirmed by Weirick(96) in a study of the area ratio of nickel to U-3/4 Ti. Theory predicts for this system a linear relationship between open-circuit mixed potential and $\log(A_{\text{U alloy}}/A_{\text{Ni}})$, the sensitivity of the technique depending on the difference in activity of the two metals. This belief was confirmed for a certain range of the log function, but only with Cl^- and Br^- (the Br^- being a less sensitive indicator). Other ions which were known to complex uranium ions, such as thiosulfate, carbamate, and oxalate, did not detect changes in the potential as a function of changes in the surface-area ratio. This fact reflects the almost unique capability of halide ions to "penetrate" oxide films on uranium alloys.

Bullock and Condon(14) have also shown that mulberry corrodes, with pitting, in a polarization cell using, as an electrolyte, water films adsorbed from air with a relative humidity of 62%. (In retrospect, the adsorbed water films probably contained a small quantity of the chloride ion.) Corrosion currents were found to be about 3×10^{-7} A/cm² (based on the gross surface area).

Weirick⁽⁷⁾ has found that, following the customary gamma quench, an aging treatment of 450, 550, or 600° C for about nine hours will lower the rest potential by about 0.35 V from the value observed with material aged one hour at 150° C. Alpha uranium was deposited at the grain boundaries at the higher aging temperatures, and the anodic polarization behavior, from his data, falls into two groups: one obtained with low-temperature and another obtained with high-temperature aged material.

Jackson and Wickland⁽⁹⁸⁾ studied the electropolishing of U-Nb alloys in 60/40 H₃PO₄/H₂O solutions. A current density of 0.12 A/cm² was used, the species going into solution being U⁺⁴. The polished surface had good resistance to attack by a refluxing HCl/acetic acid mixture at 61° C.

Bullock and Condon⁽¹⁴⁾ reported results of an experiment in which a mulberry electrode was continuously abraded in air-equilibrated solutions. At low pH values (< 7), the open-circuit potential was made more negative by both increases in chloride concentration and increases in pH. Above a pH of 7, the potentials began to increase with pH (evidence of passivation becoming faster than abrasion) although increases in chloride concentration continued to lower the potential. They also found that the critical current density of passivation of mulberry in 1.0 N KOH was increased by a factor of three if 0.01 N chloride ion was added to the solution.

RECENT EXPERIMENTAL WORK AT THE OAK RIDGE Y-12 PLANT

Experimental Variables

The philosophy of the basic experimental approach consisted of surveying the gross electrochemical properties over a substantial potential range (for pH = 13.7, typically - 1.5 to + 1.3 V vs the SCE)^(e) of several uranium-base alloys which were thought to represent most of the types of uranium alloys currently in use or being considered for use for various structural purposes. The bulk of the alloys studied were: αU, U-Ti, U-Zr, U-Nb, and U-Nb-Zr.

The α-U specimens were of three types: low carbon (60 ppm), cold-worked material of (probable, but undetermined) preferred orientation; recrystallized material which contained 680 ppm carbon; and zone-refined uranium (50 ppm carbon) preferentially oriented along the [010] direction⁽⁹⁹⁾ and sliced perpendicularly across that axis.

The U-Ti alloys were 0.3 to 1.2 wt % titanium, with some studies conducted around the U₂Ti composition (~ 8.5 wt %). Metallography showed the presence in all the low-titanium alloys of small quantities of a second phase which was identified as U₂Ti.⁽¹⁰⁰⁾ The material had an alpha-prime structure.

(e) Experimental data reported here referenced against the SCE was obtained using an SCE calibrated to be + 0.235 V vs the NHE.

Table 1
ALLOY CONSTITUTION

Chemical Composition		Phase(1)	Predominant Microstructure
Weight Percent	Atomic Percent		
U-60 ppm C-300 ppm Remainder	U-0.06 C-0.3 Remainder	α	Banded (very slightly recrystallized)
U-680 ppm C	U-0.6 C	α	Equiaxed Grains
U-50 ppm C-100 ppm Remainder	U-0.05 C-0.1 Remainder	α	Cut Across Probable [010] Orientation of Zone-Refined Rod
U-0.5 Zr	U-1.3 Zr	α'	Martensitic Plates
U-1.0 Zr	U-2.6 Zr	α'	Martensitic Plates
U-1.4 Zr	U-3.5 Zr	α'	Martensitic Plates
U-0.3 Ti	U-1.5 Ti	α'	Martensitic Plates
U-0.6 Ti	U-2.9 Ti	α'	Martensitic Plates
U-0.75 Ti	U-3.6 Ti	α'	Martensitic Plates
U-0.8 Ti	U-3.9 Ti	α'	Martensitic Plates
U-1.2 Ti	U-5.7 Ti	α'	Martensitic Plates
U-1.0 Zr-0.3 Ti	U-2.5 Zr-1.5 Ti	α'	Martensitic Plates
U-0.5 Zr-0.6 Ti	U-1.3 Zr-2.9 Ti	α'	Martensitic Plates
U-3.91 Ti	U-16.8 Ti	α (U phase)	U ₂ Ti in α -U matrix
		Hex AlB ₂ (2) (U ₂ Ti phase)	
U-8.86 Ti	U-32.6 Ti	α (U phase)	U ₂ Ti in α -U matrix
		Hex AlB ₂ (2) (U ₂ Ti phase)	
U-9.16 Ti	U-33.4 Ti	α (U phase)	U ₂ Ti in α -U matrix
		Hex AlB ₂ (2) (U ₂ Ti phase)	
U-4.5 Nb	U-10.8 Nb	γ	Equiaxed Grains (γ quench, 200° age) ⁽³⁾
U-6 Nb	U-14.1 Nb	γ	Equiaxed Grains (γ quench, no age)
U-6 Nb	U-14.1 Nb	γ	Equiaxed Grains (γ quench, 200° age)
U-6 Nb	U-14.1 Nb	γ	Equiaxed Grains (γ quench, 300° age)
U-8 Nb	U-18.2 Nb	γ	Equiaxed Grains (γ quench, 200° age)
U-7.5 Nb-2.5 Zr (mulberry)	U-16.6 Nb-5.6 Zr	γ	Equiaxed Grains (γ quench, 200° age)
U-10 Mo	U-21.6 Mo	γ	Equiaxed Grains (furnace cooled from γ region)

(1) α or α' = orthorhombic; γ = body-centered cubic.

(2) From Wernick.⁽¹⁰¹⁾

(3) All ages were for two hours.

The U-Zr alloys were 0.5 to 1.4 wt % zirconium. Metallography showed the presence of small quantities of a second phase which was apparently UZr_2 .⁽¹⁰⁰⁾ The material had an alpha-prime structure.

The U-Nb and U-Nb-Zr alloys were gamma-phase alloys with no second phases except the usual small quantities of oxides and carbides which were contained in all the alloys studied. Details of the alloy constitutions are given in Table 1.

Preparation of the α -U and U-alloy specimens is given in detail in Appendix B. Briefly, the specimens were mounted in an epoxy resin after attaching a contact wire to the back of the specimen and projecting the wire out the top of the mount. The specimens were given a typical metallographic polish under ethanol through 1- μm diamond abrasive and stored under 1.3×10^{-4} Pa (1×10^{-6} torr) vacuum (or absolute ethanol for times less than a few hours) until used. The electrochemical cell used was a three-compartment cell with glass frits and stopcocks separating the two-liter sample compartment from the counter electrode and reference compartments. Stirring was applied using a magnetic stirrer with a Teflon stir bar. The temperature was uncontrolled, but room temperature was typically $22 \pm 1^\circ \text{C}$. Specimens were held in the cell using a polymethylmethacrylate coupling which sealed the mount around its diameter using a trapped Neoprene gasket.

The environment in which most of the studies were made was 1 N KOH, pH = 13.7, and argon purged. This choice was made because two active/passive transitions could be observed over the potential range studied, and the usable potential range was quite large. Other environments of varying pHs were used as became appropriate. Chemicals used were reagent grade, and solutions were made up using deionized water. Appropriate analyses of the fresh and used solutions were made. Environments used are listed in Table 2.

Table 2
EXPERIMENTAL ENVIRONMENTS

Solvent	Solute	Solution pH	Purge Gas	
			Argon	Oxygen
H ₂ O	KOH, 1.0 N	13.46 - 13.99 13.76 (typ)	X	X
H ₂ O	KOH, 0.3 N	13.22	X	-
H ₂ O	KOH, 0.1 N	12.72	X	-
H ₂ O	KOH, 1.0 N K ₂ SO ₄ , 0.5 N	13.79	X	X
85% H ₃ PO ₄		- 1.5	X	-
85% H ₃ PO ₄	K ₂ Cr ₂ O ₇ (sat)	- 1.5	X	-
H ₂ O	H ₂ SO ₄ , 1 N	0.5 (typ)	X	X
H ₂ O	K ₂ SO ₄ , 1 N	5.55 - 9.48 6.5 (typ)	X	X
H ₂ O	KOH, 1 N H ₂ O ₂ , 0.1 to 0.0001 N	13.76	X	

Experimental methods used included: potentiometry, potentiostatic and potentiodynamic voltammetry, microscopy, coulometry, X-ray diffraction, and low-angle electron diffraction.

Experimental Observations and Discussion

Open-Circuit Potentials -

Air-Oxidized Specimens - Data reported previously⁽¹⁴⁾ (see REVIEW OF LITERATURE) describing the change in the open-circuit potential of alpha uranium and the U-7.5 Nb-2.5 Zr (mulberry) alloy as a function of time into a 90° C air oxidation, were replotted in Figure 1 to illustrate their relationship to the pH and chloride content of the solution. The potentials plotted are those which were attained by the specimens at long oxidation times; the solutions were air equilibrated. Mulberry was in two different states due to different heat treatments: standard mulberry, treated as noted in Table 1; α, γ_3 mulberry, annealed at 500° C for two hours, causing segregation into a niobium-rich gamma phase and an alpha-uranium phase. It is noted that the potential of the oxidized metals is pH dependent, but that this condition is complicated by the introduction of chloride which makes the metals more active. This situation would be effected by increasing the anodic dissolution rate, making the mixed potential move away from the oxygen reduction potential and toward the dissolution potential (cf, the Evans diagrams). Also, apparently, air-grown mulberry oxides are more soluble in strong base than around pH 7, because mulberry is relatively more noble in neutral solution than in a pH of 13.7. Uranium is almost as noble as mulberry in strong base; but, in neutral solution, the higher activity of the uranium is apparent. Finally, the two-phase, α, γ_3 mulberry is less noble than standard mulberry in all cases and is even less noble than uranium in some solutions, a fact about which there will be no speculation.

M + S Open-Circuit Potentials - A set of specimens of alpha U, U-3/4 Ti, and mulberry were prepared in metallographic mounts, as described earlier (Page 15). The specimens were immersed in oxygenated 1 N H₂SO₄, 1 N K₂SO₄, 1 N KOH/0.5 N K₂SO₄, and 1 N KOH solutions. Open-circuit potentials of the specimens were taken immediately, after which the specimens were cycled from a potential of around - 1.4 V vs SCE in the positive direction to about + 1.5 V vs SCE in the alkaline solutions. For the other solutions, depending on the alloy, the upper positive limit was the highest potential (up to + 1.5 V) within the current capacity of the potentiostat used. (For alpha uranium in 1 N H₂SO₄, for example, this value was about + 0.4 V vs SCE.) The specimen was then cycled back to - 1.4 V vs SCE and, at that point, allowed to assume a stable, open-circuit potential (usually reached within 20 minutes). The scan rate used was about 1×10^{-2} V/sec. This procedure, which may be remembered for the moment as the M + S procedure, artificially corroded the material and caused it to grow an oxide film in the presence of the oxygenated solution.

The initial and final values of the open-circuit potentials are plotted versus the pH of the solution as Figure 2. There is little difference between the potentials of the specimens in the two alkaline solutions, with the alpha uranium and mulberry becoming more positive after the procedure and the U-3/4 Ti alloy becoming more

Figure 1. OPEN-CIRCUIT POTENTIALS FOR ALPHA URANIUM AND MULBERRY. (AFTER LONG OXIDATION TIMES) AS A FUNCTION OF THE pH. (Potentials Referenced to the Normal Hydrogen Electrode; Data Taken from Bullock and Condon⁽¹⁴⁾)

negative. The potential of the group places all the materials in a region in which the potential-determining reactions could reasonably be the $UO_2 \rightarrow UO_3 \cdot 2H_2O$ (anodic) and $O_2 \rightarrow HO_2^-$ (cathodic) reactions. This explanation, of course, does not prove the identity of the oxide on the materials, but is suggestive.

Specimens in the K_2SO_4 solution are seen to have assumed a potential near that for the $U(OH)_4/UO_3 \cdot 2H_2O$ equilibrium. This observation suggests that the oxide on the materials is in the hydrated $[U(OH)_4]$ form; however, a cathodic process ($O_2 \rightarrow HO_2^-$) could interact with an anodic process at lower potentials (such as $U^{+3} \rightarrow UOH^{+3}$) to produce a mixed potential of the value seen.

Figure 2. M + S INITIAL AND FINAL OPEN-CIRCUIT POTENTIAL VALUES AS A FUNCTION OF THE pH. (Potentials Referenced to the Saturated Calomel Electrode)

Specimens in the H_2SO_4 solution clearly lie below the $\text{U(OH)}_4/\text{UO}_3 \cdot 2\text{H}_2\text{O}$ equilibrium potential, which indicates a necessity for participation by lower-potential anodic processes. In line with the observations of several workers, (70, 74, 89) oxides with higher valences than U(IV) might not be expected under these conditions (at least in quantity); but, at pH 13.70 to 14.00, the possibility cannot be discounted due to the position of the open-circuit potentials above the $\text{UO}_2/\text{UO}_3 \cdot 2\text{H}_2\text{O}$ equilibrium potential.

In the acidic solution, the initial open-circuit potentials of uranium and mulberry are noted to lie in this order: $E_U > E_{Mu}$. This behavior has been seen repeatedly on freshly polished specimens. It is possible that an explanation for this action lies in the rapid oxidation of alpha uranium. It is impossible to prepare alpha-uranium specimens free of oxide layers of some thickness without using high-vacuum techniques. Freshly electropolished alpha uranium is reported to always have several monolayers of perfectly stoichiometric UO_2 at its surface.⁽¹⁰²⁾ Thus, the potential of mulberry seen initially may reflect, in part, the lower Zr/Zr(IV) potential⁽¹⁰³⁾ before layers of oxide of comparable thickness are achieved. The post-treatment potentials of the materials are in the more reasonable relation $E_{Mu} > E_U$, mulberry being recognized as a more corrosion-resistant material.

It should be noted that certain of the materials in certain solutions exhibited systematic changes in their initial and final potentials as a function of repetitive tests in the same solution (the potentials of Figure 2 are averages of four repetitions). Final solutions were anywhere from 8×10^{-7} to 8×10^{-6} M in uranium, which could have been the responsible species. This fact points up the necessity for considering all possible species in the solution, and to test materials as a function of concentration of their own ions.

Open-Circuit Potentials in Deoxygenated Solutions - Specimens prepared in metallographic mounts, as described earlier (Page 15), were immersed in a variety of deoxygenated solutions and their initial potentials noted. These potentials are plotted as a function of pH in Figure 3. The potential values are even more strongly related to the pH for these solutions than they are for the oxygenated solutions. The potentials of the specimens under very alkaline conditions have not been elevated above the $UO_2/UO_3 \cdot 2H_2O$ equilibrium line by mixing of the $UO_2 \rightarrow UO_3 \cdot 2H_2O$ process with the oxygen-reduction process. In neutral-to-acidic solution, the potentials of the U-Ti alloy and of uranium, generally, have values between the $UO_2/UO_3 \cdot 2H_2O$ and $U(OH)_4/UO_3 \cdot 2H_2O$ equilibrium lines, reflecting a probable state of hydration of the oxides in these media. Mulberry values in neutral or acid solution tend to lie around the H_2/H^+ equilibrium line, possibly a reflection of the high exchange current of the active mulberry surface for the H_2/H^+ reaction.⁽⁸⁹⁾ One point for mulberry at pH 2 was taken from previously published data—a 0.01 N HCl solution.⁽¹⁴⁾ The chloride would be expected to keep the surface in an active state. The zone-refined, alpha-uranium specimen cut across the [010] orientation had a significantly lower potential than the other alpha-uranium specimens. Values at pH - 1.5 were taken in orthophosphoric acid and orthophosphoric acid saturated with $K_2Cr_2O_7$. The dichromate passivates both uranium and mulberry, elevating their open-circuit potentials. In a neutral solution, the U-Ti alloy seems initially more noble than either uranium or mulberry.

Relationship of Additive Elements to the Corrosion Rate - It is known that increasing the percentage of niobium in a U-Nb alloy, for example, decreases the corrosion rate in certain media. Data on the corrosion rate of U-(4.5, 6, and 8) Nb, mulberry, and U-10 Mo, taken from Macki and Kochen,⁽⁹⁵⁾ have been plotted as a function of the total atomic percent addition in Figure 4. An essentially linear relation is obtained for the U-Nb alloys and mulberry, with the U-Mo alloy

Figure 3. INITIAL OPEN-CIRCUIT POTENTIALS OF SPECIMENS IMMERSED IN A VARIETY OF DEOXYGENATED SOLUTIONS AS A FUNCTION OF THE pH. (Potentials Referenced to the Saturated Calomel Electrode)

apparently belonging to a different class. (It could be postulated that similar results for varying concentrations of molybdenum would produce a similar straight line, possibly of different slope, when so plotted.) A linear (or otherwise regular) relation should be expected between electrochemical properties and the atomic percent of additive elements.

Figure 5 reports the potentials of alpha uranium, U-3/4 Ti and mulberry as a function of the atomic percent of additive elements. The potentials plotted are: (1) those taken initially on freshly polished specimens in a deaerated solution,

and (2) those taken after performing the M + S procedure (described previously) in an oxygenated solution. The solutions used were the four solutions used in the M + S studies. The results for the deaerated solutions emphasize again that for relatively fresh metal surfaces in some media, higher alloying additions of some elements lower the open circuit potential of uranium alloys. It is obviously (from Figure 5) not a simple relation, however. The post-M + S specimens reflect the potentials in an oxygenated solution of specimens with thin coatings of oxide. One caution that must be noted is that the specific mode of forming the surface can have a great influence on its properties due to possible enrichment differences (cf, Jenks(89)). With that in mind, however, the potentials of the post-M + S specimens treated in the media specified have not been found to be in good correlation with the results of preliminary corrosion tests in the same media.(104)

Figure 4. CORROSION RATES OF URANIUM-(4, 4.5, 6, and 8) NIOBIUM, MULBERRY, AND URANIUM-10 MOLYBDENUM AS FUNCTIONS OF THE TOTAL ATOMIC PERCENT ADDITION. (Data Taken from Macki and Kochen(95))

The principal problem with simply measuring potentials is that, from the position on the potential/pH diagram, the state of the surface and what reactions are occurring must be inferred. In a rough sense, this inference is permissible, but complications prohibit a single measurement of potential from being a sensitive indicator of the corrosion rate. The main complication is that, especially in a complex system like uranium/uranium ions/uranium oxides, there is a choice of more than one set of potential-determining reactions, each with different properties with regard to corrosion. One device for circumventing this problem is the introduction of a suitable redox couple which will act as an electron acceptor for the anodic corrosion reaction. Acceptance of electrons into the redox couple can take place at a certain rate, dependent on its cathodic polarization characteristics and its concentration. By changing the concentration of the species being reduced and observing the shift in the (mixed) corrosion potential, the corrosion rate of the specimen under study can be determined. The greater the relative shift of the corrosion potential, the lower the corrosion current, and vice versa.

An example can be taken (using the HO_2^-/O_2 redox couple) again from Macki and Kochen.(94) The difference in potential for each alloy between aerated (O_2 pressure probably 0.16 atm at Golden, Colorado) and oxygenated [O_2 pressure perhaps 1.0 atm (supersaturated)] solutions of 0.1 N HCl was noted and has been plotted in

Figure 6 as a function of the log of the weight loss rate found for the alloys. (95) (± 0.0025 V error has been assumed.) The data have a roughly linear relationship as might be expected since potential is exponentially related to current through the Butler-Volmer equation.

Essentially, then, the method consists of displacing the potential of the specimen, using a redox couple with known polarization properties so that the currents drawn (at least in a relative sense) can be inferred. This technique does have the drawback that the properties of the redox couple on different alloys may differ, introducing error into the determination. One method which performs the same function and circumvents this problem is the polarization-resistance method. This method is well known (105 - 108) and is slightly more demanding of careful experimentation than some other techniques. The potential of the specimen is displaced by a small amount (a few millivolts) and the current drawn is determined. (In some cases the potential/current relation is determined.) From these data, a direct determination of the corrosion rate can be made. It is not known whether there are any experimental programs presently underway using this method to study uranium alloy corrosion, but it is a powerful technique for determining corrosion rates.

Figure 5. OPEN-CIRCUIT POTENTIALS OF ALPHA URANIUM, URANIUM-3/4 TITANIUM, AND MULBERRY IMMERSSED IN VARIED SOLUTIONS AS FUNCTIONS OF THE ATOMIC PERCENT ALLOYING ADDITIVE CONCENTRATION. (Potentials Referenced to the Saturated Calomel Electrode)

Voltammetric Studies - Voltammetric studies were performed in the three-compartment cell described earlier (Page 15). The cell was purged with argon. An electronic potentiostat, driven by a function generator, was used to make the specimens assume whatever value of the potential difference with respect to the SCE was desired. The current supplied by the potentiostat was processed in a log converter and real-time plots of $\log i$ as a function of the potential were obtained on an X-Y recorder. Typically, the potential was dynamically controlled at sweep rates varying from 5.6×10^{-4} to 1.68×10^{-2} V/sec. The sweep rate chosen for most of the studies was 5.6×10^{-3} V/sec. Those desiring more detailed information about the rapid sweep rate are referred to Appendix C.

Representative polarization curves are given in Figures 7 through 9 for alpha uranium, U-1.2 Ti, and mulberry, respectively, all in 1 N KOH solutions. Figure 7 also shows data for the

high-carbon uranium (680 ppm) where it deviates from the curve for standard uranium (60 ppm). A third set of data on Figure 7 is from a different (and atypical) specimen. The run from which this set of data were taken on the source of the singular datum mentioned later (Pages 36 to 42). Sweeps for the alpha-uranium and uranium-1.2 titanium specimens were begun in the cathodic region and that for the mulberry near the open-circuit potential (the potential sweep rate was 5.6×10^{-3} V/sec). Two complete cycles through the potential range covered were completed for the alpha-uranium and uranium-1.2 titanium specimens and 1 3/4 cycles for the mulberry specimens. The reverse sweeps are shifted down one power of ten for clarity.

Polarization Behavior of Uranium

The two regions of active/passive behavior for uranium mentioned earlier (REVIEW OF THE LITERATURE) can be seen in Figure 7. One is between the potential at which the polarity of current changes from (-) to (+) [about - 1.1 V vs SCE (cf, Ward and Waber(27))] and about - 0.4 V vs SCE. As the potential is raised from - 1.1 V, the anodic current first rises and then falls. However, it should be noted that on the first scan with a freshly polished surface, this trend is not observed. On the second scan, when thin oxide has already been grown, active/passive behavior is obtained. The second region is between about - 0.3 to + 0.1 V vs SCE and is observed on the first and succeeding scans; however, the critical current (which will be called i_{crit}) at the peak of this transition is higher for the second scan, and the potential at the current peak (which will be called E_{crit}) is lower for the second scan.

The reverse scan shows a potential of changeover from (+) to (-) current at about the same potential (- 0.4 V vs SCE) that the forward scan has a drop in current. This potential is approximately the UO_2/UO_3 equilibrium potential.

The two active/passive regions behave differently regarding reproducibility. The one with an $E_{crit} \sim - 0.1$ V vs SCE is quite reproducible and apparently insensitive to slight changes in experimental variables, whereas the one between - 1.1 and - 0.4 V vs SCE seems to vary with (presumably) slight changes in surface preparation and solution composition. This region is, in fact, the critical one for consideration in uranium corrosion in the high pH region, since a freely corroding specimen in the absence of inhibitors will assume a potential somewhere in this region; or, possibly, as high as - 0.3 V vs SCE—the HO_2^-/O_2 equilibrium potential.

Figure 6. WEIGHT-LOSS RATE OF URANIUM-(4.5, 6, and 8) NIOBIUM, MULBERRY, AND URANIUM-10 MOLYBDENUM AS FUNCTIONS OF THE POTENTIAL SHIFT FOR EACH ALLOY BETWEEN AERATED AND OXYGENATED SOLUTIONS OF 0.1 NORMAL HYDROCHLORIC ACID. (Data Taken from Macki and Kochen(94, 95))

Figure 7. REPRESENTATIVE POLARIZATION CURVES FOR ALPHA-URANIUM SPECIMENS IN A ONE-NORMAL POTASSIUM HYDROXIDE SOLUTION. [Deviations are Shown for the High-Carbon Uranium (680 ppm) and One Singular Run for Standard Uranium; Potentials are Referenced to the Saturated Calomel Electrode; Cathodic-to-Anodic Sweep Ordinate is Defined on the Left of the Graph, Anodic-to-Cathodic Sweep Ordinate is Defined on the Right of the Graph]

Figure 8. REPRESENTATIVE POLARIZATION CURVES FOR URANIUM-1.2 TITANIUM SPECIMENS IN A ONE-NORMAL POTASSIUM HYDROXIDE SOLUTION. (Potentials are Referenced to the Saturated Calomel Electrode; Cathodic-to-Anodic Sweep Ordinate is Defined on the Left of the Graph, Anodic-to-Cathodic Sweep Ordinate is Defined on the Right of the Graph)

Figure 9. REPRESENTATIVE POLARIZATION CURVES FOR MULBERRY SPECIMENS IN A ONE-NORMAL POTASSIUM HYDROXIDE SOLUTION. (Potentials are Referenced to the Saturated Calomel Electrode; Cathodic-to-Anodic Sweep Ordinate is Defined on the Left of the Graph, Anodic-to-Cathodic Sweep Ordinate is Defined on the Right of the Graph)

Processes Occurring Between - 1.1 and - 0.4 V vs SCE - Reproducibility of the second active/passive peak lent itself to correlation with corrosion-related properties, as will be shown later. For the moment, however, speculation will center on the process occurring in the first active/passive region for the cathodic-to-anodic scan. There seem to be three likely processes: (1) oxidation of H_{adsorb} to H^+ (the equilibrium potential at this pH being - 1.05 V vs SCE), (2) current due to charging the electrode capacitance, and (3) oxidation of the UOH^{+3} species (dissolved in the stagnant layer next to the electrode) to UO_2^{+2} . Production of the hydrogen ion seems unlikely since the freshly polished surface has lower currents in this region. In addition, uranium seems to have a rather low H_2/H^+ exchange current (10^{-10} A/cm²),⁽⁸⁹⁾ although the state of the uranium surface from which this value was taken was not well defined. A capacitance-charging current seems unlikely since in this region the capacitance is continuously increasing as the potential is increased.⁽¹⁰⁹⁾ In addition, sweeping the potential a factor of 10 slower (5.6×10^{-4} V/sec) revealed the same behavior, as did sweeping at 5.6×10^{-3} V/sec with ten-second holds at regular intervals.

Apparently, then, the current being drawn in this area is related to oxidation of a U(IV) species in solution in a layer next to the electrode. The source of this species would be the chemical dissolution of the UO_2 film known to exist in this potential region. It is interesting that currents in this region (from Figures 7 through 9) are in the order $i_U > i_{U-1.2} Ti > i_{Mu}$. This could well be a direct indicator of the solubility of the oxide films on these metals; in other words, of their corrosion rate. Careful studies in this area, possibly using techniques such as chronopotentiometry, might be of value in measuring the corrosion rates of such materials. It remains to be shown, of course, that the idea is valid for other pH regions and for the presence of complicating factors such as the presence of inhibitor and aggressor species.

Processes Occurring Above - 0.4 V vs SCE - Rise in current above - 0.5 V vs SCE has been attributed by Jenks to the $UO_2 \rightarrow UO_3$ reaction.⁽⁸⁹⁾ Other investigators⁽⁷⁰⁾ have found $UO_3 \cdot 2H_2O$ to be the species formed above this region. The potential of current rise is above the $UO_2/UO_3 \cdot 2H_2O$ equilibrium (- 0.655 vs SCE in a pH of 13.7); however, a nucleation overpotential could exist, making the $UO_2 \rightarrow UO_3 \cdot 2H_2O$ reaction occur at a higher potential than the equilibrium value. This possibility would not explain, however, why the reverse (anodic-to-cathodic) sweep changes polarity at - 0.4 V vs SCE, a value also obtained at a sweep rate of 5.6×10^{-4} V/sec. The state of hydration of the oxide above - 0.1 V vs SCE would then seem to be in question.

Data for the high-carbon uranium show a rise in current in the passive region at potentials of + 0.4 to + 0.5 V vs SCE, forming a small peak at + 0.8 V vs SCE. Prepolarization microscopic examination showed evidence of many generally cubic inclusions, which were probably UC.⁽¹¹⁰⁾ Postpolarization examination revealed localized attack on and immediately around the inclusions, which was, in all probability, due to the polarization treatment. This conclusion can be stated since, over the length of time of the experiment, the extent of chemical reaction of UC with the 1 N KOH would be expected to be minimal.⁽¹¹¹⁾ Additionally, Gmelin⁽⁵⁶⁾ reported evolution of CO_2 from anodically polarized high-carbon uranium.

An attempt has been made to identify the oxides present on the uranium surface by the electron diffraction method. Specimens were held in a 1 N KOH solution at potentials of - 0.7, - 0.1, and + 0.4 V vs SCE for periods of 30 minutes. Results indicated(112) that materials on the surface which exhibited diffraction patterns were different from known uranium oxides. The specimen held at - 0.7 V had a diffuse pattern characteristic of a crystallite size < 50 angstroms. The other two specimens had a different pattern, with a probable crystallite size in the 50 - 150-angstrom range. Diffuse electron diffraction patterns have been seen on uranium under similar circumstances.(74)

Films formed on uranium and uranium alloys at potentials positive to the - 0.1 V vs SCE current peak apparently have a different structure than those formed by simple oxidation. Stebbens and Shreir(68) found their films to have a refractive index of $n_1 = 1.93$ to 1.95 in contrast to the values obtained for films formed by simple air oxidation [Sladky,(113) 2.35 - (0.2 to 0.4) i ; Larson,(114) 2.2 - 0.44 i]. In addition, Sladky, in unreported work, anodized mulberry in 1 N KOH, obtaining oxide properties and growth characteristics (determined by ellipsometry) which were distinctly different from the oxide properties and growth characteristics found for air oxidation of mulberry. Sladky(113) also determined that the initial oxide (at low thickness) produced on mulberry by air oxidation had the same refractive index as that formed on uranium.

Effect of Passivators on the Hydrogen Evolution Reaction of Uranium - Uranium and mulberry specimens were cycled at a sweep rate of 5.6×10^{-3} V/sec over a wide potential range in orthophosphoric acid and orthophosphoric acid saturated with $K_2Cr_2O_7$. Characteristics of the hydrogen evolution reaction (HER) on uranium were found to depend on the presence or absence of the dichromate. Without dichromate, the overvoltage observed at a current density of $- 10^{-3}$ A/cm² on uranium was - 1.01 V; with dichromate, the overvoltage at this current density was - 0.89 V. For mulberry, the values observed under both conditions were - 0.65 V, not dependent on the presence of $K_2Cr_2O_7$. Pitting of uranium and grain-boundary etching of mulberry were observed with either solution in a postpolarization microscopic examination. The zero current potential for uranium in the orthophosphoric acid (determined at a 5.6×10^{-4} V/sec sweep rate) was - 0.83 V vs SCE, which is approximately the U^{+3}/U^{+4} equilibrium potential.

Polarization Behavior of the Alloys - Overall behavior of the U-1.2 Ti and mulberry alloys is similar to that of alpha uranium; however, there are several interesting differences:

1. For both active/passive peaks, the currents are in the order $i_U > i_{U-1.2 Ti} > i_{Mu}$. The current at the peak (around - 0.1 V vs SCE for mulberry) is about a power of ten lower than that for uranium, a ratio which is in fair agreement with preliminary corrosion tests that have been made on uranium and mulberry in 1 N KOH.(104)
2. For mulberry, currents in the region positive to the - 0.1 V vs SCE peak are little less than the current at the peak, somewhat noisy, and essentially independent of

the potential. The U-1.2 Ti alloy also maintains a high, noisy, current positive to the active/passive peak, but this value drops as the sweep continues in the positive direction. In addition, slow scans (5.6×10^{-4} V/sec) yield almost no currents in this region above what would be expected for the i_{pass} on uranium. However, a sweep at 5.6×10^{-3} V/sec with 10-second holds at regular intervals also indicated increased currents in this region. In contrast, the active/passive peak at about -0.1 V for alpha uranium is quite sharp and the current i_{pass} quite low.

- Concerning the possible effect of trace oxygen contamination leading to the production of H_2O_2 in the solutions, known amounts of H_2O_2 have been introduced into 1 N KOH solutions and preliminary polarization experiments have been performed using uranium and mulberry. Effect on the mulberry trace seems, principally, to be an increase in the cathodic currents, probably due to the $\text{HO}_2^- \rightarrow \text{H}_2\text{O}$ reaction. The anodic curves are little affected. However, uranium is profoundly affected, as can be seen in Figure 10. Increasing the H_2O_2 concentration sufficiently makes the cathodic $\rightarrow$ anodic polarization curve of uranium (above -0.3 V vs SCE) closely resemble that for mulberry. An interesting fact here is that, at the higher concentrations of H_2O_2 , the alpha-uranium specimen comes through two polarization cycles while retaining a shiny, microscopically smooth surface; whereas, alpha uranium in 1 N KOH under the same sweep conditions becomes noticeably oxidized.

Behavior of the U_2Ti Intermetallic Compound - Interested by the fact that alloys with lower concentrations of titanium exhibited lower postpassive-peak currents, it was decided to prepare U-Ti alloys with sizable concentrations of titanium, up to and around the U_2Ti composition. Figures 11 and 12 show a U-8.86 Ti specimen in the as-cast and in the heat-treated condition (see Table 1). Electron microprobe data verified⁽¹¹⁵⁾ that the phases present in the heat-treated material had the compositions of U_2Ti , $\alpha\text{-U}$, and Ti. When carried through polarization cycles in 1 N KOH, the heat-treated material revealed an active/passive peak at the usual potential for uranium and another peak at a potential of $E_{\text{crit}} = -0.22$ V and a current of $i = \text{alog}(-3.3)$, which must be characteristic of U_2Ti . The postpassivation currents were higher than would be expected for alpha uranium. There was an increase in current above $+0.5$ to $+0.6$ V vs SCE (which was similar to that seen in the high-carbon uranium specimens) which may be due to the $\text{H}_2\text{O} \rightarrow \text{O}_2$ reaction. This current increase was also noted for beta-titanium samples polarized in 1 N KOH. Another difference seen with the high-titanium, heat-treated specimens was that the hydrogen evolution reaction apparently has a relatively high exchange current on U_2Ti —about $i_0 = \text{alog}(-6.8)$. This value is about equal to that of titanium in this solution.⁽¹⁰⁴⁾ The Tafel region for hydrogen evolution extended over 3.5 powers of ten in current. The Tafel ($dE/d \log i$) slope was -0.147 . It is interesting that U-Zr alloys having small quantities of (apparently) the UZr_2 intermetallic compound exhibit no indication of high postpassive-peak currents. The mechanism operating to produce high postpassive-peak currents may, then, be due to some property of, specifically, the U_2Ti intermetallic compound. That this property may be related to H_2O_2 production and subsequent decomposition is an intriguing possibility in light of the results of the alpha-uranium/1 N KOH/ H_2O_2

Figure 10. POLARIZATION CURVES FOR ALPHA-URANIUM SPECIMENS IN ONE-NORMAL POTASSIUM HYDROXIDE SOLUTIONS WITH VARYING CONCENTRATIONS OF HYDROGEN PEROXIDE. (Potentials Referenced to the Saturated Calomel Electrode; Cathodic-to-Anodic Sweep Ordinate is Defined on the Left of the Graph, Anodic-to-Cathodic Sweep Ordinate is Defined on the Right of the Graph)

experiments. The work of Gerischer and Gerischer⁽¹¹⁶⁾ is interesting in this regard. They found a limiting current density for the $\text{H}_2\text{O}_2 \rightarrow \text{O}_2$ reaction of $i = \text{alog}(-2.7)$ on bright platinum in a 1 N H_2SO_4 solution that was 0.01 N in H_2O_2 . The current found for the postpassive-peak region of alpha uranium (in the 0.01 N H_2O_2 solution of Figure 10) is $i = \text{alog}(-2.8)$. It is in no way clear, however, why, at lower concentrations, the currents in this region decrease with increasing potential. This region is the one for the H_2O_2 concentration, however, below which specimens that have been through polarization cycles become noticeably oxidized.

Extended Potential Sweep Corrosion Rate Test - It is possible, in some cases, to determine the corrosion rate by an extrapolation of the cathodic reduction Tafel line (if one should exist) to the (mixed) open circuit potential. This intersection would occur at the corrosion current, i_{corr} . One example of this approach is the work of Morris and Scarberry⁽¹¹⁷⁾ on corrosion-rate tests of nickel alloys in sulfuric acid solutions. They developed a specific method for carrying a specimen through a polarization cycle. This method is essentially the same as the M + S procedure (Page 16). The difference in the experimental method was that the work described here was in an oxygenated solution and their work was in a deaerated solution. The difference in mechanism of corrosion is that Morris and Scarberry were working with a system in which the cathodic (electronation) reaction was the $\text{H}^+ \rightarrow \text{H}_2$ reaction; in the work described here, the cathodic reaction was the $\text{O}_2 \rightarrow \text{HO}_2^-$ reaction. The objective was the same; namely, to bring the electrode into

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Figure 11. MICROSTRUCTURE OF AS-CAST URANIUM-8.86 TITANIUM ALLOY. [Light Phase (U_2Ti), Dark Phase (U), and Minor Phase (Ti) are Shown; Bright Field Illumination; 500X]

1416-1e

Figure 12. MICROSTRUCTURE OF HEAT-TREATED URANIUM-8.86 TITANIUM AFTER SEVERAL ELECTROCHEMICAL POLARIZATION CYCLES. [Light Phase (U_2Ti), Dark Phase (U), and Minor Phase (Ti) are Shown; Bright Field Illumination; 600X]

a state representative of a freely corroding specimen and to determine the rate of the electronation reaction on the surface of the electrode.

Due to complications in the nature of oxide reduction processes occurring simultaneously with oxygen reduction processes, Tafel lines for the oxygen reduction could not be obtained for the experimental conditions used (although cathodic currents representative of oxygen reduction were clearly obtained). This observation is not to slight the technique used by Morris and Scarberry, as they obtained very good correlations in their tests between electrochemically and conventionally determined corrosion rates. The problem in transplanting this exact procedure, from a case of hydrogen ion reduction to a case of oxygen reduction, is that there is no presumptive reason to expect the exact experimental parameters used in the first case to apply to the second case. The M + S procedure studies were performed using the same experimental parameters as those of Morris and Scarberry as a starting point; and, obviously, judicious changes in method are needed. Basically, however, extrapolation of the electronation process Tafel line to the (mixed) corrosion potential is another procedure which can make good predictions of corrosion rates under the proper conditions.

Polarization Behavior as a Function of the Number of Cycles - Data reported in Figures 7 - 9 for the general polarization behavior of the three materials carries the material through two cycles over the potential range used. Early in the Y-12 investigation it had been determined that the first cycle through the wide potential range used was atypical with respect to the other cycles. Behavior of the active/passive peak around -0.1 V vs SCE for uranium was studied as a function of the sweep cycle number. Results for three specimens were averaged. These results are given in Figure 13 and are reported as two current densities—one at E_{crit} and the other at 0.1 V more positive than E_{crit} . From Figure 13 it can be seen that the form factor of the peak changes with cycle number and that the second cycle produced the maximum i_{crit} . The i_{crit} dropped with succeeding cycles to a much lower value, and the form factor changed also so that, at higher numbers of cycles, the i_{crit} was not much greater than what became the i_{pass} . In fact, the i_{pass} for alpha uranium after very few cycles dropped below the i_{pass} for mulberry (whose behavior was not influenced greatly by the number of cycles).

This fact seems to point up an important difference in the behavior of mulberry and uranium in the postpassive-peak region. The behavior of uranium is suggestive of an oxide film thickening to some limiting thickness. Similar conclusions cannot be drawn about mulberry because the currents positive to the active/passive peak apparently arise from a different process, such as (possibly) the one responsible for high-postpassive currents in U-Ti alloys. It should be noted: (1) that the behavior (in this respect) of the U-low Zr alloy studied is similar to that of alpha uranium, (2) that the behavior of the U-low Zr-low Ti alloys studied is similar to that of U-Ti alloys with the same titanium content, and (3) that the behavior of U-Nb alloys with a niobium content comparable to that of mulberry is similar to that of mulberry.

It was decided, then, to choose the second sweep as the one from which to take derived data in the analysis of the polarization curves for the several combinations of materials and environments.

Figure 13. CURVES OF CURRENT DENSITY AS A FUNCTION OF THE SWEEP NUMBER FOR E_{crit} , AND FOR 100 MILLIVOLTS FURTHER POSITIVE FROM THIS PEAK, FOR THREE ALPHA-URANIUM SPECIMENS IN ONE-NORMAL POTASSIUM HYDROXIDE.

Derived Parameter Correlation -

Parameters Used - Hoar(11) has emphasized the importance of the potential of passivation (E_{crit}), and the anodic current flowing in the passive region (i_{pass}), as criteria for the resistance of metals to corrosion. In this regard he is speaking of regions of potential ordinarily accessible to the metal in a natural corrosion situation. For alpha uranium in 1 N KOH, this region would be between - 1.1 and - 0.3 V vs SCE. Due to the survey nature of these investigations, no attempt was made to exert precise control over all parameters in order to reproduce the polarization results in this area with precision. Thus, because of an apparent sensitivity to minor changes in the experimental parameters, data in this region were not as consistent as other features observed in the polarization studies.

In particular, the passivation phenomenon occurring around - 0.1 V vs SCE in 1 N KOH (for sweeps of increasing potential with time) was fairly well reproduced with regard to its potential (E_{crit}) and its current (i_{crit}). These parameters, then, plus the current flowing beyond this passivation peak (i_{pass}) are the derived parameters which were correlated with environmental and material variables. In light of the fact that these parameters have been taken from a potential region into which the alloys must be artificially driven, the correlations which were found are interesting. Their significance is that the properties of films on active metals or alloys, which are related to the corrosion resistance properties of the metals or alloys, can be studied in potential regions remote from their natural potential regions. However, the correlations in some cases may not have the simple form achieved for the same type of parameters determined in naturally achieved potential regions.

rather the hexagonal AlB_2 structure,⁽¹⁰¹⁾ then the rather low value should not be surprising. The alpha-uranium and mulberry values obtained at pH values of 12.7 and 13.2 seem in line with those obtained at a pH of 13.7. Since these solutions were 0.1 and 0.3 N KOH, respectively, the E_{crit} is apparently not a strong function of the ionic strength. (However, the i_{crit} is such a function, as will be mentioned shortly.)

In an H_2SO_4 solution of pH 0.5 (with known O_2 contamination) an E_{crit} was observed for mulberry in a position on Figure 14 comparable to that observed for the very alkaline solutions and at a current density of $i = \text{alog} (-1.5)$. For the alpha uranium and U-3/4 Ti alloy, the current capacity of the potentiostat was reached at about +0.4 V vs SCE [and $i = \text{alog} (-1.7)$] and no evidence of passivation had been observed.

Values at a pH of -1.5 for H_3PO_4 and $\text{H}_3\text{PO}_4/\text{K}_2\text{Cr}_2\text{O}_7$ fall in line with the rest of the values; but, due to the complication of high viscosity and low water content (15%) of this medium, the interpretation of these data is uncertain.

In the solution with a pH of about 6 (1 N K_2SO_4), only alpha uranium, U-3/4 Ti, and mulberry were studied. The alpha-uranium and U-3/4 Ti specimens had not exhibited passivation at +0.4 V vs SCE [and $i = \text{alog} (-2.5)$], where the current capacity of the potentiostat was reached. Mulberry, however, revealed a rather broad active/passive peak in this solution. As shown in Figure 14, the E_{crit} value for the first sweep was consistent with values obtained at very alkaline and very acid pH values. The i_{crit} , however, was low at $i = \text{alog} (-4.30)$. The second sweep showed a considerably lower E_{crit} at a value of -0.15 V vs SCE [$i = \text{alog} (-4.62)$]. This value is low enough to postulate, for near-neutral pH values, selective dissolution of uranium [and zirconium(?)] from the mulberry surface, leaving it enriched in niobium oxides. This action would be compatible with similar proposals by Jenks⁽⁸⁹⁾ and Zehr.⁽⁹²⁾ Data for U-3/4 Ti and mulberry at a pH of about 8.2 (0.5 N K_2SO_4) seem intermediate between the data at a pH of about 6 and those at a pH of about 13.7.

The artificiality of the enrichment proposed for the specimens studied here and those studied by Jenks would cause doubt as to the applicability of data taken on mulberry in this manner; and, in this pH region, to real (simple) corrosion situations. It would clearly have applicability, however, to stress-corrosion cracking of mulberry (assuming the Zehr model to be correct).

It seems apparent, then, that the easily accessible active/passive region seen for the uranium alloys around -0.1 V vs SCE in a very alkaline solution should be more closely related to the real corrosion properties of the alloys than similar data taken in near-neutral pH solutions.

What Causes the Passivation? - Identification of the mechanism of the passivation process observed (around -0.1 V vs SCE) in these experiments would be a significant breakthrough; unfortunately, at this writing, this goal does not seem possible. A few facts, however, will be offered:

1. For surfaces not suspected of enrichment (uranium depletion), E_{crit} falls in a band across the potential/pH field which lies between the HO_2^-/O_2 and H_2O/O_2 equilibria. Since trace oxygen contamination was possible for these solutions (argon purge times before sample immersion were typically 30 minutes, but most investigators advise longer times), the possibility of trace H_2O_2 formation in the cathodic region and subsequent decomposition back to O_2 on the electrode cannot be discounted. Oxygen adsorption is one mechanism proposed for the passivation phenomenon.
2. Another factor involved (for nickel passivation, at any rate⁽¹¹⁸⁾) may be the transition in the film from ionic to electronic conductivity. This transition for nickel films occurs simultaneously with passivation. No longer having a large potential gradient, the film cannot maintain growth. However, as Jenks⁽⁸⁹⁾ points out, electronic conductivity should be accompanied by the $H_2O \rightarrow O_2$ reaction. Jenks did not observe this for mulberry in K_2SO_4 and it was not observed in this investigation. Exceptions to this generality were in the case of the heat-treated U-high titanium alloys (U - 680 ppm C) and also titanium, where increases in current were observed in the "passive" region. It should be noted, however, that Koger⁽¹¹⁹⁾ has routinely observed such increases in current on machined uranium alloy specimens studied in 0.1 N KOH solutions. The machining process may leave the surface in a condition wherein the electronically conducting state is easily accessible.
3. Since the current rise leading to the active/passive transition seems basically oxidation of a U(IV) oxide to a U(VI) oxide, coulometric analysis in this area might be of interest. Preparation of specimens for the electron diffraction analyses mentioned earlier (Page 22) offered an opportunity to perform such an analysis. Referring to Figure 7, the specimens were carried through one complete cycle in the usual manner before increasing the potential to the desired value. For a specimen so cycled, then held at + 0.62 V vs SCE in the passive current region, an immediate drop in current of 0.1 log unit was observed, corresponding to the capacitance charging current. But, after ten minutes, a second drop in current of about 0.2 log unit was observed. The drop after ten minutes could be interpreted as a completion of the oxidation of the remaining U(IV) oxide to the U(VI) state. The anodic current passed across the specimen was graphically integrated from - 0.30 V to + 0.62 V vs SCE (including the ten-minute period) and a charge density of 0.255 coulomb/cm² was found, of which 40% was passed during the ten-minute "transition time" after holding at + 0.62 V. Considering all the current to be used in a U(IV) oxide $\rightarrow$ U(VI) oxide process, this charge density leads to an oxide film thickness of 320 angstroms. This value is reasonable for the thickness (although part of the current could have been used to oxidize uranium metal directly to the U(VI) oxide), being in rough agreement with the thickness estimated from the interference color of the film. Therefore, the U(IV) $\rightarrow$ U(VI) process seems to occur all through the potential region mentioned, the attainment of E_{crit} having no obvious association with the oxidation state.

Correlation of E_{crit} with the Alloying Additive Concentration - The criterion of lower E_{crit} for better corrosion resistance and the relation of the corrosion rate to the alloying additive concentration (Figure 14) would suggest correlation of E_{crit} with the percent additive concentration. Figure 15 would suggest that, for total additive concentrations less than approximately four atomic percent, the E_{crit} (in pH = 13.7 KOH solution) does drop with the additive concentration. For gamma-phase niobium alloys at higher concentrations, however, the E_{crit} rises with the niobium concentration. Addition of zirconium to produce mulberry seems to have a greater effect than would an equal amount of niobium. Additions of titanium above a certain concentration (~ 4 at %) produce irregular behavior, probably associated with the process described in the section on polarization of uranium-titanium alloys (Page 26). This process may also be the reason for the behavior of the uranium-niobium (+Zr) alloys, but no real explanation can be offered at this time.

Figure 15. E_{crit} (FOR SECOND SWEEPS) OF ALPHA-URANIUM AND URANIUM-ALLOY SPECIMENS AS A FUNCTION OF THE ATOMIC PERCENT ALLOYING ADDITIVE CONCENTRATION. (Potentials Referenced to the Saturated Calomel Electrode)

The E_{crit} for U_2Ti is much lower than for the other materials, as has been mentioned. At the same time, the E_{crit} for the uranium phase in the high-titanium alloys (see Figure 15) is elevated. The E_{crit} and i_{crit} values for alpha uranium and U_2Ti passivation may be distorted by the proximity of the two processes, but the increase of E_{crit} for alpha uranium in high-titanium alloys is judged to be real.

E_{crit} for this passivation process, then, seems related to alloy properties which relate to corrosion resistance, but the relations are complex and apparently depend on side reactions occurring simultaneously with the metal and metal oxide dissolution processes.

Correlation of $\log i_{pass}$ with Alloying Additive Concentration - The second parameter proposed⁽¹¹⁾ as an indicator of corrosion resistance is the anodic current flowing in the passive region (i_{pass}). As can be seen from Figure 18, there is a correlation of sign opposite to that postulated for the uranium-low titanium alloys. As has been discussed, this may be related to a side reaction and not to metal or metal oxide dissolution. Data for the uranium-niobium alloys, overall, are correlated in the expected manner, but the precision is unexceptional and data for first and second scans are not differentiated. For the uranium-low zirconium alloys, however, lower i_{pass} values are observed for higher zirconium contents, which is the expected relation. The value for the high-carbon alpha uranium is higher than that for standard low-carbon uranium, a relationship that is expected. Finally, the zone-refined rod cut across the [010] direction had a lower i_{pass} than standard uranium.

Figure 16. $\log i_{pass}$ (FOR SECOND SWEEPS) OF ALPHA-URANIUM AND URANIUM-ALLOY SPECIMENS AS A FUNCTION OF THE ATOMIC PERCENT ALLOYING ADDITIVE CONCENTRATION.

Correlation of Log i_{crit} with Alloying Additive Concentration - This correlation, shown in Figure 17, was the most successful of the three. Linear relationships were obtained for the uranium-zirconium, uranium-low titanium, and uranium-niobium alloy systems, with the correct sign for the slope $d(\log i_{crit})/d(\text{at } \%)$.

Figure 17. i_{crit} (FOR SECOND SWEEPS) OF ALPHA-URANIUM AND URANIUM-ALLOY SPECIMENS AS A FUNCTION OF THE ATOMIC PERCENT ALLOYING ADDITIVE CONCENTRATION.

The i_{crit} for alpha uranium with a 680-ppm carbon content is higher than that for most standard 60-ppm carbon uranium specimens, indicating a probable higher corrosion rate. The i_{crit} for the zone-refined uranium, cut across the [010] direction, was also higher than that for most standard uranium specimens. It is difficult to compare highly oriented material with material of randomized, if somewhat preferred, orientation. The free enthalpy of formation (and thus the E^0) of oxides from the substrate may be different from that on randomized orientation material. That this difference exists is strongly suggested by the considerably lower open circuit potential for the zone-refined material compared to the standard material, and also by the different E_{crit} and i_{crit} .

The i_{crit} for standard uranium in 1 N KOH solution (0.01 to 0.001 N in H_2O_2) is noticeably lower than that for standard uranium in 1 N KOH only. This difference is consistent with the unoxidized appearance of the specimens run using these additions of H_2O_2 . It is interesting, if probably fortuitous, that the i_{crit} value for alpha uranium in H_2O_2 /1 N KOH solution is approximately the value of the zero-addition intercept of the line through the uranium-niobium alloy specimens. A more detailed discussion of the alpha-phase and gamma-phase alloys follows.

1. Alpha-Phase Alloys - In fact, it seems that each family of alloys has a different $i_{crit}/\%$ addition relationship. The uranium-low zirconium data would seem to be parallel to the uranium-low titanium data. Both, if extrapolated to zero percent addition, would indicate a higher corrosion rate than pure uranium except for the singular datum at $i_{crit} = alog (-2.15)$. These measurements may be sensitive to trace concentrations of contaminants (of which oxygen is one possibility). It may be that the singular datum was taken from the most oxygen-free run. Further data shown for alpha uranium and U-3/4 Ti using two different solutions were taken using the M + S procedure previously described (oxygenated solutions) (Page 16). The two slopes $[d(\log i_{crit})/d(at \%)]$ are identical to each other and to that of the series of uranium-low zirconium and uranium-low titanium alloys. This similarity indicates that the i_{crit} of alpha-phase material for constant environmental composition is probably a linear function of the percent additive element when the element is zirconium or titanium, which probably applies to other "film-forming" elements as well.
2. Gamma-Phase Alloys - Data are available for only one alloy system as a function of the atomic percent addition—the uranium-niobium system. Position of the mulberry value indicates that addition of an increment of zirconium to bring the total atomic addition to 22.2% is more effective in lowering the corrosion rate than would be a similar increment of niobium. This effect is possibly a manifestation of the proposition that more amorphous oxide layers are more protective,⁽¹¹⁾ a multiplicity of components tending to decrease the crystallinity of materials.

Data for the U-6 Nb (14.1 at %) alloys in different heat-treated states are consistent with the data of Draley, et al⁽¹²⁰⁾ who found that aging U-6 Nb at 350° C doubled the corrosion rate of the alloy in degassed, distilled water at 260° C.

Koger⁽¹¹⁹⁾ has determined the i_{crit} of a U-10 Mo gamma-phase alloy (in the machined condition) to be $i_{crit} = alog (-3.92)$ in 0.1 N KOH. Accepting this datum as roughly comparable to that obtained by the previously described procedure, the i_{crit} for this material in 1.0 N KOH has been estimated (see Appendix D) as $i_{crit} = alog (-3.06)$ and so plotted. This value places the U-Mo alloy well above the U-Nb alloys in its corrosion rate in this medium, a situation that is hardly surprising in light of the fact that the compound $K_2MoO_4 \cdot xH_2O$

is soluble in water at 25° C to the extent of 185 g/100 ml.(121)(f) Koger also found for this alloy that the i_{crit} in 0.1 N KOH was scarcely changed by the addition of 0.01 N chloride ion, although that of mulberry was increased by a factor of 50 by such addition.

Accepting the premise that extrapolation of the respective $\log i_{crit}$ vs % addition functions to zero percent addition would yield numbers proportional to the corrosion rate of pure, unalloyed alpha-phase and pure, unalloyed gamma-phase uranium; then, the corrosion rates of the two pure phases are shown to be different by an inspection of Figure 17. In addition, the lower $d(\log i_{crit})/d(at \%)$ for the gamma-phase material compared to the alpha-phase material indicates that a given addition of additive element is relatively more effective in reducing the corrosion rate in alpha-phase than in gamma-phase material. In all probability, continuous additions of increments of one element (such as Nb) would produce a plot of $\log i_{crit}$ vs % addition with a low-niobium slope and a high-niobium slope, the break being at the point where the gamma phase was stabilized at room temperature. This argument, of course, would only apply for comparable heat-treatment conditions.

Correlation of Parameters with Solution Analyses - Analyses of the solutions used in the polarization experiments were performed to determine the pH, uranium content, and chloride and carbonate concentration, both before and after the experiments. Cognizance of the solution pHs has already been taken. The results of the other analyses (on KOH solutions) were statistically correlated with various measured parameters of the polarization experiments on unalloyed α -U, U-3/4 Ti, and mulberry, using the CORREL program. This program is a BASIC-language program which is used in the KRONOS (CDC 6600) time-shared computer system library. Figure 18 gives a listing of the program. Essentially, the correlation coefficient is a number of value $0 < x < 1$ which, together with the degrees of freedom of the system (number of sample pairs - 1), determines the level of confidence to be assigned to the hypothesis that two sets of data are linearly correlated.

No control was exerted over the chloride and carbonate content of the solutions other than the choice of high-purity water and reagent-grade KOH. This limitation meant that the concentrations of these species, in the solutions used, assumed a variety of values which depended on the individual bottle of KOH used. The statistical consequence of this randomization is that specific levels of variables were not used; and, therefore, detailed analysis that might avoid the confounding of variables was not possible. However, it was felt that pairwise correlations might be of interest and, therefore, they were performed for selected parameters and analysis results.

(f) However, (by the relationship of oxide thickness to i_{crit} shown in Figure 13), this value, if taken in exactly the same manner as described in this report, should be even higher than is shown in Figure 17.

```

LIST
  74/02/08. 12.59.09.
PROGRAM CORREL

10 REM THIS PROGRAM COMPUTES A CORRELATION COEFFICIENT FOR TWO SETS
15 REM OF DATA HAVING EQUAL NUMBERS OF ELEMENTS. DATA SHOULD BE
20 REM ENTERED BEGINNING IN LINE 900. MAKE SURE THAT THE DATA LINE
25 REM NUMBERS DO NOT EXCEED 99998. THE FIRST INPUT ITEM IS THE NUMBER
30 REM OF DATA ELEMENTS IN EACH SET, N, WHICH IS FOLLOWED BY THE X AND
35 REM Y VALUES, ENTERED AS PAIRS. AN EXAMPLE OF THE INPUT FORMAT IS
40 REM SHOWN BELOW :
45 REM
50 REM          900 DATA N
55 REM          901 DATA X(1),Y(1),X(2),Y(2),.....X(N),Y(N)
60 REM
65 REM WHERE : N = THE NUMBER OF DATA ELEMENTS IN EACH SET OF DATA
70 REM          X(K) = THE VALUE OF THE KTH DATA ELEMENT IN THE FIRST
75 REM                  SET OF DATA
80 REM          Y(K) = THE VALUE OF THE KTH DATA ELEMENT IN THE SECOND
85 REM                  SET OF DATA
90 REM
100 READ N
110 LET S1 = 0
120 LET S2 = 0
130 LET S3 = 0
140 LET S4 = 0
150 LET S5 = 0
160 FOR I = 1 TO N
170 READ X, Y
180 LET S1 = S1 + X
190 LET S2 = S2 + Y
200 LET S3 = S3 + X*Y
210 LET S4 = S4 + X*X
220 LET S5 = S5 + Y*Y
230 NEXT I
240 PRINT "THE CORRELATION COEFFICIENT = ";
250 LET A = N*S3 - S1*S2
260 LET B = SQR((N*S4 - S1^2)*(N*S5 - S2^2))
270 LET A = INT(A/B*1000+.5)/1000
280 PRINT A
00900 DATA 6
00901 DATA 1.842,2.57,1.764,2.57,1.745,2.76,2.036,2.65,1.638,2.58,
00902 DATA 1.539,2.66
99999 END
READY.

```

Figure 18. LISTING OF THE CORREL PROGRAM USED TO CALCULATE THE SIMPLE CORRELATION COEFFICIENT.

Table 3 summarizes the results of these correlations. Where concentration values are given as "initial" they are the values determined for the solutions before the experiments; where the values are given as "average" the means of the values determined before and after the experiments were used. The uranium concentrations were divided by the number of specimens run per solution to normalize the data on a per-specimen basis. The maximum range of variation of the uranium, chloride, and carbonate concentrations is given in a footnote to Table 3.

The uranium taken into solution from the specimens is correlated with the i_{crit} values best for the unalloyed α -uranium specimens and worst for mulberry. On first thought, it would be expected that there would be a high degree of correlation for all the alloys. It is possible that, at the lower current levels for the mulberry i_{crit} ,

Table 3
SIMPLE CORRELATION COEFFICIENT VALUES FOR THE RELATIONSHIPS
BETWEEN VARIOUS PARAMETERS

Parameter	ppm U Specimen (1)	Log ppm U Specimen (2)	Average Open-Circuit Potential	Log i_{crit}	
				1st Sweep, 1st Specimen	2nd Sweep, 1st Specimen
$\log i_{crit}$ (2nd sweep, 1st specimen)		+ 0.536 (7) + 0.398 (7) + 0.291 (6)			
ave $[Cl^-]$ (3)	+ 0.069 (12) + 0.456 (7) - 0.093 (5)				
ave $[CO_3^{=}]$ (4)	- 0.194 (12) - 0.075 (7) + 0.63 (6)				
$\log [Cl^-]_{init}$ (3)				+ 0.131 (10) + 0.199 (6) - 0.131 (5)	+ 0.003 (7) + 0.553 (7) + 0.261 (6)
$\log [Cl^-]_{ave}$ (3)			+ 0.463 (11) - 0.912 (7) - 0.125 (6)		- 0.074 (7)
$\log [CO_3^{=}]_{init}$ (4)				- 0.122 (10) - 0.033 (6) + 0.055 (5)	+ 0.416 (7) - 0.239 (7) + 0.273 (6)
$\log [CO_3^{=}]_{ave}$ (4)			+ 0.173 (11) + 0.062 (7) + 0.112 (6)		

(1) The values are given in the order: α -U, U-3/4 Ti, and mulberry. Integers in parentheses following the values are the number of sample pairs used in the correlations.

(2) $8 \times 10^{-7} \text{ m} \leq [U] \leq 8 \times 10^{-6} \text{ m}$.

(3) $2.8 \times 10^{-5} \text{ m} \leq [Cl^-] \leq 1.04 \times 10^{-3} \text{ m}$.

(4) $7.7 \times 10^{-4} \text{ m} \leq [CO_3^{=}] \leq 8.2 \times 10^{-3} \text{ m}$.

side reactions are more prominent. The uranium content is also seen to be correlated somewhat with the carbonate concentration for mulberry and with the chloride concentration for U-3/4 Ti. Likewise, the average open circuit potential and i_{crit} (2nd sweep) for U-3/4 Ti are correlated with the chloride concentration. In the case of the average open-circuit potential, there is a correlation to the chloride concentration at the > 99% confidence level. It would also appear that there are some changes in correlation of the i_{crit} values with the chloride and carbonate concentrations between the first and second sweeps. This observation is entirely plausible due to the changing nature of the surface. The surface (oxide?) film is apparently thickening and may be changing in oxidation state and composition (for the alloys).

The significance of these correlations can easily be overestimated, due to the problems just described. However, they point the way to specific experiments which can verify the possible relations seen here; and, what is more important, they illustrate a method for determining, simultaneously, the effect of many components of an environment. Properly performed according to statistical principles, such experiments could give considerable information per unit time invested.

Tests of Surface Treatments - It was found possible to rapidly show the differences in several surface treatments on several alloys using an anodic polarization technique. The surface treatments were electropolishes, applied using several different solutions, with the standard 1- μ m diamond mechanical polish as a reference. The treatments were: (1) none (mechanical polish), (2) $\text{H}_3\text{PO}_4/\text{C}_2\text{H}_4(\text{OH})_2/\text{C}_2\text{H}_5\text{OH}$, (3) CrO_3 /acetic acid, (4) $\text{C}_2\text{H}_5\text{OH}$ /butyl cellusolve/perchloric acid, and (5) $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$.

The alloys used were: α -U, U-1.4 Zr, U-3/4 Ti, and mulberry. The polishing conditions were varied by trial and error to obtain the most perfect bright finish possible. Details of the treatment conditions are given in Appendix E. It was found difficult to obtain a perfect polish using the $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ treatment on any of the alloys but mulberry, so that mulberry was tested using all five surface treatments while the others had only the first four.

The anodic polarization technique consisted in starting from the open-circuit potential assumed by the treated specimen in argon-purged 1 N KOH and carrying the potential in the positive direction, using the potentiostat system in the normal manner. The anodic current typically rose immediately and soon went through the U(IV) oxide $\rightarrow$ U(VI) oxide process, the active/passive transition, and dropped to the i_{pass} . Data for the U-3/4 Ti alloy again showed large postpassive currents which, in this case, cannot be attributed to prior cathodic reduction of trace oxygen. This problem leaves the source of these currents a mystery at this time.

The data show that for all the alloys, the CrO_3 /acetic acid treatment suppresses the current rise furthest in the positive direction, that the $\text{C}_2\text{H}_5\text{OH}$ /butyl cellusolve/perchloric acid treatment actually activates the surface with respect to the mechanically polished condition, and that the other solutions are generally in between these two extremes. Two facts are of note: drastically changing the polishing conditions, as in Figure 19 for (2) and (2'), changes substantially the anodic polarization behavior; and, for mulberry, the perchloric acid treatment has not simply shifted the dissolution curve but has changed the dissolution process, as can be seen by an inspection of Figure 20. There is no explanation for this phenomenon at this time. For all the cases described in Figures 19 - 22, the second cycle through the active/passive transition area was the same as for the nonelectropolished specimens.

CONCLUSIONS

Uranium alloys up to and around an alloying concentration of about 25 atomic percent have essentially the electrochemical behavior associated with pure uranium, due to the predominance of uranium oxides in the composite oxides formed as films on the surface of the alloys. Because of this, the uranium alloys possess a profound dependence for their corrosion properties on the pH of the medium, which is a trait of uranium due to the

Figure 19. ANODIC POLARIZATION CURVES IN ONE-NORMAL POTASSIUM HYDROXIDE OF URANIUM-3/4 TITANIUM SPECIMENS SUBJECTED TO DIFFERENT SURFACE TREATMENTS. (Potentials Referenced to the Saturated Calomel Electrode; (2) -50-Volt Electropolish, (2) -100-Volt Electropolish)

Figure 20. ANODIC POLARIZATION CURVES IN ONE-NORMAL POTASSIUM HYDROXIDE OF MULBERRY SPECIMENS SUBJECTED TO DIFFERENT SURFACE TREATMENTS. (Potentials Referenced to the Saturated Calomel Electrode)

Figure 21. ANODIC POLARIZATION CURVES IN ONE-NORMAL POTASSIUM HYDROXIDE OF ALPHA-URANIUM SPECIMENS SUBJECTED TO DIFFERENT SURFACE TREATMENTS. (Potentials Referenced to the Saturated Calomel Electrode)

Figure 22. ANODIC POLARIZATION CURVES IN ONE-NORMAL POTASSIUM HYDROXIDE OF URANIUM-1.4 ZIRCONIUM SPECIMENS SUBJECTED TO DIFFERENT SURFACE TREATMENTS. (Potentials Referenced to the Saturated Calomel Electrode)

participation of H^+ in the redox reactions involved in corrosion. This broad generality has, however, several qualifying points.

Solubility of the oxide films formed on the alloys is apparently, in general, lower than that of pure uranium oxide films. This difference could be due to the formation of mixed oxides in the films, especially those oxides with a "salt-like" structure,⁽¹¹⁾ of lower solubility than that of the pure uranium oxide films. Such a lower solubility leads directly to a lower rate of anodic (deelectronation) reaction. This effect, in turn, generally leads to a higher value of the (mixed) corrosion potential. "Enrichment" processes of the type proposed for mulberry could profoundly affect the solubility properties of the surface films and may be a factor in the corrosion resistance of such alloys. Another highly speculative possibility in some cases might be the formation of "tungsten bronze"-type compounds^(122, 123) in the surface film, providing a high electronic conductivity and thus a low driving force for ionic migration.

It should be appreciated that general corrosion in aqueous solutions in the presence of oxygen normally proceeds by coupling the anodic dissolution reaction to the $O_2 \rightarrow HO_2^-$ (or H_2O_2) cathodic reaction. The $H^+ \rightarrow H_2$ reaction does not seem to become significant until a low pH is reached; and, even then, it seems to proceed more readily on some uranium alloy surfaces than on uranium surfaces. Low-pH conditions, of course, are achieved in stress-corrosion cracks (SCC) (the faster $H^+ \rightarrow H_2$ kinetics might be one factor in the greater SCC susceptibility of some alloys compared with pure uranium). Factors in the specific corrosion mechanism leading to the accumulation of hydrogen in the region of the surface film and film/metal interface cause increased general corrosion rates. This accumulation of hydrogen can be decreased by increasing the solubility of the metal for hydrogen or by increasing the rate of the $2H_{adsorb} \rightarrow H_2(gas)$ reaction. The H_{adsorb} - H_2 reaction is effectively the same as increasing the exchange current i_0 for the H_2/H^+ equilibrium, and can be electrochemically measured. Other cathodic (electronation) processes can also drive the corrosion reaction, of which $Fe^{+3} \rightarrow Fe^{+2}$ and $NO_3 \rightarrow NO$ are examples.

Electrochemical experiments reported here have strongly suggested that gamma-phase uranium may have a higher corrosion resistance than alpha-phase uranium, the difference being independent of the presence of the alloying elements. This postulate remains to be verified by tests of a variety of alloy systems.

The most promising technique for obtaining absolute corrosion rates of uranium alloys in specific media may be the polarization resistance technique; however, other and somewhat simpler methods, such as potential shifts due to coupling of the anodic dissolution reaction with a redox couple, can give at least qualitative data of the same significance. An interesting example of this method was given by Reid⁽³⁰⁾ for the corrosion of iron samples in sulfuric acid solutions. Another possible technique could be chronopotentiometry at the corroding electrode to reveal the concentration of dissolved uranium species, thus measuring the rate of solubility of the protective film. This study has shown that polarization techniques can reveal differences in surface treatments by a simple test procedure.

At this point, some speculation could be offered on the mechanism for general corrosion of uranium and uranium alloys in oxygenated aqueous environments. The mechanism may involve a rate-determining step consisting of a coupling of the electronation of oxygen to

the deelectronation of a U(IV) oxide, forming a U(VI) oxide which is soluble. This action would tend to thin the oxide film, promoting formation of more U(IV) oxide by reaction of the underlying metal with water. One aspect of this mechanism that needs emphasis is that the oxide structure must be changed during the $\text{U(IV)} \rightarrow \text{U(VI)}$ process, an effect that would be a disruption, probably causing a higher oxide solubility rate than would otherwise exist. Thus, if a film on the metal surface is a U(IV) compound, there are two factors contributing to the corrosion rate: (1) the inherent solubility of the compound, and (2) the disruption caused by the change in structure during the $\text{U(IV)} \rightarrow \text{U(VI)}$ process. Such considerations would lead to the prediction that an oxide film grown under oxidizing conditions [and in the (VI) state] would be superior to one grown under nonoxidizing conditions [and in the (IV) state] with respect to corrosion in oxygenated aqueous environments. This relationship would be separate and independent from the relative inherent solubility of the two films. The example provided by the polarizations, performed on the variously treated surfaces of uranium and its alloys, shows that the phosphate treatment does not suppress the current rise nearly as far in the positive direction as does the chromic acid treatment. Indeed, the suppression is minimal except for mulberry, indicating that, while the uranium in the surface film formed with the other media is in the (IV) state, that formed with the chromic acid medium is in the (VI) state. The current rise for the chromic acid-treated surface, then, may be due largely to direct oxidation of the underlying metal through the surface film (resulting in the destruction of the original compact film). It is not unreasonable that this should occur at potentials higher than those for the $\text{U(IV)} \rightarrow \text{U(VI)}$ reaction. The optimum oxidation state for the uranium in a film on uranium or uranium alloys, at least in oxygenated aqueous environments, would apparently then be the (VI) state.

The inhibitive action of phosphate on uranium corrosion,⁽¹²⁴⁾ under conditions where the (IV) state of uranium would be expected for the surface film, can be interpreted in terms of the disruptive facet of this corrosion mechanism. Schreyer⁽¹²⁵⁾ has shown that U(IV) solutions high in phosphate are quite stable to oxidation by oxygen, and Schreyer and Baes⁽¹²⁶⁾ have shown that similar solutions are more stable to oxidation by Fe(III) than solutions not containing high phosphate concentrations. Therefore, phosphate would seem to retard the $\text{U(IV)} \rightarrow \text{U(VI)}$ process, which would impede corrosion by preventing disruption of the surface film structure. (In the absence of oxygen or another oxidizing species, the mechanism just discussed would not apply; however, the incorporation of hydrogen under these conditions would be a disruptive process, albeit of a different type.)

It would appear from the data presented here that oxides formed on the metal surfaces in solution are more highly hydrated at lower pH values. A complementary thesis would be that, in addition, at a very low pH, the oxide film material is more soluble than at medium or high pH values. This solubility would tend to create a thinner film. Since the electric field strength in the oxide film cannot exceed a given material-dependent value, the potential at the electrode would necessarily drop. In essence, lower-valence processes such as $\text{U} \rightarrow \text{U}^{+3}$ and $\text{U}^{+3} \rightarrow \text{U}^{+4}$ (with a lower equilibrium potential) would begin to affect the value of the (mixed) corrosion potential. Hydrogen charging, or presence of the chloride ion, should complicate this picture. Chloride ion has been seen to lower the potential of oxidized uranium and uranium alloy specimens. Operationally, the only conclusion that can be drawn from this fact is that the rate of the anodic (deelectronation) process has increased (and lower-valent processes have begun to participate in the mixed potential), shifting the (mixed) corrosion potential in the negative direction.

The complexity of the variables involved in corrosion dictates the use of statistical methods in planning and analyzing electrochemical studies of corrosion. Cleary and Greene,⁽¹²⁷⁾ and Legault, et al,⁽²⁰⁾ have used such methods to study the effects of material and environmental composition on the corrosion rate of iron and steels.

In brief, electrochemical methods can effectively be used to study many fundamental and practical aspects of corrosion behavior of uranium alloys.

APPENDIX

FUNDAMENTALS OF CORROSION ELECTRODICS

Definition of the Corrosion Process in Electrochemical Terms

Variables Usable in Electrochemical Corrosion Studies

Specific Electrochemical Methods Used to Study Corrosion(28,29)

APPENDIX B

SURFACE PREPARATION OF ALPHA-URANIUM AND URANIUM ALLOY SPECIMENS FOR ELECTROCHEMICAL STUDIES

Objective of the specimen preparation is to provide a flat, distortion-free surface of known area for exposure to a variety of conditions of electrochemical studies.

To meet this objective it is necessary to mount the specimen in a stable, nonconducting, nonreacting mounting material. Ciba-Geigy epoxy (Araldite 502) and hardener (TETA 951) were chosen to give a room-temperature curing medium with all the other needed characteristics. Specimens are degreased; and, when surface oxide is present it is removed before mounting in epoxy.

Mechanical polishing is the preferred method of specimen preparation to achieve the flatness to give an easily measured surface area. Samuels⁽¹²⁸⁾ has shown that despite fears of the "Beilby layer" (an amorphous layer considered by some to be approximately 50 angstroms thick), a true structure can be exposed by careful mechanical polishing. It is his opinion also that complex films are left on electropolished surfaces that may cause variation in subsequent electrochemical studies. Electropolishing gives an undulating surface with inclusions vigorously attacked and any void enlarged; and, often, a preferential attack on certain phases in the case of alloys. For these reasons, the distortionless, scratch-free surface from electropolishing did not seem to be consistent with the needs of the bulk of this study. Effects of the surface preparation of some specimens are discussed in Appendix E.

After careful grinding on silicon carbide papers, a diamond polishing sequence is used. This process gives a flat surface, but at the price of having some fine scratches remain. It is a fast method, especially when compared to vibratory polishing, and is suitable for hand polishing that is preferred as the best way to protect the contact wire that extends from the back of the specimen mount.

Use of alcohol as a polishing lubricant has the advantage over most diamond lubricants of being more easily removed after polishing with no oily residue to "ooze" from voids or around specimen edges and contaminate the surface.

Table B-1 outlines the grinding and polishing sequence.

After polishing, a photomacrograph at approximately 10X records the surface area and any gross irregularities of the specimen surface, such as voids and inclusions. The microstructure is then developed with a suitable etch to establish the condition of the metal; ie, cold worked, annealed, or cored (if a casting), and the necessary photomicrographic record made. The specimens are then repolished to remove the etched surface and produce a clean, "as-polished" surface for the electrochemical studies.

Table B-1
STEPS IN GRINDING AND POLISHING ALPHA URANIUM
AND URANIUM ALLOYS

Step (1)	Polishing/Grinding Media and Backing Material	Abrasive Size	Time	Comments
1	SIC, Paper	180 Grit	Necessary to Flatten	Coarse grinding; rotating lap.
2	SIC, Paper	320 Grit	Necessary to Remove Prior Scratches	Still lap.
3	SiC, Paper	400 Grit	Necessary to Remove Prior Scratches	Still lap.
4	SiC, Paper	600 Grit	Necessary to Remove Prior Scratches	Fine grinding; still lap.
5				Ultrasonic cleaning.
6	Diamond on Cotton (Metcloth)	6 μm	5 Min (avg)	Time varied to remove prior abrasive scratches.
7	Diamond on Nylon	3 μm	5 Min (avg)	Time varied to remove prior abrasive scratches.
8	Diamond on Gamal	1 μm	5 Min (avg)	Time varied to remove prior abrasive scratches.
9				Ultrasonic cleaning in alcohol.

- (1) Notes: 1. In all procedures, the specimen is hand held.
 2. All grinding is done with water as the lubricant and coolant.
 3. All polishing is lubricated with ethanol and most often is on a still lap.
 4. Specimens are cleaned ultrasonically between the polishing steps.

APPENDIX C

EFFECT OF THE SWEEP RATE ON POLARIZATION CURVES

In much of the electrochemical literature that describes polarization work using potentiodynamic methods, there are attempts to justify the use of potential sweep rates of smaller and smaller dE/dt , as approaching "steady-state" conditions. In fact, very low potential sweep rates are not necessary for examining some electrochemical properties of some systems. What is necessary is that the properties examined be a regular function of the sweep rate and that this function be taken into account in the interpretation of the results. Reinehl, et al,⁽³¹⁾ in a study of current densities in the passive region of iron in 1 N H_2SO_4 , as a function of the polarization rate, have shown these currents (within the range of sweep rates studied) to be a regular function of the logarithm of the sweep rate. Morris and Scarberry⁽¹¹⁷⁾ have shown the utility of fast potential sweep rates in their investigation of the corrosion of nickel alloys in sulfuric acid solutions. Their studies permitted the isolation of the true anodic curve for the alloys free of interference by self passivation.

The decision to use high potential sweep rates in this study was made for two reasons: (1) these studies were to be a survey of the overall electrochemical properties of numerous uranium alloys in several environments, entailing the performing of a large number of experiments in a reasonable period of time, and (2) it was decided that the marked and irreversible changes in surface constitution accompanying lengthy transits over extended potential ranges would not be acceptable. Justification of this approach can be found in Figure C-1 wherein the Tafel slope ($dE/d \log i$) for the process $U(IV)$ oxide $\rightarrow$ $U(VI)$ oxide, and the critical potential for passivation (E_{crit}) from this process are plotted as a function of the logarithm of the sweep rate in volts per second. The materials were alpha uranium and U-1.2 Ti; the polarizations were performed in 1 N KOH. It is seen that both parameters are generally a regular function of the sweep rate.

It would be appropriate at this time to offer some comments on the significance of Tafel slopes in regard to the types of reactions just mentioned. Linear (Tafel) regions in $\log i$ vs E plots are a result of electron-transfer control, as described by the Butler-Volmer equation. One implicit assumption in the Butler-Volmer equation is that the concentration of reactant species at the electrode surface [for redox reactions on inert electrodes, this location is the outer Helmholtz plane (OHP)] is constant. If (as an example) the UO_2 film is being oxidized to a $U(VI)$ oxide, two limiting cases could exist: (1) that the kinetics of dissolution of the $U(VI)$ oxide is rapid enough to present the solution with a fresh plane of UO_2 throughout the oxidation, or (2) that the kinetics of dissolution of the $U(VI)$ oxide is slow enough so that the UO_2 layer gradually (from the outside in) becomes a $U(VI)$ oxide layer. These two limiting cases would lead to entirely different $E-i$ relationships. [These considerations can be complicated by factors such as oxide porosity and conductivity, which can make valency change processes (effectively) bulk processes instead of diffusion-layer processes.] It may be noted that Katz and Rabinowitch report the solubility of $UO_3 \cdot 2H_2O$, in water at $27^\circ C$, to be 0.16 g/l ($4.52 \times 10^{-4} M$).⁽¹²⁹⁾ Gayer and Leider report the solubility of $UO_3 \cdot H_2O$ in water at $25^\circ C$ to be $3.95 \times 10^{-5} M$, and in 0.77 M NaOH to be $1.47 \times 10^{-4} M$.⁽¹³⁰⁾

Figure C-1. TAFEL SLOPE FOR THE PROCESS U (IV) OXIDE $\rightarrow$ U (VI) OXIDE, AND E_{crit} FOR PASSIVATION FROM THIS PROCESS, PLOTTED AS A FUNCTION OF THE LOGARITHM OF THE SWEEP RATE. (Utilizing Data Obtained from the Polarization of Alpha Uranium and U-1.2 Ti Alloy in One-Normal Potassium Hydroxide)

APPENDIX D

ESTIMATION OF i_{crit} AT A pH OF 13.76 FROM DATA AT A pH OF 12.72

Estimation of i_{crit} for U-10 Mo for the 1.0 N KOH medium, from the value obtained at 0.1 N KOH, was based on an empirically found relationship. Log of the current density of the process: U(IV) oxide $\rightarrow$ U(VI) oxide, and the pH of the medium to which no components other than KOH were added, were found to be linearly related, as illustrated in Figure D-1. The potentials at which the current densities were measured are indicated next to each point and were chosen by picking an optimum potential in the Tafel region of the process in 1 N KOH, then changing this potential by $(-0.0591 \times \Delta pH)$ for each pH unit change. This method provides a constant overpotential for the process, compensating for the change in position of the U(IV) oxide/U(VI) oxide equilibrium with change in pH. The slope is essentially the same for alpha uranium and for mulberry; therefore, the average value (0.86/pH) was used to correct the i_{crit} for U-10 Mo from -3.92 at 0.1 N KOH (pH = 12.72) to -3.03 at 1.0 N KOH (pH = 13.76).

Figure D-1. LOGARITHM OF THE CURRENT DENSITY OF THE PROCESS U (IV) OXIDE $\rightarrow$ U (VI) OXIDE AS A FUNCTION OF THE pH IN A MEDIUM TO WHICH NO COMPONENTS OTHER THAN POTASSIUM HYDROXIDE WERE ADDED. (Changing Ionic Strength)

APPENDIX E

ELECTROLYTIC POLISHING OF ALPHA-URANIUM AND URANIUM-ALLOY SPECIMENS FOR ELECTROCHEMICAL STUDIES

Samples of α U, U-1.4 Zr, U-0.8 Ti (nonhomogenized), U-0.75 Ti (homogenized), and mulberry were spot welded to platinum wires and potted into standard one-inch Araldite (epoxy) metallographic mounts. Surface preparation for electropolishing was that given in Appendix B, ending with 1- μ m diamond in all but one case. A perchloric acid electropolish works best on a 6- μ m finish. This observation is in agreement with that mentioned by Tegar⁽¹³¹⁾ that some electropolish solutions work best on less finely polished surfaces, although the great majority of electropolish solutions give the best final surface from a highly polished mechanical prepolish.

The Disa Electropol pumps solution across the face being polished, providing fresh electrolyte to the surface as it sweeps away the viscous layer produced in the cell (that has a 1/4-inch electrode spacing). This sweeping action can produce a badly distorted surface, as can the voltage applied and time of polish. The best conditions were arrived at by trial and error, and the samples were prepared with the least rigorous treatment which would clean up the surface and leave it bright. The controls available with this electropolisher [ie, polishing time, electrode distance, agitation of electrolyte (flow rate), and voltage] were desirable so that as far as possible all specimens received an equivalent electropolishing treatment.

The four solutions used as electrolytes were: phosphoric acid/glycol/alcohol, chromic acid/acetic acid, alcohol/butyl cello-

Table E-1
PREPARATION OF THE
ELECTROPOLISHING SOLUTION

Solution	Formulation (parts by volume)
1. Phosphoric/ Glycol/ Alcohol	Mix 8 parts ethanol with 5 parts ethylene glycol and 5 parts orthophosphoric acid.
2. Chromic/ Acetic	Dissolve 118 grams of CrO_3 in 100 ml H_2O . Use 1 part of this solution with 4 parts of glacial acetic acid.
3. Alcohol/ Butyl Cellosolve/ Perchloric Acid	Mix 7 parts ethanol and 1 part 2-butoxyethanol (butyl cellosolve) with 2 parts perchloric acid (30%).
4. Phosphoric/ Sulfuric/ Water	Mix 1 part H_3PO_4 and 2 parts H_2SO_4 with 2 parts H_2O .

Table E-2
ELECTROPOLISHING CONDITIONS FOR
ALPHA URANIUM

Conditions	Solutions ⁽¹⁾		
	1	2	3 ⁽²⁾
Flow Setting ⁽³⁾	0	0	5
Voltage (V)	40	30	25
Current ⁽⁴⁾ (A)	~ 0.1	0.2	~ 0.9
Time (sec)	12	10	9

(1) Solution number as given in Table E-1.

(2) All samples were subjected to a 6- μ m diamond finish prior to the electropolish.

(3) On the Disa Electropol polishing apparatus.

(4) The typical surface area was $\sim 0.32 \text{ cm}^2$. Current values preceded by the approximation symbol (~) were variable during or between runs.

Table E-3
ELECTROPOLISHING CONDITIONS FOR
URANIUM-0.8 TITANIUM
(Nonhomogenized)

Conditions	Solutions ⁽¹⁾		
	1	2	3 ⁽²⁾
Flow Setting ⁽³⁾	0	0	7
Voltage (V)	40	30	25
Current ⁽⁴⁾ (A)	~ 0.1	0.2	0.75
Time (sec)	12	10	11.5

- (1) Solution number as given in Table E-1.
 (2) All samples were subjected to a 6- μ m diamond finish prior to the electropolish.
 (3) On the Disa Electropol polishing apparatus.
 (4) The typical surface area was ~ 0.32 cm². Current values preceded by the approximation symbol (~) were variable during or between runs.

Table E-4
ELECTROPOLISHING CONDITIONS FOR
URANIUM-0.75 TITANIUM
(Homogenized)

Conditions	Solutions ⁽¹⁾		
	1	2	3 ⁽²⁾
Flow Setting ⁽³⁾	1 (0)	0	9
Voltage (V)	50 (100)	30	31
Current ⁽⁴⁾ (A)	~ 0.17 (1.2)	0.15	~ 1.2
Time (sec)	20 (10)	10	5.5

- (1) Solution number as given in Table E-1.
 (2) All samples were subjected to a 6- μ m diamond finish prior to the electropolish.
 (3) On the Disa Electropol polishing apparatus.
 (4) The typical surface area was ~ 0.32 cm². Current values preceded by the approximation symbol (~) were variable during or between runs.

Table E-5
ELECTROPOLISHING CONDITIONS FOR
URANIUM-1.4 ZIRCONIUM

Conditions	Solutions ⁽¹⁾		
	1	2	3 ⁽²⁾
Flow Setting ⁽³⁾	0	0	9
Voltage (V)	40	30	40
Current ⁽⁴⁾ (A)	0.07	~ 0.2	1.2
Time (sec)	10	10	3

- (1) Solution number as given in Table E-1.
 (2) All samples were subjected to a 6- μ m diamond finish prior to electropolish.
 (3) On the Disa Electropol polishing apparatus.
 (4) The typical surface area was ~ 0.32 cm². Current values preceded by the approximation symbol (~) were variable during or between runs.

Table E-6
ELECTROPOLISHING CONDITIONS
FOR MULBERRY

Conditions	Solutions ⁽¹⁾			
	1	2	3 ⁽²⁾	4
Flow Setting ⁽³⁾	0	2	9	5
Voltage (V)	100	50	35	25
Current ⁽⁴⁾ (A)	1.0	~ 0.5	~ 1.3	1
Time (sec)	10	10	6	15

- (1) Solution number as given in Table E-1.
 (2) All samples were subjected to a 6- μ m diamond finish prior to electropolish.
 (3) On the Disa Electropol polishing apparatus.
 (4) The typical surface area was ~ 0.32 cm². Current values preceded by the approximation symbol (~) were variable during or between runs.

solve/perchloric acid, and phosphoric acid/sulfuric acid/water. Their preparations are described in Table E-1. All specimens were electropolished using the conditions given in Tables E-2 through E-6.

REFERENCES

- (1) Moore, W. J.; "Electrochemical Cells", *Physical Chemistry*, pp 379 - 413; Prentice-Hall, Englewood Cliffs, New Jersey (1962).
- (2) Pourbaix, M. J. N.; *Atlas of Electrochemical Equilibria* (translated from the French by J. A. Franklin); Pergamon Press, Oxford (1966).
- (3) Bockris, J. O'M. and Reddy, A. K. N.; *Modern Electrochemistry*, 2, pp 738 - 752; Plenum Press, New York (1970).
- (4) *Ibid*; p 706.
- (5) *Ibid*; p 876.
- (6) *Ibid*; p 879.
- (7) *Ibid*; p 1052.
- (8) *Ibid*; p 1072.
- (9) Tomashov, N. D. and Chernova, G. P.; *Passivity and Protection of Metals Against Corrosion*, (translated from the Russian by B. H. Tytell; Translation Editor, H. H. Uhlig); Plenum Press, New York (1967).
- (10) West, J. M.; *Electrodeposition and Corrosion Processes*, pp 41 - 43; Van Nostrand Reinhold, London (1971).
- (11) Hoar, T. P.; "On Corrosion-Resistant Materials", *J Electrochem Soc*, 117, (1), pp 17C - 22C (1970).
- (12) Bockris and Reddy; *Op Cit*; p 1291.
- (13) Andersen, T. N., Anderson, J. L., and Eyring, H.; "The Nature of Fresh Metal Surfaces in Aqueous Solutions", *J Phys Chem*, 73, (11), pp 3562 - 3570 (1969).
- (14) Bullock, J. S. and Condon, J. B.; *Electrochemical and Other Studies of a Uranium Alloy Exhibiting Stress-Corrosion Cracking*, Y-1821; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; February 29, 1972.
- (15) Tegart, W. J. McG.; *The Electrolytic and Chemical Polishing of Metals*; Pergamon Press, London (1959).
- (16) Moore; *Op Cit*; p 348.
- (17) *Ibid*; p 126.

- (18) Foley, R. T.; *The Role of Chloride Ion in Corrosion, Part II*; The American University, Washington, DC; Office of Naval Research, Contract N-00014-66-C-0225; NBS Clearinghouse AD-686-518.
- (19) Putilova, I. N., Balezin, S. A., and Barannik, V. P.; *Metallic Corrosion Inhibitors* (translated from the Russian by G. Ryback; Translation Editor, E. Bishop); Pergamon Press, New York (1960).
- (20) Legault, R. A., Mori, S., and Leckie, H. P.; "An Electrochemical-Statistical Study of Mild Steel Corrosion Inhibition in Oxygen Containing Environments", *Corrosion*, 27, (10), pp 418 - 423 (1971).
- (21) Rajagopalan, K. S., Venu, K., and Balakrishnan, K.; *J Sci Ind Res (India)*, 20D, pp 358 - 359 (1961); in Foley; *Op Cit*; p 11.
- (22) Bockris and Reddy; *Op Cit*; p 1055.
- (23) *Ibid*; p 1143.
- (24) Jones, D deG. and Masterson, H. G.; "Techniques for the Measurement of Electrode Processes at Temperatures above 100° C", *Adv in Corr Sci and Tech*, 1, pp 1 - 49 (1970).
- (25) MacDonald, D. D., Shierman, G. R., and Butler, P.; *The Thermodynamics of Metal-Water Systems at Elevated Temperatures, Part 3: The Cobalt-Water System*, AECL-4138; Atomic Energy of Canada, Limited (1972).
- (26) Hills, G. J. and Ovenden, P. J.; "Electrochemistry at High Pressures", *Advances in Electrochemistry and Electrochemical Engineering*, 4, (Edited by P. Delahay); Interscience; New York (1966).
- (27) Ward, J. W. and Waber, J. T.; "The Electrochemical Behavior of Uranium", *J Electrochem Soc*, 109, (2), p 80 (1962).
- (28) Delahay, P.; *New Instrumental Methods in Electrochemistry*; Interscience, New York (1954).
- (29) Damaskin, B. B.; *The Principles of Current Methods for the Study of Electrochemical Reactions* (translated from the Russian by G. Mamantov); McGraw-Hill, New York (1967).
- (30) Reid, W. E., Jr; "Dissolution of Iron in Sulfuric Acid Solutions", *Corrosion*, 27, (10), pp 407 - 471 (1971).
- (31) Reinoehl, J. E., Beck, F. H., and Fontana, M. G.; "Effect of Polarization Rate in Potentiokinetic Anodic Polarization of Iron in 1 N H₂SO₄", *Corrosion*, 26, (4), pp 141 - 150 (1970).
- (32) Damaskin; *Op Cit*; p 61.

- (33) Isaacs, H. S. and Leach, J. S. LI.; "Valency Changes in the Surface Oxide Films on Metals", *J Electrochem Soc*, 110, (6), pp 680 - 687 (1963).
- (34) Leach, J. S. LI and Nehru, A. Y.; "The Effect of an External Electrical Field on the Oxidation Rate of U", *Corrosion Science*, 9, pp 447 - 453 (1969).
- (35) Andrews, C. L.; "Interference in Thin Films", *Optics of the Electromagnetic Spectrum*, pp 159 - 194; Prentice-Hall, Englewood Cliffs, New Jersey (1960).
- (36) Reddy, A. K. N. and Bockris, J. O'M.; "Ellipsometry in Electrochemical Studies", *Proceedings of the Symposium on the Ellipsometer and Its Use in the Measurement of Surfaces*, US Nat Bur Stand Misc Publication 256, pp 229 - 244 (1963).
- (37) Myamlin, V. A. and Pleskov, Yu. V.; *Electrochemistry of Semiconductors* (translated from the Russian); Plenum Press, New York (1967).
- (38) Tomashov, N. D.; *Theory of Corrosion and Protection of Metals* (translated and edited by B. H. Tytell, I. Geld, and H. S. Preiser); MacMillan, New York (1966).
- (39) Uhlig, H. H.; *Corrosion and Corrosion Control*; John Wiley and Sons, New York (1963).
- (40) Hampel, C. A. (Editor); *The Encyclopedia of Electrochemistry*; Reinhold, New York (1964).
- (41) Hoare, J. P.; *The Electrochemistry of Oxygen*; Interscience, New York (1968).
- (42) *Manual of Symbols and Terminology for Physico-Chemical Quantities and Units*, International Union of Pure and Applied Chemistry; Butterworths, London (1970).
- (43) Cotton, F. A. and Wilkinson, G.; "The Actinide Elements", *Advanced Inorganic Chemistry*, pp 891, 898; Interscience (1962).
- (44) Katz, J. J. and Rabinowitch, E.; *The Chemistry of Uranium*; McGraw-Hill, New York (1951).
- (45) Belle, J. (Editor); *Uranium Dioxide: Properties and Nuclear Applications*, United States Atomic Energy Commission (1961).
- (46) Cotton and Wilkinson; *Op Cit*; pp 891 - 902, pp 908 - 914.
- (47) Chernyaev, I. I. (Editor); *Complex Compounds of Uranium* (translated from the Russian by L. Mandel); Israel Program for Sci Trans, Jerusalem (1966).
- (48) Fields, P. R. and Moeller, T. (Chairmen); *Lanthanide/Actinide Chemistry* (a symposium); Adv in Chem, Series 71; Amer Chem Soc, Washington, DC (1967).
- (49) Tsymbal, C.; "Contribution a la Chimie de l'Uranium(VI) en Solution", *Centre d'Etudes Nucleaires de Grenoble, Rapport CEA-R-3476*.

- (50) Caja, J. and Pravdic, V.; "Contribution to the Electrochemistry of Uranium(V) in Carbonate Solutions", *Croatia Chemica Acta*, 41, pp 213 - 222 (1969).
- (51) Stabrovskii, A. I.; "Oxidation-Reduction Potential on Platinum Electrode in Solutions Containing Salt Mixtures of U(VI) and U(IV) and Equilibrium Concentration of U(V) Ions in the System U(VI) - U(V) - U(IV)", *Elektrokhimiya*, 6, (10), pp 1471 - 1477 (1970).
- (52) Chadwick, P. H. and McGowan, I. R.; "Determination of Plutonium and Uranium in Mixed Oxide Fuels by Sequential Redox Titration", *Talanta*, 19, pp 1335 - 1348 (1972).
- (53) Goto, M. and Ishii, D.; "Chronopotentiometry in Strong Phosphoric Acid. II. Chronopotentiometry of Uranium (VI) Ion in Strong Phosphoric Acid", *Nippon Kagaku Zasshi*, 91, pp 343 - 346 (1970).
- (54) Adegitte, A. and Ford-Smith, M. H.; "Kinetics of the Oxidation of Uranium (IV) Ions by Halogens in Aqueous Solution. Part I. Iodine and Bromine; Part II. Chlorine", *J Chem Soc*, pp 134 - 143; Dalton Transactions (1973).
- (55) deZoubov, N.; "Actinides", *Atlas of Electrochemical Equilibria*, by Pourbaix, M. J. N. (translated from the French by J. A. Franklin), pp 198 - 212; Pergamon Press, Oxford (1966).
- (56) *Uran and Isotope*, System-Nummer 55, aus *Gmelins Handbuch der anorganischen Chemie*, p 64; Verlag Chemie, Berlin (1936).
- (57) Muthmann, W. and Fraunberger, F.; *Ber Bayr Akad*, 34, pp 205, 207, 221 (1904).
- (58) Sborgi, U.; *Z Elektrochemie*, 19, p 115 (1913).
- (59) West; *Op Cit*; pp 112 - 114.
- (60) Hoar, T. P., Mears, D. C., and Rothwell, G. P.; "The Relationships Between Anodic Passivity, Brightening, and Pitting", *Corrosion Sci*, 5, pp 279 - 289 (1965).
- (61) Chipman, J.; *Metallurgy in the Development of Atomic Power*, United States Atomic Energy Commission Publication MDDC 539 (1946).
- (62) Jacquet, P. A. and Caillet, R.; "Electrolytic Polishing of U for Physicochemical and Metallographic Studies", *Comptes Rendus*, 228, p 1224 ff (1949).
- (63) Mott, B. W. and Haines, H. R.; "The Electrolytic Polishing and Etching of Uranium", *Metallurgia*, 43, pp 255 - 257 (1951).
- (64) Kocik, J., Mance, A., and Mihajlovic, A.; "The Use of the Potentiostat in the Microstructural Examination of Uranium", *J Nucl Mat*, 37, pp 243 - 247 (1970).

- (65) Katz and Rabinowitch; *Op Cit*; p 301.
- (66) Flint, O., Polling, J. J., and Charlesby, A.; "The Anodic Oxidation of Uranium", *Acta Metallurgica*, 2, pp 696 - 712 (1954).
- (67) Young, L.; *Anodic Oxide Films*, pp 273 - 274; Academic Press, London (1961).
- (68) Stebbens, A. E. and Shreir, L. L.; "Refractive Index of Uranium Oxide Produced by Anodic Oxidation", *Nature*, 183, p 1113 ff (1959).
- (69) Vijh, A. K.; "Influence of Bond Energies of Oxides on the Kinetics of Anodic Oxide Growth on Valve Metals", *J Electrochem Soc*, 116, pp 972 - 975 (1969).
- (70) Jouve, G., Aucouturier, M., and Lacombe, P.; "Sur le Comportement Electrochimique de l'Electrode d'Uranium au Contact de Solutions Aqueuses et sur la Nature des Phases Formees en Fonction du pH", *Comptes Rendus, t.272 Serie C*, pp 598 - 601 (1971).
- (71) Jouve, G., Aucouturier, M., and Lacombe, P.; "Etude Cinetique de la Croissance des Couches d'Oxyde Anodique sur l'Uranium en Milieu Basique par Une Methode Interferometrique en Continu", *J Nucl Mat*, 39, pp 339 - 344 (1971).
- (72) Jouve, G.; "Sur les Proprietes Electriques d'Une Couche d'Oxyde Anodique Formee sur l'Uranium a Potential Controle en Milieu de pH 13", *J Nucl Mat*, 41, pp 221 - 226 (1971).
- (73) Jouve, G.; *Relations entre les Proprietes Structurales et Electriques des Films d'Oxydes Anodiques*, Formes sur l'Uranium, et le Comportement Electrochimique du Metal en Milieu Aqueux, *Centre d'Etudes de Bruyeres-le-Chatel, Rapport CEA-R-4374*.
- (74) Leach, J. S. LI. and Nehru, A. Y.; "The Corrosion of Uranium, Zirconium, and Some Alloys in Alkaline Solutions", *J Electrochem Soc*, 111, (7), pp 781 - 787 (1964).
- (75) Leach, J. S. LI.; "Some Properties of Oxide Films Formed During Aqueous Corrosion", *J Inst Metals*, 88, pp 24 - 30 (1959 - 60).
- (76) Elsayed, A. A.; *Corrosion Behavior of Uranium and Other Transition Metals in Relation to the Properties of the Surface Oxide Films*, Thesis, London University (1969):Cited in *Nucl Sci Abst*, 23, (18); 36001.
- (77) Draley, J. E. and Ruther, W. E.; "Some Unusual Effects of Hydrogen in Corrosion Reactions", *J Electrochem Soc*, 104, (6), pp 329 - 333 (1957).
- (78) McGeary, R. K. (Editor); *Development and Properties of Uranium-Base Alloys Corrosion Resistant in High Temperature Water. Part I.*, Westinghouse Electric Corporation, Report WAPD-127; April 25, 1955.
- (79) Baker, M. McD., Less, L. N., and Orman, S.; "Uranium + Water Reaction; Part I - Kinetics, Products and Mechanism", *Trans Faraday Soc*, 62, pp 2513 - 2524 (1966).

- (80) Leach, J. S. LI.; "Surface Films and the Breakaway Corrosion of Uranium", *Nature*, 182, pp 1085 - 1086 (1958).
- (81) Isaacs, H. S.; *The Cathodic Behavior of Gamma Uranium 10% Mo Alloy*, DIC Dissertation; Imperial College of Sci and Tech; November 1960.
- (82) Isaacs, H. S. and Leach, J. S. LI.; "Some Aspects of the Parallel Differential Conductance Measured at an Electrode-Electrolyte Interface", *J Electrochem Soc*, 115, (3), pp 237 - 242 (1968).
- (83) Slaidin, G. Ya.; "Diffusion of Protons Through Oxide Electrodes", *Elektrokhimiya*, 8, (12), pp 1783 - 1785 (1972).
- (84) Schroeder, J. B., Vaughan, D. A., and Schwartz, C. M.; "Aqueous Uranium Corrosion at 100° C", *J Electrochem Soc*, 106, (6), pp 486 - 489 (1959).
- (85) Baker, M. McD., Less, L. N., and Orman, S.; "Uranium + Water Reaction: Part II - Effect of Oxygen and Other Gases", *Trans Faraday Soc*, 62, pp 2525 - 2530 (1966).
- (86) Butler, G. and Ison, H. C. K.; *Corrosion and Its Prevention in Waters*, pp 97 - 98; Reinhold, New York (1966).
- (87) West; *Op Cit*; p 141.
- (88) Werd and Waber; *Op Cit*; pp 76 - 81.
- (89) Jenks, G. H.; *Electrochemistry of Uranium and Uranium Alloys in Aqueous Solutions*, ORNL-4651; Union Carbide Corporation-Nuclear Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; June 1971.
- (90) Seitz, F.; *The Modern Theory of Solids*, p 70; McGraw-Hill, New York (1940).
- (91) Leach, J. S. LI. and Nehru, A. Y.; "The Temperature Dependence of the Corrosion of Uranium in Aqueous Solutions", *J Nuclear Mat*, 13, (2), pp 270 - 274 (1964).
- (92) Zehr, S. W.; "A Study of the Intergranular Cracking of U-7.5 Wt % Nb-2.5 Wt % Zr (Mulberry) Alloy in Aqueous Chloride Solutions", *Corrosion*, 28, (5), pp 196 - 205 (1972).
- (93) Stephenson, L. L.; *A Survey of Factors Which Influence Stress Corrosion Crack Initiation in Several Uranium Base Alloys*, SC-DR-70-718; Sandia Laboratories; October 1970.
- (94) Macki, J. M. and Kochen, R. L.; *The Galvanic Corrosion Behavior of Uranium Alloys in Hydrochloric Acid and Ocean Water*, RFP-1592; Dow Chemical Company, Rocky Flats, Colorado; February 24, 1971.

- (95) Macki, J. M. and Kochen, R. L.; *The Corrosion Behavior of Uranium-Base U-Nb, U-Nb-Zr, and U-Mo Alloys in Hydrochloric Acid and Ocean Water*, RFP-1586; Dow Chemical Company, Rocky Flats, Colorado; February 26, 1971.
- (96) Weirick, L. J.; to be published.
- (97) Weirick, L. J.; to be published.
- (98) Jackson, R. J. and Wickland, C. E.; *Electrocleaning of Uranium Alloys*, RFP-1596; Dow Chemical Company, Rocky Flats, Colorado.
- (99) Holden, A. N.; *Physical Metallurgy of Uranium*, p 144; Addison-Wesley, Reading, Massachusetts (1958).
- (100) Johnson, J. R.; *Personal Communication*; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee.
- (101) Wernick, J. H.; "Topologically Close-Packed Structures", *Intermetallic Compounds*, p 213 (Edited by J. H. Westbrook); John Wiley and Sons, New York (1967).
- (102) Allen, G. C. and Tucker, P. M.; "Surface Oxidation of Uranium Metal as Studied by X-ray Photoelectron Spectroscopy", *J Chem Soc Dalton Trans*, p 470 - 474 (1973).
- (103) Maraghini, M., Deltombe, E., deZoubov, N., Van Rysselberghe, P., and Pourbaix, M.; "Zirconium", *Pourbaix, Ref 2*, pp 223 - 229.
- (104) Bullock, J. S. and Brown, A. D.; unpublished work.
- (105) Wagner, C. and Traud, W.; "Über die Deutung von Korrosions-Vorgängen durch Überlagerung von Elektrochemischen Teilvorgängen und über die Potentialbildung an Mischelektroden", *Z für Elektrochemie Bd, 44, (7)*, pp 391 - 402 (1938).
- (106) Stern, M. and Geary, A. L.; "Electrochemical Polarization. I", *J Electrochem Soc*, 104, (1), pp 56 - 63 (1957).
- (107) Oldham, K. B. and Mansfeld, F.; "On the So-Called Linear Polarization Method for Measurement of Corrosion Rates", *Corrosion*, 27, (10), pp 434 - 435 (1971).
- (108) Mansfeld, F.; "Tafel Slopes and Corrosion Rates from Polarization Resistance Measurements", *Corrosion*, 29, (10), pp 397 - 402 (1973).
- (109) Isaacs and Leach; *Op Cit*; p 684.
- (110) Meredith, K. E. G. and Waldron, M. B.; "Inclusions in Uranium Metal", *J Inst Metals*, 87, pp 311 - 317 (1958 - 59).
- (111) Sears, M. B. and Ferris, L. M.; *Rates of Gas Evolution from the Reactions of Uranium and Thorium Carbides with Aqueous Solutions of HCl, H₂SO₄, NaOH, and NH₄F*,

- ORNL-4381; Union Carbide Corporation-Nuclear Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- (112) Nolan T. A.; *Personal Communication*; Union Carbide Corporation-Nuclear Division, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee.
- (113) Sladky, R. E.; *An Ellipsometric Study of the Corrosion of Uranium and Uranium-7.5 Weight Percent Niobium-2.5 Weight Percent Zirconium Alloy*, Y-1829; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee (1972).
- (114) Larson, D. T., Lott, L. A., and Cash, D. L.; *Surface Film Thickness Determination by Reflectivity Measurements*, RFP-1911; Dow Chemical Company, Rocky Flats, Colorado.
- (115) Ferguson, J. R.; *Personal Communication*; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee.
- (116) Gerischer, R. and Gerischer, H.; *Z Physik Chem (Frankfurt)*, 6, p 178; Cited in Hoare, *Op Cit*, pp 136 - 137 (1956).
- (117) Morris, P. E. and Scarberry, R. C.; "Predicting Corrosion Rates with the Potentiostat", *Corrosion*, 28, (12), pp 444 - 452 (1972).
- (118) Bockris and Reddy; *Op Cit*; pp 1318 - 1321.
- (119) Koger, J. W.; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; unpublished work.
- (120) Draley, J. E., Greenberg, S., and Ruther, W. E.; *The High Temperature Aqueous Corrosion of Uranium Alloys Containing Minor Amounts of Niobium and Zirconium*, ANL-5530; Argonne National Laboratory; April 1957.
- (121) Weast, R. C., (Editor); *Handbook of Chemistry and Physics, 47th Edition*; p B-211; Chemical Rubber Company (1966).
- (122) Bockris and Reddy; *Op Cit*; p 1169.
- (123) Dickens, P. G. and Whittingham, M. S.; "The Tungsten Bronzes and Related Compounds", *Quarterly Reviews*, 22, pp 30 - 44, The Chemical Society, London (1968).
- (124) Sprague, T. P.; "Inhibition of Uranium Metal Corrosion", *US Patent 3,450,576*, assigned to United States Atomic Energy Commission; October 20, 1965.
- (125) Schreyer, J. M.; "The Solubility of Uranium (IV) Orthophosphates in Phosphoric Acid Solutions", *JACS*, 77, pp 2972 - 2974 (1955).

- (126) Schreyer, J. M., and Baes, C. F., Jr; "Volumetric Determination of Uranium (VI) in Phosphate Solutions", *Analytical Chem*, 25, pp 644 - 645 (1953).
- (127) Cleary, H. J. and Greene, N. D.; "Corrosion Properties of Iron and Steel", *Corrosion Sci*, 7, pp 821 - 831 (1967).
- (128) Samuels, L. E.; *Metallographic Polishing by Mechanical Methods*, 2nd Edition, pp 88 - 93; American Elsevier (1971).
- (129) Katz and Rabinowitch; *Op Cit*; p 283.
- (130) Gayer, K. H. and Leider, H.; "The Solubility of Uranium Trioxide, $\text{UO}_3 \cdot \text{H}_2\text{O}$, in Solutions of Sodium Hydroxide and Perchloric Acid at 25°C ", *JACS*, 77, pp 1448 - 1450 (1955).
- (131) Tegart; *Op Cit*; p 29.

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Rohde, R. W.

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Stephenson, L. L.

Sandia - Livermore

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