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Galvanic Corrosion of Tungsten Coupled With Several Metals/Alloys

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Abstract

From an environment perspective, tungsten is a more desirable material than depleted uranium (DU) for penetrator applications. However, the ballistic performance attained by current tungsten (W) alloys is inferior to DU. Recently, advanced tungsten-metal (W-M) composites have been developed to improve their ballistic penetration, but the corrosion properties are unknown and need to be determined. In this work, the galvanic corrosion behavior of W coupled with several selected metals/alloys was investigated. Electrochemical potentiodynamic polarizations and galvanic couplings were employed. The testing was conducted in a 1 wt-% sodium sulfate solution. The selected metals/alloys were: pure W, pure titanium (Ti), Ti 6Al-4V (Ti-6-4), hafnium (Hf), 36Ni64Fe0.03C (Invar), pure iron (Fe), and brass (CDA 260). The galvanic corrosion of these couples is examined and discussed based on the results from electrochemical tests and visual observations.

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1. Introduction

Depleted uranium (DU)- and tungsten (W)-based alloys are attractive candidate materials for kinetic energy (KE) penetrator applications (Cai et al. 1995; Chang, Levy, and Lin 1985; Levy and Chang 1981; Stein and Geary 1957) because of their unique combination of mechanical properties and high density. Traditionally, DU penetrators have better ballistic properties than W penetrators, but the toxicity and radioactivity of DU creates environmental repercussions. Thus, efforts to develop W alloys to replace DU have been undertaken by the U.S. Army and Department of Defense (DOD). Potential tungsten alloys have included W-Ni-Fe-Co, W-Ni-Co, W-Ni-Mn, W-Hf, W-Ti, and others (Cai et al. 1995).

These new W alloys are being developed strictly for improved ballistic performance; their corrosion properties are of secondary importance. However, this study is looking to uncover potential galvanic corrosion issues in tandem with the alloy development. Tungsten alloys generally contain at least two discrete phases. In most alloys under consideration, relatively pure W grains are encapsulated by a matrix consisting of the other alloying elements (Cai et al. 1995), as shown in Figure 1 for W-Ni-Fe. Galvanic corrosion can occur between these two discrete phases. The work reported herein is a preliminary study of the galvanic corrosion behavior of tungsten-metal (W-M) couples immersed in test solutions. Both potentiodynamic scans and galvanic couple experiments were performed.

2. Experimental Procedure

Samples for electrochemical testing were made from pure W, and other seven other metallic materials selected for study, namely: brass (CDA 260), hafnium (Hf), 36Ni64Fe0.03C (Invar), iron (Fe), nickel (Ni), titanium (Ti), and titanium 6Al-4V(Ti-6-4). Their typical chemical compositions are listed in Table 1. Disk-type specimens 0.318 cm thick and 1.588 cm in diameter were used in all of the tests. Immediately before initiating electrochemical tests, the specimens were polished with 600-grit silicon carbide (SiC) paper, rinsed with distilled water, acetone degreased, and air dried. One square centimeter of each specimen was exposed to the test solution.

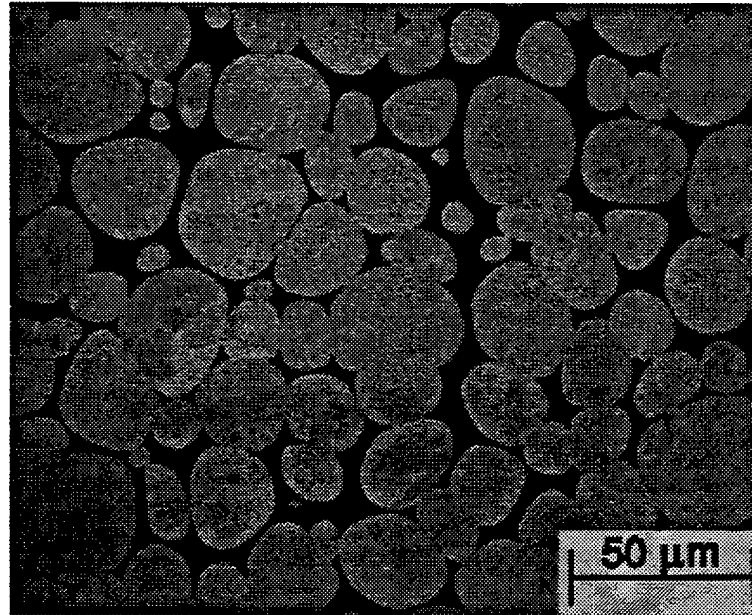


Figure 1. Typical Microstructure of W-Ni-Fe Alloys, Taken From Cai et al. (1995). The Solubility of Fe and Ni in W Is Extremely Low, Leading to Almost Pure W Grains Surrounded by an Fe-Ni Matrix. The Alloy Shown Is 95W-3.5Ni-1.5Fe.

Table 1. Chemical Compositions of Metals and Alloys Selected for This Study

Material Studied	Nominal Composition
Pure W	99.99 W
Fe	99.99 Fe
Ni	99.7 Ni
Hf	95.3Hf-3.5Zn-1.2Fe
Ti	99.9 Ti
Ti-6-4	90Ti-6Al-4V
CDA 260	70Cu-30Zn
Invar	36Ni64Fe0.03C

Tests were performed in a dilute sodium sulfate solution (1 wt-% Na₂SO₄) to simulate the humid industrial atmosphere. Potentiodynamic tests were conducted at room temperature in a cell manufactured by Princeton Applied Research (PAR) Model K0235 containing about 325 ml of test

solution. A computer-controlled PAR M273 potentiostat was used, with a sweep rate of 0.166 mV/s. Separate specimens were used for the anodic and cathodic portions of the curves. The solution was deaerated with argon gas. The open-circuit corrosion potential was measured for a period of 1 hr before the scans commenced. Potentials were measured against the saturated calomel electrode (SCE).

The galvanic corrosion tests were conducted in a modified version of the PAR Model K0235 flat cell, as shown in Figure 2. Two PAR M273 potentiostats were utilized. A W specimen is placed at one end of the cell, while the other specimen is clamped to the opposite end. The first potentiostat is set to keep the potential difference between the W and the other sample at 0 V (effectively a short circuit) and simultaneously measure the galvanic current (I_g) generated. A second potentiostat is used to monitor the open circuit potential of the corroding couple (E_g) vs. SCE. The galvanic couple cells were not deaerated, and galvanic currents were measured for a period of 3 days.

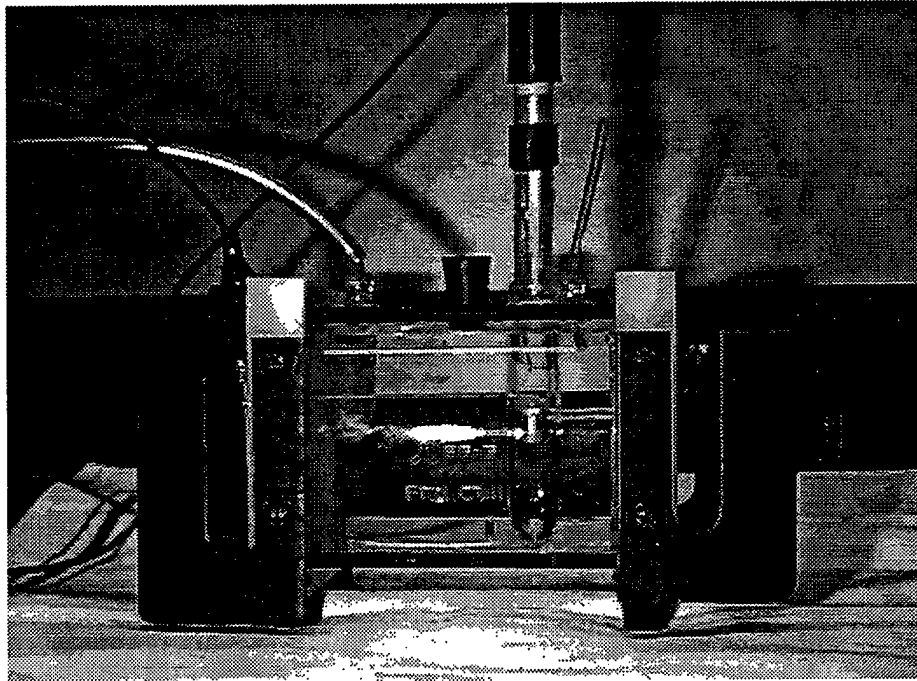


Figure 2. Experimental Setup Used for Galvanic Testing. Clamps at Both Ends Secure Each Material of the Couple Being Tested. The Potentiostat Is Used to Effectively Short-Circuit Each Specimen and Measure the Galvanic Current.

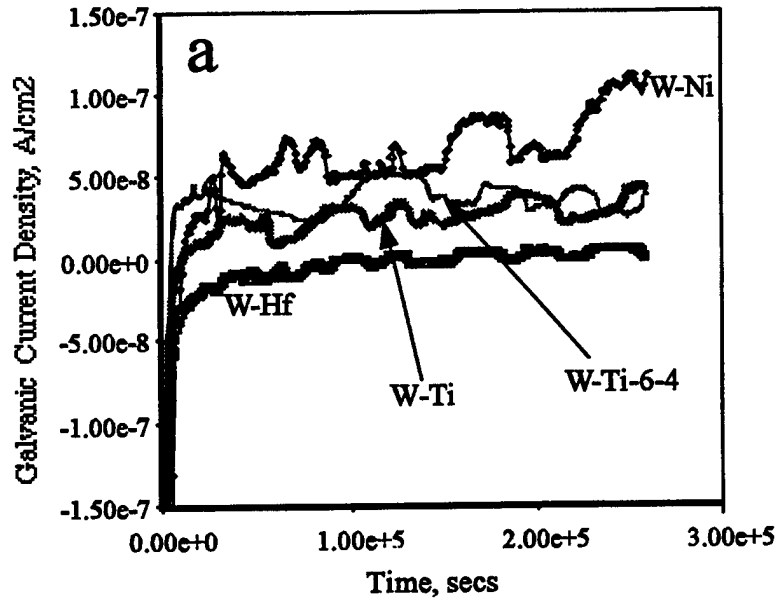
3. Results and Discussion

In the galvanic tests, variations of the galvanic currents, I_g vs. time, were recorded for the 72 hr of testing. The I_g is useful as an indicator of the severity of galvanic corrosion. Additionally, potentiodynamic scans are often used to predict galvanic corrosion behavior using mixed potential theory. The following results compare the predictions of mixed potential theory to the actual galvanic tests and comment on the implications this will have on the corrosion resistance of W alloys under development.

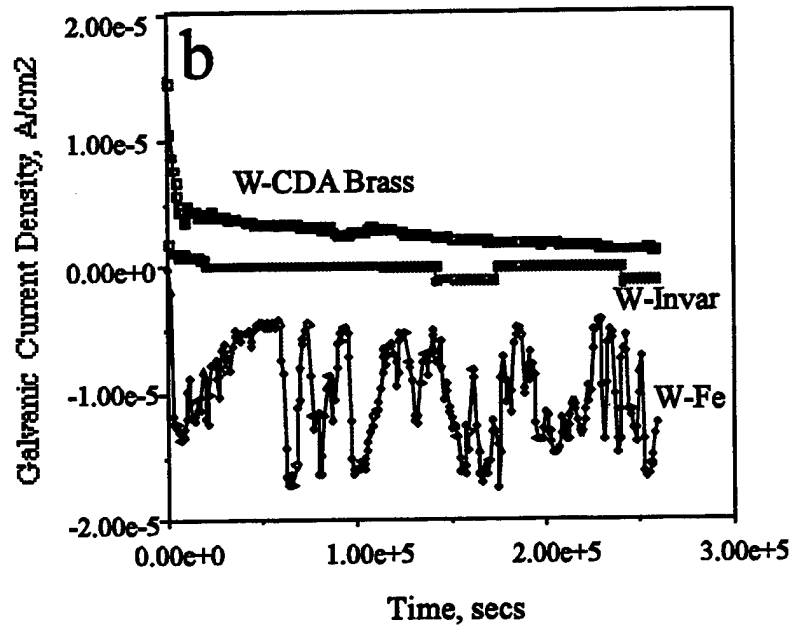
Figures 3a and b show the variation in galvanic current, I_g , as function of time. "Positive" currents in this case mean that the W is behaving as the anode, while negative currents denote that W is behaving as the cathode. These curves show that at the end of the 72-hr test, only Fe and Invar behaved as anodes with respect to W. Iron was more anodic than W throughout the test, while Invar changed behavior from cathodic to anodic after a few hours of immersion. At the outset of the test Ni, Hf, Ti, and Ti-6-4 were anodic with respect to W in the W-M couples, but they all became more noble (cathodic) in less than 10 hr.

The results of the galvanic corrosion tests are summarized in Table 2. The couples are ranked in decreasing order of the magnitude of the galvanic current density.

When two metallic specimens are coupled together and immersed in an aqueous electrolyte, the well-established mixed potential theory states that the corroding potential and corresponding galvanic current can be predicted from the potentiodynamic scans of each metal. Figure 4 shows a schematic illustrating this method. The mixed potential of the couple, E_m , and the galvanic current, I_m , can be represented by the intersection of the anodic polarization curve of the anode (the alloy/metal with the more active E_{corr}) and the cathodic polarization curve of the cathode (the alloy/metal with the more noble E_{corr}) as the two polarization curves are overlapped. Generally, I_m may be considered the corrosion rate of the anode in the couple.



(a)



(b)

Figure 3. Galvanic Corrosion Current Densities as a Function of Time: (a) W Coupled With Ti, Ti-6Al-4V, Hf, and Ni; (b) W Coupled With CDA, Fe, and Invar.

Table 2. Summary of Galvanic Corrosion Tests

W Coupled To	I_g (A/cm ²)
Fe	-1×10^{-5}
CDA	1×10^{-6}
Invar	-1×10^{-6}
Ni	1×10^{-7}
Ti	3×10^{-8}
Ti-6Al-4V	3×10^{-8}
Hf	0×10^{-8}

Note: Negative sign indicates that the material was anodic with respect to W.

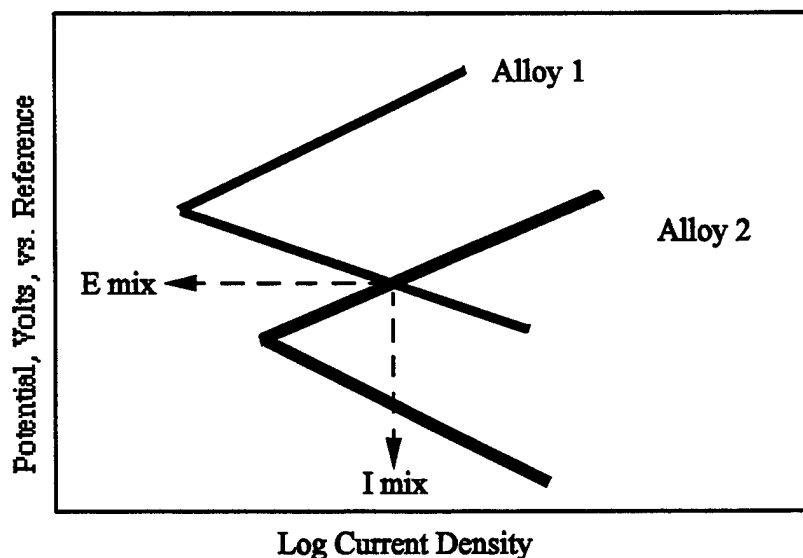
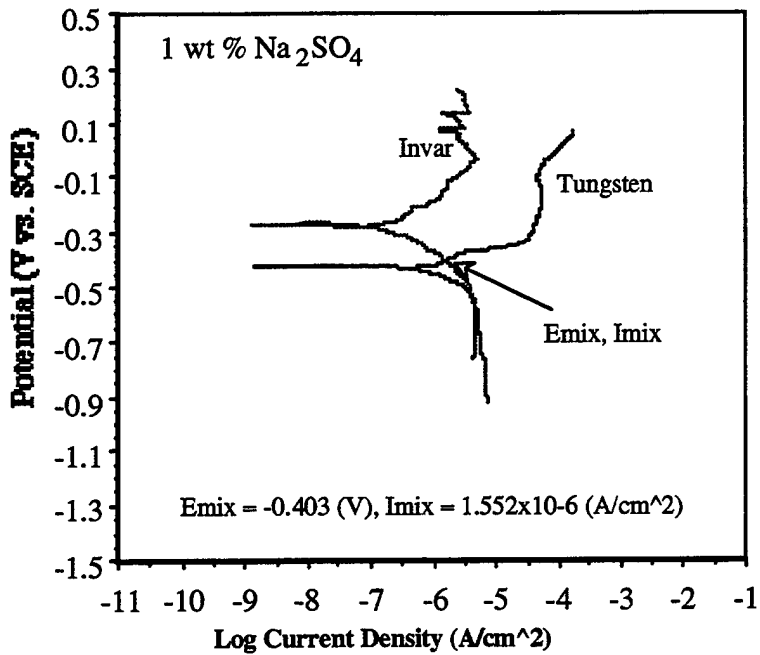
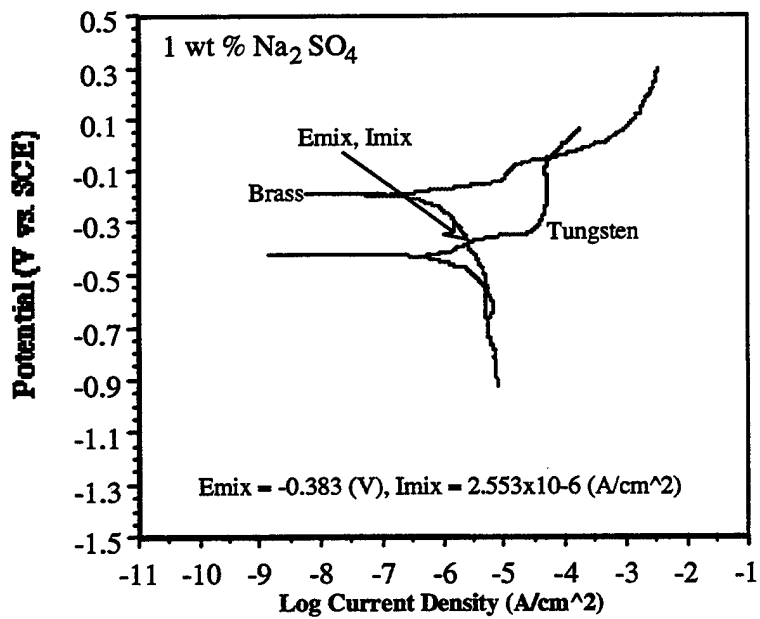


Figure 4. Schematic Illustrating the Mixed Potential Theory. The Combined System Must Equilibrate to a Common Potential and Common Current Density When the Specimens Are Electrically Connected. The Common (Mixed) Potential Is Designated E_m , and the Current Density Obtained Is I_m .

Figures 5 a–g show the overlapped potentiodynamic scans of the couples under investigation and the corresponding values of E_m and I_m . Tables 3 and 4 summarize these results, providing the open-circuit potentials (E_{corr}) for each metal/alloy studied, as well as the E_m and I_m predicted from

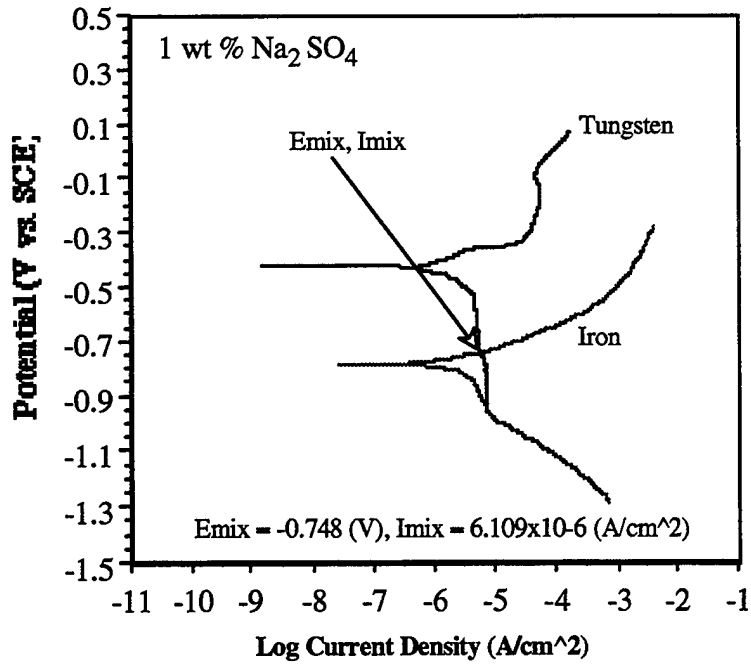


(a) W and Invar.

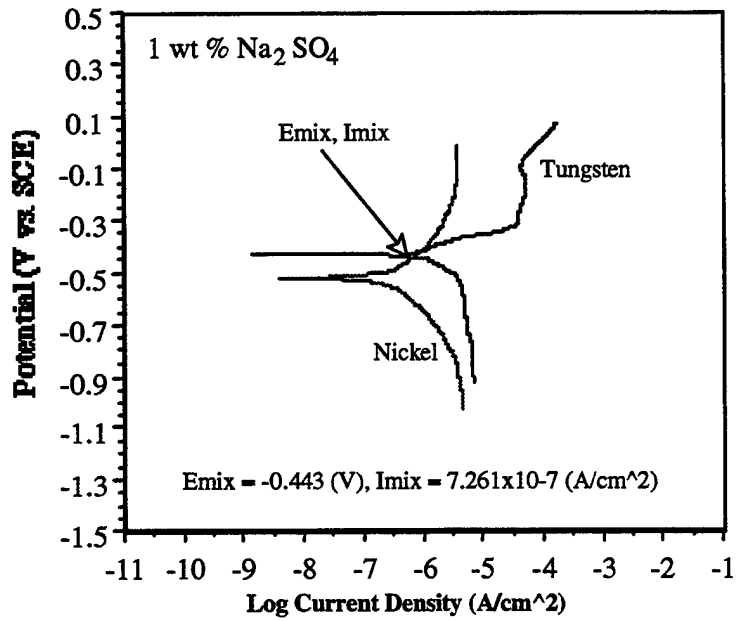


(b) W and CDA.

Figure 5. Potentiodynamic Scans and Mixed Potentials.

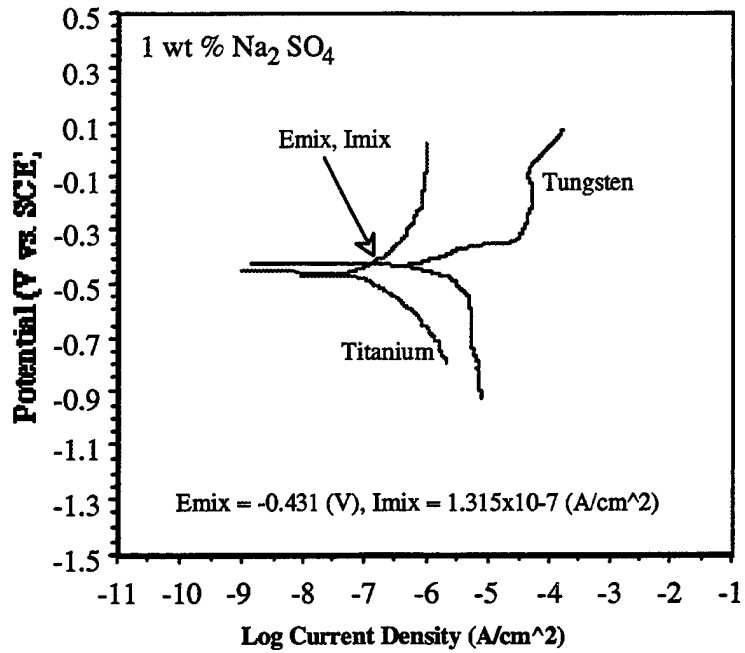


(c) W and Fe.

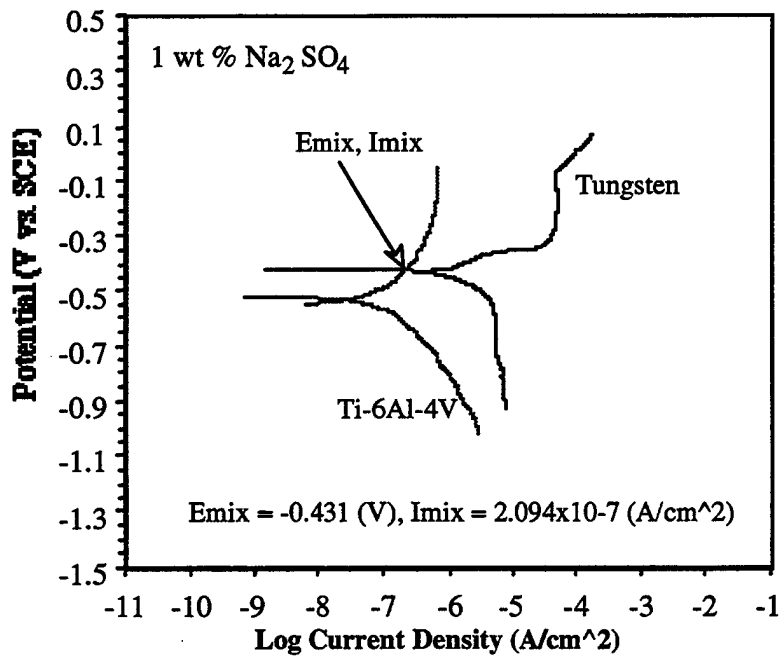


(d) W and Ni.

Figure 5. Potentiodynamic Scans and Mixed Potentials (continued).

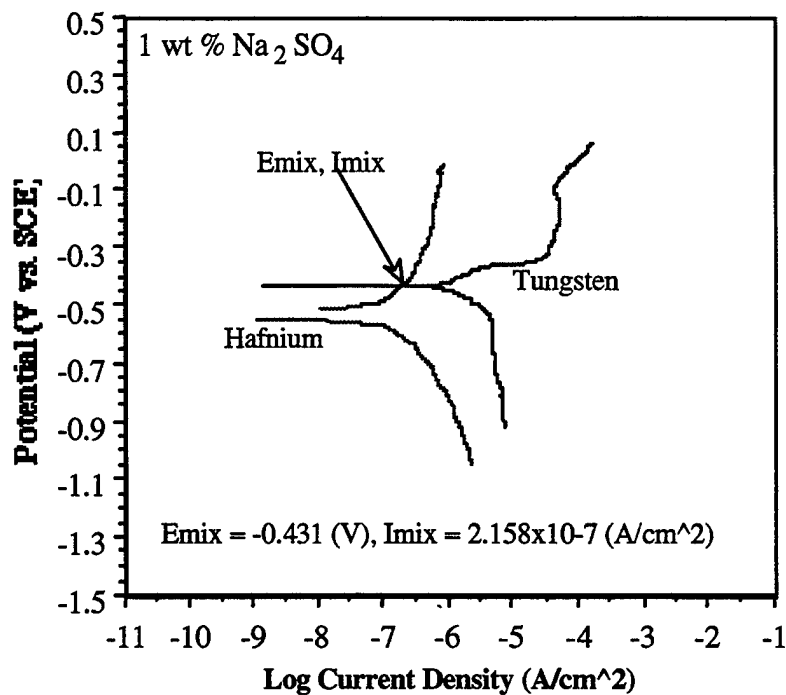


(e) W and Ti.



(f) W and Ti-6Al-4V.

Figure 5. Potentiodynamic Scans and Mixed Potentials (continued).



(g) W and Hf.

Figure 5. Potentiodynamic Scans and Mixed Potentials (continued).

Table 3. Mixed Potentials and Mixed Current Densities as Determined From Polarization Curves

W Coupled To	W is More	E_m (V vs. SCE)	I_m (A/cm ²)
Fe	Noble	-0.748	6.109×10^{-6}
Ni	Noble	-0.443	7.261×10^{-7}
Hf	Noble	-0.431	2.158×10^{-7}
Ti-6-4	Noble	-0.431	2.094×10^{-7}
Ti	Noble	-0.431	1.315×10^{-7}
Invar	Active	-0.403	(1.552×10^{-6})
CDA	Active	-0.383	(2.553×10^{-6})

Table 4. Average Open-Circuit Potentials Measured After 1 hr of Immersion

Material	E_{corr} (V vs. SCE)
CDA	-195
Invar	-277
W	-431
Pure Ti	-463
Pure Ni	-522
Hf	-533
Ti-6Al-4V	-535
Pure Fe	-785

mixed potential theory. Comparing I_m to I_g shows that the mixed potential theory agrees reasonably well with the longer term galvanic couple data. The materials with large I_m 's (Fe, CDA, Invar) show the largest I_g 's. The Fe:W couple sustained the largest current density, at 1×10^{-5} A/cm². The Invar:W couple shows a reversal of current that is not easily explained. The remaining materials (Ti, Ti-6-4, Ni, and Hf) have E_m 's close to the E_{corr} of W. This means that the W, which is near its free-corrosion potential, can behave either as an anode or a cathode as drifting of the corrosion potential occurs. Long-term measurements of E_{corr} often show "drifting" from 10-30 mV, suggesting that changes in the anodic/cathodic relationship (current reversals) should be expected if the E_m is near E_{corr} of either material in the couple. Current reversals are seen for all of the couples except W-Fe and W-CDA. However, relatively small galvanic currents would be expected, and this is precisely what is observed.

It should be noted that there are certain limitations of the methods used in this preliminary study; for instance, the effect of grain boundaries, solid solubility, and intermetallic compound formation that may result in certain processes have been ignored. Also, other factors such as the ratio of anode/cathode surface area must be accounted for. However, because of the two discrete phases found in W alloy composites (Figure 1), it is reasonable to assume that the galvanic effects measured in this study will agree well with the general corrosion behavior of the W alloys under development.

4. Conclusions

Comparison of mixed potential theory and galvanic corrosion tests provided good agreement for the materials studied. Pure Ti, Ti-6Al-4V, Ni and Hf when coupled with W showed small galvanic current densities ($< 1.0 \times 10^{-7} \text{A/cm}^2$) and maintained galvanic corrosion potentials near the E_{corr} of W. Tungsten alloys utilizing these materials as the matrix material should show little or no galvanic corrosion. When W was coupled to Fe, CDA, and Invar, significantly larger current densities were measured. This suggests that corrosion protection schemes will need to be developed for W alloys under development using these materials in the matrix.

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