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GALVANIC CORROSION STUDY OF CONTAINER MATERIALS USING ZERO RESISTANCE AMMETER

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ABSTRACT

Galvanic corrosion behavior of A 516 steel separately coupled to six different corrosion-resistant alloys was investigated in an acidic brine ($\text{pH} \approx 2.70$) at 30°C , 60°C and 80°C using zero resistance ammeter technique. The corrosion-resistant alloys include Alloys 825, G-3, G-30, C-4 and C-22; and Ti Grade-12, which were coupled to A 516 steel at an anode-to-cathode area ratio of one. The galvanic current and galvanic potential were measured as a function of time at all three temperatures. Optical microscopic examination was also performed on all tested specimens to evaluate the extent of surface degradation due to galvanic coupling. The overall results are presented in this paper.

Keywords: Galvanic corrosion, carbon steel, nickel-rich and nickel-base alloys, titanium alloy, galvanic current, galvanic potential, temperature effect.

INTRODUCTION

The current high-level nuclear waste package design is focused on all-metallic multi-barrier concepts to accommodate the nation's spent nuclear fuel and vitrified high-level nuclear waste for geologic disposal in the potential Yucca Mountain repository. This design incorporates an outer corrosion-allowance metal barrier over an inner container made of suitable corrosion-resistant metal. The corrosion-allowance barrier, which will be thicker than the inner corrosion-resistant barrier, is being designed to undergo environment-induced degradation at a very slow rate, thus providing the inner container protection from the potential repository environment for an extended period.

The precise method of fabricating these waste packages is yet to be finalized. Two alternate approaches are currently being considered. One approach is to fabricate the two barriers separately, and then to shrink-fit the inner barrier inside the outer barrier by slipping the inner container into the outer one which will be expanded by heating prior to insertion of the inner container. Although this method may provide sufficient bonding between these two barriers, it is likely that there will

be gaps at some locations where breached liquid may be trapped, thus causing galvanic interaction between the two barriers. Under this scenario, the more electronegative outer container material may undergo increased corrosion attack while protecting the more noble inner container material. The alternate method is to fabricate these waste packages from clad or weld-overlay materials. In this case, the outer corrosion-allowance metallic barrier will have a thin layer of corrosion-resistant clad material inside, thus eliminating the gap between the two barriers while still providing galvanic protection to the more noble material. In view of these waste package design considerations, an investigation was pursued to evaluate the corrosion behavior of galvanically-coupled candidate inner and outer container materials, the results of which are presented in this paper.

MATERIALS AND EXPERIMENTAL PROCEDURE

Materials tested include iron-nickel-chromium-molybdenum (Fe-Ni-Cr-Mo) Alloys 825, G-3 and G-30; Ni-Cr-Mo Alloys C-4 and C-22; a titanium-base alloy Ti Grade-12; and a carbon steel (A 516). Their chemical compositions are given in Table 1. Test specimens in the form of 2" x 2" square were fabricated from heat-treated materials by a qualified vendor, and additional thermal treatments were not given to these specimens prior to their exposure to the test environments. Since the precise environment surrounding the waste packages is unknown, tests were performed in a deaerated acidic brine containing 5 weight percent NaCl at 30°C, 60°C and 80°C. Acidification was done by adding sulfuric acid to the brine. The pH of this salt solution was in the vicinity of 2.70. The rationale for selecting an acidic brine as a test environment has been provided elsewhere.⁽¹⁾

Galvanic contact between A 516 steel and a corrosion-resistant alloy was established by short circuiting them through use of a computer controlled EG&G Model 283 potentiostat which acted as a zero resistance ammeter. Cell connections were made using A 516 steel as an anode, and a corrosion-resistant alloy as a cathode. A modified EG&G Pyrex cell was used to contain these two working electrodes and a Ag/AgCl reference electrode, as illustrated in Figure 1. Equal exposed areas (one cm² each) of anodic and cathodic materials were tested with a separating distance of 12 cm between them. A controlled temperature liquid (water/ethylene glycol mixture) bath maintained the desired test temperature. Tests were performed for periods ranging between seven and eight days. Both measured galvanic current and galvanic potential were monitored as a function of time.

The specimens were cleaned with distilled water, acetone and ethanol prior to their exposure to the test solution. The pH of the test solution was measured at room temperature both before and after each experiment. At the conclusion of each test, the specimen was cleaned with distilled water, acetone and ethanol. The cleaned specimen was visually examined, followed by an optical microscopic examination to evaluate the extent of damage in both electrodes resulting from galvanic interaction.

RESULTS AND DISCUSSION

The optical microscopic examination revealed that A 516 steel individually coupled to corrosion-resistant alloys suffered from general corrosion and crevice corrosion at all three test temperatures, the extent of damage being more pronounced at higher temperatures. Formation of shallow pits was also observed on the exposed surface of a few specimens. Some of the A 516 steel specimens were covered with thick brownish corrosion products, which were not analyzed. Appearances of two surfaces of A 516 steel galvanically coupled to Alloys 825 and G-30, respectively in the 80°C acidic brine are illustrated in Figure 2, showing severe general corrosion and crevice corrosion tendency. As to the surface characteristics of corrosion-resistant alloys due to galvanic interaction with A 516 steel, it appears that Alloys 825, G-3 and G-30 suffered from moderate crevice corrosion at 60°C and 80°C. Slight crevice corrosion tendency was also observed with Alloys C-4 and C-22, and Ti Grade-12 at these two temperatures. One interesting observation with these three alloys was that they were covered with black surface films at these temperatures, with the maximum amount of film being formed on Ti Grade-12.

The results indicate that at 30°C, the equilibrium or steady-state galvanic current for A 516 steel coupled to Alloys 825, G-3, G-30, C-4 and C-22 ranged between 17 µA and 30 µA. But the galvanic current for A 516 steel/Ti Grade-12 couple was substantially higher (86 µA) at the same temperature. At higher temperatures (60°C and 80°C), the value of the steady-state galvanic current in all couples ranged between 20 µA and 56 µA, with a value of 34 µA for A 516 steel/Ti Grade-12 couple. As to the equilibrium galvanic potential of these couples at 30°C, its value was in the vicinity of -670 to -682 mV, with an exception of higher galvanic potential of -785 mV for A 516 steel/Ti Grade-12 couple. Except for A 516 steel/Alloy C-4, A 516 steel/Alloy C-22, and A 516 steel/Ti Grade-12 couples, the magnitude of the galvanic potential value did not change significantly at 60°C and 80°C. The galvanic potential for these three couples became more noble at higher

temperatures. For A 516 steel/C-4 couple, the galvanic potential was -240 mV and -390 mV, respectively at 60°C and 90°C. Similarly, a positive shift in galvanic potential (-680 mV to -530 mV) was observed for A 516 steel/Alloy C-22 couple at higher temperatures. Noble galvanic potential of -215 and -303 mV, respectively were also observed for A 516 steel/Ti Grade-12 couple at these temperatures. A comparison of galvanic current and galvanic potential as a function of test duration for all six couples at three temperatures is illustrated in Figures 3 through 8.

The excellent corrosion resistance of titanium alloys, which are known to exhibit active-passive transition behavior, is primarily due to the inert, tightly adherent protective oxide films that cover their surfaces. Although the passive oxide film covering the titanium alloy surface is effective in avoiding or limiting hydrogen uptake, under certain conditions, hydrogen may be evolved on the alloy surface causing hydrogen embrittlement of the alloy.^(2,3) Conditions that must be met for hydrogen attack to occur are: the generation of critical concentration of atomic hydrogen on the titanium alloy surface resulting from galvanic coupling, the exposure of the alloy surface at temperatures at which the hydrogen diffusion rate is significant, and the maintenance of solution pH at or below 3. A natural result of galvanic coupling is the evolution of hydrogen gas and absorption of atomic hydrogen at the surface of the cathodic member while the anodic material undergoes dissolution. A temperature of 80°C has been cited⁽⁴⁾ to be the critical temperature above which hydrogen diffusion through the titanium surface oxide film may be significant. As mentioned earlier, Ti grade-12 coupled to A 516 steel showed adherent black surface film at 60°C and 80°C along with a slight crevice corrosion tendency, even though its surface was shiny and unattacked at 30°C. It is possible that hydrogen evolution and absorption at 30°C was quite insignificant, and that hydrogen gases formed at 60°C and 80°C were precipitated on the alloy surface as black hydride films which were not detrimental from a corrosion viewpoint.

The iron content in the corrosion product resulting from the dissolution of A 516 steel in the acidic brine is most frequently in the form of ferric ions. It has been suggested^(5,6) that ferric ions may act as cathodic depolarizers and shift the corrosion potential of titanium alloys in the positive direction, a phenomenon which was also observed in this study. As mentioned earlier in this paper, the galvanic potential of the A 516 steel/Ti Grade-12 couple was shifted to more noble values (-785 mV versus -215 and -303 mV) at higher temperatures that resulted in more dissolution product and, thus produced more ferric ions. It is possible that a similar mechanism of ennoblement of steady-state galvanic potential may be applicable to A 516/Alloy C-4 and A 516/Alloy C-22 couples at higher temperatures, since adherent black films were also formed on the exposed surfaces of Alloys C-4 and C-22 while galvanically coupled to A 516 steel.

SUMMARY AND CONCLUSIONS

A zero resistance ammeter method was used to evaluate the galvanic corrosion susceptibility of candidate nuclear waste package container materials. A 516 steel, a corrosion-allowance material, was galvanically coupled to corrosion-resistant materials such as Alloys 825, G-3, G-30, C-4 and C-22; and Ti Grade-12 in an acidic brine at 30°C, 60°C and 80°C. The steady-state galvanic current and galvanic potential were recorded as a function of test duration. The significant conclusions drawn from this investigation are given below:

- A 516 steel suffered from general corrosion and crevice corrosion while galvanically coupled to corrosion-resistant alloys, the extent of attack being more severe at 60°C and 80°C. Shallow pits were observed on a few test specimens.
- Moderate crevice corrosion tendency was observed with Alloys 825, G-3 and G-30 at 60°C and 80°C.
- Alloys C-4 and C-22; and Ti Grade-12 were covered with adherent black surface films at 60°C and 80°C.
- With an exception of higher galvanic current for A 516 steel/Ti Grade-12 couple at 30°C, the magnitude of galvanic current ranged between 17 μ A and 56 μ A.
- The galvanic potential for A 516 steel coupled to Alloys C-4 and C-22; and Ti Grade-12 was shifted to more noble values at 60°C and 80°C possibly due to the beneficial effect of increased concentration of ferric ions formed at higher temperatures.

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Table 1

Chemical Composition of Materials Tested (wt%)

Material	Heat #	C	Mn	P	S	Si	Ni	Cr	Mo	Fe	Ti	Al	Cu	Others
Alloy 825	J927	0.01	0.39	—	0.001	0.12	Bal	22.80	3.30	26.42	0.97	0.10	1.70	—
Alloy G-3	J432	0.004	0.77	0.016	<0.001	0.21	Bal	21.72	6.73	19.40	—	—	1.77	Nb+Ta: 0.2 Co: 1.86 W: 0.89
Alloy G-30	L731	0.01	1.10	0.009	0.004	0.28	Bal	28.81	5.09	14.28	—	—	1.93	Nb+Ta: 0.8 Co: 2.66 W: 2.76
Alloy C-4	K933	0.003	0.21	0.005	0.004	0.03	Bal	15.43	15.66	0.29	0.21	—	< 10	—
Alloy C-22	H157	0.005	0.34	0.02	<0.001	0.05	Bal	22.10	13.30	4.50	—	—	—	W: 2.90 Co: 1.30
Ti Gr-12	E133	0.018	—	—	—	—	0.82	—	0.29	0.11	Bal	—	—	—
A 516 Steel	K963	0.14	0.72	0.01	0.021	0.25	0.02	0.04	0.01	Bal	—	.047	0.04	Nb: 0.001 V: 0.002

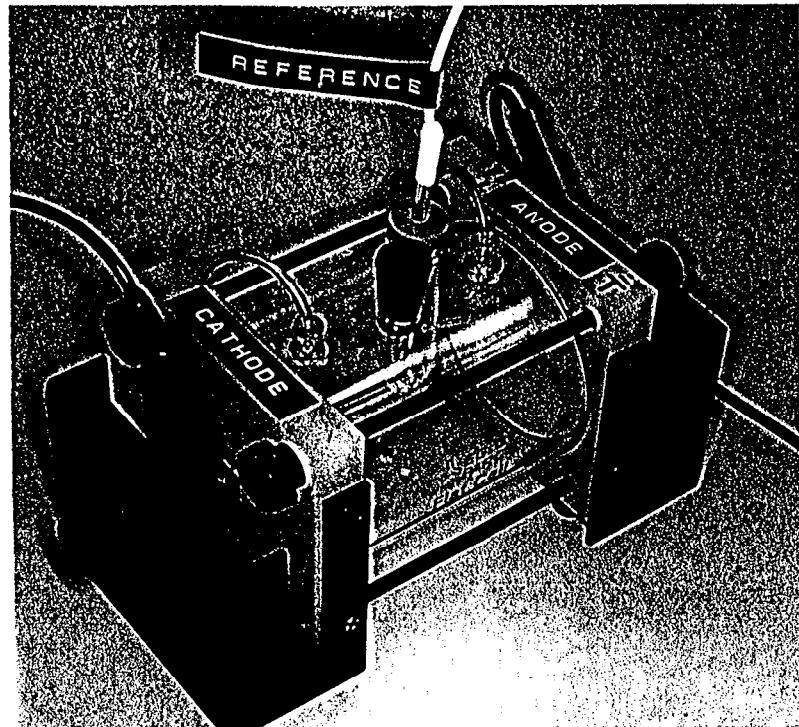
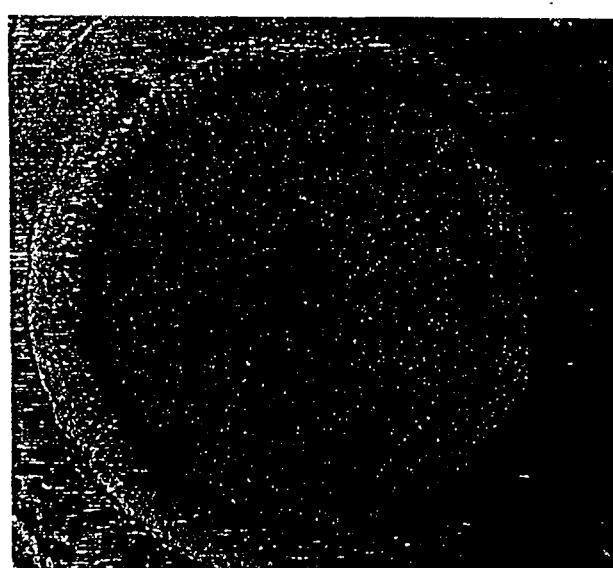
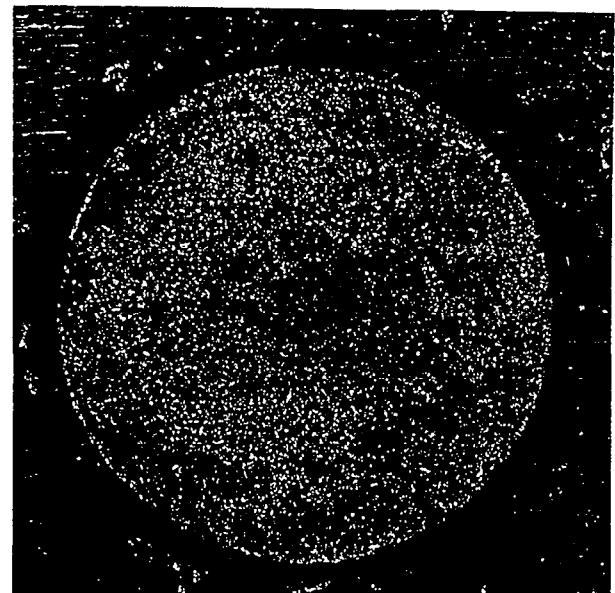


Figure 1. Galvanic Corrosion Test-Setup



(a)



(b)

Figure 2. Surface Appearance of A 516 Steel Galvanically Coupled to (a) Alloy 825, and (b) Alloy G-30 in 80°C Acidic Brine

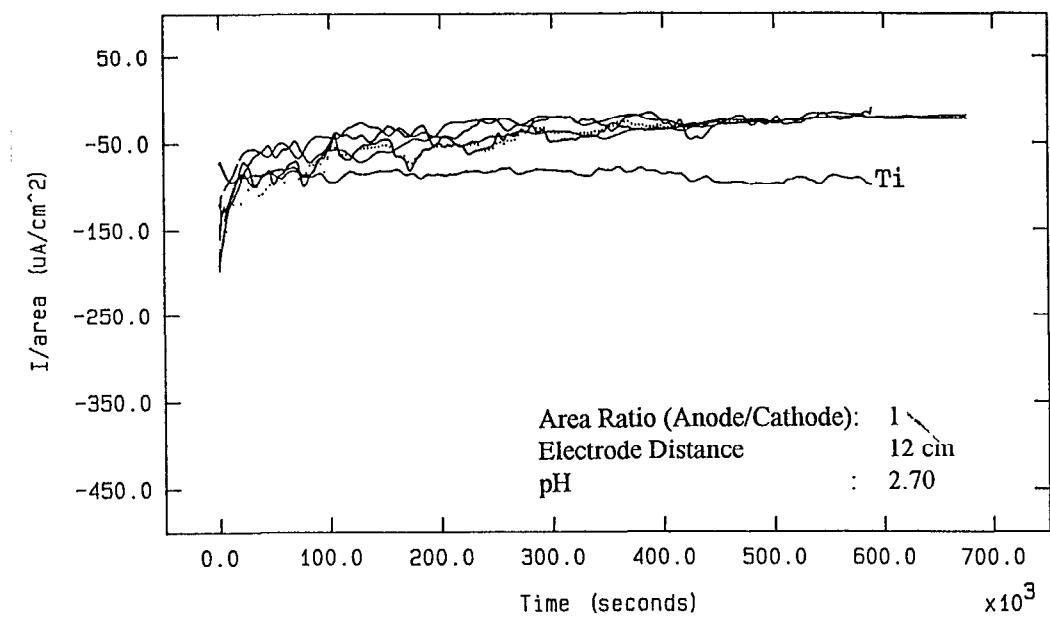


Figure 3. Galvanic Current Density vs Time for all six Couples at 30°C

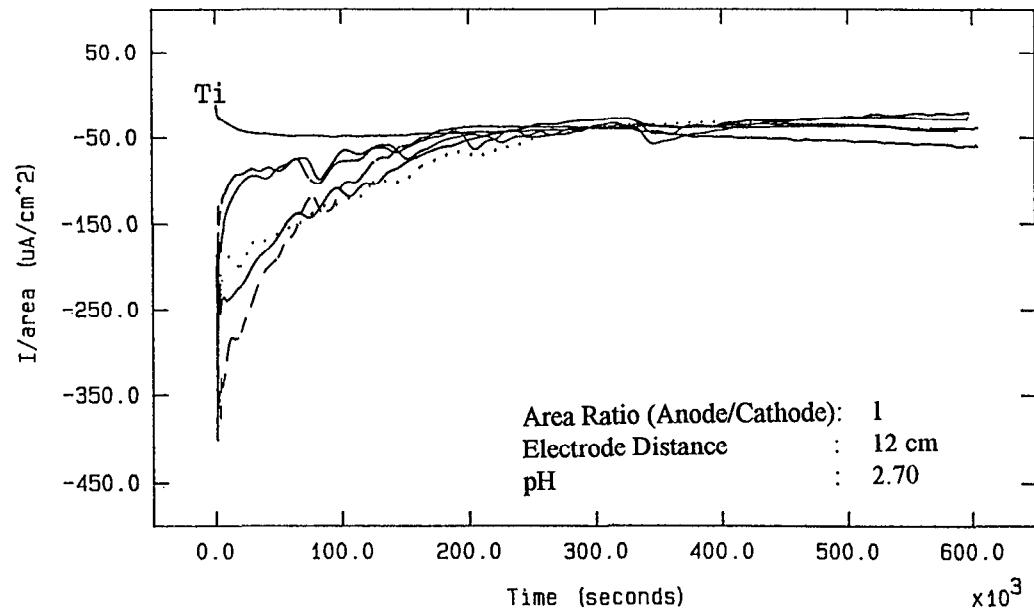


Figure 4. Galvanic Current Density vs Time for all six Couples at 60°C

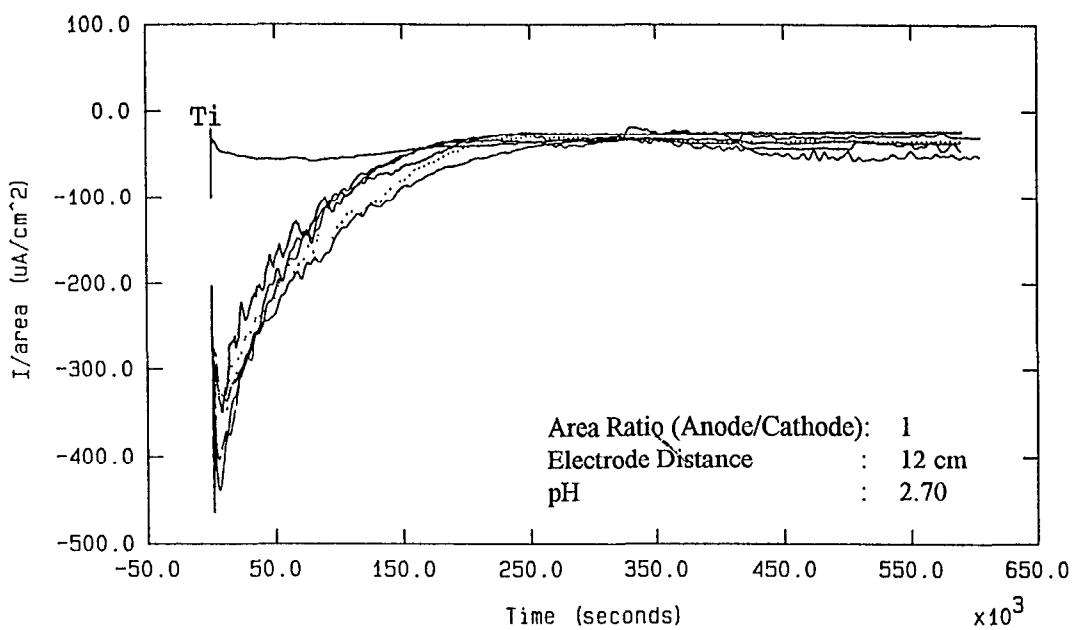


Figure 5. Galvanic Current Density vs Time for all six Couples at 80°C

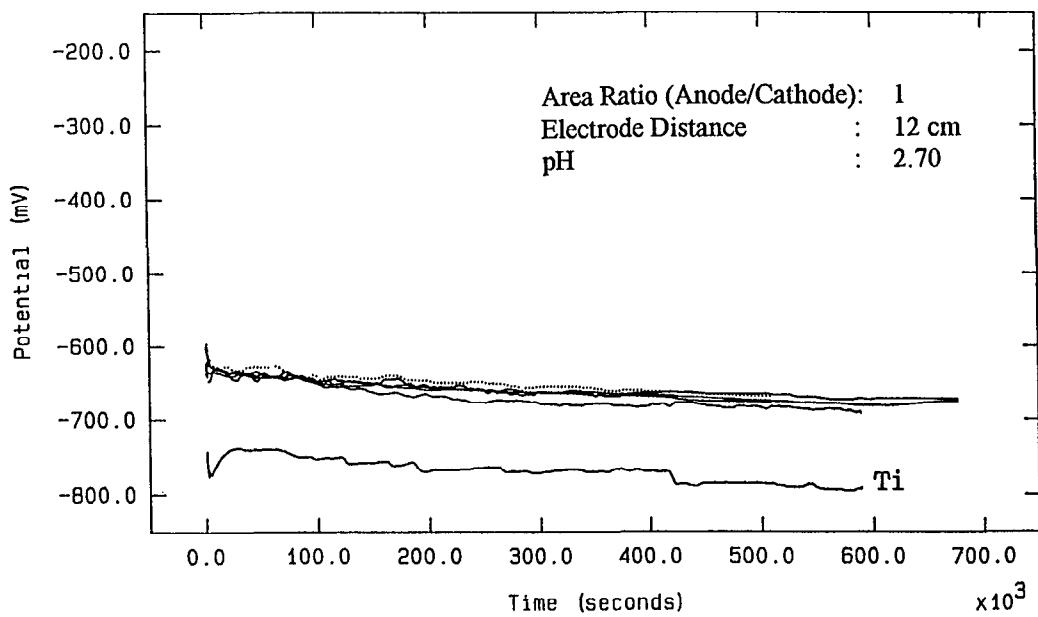


Figure 6. Galvanic Potential vs Time for all six couples at 30°C

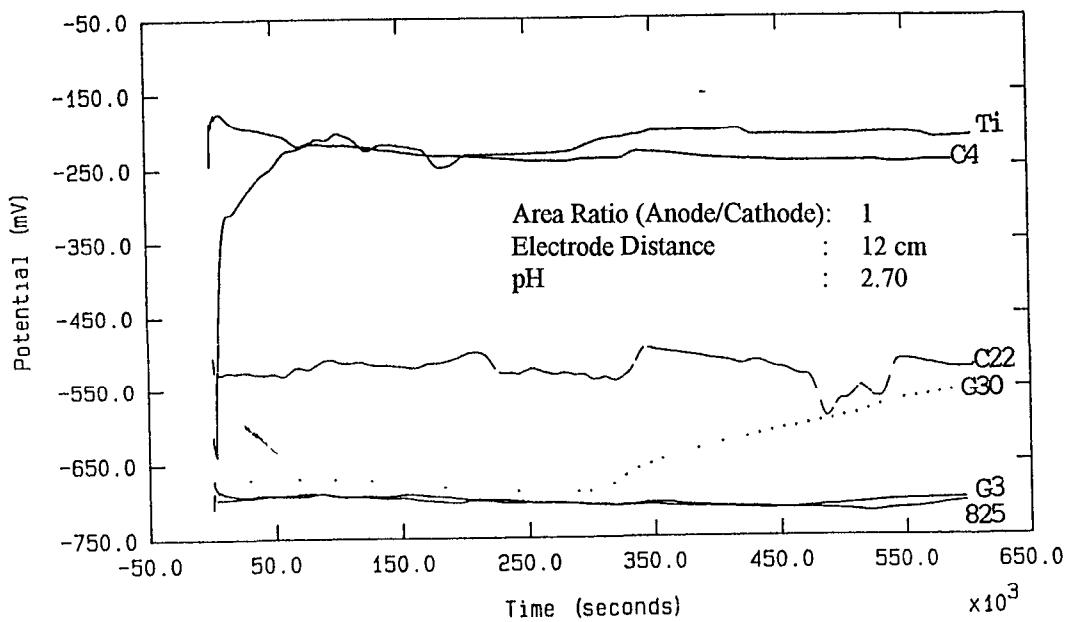


Figure 7. Galvanic Potential vs Time for all six Couples at 60°C

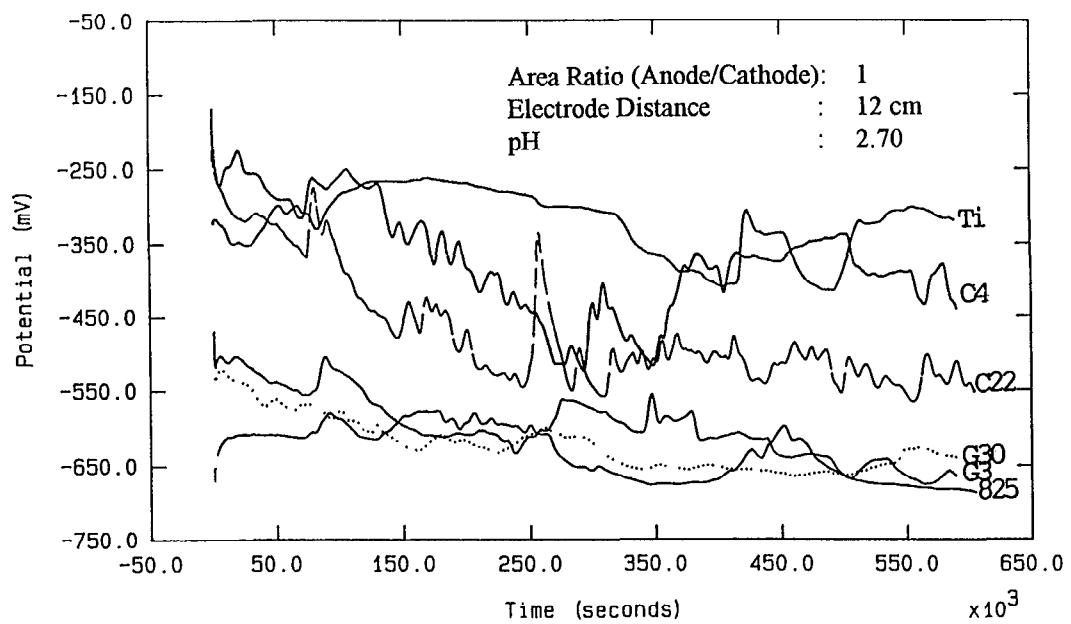


Figure 8. Galvanic Potential vs Time for all six Couples at 80°C

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