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INVESTIGATION OF STRESS CORROSION CRACKING OF TITANIUM ALLOYS

Semi-Annual Progress Report No. 1

for the Period

June 1, 1966 through November 30, 1966

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Prepared by:

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Abstract

In studies of the mechanism of stress corrosion cracking of titanium alloys, the foil form has been found to be advantageous. The experimental equipment utilized to test foil by dead weight loading has been described. The apparatus and procedures used to make electrode potential and potentiostatic measurements have been presented in detail.

The two alloys investigated, Ti-6Al-4V and Ti-13V-11Cr-3Al, were not susceptible to stress corrosion cracking in aqueous solutions with pH values from 0 to 13 and Cl^- ion added. These alloys failed readily in methanol solutions containing less than about one percent water. Electrochemical measurements indicate that the mechanism of cracking was associated with onset of passivation as a function of water content.

Introduction

A research proposal was submitted to NASA in July 1965 concerning "Stress Corrosion Cracking of Titanium Alloys" in response to the NASA Research Suggestion (RS-4-Stress Corrosion), dated June 1965. A grant was awarded, effective June 1, 1966. In the interim period, a start was made on the problem under Mellon Institute sponsorship. This preliminary work served to assure that titanium alloy specimens in foil form were adaptable to existing procedures worked out for ultra-high strength steels.

More recently, it has been possible to make correlations between electrode potential measurements and the more susceptible conditions for stress corrosion cracking of 18Ni maraging steel foil.¹ As a function of the pH of aqueous solutions, the maximum susceptibility occurred just prior to the onset of passivation. Similar work on commercial titanium alloys is presently underway and partial results are reported herewith.

Materials

Commercially produced titanium alloys were used in this investigation. The foil (.002-.003" thick) was obtained from companies which reroll sheet and strip on a Sendzimir mill. Not all of the alloys to be investigated have been received as yet, so that the present work has been limited to two alloys whose mill compositions are listed in Table I, i.e., Ti-6Al-4V and Ti-13V-11Cr-3Al.

Quarter-inch and half-inch strips were slit from the foil parallel with the rolling direction by automatic machinery. Heat treating was accomplished by sealing specimens in vycor tubes under partial pressure

of helium. Tension tests were performed on an Instron Testing Machine, and the resulting tensile properties are presented in Table II.

Reagent grade chemicals were used throughout in the preparation of solutions without additional purification. The water was first distilled and then passed through a commercial ion exchanger; the electrical conductivity was of the order of 6×10^{-7} ohms⁻¹.

Experimental Apparatus and Procedures

Stress corrosion testing of foil was carried out with dead weight loading, but specimens could be either pin-loaded or clamp-loaded. The pin-loaded specimens were half-inch wide and generally notched by tearing. In either case, the corrosive atmosphere was applied over only a portion of the test specimen and was contained in a polyethylene bottle. The apparatus for clamp-loaded specimens has provision for testing ten specimens at one time. Figures 1 and 2 show it with all positions loaded.

Figure 1 presents the overall view of the apparatus with the auxiliary equipment. To the right on the wall are ten counters which record the time to failure of the individual specimens. The counters are activated by micro-switches seen at close range in Figure 2. Also visible is one of the broken specimens, approximately four inches long, after the plastic bottle has been removed. In the far testing position in Figure 2, the loaded specimen threaded through the bottle containing the testing solution may be seen. The specimen was clamped to straps on each side and the tension applied over a ball bearing on one side with dead weight. The versatility of the apparatus can be noted at the end position where the test specimen was loaded in a vertical position rather

than the horizontal position, which facilitates the testing of partially immersed specimens.

It was also possible to use an alternate immersion type of testing by means of a gravity feed system for moving the liquid solution in and out of the bottle by a reciprocating motion of a reservoir of solution (see extreme right in Figure 1). In response to the timers, the exposure and immersion times of a specimen could be varied as well as the exposure/immersion ratios. The small motor and fan directly above the testing apparatus in Figure 1 was sometimes used to increase the rate of drying of alternate immersion specimens. The gravity feed equipment could also be used for reciprocally flowing solutions.

The pin-loaded specimens are shown in Figures 3 and 4. The test specimen is loaded by means of a weighted lever arm. The load can be dead weight or the lever arm may be locked in position at a given load.

All test specimens were cleaned with methyl-ethyl-ketone before threading through a 1 1/4 inch diameter polyethylene bottle. A detailed description of the experimental arrangement for the clamp-loaded specimens has already been given.² The pin-loaded specimens were notched by tearing to the center line between punched holes.

Apparatus for measuring electrode potentials is pictured in Figure 5. A specimen of quarter-inch foil, about one-half inch long, was degreased in methyl ethyl ketone and then screw-clamped into a plastic holder to make electrical contact with a platinum wire lead. A Luggin capillary was placed in a fixed position in front of the foil and was connected by a KCl salt bridge to a silver/silver chloride reference

electrode. The plastic holder, when assembled, was immersed in the test solution. This whole assembly, including the reference electrode, was immersed in a constant temperature bath maintained at $30^{\circ} \pm 1^{\circ}\text{C}$.

Values of electrode potential were measured as a function of time for periods of one to two hours. Zero time was taken as the moment of immersion of the specimen in the test solution. A compensating device, consisting of a micro-potentiometer, converted the values directly to the calomel scale, and these values were measured with a 610B Keithley electrometer.

The experimental set-up for potentiostatic measurements is pictured in Figure 6 and shows an Anotrol Model 4700 potentiostat, voltmeter, calomel half cell, salt bridge and working cell. The working cell has a volume of 750 ml, inlets for gas, thermometer, reference electrode, and working electrode. The auxiliary electrodes are platinum. A magnetic stirrer was used to gently stir the test solution. The working electrode was made by spot welding a square centimeter of titanium to the end of a piece of platinum wire. The wire, back of sample and edge were coated with several layers of epoxy resin leaving an exposed surface area of a quarter of square centimeter. The Luggin capillary is positioned at one of the top corners and about 2 mm away from the electrode surface. This capillary is filled with saturated KCl and connected, via the bridge, to a saturated calomel electrode.

Nothing was done to prepare the electrode surface except degreasing in methyl ethyl ketone which duplicates the conditions that were encountered on the stress corrosion testing apparatus. Likewise, no attempt was made to control the gaseous content of the electrolyte.

The values of potential set with the potentiostat were measured using an externally connected vacuum tube voltmeter that had been previously calibrated. Measurements of current were taken five minutes after the adjustment of potential. The temperature of the electrolyte was $28^{\circ} \pm 1^{\circ}\text{C}$ throughout the experiments.

Experimental Results and Discussion

Aqueous Solutions

The initial approach to the stress corrosion cracking of titanium alloys was to investigate the possibility of the foil exhibiting cracking in aqueous solutions containing NaCl or in substitute ocean water. Although it has been generally believed that titanium alloys do not stress crack in the aforementioned environments without precracking,^{3,4} nevertheless, recent work with maraging steel foil indicates that this foil was more sensitive to stress corrosion cracking than was sheet from the same heat.¹ Foil specimens and precracked specimens may, under some conditions, show a similar high sensitivity to stress corrosion cracking that cannot be detected with the more conventional U-bend or bent-beam specimens made from sheet or bar. The possibility that titanium alloys in foil form might also stress crack, even as precracked specimens, required investigation.

Attempts to crack alloys Ti-6Al-4V and Ti-13V-11Cr-3Al as foil in aqueous salt solutions loaded to 75-85 percent of yield strength were without success. Stagnant immersion as well as alternate immersion tests were run. Both cold rolled and heat treated foil was tried. Substitute ocean water (ASTM: D1141-52) and aqueous solutions with varying amounts

of NaCl were tried. Pin-loaded specimens pretorn were not effective.

Electrode potential measurements as a function of pH and NaCl content were useful in predicting the environmental conditions for maximum susceptibility to stress corrosion cracking with maraging steel.¹ Similar curves were made for the titanium alloys and an example of one of them is presented in Figure 7. The points on the curve represent values of electrode potential after one hour's time, e.g., see Figure 11. The curve deflects sharply at high and low pH values which would suggest the regions of susceptibility to stress corrosion cracking. Tests were made using environments similar to those in the region of the deflections in the curve, but no failures occurred in 2-3 month's time.

Methanol Solutions

It has recently been demonstrated by Mori et al⁵ that commercially pure titanium and zirconium will stress crack as U-bend specimens in alcohol solutions containing 0.4 to 1.0 percent hydrochloric or sulfuric acid. Small amounts of water were found to prevent cracking and the authors suggested about 1.5 percent water as sufficient for titanium. The authors were not able to determine a mechanism of stress corrosion cracking for titanium and zirconium in HCl-methanol.

In order to help elucidate the mechanism of the cracking of titanium in alcohol solutions, the project emphasis has recently turned to this problem. It was found that NaCl additions to methanol would decrease the time to failure of the clamp-loaded specimens stressed to 75-85 percent of yield strength (see Table 3).

The optical microscope reveals very few cracks forming in specimens that have failed. The cracking that was observed exhibits side branching characteristic of stress corrosion cracking, see Figures 8 and 9. In the heat treated foil, the cracking appears to be predominately intergranular.

Present work confirms the observations of Mori et al⁵ that the addition of water will prevent cracking, at least up to 300 hours. The amount of water required varies somewhat with alloy and heat treatment, but no failures have been observed thus far with two percent or more water. Figure 10 illustrates how the Ti-13V-11Cr-3Al alloy reacts when exposed to methanol^{*}-water solutions containing 0.15 N NaCl. The water seems to prevent cracking even when less than one percent is added. The minimum in the curve occurs at about 0.35 percent water.

To better understand the nature of the cracking, electrode potential and potentiostatic measurements were made. Typical measurements of specimen electrode potentials as a function of time are plotted in Figure 11 for the Ti-13V-11Cr-3Al alloy immersed in methanol-water solutions containing 0.15 N NaCl. The curves fall into two distinct types, those that increase and those that decrease the potential within the first quarter hour. This separation between the two groups of curves falls between 0.30 and 0.38 percent water, which covers the range where the maximum susceptibility to stress corrosion cracking occurs. If the values for electrode potential for any given time, i.e., quarter, half or full hour, are plotted, an abrupt change in the resulting curve occurs near 0.35 percent water and at a potential of about -150 mv with respect to saturated calomel electrode

* Methyl alcohol absolute, low in acetone, containing 0.036 percent water.

(S.C.E.), e.g., see Figure 12 for a plot of one-hour values of electrode potential.

It was thought that the correlation of the maximum stress corrosion susceptibility and measurements of electrode potential as a function of water content in methanol solutions containing 0.15 N NaCl were possibly associated with the onset of passivation. Such an association has been found for 18Ni maraging steel¹ as a function of pH of aqueous solutions. Potentiostatic measurements recorded in Table 4 for the Ti-13V-11Cr-3Al alloy indicate that two percent water sustains passivation over the range of potential values of interest. The test run with methanol without added water indicates no passivation. The solution which corresponds to that which produces the maximum susceptibility to stress corrosion cracking, 0.35 percent water, exhibited a small region of passivation. That is, with this solution, the alloy was close to the onset of passivation as a function of water content.

Although the experimental data are limited at this time, the following explanation may be applicable to the stress corrosion behavior of titanium alloys in methanol solutions containing small amounts of water and Cl⁻ ion. Passivation does not occur completely at any definite value of electrode potential or water. It would occur over a short range of values. Within the range of water contents up to about one percent, passivation is occurring. As the water is increased, more of the surface is passivated and the corrosion currents generated at the remaining active areas become progressively more intense. Ultimately this leads to the nucleation of a site susceptible to stress corrosion cracking and thus produces a

a minimum in the percent water versus time to failure curve. It is probably that the Cl^- ion plays a part in the overall mechanism, and work is presently progressing in this direction.

Conclusions

The following conclusions are based on the work accomplished in the period of June 1 to November 30, 1966.

1. The two alloys investigated, Ti-6Al-4V and Ti-13V-11Cr-3Al, in foil form did not stress crack in aqueous solutions with pH values from 0 to 13 even with NaCl added or in substitute ocean water.

2. These same two alloys were very susceptible to stress corrosion cracking in methanol solutions containing less than about one percent water. Increasing the water tends to prevent cracking.

3. A minimum in the time to failure curve as a function of water content in methanol solutions containing 0.15 N NaCl was attributed to electrochemical factors.

4. Electrode potential measurements indicated the amount of water needed to obtain the minimum. Potentiostatic tests suggest that the maximum susceptibility was associated with the onset of passivation as a function of water content.

Future Work

The following items of work are planned for the immediate future.

1. Continued studies are planned of the correlation of electrochemical measurements with stress corrosion susceptibility in alcohol solutions on the two alloys already being investigated.

2. Three more commercial alloys in foil form should be received from the rolling mill around the first of the year, namely: Ti-8Al-1Mo-1IV, Ti-5Al-5Sn-5Zr, and Ti-6Al-2Sn-4Zr-2Mo. Initial plans would call for following present procedures using alcohol solutions with these alloys. No extensive tests with aqueous solutions are anticipated.

3. Electron microscopy is planned for certain of the alloys which show significant differences in susceptibility to stress corrosion cracking as a function of structure.

4. Studies of the rate of crack propagation using a hard-beam tensile machine and specimens cut from rod will be initiated.

References

1. J. A. S. Green and E. G. Haney, "Relationships between Electrochemical Measurements and Stress Corrosion Cracking of Maraging Steel"; to be published in Corrosion.
2. J. A. S. Green and E. G. Haney, "A Stress Corrosion Test for Foil and Strip"; presented at the Annual Meeting of A.S.T.M., Atlantic City, June 27, 1966.
3. D. W. Stough, F. W. Fink, and R. S. Peoples, "Stress Corrosion and Pyrophoric Behavior of Titanium and Titanium Alloys"; TML Report No. 84, Battelle Mem. Inst., September, 1957.
4. B. F. Brown, "A New Stress-Corrosion Cracking Test for High-Strength Alloys", Materials Research and Standards, Vol. 6, March 1966, pp. 129-133.
5. K. Mori, A. Takamura and T. Shimose, "Stress Corrosion Cracking of Ti and Zr in HCl-Methanol Solutions," Corrosion, Vol. 22, Feb. 1966, pp. 29-31.

Table 1

Chemical Composition, Weight Percent

Alloy	C	O	V	Al	H	N	Fe	Cr
6Al-4V	.02	.134	4.0	6.0	.001	.01	.21	--
13V-11Cr-3Al	.016	--	13*	3*	.007	.017	.08	11*

*Nominal

Table 2

Mechanical Properties of Titanium Alloy Foil

Alloy	Treatment	Tensile Strength, KSI	Yield Strength KSI, 0.2% off set	Elongation, percent in 4 in.
13V-11Cr-3Al	Cold rolled	181.6	172.8	3.75
13V-11Cr-3Al	Slow heat to 1400°F, held 10 min. and C.W.Q. + 24 hr. at 900°F	175.2	165.6	4.88
6Al-4V	1 hr. at 1750°F, A.C. + 2 hr. at 900°F	187.5	165.5	~
6Al-4V	Cold rolled and annealed	161.6	129.6	11.2 (in 2")

Table 3

Effect of Metal Treatment and NaCl on Time to Failure
of Titanium Alloy Foil in Methanol Solutions

Alloy	Treatment	Time to Failure, minutes	
		Methanol	Methanol saturated with NaCl
13V-11Cr-3Al	Cold rolled	92	30
13V-11Cr-3Al	Slow heat to 1400°F, held 10 min. and C.W.Q. + 24 hr. at 900°F	779	7
6Al-4V	Cold rolled and annealed	3,750	2,780
6Al-4V	1 hr. at 1750°F, A.C. + 2 hr. at 900°F	No failure after 20,000	450

Table 4

Potentiostatic Measurements on Ti-13V-11Cr-3Al
Heat Treated at 1400°F + C.W.Q. + 24 hr. at 900°F

Potential (mv) S.C.E.	Current Density μ amp/cm ²		
	Percentage of water in methanol with 0.15 N NaCl		
	0.036%	0.35%	2.0%
-1000	-15.8	-44.0	-16.0
-900	-11.3	-19.2	-6.4
-800	-8.1	-6.8	-2.4
-700	-4.5	-2.4	-0.8
-600	-2.3	-0.8	-0.4
-500	-0.9	-0.4	-0.2
-400	+1.8	0.0	0.0
-300	+171.0	0.0	0.0
-200	+441.0	+40.0	0.0
-100	+900.0	+560.0	0.0
0	+2070.0	+1360.0	0.0
+100	+2970.0	+2160.0	+25.2
+200	+3555.0	+2960.0	+352.0
+300	+3960.0	+3600.0	+2160.0
+400	+4320.0	+4200.0	+2760.0
+500	+4950.0	+4400.0	+3400.0
+600	+5400.0	+5200.0	+3800.0
+700	+5850.0	+5600.0	+4400.0
+800	+6300.0	+6000.0	+5200.0
+900	+6750.0	+6400.0	+5600.0
+1000	+7200.0	+6800.0	+6000.0

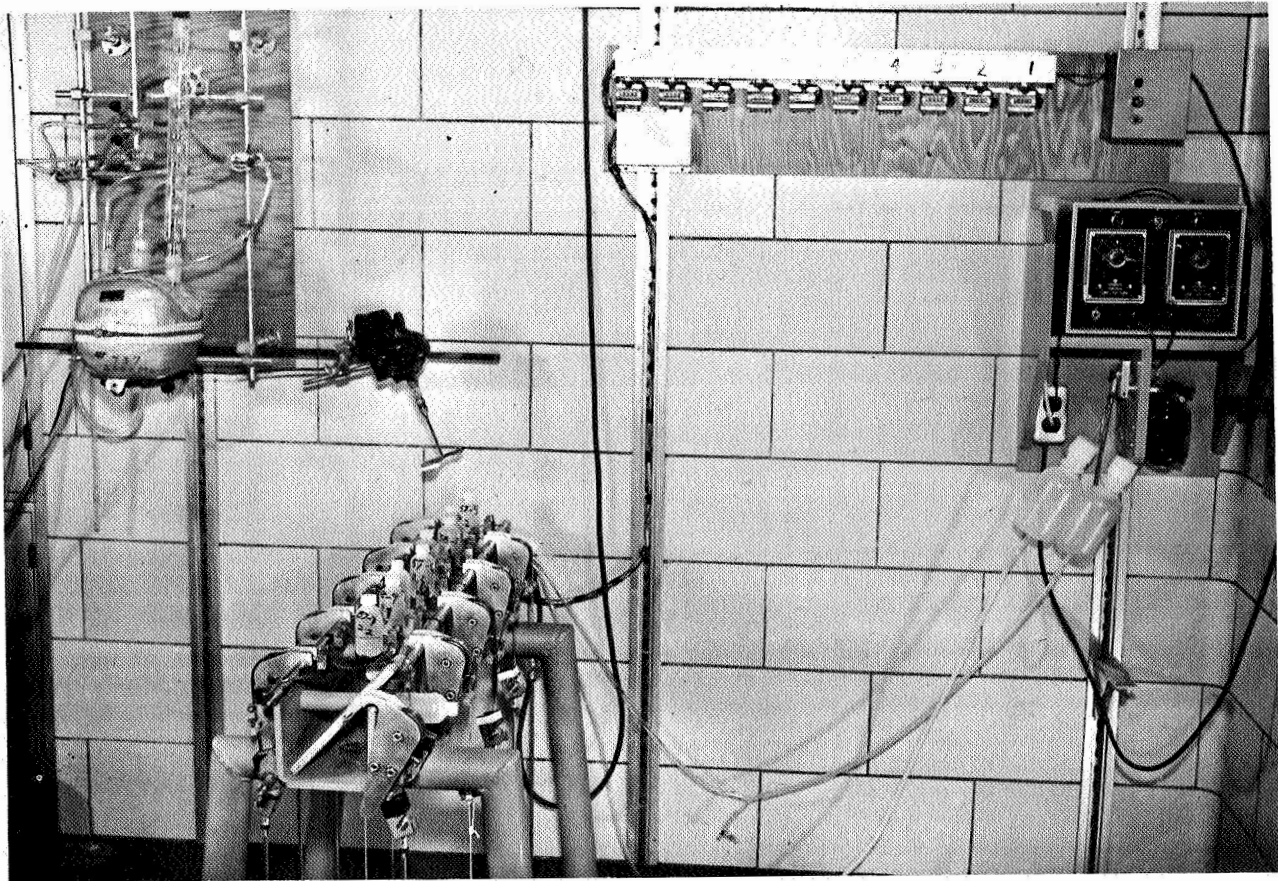
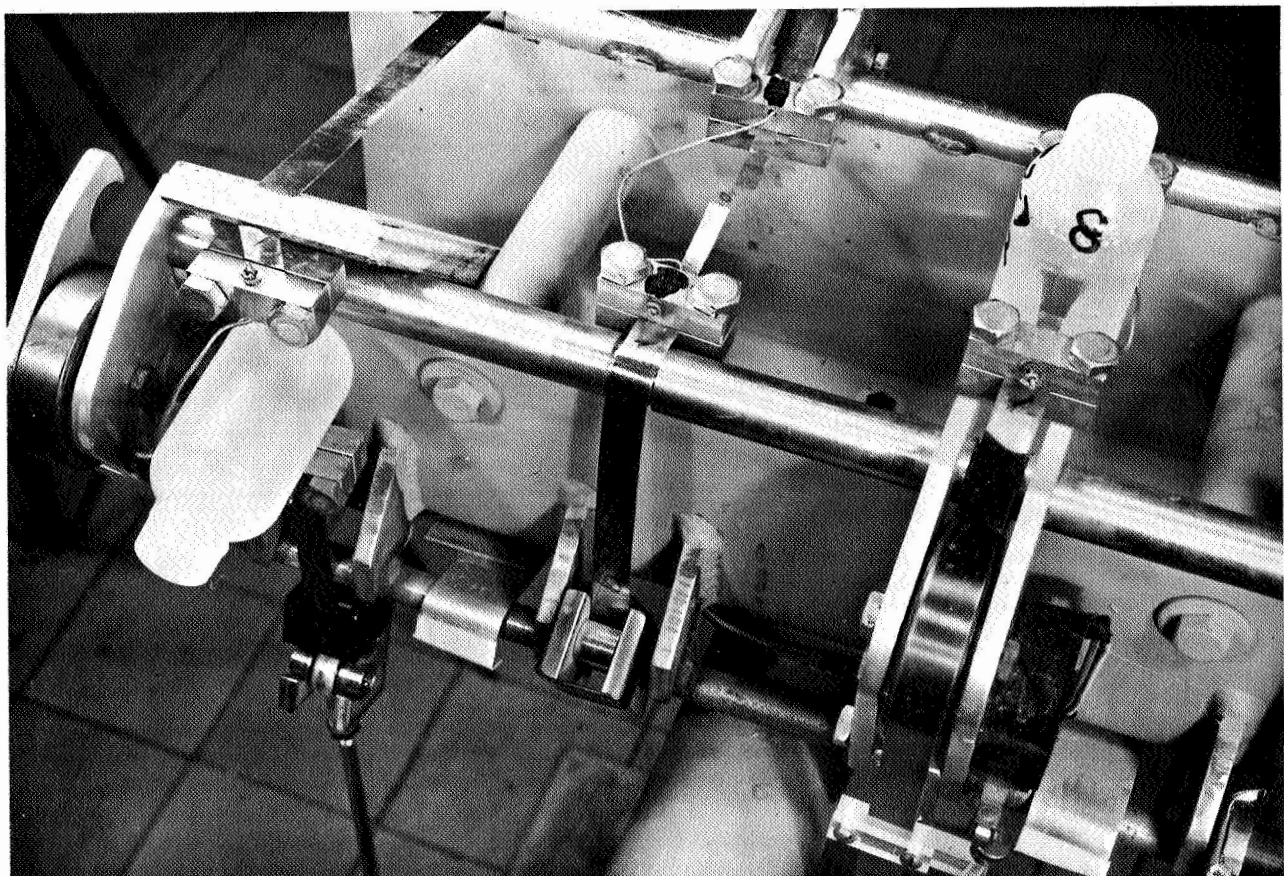


Figure 1--Apparatus for Stress Corrosion Testing of Foil at Constant Stress and its Auxiliary Equipment.

Figure 2--A closer view of stress corrosion testing apparatus showing partial immersion set-up (left), a cracked specimen with bottle removed (center), and a stagnant immersion test in progress (right).



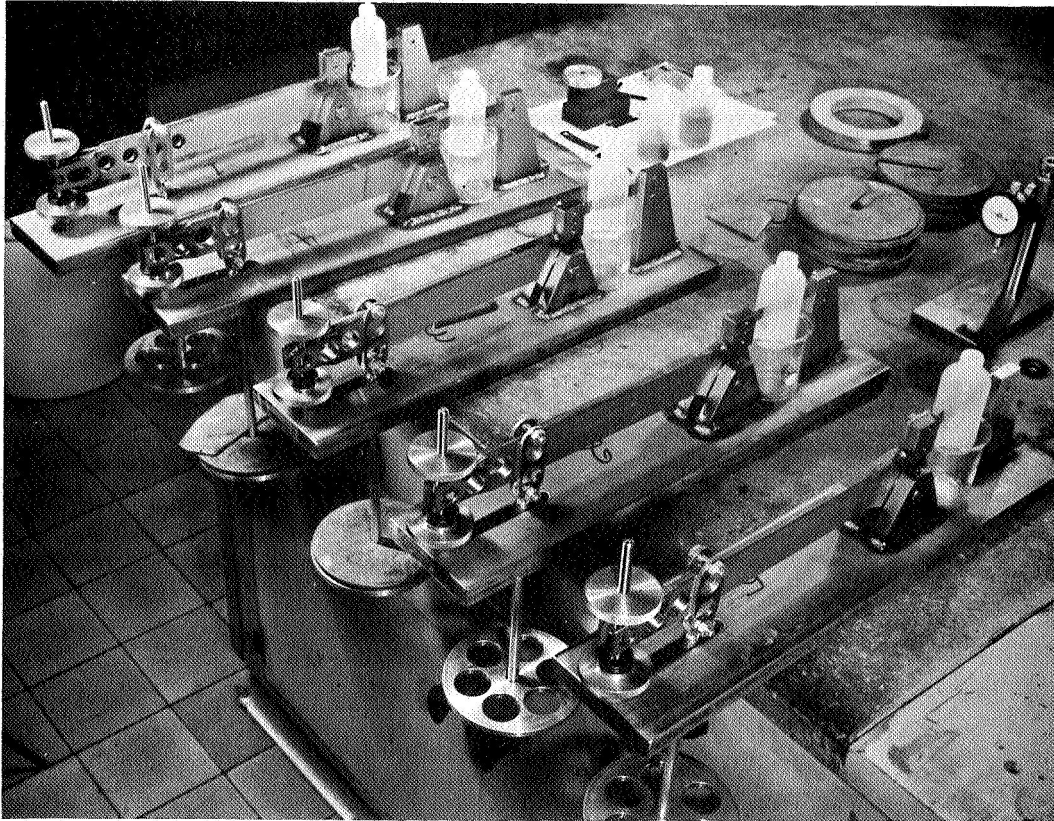
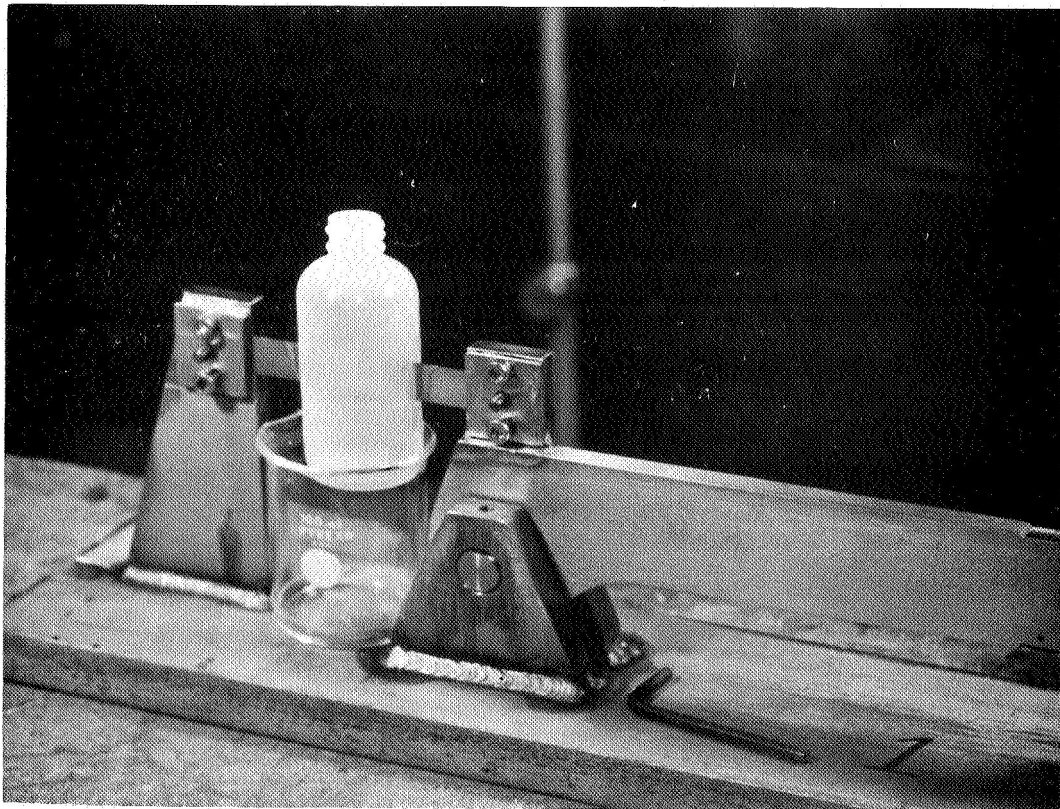


Figure 3--Apparatus with lever loading for Stress Corrosion Testing of Foil and its Auxiliary Equipment.

Figure 4--Closer view of the apparatus showing a pin-loaded specimen ready for testing.



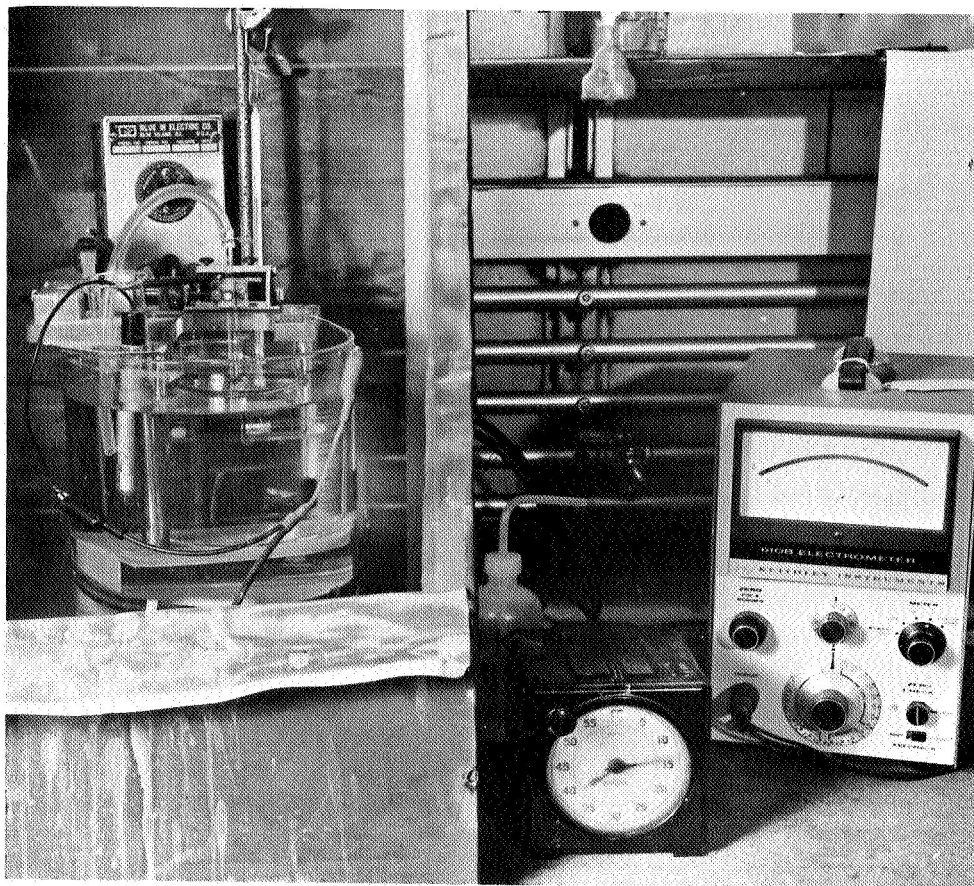
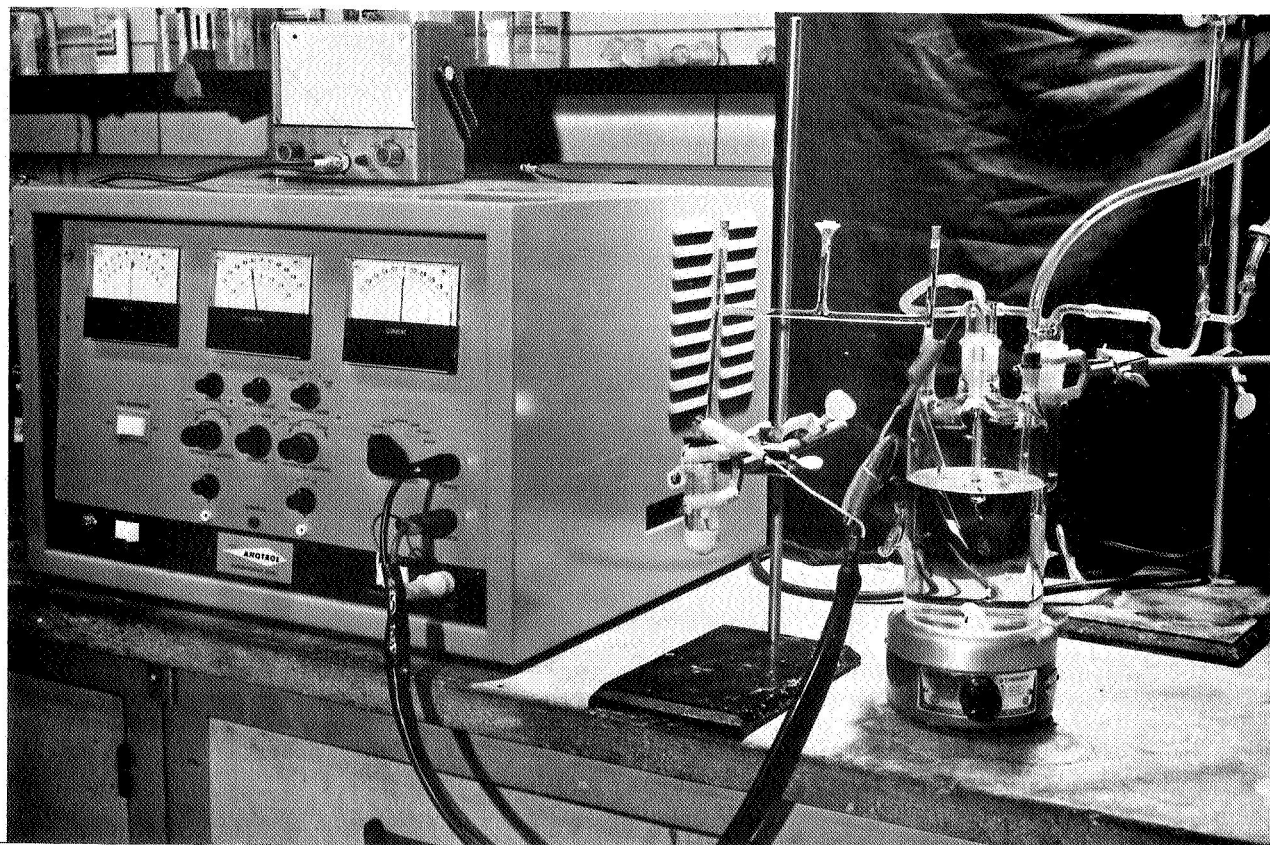


Figure 5--View of set-up for measuring electrode potentials showing the cell enclosed in copper-wire shield, a timer and the electrometer.

Figure 6--View of set-up used for potentiostatic measurements with the working cell to the right, the potentiostat on the left and the saturated calomel electrode in center.



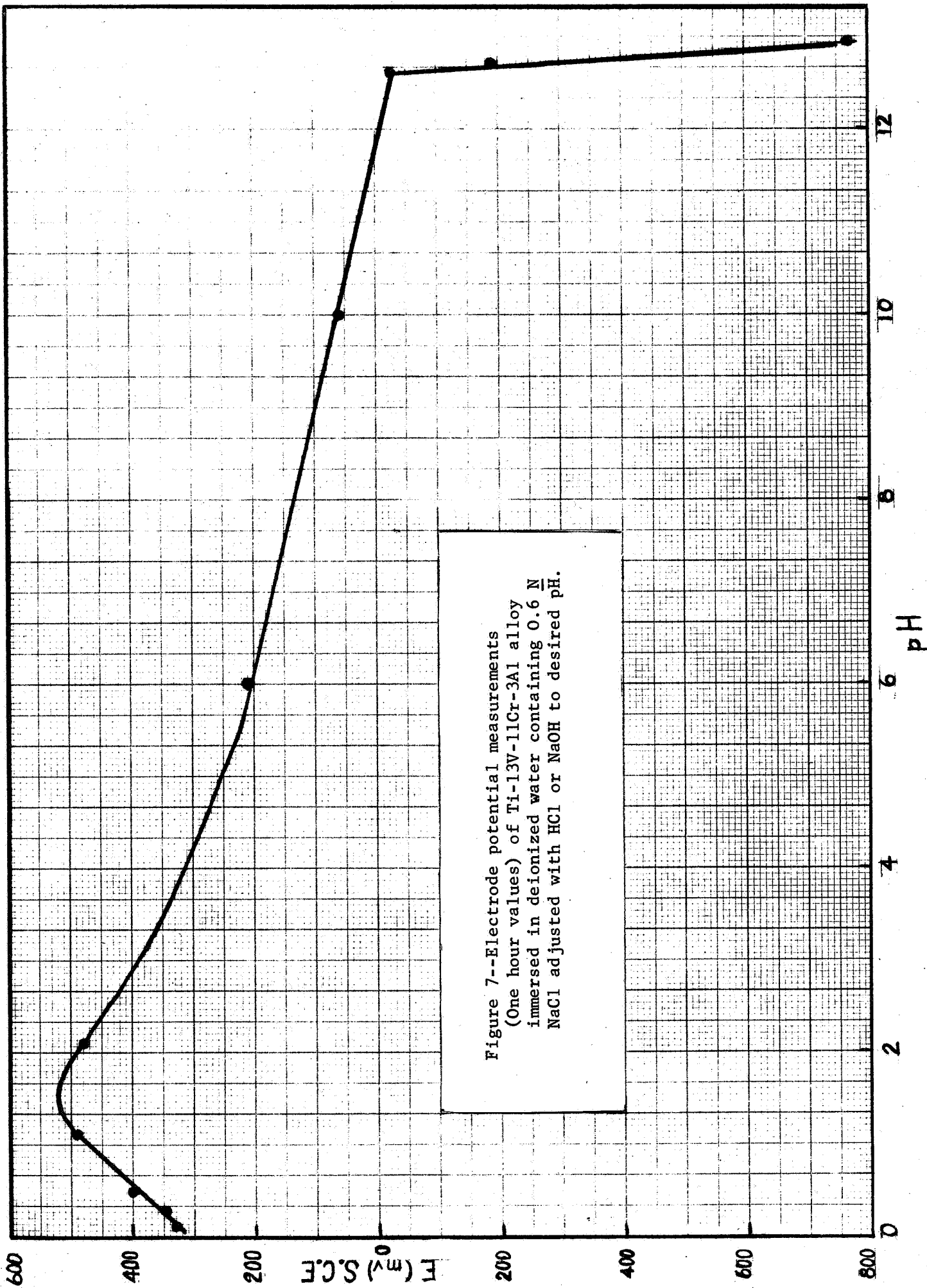


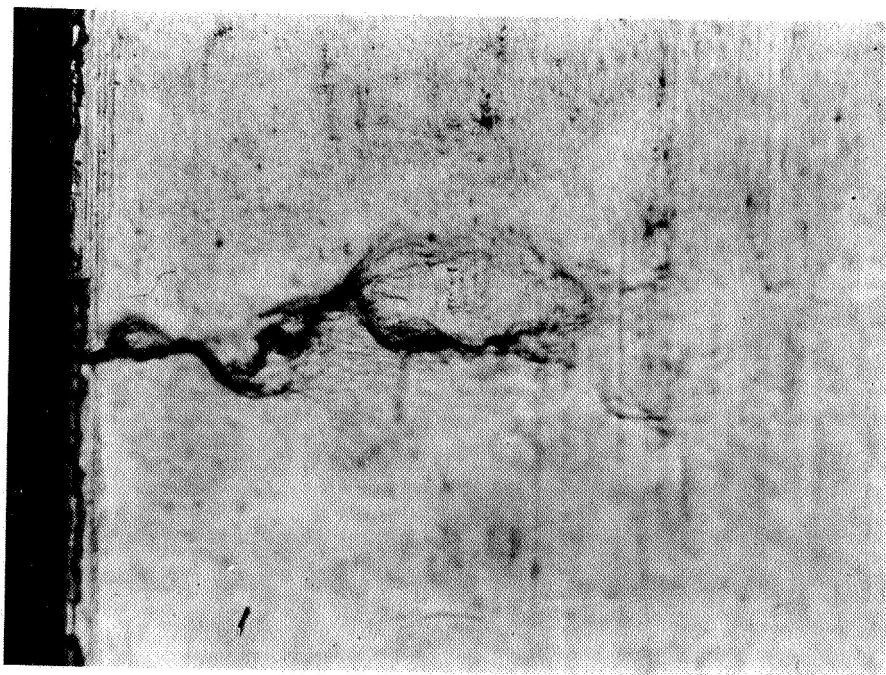
Figure 7--Electrode potential measurements
 (One hour values) of Ti-13V-11Cr-3Al alloy
 immersed in deionized water containing 0.6 N
 NaCl adjusted with HCl or NaOH to desired pH.

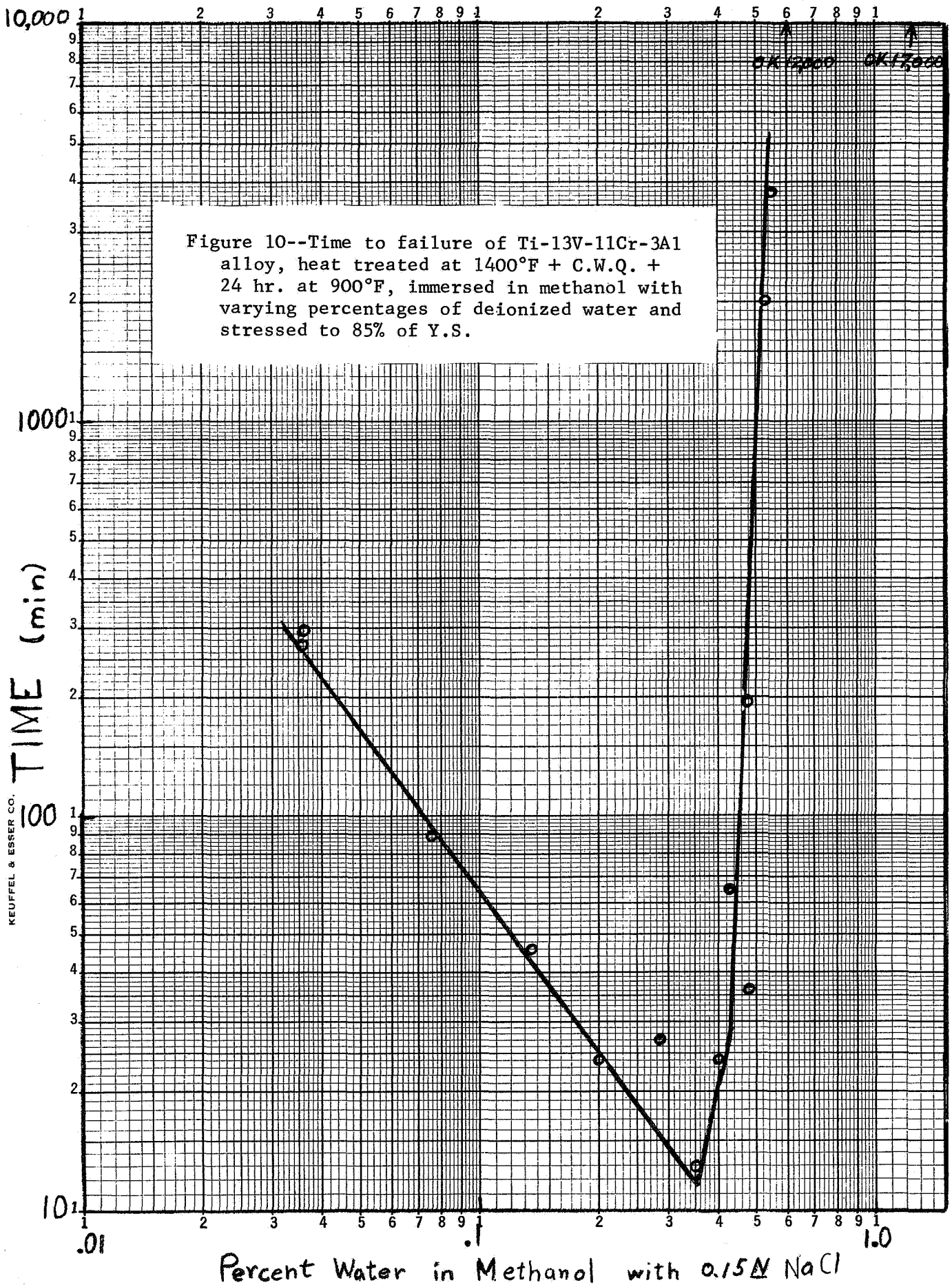


Photomicrographs of the surface of foils showing stress corrosion cracks in an area near the fracture.

Figure 8--Ti:6-4 alloy, cold rolled and annealed, broke after 975 min. exposure to solution of methanol saturated with NaCl; stressed 75% Y.S., Mag. 100X.

Figure 9--Ti:13-11-3 alloy, heat treated at 1400°F + C.W.Q. +34 hr at 900°F broke in a few minutes exposure to solution of methanol saturated with NaCl + 0.2% H₂O; stressed 85% Y.S., Mag. 250X.





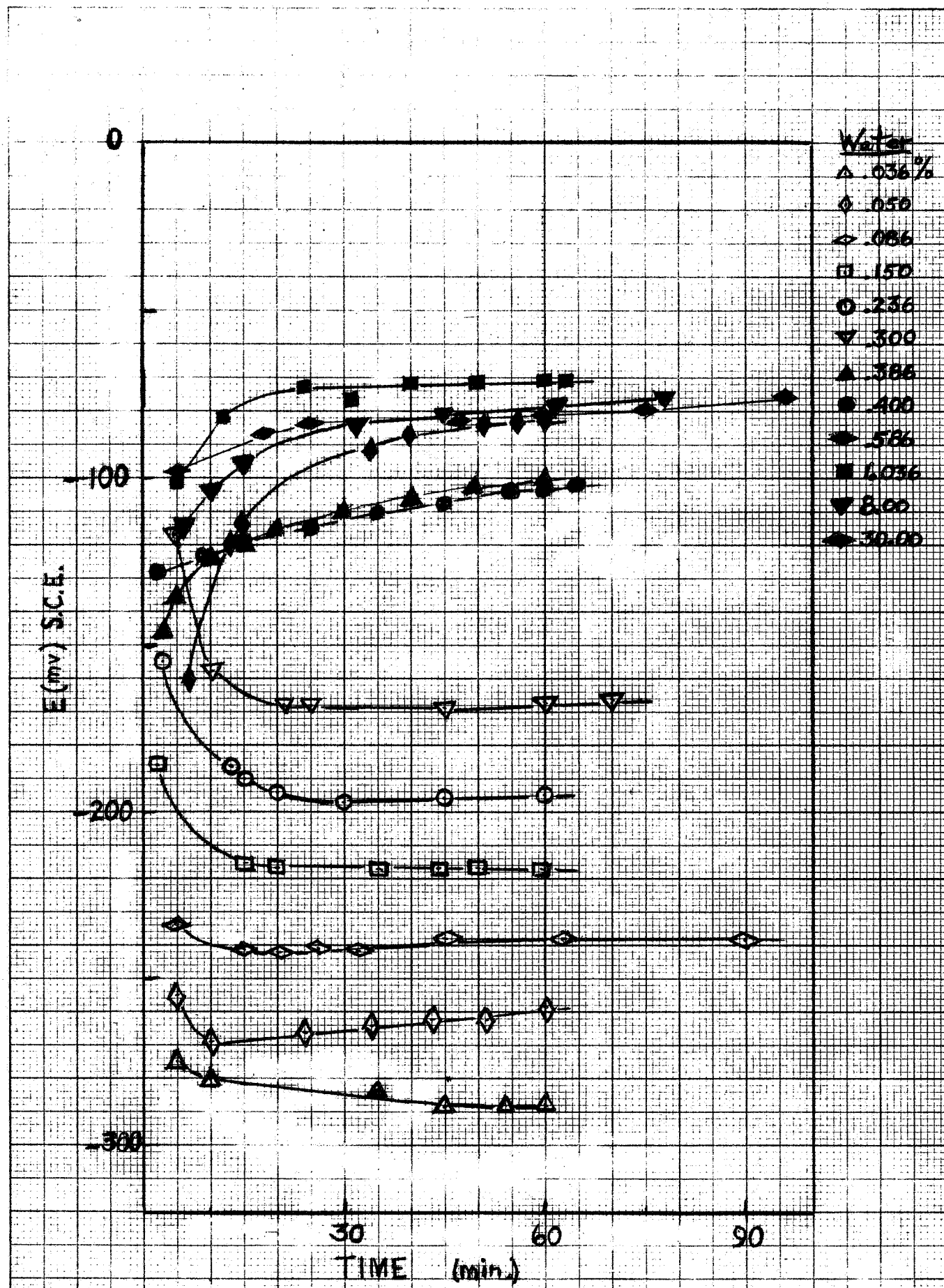


Figure 11--Variation with time of electrode potential for Ti-13V-11Cr-3Al alloy, heat treated at 1400°F + C.W.Q. + 24 hr. at 900°F, immersed in methanol containing 0.15 N NaCl with varying percentages of deionized water.

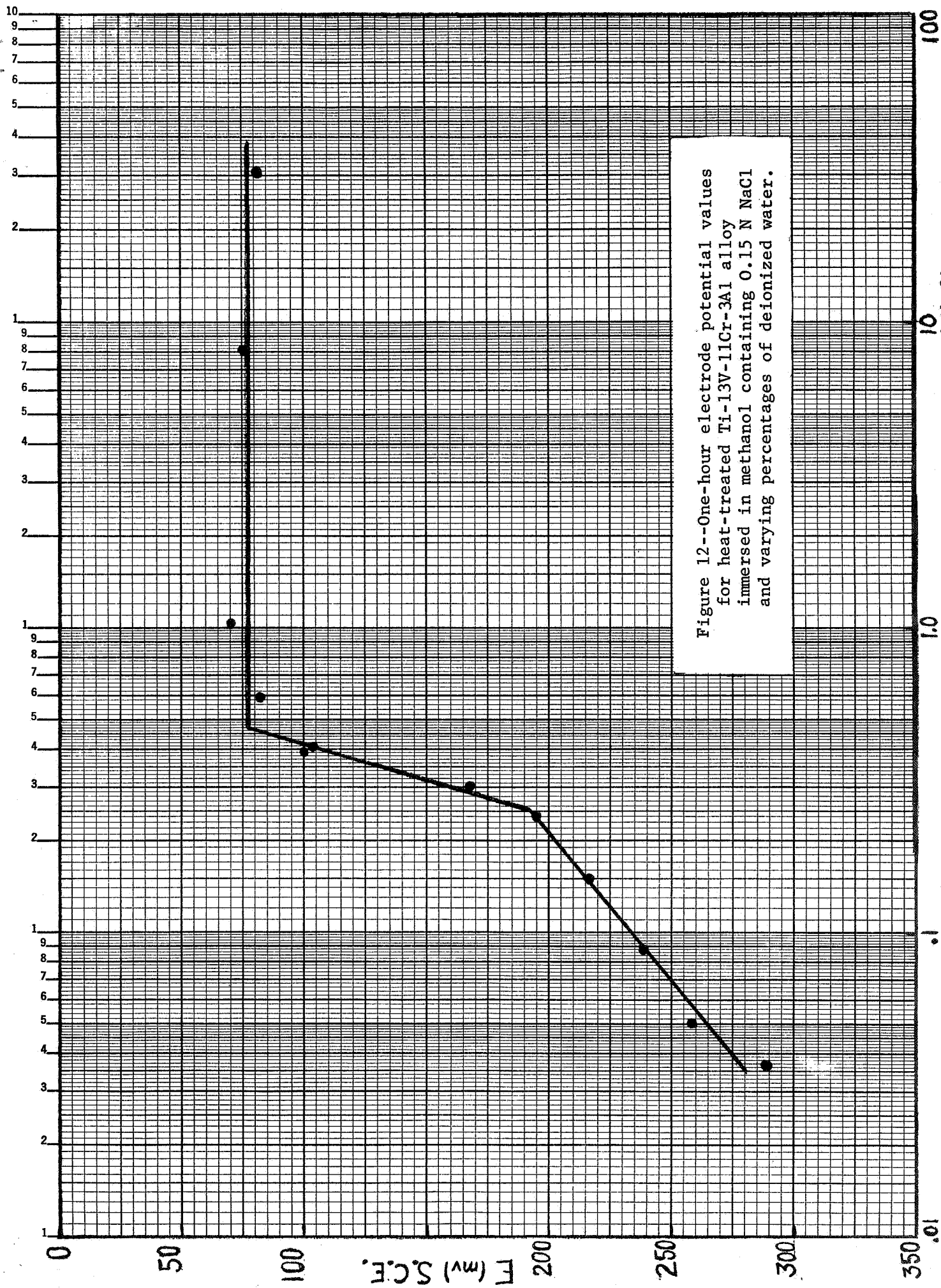


Figure 12--One-hour electrode potential values for heat-treated Ti-13V-11Cr-3Al alloy immersed in methanol containing 0.15 N NaCl and varying percentages of deionized water.