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DISSOLUTION BEHAVIOR OF Fe AND Ni IN THE ACTIVE REGION OF DISSOLUTION IN SULFURIC ACID

DALE O. CONDIT, 2ndLt, USAF
METALLURGY AND CERAMICS RESEARCH LABORATORY

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AEROSPACE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This technical report was prepared by the Metallurgy and Ceramics Laboratory of the Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio. The research was conducted in conjunction with similar corrosion research at the Ohio State University under the supervision of Dr. Roger W. Staehle and the sponsorship of the United States Atomic Energy Commission.

The author wishes to acknowledge the assistance of Dr. Staehle and the help of the members of the Metallurgy and Ceramics Laboratory of ARL, namely Major William E. Craven, Darrell Frank, and Jack Smith.

ABSTRACT

The dissolution characteristics of high purity Fe and high purity Ni in 1N H_2SO_4 at 25° C were investigated using atomic absorption analysis. The specimens were dissolved potentiostatically and samples of solution were analyzed for Fe and Ni ions.

The analyses showed that the dissolution was a logarithmic function of time, the exponent of time being about 1.0 for Fe and 0.7 for Ni. Anodic polarization curves indicated that dissolution of Fe was larger than for Ni. The mechanism for Fe involved two electrons; whereas, for Ni it involved three electrons. Determination of zero-order rate constants indicated that the constants for both Fe and Ni increase with potential, the constant for Fe at a given potential always being much larger than the constant for Ni.

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Section I

INTRODUCTION TO THE PROBLEM

INTRODUCTION

The purpose of this investigation was to study the active dissolution behavior of pure Fe and pure Ni in acid medium at low pH. This investigation was a first step in a program whose ultimate aim is to determine the relative rates of dissolution of Fe and Ni from Fe-Ni binary alloys and the residual composition of the alloy surface. The incentive for such a program was the intense current interest in passivity and stress corrosion cracking which depend for their peculiar behavior on the composition of the surface of aloys containing Fe and Ni.

The results of any investigation of this type do not reflect the equilibrium states of the system but rather the rates of the dissolution processes. In order to determine the changes in dissolution behavior that occur when two metals are alloyed, it is important to first understand the dissolution behavior of the pure components.

SINGLE METAL ELECTRODES

The standard electrode potential E^o_o of a pure metal is defined as the potential where metal and metal ions of unit activity are in equilibrium. This equilibrium can be represented by the following equation:

$$M \rightleftharpoons M^{+z} + ze^- \qquad (1)$$

for which the Nernst equation gives the potential

$$E_o = E^o_o - \frac{RT}{zF}\left[\frac{a_{M^{+z}}}{a_M}\right] \qquad (2)$$

This equation establishes the standard equilibrium potential for the metal, E_o being the equilibrium potential at any given activity of metal ions $a_{M^{+z}}$. As Tomashov(1) points out, the equilibrium thus established is a dynamic equilibrium, the transfer of charges continuing at equal rates, forward and reverse. The rate of charge transfer at which the reversible equilibrium is established is given by the exchange current which Vetter$^{(2)}$ shows to be:

$$i_o = \overrightarrow{i} = zF\,K_+\,C_r \exp-(\Delta\bar{G}^*/RT) \tag{3}$$

$$= \overleftarrow{i} = -zF\,K_-C_o \exp-(\Delta\bar{G}^*/RT)$$

where

$$K_+\,C_r \exp-(\Delta G^*/RT)$$

and

$$K_-\,C_o \exp-(\Delta G^*/RT)$$

represent the number of surface atoms that are dissolving and the number of atoms redepositing on the surface, respectively; and zF is the conversion factor to current.

If the potential of this electrode deviates from the equilibrium potential by a value $\eta = E - E_o$, the current flow is altered in either the forward or the reverse direction depending on the sign of η. This current flow is given by:

$$\overrightarrow{i} = zF\,K_+\,C_r \exp - (\Delta\bar{G}^* - \alpha zF\eta)/RT$$

$$= i_o \exp(\alpha zF\eta/RT) \tag{4}$$

and

$$\overleftarrow{i} = -zF\,K_-\,C_o \exp\left[-\left\{\Delta\bar{G}^* + (1-\alpha)zF\eta\right\}/RT\right]$$

$$= -i_o \exp\left[-(1-\alpha)zF\eta/RT\right] \tag{5}$$

The net current for a given overpotential η is thus

$$i_{net} = \overrightarrow{i} - \overleftarrow{i} \tag{6}$$

which for overpotentials of 30 mV or more in either the positive (anodic) or the negative (cathodic) direction can be approximated by the current for that direction only.(3) This approximation yields Tafel's equation which for anodic polarization is as follows:

$$\eta = -\frac{2.303\,RT}{\alpha z F} \log i_o + \frac{2.303\,RT}{\alpha z F} \log i \tag{7}$$

This equation is in the form of the following straight line:

$$\eta = a + b \log i \tag{8}$$

where η is linearly dependent on logi. The intersection of plots of anodic and cathodic polarization curves is at the equilibrium potential and the exchange current as shown in Figure 1.

When a metal is immersed in a solution containing ions other than its own ions, it will establish a potential different from the equilibrium potential. This potential is commonly called the corrosion potential; and the current at which this potential obtains, the corrosion current. In many cases the cathodic reaction is not the redeposition of metal ions as in the previous equilibrium case. The cathodic reaction is often an irreversible process such as the evolution of hydrogen in deoxygenated acid media. Tafel's equations still apply. The system of metal electrode in aqueous acid solution is shown in Figure 2 where the anodic reaction is metal dissolution and the cathodic reaction is hydrogen gas evolution. In such cases, the corrosion current is a reflection of the actual rate of corrosion.

Some metals, like Fe or Ni in sulfuric acid, display an active-to-passive transition. This behavior is marked by a large current in the

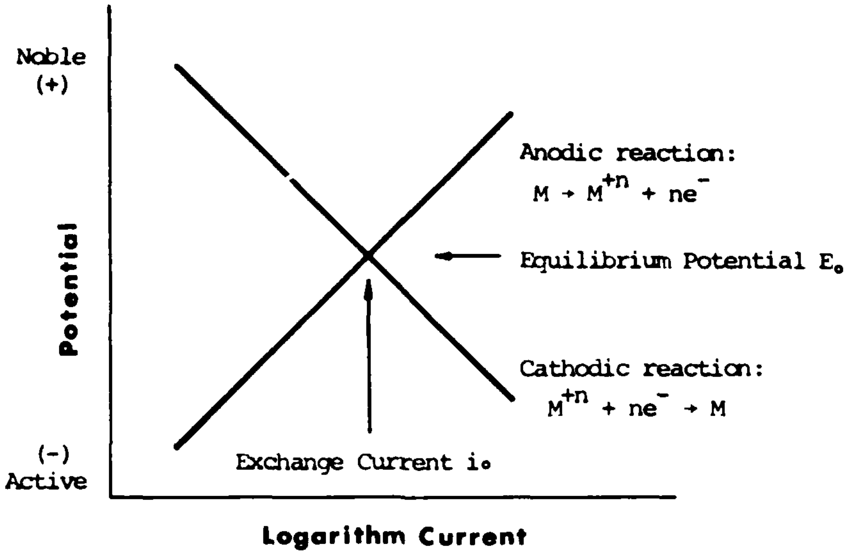

Figure 1. Polarization behavior for a single electrode system

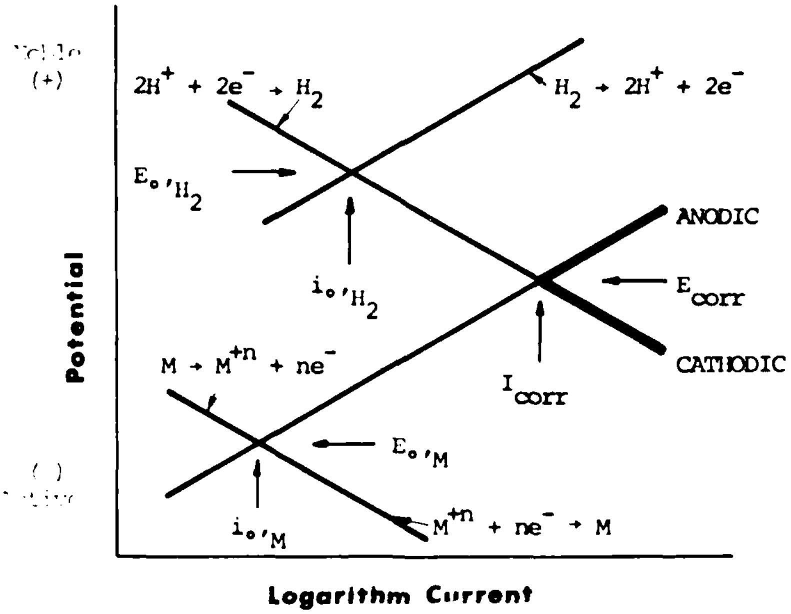

Figure 2. Polarization curves for a corroding electrode system

low overpotential region of the anodic polarization curve. As the overpotential is increased, however, the current begins to decrease as a passive layer is formed on the metal surface. This condition continues for a few hundred millivolts; then the current begins to increase due to breakdown of the passive film, metal dissolution in higher valence states, and oxygen evolution. This phenomenon is illustrated in Figure 3. The dotted lines in this figure indicate the anodic and cathodic polarization curves that would be obtained experimentally; these curves approach the actual polarization curves (solid lines) as the overpotential becomes greater than 30 mV. The present investigation was restricted to observing dissolution in active dissolution region.

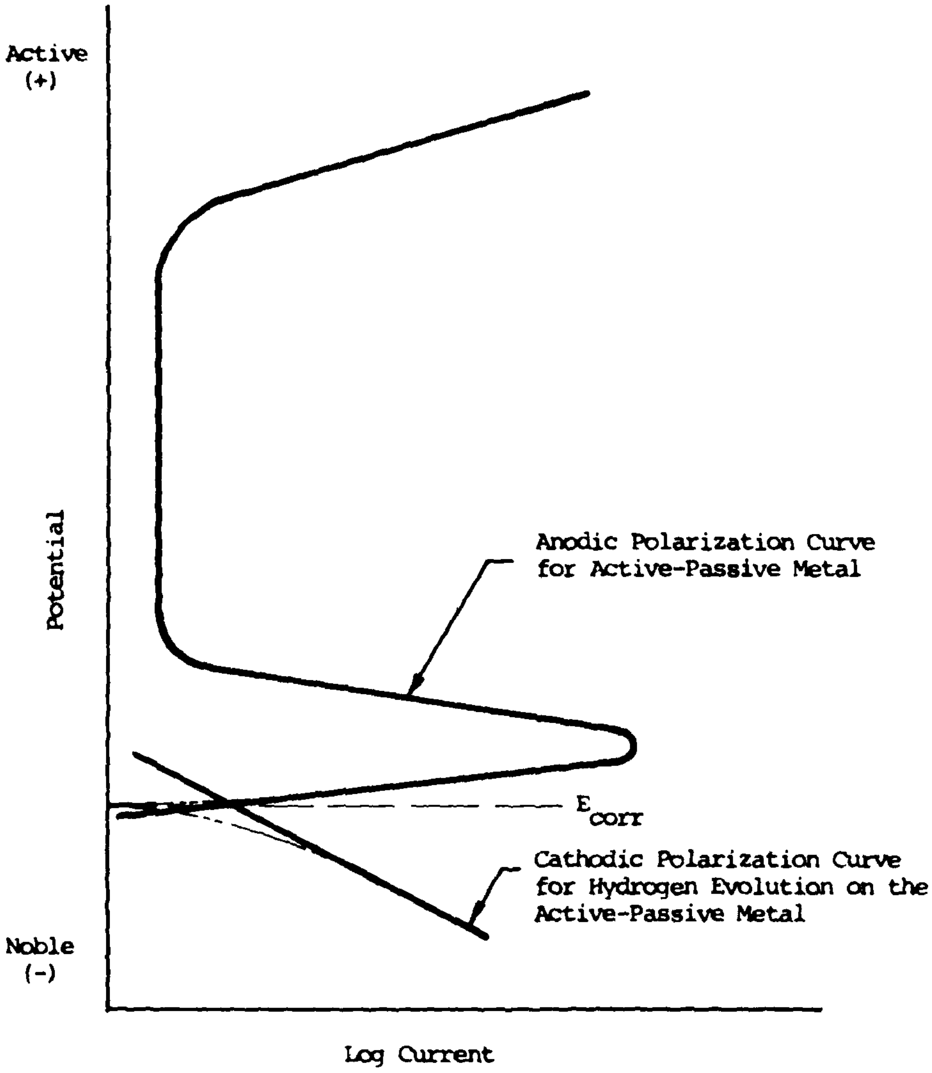

Figure 3. Polarization curves for an alloy exhibiting active-passive behavior

Section II

EXPERIMENTAL

Previous investigations of metals and alloys have revealed semi-quantitative results on their dissolution behavior, relying heavily on electrochemical parameters as a basis for conclusion. However, no strictly quantitative work involving the measurement of the actual amounts of Fe or Ni dissolving and comparing these values with the weight changes has been done. The present investigation endeavored to determine the actual rates of dissolution using atomic absorption analysis and compare these values with the measured electrochemical currents and the specimen weight changes.

The electrochemical portion of the experiment involved dissolution of pure Fe and pure Ni at constant potential. By applying various potentials on the specimen with a potentiostat, the dissolution rate could be changed; and the resulting changes in dissolution behavior determined. Atomic absorption analysis was conducted on samples of the solution taken from the electrochemical cell at various times during the dissolution process. From these data the rates of dissolution for Fe and Ni were determined.

The specimens were very high purity polycrystalline Fe and Ni which had been machined into cylinders one half inch long and two-tenths inches in diameter. As a final preparation, the specimens were abraded on metallographic paper to a 600 grit finish, degreased with acetone, washed thoroughly, and weighed. The specimens were mounted in a modified Stern-Makrides mount shown in Figure 4 and placed into the electrochemical cell without prior activation treatment.

The electrolyte, 1N H_2SO_4 (pH = 0.30), was placed in the cell shown in Figure 5. Only the central compartment for the specimen and one of the outer compartments for the auxiliary electrode were used in the experiment. The cell was placed in a constant temperature bath at 25° C. Hydrogen gas was used to purge the solution of oxygen for two hours prior to a test.

All tests were conducted in static solutions with the long axis of the electrode vertical in the solution. This specimen position allowed

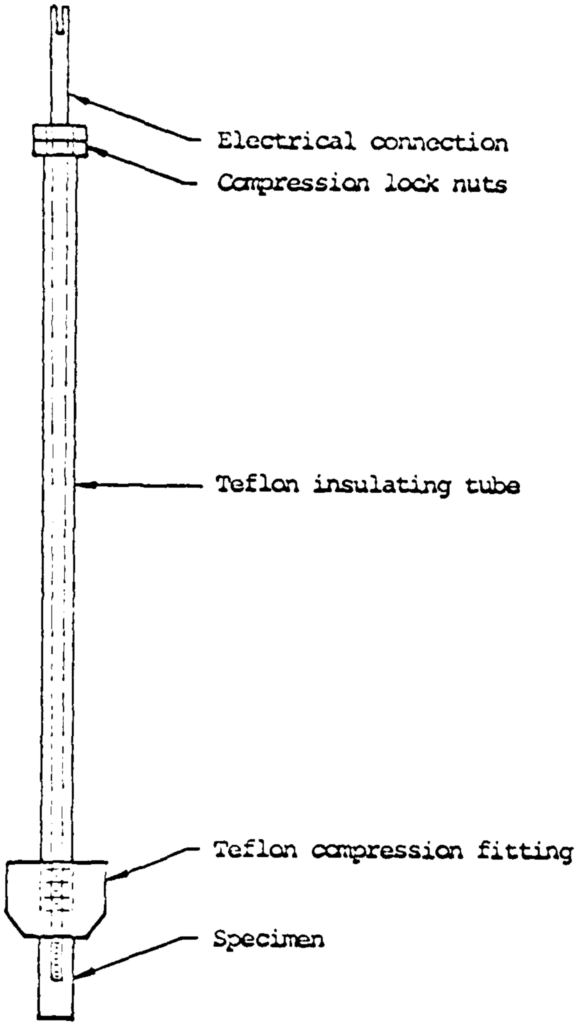

Figure 4. The specimen mount with specimen

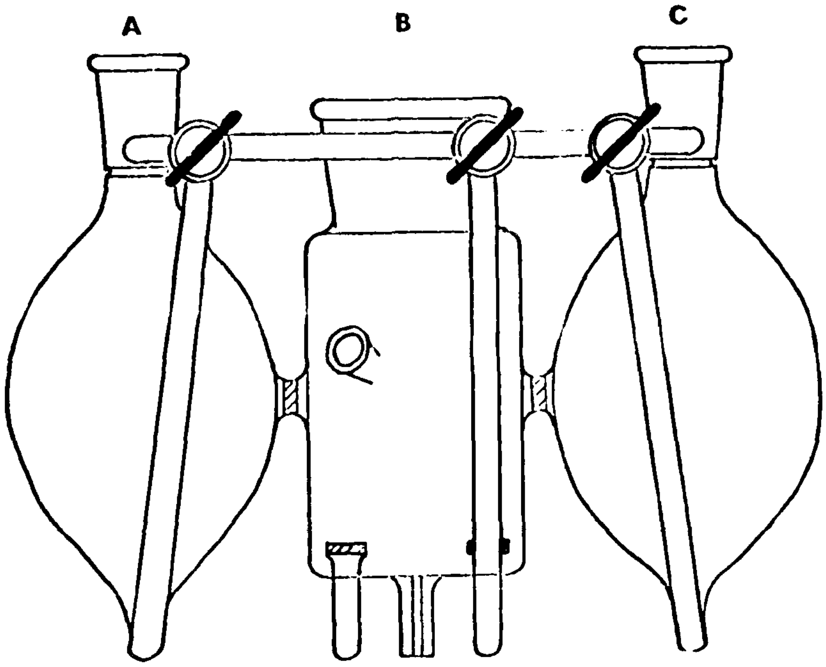

Figure 5. The polarization cell

natural convection forces to remove the dissolved ions away from the surface of the specimen. Hydrogen gas was used, however, to stir the solution for a short time prior to removal of solution samples in order to assure uniform ion concentration.

An Anotrol Model 4100 Research Potential Controller was used to dissolve the specimens at constant potential. The potentiostatic circuit is shown in Figure 6. The potential was monitored with a Keithley Model 610B Electrometer and the current was constantly monitored on a Bristol 560 Dynamaster Potential Recorder. The Fe specimens were dissolved at -390, -340, -248, -163, -128, -83, and 0 mV (SHE) while Ni was dissolved at -150, -105, -60, + 22, + 90, + 162, + 142 mV (SHE). The test times depended on the rate of dissolution and varied from 15 minutes to 9 hours.

Samples of solution were taken for atomic absorption analysis at regular intervals during the dissolution process. These samples were analyzed and concentration-time curves plotted. The specimens were weighed at the completion of each test. This weight was used to calculate the anodic current and the total anodic polarization curves.

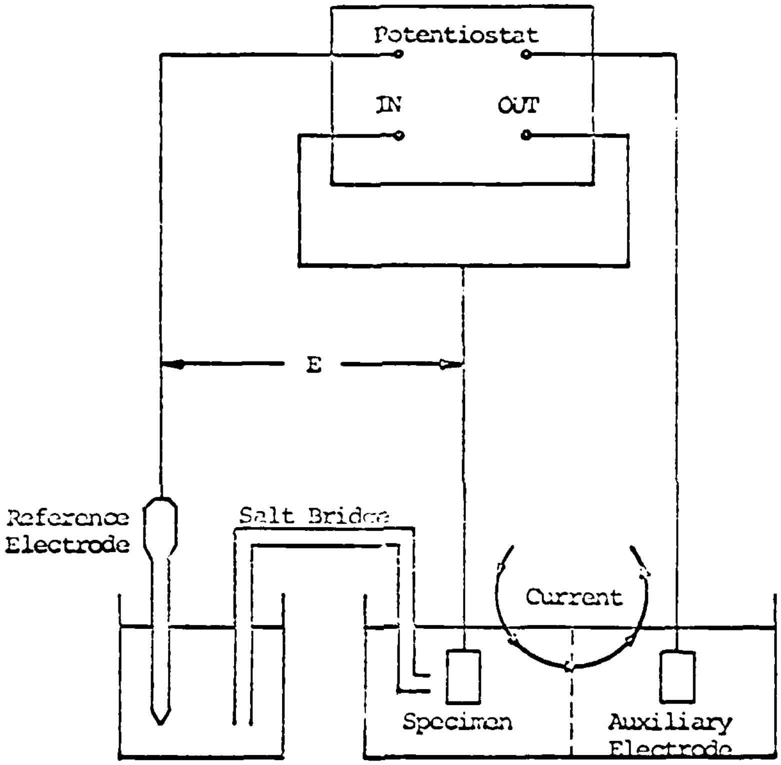

Figure 6. Schematic of the potentiostatic apparatus

Section III

RESULTS AND DISCUSSION

DISSOLUTION AT CONSTANT POTENTIAL

The data obtained using atomic absorption analyses for the dissolution of pure Fe and pure Ni are shown in Figures 7 and 8. The curves for these data are expressed as straight lines on a logarithmic plot. Points that lie in the region where the accuracy of the atomic absorption analysis is not totally reliable (concentrations of 2 ppm or less) are omitted in plotting the curves. Using a computer solution for the method of least squares, a straight line was fitted to each set of data points, the form of the equation being

$$C_i = a_i t^{n_i} \tag{9}$$

where

C_i = concentration of Fe or Ni in solution, ppm

a_i = concentration of Fe or Ni in solution at $t = 1$ second, ppm

t = time, seconds

n_i = slope of the log-log, concentration time curve

The values of a_i and n_i are given in Tables I and II.

The essential conclusions illustrated by these curves are that:

(1) The rate of dissolution increases as the potential becomes more noble,
(2) The slope of the log-log, concentration time curves for Fe is approximately 1.0; whereas, for Ni it is approximately 0.7, and
(3) The intercepts of $t = 1$ second decrease with decreasing potential.

In order to determine a potential for Fe and for Ni when it could be assumed that the surface was undisturbed, the concentrations at $t = 1$

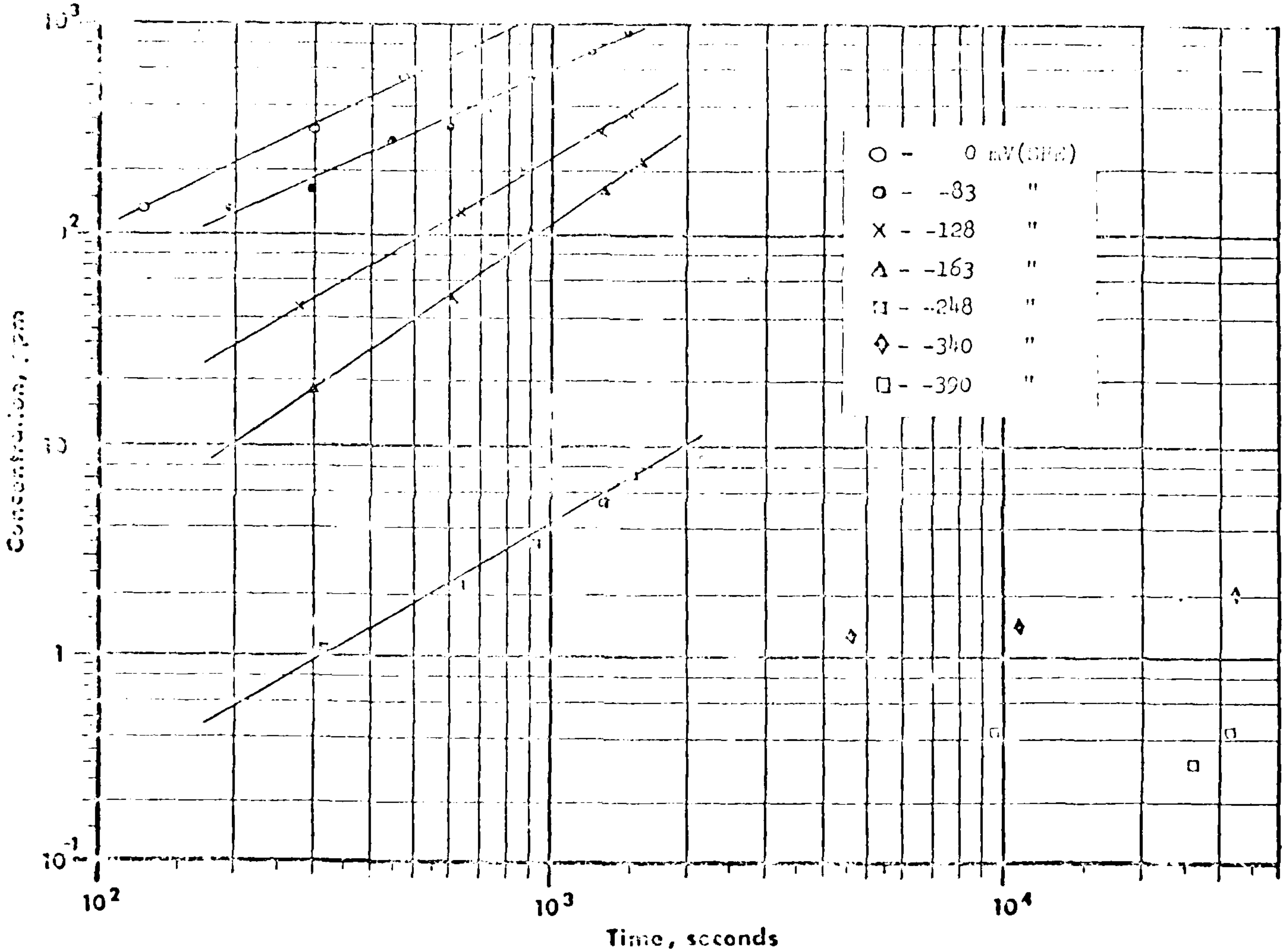

Figure 7. Concentration-time Behavior for Pure Fe [E_{corr} = -274mV (SHE)].

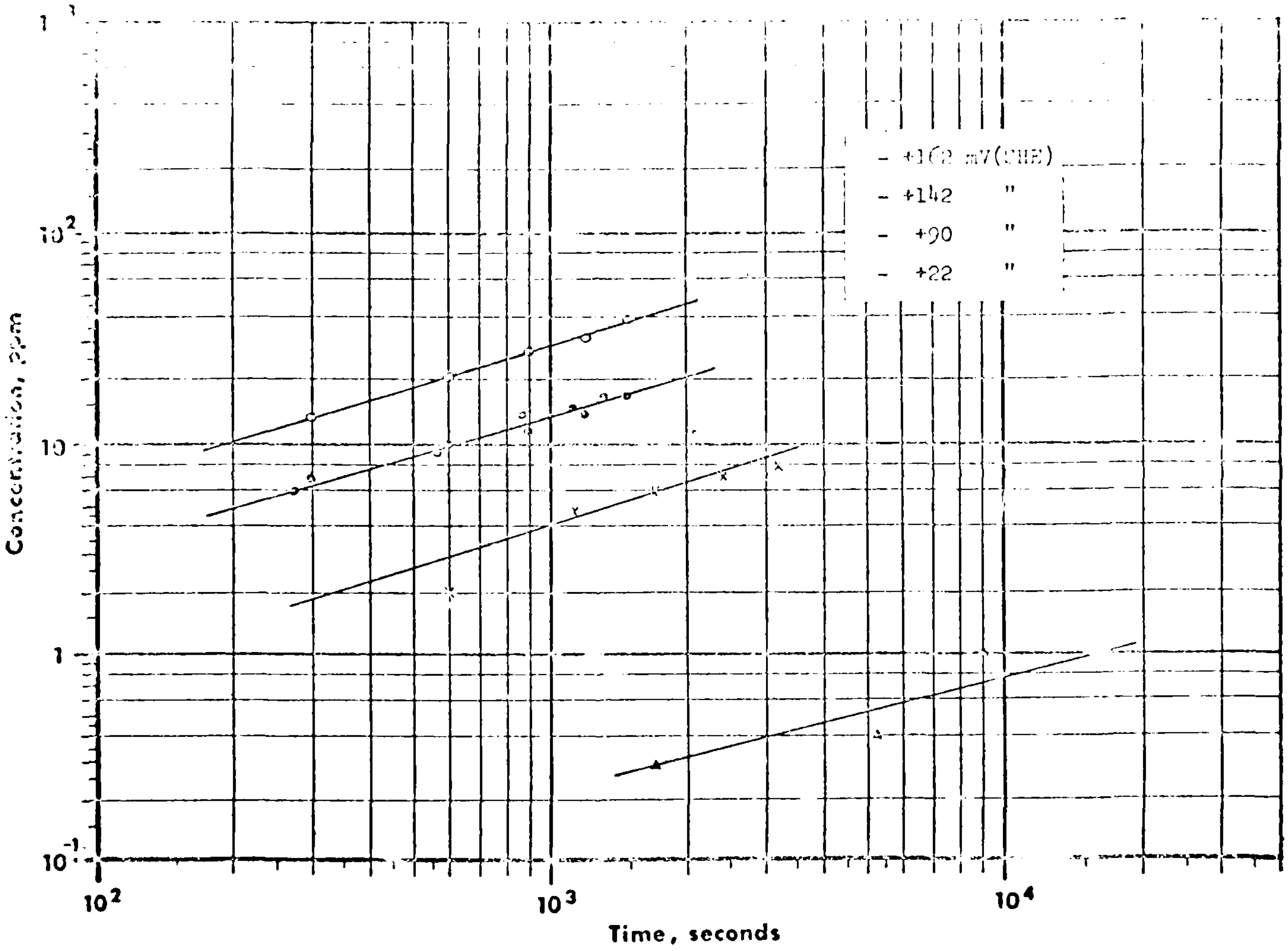

Figure 8. Concentration-time Behavior for Pure Ni [E_{corr} = -22mV(SHE)].

Potential mV(SHE)	n_{Fe}	a_{Fe} ppm
0	1.02	1.01
-83	0.973	7.32×10^{-1}
-128	1.30	3.04×10^{-2}
-163	1.01	1.76×10^{-3}
-248	1.26	6.78×10^{-4}

Table I. Values of slope and the intercept at t = 1 for the log-log, concentration-time curves for Alloy 1, pure Fe

Potential mV(SHE)	n_{Ni}	a_{Ni} ppm
+162	0.690	2.52×10^{-1}
+142	0.627	1.73×10^{-1}
+90	0.803	1.38×10^{-2}
+22	0.671	1.77×10^{-3}

Table II. Values for slope and the intercept at t= 1 for the log-log, concentration-time curves for Alloy 12, pure Ni second were plotted as a function of the potentials of dissolution using the method of least squares. An equation of the following form was obtained:

$$E_i = b_i \log C_i + E_i^{1\ \mathrm{ppm}} \tag{10}$$

where

E_i = potential of Fe or Ni at a given concentration, mV

b_i = slope of the curve, mV

C_i = concentration of Fe or Ni, ppm

$E_i^{1\ \mathrm{ppm}}$ = potential of Fe or Ni in alloy at 1 ppm, mV

It is assumed that the condition of one atom layer per square centimeter per second would be a reasonable value to select for the undisturbed condition. This value is equivalent to a one-third part per billion (1/3 ppb) concentration in solution at 1 second. This concentration is substituted into Eq. (10) to give the potential for an undisturbed surface. This potential for Fe is -240 mV (SHE) and for Ni is + 18 mV (SHE). These values are very much larger than the standard electrode potentials for Fe and for Ni, -440 mV (SHE) and -250 mV (SHE), respectively.

ANODIC POLARIZATION BEHAVIOR

The weight change of a given specimen at a given potential was converted to current using Faraday's Equation with a value of z = 2. These currents agreed very closely with the integrated current recorded during the test which means that the assumed value for z was correct. These total anodic polarization curves for Fe and Ni are shown in Figure 9.

Once again using the method of least squares, the corrosion currents and the Tafel slopes were determined. The corrosion current for Fe was 5.94×10^{-1} mA/cm^2 and for Ni was 1.47×10^{-3} mA/cm^2. The Tafel slopes for Fe and Ni were 53 mV and 43 mV, respectively.

The Tafel slope for Fe indicates the mechanism of dissolution would be as follows, as discussed by Felloni:(4)

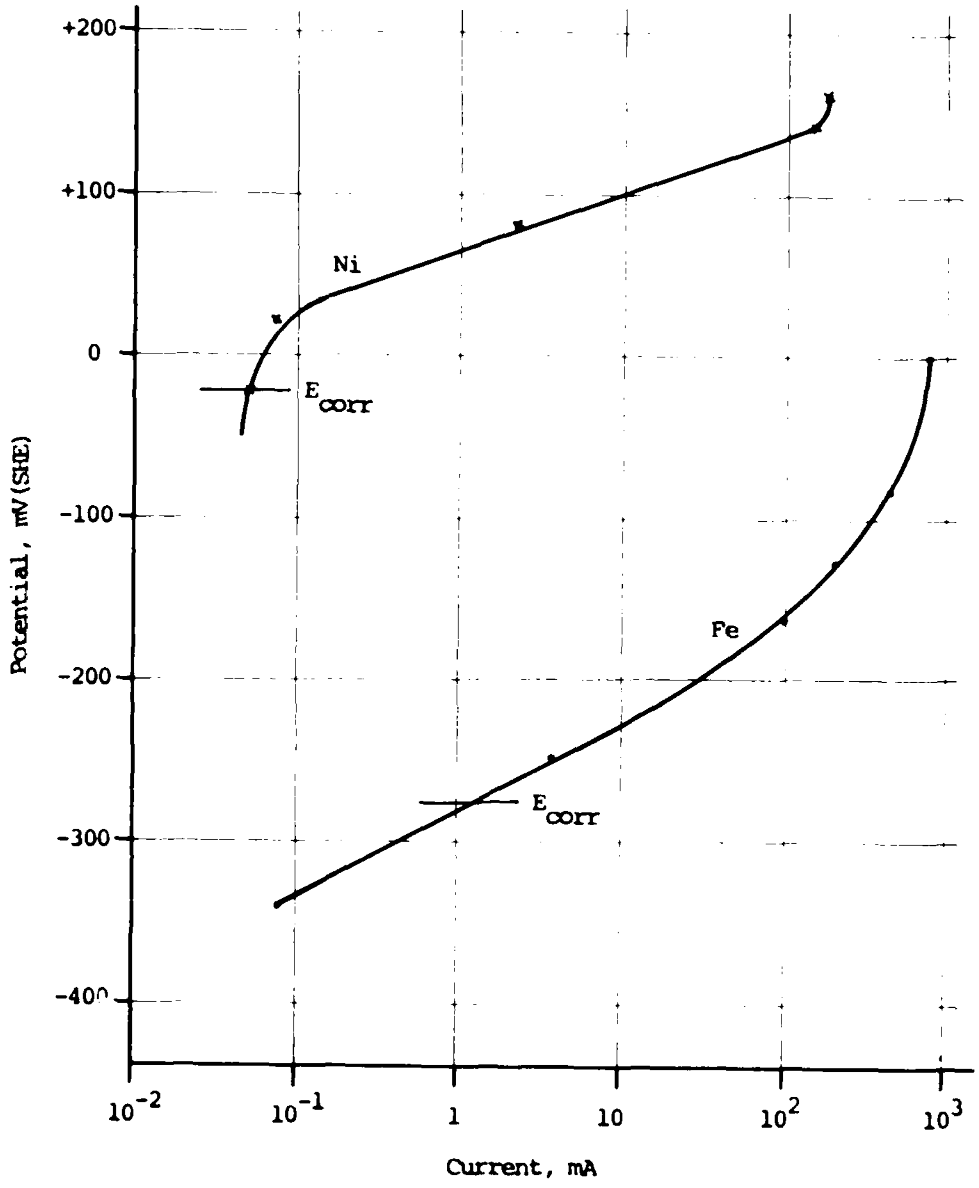

Figure 9. Total anodic polarization curves for pure Fe and pure Ni

$$\mathrm{Fe} + \mathrm{OH}^- \rightleftharpoons \mathrm{Fe\,OH}^-_{ads}$$

$$\mathrm{FeOH}^-_{ads} \longrightarrow \mathrm{FeOH}^+ + 2e^- \text{ (rate controlling)}$$

$$\mathrm{FeOH}^+ + \mathrm{H_2O} \rightleftharpoons \mathrm{Fe}^{+2}_{ag} + \mathrm{OH}^- + \mathrm{H_2O}$$

The Tafel slope for Ni, however, is closer to a value of 40 mV and would suggest the mechanism similar to that given by Kelly(5), (6) for Fe:

$$\mathrm{Ni} + \mathrm{OH}^- \rightleftharpoons (\mathrm{NiOH})_{ds} + e^-$$

$$\mathrm{Ni} + \mathrm{OH}^- + (\mathrm{NiOH})_{ads} \longrightarrow \mathrm{Ni(OH)}_{ads} + (\mathrm{NiOH})^+ + 2e^-$$

$$\mathrm{Ni(OH)}^+ + \mathrm{H}^+ \rightleftharpoons \mathrm{Ni}^{+2} + \mathrm{H_2O}$$

SECTION IV

CONCLUSIONS

The dissolution of Fe and Ni in IN H_2SO_4 at 25° C is logarithmic function of time with the slope of the curve for Fe being close to 1.0 and for Ni being close to 0.7. These slopes would indicate that the dissolution of Ni is not as active as that of Fe. Furthermore, the fact that the amount of Ni in solution was approximately equal to the weight loss of the Ni specimen at every potential indicates that the lower value of the slope is not manifested by a passivation process.

The values of n_i were assumed to be 1.0 in order to calculate intrinsic rate constants for Fe and Ni as a function of potential. Linear solutions for the method of least squares were calculated on the computer for the slope b of curves of the form

$$C_i = b_i t^{1.0} \tag{11}$$

where

C_i = concentration of Fe or Ni, ppm

b_i = slope of the curve, ppm/sec

t = time, seconds

These slopes were substituted into the following equation to yield zero-order intrinsic rate constants for the dissolution of Fe and Ni

$$K_i = \frac{ms}{M_i A} \left(\frac{dCi}{dt} \right)_E \times 10^{-6} \tag{12}$$

where

K_i = intrinsic rate constant for Fe or Ni, moles/cm^2 sec

ms = mass of solution, gms

M_i = molecular weight of Fe or Ni, gms

A = specimen area, cm^2

$\left(\frac{dCi}{dt} \right)_E$ = slope of concentration time curve, ppm/sec

Using this equation, the intrinsic rate constants for Fe and Ni were calculated for three potentials. The results are shown in the table below.

Table III. Intrinsic Rate Constants for Fe and Ni at Constant Potential.

Potential, mV(SHE)	-100	0	+ 100
K_{Fe}	8.10×10^{-7}	2.06×10^{-6}	2.61×10^{-6}
K_{Ni}	5.70×10^{-14}	3.78×10^{-11}	4.85×10^{-9}

The rate constants for both metals each increase with increasing potential, K_{Ni} being less than K_{Fe} for all potentials.

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13 ABSTRACT

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The analyses showed that the dissolution was a logarithmic function of time, the exponent of time being about 1.0 for Fe and 0.7 for Ni. Anodic polarization curves indicated that dissolution of Fe was larger than for Ni. The mechanism for Fe involved two electrons; whereas, for Ni it involved three electrons. Determination of zero-order rate constants indicated that the constants for both Fe and Ni increase with potential, the constant for Fe at a given potential always being much larger than the constant for Ni.

14 KEY WORDS	LINK A		LINK B		LINK C	
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Corrosion of Iron						
Corrosion of Ni						
Polarization Behavior of Fe and Ni						