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BEHAVIOR OF IRON-NICKEL ALLOYS IN
SULFURIC ACID SOLUTIONS.**

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ANODIC POLARIZATION BEHAVIOR OF IRON-NICKEL ALLOYS
IN SULFURIC ACID SOLUTIONS

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University

By

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The Ohio State University

1960

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ANODIC POLARIZATION BEHAVIOR OF IRON-NICKEL ALLOYS IN SULFURIC ACID SOLUTIONS

I. INTRODUCTION

Studies on the anodic behavior of pure iron and nickel in various media have received the attention of many investigators, some of the more pertinent work being reviewed in Part IV of this dissertation. While the commercial importance of these metals is no doubt a stimulus to their investigation, the complex nature of their active and passive reactions is an incentive to their study, and the heated controversy on theories of passivity has probably stirred additional interest. The iron-nickel system is thus of particular interest, since it combines these two metals which have been the subject of so much controversy.

Iron-nickel alloys are of commercial interest, mainly because of their thermal, elastic, and magnetic properties, but the additional corrosion resistance on adding nickel to iron is sometimes advantageous. Invar, an alloy containing 36% nickel, has a coefficient of expansion close to zero over a wide temperature range. Alloys having a nickel content between 27 and 44% have the unusual property of becoming stiffer with increasing temperature. A wide range of magnetic properties is obtained by varying the iron-nickel

ratio. High permeability alloys such as Permalloy occur at about 80% nickel. At 30% nickel, there is a sharp minimum in the magnetic saturation intensity.

The study of electrode polarization is an important part of electrode process chemistry, and has received increasing attention since the early investigations on hydrogen overvoltage by Tafel at the beginning of this century. Reaction mechanisms may in many cases be deduced from the potential-current characteristics of an electrode. The method of investigating these Fe-Ni alloys has been the determination of the potential-current characteristics of twelve alloys ranging in composition from 0 to 100% nickel in five concentrations of sulphuric acid varying from 0.001 to 10.0 N. Particular attention was focused on determinations of corrosion potential, passivation current, passive current, and activation (Flade) potential.

The results of this investigation are summarized in Part II of this dissertation. Part III is a brief review of electrode potential theory, including pertinent references to the literature. Part IV consists of a survey of the relevant literature on iron, nickel, and iron-nickel alloys. The results are presented and discussed in Part VI.

II. SUMMARY AND CONCLUSIONS

A. Scope

The anodic behavior of annealed iron-nickel alloys in H_2SO_4 solutions was investigated at $25^\circ\text{C} \pm 1^\circ\text{C}$ by galvanostatic and potentiostatic techniques. Twelve alloy compositions, ranging from 0 to 100% nickel by increments of 10 atomic % nickel (plus a 95 at.% Fe - 5 at.% Ni alloy) were chosen to represent the entire iron-nickel system. The electrolyte was hydrogen saturated 0.5 N K_2SO_4 and H_2SO_4 , utilizing five concentrations of H_2SO_4 (0.001 to 10.0 N) to vary the pH from 3.73 to -0.47. The electrochemical behavior was analyzed in terms of the metallurgical structure and environment.

B. Summary

1. Metallurgical Structure

The structures of the annealed (one hour at 1000°C) alloys were studied with X-rays. The structure was single phase (α) up to 5 atomic % nickel, two phase ($\alpha + \gamma$) from 10 to 40 atomic % nickel, and single phase (γ) with 50 atomic % or more nickel. The experimental structures correspond to those expected for annealed alloys.

2. Anode Polarization Curves

Since the passivation reaction occurred for every alloy composition and at every pH, all the polarization curves were of a general S-shape. The porous salt film formed at the limiting current density (I_L) was stable over a wide potential range (0.5 - 0.6 volt) for pure iron. With increasing nickel, the Tafel curve for anodic dissolution shifted to a more noble potential, and the active-passive transition curve shifted to a more active potential, so that with pure nickel the I_L plateau had a potential range of only 0.1 - 0.2 volt. The effect of increasing pH was to shift the entire polarization curve to more active potentials.

3. Corrosion Potentials

The corrosion potentials of each alloy acted in the same manner as a reversible hydrogen electrode

$$\left(\frac{dE}{d\text{pH}} = -0.059 \right),$$

except that the experimental $\frac{dE}{d\text{pH}}$ values (-0.035 to -0.046) were slightly lower. Though the corrosion potential became more noble with increasing nickel, the best correlation was with metallurgical structure. Corrosion potentials of the γ -alloys are approximately 0.20 volt noble with respect to the α -alloys. For the two-phase alloys, there is a regular increase in corrosion potential

from the α -potential (minimum γ area) to the γ -potential (minimum α area), indicating control of the potential by the major constituent and polarization of the minor constituent.

4. Passivation Current

No special trend in passivation current density (I_p) was noted with changing composition. However, the I_p value of each alloy went through a characteristic maximum with changing pH, the maximum occurring in the pH range 0-2. Since the passivation current is dependent on the precipitation of a porous film, the maximum could be explained on the basis of a change in the metal ion concentration required to precipitate a film as the H_2SO_4 concentration varies. A low acid concentration favors the precipitation of metal hydroxide, while a high acid concentration favors the precipitation of metal sulfate. Intermediate acid concentrations thus require a higher nickel ion concentration for precipitation, and consequently the I_p value is higher.

5. Passive Current

The passive current density, or minimum current density required to maintain passivity, did not vary significantly with changing composition. For each alloy, the

passive current density increased very rapidly with increasing acidity according to the relation

$$\log I = a - b \text{ pH} .$$

The equation was also deduced theoretically from a consideration of absolute rate theory.

6. Passive-Active Transition

Flade potentials (E_f) were obtained from potential decay traces, and indicated that each alloy followed the Flade relation

$$E_f = E_f^0 - 0.059 \text{ pH} .$$

The standard Flade potential ($E_f = E_f^0$ at $\text{pH} = 0$) was approximately 0.58 volt for α - and two-phase alloys and 0.47 volt for γ -alloys, indicating that the active constituent of the two-phase alloys controlled E_f^0 . However, the 60 at.% Fe - 40 at.% Ni two-phase alloy had an E_f^0 characteristic of γ -alloys, indicating that the change in electron configuration at 33 at.% Ni might be meaningful.

The potential-current relationship for the passive-active transition is described by the equation

$$\frac{d \ln I}{d E} = - k .$$

The transition curve is shifted to more active potentials with increasing pH. Increasing nickel content also shifts the transition curve in the anodic direction.

7. Galvanic Experiment

A binary electrode, consisting of an α -phase and γ -phase alloy electrically connected, was used to simulate the anodic behavior of a 70 at.% Fe - 30 at.% Ni two-phase alloy. However, the tendency of the γ constituent to form films resulted in values characteristic of α -alloys. The corrosion potential was characteristic of the α -phase constituent because of polarization of the γ -phase constituent. Values for passivation current were also considerably reduced. However, the pH dependence of the corrosion potential and passivation current was similar to that of normal two-phase alloys. The Flade relation was valid for the binary electrode, and E_f^0 was characteristic of the α -phase constituent (as in the case of the 70 at.% Fe - 30 at.% Ni alloy).

C. Conclusions

It was possible to analyze and explain the anodic behavior of iron-nickel alloys in sulfuric acid solutions in terms of metallurgical structure and electrochemical environment.

III. THEORY OF ELECTRODE POTENTIALS

A. Simple Electrodes

Simple electrode signifies an electrode at whose surface only one reaction is taking place. The case where two or more reactions occur will be covered in the section on complex electrodes. The sections are further divided as to whether the electrode is carrying an external current (i.e., polarized) or not (i.e., insulated).

1. Insulated Electrodes

a. Reversible

When a metal is immersed in a solution of its own ions, there arises a dynamic equilibrium, $M \rightleftharpoons M^{n+} + ne$, whereby an electrical double layer is set up at the metal solution interface. The current is the same in each direction and is designated the exchange current, I_0 . The simplest picture of the double layer is that of Helmholtz, who proposed two parallel layers of charge whose capacity, C , should be given by

$$C = \frac{K}{4\pi d} ,$$

where d is the thickness and K , the dielectric constant of the medium. The actual picture is much more complicated because of the diffuse nature of the double layer.

There are several types of reversible electrodes, the simplest being "electrodes of the first kind," where the electrode is reversible to ions of the electrode material:

"Electrodes of the second kind" involve a metal, an insoluble salt of the metal, and a solution of a soluble salt of the same anion, and are reversible to the common anion:

"Electrodes of the third kind" consist of a metal M_1 , an insoluble salt M_1X_1 , an insoluble salt of another metal M_2X_1 , and a solution of a soluble salt M_2X_2 , and behave reversibly with respect to M_2 :

Redox electrodes involve an inert electrode and the oxidized (n) and reduced (m) forms of the redox system:

The potential of a reversible electrode is given by the Nernst equation:

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} .$$

It should be noted that the plus sign after E° corresponds to the use of the European sign convention, wherein potentials more noble than the standard hydrogen electrode (SHE) are given a positive sign. This convention is used in

Europe and by electrochemists and corrosion engineers in the United States. The American convention is used by physical chemists of this country, assigning a negative sign to potentials more noble than the SHE, and requiring a change of sign in the Nernst equation as used above. The European system has the advantage that the sign of the electrode corresponds to the polarity of a D.C. voltmeter (more positive electrode connected to the plus terminal). The American system is consistent in that the electropositive elements have positive potentials.

b. Irreversible

A metal immersed in a solution of foreign ions exhibits an irreversible potential, i.e., the Nernst equation is not applicable. Some of these cases may be considered as distorted reversible potentials. Zinc dipped into a 1.0 N KCl solution exhibits a potential about 0.1 volt anodic to its E^0 (1)* The measured potential corresponds to a reversible potential with a zinc ion concentration of about 0.001 N. Since zinc is very electropositive, some zinc could go into solution to set up a pseudo "electrode of the first kind." Similarly, a metal could react with the solution to form a sparingly soluble precipitate--analogous to an "electrode of the second kind."

*Refers to Bibliography

2. Polarized Electrodes

If one disturbs the dynamic equilibrium of the reversible electrode by passing a current through it, the potential of the electrode changes in such a way as to sustain the flow of current. The difference between the reversible and measured potential is the overvoltage η , and is the sum of the effect of all the irreversible processes. In particular, slow ionic diffusion leads to concentration polarization and slow ionic dissolution or discharge leads to activation overvoltage. In addition, there is a measurement error, sometimes referred to as ohmic overpotential, which is caused by the IR drop in the solution between the electrode and the reference probe.

a. Concentration Polarization

Ions are transported to or from the surface of the electrode by migration and diffusion. If the rate of electrolysis exceeds the rate at which ions can migrate, ionic diffusion commences and the concentration at the surface of the electrode becomes different from that in the bulk of the solution (i.e., surface concentration is greater for anodic current and less for cathodic current). As the rate of electrolysis is increased still further, the concentration gradient approaches a maximum, and the corresponding current density is referred to as the limiting current density, I_L .

Using a modified form of Fick's law,

$$I = k (a_{\text{bulk}} - a_{\text{el}}) \text{ for cathodic current,}$$

or

$$I = -k (a_{\text{bulk}} - a_{\text{el}}) \text{ for anodic current,}$$

one may substitute the activities into the Nernst equation to obtain an expression for the concentration polarization,

η_c :

$$\eta_c = \frac{RT}{nF} \ln \frac{I_L}{I_L - I} \text{ for cathodic current}$$

or

$$\eta_c = \frac{RT}{nF} \ln \frac{I_L + I}{I_L} \text{ for anodic current.}$$

As I approaches I_L , concentration polarization will be much more serious for a cathodic current. Concentration polarization may be decreased by stirring, increasing the bulk concentration, or increasing the temperature.

b. Activation Overvoltage

If discharge or dissolution of the ion at the electrode is the slow step, this leads to activation overvoltage. Using absolute rate theory, one may write for the electrode at equilibrium

$$I_a = K_1 e^{-\Delta G_1^*/RT}$$

$$I_c = K_2 a_+ e^{-\Delta G_2^*/RT} \text{ (where } a_+ = \text{activity of the ion in solution)}$$

since $\Delta G_1^* - \Delta G_2^* = \Delta G = -nFE;$

$$E = \frac{RT}{nF} \ln \frac{K_2}{K_1} + \frac{RT}{nF} \ln a_+ .$$

When a net reaction takes place ($I_c \neq I_a$), the effect of the overvoltage is to make one of the reactions easier and the other more difficult. For the case of anodic dissolution ($I_a > I_c$), η aids the dissolution by decreasing ΔG_1^* to $\Delta G_1^* - \alpha \eta F$ and hinders discharge by increasing ΔG_2^* to $\Delta G_2^* + (1 - \alpha) \eta F$, where α is the fraction of η assisting dissolution. In this case

$$I_a = K_1 \exp \left[\frac{-\Delta G_1^* + \alpha \eta F}{RT} \right] = I_0 \exp \left[\frac{\alpha \eta F}{RT} \right] ,$$

$$I_c = K_2 a_+ \exp \left[\frac{-\Delta G_2^* - (1 - \alpha) \eta F}{RT} \right] =$$

$$I_0 \exp \left[-\frac{(1 - \alpha) \eta F}{RT} \right] \text{ and } I = I_a - I_c =$$

$$I_0 \exp \left[\frac{\alpha \eta F}{RT} \right] - I_0 \exp \left[-\frac{(1 - \alpha) \eta F}{RT} \right] .$$

For small overvoltages, one obtains the linear relationship

$$I = I_0 \frac{\eta F}{RT} .$$

If $\eta > 0.05$ volt, $I_a \gg I_c$, and $I = I_0 \exp \left[\frac{\alpha \eta F}{RT} \right] .$

Then $\eta = -\frac{RT}{\alpha F} \ln I_0 + \frac{RT}{\alpha F} \ln I$, which is of the same form as that proposed empirically by Tafel:

$$\eta = a + b \log I .$$

A Tafel plot (i.e., η vs. $\log I$) yields valuable information. Evaluation of the slope and the intercept permits the determination of the exchange current

$$\log I_0 = -\frac{a}{b}.$$

The value of the Tafel constants is dependent on the mechanism of the reaction. For hydrogen evolution on mercury, nickel, and copper, b is 0.12 volt and the discharge step is rate-determining; for smooth platinum cathodes, b is 0.03 volt and the recombination step is rate-determining (2). Bockris and co-workers have given a comprehensive treatment of the kinetics (3) and the mechanism (4) of the hydrogen evolution reaction. King (5) discusses the magnitude of concentration polarization to be expected in measurements of hydrogen overvoltage. As a general rule, the overvoltage for metal dissolution or deposition is not large, but, in the case of iron, nickel, and cobalt, it is about 0.2 or 0.3 volt for deposition at appreciable rates and about 0.3 to 0.4 volt for anodic dissolution (6).

c. Ohmic Overpotential

At high currents, the potential drop in the solution between the reference probe and the electrode surface becomes appreciable, even though the probe is quite close to the electrode. Since Ohm's law is applicable, current is the

chief factor in ohmic overpotential, though the change in the conductivity of the solution near the electrode also has some effect, especially at a cathode. The activation overpotential may also be considered as ohmic:

$$R = \frac{d\eta}{dI} = \frac{b}{2.303 I} .$$

The two can be distinguished since the decay of the ohmic overpotential is almost instantaneous on stopping the current, while the decay of the activation overpotential is rapid, but measurable.

One method of correcting for the ohmic error is to interrupt the current at small intervals of time, measure the potential decay, plot the potential versus decay period, and extrapolate to zero time. Another method holds the current constant while measuring the potential at various distances from the electrode, and extrapolating to zero distance. The first method was used by Le Boucher (7) who used a rectangular current pulse to cut off the current only once, and by Cahan and Rüetschi (8) who used a square wave superimposed on a constant D.C. current.

d. Surface Roughness

The current density terms in the expressions for η_c and η are based on real area, which is generally different from the geometrical area because of surface roughness. The

Tafel intercept will be affected by the surface roughness, but the slope remains the same. It is desirable that the real area be determined in the aqueous environment, rather than by gas adsorption as in the B.E.T. method. The fact that real and geometrical areas are identical for liquid electrodes (e.g., mercury) is the basis for a method of roughness determination. The assumption is made that the double layer capacity is the same for different metals at which hydrogen is evolving; the roughness is then the ratio of the capacity of the metal to the capacity of the mercury. In recent work, Wagner (9) has evaluated the capacity from

$$C = \frac{I}{A} \cdot \frac{\Delta t}{\Delta E} ,$$

evaluating the current time integral by means of a ballistic galvanometer. Brodd and Hackerman (10) evaluated the capacity from constant current curves:

$$C = I (dt/dV) ,$$

where (dt/dV) is the reciprocal of the slope of the charging curve.

3. Polarization Diagrams

a. Passive vs. Non-passive Behavior

A polarization diagram is a convenient method of representing the potential-current relationship of an electrode. Typical anodic behavior of metals is shown in Figure 1. A

Fig. 1 - Schematic Polarization Diagram

logarithmic current scale permits the presentation of both active and passive currents, and also shows up any process controlled by activation overvoltage through the presence of Tafel curves. Curve ABC represents the anodic behavior of a metal which does not undergo the phenomenon of passivity. The dissolution rate increases along AB as the potential becomes more noble, the decreasing slope near B indicating the onset of concentration polarization. Along BC, the current is relatively constant (I_L is the limiting current density) with increasing potential. At C, the current starts to rise because a new reaction (e.g., O_2 evolution) becomes possible at this potential, and, as the potential increases, the shape of ABC will be repeated for the new reaction. The total current will be the sum of the current of all the reactions.

Curve DEFGHI represents the anodic behavior of a metal which forms a passive film. The behavior along DEF is much the same as along ABC, and, at F, a new reaction (formation of a passive film) starts. In this case, however, the I_L 's are not additive since the passive film stifles the first reaction, and the total current along GH is the amount required to sustain the film. Along HI, the current again rises because of oxygen evolution.

b. Constant Potential vs.
Constant Current Measurements

A constant current, or galvanostatic technique, is convenient since all that is required is a large resistor R , and a large D.C. potential E , in series with the cell. Since R is much larger than the resistance (R_{anode}) of the anode under study, the current is controlled by

$$I = \frac{E}{R}.$$

In curve ABC of Figure 1, the inability to get a steady state point between B and C is no limitation since the determination of points B and C has effectively characterized the behavior between these two points.

The situation is different where a passive film forms. Under conditions of constant current, the potential goes from E to I when the current is equal to or a little greater than I_L . On decreasing the current from I, the potential becomes more active along IH, but at H, the potential shifts to point A. Therefore, the behavior along EFGH is not open to determination by constant current methods.

A constant potential, or potentiostatic technique, is required for a determination of EFGH. Greene (11) treated the requirements for a potentiostatic system from a theoretical viewpoint, and also described an electrical circuit and polarization cell which yielded good potentiostatic control.

The essential condition is that the polarizing potential be applied through a low resistance circuit, i.e., $R_{\text{anode}} \gg R_{\text{external}}$, where R_{external} includes the resistance of the electrical circuit, resistance of the solution between the anode and cathode, and the polarization resistance of the cathode.

The "classical potentiostat" described by Greene is not usable when the external resistance is on the same order of magnitude or greater than the anode resistance (e.g., when using a cell with high internal resistance). In this case, an automatic potentiostat must be used to control the potential of the anode. Lingane (12) describes a number of electronic circuits which may be used for controlled potential electrolysis; the recent literature indicates a growing use of this type of instrument (13-16).

B. Complex Electrodes

Because of complex structure or films, many metals exhibit irreversible potentials when dipped into solutions of their own ions. It is to be noted that when more than one electrochemical reaction takes place at an electrode, all the reactions proceed at the same electrochemical potential. The complex electrode has a surface that is subdivided into micro-anodes and -cathodes, but the micro-cells are not permanent and may change position with time and

environment. Possible sources of local anodes and cathodes are

- 1) a two-phase structure,
- 2) impurities,
- 3) stresses,
- 4) a non-homogeneous composition,
- 5) grain structure,
- 6) a layer of oxide or other corrosion products,
- 7) crystal orientation.

1. Insulated Electrodes

The case of the insulated complex electrode is illustrated graphically in Figure 2. For the insulated electrode, a necessary condition is

$$\sum I_{\text{anodic}} = \sum I_{\text{cathodic}}.$$

Therefore, it is essential to plot current, instead of current density, in the combined diagram of anodic and cathodic polarization. Only for the case of equal anodic and cathodic areas is it possible to plot current density.

Figure 2 (a) describes the situation where the local anodes and cathodes are approximately equally polarized. When the solution resistance is zero, the micro-cells polarize to E_1 , the corrosion potential, where I_1 is the corresponding corrosion current. Actually, there is always some solution resistance and, consequently, a small potential difference between E_a and E_c at I_1 . As the solution resistance increases, the potential difference between the anodes and cathodes increases, and the current decreases as shown by E_2 and I_2 .

(a) Mixed Control

(b) Cathodic Control

(c) Anodic Control

Fig. 2 - Schematic for Mixed Potentials

The case where the anodes polarize only slightly compared with the cathodes is illustrated in Figure 2 (b), and is referred to as cathodic control. The opposite situation is referred to as anodic control and is described in Figure 2 (c). Since it is current density which is linearly related to potential, it becomes necessary to change the slopes of the polarization curves as the areas change. Referring to Figure 2 (b) and assuming a 50% reduction in the anodic area, it is clear that the anodic slope will double. Since the process is under cathodic control, the current will decrease only slightly from I_1 , but the anodic current density, or intensity, is almost doubled. If the cathodic area is halved, a similar analysis will show both current and intensity to diminish substantially. This is the well known "area effect" in corrosion. For a process under anodic control, a change in cathode area has very little effect on the anodic current, whereas a decrease in anodic area will decrease the anodic current, leaving the anodic intensity relatively unaffected.

2. Polarized Electrodes

When an external anodic current I_{ext} is applied to an electrode at which two or more redox systems are operating, the relationship between the currents may be expressed as

$$I_{\text{ext}} = \sum I_{\text{anodic}} - \sum I_{\text{cathodic}} .$$

An alternate form of the Tafel equation is

$$\eta = b \log \frac{I}{I_0}.$$

For anodic polarization of a combined system $M - M^+$, $H - H^+$, one is then able to write

$$I_{\text{ext}} = I_{\text{anodic}} - I_{\text{corrosion}}$$

$$\eta_m = b_m \log \frac{I_{\text{ext}} + I_{\text{corrosion}}}{I_0 (m)},$$

where $I_{\text{corrosion}}$ is the local cell current at η_m .

Thus in plotting η_m vs. I_{ext} , one does not obtain true Tafel behavior until the external current is much larger than the corrosion current. If concentration and ohmic overvoltage are included, the expression for overvoltage becomes

$$\eta_m = b_m \log \frac{I_{\text{ext}} + I_{\text{corrosion}}}{I_0 (m)} +$$

$$2.3 \frac{RT}{nF} \log \frac{I_L + I_{\text{ext}} + I_{\text{corrosion}}}{I_L} +$$

$$I_{\text{ext}} R_{\text{solution}}.$$

A more comprehensive treatment of the above may be found in papers by Stern and Geary (17-18) and Posey (19).

3. Polarization Diagrams

Where it is possible to isolate electrically the local anodes and cathodes, a direct determination of the polarization curves of the local anodes and cathodes is possible. In general, this is not possible, and Mears and Brown (20) discuss several indirect methods. The "potential break" method uses an external current to obtain a cathodic and anodic polarization curve. The corrosion current is determined in a separate test, and the results combined so as to obtain the approximate average slopes of the polarization curves of the local anodes and cathodes. This method requires that the anodic and cathodic areas be approximately equal.

The basis of the "equivalent corrosion current" method is the fact that corrosion is proportional to current and time:

$$\text{weight loss } w = k I_w t .$$

To obtain the curve for the local anodes, cathodic current (I_{ext}) of various magnitudes is impressed, corrosion current measured, and I_{ext} plotted vs. I_w . Another plot is made of E vs. I_{ext} , and, since with cathodic current $I_w = I_a$ (local anode current) and $E = E_a$ (local anode potential), a plot of E_a vs. I_a gives the polarization curve for the local anodes. Similarly, cathodic curves are obtained by impressing anodic current and using the fact that $I_c = I_w - I_{\text{ext}}$ and $E = E_c$.

C. Passivity

This section contains only general remarks on passivity, specific theories being considered later under iron and nickel. Passivity has recently been defined by Evans as "the case where metal, after suitable treatment, becomes indifferent to a reagent or environment which would attack the untreated metal" (21). It is a property exhibited by most metals under suitable conditions; for example, copper is passive, and zinc and magnesium show signs of passivity in concentrated nitric acid at -11°C (22).

In reviewing his own work and that of Müller, Evans and others, Hedges (23) concluded that a passive film is formed as follows:

1. When the dissolving metal anode reaches a sufficiently high current density, hydroxyl or acid anions accumulate at the surface of the metal.
2. The solution in the vicinity of the electrode becomes super-saturated, and a porous non-protective solid crystallizes on the surface.
3. The relatively thick visible film greatly increases current density at the pores so that at isolated spots a perfectly continuous oxide film is formed.
4. The thin invisible film does not grow in thickness, but extends sideways rapidly covering the whole electrode.
5. The non-protective film is thrown off.

In September, 1957, an international conference on the passivity of metals was held in Darmstadt, Germany, and the conditions for passivity were summarized in the following terms:

1. The protective film must be less than 100 Å thick.
2. The film must require no more than 10^{-2} coulombs/cm² to be formed.
3. The film must be an electronic conductor.
4. The E vs. I characteristics defined by a curve such as curve DEFGHI of Figure 1 must be satisfied.
5. The film must be formed very rapidly.
6. The passivated metal must be oxidized.
7. The passive film must be hydrophobic.
8. The passive film must be relatively acid insoluble (16).

It is important to know whether salts or hydroxides will form on the anode, and the factors are discussed by Evans (24). Low E.M.F.'s favor the formation of soluble salts (e.g., metal sulphates), whereas high E.M.F.'s favor the formation of hydroxide. Salt formation is more likely in acid solution, and hydroxide formation in alkaline solution, and "the criterion between activity and passivity becomes the question whether the solution can or cannot dissolve the metallic hydroxide." Additional conditions favoring passivity are

- 1) stagnant liquid and horizontal electrode,
- 2) high current density,
- 3) initial porous protective layer.

The behavior of a passive metal in the vicinity of the passivation potential E_p and activation potential E_a is discussed by Franck (25) on the basis of a mixed potential. Where E_f is the equilibrium potential of the reaction of the passive layer, the condition for a corroding anodic (i.e., formed by oxidation) layer is $E_p > E_f$; for a cathodic layer, however, $E_p < E_f$. Depending on the form of the current voltage curve and the position of the resistance line, four types of transitions are possible, giving rise to N-shape or S-shape current-voltage curves. It is found that mixed electrode states on S-form curves are stable, and on N-form curves unstable. For anodic layers, degree of coverage α measures the ratio $\frac{\text{passive area}}{\text{total area}}$, ($\alpha = 1$ for passivity), and the polarization current I is then given by

$$I = \alpha I_p - (1 - \alpha) I_a ,$$

where I_p represents the passive current and I_a , the active current. In phosphoric acid, passive iron activates when the ratio of active to passive area becomes 1 : 6000, but remains passive when the ratio is 1 : 6600.

In his latest paper on electron configuration in alloys and passivity, Uhlig (26) reviews his earlier work, and presents an improved theory. The original theory proposed that the active state of a metal corresponds to the situation of filled d band energy levels, and the passive

state to unfilled d bands (27). Thus electron absorbers (oxygen or oxidizing agents) would tend to impart passivity, whereas hydrogen would favor the active state.

Chromium, which is inherently passive and has five vacancies in the 3d band, could passivate five iron atoms. This corresponds to 15.7 weight percent chromium, which is in agreement with the observed critical amount (about 12%) necessary to produce stainless Cr-Fe alloys.

The early theory did not explain the effect of environment in shifting critical compositions. If sufficient hydrogen is adsorbed or absorbed, no critical composition is observed for Cr-Fe alloys, whereas oxidizing environments can reduce the critical amount of chromium to 4%. Calculations are made showing the number of electrons shifted from or to the adsorbed species. The theory is extended to two-phase alloys, the conditions for passivity being that each of the phases exceeds the critical composition. If one of the phases is active, the passivity is destroyed by galvanic contact.

IV. ANODIC BEHAVIOR OF IRON, NICKEL, AND IRON-NICKEL ALLOYS

A. Iron

The anodic behavior of iron has received much attention in the literature, and there is substantial agreement on the results. However, these results have led to a variety of interpretations, particularly with respect to theories of passivity.

1. Active State

The behavior of iron in the active state can roughly be described by stipulating the open-circuit (o.c.) potential, the Tafel slope, and limiting current density to define curve DE of Figure 1. The pH dependence of the o.c. potential has been investigated by Stern (28), who found that the steady-state corrosion potential of iron in deaerated acidic NaCl behaved in the same manner as a reversible hydrogen electrode

$$\left(\frac{d E}{d \text{ pH}} = - 0.059 \right)$$

over the pH range 1-5; the experimental slope was slightly less,

$$\frac{d E}{d \text{ pH}} = - 0.0559 .$$

In the same pH range, corrosion rate was essentially constant

(27-29 mdd). Combining this information with a series of local cathodic polarization curves, he concluded that the local anodic polarization curve for iron was extremely steep. This was attributed to a very large cathode-to-anode area ratio which increased with decreasing pH in the vicinity of the corrosion potential. A later paper by Stern and Roth (29) discussed the possibility of attributing the pH dependence of the o.c. potential to a reduction of the I_0 for the reaction,

as the pH decreased. Tafel slopes of 0.068 to 0.078 were found for anodic dissolution. It was concluded that no obvious experiment could distinguish between the two proposed mechanisms, but that the explanation based on decreasing anode area appeared to be better.

Pourbaix (30) studied the o.c. pH dependence on iron in deaerated HCl and found that the potential could be deduced from the Nernst equation, where the instantaneous concentration of ferrous ions was a function of pH. In the same environment, Makrides, Komodromos, and Hackerman (31) found that o.c. potential was a linear function of pH, and the corrosion rate a linear function of HCl activity.

$\frac{d E}{d \text{ pH}}$ was -0.047, less than the value found by Stern.

Experimenters are agreed that passivation currents (I_p) are not very reproducible, though no explanations are advanced as to why this should be so. Bartlett and Stephenson (32) studied iron in 2.0 N H_2SO_4 , and found $I_p = 600 \text{ ma/cm}^2$, and $I_L = 200 \text{ ma/cm}^2$, though "the exact values of the currents will differ somewhat from experiment to experiment." The decrease in current density from I_p to I_L was due to the formation of a ragged, gelatinous brownish coat. Bonhoeffer (33), reporting on the results of U. F. Franck, found that iron in 1.0 N H_2SO_4 had a minimum passivation current density of about 300 ma/cm^2 , which decreased to about 200 ma/cm^2 , because of the formation of a porous protective layer whose chemical nature is not known. I_p was very much dependent on the velocity of stirring, I_p being 17 amps/cm^2 with vigorous stirring. Pourbaix (30) found a linear decrease of the passivation current density with increasing pH, though he states "results indicated in this table seldom are reproducible, therefore, particularly those concerning the current density of passivation." I_p varied from 113 ma/cm^2 to 362 ma/cm^2 in 0.1 N H_2SO_4 .

2. Passive State

The study of the passive behavior of iron has been a subject of scientific observation for many years, as

indicated in a historical review by Uhlig (34):

- 1782 C. F. Wentzel observed iron unattacked by concentrated nitric acid.
- 1807 W. Hisinger and J. Berzelius pointed out that anodic polarization aids passivity.
- 1836 C. Schonbein used the word "passivity" to describe the behavior of iron in concentrated nitric or when anodically polarized.
- 1844 M. Faraday attributed passivity of iron in nitric to an oxide film.
- 1912 H. Brearly and, independently, B. Strauss and E. Maurer discovered the passivity of iron stabilized by alloying with 12% chromium.
- 1919 G. Tammann suggested that a film of adsorbed oxygen, rather than the oxide, is responsible for the passivity of iron.

The present picture has not clarified; there is still much controversy about the merits of an oxide film versus an adsorbed oxygen monolayer as the cause of passivity. It is generally agreed that when iron is activated from the passive state, it does so at a fairly reproducible potential, E_f , the Flade potential. The potential has the value $E_f = 0.58 - 0.059 \text{ pH}$ at 25°C , and any proposed mechanism must be formulated so as to correspond to this pH dependence. The standard Flade potential ($E_f = E_f^\circ$ at $\text{pH} = 0$) of 0.58 is reported by most observers, though Uhlig and King (35) found that E_f° depended on the nature of the passivating solution,

<u>Passivator</u>	<u>E_f^0</u>
1. NaNO_2	+ 0.50
2. K_2CrO_4 , K_2FeO_4 , Na_2MoO_4	+ 0.54
3. Na_2WO_4	+ 0.61
4. Anodic polarization in H_2SO_4 ; concentrated HNO_3	+ 0.64

However, $\frac{d E_f}{d \text{pH}}$ was about -0.059 for each solution. Cartledge and Sympson (36) conducted 21 experiments in which the average deviation from the theoretical value was only 8 m.v., with E_f independent of the identity of the passivating solution in the pH range 5.6 - 7.0.

Since E_f is independent of iron concentration, it is necessary to assume a process in which iron does not react. Uhlig (35, 37) assumed the model

for which thermodynamic calculations gave E_f^0 of +0.56 v. Breakdown of passivity followed the reaction

to account for the residual film of Fe_2O_3 reported by other investigators. In earlier work, Uhlig and Geary (38) showed that iron in chromate solutions showed a potential dependence suggesting a Langmuir adsorption isotherm, and Uhlig and

O'Connor (39) found evidence of adsorbed ferrate for passive iron in concentrated nitric acid.

The oxide theory for the passivity of iron is faced with the problem that E_f^0 does not correspond to the free energy difference between any known oxides of iron, so that it is necessary to assume an abnormal oxide either on the surface, or between the surface oxide and the iron. Evans and co-workers (40, 41) have given evidence that Fe_2O_3 is the outer protective layer. Assuming Fe_2O_3 to be the protective surface layer, Cartledge (42) proposed an "abnormal FeO" for the inner layer:

This required that "FeO abnormal" have a ΔF_f^0 of formation of -73.6 K cal/mol, compared to a ΔF_f^0 of -58.4 for bulk FeO, which seemed reasonable to Cartledge for a surface film.

A mechanism in which Fe_3O_4 is the inner oxide is favored by Weil (43) where the Flade potential is the equilibrium potential of the reaction

Vetter (44) also has the scheme, $Fe/Fe_3O_4/Fe_2O_3$ /electrolyte, but considers the reaction

to occur completely irreversibly. This results in a potential difference $\Delta\phi = 0.66$ in the Fe_3O_4 layer which explains

the difference between the experimental and theoretical values of E_f .

Oxygen overpotential curves and forced decay traces on passive iron were interpreted by Wade and Hackerman (45) as suggesting adsorbed hydroxyl radicals in acid solution and adsorbed hydroxide ions in alkaline solution. Using constant current charging and discharge curves, Snavelly and Hackerman (46) found that a potential near the reversible oxygen potential must be achieved before a complete passive layer is formed. Coulombs involved at the Flade region represented only 10% of the passive layer and the remainder decayed when the iron was exposed.

Recently, Hackerman (47) proposed a generalized theory of passivity in which the following sequence of steps occurred, though not all steps were meaningful in all reactions:

1. Adsorption of O_2 monolayer or less (or OH or OH^-)
2. Splitting of O_2 and association with atoms of metal
3. Electron displacement to produce monolayer of oxygen ions (probably O^-)
4. Intrusion of metal ion from lattice into sorbed layer
5. Formation of three-dimensional crystalline oxide
6. Regeneration.

If the rates of steps 2 and 3 are fast relative to step 4, a thin passive film will form, whereas if step 4 is relatively fast, a bulk oxide is formed. Though step 3 was complete before step 4, tenuous passivity of iron was attributed to the slowness of steps 3 and 4, compared to that of aluminum.

Another recent theory to explain the passivity of iron was advanced by Pryor (48) and based on a single phase passive film of $\gamma - \text{Fe}_2\text{O}_3$ having a non-uniform defect concentration. The $\gamma - \text{Fe}_2\text{O}_3$ varies from an outer p-type layer with excess oxygen to an inner n-type oxide. To prevent dissolution of the $\gamma - \text{Fe}_2\text{O}_3$, excess oxygen could be reduced by the following electrochemical reaction,

for which an equilibrium potential could be written as follows:

$$E = E^0 + \frac{RT}{2F} \log (\text{H}^+)^2 (\text{O}^{--}) \left(\begin{array}{|c|} \hline + \\ \hline + \\ \hline \end{array} \right) .$$

Comparing this equation with the Flade relationship, it is deduced that

$$E_f = E^0 + \frac{RT}{2F} \log (\text{O}^{--}) \left(\begin{array}{|c|} \hline + \\ \hline + \\ \hline \end{array} \right) .$$

By this model it becomes erroneous to treat E_f as a thermodynamic potential since it is uncorrected for the activities of the excess oxygen. The variation in E_f found by Uhlig and King (35) is attributed to variations in the defect structure of the outer layer of passivating oxide formed under different conditions.

Pryor (49) has shown that the pH dependence of the passive potential of iron depends on the nature of the protective film. In solutions where the iron formed hydrated oxides, a pH dependence similar to that in the Flade equation was found. However, where the protective film consisted of iron phosphates, the passive potential became more noble with increasing pH. This behavior is explained by the dependence of the solubility product on pH; with increasing pH, the solubility of iron phosphate increases and that of iron hydroxide decreases.

B. Nickel

The electrochemical behavior of nickel is quite similar to that of iron in both the active and passive states. Similarly, there is a divergence of opinion as to the interpretation of this behavior. The situation is somewhat simplified in comparison to iron since the +2 state of nickel and its compounds is by far the most important in aqueous solution (50).

1. Active State

The pH dependence of the o.c. potential of nickel has not been investigated to the degree of that of iron. Piontelli and Serravalle (51) found that in the absence of current, the potential of the nickel electrode corresponded as a rule to a more or less reversible hydrogen electrode, without any direct influence of the activity of the nickel ions. Experiments were carried out in various electrolytes, using a current pulse technique. Chloride ions prevented the formation of a passive film, whereas chlorate, sulfate, and fluoride ions did not. In 4.0 N H_2SO_4 , passivation current was 80 ma/cm^2 , while in 6.0 N H_2SO_4 , I_p decreased to 40 ma/cm^2 .

Turner (52), working with nickel in 2 N H_2SO_4 and at constant current, found that a nickel anode became passive when the current density exceeded 300 ma/cm^2 . At lesser current values, an initial maximum was noted when the current was switched on. This was attributed to the precipitation of nickel sulfate at the anode surface

causing a decrease in nickel ion activity. The electrode potential decreased to a steady value where the rate of film formation was equal to the rate of film dissolution.

Hickling and Spice (53) investigating nickel over a wide pH range, found that in alkaline (pH of 12-14) solutions, nickel existed in the passive condition at both 25°C and 65°C. The presence of 0.2 N Na_3PO_4 , $\text{Na}_2\text{B}_4\text{O}_7$, KNO_3 , K_2SO_4 , or KCl had little or no effect. In buffer solutions (pH of 5-10) of phosphate or borate, a current density of 100 ma/cm^2 was sufficient to passivate the nickel by primary formation of a sparingly soluble salt film followed by oxide formation. Short pulses of very high current density were necessary to passivate a phosphate solution at a pH of 1.8, and in 1.0 N H_2SO_4 , the electrode was continually active. A determination of surface roughness indicated that the true area was about 3.6 times the apparent area.

Nickel in solutions of 0.1 N to 10.0 N HCl was studied by Higgins (14). The anodic dissolution was diffusion controlled at higher current density so that it was possible to obtain a linear decrease in limiting current density as the solution was saturated with nickelous ion. The precipitation of a green salt film, $\text{NiCl}_2 \cdot \text{H}_2\text{O}$, decreased the current density from 400 to 100 ma/cm^2 in 9 N HCl. The tetrahydrate of NiCl_2 stable in HCl greater than 7.5 N, was less soluble than the more hydrated (penta and tetra) form.

2. Passive State

Piontelli and Serravalle (51) concluded that from a thermodynamic point of view, it would be difficult to distinguish between passivity by adsorption on the one hand or by formation of oxides or hydroxides on the other. Though the structure of the passive films could not be determined by structural identification methods (including electron diffraction), they concluded, based on their results, that a true oxide film was present in the condition of complete passivity. However, the passive potential made any of the following reactions energetically possible:

Turner (52) did not determine specifically the composition of the oxide he felt was present, but thought that

the decay of anode polarization indicated the presence of some NiO_2 . Hickling and Spice (53) believed that the protective film on nickel was Ni_2O_3 .

Since Ni is one of the plates in nickel-cadmium and nickel-iron batteries, the behavior of nickel in alkaline solutions is of special interest. Conway and Bourgalit (54) studied the discharge characteristics of the nickel-nickel oxide electrode in 0.0015 to 15.0 N KOH. Results indicated that in the decay from the passive state, there were two consecutive processes in the reduction of the Ni^{4+} to the Ni^{3+} state; adsorption of OH^- followed by proton transfer. The Ni^{3+} state could also be reduced to the Ni^{2+} state by the same mechanism, if the potential of the electrode remained positive to that of the reversible oxygen electrode.

Okamoto, Takaishi, and Sato (55) have attempted to explain the difference between the experimental and thermodynamic Flade potential for nickel by taking into account the surface free energy of the thin oxide film. Since they found passive nickel dissolves as an ion of Ni^{++} , they assumed the passive film is NiO , and the reaction which determines the Flade potential is

They also found the Flade potential of nickel in 1.0 N H_2SO_4 to be +0.43 volt, or +0.32 volt greater than E° . The free energy of formation of the film is

$$F = F_{\text{bulk}} + \frac{F_{\text{surface}}}{L},$$

where L is the film thickness. F_{surface} was estimated from other data to obtain $L \simeq 70\text{\AA}$, a reasonable value for film thickness.

In another paper, Okamoto and co-workers (56) investigated the effect of temperature on the passivity of nickel. In the passive state, dissolution rates were in good agreement with anodic currents, assuming nickel dissolves in the divalent state. The linear relation between $\log I_{\text{passive}}$ and $1/T$ had a break at 60°C . It was suggested that the film was pseudomorphic below 60°C , and crystalline above 60°C , crystallization reducing the protective capacity of the film.

Kolotyrkin (57) reported on the results of some work by himself and co-workers. The electrochemical behavior of nickel, platinum, and other metals in sulfuric acid was investigated potentiostatically. In 1.0 N H_2SO_4 , the passivation current for nickel was about 10 ma/cm^2 and was obtained at a potential of +0.150 v. There was no plateau, the curve dropping in a straight

line to a passive current of about $20 \mu\text{a}/\text{cm}^2$ at a potential of +0.430. With additional data from capacitance and resistance values, it was concluded that the mechanism of passivity for chromium, nickel, and stainless steel was the same as that for platinum, namely the activated adsorption of oxygen (or other anions). However, adsorption may in some cases lead to increased anodic dissolution, because of the weakening of the bond of the metal with the crystalline lattice. For adsorption to lead to passivity, it is necessary that adsorption lead to a surface complex of the type MeO_n^{-2n} , which has a lower hydration energy than the ordinary ion.

C. Iron-Nickel Alloys

1. Metallurgy

Owing to the formation of metastable structural states which vary according to composition and heat treatment, and the sluggishness of diffusion at temperatures below 500°C , the exact placing of the equilibrium phase boundaries has met with great experimental difficulties. The iron-nickel constitution diagram shown in Figure 3 is after Hansen (58), and is based on the most reliable data published up to 1954. The transformation is affected with temperature hysteresis which increases with increasing

Fig. 3 - Constitution of Fe-Ni System (after Hansen)

nickel. The transformation has features of a diffusionless, martensitic type transformation.

Crystal structures include a B.C.C. α -phase, and a F.C.C. γ -phase, and in his treatise on the iron-nickel system, Marsh (59) summarized the following compounds as having been reported:

However, according to Hansen, later work has shown the existence only of a super-lattice of FeNi_3 , this compound (Cu_3Au type) covering the composition range approximately 50-80 atomic % Ni. The addition of nickel expands the iron lattice.

The importance of heat treatment and composition is shown by the following taken from the ASM Metals Handbook:

- a. Alloys that contain up to 6% Ni are ferritic. With increasing nickel content, the alloys become increasingly subject to air hardening on slow cooling.
- b. Between 6 and 25% Ni, the alloys are martensitic after fast cooling; after slow cooling or reheating, they decompose into $\alpha + \gamma$. The structure varies from the martensitic to the Widmanstätten type observed in meteorites.
- c. Between 25 and 30% Ni, the alloys may consist either of a mixture of α and γ , or of pure γ , after fast cooling. They decompose into $\alpha + \gamma$ on reheating to 350 or

450 C. Cold working at room temperature may transform them completely into α .

- d. Between 30 and 45% Ni, the structure of the alloys appears to be γ , after either rapid or slow cooling. However, the lattice parameters are slightly affected by the rate of cooling and reheating, indicating some decomposition of an unknown nature. Long-time heating at a temperature of 350 C causes a definite decomposition into $\alpha + \gamma$. These observations may also explain the maximum value of lattice parameter at 38 to 39% Ni, and the low expansion of the alloys in this range (invar).
- e. Alloys with more than 50% Ni are, for all practical purposes, γ or austenitic, and possess the characteristics of nickel-base solid solutions. The existence of $\alpha + \gamma$ in the lower-nickel part of this range, at temperatures below 400 C, has no practical significance (60).

2. Electrochemistry

Investigations on the electrochemical behavior of iron-nickel alloys have been principally confined to studies on hydrogen and oxygen over-voltage, and evaluations of corrosion resistance. Gas overvoltages have been determined mainly in alkaline solutions (61-64). The results of these studies indicate that for H_2 evolution, the Tafel slope b increased with iron and temperature, and no sharp effect was found corresponding to a phase change. For O_2 evolution, pure nickel was the only composition which had a regular Tafel curve; all other alloys required two sets of Tafel constants to fit the data.

Results of corrosion tests on the iron-nickel alloys in sulfuric acid and other media have been summarized by Uhlig (65) and Marsh (66). The data for 5 and 10% H_2SO_4 indicate that there is a marked improvement in resistance to attack as the nickel content is increased up to 35 to 40% nickel, and thereafter little change. Higher acid concentrations resulted in minimum corrosion rate in the vicinity of 50% nickel.

Uhlig has used the corrosion data for iron-nickel alloys in 5 and 10% H_2SO_4 as additional verification of his electron configuration theory (26-27). Nickel exhibits greater passivity than iron in aqueous solution due to its higher heat of adsorption of oxygen (130,000 cal and 75,000 cal/mol O_2 respectively). According to the theory, nickel is the electron acceptor and iron the donor, and the critical composition is calculated to be 33.3 atomic % nickel, in fair agreement with the corrosion data.

In the course of the corrosion studies of iron with small nickel additions, Herzog (67) found that 2 to 6% nickel reduces corrosion by 40 to 50% in sea-water and fresh water. Adherent deposits on the surface were found to contain hydrated oxide of nickel.

A systematic study of the anodic behavior of iron-nickel alloys in sulfuric acid at 25°C was conducted by

Morioka and Sakiyama (68). They investigated 16 alloys ranging in composition from 0 to 100% nickel in 1.0 and 5.0% deaerated H_2SO_4 (0.205 N and 1.01 N respectively). Alloys were annealed at 900°C for five hours. Potential-current curves were obtained by increasing and decreasing the electrolysis voltage at a rate of 0.3 volts/minute (evidently using a motor driven potentiometer).

Passivation current I_p was rather irregular, an increase in nickel content making it smaller for the 1% H_2SO_4 solution. In the 5% solution, I_p reached minimums at about 40 and 70% nickel. Some representative values estimated from the potential-current curves are as follows:

% Ni	1% H_2SO_4	I_p (ma/cm ²)	5% H_2SO_4
0	160		300
22	110		220
39	50		100
50	40		160
70	20		60
100	10		230

The I_p value for 100% nickel in 5% H_2SO_4 was as low as about 20 ma/cm² in one trial.

In the active state of iron a linear relationship was found between overvoltage and anodic current, whereas for active nickel, the Tafel equation could be applied up to 150 ma/cm². The polarization curves changed from a linear to a logarithmic relationship with increasing nickel content.

In the passive state, the potential at which significant currents could be noted because of oxygen evolution varied with composition. From 0 to about 50% nickel, this potential was around 1.7 volts. With increasing nickel, the potential for oxygen evolution decreased to around 1.1 volts. Anodic dissolution in the form of Fe^{+++} and Ni^{++} was detected at potentials more noble than that for oxygen evolution, though it was felt that the nickel dissolved as Ni^{+++} and was directly reduced. The active state was recovered for all alloys when the potential was set at active values. Passive current increased when nickel content exceeded 60%, but it was not possible to check their current values since a linear, instead of logarithmic, current scale was used.

Corrosion potential became more noble with increasing nickel content. The potentials were slightly more active after electrolysis. There was a sharp effect at 30% nickel, α -phase alloys containing less nickel being about 0.15 volt more active than γ -phase alloys with more nickel.

V. PROCEDURE AND APPARATUS

A. Specimen Preparation

Anodes were prepared from pure iron and nickel. The nickel was reagent grade shot from the J. T. Baker Chemical Company and assayed 99.99% nickel. The iron was Ferrovac E half-inch diameter rod from the Crucible Steel Company and contained 99.97% iron. The nickel and iron were degreased in acetone and pickled for 15 minutes at 180°F in 30% HCl and 10% HCl respectively. The pickled metal was neutralized in 5% NH_4OH , rinsed in double distilled H_2O , and dried. Specimens of about 30 grams each were prepared at the following compositions:

<u>Atomic % Fe</u>	<u>Atomic % Ni</u>
100	0
95	5
90	10
80	20
70	30
60	40
50	50
40	60
30	70
20	80
10	90
0	100

The pure metal specimens were arc-melted three times and the alloy specimens were arc-melted six times for homogenization. The arc furnace was gettered by

arc-melting titanium and the melting was done under a partial pressure of argon.

The arc-melted buttons were milled into square rods about 0.2 inch by 0.2 inch, and about one inch long. One end was drilled and tapped with a 6-32 thread for connection to the cell. The other end was polished through 000 paper.

The specimens were then vacuum annealed at 1000°C for one hour, and furnace-cooled to room temperature in three hours. The sides of the specimens were coated with Varno cement so that when the specimen was screwed into the polarization cell, only the polished end (about 0.25 cm²) was exposed to the solution.

B. Electrolyte

The solution used was H₂SO₄ with 0.5 N potassium sulfate as supporting electrolyte. The pH was adjusted by varying the concentration of the acid. The supporting electrolyte was necessary to give sufficient conductivity at the higher pH's (0.1 N and lower). Following is a list of the solutions used and their experimental pH:

<u>N H₂SO₄</u>	<u>pH</u>
10.0	-0.47
1.0	0.56
0.1	1.67
0.01	2.73
0.001	3.73

The pH's of the 0.001-0.1 N solutions were checked with a Beckman glass electrode and the pH's of the 1.0 N and 10 N solutions were checked with a platinized platinum hydrogen electrode. The pH's are higher than normal for H_2SO_4 because of the increase in ionic strength from the supporting electrolyte and consequent decrease in the activity coefficient (as predicted by the Debye-Hückel Theory).

C. Polarization Cell

The polarization cell used in the experimental work is shown in Figure 4, and was designed to have a low internal resistance. The large area platinized platinum cathode provided a low polarization resistance, and the proximity of the anode and cathode (with porous tube removed) provided a low solution resistance.

Preliminary work was carried out in a cell which consisted of separate anode and cathode compartments connected by a fritted disc. This gave a good separation of anode and cathode gas products and allowed control of the gas environment in each compartment, but the internal resistance was approximately 15 ohms. Since the external resistance was greater than the anode resistance, the system acted as a constant current source.

The new cell had a potentiostatic resistance of about one ohm, with the porous tube removed. This gave good potentiostatic control, but allowed only for a uniform gas

● O Rings	F Calomel Probe
A 3/4", 3 1/2" D Teflon Gaskets	G Gas In
B 70 mm D Pyrex Cylinder, 33 4" h	H Gas Out
C Removable Porous Tube	I Threaded Teflon Plug
D 40 mm D pt Electrode, or 18 mm D if Porous Tube Out	J Threaded Metal Rod for Electrical Contact
E Threaded Specimen	K Clamp

Fig. 4 - Low Resistance Polarization Cell

environment (H_2) for both electrodes. The cell permitted individual control of the gas environment by insertion of a porous alundum tube. The resulting increase in resistance requires the use of an electronic potentiostat (see V, E).

The Luggin tubulus used as a probe for the saturated calomel reference electrode had a diameter of approximately one millimeter. It was filled with a 4% agar-saturated KNO_3 gel. An agar-KCl gel interfered with the reactions under study and an agar- K_2SO_4 solution would not gel.

The platinized platinum cylindrical cathode was 18 millimeters in diameter if the porous tube was removed or 40 millimeters in diameter if the tube was in place. The platinization was carried out by cleaning the platinum metal in hot aqua regia and electrolyzing in a 1.0 N HCl solution containing 2% chloroplatinic acid and 0.02% lead acetate. The current density was about 0.1 amp/cm² and the current was reversed about once a minute to decrease gases in the deposited platinum. The electrodes were then rinsed, soaked, and stored in double distilled water.

Convection in the vicinity of the anode was decreased by having the anode surface face upwards. This decreased the current requirements and, consequently,

aided the potentiostatic control. With the specimen E screwed onto plug I and the platinum cathode D inserted into the top gasket, the cell was assembled and the nuts tightened. The solution was poured through the top middle hole and probe F inserted. With the stopcocks on the gas inlets and outlets shut off, the "O" ring seals provided an air tight cell. The stopcocks on the gas inlets were made of teflon to avoid contamination of the solution.

D. Constant Current Apparatus

Figure 5 illustrates the electrical circuit used for constant current measurements. The regulated D.C. power supply and 12 resistors provided 12 current ranges from 0-200 milliamps down to 0-1 microamp. The range selector switch S-3 was a shorting switch, so that the circuit was not opened while operating the switch.

A.C. ripple from the power supply was very small, but its effect on passivity could be checked by using switch S-1 to change the power supply to a 225 volt battery. The choice of anodic or cathodic current was made with switch S-2.

E. Constant Potential Apparatus

The constant potential supply is shown in Figure 6. Switch S-3 chooses between the battery operated "classical" potentiostat and the electronic potentiostat P, the details of which follow in Figures 7 and 8. Low resistance

P-S Heath-kit PS-3 Regulated power supply;
0-500V, 0-200 ma.

B 225V Battery

S-1 D. P. D. T. Power selector

V 0-600V Voltmeter

S-2 S. P. S. T. Voltmeter on-off

C 0.1 ufd, 1000 V

S-3 12 Position rotary shorting switch

R 12 Resistors; 1K, 3K, 10K, 30K, 100K at
100 watts, 330K, 1Meg, 3.3 Meg, 10 Meg,
33 Meg, 50 Meg, 480 Meg, at 2 watts.

S-4 D. P. D. T. Current reverse

Fig. 5 - Constant Current Supply

B 6 Volt, 216 Amp. hour Ni-Cd Battery

L Pilot Lamp

P₁ .5 Ohm, 100 Watt Potentiometer

P₂ 10 Turn, 3 Ohm, 2 Watt Precision Potentiometer

P Electronic Potentiostat

S₁ DPDT Middle Position off, Current Reverser

S₂ DPDT Potentiometer Selector

S₃ SPDT Potentiostat Selector

Fig. 6 - Constant Potential Supply

Fig. 7 - Potentiostat Block Diagram

- Fig. 8 - Potentiostat Circuit

potentiometer P_1 was used for potential control in the active region where the current was high, while a precision potentiometer P_2 was used in the passive region where currents were low and resistance not as critical, but where precise control of the potential was necessary. Switch S-2 selected the potentiometer and switch S-1 reversed the current.

The original scope of this work was to have covered various gas environments for the anode, using the electronic potentiostat shown in Figures 7 and 8 which was designed to function as a potential controller for a high resistance cell. It was later decided that work would be limited to an H_2 gas saturated solution, making the use of the electronic potentiostat unnecessary. Future work will require the use of this instrument; therefore, a description of its principles and operation are included for the use of future experimenters.

An electronic potentiostat is essentially an electronic servomechanism, controlling the anode-reference electrode potential by means of an amplified error signal. A block diagram, Figure 7, facilitates an understanding of this instrument. The anode-reference electrode potential is measured by the D.C. amplifier and compared with a reference voltage (bucking potential) in the chopper. The

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chopper converts the D.C. difference into a 400 cycle A.C. error signal, which is amplified by the error amplifier and fed to a phase sensitive detector. The error and carrier signals are compared in the detector to differentiate between a positive and negative error. The detector is phased so that a positive error signal (i.e., an anode-reference potential higher than desired) will decrease the polarizing potential applied to the cell, thereby decreasing the cell current and, likewise, the anode reference potential. The action is reversed for a negative error signal, the polarizing potential applied to the cell always being changed so as to make the error signal approach zero.

The procedure for operating the electronic potentiostat is as follows:

1. Turn on equipment and set oscillator at 400 cycles. The chopper should give an audible 400 cycle tone.
2. Disconnect the platinum cathode lead, set A-2 volume control for 20 volts A.C. at T-2, disconnect input to A-1, and adjust R-3 for zero D.C. volts from the cathode lead to ground. The setting of R-3 may be changed if a rest point other than zero volts is desired.
3. Reconnect A-1 input and set A-1 volume control for output of 5 to 10 volts. The first amplifier stage of A-2 was converted to a phase shifter, and brings the carrier

and error signal into phase. This condition may be achieved by using an oscilloscope and adjusting the phase shifter to obtain the proper Lissajous figure (a straight line). Alternately, one may adjust for a maximum D.C. output from the cathode lead to the ground.

4. The control potential is set by 10 turn precision potentiometer P (see Figure 8). The setting is not calibrated, but one may easily set the dial at the o.c. (corrosion) potential as follows: disconnect the connection to the platinum cathode so that the electrometer measures the o.c. potential. If potentiometer P is adjusted for zero D.C. output, the potentiostat will control at the o.c. potential when operated. Counterclockwise turning of the potentiometer sets the control potential at more cathodic values.

5. The volume control of A-1 sets the amplification of the error signal. With high amplification, the control potential changes more rapidly as the potentiometer is turned. Since the error signal for any setting is smaller, closer control is obtained. The limiting factor is the stability of the potentiostat; the greater the amplification, the greater the tendency for instability with the Pt cathode connected.

6. R-2 and C-1 make up the R.C. lag network which tends to decrease the instability mentioned in (5) above.

However, increasing the R.C. lag also slows the response time of the potentiostat, and a balance is found between response time and degree of control (instability must be absent) using the R.C. lag and A-1 volume controls.

F. Measurement Circuit

The potential and current measuring circuits are represented in Figure 9. Switch S-1 selects between the constant potential and constant current sources, and has an off position for o.c. potential measurements. REC-1, the cell current recorder is a Bristol high speed (0.4 second full scale) recorder and has three ranges: 0-1 mv, 0-10 mv, and 0-100 mv. The current range is further extended by using shorting switch S-2 to select one of six precision current resistors. For currents less than a microamp, the recorder was replaced by a galvanometer with an internal resistance of 27 ohms, a sensitivity of 1.6 microvolts per millimeter, and a 10 millimeter scale.

The anode reference cell potential is measured by electrometer E which has three scales: 0-10 mv, 0-100 mv, and 0-1000 mv. The range can be extended to two volts by the use of bias cell B, a Weston standard cell ($E = 1.019$ volts). The electrometer has an output jack for the Brown recorder, and both the electrometer and recorder were calibrated using the Weston standard cell. Using a Poggendorff

A Anode
 C Cathode
 REF Saturated calomel reference electrode
 S-1 D. P. D. T. Selector
 C-C Constant current source (see Fig. 5)
 C-P Constant potential source (see Fig. 6)
 S-2 6 position rotary shorting switch

R 6 1% resistors; 0.1, 1.0, 10, 100, 1000, and 10,000 ohm
 E Curtiss Wright electrometer
 REC-1 Cell current recorder
 REC-2 Anode-calomel potential recorder
 S-3 SPDT Bias cell on-off
 B Bias cell

Fig. 9 - Measurement Circuit

compensation circuit as the input to the electrometer, the recorder was found to be accurate to within one millivolt over the entire range.

G. Determination of a Polarization Diagram

All measurements were conducted in a room maintained at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$. After assembly of the cell (see V, C), hydrogen gas was vigorously bubbled through it for 15 minutes to deaerate and saturate the solution with hydrogen. The hydrogen was passed through a Deoxo Purifier, which decreases the oxygen content down to one part per million. The anode was electropolished for 20 minutes at a current density of about 40 ma/cm^2 . It was necessary that the anode be active during this treatment, for, if a film were initially present, this current density would lead to oxygen evolution. Film reduction was accomplished by (1) cathodic polarization of the specimen, or (2) constant potential electrolysis at an active potential, or (3) the first treatment quickly followed by the second.

The anodic reaction was in some cases disturbed with the reference probe touching the anode. A cathetometer was used to set the probe at a distance of 2.0 millimeters from the anode. This introduced an ohmic overpotential because of the resistance of the solution, the

error becoming more serious at higher currents. To correct for this, the ohmic overpotential was determined at various current densities and a correction plot made. The ohmic drop was linear and relatively insensitive to anode composition. The error was higher in the less conductive solutions, and became constant for 0.1 N solutions and lower since their conductivities were in this case mainly dependent on the supporting electrolyte.

<u>Solution</u>	<u>Correction</u> (mv per ma/cm ²)
10.0 N	0.20
1.0 N	0.75
0.1 N	2.00

The electrical connection to the cathode was opened, and the o.c. potential noted after it had reached a steady value. The rate of hydrogen bubbling was reduced so as not to stir the solution. The general procedure was to use constant current measurements when the polarization resistance was low (i.e., E relatively insensitive to changes in I/A), and constant potential measurements where the polarization resistance was high and constant current measurements impossible. Starting at a current density of one $\mu\text{a}/\text{cm}^2$, the current was increased by factors of ten, noting the steady state potential at each current density value. As the current density required for oxygen evolution was

neared, current increments were decreased to obtain a value for the passivation current density. As O_2 evolution started, the anode potential took a characteristic jump in the noble direction, and the steady state value of the potential was read off. Current density was decreased in tenfold increments starting with 10 ma/cm^2 , until the potential started a definite drift in the active direction. The Bristol recorder was plugged into the electrometer to obtain a high speed trace of the potential as the anode activated.

The anode was activated and measurements made at constant potential, reading the steady state current at each potential. Several potentials were chosen to verify the constant current determinations and the shape of the curve up to the passivation potential was determined. When the anode became passive, as indicated by a sudden decrease in current (fast decrease in the case of iron, and slower for nickel and the alloys), the potential was set at +1.200 volts. The potential was decreased in steps of 0.2 volt to the point where the current started to increase, and the steady state passive current noted at each potential. The potential was then decreased slowly and the activation potential noted, the method of determining the activation potential varying with the anode composition. Iron gave an unmistakable sharp jump in current

and potential on activation. However, the passive film on the nickel and alloy anodes decomposed very slowly, and a pseudo-constant current technique was used in this case.

Any point on this activation (negative resistance) curve is inherently unstable, the degree of instability increasing with the steepness of the slope. A regular constant current source was not usable since the potential would always go to the equivalent value of O_2 evolution. A constant potential source, whose potentiostatic resistance cannot experimentally be zero, would tend toward higher or lower currents, depending on the position on the curve. Since the actual slope had a finite value, and the film decomposed slowly, it was possible to achieve a momentary (two or three minutes) steady state on the curve. The procedure was to choose an approximate current value at which the potential was to be determined, and set the potential at some active value until the current built up to the desired magnitude. The potential was then made more noble until the current started to decrease slowly. By manipulating the potential, the current was made to increase and decrease at a slower and slower rate, until a steady current value was attained, and the value of both potential and current was recorded.

The above procedure was followed for all specimens in 10.0 N, 1.0 N, 0.10 N, and 0.01 N solutions. For the 0.001 N solution, the test was abbreviated to the determination of the o.c. potential, passive current density, activation potential, and passivation current density. Otherwise, the 0.001 N solution would undergo a significant rise in pH (the 0.01 N solution had a rise of 0.04 to 0.06 pH units during a regular test).

H. X-ray Investigation

An X-ray investigation was made of the variation in alloy metallurgical structure with composition. Using molybdenum K α radiation, an X-ray traverse of the specimen was made using a Norelco X-ray Diffractometer. Identification was made by comparing the 2θ values of the peaks with values for iron and nickel computed from the ASTM X-ray Powder Data File.

VI. RESULTS AND DISCUSSION

In the presentation and discussion of the results, the following will be understood:

1. The European sign convention is used for potentials.
2. Potentials are referred to the standard hydrogen electrode (SHE).
3. Current density is calculated on the basis of geometric area.
4. The composition of an alloy is given in the order atomic % Fe - atomic % Ni (i.e., 80-20 alloy will signify 80 at.% Fe - 20 at.% Ni alloy).

A. Metallurgical Structure

Since the structures of the alloys are a function of both heat treatment and composition, an X-ray investigation was conducted to determine the structures of the heat-treated (one hour at 1000°C) specimens, and the structures are as follows:

<u>Composition (at.% Ni)</u>	<u>Structure</u>
up to 5	α
10 - 40	$\alpha + \gamma$
50 - 100	γ

These results correspond to the structures obtained on re-heating according to the ASM Metals Handbook (60). Though the position of the diffractometer peaks was adequate for identification purposes, the peak intensity values were

not sufficiently reliable for a quantitative determination of the amount of each phase in the two-phase alloys.

No significant information was obtained in a microscopic examination of the alloy specimens after electrolysis. As might be expected, there was a marked attack of the grain boundary for all alloys, and in the two-phase alloys, there was additional selective attack of some of the grains. The attack of the selected grains initiated at the grain boundary and proceeded inwards. The surface of these alloys was deformed with a Rockwell hardness indenter in order to identify the selectively attacked grains by their slip pattern. However, no meaningful slip patterns could be discerned.

B. Anodic Polarization Curves

The anodic polarization curves of twelve Fe-Ni alloys were determined by means of galvanostatic and potentiostatic techniques. The curves for the 95-5, 70-30, 40-60, and 0-100 alloys are shown in Figures 10 to 13. These four compositions were chosen as representative of the twelve Fe-Ni alloys and adequately show the transition behavior with changing composition.

1. Effect of Composition

With respect to the general shape of the curves, there was no sharp effect found with either changing

Fig. 10 - Anodic Polarization of 95 at % Fe -
5 at % Ni Alloy at Various pH

Fig. 11 - Anodic Polarization of 70 at % Fe -
30 at % Ni Alloy at Various pH

Fig. 12 - Anodic Polarization of 40 at % Fe -
60 at % Ni Alloy at Various pH

Fig. 13 - Anodic Polarization of 0 at % Fe -
100 at % Ni Alloy at Various pH

composition or changing structure. Changes in o.c. potential, passivation current I_p , passive current, and Flade potential will be discussed in detail later. The 95-5 alloy was presented in preference to pure iron since the behavior of the latter is already quite well known, and, in any case, the two were much alike in their behavior. The decrease, with increasing nickel content, in the potential span over which the current I_L is relatively constant should be noted. With increasing nickel, the most active potential (potential corresponding to I_p) becomes more noble and the passivation potential becomes more active, so that the two potentials converge and form a sharp peak in the case of nickel.

2. Effect of pH

In Figures 10-13, a massive shift of the potential to the left is noted with increasing pH. The shift at the left (Tafel slope for anodic dissolution) and center (active-passive transition) is discussed later, but the shift at the right is a consequence of the change in the potential of the reversible oxygen electrode,

$$E_{O_2} = 1.23 + \frac{RT}{4F} \log (a_{H^+})^4 (p_{O_2}) ,$$

and at 25°C and $p_{O_2} = 1$ atmosphere,

$$E_{O_2} = 1.23 - 0.059 \text{ pH} .$$

The pH-potential relationship indicated by this equation was not valid for the 0-100 alloy in 10.0 N H_2SO_4 (Figure 13), the oxygen evolution potential shifting to a more active value for the highest acidity. This abnormal shift at high acidity was also noted for the 10-90 alloy. If the passive nickel layer were oxidized to NiO_2 , which is unstable in acid solution, the current could be attributed to anodic dissolution instead of oxygen evolution. Latimer (69) gives

with $E^\circ = + 1.32$, which is in the correct potential range. A similar phenomenon was noted by Tomashov (70) in the transpassivity of stainless steel where the protective chromium oxide at very noble potentials dissolves as soluble dichromate. The anomalous maximum in passive current for nickel in 10.0 N H_2SO_4 (Figure 13) was reproducible and is reminiscent of the passive behavior of stainless steels.

3. Tafel Slopes

Tafel slopes for anodic dissolution and for oxygen evolution were measured for all alloys; however, the experimental conditions were such as to interfere with true Tafel behavior. For anodic dissolution, a linear slope is obtained only after the impressed current is much larger than the corrosion current, but at higher impressed currents,

the limiting current is approached and concentration polarization causes deviation. Similar conditions exist for Tafel curves in oxygen evolution, where the oxygen evolution current should be much greater than the anodic dissolution current, but much less than the limiting current. Compensation was made for ohmic overpotential, but the correction became so large (up to 0.4 volt) at the higher current densities, that a small error in the correction could noticeably influence the results.

Using only the slope values which exhibited Tafel behavior over at least a hundred-fold range of current, the b values for anodic dissolution ranged from 0.034 to 0.074. These values are generally lower than the values (0.07 to 0.10) normally reported, but no significance is attached to these results because of the irregularity of the data. No regular progression of b values was found with either pH or composition, though the high nickel alloys tended to have greater slopes. For oxygen evolution, b values ranged from 0.033 to 0.092 with no regular dependence on pH or composition.

It can probably be concluded from the foregoing that one should not attempt to obtain information on Tafel slopes and passivity phenomena under the same experimental conditions. This study was principally focused on

a potentiostatic study of the alloy system, in which case smaller currents (i.e., no stirring) are desired to approach a true potentiostatic condition. To obtain better Tafel behavior, on the other hand, would require vigorous stirring to eliminate concentration polarization. A more sophisticated method of compensating for ohmic overvoltage (e.g., the interrupter method) would also be required for the higher current values.

4. Periodic Phenomena

In certain potential and current ranges, the potential and current of an electrode may undergo rhythmic fluctuations. The simplest type is the active-passive oscillation, and this type of fluctuation is pictured in Figure 14 for iron in 1.0 N H_2SO_4 . The time-current trace was obtained with a Bristol high speed recorder at a chart speed of six inches per minute. The trace at the top was at a frequency of 18 cycles per minute and the trace at the bottom at 6 cycles per minute. This type of oscillation was obtained only in the α - and two-phase alloys, and in all concentrations H_2SO_4 , except 10.0 N. As the true passivation potential was approached from the active direction, the frequency of the oscillations decreased; the frequencies ranged from 150 to 2 cycles per minute. Bonhoeffer (33) explains this active-passive behavior on the basis of a dependence of passive potential

Fig. 14. Active-Passive Current Fluctuation
for Iron in 1.0 N H_2SO_4 .

on pH in the active and passive state. The pH at the surface of an active electrode is higher (preservation of electrical neutrality) and the electrode passivates at a more active potential according to the Flade relation. The rate of activation from the passive state is greater with a large difference between true and apparent passivation potential, explaining the experimental frequency dependence.

Ludering (71) has shown that for certain critical values of anode area and external resistance, one may obtain periodic dissolution and formation of a ferrous sulfate film. In the present study, this type of oscillation was noted in the high iron alloys, though it was not as regular as the active-passive type. It occurred in the area of constant high current density (I_L), and frequencies were in the range 200-240 cycles per minute, and independent of potential.

Piontelli (51) reported periodic behavior for a passive nickel electrode at constant current (during oxygen evolution). This type of oscillation was noted in this work at an 80% or greater nickel content, but only in 10.0 N H_2SO_4 . The oscillation was irregular and required high current density (10-100 ma/cm^2).

C. Corrosion Potential

1. Dependence on Composition

The corrosion, or open-circuit (o.c.) potential shows a dependence on both composition and pH. The variation in o.c. potential with composition is shown in Figure 15. The potentials correlate quite well with the structure at each composition. The γ -phase alloys are about 0.20 volt noble with respect to the α -phase alloys. This is in agreement with the results of Morioka and Sakiyama (68), except that they did not indicate the existence of a two-phase field in the range 10-40 at.% Ni, but showed the α -phase up to 30 at.% Ni and the γ -phase at higher Ni content. However, they do not mention an independent determination of alloy structure, and it is likely their remarks on structure are based on their o.c. potential data, since the heat treatment they used, 900°C for five hours, would ordinarily yield a two-phase structure in the range 10-40 at.% Ni.

The o.c. potential behavior in the single-phase range can be predicted from the theory of mixed potentials:

with predominant polarization of the anodic reaction to give anodic control. This is particularly true of the

Fig. 15 - Corrosion Potential vs. Composition at Different pH

γ -alloys, which are seen to agree fairly well with the corresponding reversible hydrogen potential scale indicated on the right-hand ordinate of Figure 15. The more noble o.c. potential of the α -alloys with the addition of 5% nickel is the result of a more noble reversible potential. The o.c. potential was insensitive to ferrous or nickelous ion concentration in solution, additional proof of anodic control.

The behavior in the two-phase range is more complicated. In this case, the condition, $\Sigma I_a = \Sigma I_c$, is met by summing the local current for each phase, and a polarization diagram to deduce the o.c. potential would require four polarization curves, an anodic and a cathodic curve for each of the phases. Since information of this type would be difficult, if not impossible, to obtain, a qualitative analysis is made to explain the o.c. potential behavior with changing composition in the two-phase range.

Since the Tafel slope for hydrogen evolution is less for nickel than for iron in acid (72, 73), and Tafel slopes for hydrogen evolution in the Fe-Ni system increase with increasing iron content in alkaline solution (61, 63), it is assumed that the hydrogen evolution Tafel slope for the α -phase is greater than for the γ -phase in acid solution. In a galvanic experiment (see VI, G) with a binary electrode, anodic current flowed from the α - to the γ -phase

constituent, indicating that the α -phase is attacked anodically in preference to the γ -phase.

Based on this information, the more noble o.c. potential of the 90-10 alloy may be attributed to the first increments of γ -phase area, which depolarizes the hydrogen reaction, since the new phase has a completely cathodic area with a relatively low hydrogen overvoltage. As the nickel content is increased from 10 to 50 at.%, the o.c. potential becomes yet more noble because of the increase in the ratio of γ -phase to α -phase area. As this ratio increases, the ratio of polarization of γ -phase to polarization of α -phase decreases, so that the phase with the greater area controls the potential of the two-phase electrode.

2. pH Relation

Since iron in HCl acts in the same manner as a reversible hydrogen electrode ($\frac{dE}{d\text{pH}} = -0.059$) in the pH range 1-4, a similar relationship might be expected for the iron-nickel alloys in H_2SO_4 . The data from Figure 15 was accordingly replotted in the form shown in Figure 16.

An explanation of the method of determining the o.c. potential value plotted should be made at this point. The tendency for film formation, which increased with increasing nickel content and with increasing pH, sometimes

Fig. 16 - Corrosion Potential vs. pH for Each Alloy

resulted in widely divergent values for the o.c. potential. The o.c. potential with a film present was always noble with respect to an active, film-free surface, the difference in some cases being as high as 0.08 volt. Therefore, the noble values were not used, and the o.c. potential plotted was the active value, or the average of active values.

An inspection of Figure 16 shows that the anticipated o.c.-pH relationship does exist. Values for $\frac{dE}{d\text{pH}}$ vary from -0.035 to -0.046, less than the value of -0.059 for a reversible hydrogen electrode, or Stern's (28) value of -0.056. The slopes of Figure 16 are somewhat closer to the value of -0.047 found by Makrides, Komodromos, and Hackerman (31); however, the other two investigations were in HCl so that substantial agreement is not necessarily expected. The literature did not indicate whether the linear relationship should exist for negative or very low pH values. Approximately half of the Fe-Ni alloys studied deviated from the linear relationship at very high acidities.

The pH dependence of the o.c. potential is explained by Stern and Roth (29) on the basis of a decreasing area of local anodes with decreasing pH, possibly caused by greater hydrogen adsorption. This seems reasonable and

the argument could be applied to the present system. A simple qualitative explanation might be based on anodic control of the o.c. potential, the o.c. potential polarizing to the potential of the local cathodes, i.e., the potential of a hydrogen electrode.

D. Passivation Current

1. Measurement

Passivation current I_p was measured under galvanostatic conditions by increasing the current in small steps and noting the current at which the potential started a definite drift in the noble direction. The film formation noted previously sometimes interfered resulting in abnormally low values. A rapid determination also tended to give lower values. A method for evaluating I_p was described by Stern (74), in which various current densities greater than I_p were impressed and the time for passivity (t_p) noted. A plot of I versus $\frac{1}{t_p}$ was extrapolated to $\frac{1}{t_p}$ equal to zero (infinite time), the corresponding I value being considered as I_p . However, Stern could be relatively sure of an initially active surface since the environment was boiling 1 to 5% H_2SO_4 . Though Stern's method yields more reproducible results, it was not used in this work because of the limitations (film, etc.) noted previously.

2. Effect of pH and Composition

The passivation currents for the Fe-Ni system are shown in Figure 17 by a current-pH plot for each alloy. A composition-current plot was not made since no special trend was noted on this basis. For each alloy, the passivation current I_p passes through a maximum value in the pH range 0-2. Since the highest corrosion rates reported (65, 66) are the current equivalent of only 1 ma/cm², the variation in local cell current is probably a negligible factor in explaining the maximum in I_p .

The explanation for the variation in I_p with pH must therefore lie in the nature of the porous non-protective films formed at high current densities. These films ranged in color from gray-black for high iron alloys, to a greenish black for the 50-50 alloy, to a light green for the high nickel alloys. The colored films disappeared when the alloy became passive. The following reactions are of possible interest here:

Fig. 17 - Passivation Current Density vs. pH for Each Alloy

If the basis for I_p is an adequate ionic concentration to precipitate the hydroxide, the controlling factor should be

$$K_{sp} = [M^{++}] [OH^-]^2,$$

so that a decrease of one unit of pH would require a hundred-fold increase in metal ion concentration for precipitation. Starting with the highest pH, a marked increase in I_p is noted as pH decreases, the higher current value being required to achieve a greater metal ion concentration at the surface of the electrode. The erratic behavior of iron probably resulted from difficulties in measurement because of periodic fluctuations. Pure nickel had abnormally low I_p values at higher pH's, which is probably one of the reasons it is so useful in caustic solutions.

As the pH is reduced further, the metal ion concentration required is increased still more, but now the possibility of the precipitation of the metal sulfate must be considered. Sulfate ion concentration was essentially constant down to pH = 1.67 because of the supporting electrolyte (0.5 N K_2SO_4). At lower pH, the sulfate ion concentration increases at an increasing rate, so that the metal sulfate precipitates at a lower current density than the hydroxide. There is a tendency for the maximum to

shift to larger pH values for the iron-rich alloys, possibly because of the lower solubility of the $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ compared to the $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$.

E. Passive Current

1. Measurement

The passive current density is defined as the minimum current density required to maintain passivity. The minimum current was evaluated from anodic polarization curves such as in Figures 10-13. It is necessary to prevent crevice corrosion and insure optimum passivity by providing leak-proof electric connections of the electrodes. Occasional faulty connections (in some cases giving a hundred-fold current increase) were detected by comparison with other values. Whereas the criterion for o.c. potential and I_p was that the best values were the most active values, the criterion for passive current was that the best values were the most passive values. The time required to reach a steady-state current, or optimum passivity, varied with the acidity. Approximately fifteen minutes were required for the 0.001 N H_2SO_4 solution, but this increased to approximately two hours for the 10.0 N solution.

2. Effect of pH and Composition

The variation of passive current density with composition at constant pH showed no special trend, the current values being roughly the same across the whole composition range. However, a semi-logarithmic plot of passive current density versus pH for each alloy indicates a remarkable increase in passive current density with increasing acidity as shown in Figure 18. The passive film is free of pores under these conditions so that the passive current represents dissolution of the passive film instead of dissolution of the metal. However, the dissolution of the film is counterbalanced by film formation by the process which determines the Flade potential, and at the steady state, the rates of dissolution and formation are equal.

Weil (43) has reported that the dissolution rate of the passive layer of iron follows the relation,

$$\log J_k = \log J_{k_0} - a \text{ pH} ,$$

up to a pH value of 6.0, where J_k is the passive current density. The current-pH data in Figure 18 shows that the equation proposed by Weil is more or less followed by each alloy.

If the passive film is represented by Me_2O_3 (either an oxide or adsorbed O_2), the dissolution could proceed by the over-all reaction,

Fig. 18 - Passive Current Density vs. pH for Each Alloy

However, this type of reaction probably takes place by proton penetration of the electron cloud of the oxygen atom, the rate of this proton jump increasing with increasing acidity (78). The dissolution reaction is therefore rewritten in the general form

The formation of the passive film may be written

The rate of formation R_f of the passive film at a film-free surface, according to the absolute rate theory, is

$$R_f = [\text{OH}^-]^m k_1 \exp \left[\frac{\alpha n F}{RT} (E - E_f) \right]$$

where α = symmetry factor, E = electrode potential, and E_f = Flade potential.

If the same potential barrier is assumed for the dissolution reaction as for the passivation reaction, one may write

$$R_d = [\text{H}^+]^n k_2 \exp \left[\frac{\alpha n F}{RT} (E - E_f) \right] .$$

Since at the steady state, $R_f = R_d$, and the passive current

$$I = k_3 R_f, \quad I = [\text{H}^+]^n k_4 \exp \left[\frac{\alpha n F}{RT} (E - E_f) \right]$$

$$\log I = -n \text{pH} + k_5 + k_6 (E - E_f) .$$

Since $E \simeq E_f$ at the minimum current required to maintain passivity,

$$\log I = a - n \text{ pH}$$

as proposed by Weil and supported by the data of Figure 18.

F. Active-Passive Transition

1. Flade Potential

a. Measurement

Flade potentials were determined from high speed recorder traces of the potential decay of the passive alloys. In the decay trace, there is a halt in the potential corresponding to dissolution of the passive film. Uhlig (35), following the method of Flade, obtained the decay trace without impressing an external current, and recorded the Flade potential as the potential value just before the abrupt drop. Uhlig's method was adequate for evaluation of Flade potentials in this study for moderate acidities. However, at the highest acidity, the potential decay was so rapid that the halt disappeared completely, and at the lowest acidity, the decay was so slow that the halt was indistinct. The rate of decay also depended on the composition, the decay time increasing with increasing nickel content. To compensate for the different decay rates, small cathodic currents were impressed to speed up

sluggish reactions, and small anodic currents (but less than the passive current) were impressed to slow down the fast reactions.

Prominent halts were obtained for the α - and two-phase alloys. The γ -alloys had less definite halts because of the slower transition between the active and passive states. The decay traces for the γ -alloys were examined visually from all angles to deduce "breaks" in the curve. In extreme cases, it was necessary to assume that an inflection point in the decay trace was the Flade potential. Such tenuous criteria gave considerable scatter in the data as shown in Figure 19.

b. pH Relation

The Flade potential as a function of pH is shown for each alloy in Figure 19. The range of the data is shown by the vertical dotted lines. Since the Flade potentials of both iron and nickel are known to have a 0.0591 pH dependence, the assumption is made that all the Fe-Ni alloys will have the 0.0591 pH dependence. Linear dependence of data may be represented by an equation of the form

$$\Sigma y = na + b \Sigma x ,$$

where n = number of data points.

The E_f —pH data were therefore accumulated according to the equation

Fig. 19 - Flade Potential vs. pH for Each Alloy

$$\sum E_f = n E_f^{\circ} - 0.0591 \sum \text{pH}$$

to evaluate E_f° , the standard Flade potential ($E_f = E_f^{\circ}$ at $\text{pH} = 0$), for each alloy. The curves of Figure 19 were drawn through the E_f° value at $\text{pH} = 0$ and at a slope of -0.0591 . The relatively good fit with the data justifies the value assumed for the slope, and indicates that the Flade relation ($E_f = E_f^{\circ} - 0.0591 \text{ pH}$) is substantially followed at every composition.

c. Effect of Composition

The experimental standard Flade potentials (E_f°) are plotted versus composition in Figure 20. The E_f° value of $+0.59$ for iron is slightly higher than the accepted value of $+0.58$. The E_f° value for the 95-5 α -alloy is about the same as for iron. An E_f° value of $+0.45$ for nickel was computed from the E_f value of $+0.43$ for nickel in $1.0 \text{ N H}_2\text{SO}_4$ reported by Okamoto, Takaishi, and Sato (55). The experimental E_f° for nickel was $+0.49$, but this value is not as reliable as the experimental E_f° of iron because of the difficulty in evaluating the decay traces for high nickel alloys. This difficulty in the high nickel range manifests itself in Figure 20 where the E_f° values for the γ -alloys show an erratic trend with changing composition. However, the median E_f° value of $+0.47$ for the γ -alloys is

Fig. 20 - Standard Flade Potential vs. Composition

only 0.02 volt higher than the value for nickel reported in the other investigation.

One would predict that a two-phase alloy should be as noble as its most active constituent, i.e., the E_f^O of the two-phase alloys should be controlled by the E_f^O of the α constituent. This behavior is followed by the 90-10, 80-20, and 70-30 alloys. However, the E_f^O value of the 60-40 alloy does not follow the predicted behavior, but is apparently controlled by the E_f^O of the γ -phase. This effect at 40 at.% nickel could be attributed to a small α -phase area, the active current of the α -phase being insufficient to activate the γ -phase through galvanic contact.

The explanation of this effect could also lie in the change of the occupancy of the d band energy levels with changing composition, the passive state corresponding to unfilled d bands, according to Uhlig's Electron Configuration Theory (26, 27). In this theory, nickel is an electron acceptor, and at a certain critical composition of nickel, the alloy becomes passive because the d levels of iron are no longer full. The critical composition is calculated by Uhlig to be 33.3 at.% Ni. The effect at 40 at.% Ni shown in Figure 20 could be considered a remarkable verification of Uhlig's theory for the Fe-Ni alloy system.

2. Transition from Passive to Active State

a. Measurement

Steady-state potential current values were determined for the curve defining the transition from the passive to the active state by a pseudo-galvanostatic technique. Though the electrical circuit for these measurements was actually potentiostatic, the potential was closely adjusted with a 10 turn precision potentiometer to obtain a steady-state current value. This approach was required because of the steep negative slope of the transition.

b. Relation between E and I

The steady-state potential-current values for the passive-active transition are shown in Figures 10-13. In some cases, the potential became completely unstable as the current increased from the passive value. This situation arose for the 95-5 alloy (Figure 10) in 0.01 N H_2SO_4 . The instability of the other alloys ensued at current values much higher than the passive current, compared to the 95-5 alloy. The current at which instability set in tended to be lower with increasing pH.

The criterion for stability during the passive-active transition is discussed by Franck (25). Since all the

stationary states of the electrode are given by the polarization curve, and all the stationary states of the external circuit by a "resistance line" representing the total external resistance (potentiometer, solution, etc.), the intersection of both curves represents the stationary state in which the entire circuit (electrode and external circuit) can exist. Two general cases were considered by Franck, E-I diagrams resulting in N-shaped curves and E-I diagrams resulting in S-shaped curves. An analysis of each type of curve leads to the conclusion that mixed electrode states (the electrode surface has both active areas and passive areas in the transition state) on S-form curves are stable, but on N-form curves unstable.

Since the polarization curves (Figures 10-13) are of a general S-form, the stability of points on the passive-active transition are explained by Franck's theory. The decreasing stability with increasing pH would be concerned with a changed "resistance line" because of the lowered conductivity.

The passive-active transition (Figures 10-13) gives rise to negative slopes which are in some cases quite linear. In a recent paper by Mueller (79), an equation is derived which covers the curve of the density of anodic dissolution current as a function of the potential including the active and passive states.

$$1) \quad I_c = \frac{2 I_{0.5} \exp \frac{\alpha_a n_a F}{RT} (E - E_{0.5}) + I_p \exp \frac{\alpha_p n_p F}{RT} (E - E_{0.5})}{1 + \exp \frac{\alpha_p n_p F}{RT} (E - E_{0.5})}$$

where I_c = anodic dissolution current

$I_{0.5}$ = I when surface is 50% covered by protective film

$E_{0.5}$ = E corresponding to $I_{0.5}$

I_p = passive current

α_a = symmetry factor of anodic reaction

α_p = symmetry factor of reaction forming passive film

n_a = valency of anodic dissolution reaction

n_p = valency controlling rate of passive film formation.

For the active state, the second term in each numerator and denominator is negligible, and

$$2) \quad \frac{d \ln I_c}{dE} = \frac{\alpha_a n_a F}{RT},$$

an alternate form of the Tafel equation. In the active-passive transition zone, the second term in the numerator and the first term in the denominator become negligible, and

$$3) \quad \frac{d \ln I_c}{dE} = \frac{\alpha_a n_a - \alpha_p n_p}{RT}.$$

In the passive area, the first term of each numerator and denominator becomes negligible, and

$$4) \quad I_c = I_p.$$

The ratio $\alpha_a n_a / \alpha_p n_p$ describes the form of the curve. For a ratio of unity, the curve forms a polarographic wave, but for ratios greater than unity, a negative slope is obtained for equation 3. Since Figures 10-13 are also on a semi-logarithmic basis, equation 3 adequately describes the experimental active-passive transition curve.

c. Effect of pH

Similar to the effect of pH on the Flade potential, the active-passive transition curve shifts to the left with increasing pH. It should be noted that the Flade potential obtained from a decay trace is active with respect to the potential at which the transition to the active state starts. This may be seen from a comparison of Figures 10-13 with Figure 19. The Flade potential is seen to fall between the potential limits of the active-passive transition curve, and it is not possible to differentiate the Flade potential from any of the other mixed electrode states.

d. Effect of Composition

Since the Flade potential is incorporated into the transition curve, it would be expected that the transition curve should shift with composition in much the same manner as the Flade potential. An examination of all the

polarization curves (including those not presented in Figures 10-13) indicates that the transitions are alike for all alloys up to 30 at.% Ni. Alloys with 70 at.% Ni and higher also behave alike, but the transition occurs at a potential 0.2 or 0.3 volt more active with respect to the lower nickel (up to 30 at.%) alloys. The transition for nickel contents between 40 and 60 at.% Ni is interesting. The slopes are less steep than those of alloys with either higher or lower nickel content, as shown in Figure 12 for the 40-60 alloy. The alloys with nickel content between 40 and 60 at.% thus represent a bridge between iron-like and nickel-like behavior, since the transition from the passive to the active state starts at potentials characteristic of the high iron alloys, but ends at potentials characteristic of the high nickel alloys. The change from ferritic to austenitic type behavior between 40 and 60 at.% Ni does not correlate exactly with the metallurgical structures of the alloys.

G. Galvanic Experiment

1. Scope

The purpose of this experiment was to simulate a normal two-phase alloy electrode and compare the electrochemical behavior of the artificial and normal alloy. The

artificial binary electrode consisted of two electrically connected alloys with equal areas to simulate a 50% α - 50% γ alloy (i.e., approximately the 70-30 alloy). Two types of artificial binaries, unsaturated and saturated, were investigated. The constituents of each type were as follows:

<u>Type</u>	<u>α-phase</u>	<u>γ-phase</u>
unsaturated	100-0 alloy	0-100 alloy
saturated	95-5 alloy	40-60 alloy

The results of the galvanic experiment are summarized in Figure 21.

2. Corrosion Potential

The variation in o.c. potential with pH is shown at the left side of Figure 21. The behavior is similar to that of a reversible hydrogen electrode, $\frac{dE}{d\text{pH}} = -0.50$ for the unsaturated and -0.56 for the saturated binary electrode. These slopes are less than that of a reversible hydrogen electrode ($\frac{dE}{d\text{pH}} = -0.059$), but greater than all those shown in Figure 16 for the natural alloys. It was anticipated that the artificial electrodes would simulate the behavior at or near the composition of the 70-30 alloy. However, on comparison of Figures 16 and 21, the o.c. potentials of the unsaturated binary are intermediate to the o.c. potentials of the 100-0 and 95-5 alloys, and the o.c.

Fig. 21 - Electrochemical Properties vs. pH for Binary Electrode (Equal areas of each Constituent).

potentials of the saturated binary are close to those of the 95-5 alloy.

From this behavior, one would suspect the presence of films on the γ -phase constituent, though each constituent of the binary was activated prior to connecting them together electrically. The tendency for γ -alloys to form inert films, which increases with increasing pH, has been noted previously in discussing the o.c. potential and passivation current for normal alloys. Evidently the γ -phase is partially cathodically protected by the galvanic current from the α -phase, so that the surface of the γ -phase loses its activity and forms a film. This explains the o.c.-pH behavior, since the film would cause the γ -phase to polarize to the potential of the α -phase, which is itself pH dependent. Furthermore, the stronger tendency for film formation at higher pH's would polarize the γ -potential closer to the α -phase potential more strongly with increasing pH, explaining the higher $\frac{dE}{d\text{pH}}$ values of the binary alloys compared to the normal alloys.

3. Flade Potential

In the discussion of the Flade potential (E_f^0) of the normal two-phase alloys, it was shown that the E_f^0 of the active constituent (α -phase) controlled the E_f^0 of the entire alloy. The E_f and E_f^0 values for the binary electrodes

were determined in the same manner as for the normal alloys. From the second column of Figure 21, it is seen that pH dependence of E_f predicted by the Flade equation is followed by both binary alloys. Furthermore, the E_f^0 values (0.56 and 0.57) are characteristic of the α -alloys. The binary alloys therefore exhibit normal behavior in regard to their E_f behavior.

4. Passivation Current

Passivation currents (I_p) were determined in the same manner described previously for normal alloys. A comparison of the middle column of Figure 21 with Figure 17 indicates that I_p values for binary electrodes are less than for normal alloys. This is probably a result of the tendency of the γ -alloys to form films, since the I_p value would be decreased by the loss of active surface. Since pure nickel has the strongest tendency to form films, this explains the lower I_p value of the unsaturated binary compared to the saturated binary alloy. Similar to the normal alloys, the I_p value for each type of binary, goes through a maximum with changing pH. As explained previously, this maximum

occurs because of the changing solubilities of the metal sulfates and hydroxides with changing H_2SO_4 concentration.

5. Passive Current

The passive currents for the binary electrodes were evaluated as the minimum current required to maintain passivity, just as for the normal alloys. A comparison of the fourth column of Figure 21 with Figure 18 shows no substantial difference in behavior for the artificial electrode. There is a tendency for the passive currents of the binary alloys to be higher, but this is probably a result of the difficulty in achieving the passive state. In some cases, one of the constituents would passivate and not the other. In other cases, the entire electrode was passive, but the current was five or six times too large and would not achieve a steady state. This incomplete passivity was not due to leakage currents, because activation and repassivation would ultimately yield a satisfactory passivity. The linear dependence of the passive current on pH is similar to that of the normal alloys, and is thus due to the increased solution rate of the passive film in higher acidities.

6. Galvanic Current

The galvanic current is defined here as the current flowing between the two constituents of the binary electrode

when they are electrically connected. After 15 or 20 minutes, the galvanic current reached a steady state, the current always flowing from the α -phase to the γ -phase, i.e., the major portion of the anodic dissolution was concentrated at the α constituent, and the major portion of the hydrogen evolution at the γ constituent. However, since the galvanic current density was somewhat less than the current density equivalent of the corrosion rate (65, 66), some anodic dissolution of the γ constituent and hydrogen evolution at the α constituent would be expected. In support of this, hydrogen evolution at both constituents of the binary was noted in 10,0 N H_2SO_4 .

The larger galvanic currents for the unsaturated binary electrode, compared to the saturated binary electrode, are probably caused by the greater difference in the initial o.c. potentials of the constituents of the unsaturated binary compared to the saturated binary electrode (Figure 15). The galvanic current exhibits a semi-logarithmic relation with pH similar to that of the passive current,

$$I_{\text{galvanic}} = a - b \text{ pH} .$$

Though the reactions are different (anodic dissolution versus dissolution of passive film), the hydrogen ion concentration enters both reactions in the same manner,

The hydrogen ion concentration thus shifts both reactions to the right, though the exact rate equation of each depends on the mechanism of the reaction.

VII. RECOMMENDATIONS FOR FUTURE WORK

A. Equipment and Procedure

1. Incorporate a more accurate technique, such as the interrupter method, to correct for ohmic overpotential.
2. Improve the oscillatory behavior of the electronic potentiostat according to the criteria in a recent paper on potentiostat oscillations by F. G. Will (80).
3. Incorporate a stirrer into the polarization cell to eliminate concentration polarization when it is objectionable.
4. Pre-electrolyze the solution to eliminate impurities which can be reduced or oxidized.

B. Research

1. Examine the effect of heat treatment in the composition range 5-50 at.% Ni (e.g., quench to obtain martensite in the range 10-25% nickel and γ -phase alloys in the range 25-50% nickel).
2. Continue the galvanic experiment by investigating the effect of changing the relative area of each of the phases. By combining nickel-saturated α electrodes and iron-saturated γ

electrodes of different sizes, it should be possible to compare these results with those obtained on ordinary two-phase electrodes. The additional information could aid in an understanding of the behavior of the corrosion potential and the Flade potential.

3. Investigate the anodic behavior of the Fe-Ni-Cr ternary system in the iron rich range (i.e., up to 30 at.% Ni and 30 at.% Cr).
4. Investigate the passivation current density as it is affected by
  - a) changing concentration of acid anion at constant pH
  - b) changing pH at constant concentration of acid anion
  - c) stirring
  - d) facing the electrode vertically or horizontally.
5. Examine the effect of changing the acid anion species, particularly with respect to passivity.
6. Determine Tafel slopes for
  - a) hydrogen evolution
  - b) anodic dissolution
  - c) oxygen evolution

7. Evaluate double layer capacities. An oscilloscope and square wave generator are available to set up suitable equipment (8).

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AUTOBIOGRAPHY

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