This dissertation has been
microfilmed exactly as received

69-11,622

CONDIT, Dale Osborne, 1943-
THE DISSOLUTION BEHAVIOR OF Fe-Ni ALLOYS
IN H_2SO_4 AT 25°C.

The Ohio State University, Ph.D., 1968
Engineering, metallurgy

University Microfilms, Inc., Ann Arbor, Michigan

THE DISSOLUTION BEHAVIOR OF
Fe-Ni ALLOYS IN 1N H_2SO_4 AT 25°C

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

by

Dale Osborne Condit, B. Met. Engr., M. S.

The Ohio State University
1968

Adviser
Department of Metallurgical Engineering

DEDICATION

In each of our lives we meet certain people who make life a rewarding and fulfilling adventure and who help us live up to the good image they have of us. I have known such people at this university: in its engineering college, in my department, and in the athletic department; I have known them from summer baseball programs and from high school booster clubs; I have known them in Columbus, Deerfield Beach, Denver, Doylestown, Fairborn, and Zanesville. I am proud of them, grateful for what they have done for me, and hopeful that I may someday be able to do something for them.

To these people I sincerely dedicate this dissertation.

ACKNOWLEDGEMENTS

I wish to thank my adviser, Dr. Roger W. Staehle, for his guidance, counsel, and inspiration during the course of both my research and my graduate career. His enthusiastic interest in all my endeavors is gratefully appreciated.

I also wish to thank an associate, Robert L. Cowan II, for his help during the course of my graduate study. Without the benefit of his counsel and our discussions, this dissertation might never have been completed.

The author is deeply indebted to Professors George R. St. Pierre and Gordon W. Powell whose help in the preparation of this dissertation was invaluable.

The author gratefully acknowledges the support provided by the United States Atomic Energy Commission by the award of a special fellowship in Nuclear Science and Engineering administered by the Oak Ridge Associated Universities.

The interest and support of the sponsor of this project, the Fuels and Materials Branch of the Division of Nuclear Technology of the Atomic Energy Commission, and the support of Messrs. A. vanECHO and J. M. Simmons of that organization are sincerely appreciated.

The author also wishes to acknowledge the interest and support of Mr. E. J. Hassell and the Metallurgy and Ceramics Division of the Aerospace Research Laboratories and the help of Major William E. Craven, Mr. Darrell Frank, and Mr. Jack Smith of that division.

VITA

June 24, 1943	Born - Columbus, Ohio
September, 1966	B. Met. Engr. - The Ohio State University M. S. - The Ohio State University
June, 1968 - Present	Research Metallurgical Engineer Aerospace Research Laboratories Wright-Patterson AFB, Ohio

FIELDS OF STUDY

Major Field: Metallurgical Engineering

Studies in the Corrosion of Metals and Alloys with
Emphasis on Stress Corrosion Cracking. Professor
Roger W. Staehle.

TABLE OF CONTENTS

	Page
DEDICATION	ii
ACKNOWLEDGMENTS	iii
VITA	iv
LIST OF FIGURES	vi
LIST OF TABLES	x
LIST OF PLATES	xi
SUMMARY AND CONCLUSIONS	1
INTRODUCTION TO THE PROBLEM	3
Introduction	3
Single Metal Electrodes	3
Binary and Multi-component Electrodes	5
SURVEY OF THE LITERATURE	19
Introduction	19
The Cu-Zn System	19
The Cu-Au System	22
The Stainless Steels	27
Quantitative Experimental Techniques	33
EXPERIMENTAL INVESTIGATION	40
Introduction	40
Specimen Preparation	41
The Electrolyte	44
The Polarization Cell	44
The Constant Potential Apparatus	47
The Experimental Procedure	47
RESULTS AND DISCUSSION	53
Introduction	53
Dissolution at Constant Potential	54
Anodic Polarization Behavior	88
(Fe/Ni) Ratios in Solution	93
Electron Microscopy	113
Discussion	119
APPENDIX	123
BIBLIOGRAPHY	126

LIST OF FIGURES

Figure	Page
1. Polarization Curves for Metal A and Metal B Indicating the Changes in Reaction Rates with Changes in Potential	6
2. Polarization Curves for Metal A and Metal B and for an A-B Alloy	8
3. Dissolution Model for the Surface of a 50X-50Y Alloy for the Case where $i_x > i_y$	12
4. Dissolution Model for the Surface of a 50X-50Y Alloy for the Case where $i_x \gg i_y$	13
5. Description of the Process of Noble Metal Enrichment	15
6. Micro-probe Trace for Cu-40Zn Alloy Prior to Dissolution	21
7. Micro-probe Trace for Cu-40Zn Alloy After Dissolution	21
8. X-ray Diffraction Patterns for Cu-10Au Foil for Increasing Amounts of Dissolution in 1N H_2SO_4 ...	23
9. X-ray Diffraction Patterns for Cu-10Au Foil for Increasing Amounts of Dissolution in Buffered 1N NaCl	23
10. Concentration Gradient in Cu-10Au Alloy Foil	25
11. Micro-probe Traces for Cu-10Au Foils After Dissolution	28
12. Open Circuit Potential versus Time Curves for 18-8 and 16-20 Stainless Steels	29
13. Open Circuit Potential versus Time Curves for Various Stainless Steels	29
14. Schematic of Relation Between Time to Fracture and Noble Component Concentration and Between Open Circuit Potential and Time for Active- Noble Alloys	31

List of Figures (continued)

Figure	Page
15. Effect of Ni on Time to Fracture for Fe-20Cr Alloys	32
16. Comparative Sensitivities of Neutron-Activation and Photo-colorimetric Analyses	35
17. The Method of Analysis Used in Atomic Absorption Analysis	38
18. Phase Diagram for Fe-Cr-Ni Indicating the Fe-Ni Alloys Investigated	42
19. The Specimen Mount with Specimen	43
20. The Polarization Cell	45
21. Schematic of the Potentiostatic Apparatus	48
22. Dissolution Potentials for the Low Nickel Alloys Investigated	50
23. Dissolution Potentials for the Intermediate Nickel Alloys Investigated	51
24. Concentration-time Behavior for Pure Fe	55
25. Concentration-time Behavior for Fe in Fe-5Ni	57
26. Concentration-time Behavior for Ni in Fe-5Ni	59
27. Concentration-time Behavior for Fe in Fe-10Ni	61
28. Concentration-time Behavior for Ni in Fe-10Ni	63
29. Concentration-time Behavior for Fe in Fe-20Ni	65
30. Concentration-time Behavior for Ni in Fe-20Ni	67
31. Concentration-time Behavior for Fe in Fe-45Ni	69
32. Concentration-time Behavior for Ni in Fe-45Ni	71
33. Concentration-time Behavior for Fe in Fe-65Ni	73
34. Concentration-time Behavior for Ni in Fe-65Ni	75
35. Concentration-time Behavior for Pure Ni	77

List of Figures (continued)

Figure	Page
36. Total Anodic Polarization Curves Determined for the Weight Changes for the Alloys Investigated with Corrosion Current i_{corr} Indicated by the Intersection with the Corrosion Potential E_{corr} ...	89
37. Difference Between Polarization Curves Measured Coulometrically and by Weight Change	91
38. The Phase Diagram and Corresponding Lattice Parameters for the Fe-Ni Binary System	94
39. Calculated (Fe/Ni) Ratios in Solution as a Function of Time for Fe-5Ni	96
40. Calculated (Fe/Ni) Ratios in Solution as a Function of Time for Fe-10Ni	98
41. Calculated (Fe/Ni) Ratios in Solution as a Function of Time for Fe-20Ni	100
42. Calculated (Fe/Ni) Ratios in Solution as a Function of Time for Fe-45Ni	102
43. Calculated (Fe/Ni) Ratios in Solution as a Function of Time for Fe-65Ni	104
44. Relative Difference Between the Calculated (Fe/Ni) Ratio in Solution R_C and the Alloy Ratio R_A versus Potential for Fe-5Ni	106
45. Relative Difference Between the Calculated (Fe/Ni) Ratio in Solution R_C and the Alloy Ratio R_A versus Potential for Fe-10Ni	107
46. Relative Difference Between the Calculated (Fe/Ni) Ratio in Solution R_C and the Alloy Ratio R_A versus Potential for Fe-20Ni	108
47. Relative Difference Between the Calculated (Fe/Ni) Ratio in Solution R_C and the Alloy Ratio R_A versus Potential for Fe-45Ni	109
48. Relative Difference Between the Calculated (Fe/Ni) Ratio in Solution R_C and the Alloy Ratio R_A versus Potential for Fe-65Ni	110

List of Figures (continued)

Figure	Page
49. Layers of Pure Fe or Pure Ni Remaining on the Surface of an Fe-20Ni Alloy as a Function of the Amount of Charge Passed for Given (Fe/Ni) Ratios in Solution	112
50. The Zero-order Intrinsic Rate Constants for Fe and Ni as a Function of the Ni Composition at 0mV(SHE)	120
51. The Normalized Values for the Zero-order Intrinsic Rate Constants for Fe and Ni as a Function of Ni Composition at 0mV(SHE)	122

LIST OF TABLES

Table	Page
1. Sensitivity of neutron-activation analysis for various elements	37
2. Sensitivity of atomic absorption analysis for various elements	37
3. Values of slope and the intercept at $t = 1$ second for the log-log, concentration-time curves for Alloy 1, pure Fe	79
4. Values of slope and the intercept at $t = 1$ second for the log-log, concentration-time curves for Alloy 2, Fe-5Ni	80
5. Values of slope and the intercept at $t = 1$ second for the log-log, concentration-time curves for Alloy 3, Fe-10Ni	81
6. Values of slope and the intercept at $t = 1$ second for the log-log, concentration-time curves for Alloy 4, Fe-20Ni	82
7. Values of slope and the intercept at $t = 1$ second for the log-log, concentration-time curves for Alloy 6, Fe-45Ni	83
8. Values of slope and the intercept at $t = 1$ second for the log-log, concentration-time curves for Alloy 8, Fe-65Ni	84
9. Values of slope and the intercept at $t = 1$ second for the log-log, concentration-time curves for Alloy 12, pure Ni	85
10. Values of slope and the intercept at $c = 1\text{ppm}$ and at $c = 1/3\text{ppb}$ for a semi-log, potential-concentration plot for alloys investigated	87
11. Corrosion currents and Tafel slopes for weight change data for alloys investigated	92

LIST OF PLATES

Plate	Page
I. Replica Electron Photo-micrographs for Fe-5Ni Dissolved at $\eta = +46\text{mV}$ for the Times Indicated	114
II. Replica Electron Photo-micrographs for Fe-5Ni Dissolved at $\eta = +216\text{mV}$ for the Times Indicated ...	115
III. Replica Electron Photo-micrographs for Fe-20Ni Dissolved at $\eta = +32\text{mV}$ for the Times Indicated ...	116
IV. Replica Electron Photo-micrographs for Fe-20Ni Dissolved at $\eta = +210\text{mV}$ for the Times Indicated ...	117
A-I. Microstructures for Fe, Fe-5Ni, Fe-10Ni and Fe-20Ni	124
A-II. Microstructures for Fe-45Ni, Fe-65Ni and Ni	125

SUMMARY AND CONCLUSIONS

The dissolution characteristics of Fe, Ni, and five Fe-Ni binary alloys were investigated in 1N H_2SO_4 at 25°C. The specimens were dissolved at constant potential. Atomic absorption analysis was used to analyze the solutions to determine the Fe and Ni concentrations. From these analyses the dissolution rates of Fe and Ni were determined. Electron microscopy was conducted on two alloys to determine the changes in surface topology as a function of the rate and of the magnitude of dissolution.

The results of the investigation indicate that the atomic absorption analysis technique is a useful tool in determining the dissolution characteristics of Fe-Ni binary alloys, yielding results that are quite reproducible. The technique should prove increasingly useful in investigating the corrosion behavior of metals and alloys.

The dissolution behavior of Fe-Ni binary alloys is a logarithmic function of time and of the form $c = at^n$ where c is the concentration of either Fe or Ni in solution, t is the time, n is the slope of the logarithmic concentration-time curve, and a is the intercept at $t = 1$ second. The slope of all the concentration-time curves is approximately 1.0 except those for pure Ni whose slopes are about 0.6.

The potentials for Fe and Ni in a given alloy where the surface is assumed to be undisturbed (determined for 1/3 ppb concentration) increase with increasing Ni concentration. These potentials are always

greater than their equilibrium values $E_{\text{Fe}}^{\circ} = -440\text{mV(SHE)}$ and $E_{\text{Ni}}^{\circ} = -250\text{mV(SHE)}$.

The anodic polarization curves were determined from the weight changes that occurred during the dissolution process. The Tafel slopes for the alloys are all approximately 2.0×10^{-2} V. and are in reasonable agreement with theoretically determined values. The corrosion currents show a large decrease as the Ni concentration is increased from 20 at. % to 45 at. %. X-ray investigations indicate that a structure change from body-centered cubic to face-centered cubic occurs in this region. Therefore, it might be suspected that the corrosion behavior of Fe-Ni binary alloys is a structure sensitive property.

Using zero-order rate constants and (Fe/Ni) ratios calculated from the dissolution rate equations, the nickel enrichment phenomenon is expected to occur at high dissolution potentials and at nickel concentrations between 5 at. % and 50 at. %. X-ray examinations of the surfaces of the specimens before and after dissolution give no indication of the occurrence of enrichment, mainly because of the inherent inaccuracy of the technique at the low angles necessary to study the surface. Replicas of the surfaces of two of the alloys indicate that dissolution involves the accumulation of atomic ledges into larger steps. The faces of these steps are $\{110\}$ planes which would be expected in body-centered cubic alloys.

INTRODUCTION TO THE PROBLEM

Introduction

The purpose of this investigation was to study the active dissolution behavior of binary Fe-Ni alloy with the ultimate aim of determining relative dissolution rates of Fe and Ni and the residual composition of the alloy surface. The incentive for such a study was the intense current interest in passivity and stress corrosion cracking, which depend for their peculiar behavior on the composition of the surface of the alloy.

The present investigation was a scoping study of a system that had not been previously studied and in which the individual electrode potentials of the binary system were both more negative than the H^+/H_2 equilibrium potential. The results of any such investigation do not reflect the equilibrium states of the system but rather the rates of the individual components' dissolution processes. In order to determine what changes in dissolution behavior can occur when two metals are alloyed, it is important to first understand the dissolution behavior of a pure metal.

Single Metal Electrodes

The standard equilibrium potential E_0 of a pure metal is defined as the potential where metal and metal ions of unit activity are in equilibrium. This equilibrium can be represented by the following equation

for which the Nernst equation gives the potential

$$E_o = E_o^o - \frac{RT}{zF} \ln \left[\frac{a_{M^{+z}}}{a_M} \right] \quad (2)$$

This equation establishes the standard equilibrium potential for the metal, E_o being the equilibrium potential at any given activity of metal ions. As Tomashov (1) points out, the equilibrium thus established is a dynamic equilibrium, the transfer of charges not ceasing but continuing at equal rates, forward and reverse. The rate of charge transfer at which the reversible equilibrium is established is given by the exchange current as shown by Vetter (2) to be

$$\begin{aligned} i_o = \hat{i} &= zF k_+ c_r \exp(-\Delta\bar{G}^*/RT) \\ &= \hat{i} = - zF k_- c_o \exp(-\Delta\bar{G}^*/RT) \end{aligned} \quad (3)$$

where

$$k_+ c_r \exp(-\Delta\bar{G}^*/RT)$$

and

$$k_- c_o \exp(-\Delta\bar{G}^*/RT)$$

represent the number of surface atoms that are dissolving and the number of surface sites available for discharge, respectively; and zF is the conversion factor to current.

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

$$\begin{aligned}\hat{i} &= zF k_+ c_r \exp - [(\Delta \bar{G}^* - \alpha zF \eta)/RT] \\ &= i_o \exp(\alpha zF \eta/RT)\end{aligned}\quad (4)$$

and

$$\begin{aligned}\hat{i} &= - zF k_- c_o \exp [-\{\Delta \bar{G}^* + (1 - \alpha) zF \eta\}/RT] \\ &= - i_o \exp [-(1 - \alpha) zF \eta/RT]\end{aligned}\quad (5)$$

The net current for a given overpotential η is thus

$$i_{\text{net}} = \hat{i} - \hat{i} \quad (6)$$

which for overpotentials of 150mV or more in either the positive (anodic) direction or the negative (cathodic) direction can be approximated by the current for that direction only.

Binary and Multi-component Electrodes

The determination of the electrochemical behavior of a binary or multi-component alloy presents many problems among which are:

- (1) What is the state of equilibrium for each component in the alloy, i.e., what is E_o for each component at the surface?
- (2) Knowing the individual behavior of the components of an alloy, what will be their behavior in an alloy?
- (3) How does the dissolution behavior of these components change as the dissolution proceeds?

Figure 1 illustrates the changes in electrode kinetics when two metals are connected together in solution. The dissolution rate of B is greatly decreased (this assumes the potentials of both the noble metal B and the active metal A are below the H^+/H_2 equilibrium potential for this solution) and the rate of hydrogen evolution is greatly

Figure 1. Polarization Curves for Metal A and Metal B Indicating the Changes in Reaction Rates with Changes in Potential (10).

enhanced. In contrast, the dissolution rate of A is enhanced; whereas, the rate of hydrogen evolution on A is decreased. Considering this as an alloy system as in Figure 2, the changes in the relative rates of dissolution of A and B and of the hydrogen evolution are readily observed. This, of course, assumes that these individual polarization curves can be added in proportion to the components' concentrations in the alloy.

The Nernst equation might be employed to define the equilibrium potential of each component as Pickering (3) has done

$$E_o = E_o^\circ + \frac{RT}{zF} \ln \left[\frac{a_{M_A}^{+z}}{a_{M_A}(M_A-M_B)} \right] \quad (7)$$

which in a solution of constant M_A^{+z} the potential becomes

$$E_o = E_o^\circ - \frac{RT}{zF} \ln \left[a_{M_A}(M_A-M_B) \right] \quad (8)$$

where $a_{M_A}(M_A-M_B)$ is the activity of M_A in an M_A-M_B alloy. This equation also assumes noble metals have positive electrode potentials and active metals, negative ones.

Furthermore, ideal mixing might be assumed as Scully (4) has done using the equation that

$$i_{\text{alloy}} = i_A f_A + i_B f_B \quad (9)$$

from which it might be reasoned

$$E_{\text{corr, alloy}} = f_A E_{\text{corr, A}} + f_B E_{\text{corr, B}} \quad (10)$$

where f_A and f_B are the fractions of A and B in a binary alloy. These equations also assume that there is no effect from the hydrogen evolution reaction.

Despite the fact that the previous expressions have a sound

Figure 2. Polarization Curves for Metal A and Metal B and for an A-B Alloy.

theoretical basis, they represent an oversimplified picture of the system and cannot accurately describe the behavior of a binary or multi-component system. The ultimate reason for this is that the dissolution behavior of an alloy is more complex and much less understood than that for a pure metal. This complexity might be emphasized by considering the manner in which a pure metal is believed to dissolve. The total change in free energy for the dissolution of a pure metal may be determined by summing the energies of the individual steps in the dissolution process. These steps are shown below.

Calculations for the total change in energy made from this model are in excellent agreement with experimental observations. For a pure metal the energies of these steps remain the same as the dissolution proceeds; therefore, the potential of the system would be expected to remain the same. However, this is not so for an alloy system. As dissolution proceeds in the alloy, the neighbors surrounding given atoms are likely to change. As a result, the energy to remove these atoms from their neighbors will change. This change in the value of the energy to remove an atom from the lattice will have three main effects which are

- (1) changes in the potential of the alloy,
- (2) alteration of the current flowing in the system, and
- (3) changes in the relative amounts of the components dissolving.

These last two deviations would also be suggested by equation (3)

where the activation energy $\Delta\bar{G}^*$ is an expression of the barrier to dissolution for an atom on the surface. As this energy is increased or decreased, the number of atoms of a given component that dissolve will change. If the dissolution of the components from an alloy occurs at different rates, then the value of the available atoms of a given component on the surface will change, resulting in a change in the current. Furthermore, changes in η will also result in the alteration of the value for the current and possibly the relative rates of dissolution of the components from an alloy. The dissolution of an alloy is, therefore, a complex series of steps, each depending on the previous step.

Considering the difference in dissolution rates and their effects on the character of a dissolving alloy, three particular cases, in general, should be considered:

- (1) when the dissolution rates of X and Y are approximately the same ($i_x \cong i_y$),
- (2) when the dissolution rate of X is greater than the dissolution rate of Y ($i_x > i_y$), and
- (3) when the dissolution rate of X is much greater than the dissolution rate of Y ($i_x \gg i_y$).

In these examples X may be either the more noble component or the more active component in the alloy. In each of these cases, it will also be assumed that the dissolving alloy is a 50X-50Y alloy, since the relative amounts of X and Y will also have an effect on the changes that occur in the alloy.

For the case when $i_x \cong i_y$ the surface of the 50X-50Y alloy would

remain the same, as the number of X atoms dissolving would be the same as the number of Y atoms dissolving. However, if the alloy were rich in X, these conditions of dissolution would favor the enrichment of X; whereas, if the alloy were rich in Y, dissolution under this criterion would favor the enrichment of Y.

Figure 3 illustrates the surface changes occurring when $i_X > i_Y$. The surface in this case becomes enriched in Y to a given concentration; then the rate at which the X atoms dissolve is dependent on the rate at which Y atoms dissolve. Because of this the surface of the alloy under these conditions does not become greatly enriched in Y.

Figure 4 illustrates the changes that would occur on the surface of the alloy where $i_X \gg i_Y$. In this figure the X atoms leave the surface very rapidly, leaving ledges of Y behind and, eventually, a fairly thick surface of pure Y. While this pure Y surface is relatively thin, surface diffusion by exchange of atoms just below and along the surface accounts for the continued dissolution of X. Eventually, however, the layer of pure Y becomes thick enough that volume diffusion becomes the predominant mode for atoms of X to reach the surface; and as the dissolution proceeds, it becomes exceedingly difficult for atoms of X to reach the surface by volume diffusion.

As pointed out previously, one of the primary reasons for studying the dissolution behavior of alloys is the current interest in stress corrosion cracking. Staehle (5) has proposed a mechanism for stress corrosion which is the first attempt to explain the effect of a noble component in the stress corrosion behavior of an alloy, specifically the role of Ni in the stainless steels. He suggests that

Figure 3. Dissolution Model for the Surface of a 50X-50Y Alloy for the Case where $i_x > i_y$.

Figure 4. Dissolution Model for the Surface of a 50X-50Y Alloy for the Case where $i_x \gg i_y$.

the phenomenon is a four-step process:

- (1) The surface of an alloy is enriched in its noble component by selective dissolution of the more active components,
- (2) the noble surface is disrupted when dislocations emerge creating a slip step and exposing alloy surface which is of a different composition than the surface,
- (3) dissolution at these slip step sites resulting in stress raising effects, and
- (4) subsequent fracture of the alloy.

The first step, therefore, is an essential one. Staehle illustrates the manner in which this enrichment might ideally occur and the resulting changes in electrochemical properties in Figure 5. Furthermore, according to Pickering (3,7), if this selective dissolution occurs, it can be expected to occur under the following conditions:

- (1) The difference between the single electrode potential of the component metals should be several times greater than RT/F ,
- (2) the potential of the dissolving alloy should be higher than that of the more active component, and
- (3) the potential of the dissolving alloy should be significantly lower than the more noble component.

In multi-component alloy systems, preferential dissolution of the more active components is likely to occur leaving behind the more noble components, especially if the single electrode potentials of these noble components lie close to or above the equilibrium hydrogen

Figure 5. Description of the Process of Noble Metal Enrichment (5).

potential for the system. If this selective dissolution does occur, there are three mechanisms by which it can occur:

- (1) Both metals dissolve and the more noble metal re-deposits on the surface,
- (2) the active metal dissolves while the noble metal atoms remain on the surface and the active metal atoms reach the surface by volume diffusion, or
- (3) the more active metal dissolves and the noble metal atoms redistribute on the surface by surface diffusion.

The problem as stated by Pickering is quite simple but the observable manifestation of the enrichment phenomenon may actually indicate that something else is occurring on the surface of the alloy.

Changes in the potential of the alloy could indicate

- (1) enrichment of a component on the alloy surface,
- (2) a film either being built or destroyed on the surface, and
- (3) a change in the cathodic kinetics.

A more sophisticated means of determining which of these three processes is acting at the alloy surface is required. First, it is essential to determine just how the alloy dissolves at given potentials and from this estimate what is occurring at the surface. However, in analyzing any data on the dissolution behavior of metals and alloys it is important to know how many layers of surface are dissolved for a given current flow or for a given concentration of ions in solution. With this in mind the objective of this investigation was to study the dissolution characteristics of the Fe-Ni binary system. This particular

system was chosen since it is of importance in the study of stress corrosion cracking in the stainless steels; and, furthermore, the study will provide a basis for further study of the dissolution of binary alloys.

SURVEY OF THE LITERATURE

Introduction

In general, most studies concerned with the dissolution of alloys and with the enrichment of noble species on the surface of alloys have been conducted with regard to dezincification and stress corrosion cracking phenomena. However, an excellent study of the dissolution behavior of the Cu-Au alloy system has also been done by Pickering(3,7).

The Cu-Zn System

The earliest evidence of the "enrichment" phenomenon was given by Bengough, et.al. (8,9), in which the phenomenon of dezincification of brass piping in steam condensers was investigated.

In his work with the Cu-Zn alloys, Pickering uses a ring-disc electrode system. The disc electrode is the alloy to be dissolved and the ring electrode is used to measure currents caused by any re-deposition of ions at the ring. He finds that at potentials of dissolution of +257mV to +387mV(SHE) both Cu and Zn dissolve. He obtains 100 per cent recovery of Cu at the ring electrode and concludes that no redeposition is occurring at the disc electrode. The potential of dissolution is important. In the experiments this potential is such that Cu would be expected to dissolve; and, therefore, no re-deposition should be expected. The Cu^{++} ion concentration in the vicinity of the disc electrode would have to exceed 10^{-3} for $E_{\text{diss}} = +257\text{mV(SHE)}$ and $10^{1.5}$ for $E_{\text{diss}} = +387\text{mV(SHE)}$ for redeposition to occur. Furthermore, dezincification rarely occurs in rapidly flowing

solutions (4). Thus, to study any enrichment mechanism with respect to dezincification, environments in which this phenomenon occurs would have to be duplicated.

Sugawara and Ebiko (10) conducted studies similar to Pickering's but used several potentials and electron micro-probe traces in their attempt to determine the mechanism of dezincification, whether it is bulk diffusion or an ionization-redeposition mechanism. The results of the micro-probe work on Muntz metal (Cu-40Zn) are shown in Figures 6 and 7. These figures indicate that only the zinc content in the β -phase is decreased; or, in other words, the only dezincification that occurs is in the β -phase. In the beta brass, after polishing and etching, three distinct regions appear: a yellow matrix; a reddish orange middle layer; and a red-colored, perfectly dezincified layer. The zinc detected in Figure 7 after dezincification was detected in the middle layer and not in the dezincified layer. Line analysis with the micro-probe indicated no concentration gradient from the matrix to the dezincified layer; therefore, Sugawara and Ebiko concluded that volume diffusion was not the mechanism for dezincification. They proposed that, since the grain boundary concentration of zinc is higher than for the matrix in brass and since the grain boundary is more chemically active, the grain boundary is preferentially attacked in the beginning of the process. Subsequently, the corrosive solution will penetrate into the interior of the brass along the corroded grain boundaries and attack the zinc-rich β -phase of the brass. Furthermore, accumulation of Cu ions inside the brass would allow for their redeposition.

Figure 6. Micro-probe Trace for Cu-40Zn Alloy Prior to Dissolution (10).

Figure 7. Micro-probe Trace for Cu-40Zn Alloy After Dissolution (10).

The Cu-Au System

In his experiments with Cu-Au alloys Pickering uses the same rotating, ring-disc electrode as in the studies with Cu-Zn alloys to determine whether Au is ionized from a Cu-10Au alloy.

For Cu-10Au alloys dissolving at potentials ranging from +500mV to +900mV(SHE), no appreciable change in current flow occurs at the ring electrode which is set at +1100mV(SHE). This indicates that negligible amounts of Au are ionized; and, therefore, the accumulation of Au on the surface must be occurring either by volume diffusion in the bulk or by surface diffusion. To test which of these mechanisms predominates, Pickering uses X-ray diffraction examinations of foils of Cu-10Au. Figures 8 and 9 show the data for different degrees of dissolution for the Cu-10Au alloy in 1N H_2SO_4 and buffered 1N NaCl. In "c" of each figure a region of diffracted intensity between the {111} lines for Cu-10Au and pure Au indicates the presence of a gold-rich alloy. For 1N H_2SO_4 the passage of 19.2 Coulombs/cm² (approximately 6×10^4 atom layers, 3000 atom layers/Coulomb) is sufficient to enrich the alloy to pure gold; whereas, with the buffered NaCl only a gold-rich alloy is formed with this passage of charge. The decrease in the intensity of the original alloy peak is indicative of the change in composition that is occurring. As more Cu is selectively dissolved from the alloy, the intensity of the Au lines increases since the depth of the gold zone is increasing. Metallographic examination shows a rather rich surface layer of Au and an unreacted Cu-10Au alloy layer. The depth of the gold-rich layer is 8 microns in close agreement with the theoretical value of 7 microns determined using Faraday's equation.

Figure 8. X-ray Diffraction Patterns for Cu-10Au Foil for Increasing Amounts of Dissolution (no dissolution at top, 19 Coul/cm² at bottom) in 1N H₂SO₄ (3).

Figure 9. X-ray Diffraction Patterns for Cu-10Au Foil for Increasing Amounts of Dissolution (no dissolution at top, 19 Coul/cm² at bottom) in Buffered 1N NaCl (3).

The case for bulk diffusion by di-vacancy motion in Cu-10Au as proposed by Pickering is not, however, unequivocally substantiated by these findings. Two parameters from the X-ray data can be expected to support a bulk diffusion mechanism, both of which would indicate existence of a composition gradient from the gold-rich surface to the Cu-10Au bulk on the interior. They are (1) diffracted intensity and (2) line broadening. The presence of new peaks of diffracted intensity would indicate the presence of a new phase, while increases in present peaks would indicate increasing amounts of the existing phase or phases. Line broadening could indicate a change in lattice parameter over the effective depth of penetration of the X-ray beam, provided that the broadening was asymmetrical. However, line broadening may also be manifested by internal stress on the lattice or by deformation, changes in crystalline particle size, or high temperatures. The latter two causes may be excluded as reasons for line broadening under the present conditions.

Pickering believes that the relative changes in the diffracted intensity, see Figures 8 and 9, are evidence of the change in composition and, thus, of bulk diffusion. If bulk diffusion does occur and Pickering's metallographic evidence is taken into account, then a composition gradient would exist in the metal similar to that shown in Figure 10. If the effective depth of penetration of the X-rays is sufficient, then intensities of the diffracted beam would indicate the presence of the alloy and the gold-rich regions, while line broadening could indicate the existing change in lattice parameter. However, the effective depth of penetration of the X-rays in Pickering's

Figure 10. Concentration Gradient in Cu-10Au Alloy Foil.

experiments is only about $3000\text{\AA}$ which is not, after $19.2\text{ Coulombs/cm}^2$ have been passed and a pure gold zone of 8 microns exists, sufficient to indicate the presence of the bulk alloy, or any gold-rich alloy, which is deeper than 8 microns below the surface. Furthermore, no line broadening could be caused by lattice parameter changes since to a depth of about $3000\text{\AA}$, and even deeper, pure gold is the only existing phase.

The only way Pickering's data can be interpreted is that there may be locations on the surface that are preferentially dissolved, as an alloy, more rapidly than others which means diffracted intensities for the alloy as well as those for pure gold would appear and also compositions in between. The line broadening, as previously stated, could be caused by a change in lattice parameter over the effective depth of X-ray penetration; but because of the selective dissolution of Cu out of the matrix, line broadening could also be an indication of internal stresses within the matrix. This is the most probable explanation for the broadening observed in Pickering's diffraction data.

Furthermore, it should be noted that the potential for dissolution of the Cu-10Au alloy that Pickering uses is below that for the dissolution of Au in the same solution; therefore, it would be unreasonable to expect Au to dissolve to any great extent. Under these conditions of aqueous corrosion at a $\text{pH} = 1$, the concentration of Au at the potential of dissolution, $+500\text{mV}$ to $+900\text{mV(SHE)}$, would only be of the order of 10^{-30} to 10^{-50} according to thermodynamic data. These

concentrations would be unmeasurable using Pickering's technique, even if Au were dissolving.

The only reasonable means to determine whether volume diffusion occurs is to make an electron micro-probe trace of the sample to observe whether any variations in composition occur in the specimen. Pickering (11) has done this and has obtained favorable results as shown in Figure 11.

The Stainless Steels

Experimental work conducted by Barnartt and van Rooyan (12), Hoar and Hines (13,14), and Staehle (15) in the Fe-Cr-Ni system, specifically the stainless steels, indicates that the open circuit potential of these alloys become more noble with time. This phenomenon is illustrated in Figures 12 and 13. They suggest that the increase in this potential is the result of preferential dissolution of Fe and Cr from the surface of the alloy, leaving a nickel-rich surface which controls the anodic kinetics. They also observed that hydrogen evolution decreases to almost zero during the change in potential, indicating an appreciable decrease in the rate of corrosion on the surface. Hoar and Hines also suggest that this phenomenon might be due to the presence of a passive layer on the surface of the alloy. As pointed out previously, the change could also be the result of changes in the cathodic kinetics.

These same investigators conducted experiments on alloy subjected to stress. The results were very similar to those for alloys not subjected to stress. The maximum in the curves occurs at shorter times indicating that the effect of the stress is to accelerate the process

Figure 11. Micro-probe Traces for Cu-10Au Foils After Dissolution (11).

Figure 12. Open Circuit Potential versus Time Curves for 18-8 and 16-20 Stainless Steels (12).

Figure 13. Open Circuit Potential versus Time Curves for Various Stainless Steels (13).

which is occurring at the surface to cause the increase in nobility.

Bond (16) has pointed out that the addition of 1 - 3 atomic per cent Cu, Co, or Ni to Fe-Cr alloys increases their susceptibility to stress corrosion cracking. This phenomenon might be rationalized by Staehle's theory since the open circuit potentials of Cu, Co, and Ni are all more noble than the potentials for Fe and Cr. Staehle suggests that the changes in the corrosion potential is indicative of the magnitude of the change in composition that occurs on the surface of the alloy; and also this change in composition indicates the relative susceptibility of the alloy to stress corrosion cracking. These ideas are illustrated in Figure 14. In this figure the center section of the phase diagram represents the composition of noble component where the possibility of achieving a highly noble surface is great and also where the difference in composition between the surface and the bulk is high. Therefore, in this portion of the diagram an alloy, should stress be applied and slip steps emerge at the surface, would be most susceptible to stress corrosion cracking; that is, the time-to-cracking for this alloy would be a minimum, as indicated in the figure. On either side of this portion of the diagram conditions are less favorable, due to the decreased possibility of noble metal enrichment occurring or to the convergence of the surface and the bulk compositions. These postulations are reasonable and the data of Copson (17) shown in Figure 15 lend credence to their validity.

Experimental evidence has indicated that enriched surfaces may be found in certain systems while in others the evidence may indicate that some other phenomenon is occurring on the surface causing the

Figure 14. Schematic of Relation Between Time to Fracture and Noble Component Concentration and Between Open Circuit Potential and Time for Active-Noble Alloys (6).

Figure 15. Effect of Ni on Time to Fracture for Fe-20Cr Alloys (17).

potential to change. In these systems it is necessary to find a more quantitative means of determining unequivocally what the mode of dissolution is. If this is accomplished, more insight into the stress corrosion cracking problem will be achieved.

Quantitative Experimental Techniques

Two recently refined experimental techniques may prove quite useful in a direct approach to studying the dissolution behavior of metals and alloys: neutron-activation analysis and atomic absorption analysis.

Neutron-activation analysis is a highly specific and highly sensitive technique which takes advantage of the fact that radiated elements emit gamma radiation that can be identified for given elements. The process of neutron-activation essentially involves two steps: an activation step in which the sample is exposed to a beam of neutrons and a measurement step in which the induced radioactivity is measured as a function of energy. The energy of the gamma radiation is the means of identifying the particular element while the activity, or intensity, of the radiation is a measure of the quantity of that element present.

The specific activity of a given radiation could be measured directly; but because the nuclear constants and parameters involved in making this calculation are not known precisely, a comparative technique is used. Gamma rays, because of their distinct energies, are resolved for both the sample under investigation and a standard of known mass using the technique of multi-channel scintillation gamma spectroscopy (18,19). Thus, all nuclear constants and parameters being equal, the concentration of the element under investigation

can be determined using the simple proportion that is shown below

$$\frac{a_s \text{ (sample unknown)}}{a_s \text{ (standard)}} = \frac{m_{\text{sample}}}{m_{\text{standard}}} \quad (13)$$

The concentration can be measured for most elements to 10^{-11} to 10^{-16} grams (20) with an accuracy of about two per cent of the actual concentration (21).

Neutron-activation analysis provides a very sensitive means of measuring trace elements in any system. The dissolution behavior of Fe-Cr-Ni alloys could be easily determined using this technique since three readily detectable radio-isotopes are produced in this system by neutron bombardment: Fe^{59} , Cr^{51} , and Ni^{65} .

In experiments with Ti alloys containing 0.1 to 0.2 atomic per cent Pd, Tomashov (19) used neutron-activation analysis to determine whether Pd enriched on the surface of the alloy. Concerned with the mechanism of how additions of small amounts of Pd exert such a great influence on the cathodic process and thus the dissolution characteristics, these investigators found that after treatment in boiling HCl that about 20 per cent of the surface was covered with Pd. Treatment in boiling 5 per cent HCl for 30 minutes increased the surface concentration by at least 75 times.

Dembrovshiy and Florianovich (22) have conducted experiments using neutron-activation analysis to determine the dissolution rates of Fe-Cr alloys and have compared the results with those using the photo-colorimetric method. Figure 16 illustrates the data obtained by both methods, values being converted to current densities for plotting, at various potentials for an Fe-4Cr alloy in 0.1N H_2SO_4 solution. The

Figure 16. Comparative Sensitivities of Neutron-Activation and Photo-colorimetric Analyses (22).

figure shows both methods give comparable results, the scatter being attributed to the non-reproducibility of the results of the electrochemical investigations. They concluded that the method of neutron-activation was both successful and accurate. Furthermore, the proximity of the results of both techniques indicated the absence of any specific influence of neutron bombardment on the dissolution characteristics.

These same authors have calculated the sensitivity of a radiochemical analysis on several Fe-base alloys containing such components as Cr, Mn, Co, Ni, and Mo. These results are shown in Table 1.

The other quantitative means of determining minutely small concentrations of elemental materials is atomic absorption analysis. In this technique of analysis light energy is radiated from an emitter source made of the same metal that is being detected in the sample under investigation. This beam is then focused on the sample, which has been vaporized; and the beam is attenuated because of the absorption by the metal vapor being studied. The amount of attenuation is proportional to the concentration of the element in the vaporized sample. The fact that the atoms being investigated will only absorb radiation of certain discrete wavelengths, wavelengths corresponding to its own excited states, and that unexcited atoms of the element in vapor are capable of absorption indicate why this technique also has high sensitivity and specificity. Figure 17 illustrates how the atomic absorption analysis is accomplished. The use of the double-beam atomic absorption spectrometer also permits comparative measure of the test

Recorded Radio-isotope	Radio-isotope Half-life, $t_{1/2}$	$t_{irr}/t_{1/2}$	Sensitivity q , gm.
Cr ⁵¹	27.8d	0.1	2.4×10^{-10}
Fe ⁵⁹	45.1d	0.1	2.5×10^{-7}
Mn ⁵⁶	2.6h	5.0	3.0×10^{-12}
Co ⁶⁰	5.3y	0.001	4.0×10^{-10}
Ni ⁶⁵	2.6h	5.0	2.0×10^{-8}
Mo ⁹⁹	2.8d	1.0	1.0×10^{-11}

Table 1. Sensitivity of neutron-activation analysis for various elements in a neutron flux of $10^{13}n/cm^2 \cdot sec$ for the indicated irradiation time (22).

Element	Sensitivity
Be	100
Ca	0.1
Cr	0.05
Co	0.2
Cu	0.1
Au	0.3
Fe	0.1
Mg	0.01
Ni	0.15
Pt	0.7
Ag	0.05
Zn	0.03

Table 2. Sensitivity of atomic absorption analysis for various elements, in parts per million concentration for 1% absorption (23).

Hollow-cathode lamp emits this spectrum...

Sample absorbs only at the resonance line...

Spectrum emitted from lamp looks like this after resonant absorption in the sample...

Monochromator blocks out all but a band of wavelengths around the best resonance line...

Result is this diminished resonance line which goes to the photodetector.

Figure 17. The Method of Analysis Used in Atomic Absorption Analysis (23).

beam versus the reference beam, thus allowing very accurate measure of the metal concentration.

Atomic absorption analysis has been shown to be equally as sensitive as neutron-activation analysis as indicated in Table 2.

The methods of neutron-activation analysis and atomic absorption analysis are both ideal means of investigating the dissolution characteristics of metals and alloys. These techniques would be especially useful in the Fe-Cr-Ni system since their sensitivity to these elements is never greater than 1.5×10^{-1} ppm, as indicated by Tables 1 and 2. Both the neutron-activation and atomic absorption techniques seem ideally suited to aid in the investigation of the dissolution behavior of binary alloys, especially those containing Fe, Cr, and Ni. However, because of the need for standard samples of known, and in some cases comparable, weight of the samples being investigated, the neutron-activation analysis is sometimes cumbersome. Furthermore, the presence of even the smallest amounts of sodium can lead to spurious results in this technique, especially when analyzing for very small quantities of unknown. The atomic absorption technique does not have these drawbacks and, despite its somewhat lower sensitivity, seems more suited for dissolution studies of Fe-Ni binary alloys in aqueous media.

EXPERIMENTAL INVESTIGATION

Introduction

In order to determine the dissolution behavior of Fe-Ni binary alloys and the relative concentration of Fe and Ni on the surface of these alloys after dissolution, the concentrations of Fe and Ni were measured and the residual Fe and Ni on the surface calculated. For this investigation pure Fe, pure Ni, and five Fe-Ni binary alloys were electrochemically dissolved at various potentials. The solutions in which the alloys were dissolved were analyzed using atomic absorption analysis. From this data the surface concentration of each component was deduced. X-ray studies, replica electron microscopy, and optical metallography were also conducted in the investigation.

The electrochemical portion of the experiment involved dissolution of the alloys in the Fe-Ni binary system at constant potential. By applying various potentials on the specimen with a potentiostat, the dissolution rate could be changed and the resulting changes in dissolution behavior and in the surface composition determined. Atomic absorption analysis was conducted on samples of the solution taken from the electrochemical cell at various times during the dissolution process. The concentrations of Fe and Ni in these solutions were used to determine their relative rates of dissolution. From these rates, the surface composition after a given amount of dissolution could be deduced.

X-ray and optical metallographic examinations were conducted on

each specimen prior to the electrochemical dissolution. The purpose of these examinations was to describe the surface and structure of the specimens before they underwent dissolution. X-ray examination after dissolution was intended to determine whether any shifts in the 2θ positions of the peaks of diffraction pattern would indicate a change in composition on the surface of the specimen, as Pickering (3) has done in the Cu-Au system.

Replica electron microscopy was also used to examine the surface at various stages during dissolution. Changes in the surface topology such as the amount of ledging, the ledge orientation and height, and massing of material were examined.

Specimen Preparation

Five high purity and homogeneous Fe-Ni alloys, pure Fe, and pure Ni were prepared for this investigation. The melting and fabrication techniques for these alloys are discussed in Beauchamp (24). Figure 18 shows the ternary Fe-Cr-Ni phase diagram and the location of the alloys investigated: at 0, 5, 10, 20, 45, 65, and 100 per cent Ni concentrations.

After metallurgical preparation, the specimens were machined into cylinders one-half inch long and two-tenths of an inch in diameter with a tapped hole in one end. These specimens were then mounted in a modified Stern-Makrides electrode mount for testing. The specimen mount is shown in Figure 19. This type of mounting permitted several tests with one specimen; by removing the affected surface of the specimen, it could be lowered into the cell and used for another test.

As a final preparation, the specimens were polished on 280 grit

Figure 18. Phase Diagram for Fe-Cr-Ni Indicating the Fe-Ni Alloys Investigated.

Figure 19. The Specimen Mount with Specimen.

and then on 600 grit metallographic paper, decreased with acetone, washed thoroughly, and weighed. No prior chemical activation was used, since this would have involved dissolving part of the surface of the specimen away and could have led to spurious results during the actual dissolution. The specimens did, however, without activation treatment assume an active corrosion potential in only a short time after being placed in the electrochemical cell.

The Electrolyte

The electrolyte was prepared from reagent grade stock sulfuric acid and double distilled water to provide for as little contamination as possible. The chemical analysis of the 1N H_2SO_4 solution indicated that the concentrations of Fe, Ni, and Cl^- were all less than one part per million (1 ppm).

The electrolyte, after being placed into the electrochemical cell, was purged of oxygen by bubbling high-purity hydrogen through it prior to each test. Hydrogen was used for this purpose rather than other commonly used gases because of its tendency to establish a steady-state hydrogen redox potential, enabling measurement of the pH of the solution.

The Polarization Cell

All electrochemical experiments were conducted using the multipurpose cell shown in Figure 20. In this particular investigation only the large 200ml central compartment and one of the smaller outer compartments were used, the larger for the specimen to be dissolved and the smaller for the counter electrode. The compartments were separated by fine porosity, fritted glass discs which gave good

Figure 20. The Polarization Cell (only compartments A and B used in this investigation).

separation of the anode and cathode reaction products and allowed for the control of the gaseous environment in each compartment. The hydrogen purge was accomplished by bubbling the gas through the coarse, fritting glass discs at the bottom of each compartment, thus providing wide dispersion of the gas. The gas was bubbled through the solution over platinized platinum electrodes which enabled measurement of the hydrogen redox potential, from which the solution pH was measured

All tests were conducted in static solutions with the long axis of the electrode vertical in the solution. This specimen position did allow natural convection forces to remove the dissolved ions away from the surface of the specimen. A rotating, ring-disc electrode system similar to that used by Pickering (3) was considered. However, the problem with this method in the Fe-Ni system at low pH is that, at potentials required to discharge Fe or Ni, the hydrogen evolution would be so great that it would mask any currents related to the Fe or Ni discharge. This method could, however, be used at high pH where the hydrogen evolution would be negligible.

A Haber-Luggin probe was located very close to the cylindrical surface of the specimen. The probe was filled with electrolyte through a tube which connected it to a 1N H_2SO_4 solution. This solution was connected by means of an agar salt bridge to a saturated solution of KCl. In this solution a standard calomel electrode (SCE) was placed and used for all potential measurements. Standard calomel electrode potentials are easily converted to standard hydrogen potentials (SHE) by adding 242mV to the calomel potential.

The Constant Potential Apparatus

The electrochemical dissolutions conducted during this investigation were made under conditions of constant potential, referred to as potentiostatic conditions. The potential was considered the independent variable while the current was the dependent variable. Other than the alloy electrode being investigated, a counter electrode of platinized platinum and a reference electrode (SCE) were required to provide the constant potential conditions. A schematic of the experimental apparatus is shown in Figure 21.

The instrument used to provide the potentiostatic conditions was the Anotrol Model 4100 Research Potential Controller. The current required to maintain the potential was plotted as a function of time on a Bristol Model 560 High-Speed Dynamaster Potential Recorder while the potential was constantly monitored using a Keithley Model 610B Electrometer.

The Experimental Procedure

Before each test, the test cell and the auxiliary components were thoroughly washed three times with distilled water and allowed to dry. The smaller compartments of the electrochemical cell were then filled with 140ml of a 1N H_2SO_4 solution while the alloy electrode compartment was filled with 200ml of the solution. The cell was then immersed, with Luggin probe already in place, into an electrically controlled temperature bath at $25^\circ \pm 1^\circ\text{C}$. Tygon tubing was attached to the gas inlet and two specially designed gas outlets. These outlets also had a platinized platinum electrode built into them so that the hydrogen gas purging the solution passed over them before exiting the cell.

Figure 21. Schematic of the Potentiostatic Apparatus.

This arrangement enabled measurement of the H^+/H_2 potential. Hydrogen gas was then bubbled through the solution for two hours. At this time the Luggin probe was filled completing the solution bridge.

At the end of the hydrogen purge the solution potential was measured and the pH calculated. The outlet electrode was removed from the alloy electrode compartment and the alloy to be investigated placed into the 1N H_2SO_4 solution. The stopper through which the specimen mount passed was fitted with a compression ring which allowed adjustment of the specimen close to the Luggin probe. The specimen was allowed about twenty minutes to attain a constant corrosion potential which was sufficient in all cases. At this time a sample of solution was taken from the cell to be used as a reference for samples taken during the course of the potentiostatic dissolution.

The potential controller was set to the desired dissolution potential and the dissolution process begun. Figures 22 and 23 show the potentials at which each alloy was investigated. At regular intervals, depending on the degree of dissolution, samples of solution were taken from the alloy electrode compartment. At these intervals the dissolution process was stopped for a very short time and a small amount of hydrogen gas passed through the solution for mixing. At this time a sample of solution was removed through a hypodermic needle passed through a small hole in the alloy electrode plug. The test was then continued immediately. The tests ran from fifteen minutes in some cases to nine hours in others. The samples of solution were then analyzed using the atomic absorption analyzer.

The exchange currents for the alloys were calculated from their

Figure 22. Dissolution Potentials for the Low Nickel Alloys Investigated.

Figure 23. Dissolution Potentials for the Intermediate Nickel Alloys Investigated.

anodic polarization curves. These polarization curves were determined from the weight changes of the samples which were converted to currents using Faraday's Law. These currents were compared to the recorded currents measured during the dissolution process as a means of checking the results of currents obtained from the weight changes.

In order to render an indication of the changes in surface topology and ledging as a function of the degree and rate of dissolution, replicas of the surfaces were examined with the electron microscope. The replicas were taken from the surfaces of two alloys that had been dissolved for various times at two different potentials. One of the potentials produced a high dissolution rate while the other produced a low dissolution rate.

RESULTS AND DISCUSSION

Introduction

The purpose of this investigation was to determine the relative rates of dissolution of the components of Fe-Ni binary alloys. The alloys were dissolved in acid solution at constant potential. The solutions were analyzed for Fe and Ni using atomic absorption analysis. These data were used to plot concentration versus time curves and to compute, using the method of least squares, the equations for these curves on a log-log plot. These equations, as well as the data taken from the analyses, were used to determine the (Fe/Ni) ratios in solution as function of time and potential. These ratios were used to determine what changes occurred on the surface of the alloy during dissolution.

The changes in weight for the alloy specimens were also measured, converted to currents, and plotted against potential to yield the total anodic polarization curves. The corrosion current for each alloy was determined from these curves.

The grain structure of the alloys was determined using optical metallography. X-ray diffraction patterns of the alloys were taken before and after dissolution to determine whether any changes in surface composition or structure could be detected and compared with the data from the (Fe/Ni) ratios. Replica electron photo-micrographs were taken for the Fe-5Ni and Fe-20Ni alloys at four stages during dissolution at two different potentials. These micrographs were compared to

determine the effect of alloy composition, rate of dissolution, and amount of dissolution on the surface topology of the alloy specimens.

Dissolution at Constant Potential

The data obtained using atomic absorption analyses for the dissolution behavior of the Fe-Ni binary system investigated is shown in Figures 24 through 35. For the alloys two graphs are given: one for the dissolution behavior of Fe and one for the dissolution behavior of Ni. The curves for these data are expressed as straight lines on a logarithmic plot. Points that lie in the region where the accuracy of the atomic absorption analysis is not totally reliable (concentrations of 2 ppm or less) are omitted in plotting the curves. Using a computer solution for the method of least squares, a straight line was fitted to each set of data points, the form of the equation being

$$c_i = a_i t^{n_i} \quad (14)$$

where c_i = concentration of Fe or
 Ni in solution, ppm
 a_i = concentration of Fe or
 Ni in solution at $t = 1$ second,
 ppm
 t = time, seconds
 n_i = slope of the log-log,
 concentration-time curve

The values of a_i and n_i are given in Tables 3 through 9.

The essential conclusions illustrated by these curves are that:

- (1) the rate of dissolution increases as the potential becomes more noble,
- (2) the slope of the log-log, concentration-time curves are generally close to 1.0, except in the case of pure Ni where the slopes are approximately 0.6, and

Figure 24. Concentration-time Behavior for Pure
Fe [$E_{\text{corr}} = -274\text{mV (SHE)}$].

Figure 25. Concentration-time Behavior for Fe
in Fe-5Ni [$E_{\text{corr}} = -216\text{mV(SHE)}$].

Figure 26. Concentration-time Behavior for Ni
in Fe-5Ni [$E_{\text{corr}} = -216\text{mV(SHE)}$].

Figure 27. Concentration-time Behavior for Fe
in Fe-10Ni [$E_{\text{corr}} = -197\text{mV(SHE)}$].

Figure 28. Concentration-time Behavior for Ni
in Fe-10Ni [$E_{\text{corr}} = -197\text{mV(SHE)}$].

Figure 29. Concentration-time Behavior for Fe
in Fe-20Ni [$E_{\text{corr}} = -140\text{mV(SHE)}$].

Figure 30. Concentration-time Behavior for Ni
in Fe-20Ni [$E_{\text{corr}} = -140\text{mV(SHE)}$].

Figure 31. Concentration-time Behavior for Fe
in Fe-45Ni [$E_{\text{corr}} = -78\text{mV(SHE)}$].

Figure 32. Concentration-time Behavior for Ni
in Fe-45Ni [$E_{\text{corr}} = -78\text{mV(SHE)}$].

Figure 33. Concentration-time Behavior for Fe
in Fe-65Ni [$E_{\text{corr}} = -51\text{mV(SHE)}$].

Figure 34. Concentration-time Behavior for Ni
in Fe-65Ni [$E_{\text{corr}} = -51\text{mV(SHE)}$].

Figure 35. Concentration-time Behavior for Pure
Ni [$E_{\text{corr}} = -22\text{mV(SHE)}$].

Potential mV(SHE)	n_{Fe}	a_{Fe} ppm
0	1.02	1.01
-83	0.973	7.32×10^{-1}
-128	1.30	3.04×10^{-2}
-163	1.61	1.76×10^{-3}
-248.	1.26	6.78×10^{-4}

Table 3. Values of slope and the intercept at $t = 1$ for the log-log, concentration-time curves for Alloy 1, Pure Fe.

Potential mV (SHE)	n_{Fe}	n_{Ni}	a_{Fe} ppm	a_{Ni} ppm
0	1.04	1.05	5.57×10^{-1}	2.89×10^{-2}
-100	0.470	0.851	7.02	2.43×10^{-2}
-170	1.09	0.905	1.32×10^{-2}	2.65×10^{-3}

Table 4. Values of the slope and the intercept at $t = 1$ for the log-log, concentration-time curves for Fe and Ni in Alloy 2, Fe-5Ni.

Potential mV(SHE)	n_{Fe}	n_{Ni}	a_{Fe} ppm	a_{Ni} ppm
0	0.930	0.637	9.39×10^{-1}	3.30×10^{-1}
-100	0.955	0.924	2.54×10^{-2}	1.83×10^{-2}
-160	1.46	1.40	1.59×10^{-4}	9.85×10^{-5}

Table 5. Values of the slope and the intercept at $t = 1$ for the log-log, concentration-time curves for Fe and Ni in Alloy 3, Fe-10Ni.

Potential mV(SHE)	n_{Fe}	n_{Ni}	a_{Fe} ppm	a_{Ni} ppm
+90	1.03	0.988	4.73×10^{-1}	1.55×10^{-1}
+22	1.34	1.04	2.91×10^{-2}	5.15×10^{-2}
-53	1.47	1.11	2.33×10^{-3}	7.30×10^{-3}
-83	1.01	0.883	3.11×10^{-2}	2.81×10^{-2}
-108	1.14	1.11	2.76×10^{-3}	1.11×10^{-3}

Table 6. Values of the slope and the intercept at $t = 1$ for the log-log, concentration-time curves for Fe and Ni in Alloy 4, Fe-20Ni.

Potential mV(SHE)	n_{Fe}	n_{Ni}	a_{Fe} ppm	a_{Ni} ppm
+100	1.46	1.08	5.29×10^{-3}	6.37×10^{-2}
+2	1.01	1.16	1.12×10^{-2}	3.04×10^{-3}
-18	0.506	0.848	2.26×10^{-1}	1.48×10^{-2}
-35	0.706	0.974	2.57×10^{-2}	2.79×10^{-3}
-63	1.40	1.37	1.64×10^{-5}	2.43×10^{-5}

Table 7. Values of the slope and the intercept at $t = 1$ for the log-log, concentration-time curves for Fe and Ni in Alloy 6, Fe-45Ni.

Potential mV(SHE)	n_{Fe}	n_{Ni}	a_{Fe} ppm	a_{Ni} ppm
+100	0.960	1.05	2.32×10^{-2}	1.91×10^{-2}
+32	1.07	0.964	1.32×10^{-3}	7.77×10^{-3}
+12	1.00	1.06	1.88×10^{-3}	2.61×10^{-3}
-8	1.34	1.11	1.09×10^{-4}	1.44×10^{-3}

Table 8. Values of the slope and the intercept at $t = 1$ for the log-log, concentration-time curves for Fe and Ni in Alloy 8, Fe-65Ni.

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

Table 9. Values for slope and the intercept at $t = 1$ for the log-log, concentration-time curves for Alloy 12, Pure Ni.

(3) the intercepts at $t = 1$ second decrease with decreasing potential.

In order to determine a potential for each component in a given alloy when the surface could be assumed to be undisturbed, the concentrations at $t = 1$ second were plotted as a function of the potentials of dissolution using the method of least squares. An equation of the following form was obtained:

$$E_i = b_i \log c_i + E_i^{1\text{ppm}} \quad (15)$$

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

b_i = slope of the curve, mV

c_i = concentration of Fe or Ni,
ppm

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

It was assumed that the dissolution of one atom layer per square centimeter per second would be a reasonable value to select for the undisturbed condition. This value is equivalent to a one-third part per billion (1 ppb) concentration in solution at one second. This concentration was substituted into equation (15) to give the potential for an undisturbed surface. This potential along with the values for b_i and $E_i^{1\text{ppm}}$ is given in Table 10.

The data generally indicate that the potential for both Fe and Ni increase or become more noble as the concentration of Ni in the alloy increases. No specific relation exists between the potentials for Fe and for Ni in a given alloy. However, in the cases for Fe-10Ni, Fe-20Ni, and Fe-45Ni, the potential for Ni is more noble than that for Fe.

Furthermore, the potentials calculated for pure Fe and for pure

Alloy	b_{Fe}	b_{Ni}	E_{Fe}^{1ppm} mV (SHE)	E_{Ni}^{1ppm} mV (SHE)	$E_{Fe}^{1/3ppb}$ mV (SHE)	$E_{Ni}^{1/3ppb}$ mV (SHE)
Fe	58.8		-35.4		-240	
Fe-5Ni	31.6	127	-76.4	149	-185	-285
Fe-10Ni	41.4	43.1	-11.8	2.8	-156	-147
Fe-20Ni	74.0	56.6	102	56.7	-155	-140
Fe-45Ni	10.3	38.2	-14.8	94.4	-51	-38
Fe-65Ni	45.7	89.6	162	241	+4	-70
Ni		61.6		196		+18

Table 10. Values of the slope and the intercept at $c = 1$ ppm and at $c = 1/3$ ppb for a semi-log, potential-concentration plot for the alloys investigated.

Ni are much more noble than their equilibrium potentials, -440mV(SHE) and -250mV(SHE), respectively. There is no explanation for this behavior.

Anodic Polarization Behavior

The total anodic polarization behavior of the alloys was determined from the weight changes of the specimens at the various potentials of dissolution. The specimen weight changes were converted to charge using Faraday's equation in the following form:

$$Q = It = \left[\frac{z_{Fe} F}{M_{Fe}} \text{ wt.\% Fe} + \frac{z_{Ni} F}{M_{Ni}} \text{ wt.\% Ni} \right] \Delta w \quad (16)$$

where Q = charge passed, Coul.

I = current, amps.

t = time, seconds

z_{Fe}, z_{Ni} = oxidation states of Fe and Ni

M_{Fe}, M_{Ni} = molecular weights of Fe and Ni

wt.%Fe = percentage Fe in alloy

wt.%Ni = percentage Ni in alloy

F = Faraday's constant

Δw = specimen weight change

Using this equation, individual equations for each alloy were determined; and from these the charge passed through each alloy at a given potential for a given weight change was determined. The currents were determined by dividing the appropriate Q value by the time of the experiment. These currents were plotted as a function of the potential to yield the anodic polarization curves shown in Figure 36. "Since the specimen sizes were all approximately the same, the currents calculated are comparable from alloy to alloy. Current densities can be calculated by multiplying the value for the current by 0.45 cm^{-2} .

The accuracy of the currents measured using the weight changes

Figure 36. Total Anodic Polarization Curves Determined from the Weight Changes for the Alloys Investigated with Corrosion Current i_{corr} Indicated by the Intersection with the Corrosion Potential E_{corr} .

was checked by determining the coulometric current during the experiment. The recorded current was integrated over time to yield the total charge passed. This charge was then converted to current by dividing by the total time of the experiment. In each case the coulometric current deviated from the weight change current on the average of about four per cent, as high as sixteen per cent in one case, and was lower than the weight change currents in all but two cases. Figure 37 shows why the coulometric current would be expected to be less than the current determined by weight change; the evolution of hydrogen diminishes the anodic current by a small amount depending on the overpotential.

The intersection of the anodic polarization curves with the initial corrosion potential E_{corr} yields the corrosion current i_{corr} . The corrosion current is directly determinable from the weight change data since the deviations in polarization behavior caused by hydrogen evolution are not present. Coulometric measurements are disturbed by this reaction and extrapolations of the Tafel portion of these curves must be made to determine i_{corr} . This is illustrated in Figure 37.

In order to determine a more accurate value for i_{corr} and for the Tafel slope, the method of least squares was used with the weight change data. The results are shown in Table 11. The data at high potentials was excluded for the analysis since it appeared that at this point the alloys were beginning to passivate, indicated by the deviation from straight line behavior. The overall polarization curves are in good agreement with the results of Beauchamp (24) and Condit (25). Furthermore, the corrosion currents are noticeably larger for low nickel alloys compared to high nickel alloys, the changes occurring

Figure 37. Difference Between Polarization Curves Measured Coulometrically and by Weight Change.

Alloy	i_{corr} mA	$2.3RT/\alpha zF$ V.
Fe	1.32	1.91×10^{-2}
Fe- 5Ni	2.08	2.38×10^{-2}
Fe-10Ni	3.05	1.71×10^{-2}
Fe-20Ni	4.74	1.56×10^{-2}
Fe-45Ni	3.48×10^{-1}	2.41×10^{-2}
Fe-65Ni	7.99×10^{-2}	2.40×10^{-2}
Ni	3.26×10^{-3}	2.31×10^{-2}

Table 11. Corrosion currents and Tafel slopes for weight change data for alloys investigated.

in the range between nickel concentrations of 20 at. % and 45 at. %. X-ray diffraction studies of the alloy system, as well as studies on the alloys in this investigation, indicate that for the Fe-Ni system a change in structure from body-centered cubic to face-centered cubic occurs at about 25 at. % Ni as shown in Figure 38. The corrosion current may, since its inflection point is in this range, be a structure sensitive property.

The values for the Tafel slopes given in Table 11 are in very reasonable agreement with the data obtained for Fe by Felloni (27). Felloni found the slope for Fe in 0.5M H_2SO_4 to be about 3.1×10^{-2} V.; whereas, the data for the present investigation indicate that the slope is approximately 2.1×10^{-2} V. This deviation may be due to experimental error or to the assumption that $z = 3$.

(Fe/Ni) Ratios in Solution

The change in composition on the surface of the alloy during dissolution is ascertained by determining the ratio of Fe to Ni in the solution. If this ratio is greater than the (Fe/Ni) ratio for the alloy, the surface can be assumed to be enriching in Ni since Fe is dissolving proportionately faster than Ni. Conversely, an (Fe/Ni) ratio in solution less than the alloy ratio would indicate that Fe is enriching on the surface.

The (Fe/Ni) ratios in solution were calculated by dividing the equations for the concentrations of Fe and Ni as a function of time. The data from Tables 4 through 8 were used to yield equations of the form

Figure 38. The Phase Diagram and Corresponding Lattice Parameters for the Fe-Ni Binary System (26).

$$R_C = (Fe/Ni)_E = r_o t^n$$

where $R_C = (Fe/Ni)_E$ = Fe-to-Ni ratio

in solution at a given potential E

r_o = ratio at $t = 1$ second

n = slope of the log-log, ratio-time curve

The data are plotted for times consistent with those of the experiments and are shown in Figures 39 through 43. From these curves the relative difference between the calculated (Fe/Ni) ratio R_C and the alloy (Fe/Ni) ratio R_A was determined as a function of potential for 10^2 and 10^4 seconds. These curves are shown in Figures 43 through 48 and indicate more clearly the trends in each alloy at the various potentials. The changes in the (Fe/Ni) ratios are, of course, subject to some deviation; but, generally, the essential conclusions drawn from these data are that:

- (1) for high dissolution potentials the (Fe/Ni) ratios in solution tend to be greater than the alloy ratio indicating a tendency for nickel enrichment,
- (2) for the Fe-10Ni and Fe-20Ni alloys the values of R_C tend to increase with time and to indicate nickel enrichment over a wide range of potentials, and
- (3) for alloys on either side of this region the values of R_C show reduced or inconsistent tendencies for nickel enrichment and in many cases indicate that Fe may be enriching on the surface.

In many cases even though the values for the (Fe/Ni) ratios in solution within the plotted time span are less than the alloy ratio, the slope

Figure 39. Calculated (Fe/Ni) Ratios in Solution
as a Function of Time for Fe-5Ni.

Calculated (Fe/Ni) Ratio

Figure 40. Calculated (Fe/Ni) Ratios in Solution
as a Function of Time for Fe-10Ni.

Figure 41. Calculated (Fe/Ni) Ratios in Solution
as a Function of Time for Fe-20Ni.

Figure 42. Calculated (Fe/Ni) Ratios in Solution
as a Function of Time for Fe-45Ni.

Calculated (Fe/Ni) Ratio

Figure 43. Calculated (Fe/Ni) Ratios in Solution
as a Function of Time for Fe-65Ni.

Calculated (Fe/Ni) Ratio

Figure 44. Relative Difference Between the Calculated (Fe/Ni) Ratio in Solution R_c and the Alloy (Fe/Ni) Ratio R_a versus Potential for Fe-5Ni.

Figure 45 Relative Difference Between the Calculated (Fe/Ni) Ratio in Solution R_C and the Alloy (Fe/Ni) Ratio R_A versus Potential for Fe-10Ni.

Figure 46. Relative Difference Between the Calculated (Fe/Ni) Ratio in Solution R_c and the Alloy (Fe/Ni) Ratio R_a versus Potential for Fe-20Ni.

Figure 47. Relative Difference Between the Calculated (Fe/Ni) Ratio in Solution R_C and the Alloy (Fe/Ni) Ratio R_A versus Potential for Fe-45Ni.

Figure 48. Relative Difference Between the Calculated (Fe/Ni) Ratio in Solution R_c and the Alloy (Fe/Ni) Ratio R_a versus Potential for Fe-65Ni.

of the ratio-time curve is positive, indicating a tendency for nickel enrichment at some longer time. Negative slopes indicate a long-range tendency toward the enrichment of Fe.

In some of the experiments the behavior of the corrosion potential was observed both before and after the dissolution process. For dissolution potentials above E_{corr} the value of the corrosion potential was generally more active after dissolution of the alloy than before. For dissolution potentials below E_{corr} the value of the corrosion potential after dissolution was generally more noble than before dissolution. The difference in the initial and final values for E_{corr} was never greater than 40mV. The (Fe/Ni) ratios give no explanation for this behavior.

Assuming that only one component dissolves from a binary alloy, the number of layers of the other component remaining on the surface could be calculated. For various (Fe/Ni) ratios in solution the number of layers of pure Ni or pure Fe remaining on the surface of an Fe-20Ni alloy have been calculated as a function of the amount of dissolution. The results of this calculation are shown in Figure 49. The problem in the present investigation is that pure Fe or pure Ni cannot be assumed to be on the surface after dissolution; but instead the surfaces are enriched in Fe or Ni. The process of dissolution in a binary alloy is much more complex and not as easily illustrated as it is in this figure. The process is still more complex if the (Fe/Ni) ratio in solution changes with time.

X-ray diffraction patterns before and after dissolution of Fe-20Ni, Fe-45Ni, and Fe-65Ni indicate no change in lattice parameter that would

Figure 49. Layers of Pure Fe or Pure Ni Remaining on the Surface of an Fe-20Ni Alloy as a Function of the Amount of Charge Passed for Given (Fe/Ni) Ratios in Solution.

substantiate the data obtained from (Fe/Ni) ratios in solution. The primary reason for this incapability is that at diffraction angles low enough to just analyze the surface layers of the alloy, the error of the diffraction technique is greater than any expected change in the lattice parameter. These diffraction data are, therefore, not included here.

Electron Microscopy

Carbon replicas of the surfaces of two alloys were examined to determine what changes occur on the surface of each alloy during the dissolution process. Fe-5Ni and Fe-20Ni were dissolved at two different potentials. At various stages during the dissolution the surface of the alloy was replicated and the replica observed in the electron microscope. Plates I through IV illustrate the changes in surface topology that occurred during dissolution.

The first micrograph in each plate indicates the state of the surface prior to the potentiostatic dissolution, but after the alloy had been allowed to reach its corrosion potential in the solution. The micrograph is marked to indicate the number of atom layers that are expected to be dissolved during this period. These initial micrographs indicate that the surface conditions prior to dissolution were nearly the same for both alloys.

The Fe-5Ni alloy was dissolved at $\eta = +46\text{mV}$ [$E = -170\text{mV(SHE)}$, $i = 20\text{mA}$] and at $\eta = +216\text{mV}$ [$E = 0\text{mV(SHE)}$, $i = 500\text{mA}$]. The Fe-20Ni alloy was dissolved at $\eta = +32\text{mV}$ [$E = -108\text{mV(SHE)}$, $i = 8\text{mA}$] and at $\eta = +210\text{mV}$ [$E = +70\text{mV(SHE)}$, $i = 500\text{mA}$].

Comparison of Plates I-(4) and II-(2) shows that the rate of

(1)-Test begin, 3.4 Coul.
 10^4 layers

(2)-120s, 2.4 Coul.
 7.2×10^3 layers

(3)-900s, 18 Coul.
 6.4×10^4 layers

(4)-2100s, 42 Coul.
 1.3×10^5 layers

PLATE I. Replica Electron Photo-micrographs for Fe-5Ni
 Dissolved at $\eta = +46$ mV for the Times Indicated (11,300X).

(1)-Test begin, 3.4 Coul.
 10^4 layers

(2)-120s, 60 Coul.
 1.8×10^5 layers

(3)-900s, 450 Coul.
 1.3×10^6 layers

(4)-1500s, 750 Coul.
 2.3×10^6 layers

PLATE II. Replica Electron Photo-micrographs for Fe-5Ni
 Dissolved at $\eta = +216$ mV for the Times Indicated (11,300X).

(1)-Test begin, 5.7 Coul.
 1.8×10^4 layers

(2)-120s, 1.2 Coul.
 3.6×10^3 layers

(3)-900s, 9 Coul.
 2.7×10^4 layers

(4)-2100s, 21 Coul.
 6.3×10^4 layers

PLATE III. Replica Electron Photo-micrographs for Fe-20Ni
 Dissolved at $\eta = +32$ mV for the Times Indicated (11,300X).

PLATE IV. Replica Electron Photo-micrographs for Fe-20Ni
Dissolved at $\eta = +210$ mV for the Times Indicated (11,300X).

(1)-Test begin, 5.7 Coul.
 1.8×10^4 layers

(2)-120s, 60 Coul.
 1.8×10^5 layers

(3)-900s, 450 Coul.
 1.3×10^6 layers

(4)-1500s, 750 Coul.
 2.3×10^6 layers

PLATE IV. Replica Electron Photo-micrographs for Fe-20Ni
 Dissolved at $\eta = +210$ mV for the Times Indicated (11,300X).

dissolution is very significant. It is clear that atomic ledges have accumulated into large steps and that after only 120 seconds at $\eta = +216\text{mV}$ this accumulation of atomic ledges is much more pronounced than after 2100 seconds at $\eta = +46\text{mV}$. Plates III-(4) and IV-(2) for Fe-20Ni do not indicate as pronounced an effect as in the Fe-5Ni, although the pitting shown in Plate IV-(2) would indicate some tendency for the accumulation of atomic ledges.

Comparison of Plates I-(4) and II-(4) and Plates III-(4) and IV-(4) show the effects of alloying since the charge passed in each set is the same. For the low dissolution rate, no effect of alloying is observed. However, for the high dissolution rate, the ledging is quite pronounced. The accumulation of ledges for the Fe-5Ni alloy is very regular; whereas, these steps created in the Fe-10Ni alloy do not have well-defined step intersections and seem to be much deeper. The dissolution of the Fe-20Ni at high overpotentials seems to create trenches rather than the accumulation of ledges.

The angles between the step intersections is quite pronounced, especially in the Fe-5Ni alloy, although some regularity is observable in the Fe-20Ni alloy. The angle of intersection of the steps is approximately 120° . X-ray studies indicate that there is a strong preferred orientation in both alloys with the $\{110\}$ planes being normal to the specimen axis. This agrees with previous observations that swaged and drawn body-centered cubic materials have strong $\{110\}$ textures (28). Considering these two facts, it can be deduced that the faces of the steps are also $\{110\}$ and that the intersections of the steps are $\langle 111 \rangle$ directions. The angle of emergence of these steps would be 60° . This

mode of dissolution might have been expected since the $\{110\}$ planes are one set of the planes of closest packing in body-centered cubic materials.

Discussion

The data from this investigation illustrate the feasibility of using atomic absorption analysis as a means of determining the dissolution behavior of certain metals and alloys. This technique proves to be very reproducible as the consistent straight line behavior would indicate.

The analyses indicate that the dissolution behavior of Fe and Ni, both as pure metals and in binary alloys, is a logarithmic function of time. The exponent of time was generally close to 1.0 so that the kinetic behavior could be considered as a zero-order reaction. Using equation (14), the intrinsic zero-order rate constants for Fe and Ni could be determined for each alloy at a constant potential. The following equation was used to determine the rate constants

$$K_i = \frac{M_s}{AM_i} \left(\frac{dc_i}{dt} \right) \times 10^{-6} \quad (18)$$

where K_i = intrinsic rate constant,
moles/cm²·second

M_s = mass of solution, gms.

A = area of the specimen, cm²

M_i = molecular weight of Fe or Ni

dc_i/dt = slope of the concentration-time curve, ppm/second

These rate constants for Fe and Ni are shown in Figure 50 for a potential of 0mV(SHE). The curves indicate that the rate of Fe dissolution is greater than the rate of Ni dissolution in the range of Ni compositions from 0 at. % to about 50 at. %. A more accurate interpretation

Figure 50. The Zero-order Intrinsic Rate Constants for Fe and Ni as a Function of Ni Composition, at 0mV(SHE).

of these data can be obtained by normalizing both curves. This is accomplished by dividing each data point by its respective concentration of Fe or Ni. The curves obtained from this calculation are shown in Figure 51. This figure clearly shows that the dissolution rate of Fe is proportionately greater than that for Ni in the range from 5 at.% to 50 at.% Ni. Therefore, Ni enrichment could be expected to occur in this region at this potential.

The Tafel slopes calculated for the anodic polarization curves indicate the possible mechanism of dissolution. Bockris (29) has suggested that for slopes on the order of 3.0×10^{-2} V. the mechanism for the dissolution of Fe is as follows:

Since the Tafel slopes in this investigation are approximately the same as those of Bockris, the mechanism for the dissolution of Fe and Ni may be very similar to the mechanism shown above.

Figure 51. The Normalized Values for the Zero-order Intrinsic Rate Constants for Fe and Ni as a Function of Ni Composition. at 0mV(SHE).

APPENDIX

(1) - Pure Fe

(2) - Fe-5Ni

(3) - Fe-10Ni

(4) - Fe-20Ni

PLATE A-I. Microstructures for Pure Fe, Fe-5Ni, Fe-10Ni, and Fe-20Ni (100X).

(1) - Fe-45Ni

(2) - Fe-65Ni

(3) - Pure Ni

PLATE A-II. Microstructures for Fe-45Ni, Fe-65Ni,
and Pure Ni (100X).

BIBLIOGRAPHY

1. Tomashov, N. D., Theory of Corrosion and Protection of Metals, New York: The Macmillan Company, 1966.
2. Vetter, K. J., Electrochemical Kinetics, Theoretical Aspects, New York: Academic Press, Inc., 1967.
3. Pickering, H. W. and Wagner, C., Journal of Electrochemical Society, 114, No.7, (July, 1967), 698.
4. Scully, J. C., The Fundamentals of Corrosion, Oxford: Pergamon Press, 1966
5. Staehle, R. W., "The Process of Noble Metal Enrichment", submitted to Corrosion.
6. Latanision, R. M. and Staehle, R. W., International Conference, Fundamental Aspects of Stress Corrosion Cracking, The Ohio State University, Columbus, (September, 1967).
7. Pickering, H. W., International Conference, Fundamental Aspects of Stress Corrosion Cracking, The Ohio State University, Columbus, (September, 1967).
8. Bengough, G. D. et.al., Journal of the Institute of Metals, 23, (1920), 65.
9. Bengough, G. D. et.al., Journal of the Institute of Metals, 32, (1924), 81.
10. Sugawara, H. and Ebiko, H., Corrosion Science, 7, (1967), 513.
11. Pickering, H. W., Journal of Electrochemical Society, 115, No. 2, (February, 1968), 143.
12. Barnartt, S. and vanRooyan, D., Journal of Electrochemical Society, 108, No. 3, (March 1961), 222.
13. Hoar, T. P. and Hines, J. G., Stress Corrosion Cracking and Embrittlement, ed. W. D. Robertson, New York: John Wiley and Sons, Inc., (1965), 107.
14. Hoar, T. P. and Hines, J. G., Journal of the Iron and Steel Institute, 182, (1956), 124.
15. Staehle, R. W., The Ohio State University Research Foundation Report No. OOO-1319-51 (Q-13), Columbus, (September, 1966).

16. Bond, A. P., Paper presented to NACE Conference in Cleveland Ohio, 1968.
17. Copson, H. R., Physical Chemistry of Stress Corrosion Fracture, 247.
18. Wahl, W. and Kramer, H., "Neutron-Activation Analysis," Scientific American.
19. Tomashov, N. D., et.al., Protection of Metals, 1, (1965), 113.
20. Corliss, W. R., Neutron-Activation Analysis, Washington: United States Atomic Energy Commission.
21. Friedlander, G. and Kennedy, J., Nuclear and Radiochemistry, New York: John Wiley and Sons, Inc., 1955.
22. Dembrowskiy, M. A. and Florianovich, G. M., Protection of Metals, 1, (1965), 125.
23. Kahn, H. and Slavin, W., Science and Technology, (November, 1962).
24. Beauchamp, R. L., Doctoral Dissertation, The Ohio State University, Columbus, 1966.
25. Condit, D. O., Master's Thesis, The Ohio State University, Columbus, 1966.
26. Pearson, W. B., Handbook of Lattice Spacings and Structures of Metals and Alloys, New York: Pergamon Press, 1958.
27. Felloni, L., Corrosion Science, 8, No. 3, (March, 1968), 133.
28. Barrett, C. S. and Massalski, T. B., Structure of Metals, New York: McGraw-Hill Book Company, 1966.
29. Bockris, J. O'M., et.al., Electrochimica Acta, 4, (1961), 325.