ELECTRODE KINETIC BEHAVIOR OF METALLIC SURFACES

Final Technical Report

Office of Naval Research

Contract Number - Nonr-591(17)

Norbert D. Greere

Rensselaer Polytechnic Institute
Troy, New York

February, 1968

Reproduction in whole or in part is permitted for any purpose of the United States Government
This research program was concerned primarily with the study of the influence of metallic structure and composition on the electrode kinetic and corrosion behavior of metal surfaces. Office of Naval Research support for the program covered the period of September 1, 1962 through August 31, 1966.

Since the complete details of research progress have been given in five technical reports and a patent application, only the most pertinent results are summarized briefly below.

Technical Report #1 - Electrode Mounting for Potentiostatic Anodic Polarization Studies
May, 1965

The results of this study show that even microscopic crevices at an electrode mount interface can produce pronounced error in passive current measurements during potentiostatic anodic polarization experiments. The importance of avoiding all crevices when mounting electrodes for electrochemical studies was not recognized generally prior to this study.

Technical Report #2 - Principles of Metallographic Etching - June, 1965

The field of metallographic etching has been
traditionally more an art than a science. The purpose of this study was to determine the controlling parameters in the metallographic etching of multiphase alloys and provide a more scientific basis for the development of new etches.

Tin-zinc alloys in sodium hydroxide solutions were chosen as the most suitable system for study. Etching rate and contrast were found to be unique functions of electrode potential. Identical etching results were obtained by potentiostatic, electrolytic, and chemical techniques when performed at the same electrode potential. In addition, it was found that to produce sufficient metallographic contrast, the dissolution rate of a given phase must be at least 5 times greater than the surrounding matrix unless a colored insoluble dissolution product is produced.

The results show that metallographic etches can be designed on a scientific rather than an empirical basis.

Technical Report #3 - Predicting the Intergranular Corrosion of Austenitic Stainless Steels
October, 1965

A continuous grain boundary precipitate of chromium-
rich carbide is known to be a necessary but not sufficient cause for the intergranular corrosion of austenitic stainless steels. Since intergranular attack does not occur in many environments, expensive preventive measures can often be avoided. The purpose of this investigation was to determine the precise environmental conditions under which these steels corrode intergranularly.

The results provide a method for rapidly predicting the intergranular susceptibility of various sulfuric acid-oxidized mixtures on the basis of corrosion potential measurements and controlled potential corrosion tests.

Technical Report #4 - Passivation of Crevices during Anodic Protection - February, 1968

The ability to passivate narrow crevices is an important factor in practical applications of anodic protection. The work described in Technical Report #1 was extended to investigate the factors controlling the passivation of crevices.

Theoretical analyses and experimental studies with a special crevice assembly demonstrate that the most important parameter is the critical anodic current
density; i.e., of the protected metal. Thus selecting alloys for anodic protection applications with small critical anodic current densities reduces the current requirements for initial passivation and improves the crevice-passivating ability of the system.

Technical Report #5 - The Variable Corrosion Resistance of 18 Cr - 8 Ni Stainless Steel, to be issued March, 1968

It is well known that similar heats of 18 Cr - 8 Ni can vary by as much as fifty-fold in their corrosion resistances.

Using electrochemical techniques, conventional corrosion testing, and multiple correlation analyses, the corrosion behavior of a large number of commercial heats of Types 304 and 316 stainless steel was examined in detail. It was found that the differences in behavior among the heats was due almost entirely to slight variations in chemical composition.

The following equation was developed which describes the effect of various elements on the critical anodic current density, $i_c$. Corrosion resistance is inversely proportional to critical anodic current density.
\[ I_c = 15471 + 373 \text{ (Mn)} + 7600 \text{ (S)} - 750 \text{ (Mo)} \\
- 6500 \text{ (C)} - 840 \text{ (Cr)} - 1240 \text{ (Cu)} \]

where \( I_c \) = microamperes/cm\(^2\) and alloy composition is in weight per cent.

On the basis of this study a patent application, "Stainless Steel Compositions with Increased Corrosion Resistance", was filed 31 October, 1966. The application bears Serial No. 591,352, and is further identified as Navy Case No. 41,478.

During the course of this program, two Ph. D. candidates, B. E. Wilde and W. D. France, Jr., were completely supported in their doctoral research. In addition, the research of several Masters' candidates, including France, was either completely or partially supported.
Electrode Kinetic Behavior of Metallic Surfaces

The primary purpose of this program was to relate the electrode kinetic and corrosion behavior of metallic surfaces to metallographic structure and function.

Since complete research details have previously been presented in five technical reports, and a patent application, only the most important results are briefly summarized in this final report.
Corrosion
Electrochemistry
Electrode Kinetics
Stainless Steels
Intergranular Corrosion
Anodic Protection
Crevice Corrosion
Metallographic Etching

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (corporate authority) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 3200.10 and Armed Forces Industrial Manual. Enter the group number. Also, where applicable, show that optional markings have been used for Group 3 and Group 4 on appropriate forms.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. Use a period at the end of the title. The title cannot contain subject classifications in all capitals in parentheses immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is involved.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on the report. For last name, first name, middle initial. If necessary, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, or month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total report text should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b. No. & d. PROJECT NUMBER: Enter the applicable military department identification, such as project number, project number, system number, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number(s) by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been reprinted by any other report numbers (either by the originator or by the sponsor), also enter this number(s).

10. AVAILABILITY LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified recipients may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through security classification."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through security classification."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through security classification."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or activity sponsoring (paying for) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicating the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (F2), (F3), (C3), or (F1).

There is no limitation on the length of the abstract. However, the suggested length is from 120 to 225 words.

14. KEY WORDS: Key words are technical meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be entered so that an security classification is required. Identifiers, such as equipment model designation, code name, military project code name, geographic location, may be used as key words but will be followed by an indication of restricted context. The assignment of links, values, and weights is optional.