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Annual Report
Contract No. N00014-87-K0042
December 1, 1986 - December 1, 1987

THE INFLUENCE OF CATHODIC PROTECTION ON EROSION-CORROSION OF METALS AND MODEL ALLOYS

Submitted to:

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

Submitted by:

M. E. Orazem
Assistant Professor

Report No. UVA/525418/CHE88/101
February 1988

SCHOOL OF ENGINEERING AND APPLIED SCIENCE

DEPARTMENT OF CHEMICAL ENGINEERING

UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA 22901

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The object of this program is to develop a fundamental understanding of the influence of applied potential on mechanisms for erosion-corrosion as applied to copper and copper-based alloys. This work is intended to allow application of laboratory experiments to predict the onset of erosion-corrosion failure under field conditions and to guide development of workable strategies for prevention of erosion-corrosion.

In the first year of the program, an electrochemical cell incorporating a scanning ellipsometer was designed and built. The cell uses a submerged electrolyte jet impinging on an electrode. The laser spot size is around 25 × 70 μm, and the position of the electrode-jet assembly relative to the laser spot can be controlled by stepping motor stages without altering the hydrodynamic environment. This system will be used to map local film thickness

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under well controlled fluid flow exhibiting high shear rates. The radial position at which the film thickness decreases can be related to a critical value for hydrodynamic shear required to remove the film, and the use of a well-characterized flow geometry allows separation of erosion-corrosion effects from corrosion enhancement associated with mass transfer. Experiments using this system will begin in the second year of the program. In support of the erosion-corrosion studies, electrochemical experiments are being conducted to identify the corrosion mechanisms and film composition associated with corrosion of copper in neutral and basic saline solutions. These experiments will be extended to model copper-aluminum alloys in the second year of the program.

Abstract

The object of this program is to develop a fundamental understanding of the influence of applied potential on mechanisms for erosion–corrosion as applied to copper and copper–based alloys. This work is intended to allow application of laboratory experiments to predict the onset of erosion-corrosion failure under field conditions and to guide development of workable strategies for prevention of erosion–corrosion.

In the first year of the program, an electrochemical cell incorporating a scanning ellipsometer was designed and built. The cell uses a submerged electrolyte jet impinging on an electrode. The laser spot size is around 25 × 70 μm, and the position of the electrode–jet assembly relative to the laser spot can be controlled by stepping motor stages without altering the hydrodynamic environment. This system will be used to map local film thickness under well controlled fluid flow exhibiting high shear rates. The radial position at which the film thickness decreases can be related to a critical value for hydrodynamic shear required to remove the film, and the use of a well–characterized flow geometry allows separation of erosion–corrosion effects from corrosion enhancement associated with mass transfer. Experiments using this system will begin in the second year of the program. In support of the erosion–corrosion studies, electrochemical experiments are being conducted to identify the corrosion mechanisms and film composition associated with corrosion of copper in neutral and basic saline solutions. These experiments will be extended to model copper–aluminum alloys in the second year of the program.

Scientific Research Goals

Erosion–corrosion is a pervasive and complex problem which is attributed to velocity–enhanced mass transfer as well as to a mechanical removal of protective oxide films. The objective of this contract, awarded January 20, 1987, is to identify specific modes of corrosion enhancement associated with high–speed flow. This work is necessary to provide a fundamental understanding of the mechanism for erosion–corrosion, and to allow application of laboratory experiments to field conditions. This work is intended to guide development of workable strategies for prevention of erosion–corrosion.

This objective will be accomplished by developing a new experimental system to study the erosion–corrosion of copper and model copper–based alloys in sodium chloride solutions. The growth and removal of oxide films will be observed *in–situ* by automated scanning ellipsometry. This apparatus will be used to study the electrochemistry of copper and model copper–based alloys under conditions where erosion–corrosion is expected. These materials were chosen because they are of industrial and national importance and because they are known to be susceptible to erosion–corrosion attack. Parametric studies will be conducted to identify the mode of enhanced attack, the influence of fluid composition and pH, and the influence of polarization. The ultimate goal of this work is the development of a mathematical model to predict the current requirements for the cathodic protection of complex geometries subject to high-speed flow. In order to provide a comprehensive solution to the problem, local microstructural and microchemical analyses will also be employed. The techniques to be used include scanning and transmission electron microscopy, energy dispersive X-ray analysis, and Auger spectroscopy.

Significant Results

The results of the first year include design and construction of an ellipsometer to measure local film thickness under high-speed impinging fluid, preliminary electrochemical experiments for copper in neutral and basic saline solutions, and development of an in-house capability to formulate model copper-aluminum alloys.

Cell Design

Our primary goal for the first year was to design and construct the impinging jet/ellipsometer apparatus. The cell has been designed and is under construction. A schematic representation of the cell is shown in Figure 1. This includes computer-interfaced stepping motor stages for accurate positioning of the jet nozzle and metal electrode to be studied, polarizer and analyzer components of the ellipsometer, and a plexiglas cell compartment supported in a rigid 1/2 inch aluminum frame. The flow assembly is given as Figure 2. A magnetically coupled centrifugal pump will be used to drive the flow, and the system is designed to allow study of both aerated and deaerated conditions. All components have arrived, and the flow system is now being tested. This system will be controlled by a HP 310 laboratory computer, and some of the software needed to run these experiments has been written. The underlying concept and principles for the cell design are presented in the following sections.

Concept

In the absence of impingement of particles or bubbles, hydrodynamic shear is the primary mechanism for transfer of momentum between the flowing electrolyte and the surface (see references 1-3). A nonzero value for the wall shear stress results from the relative motion between the fluid and the solid. This force acts on the surface in the direction of flow, and has been implicated in the removal of loosely adherent films. Copson[4] suggested that shear stresses are likely to be too small to cause significant erosion-corrosion. Indeed, experiments conducted in our laboratory indicate that if particles or small bubbles are present in the flowing electrolyte, attack by impingement will overwhelm attack by shear mechanisms. Efird[5] has reported critical values of shear stress for the erosion-corrosion of copper and some copper-based alloys in sea water. The temperature dependence of the critical velocity was shown to correlate well with the temperature dependence of the surface shear stress. Giralt and Trass[6] have shown that removal of solid naphthalene and trans-cinnamic acid by a submerged impinging jet of saturated solution is proportional to the wall shear stress above a critical or threshold value. Steele and Geankoplis[7] have also reported removal of material by an apparent shear erosion mechanism.

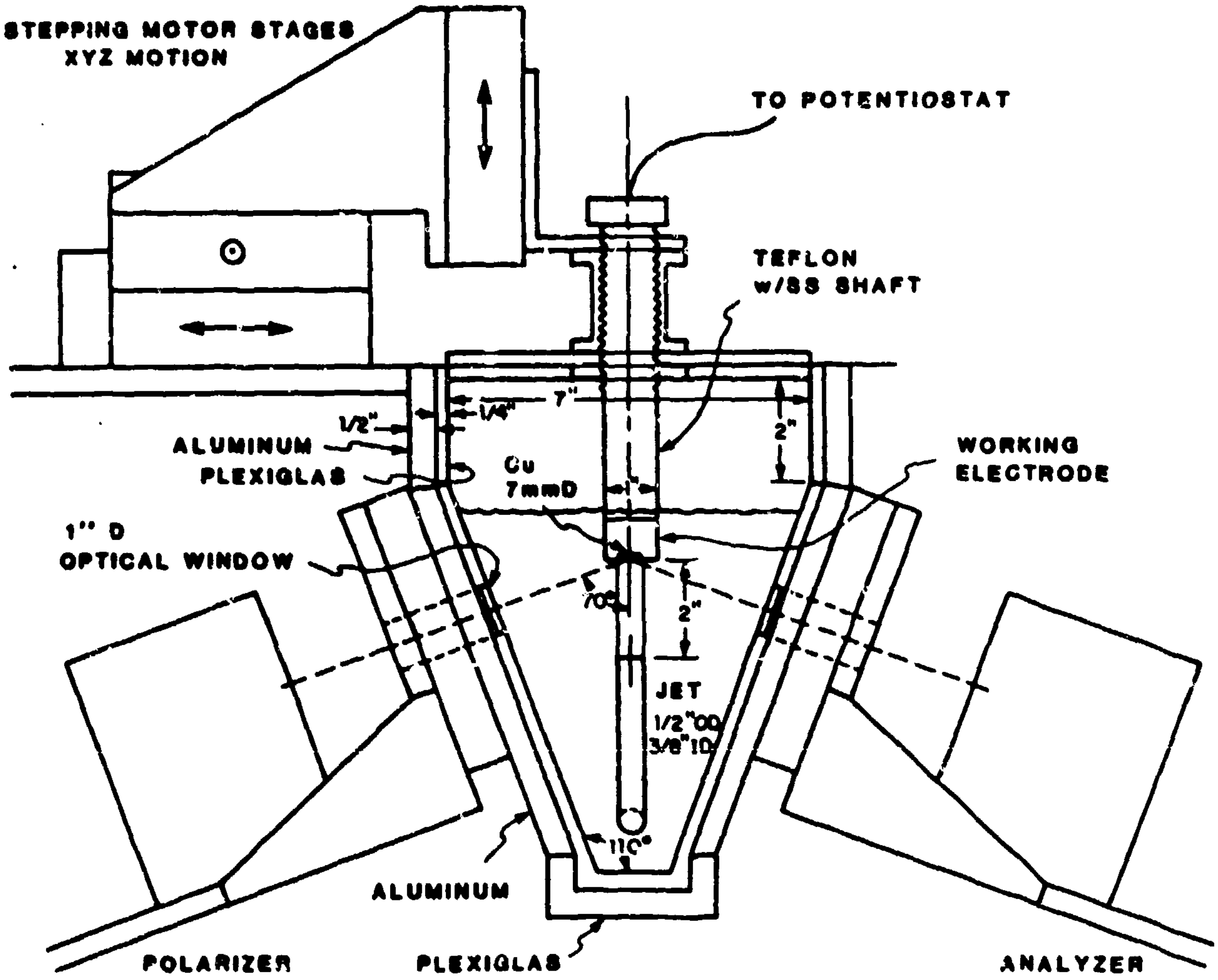

Figure 1. Schematic representation of the cell used in the impinging-jet apparatus for *in-situ* study of the erosion-corrosion of copper and copper-based alloys.

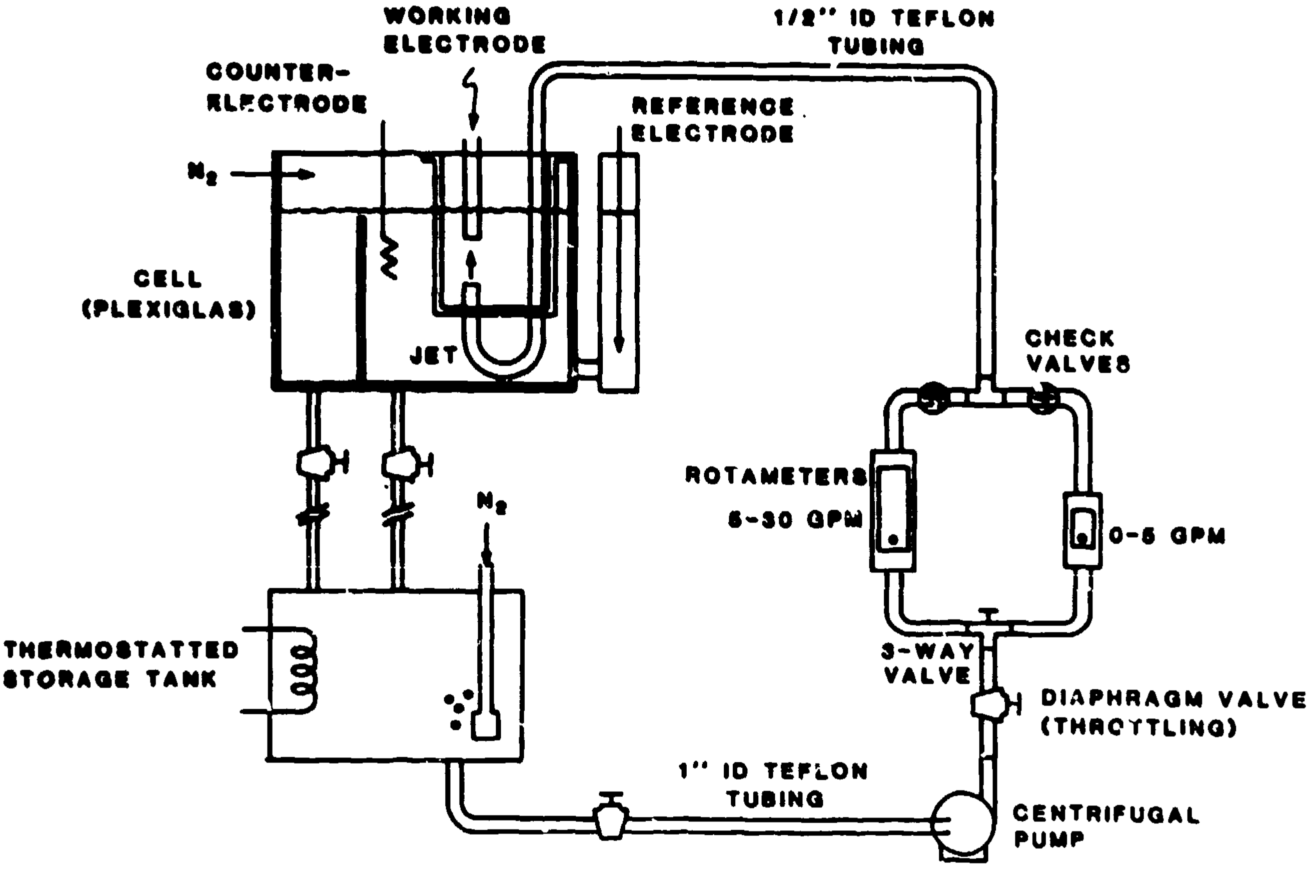

Figure 2. Schematic representation of the flow-system design for the impinging-jet apparatus for *in-situ* study of the erosion-corrosion of copper and copper-based alloys.

The concept of a critical shear stress may allow a more universal application of erosion-corrosion experiments. It is well known that values obtained for critical velocities in different experimental systems do not agree. Since, in the absence of mass transfer or impingement effects, the means of transfer of momentum from the fluid to the solid is the shear stress, the extent of erosion-corrosion by shear would be expected to be the same for different geometries only if the value of shear stress would be the same. This approach has been suggested by Efird[5] and by Silverman.[8] The use of this approach requires that experiments be conducted for which the effects of mass transfer, impingement, and shear can be quantitatively assessed.

The Impinging Jet Electrode

The impinging jet system comprises a submerged electrolyte jet impinging at 90° onto a flat specimen. The flow pattern for this system has been studied extensively[9-16] and is shown in Figure 3. Detailed mathematical analyses for this system have tended to concentrate on the stagnation and wall jet regions. The stagnation region is observed directly beneath the jet. Within the stagnation region, the axial velocity is independent of radial position. The flow in this region therefore resembles a rotating disk in that the surface is uniformly accessible to mass transfer. Further from the center line, a boundary layer is developed which is called the wall jet region.

The velocity distribution in the stagnation region has both radial and axial components. The velocity in the radial direction is given by[16]

$$v_r = ar\frac{df(\eta)}{d\eta}, \tag{1}$$

and the velocity in the axial direction is given by

$$v_z = -2\sqrt{a\mu/\rho}\, f(\eta); \tag{2}$$

where

$$f(\eta) = 0.656\eta^2 - \frac{1}{6}\eta^3 + 3.6444 \times 10^3\eta^6 + O(\eta^7),$$

and $\eta = \sqrt{a\rho/\mu}\, z$. The parameter a in equations (1) and (2) is the hydrodynamic constant with units of s^{-1}. It plays a role in the impinging jet system similar to that of rotation speed in a rotating disk system. The hydrodynamic constant is a function of jet velocity and the distance between the nozzle and the electrode and can be determined through independent electrochemical experiments. The fluid viscosity μ and density ρ are also measured independently.

The axial velocity is independent of radial position. Thus, a mass-transfer-limited current distribution across the electrode is uniform. The radial velocity is a function of radial position; it has a value of zero at the center of the disk and has a maximum value at the outer edge of the disk. Both the radial and axial velocities obey the no-slip boundary

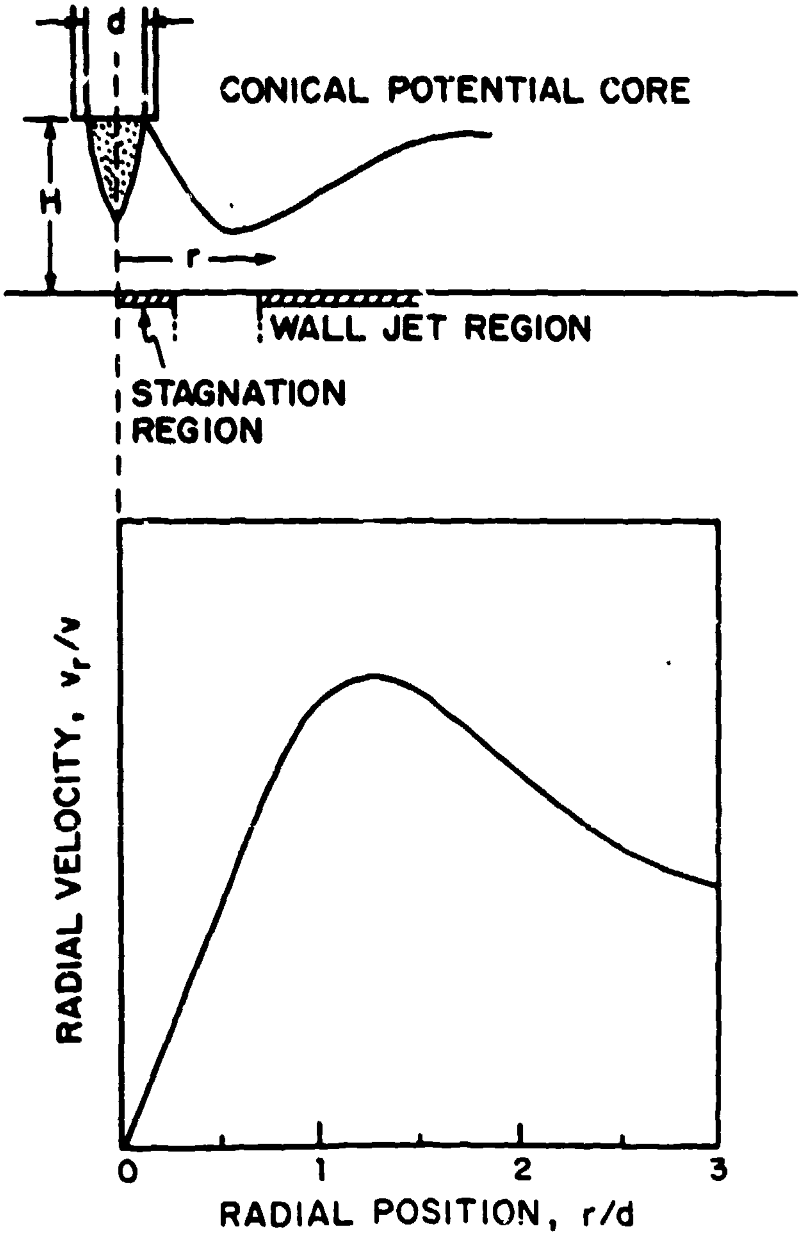

Figure 3. The flow pattern for a submerged impinging jet.

condition and are zero at the wall. The only non-zero value of surface shear stress is τ_{rz}, given by

$$\tau_{rz} = -1.312r(\mu\rho)^{1/2}a^{3/2}. \tag{3}$$

The shear stress is a linear function of radial position. It has a value of zero at the center of the disk and reaches a maximum value at the outer edge of the disk. The parameter a is the hydrodynamic constant which is proportional to the average jet velocity. The flow in the wall jet region is more complex and is described by Scholtz and Trass.[13]

Experimental Method

The impinging-jet system provides a unique environment for the electrochemical evaluation of film persistency. It can be used to distinguish clearly among the various modes of erosion-corrosion. The approach taken to identify a shear mode for removal of a film is illustrated in Figure 4. The shear stress on the electrode surface for a given average jet velocity is a linear function of radial position. The critical shear (τ_c) for removal of a protective film can, in principle, be obtained by measuring the profile of an electrode subjected to a given jet velocity. For velocity v_1, the radial position at which a sudden increase in corrosion rates is observed (r_{c1}) provides a value for the critical shear. The rate of corrosion at larger values of radial position can be determined from the electrode profiles, and these values provide the proportionality of erosion-corrosion rate to shear stress. At the higher jet velocity (v_2), the critical shear should be observed at a smaller radial position (r_{c2}). Thus, a single experiment can be used to scan a continuous distribution of wall shear stress values and thereby obtain the critical value. Experiments conducted at different velocities provide verification for the critical shear values.

Calculations similar to those presented by Newman[17] can be used to determine whether a nonuniform current distribution is expected from mass-transfer and potential distribution considerations. A numerical method for determining the current distribution from experimental current-potential data in the Tafel regime has been developed in this laboratory (see *Appendix A: Related Results from Previous Contracts*).[18-20] Usually, if a surface is protected by a film, the current distribution predicted by these calculations will be uniform. Therefore, if the corrosion is mass-transfer controlled, the enhanced corrosion rates will be uniform and not exhibit a critical radius. The use of profilometry provides information that is otherwise submerged in a simple weight-loss measurement, and these measurements provide an indirect proof of a shear mechanism for erosion-corrosion. This has been used here in the study of the persistency of inhibitor films;[21-23] however, this work also showed the need for a direct measure of film persistency (see *Appendix A*). Direct proof may be obtained by the use of scanning ellipsometry to measure local film thicknesses which should change in the presence of erosion-corrosion.

The advantages of this technique are:

- The fluid flow is well characterized. The hydrodynamic shear for the impinging-jet system in the stagnation region is a linear function of radial position and can be measured through a sensitive electrochemical technique.

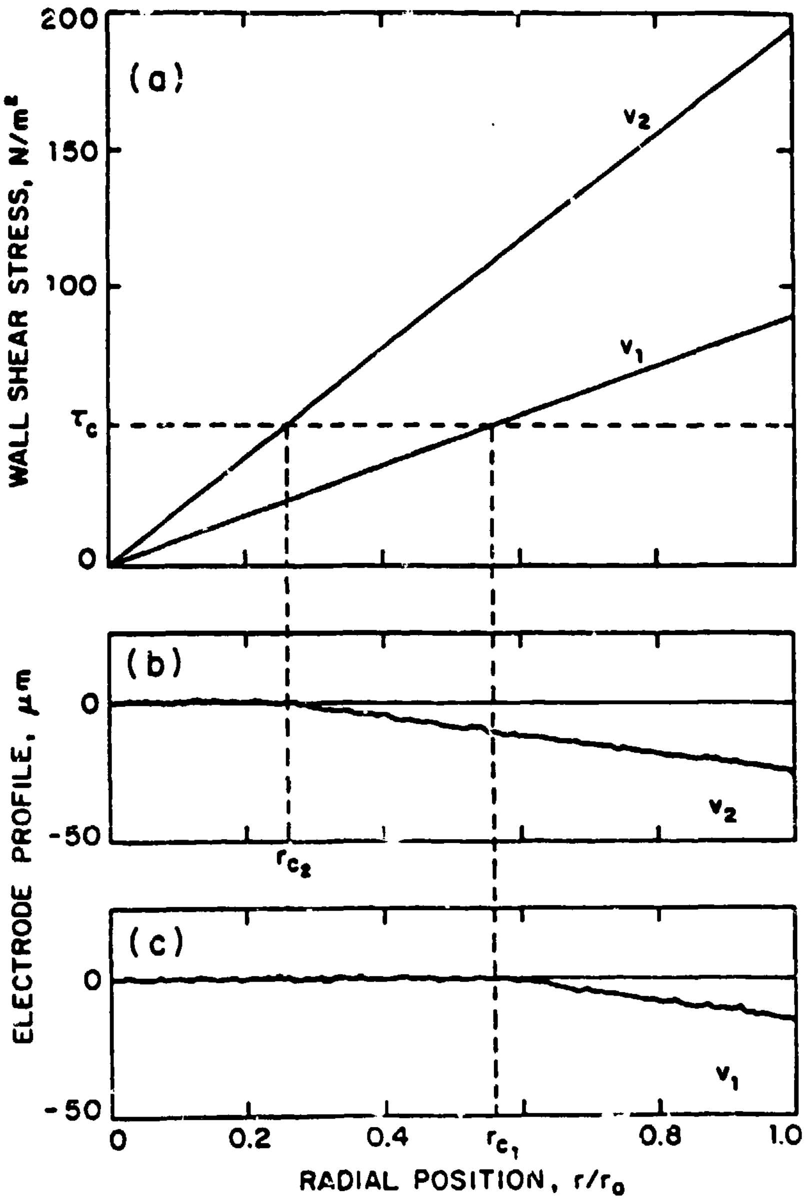

Figure 4. The use of electrode profile (or measured film thickness distribution) to identify a critical wall shear stress for removal of a protective film: a) wall shear stress as a function of radial position with jet velocity as a parameter; b) electrode profile as a function of radial position after sustained corrosion under jet velocity v_2; and c) electrode profile as a function of radial position after sustained corrosion under jet velocity v_1.

- Mass transfer to the disk is uniform. This prevents establishment of differential oxygenation cells and aids in the interpretation of experimental results. Fortunately, the constraint on electrode size given by the need for uniform mass transfer does not significantly reduce the maximum values of wall shear stress that can be reached as compared to the current practice. The wall shear stress reaches a maximum close to the radius where the mass transfer is no longer uniform.
- The electrode is stationary. This allows use of *in-situ* determination of film thickness by ellipsometry. Rotating disks and rotating concentric cylinders also provide well-characterized fluid flow with uniform mass transfer; however they cannot be used for *in-situ* ellipsometry which requires a stationary electrode.

The experimental design for the scanning ellipsometer will be presented at the T-5A Workshop on Fluid Flow Enhanced Corrosion, Corrosion/88, Saint Louis, Missouri, March 21-25, 1988.[24]

Preliminary Studies for the Corrosion of Copper in Saline Solutions

The corrosion of a rotating copper disk is being studied in aerated and deaerated 0.5M NaCl solutions as a function of applied potential, pH, and rotation rate. This work is intended to provide a foundation for the study of the influence of large values of hydrodynamic shear. Experiments are being conducted where the potential is swept from the corrosion potential to +2 V(SCE) at a constant rate, and where the potential is changed instantaneously from the corrosion potential to a potential of interest and held there for a given period of time. An example of the potentiodynamic results is presented in Figure 5 where the anodic current is presented as a function of applied potential with rotation speed as a parameter for an aerated solution with pH equal to 6.5. A significant effect of rotation speed is seen at potentials greater than 0.5 V(SCE). The may be associated with removal of a precipitated film which, at this potential, was loosely adherent.

Salt films and oxide layers were observed on the electrode surface, and these appeared either as rings growing inward with increasing potential from the periphery of the disk or as circles growing radially outward from the center. These observations can be explained in terms of the potential and current distributions expected on a disk electrode below the limiting current.[17] Rings growing inward observed during the corrosion of iron in sulfuric acid have been shown to be caused by deposition of ferrous sulfate salts.[25] The ring observed at low potentials may be associated with deposition of $CuCl_2$ which is sparingly soluble. The circles observed are probably associated with formation of copper oxides (see reference 26). This work, augmented with chemical and microscopic analyses of the corrosion products, will continue throughout the next year both for copper and for model alloys

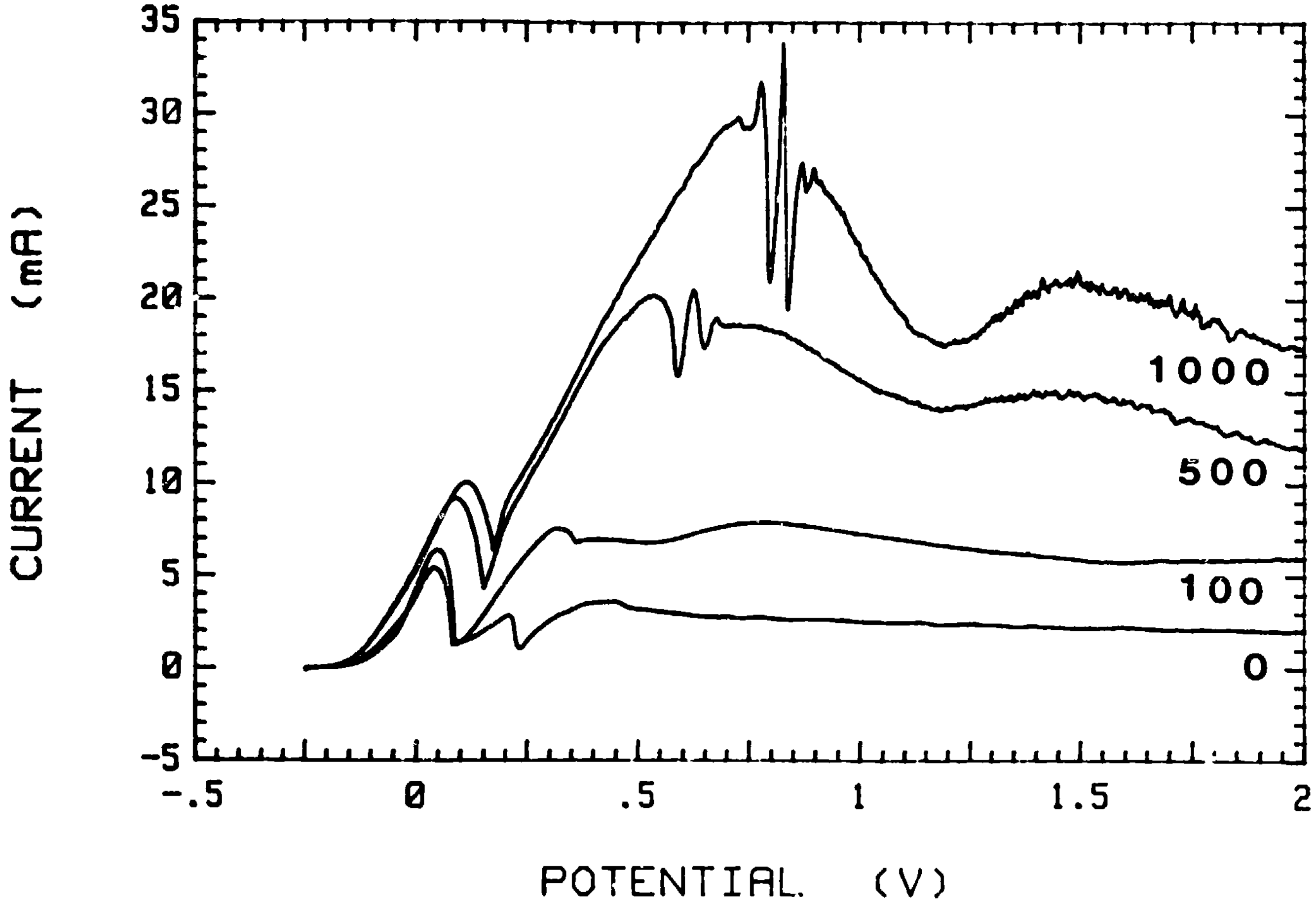

Figure 5. Current as a function of applied potential for a rotating copper disk electrode in a 0.5M aerated NaCl solution with rotation speed in rpm as a parameter.

Preparation of Copper–Aluminum Alloys

Aluminum bronzes are of two general types: the α or single–phase alloys, often referred to as homogeneous alloys, and the α–β, or two–phase alloys, known as duplex bronzes. Under perfect equilibrium conditions 9.8 percent of Al is soluble in Cu before the β phase appears, but, in practice, alloys containing in excess of 7.5 percent Al usually exhibit two phases.[27] Since the properties of the α–β alloys differ from those of the single phase, the duplex bronzes will not be prepared at this point. Also, under certain conditions of corrosion the α–β aluminum bronzes are susceptible to dealuminization.[27]

The alloys will be melted in an induction furnace located in the Department of Materials Science at the University of Virginia. The induction coils of the furnace will be concentrated near the bottom of the crucible, thus causing a temperature gradient in the crucible. To compensate for its higher melting point (1083°C as compared to 660°C for aluminum), the copper will be placed at the bottom of the crucible where it should melt first. The aluminum will be placed on the copper where it will receive less heat. The molten mixture is stirred by rocking the crucible for five minutes. A homogeneous composition and temperature distribution is obtained when the color of the melt matches that of the crucible (white). Care must be taken to avoid excessive temperatures which will cause loss of aluminum by vaporization. Some loss of aluminum will occur even under optimal conditions. The melt will be poured into a mold and slowly cooled. Impurities will presumably collect at the top of the mold, and this metal will be cut and discarded. The resulting ingot will be rolled, homogenized at about 800°C, cut turned, and annealed according to ASM standards.[28,29] Samples will be sent to outside laboratories to provide confirmation of alloy composition through chemical analysis.

Plans for Next Years Research

Our short–term plans for this work include:

- to complete construction and assembly of the ellipsometer system and to conduct preliminary experiments with copper in saline solutions to study the growth and removal of passive films under high–shear flow,
- to conduct rotating disk studies of copper electrodes in aerated and deaerated neutral and basic saline solutions to identify the conditions for passivation in the absence of erosive effects, and
- to conduct rotating disk studies of copper alloys in aerated and deaerated neutral and basic saline solutions to identify the effect of alloy composition on passivation in the absence of erosive effects.

Acknowledgement

This work is supported by the Office of Naval Research under Contract Number: N00014–87–K–0042. The support of Dr. A. John Sedriks is gratefully acknowledged.

Appendix A: Related Results from Previous Contracts

The work presented in this section was supported by the Chemical and Metals Division of Dow Chemical and the Virginia Center for Innovative Technology Grant Number MAT-86-028. An impinging jet experimental system, similar to that shown in Figure 1 but without an ellipsometer, was used to evaluate the influence of fluid flow on the performance of model corrosion inhibitors. A minimum (or critical) value for the shear required to remove the protective film was identified by profilometry (see Figure 4), and this value was found to depend on the inhibitor composition. This result indicates that it should be possible to tailor an inhibitor composition for maximizing protection under high velocities in a given fluid environment. In support of this project, a numerical method for compensation for ohmic resistance of the electrolyte was developed which identifies the current distribution on the disk expected from ohmic considerations. This is essential for separating transport effects from electrode kinetics. Another effort was identification of the reaction mechanism for corrosion in the absence of inhibitors which provides a foundation for understanding how inhibitors respond to high fluid velocities.

A New Method for Ohmic Compensation

A numerical method was developed for adjusting experimental current-potential curves for the ohmic resistance corresponding to a secondary current distribution on a (rotating) disk electrode. A novel and essential feature of this technique is that the compensation procedure also yields the extent to which ohmic effects cause the current distribution to be nonuniform. This allows the electrode profile to be used to identify enhanced corrosion caused by fluid shear.

The nonuniform current and potential distribution on the disk electrode cause the electrolyte resistance itself to be a function of measured current, a feature that cannot be seen by current-interruption methods of evaluating ohmic resistance. The method described here is employed after experiments are conducted and yields the Tafel slope as well as adjusted values for current density and surface overpotential that apply to the center of the disk. This facilitates comparison of experimental data to mathematical models of the rotating disk electrode that, in the secondary current regime, apply strictly only to the center of the electrode. The algorithm is written in interpretive BASIC 4.0 for an HP-310 computer, and iterative treatment of 25 current-potential data pairs generally requires less than 5 seconds. Analysis of 3000 data pairs requires about 3 minutes.

The Tafel slopes obtained using ohmic correction based on current interruption are only 2 to 5 mV/decade higher than those obtained by accounting for the nonlinear ohmic resistance. This agreement is seen because, at the high current densities where the ohmic correction is most significant, the resistance correction approaches the primary resistance obtained by current interruption. The Tafel slope values for the two methods differ most for solutions of low conductivity. The major advantages of the ohmic correction method described here are that the experimental condition is never perturbed and that the method indicates the extent to which the current distribution is nonuniform. This technique applies to cases where the rotation speed does not influence the measured current at a given applied potential and where the reference electrode is located far from the working electrode. Accurate values for solution conductivity and electrode diameter are also needed.

This work will be presented as an invited paper at the ASTM Symposium on Ohmic Electrolyte Resistance Measurement and Compensation, Baltimore, Maryland, May 17, 1988,[18] and will be submitted for review for the corresponding ASTM Special Technical Publication.[19] The software developed here will be used in the research on copper to help separate the effects of fluid shear on current distribution from mass transfer and ohmic contributions.

Corrosion of Iron in Chloride Solutions

Potentiostatic data were obtained for the dissolution of iron in deaerated acidic solutions with chloride concentrations of 0.1 M, 1.0 M, and 4.5 M, respectively, where the pH was adjusted by addition of HCl. The potentiostatic data were obtained for individually polished electrodes held at the applied potential for between 15 to 45 minutes. These data were corrected for the ohmic contribution to the measured potential. The ohmic correction procedure developed under this contract and described above yielded a Tafel slope value of 39 mV/decade for the 0.1 M Cl^- system, while the higher concentrations of 1.0 M and 4.5 M Cl^- gave values of 58 and 60 mV/decade, respectively. Several mechanisms have been proposed for this system. Tafel slopes of 60 mV/decade are consistent with the Lorenz mechanism; whereas, the lower value of Tafel slope obtained for the 0.1 M chloride system is consistent with a Bockris mechanism. The inhibitory effect of increased chloride ion concentration and the dependence on pH is consistent with the Lorenz mechanism, and this conclusion was supported by nonlinear regression of the data.

A paper based on this work is in preparation and will be submitted for publication.[30]

Evaluation of the Persistency of Inhibitors

The impinging jet electrode system was employed as a means of characterizing the performance of several model and commercial corrosion inhibitors, provided by the Chemical and Metals Department, DOW Chemical, USA. The objective of this study was to quantify the quality of inhibition of pure iron corroding in an aerated-acidic chloride environment in the presence of a single-phase fluid flow. Since inhibitors primarily protect the metal by adsorbing onto its surface, evaluation of its performance in the presence of fluid flow and high-shear conditions must be undertaken. Fluid flow generally increases the rate of corrosion by increasing the rate of mass transfer of species to the reactive sites; for example, the rate of the oxygen reduction reaction at the cathodic site is increased by the transport of oxygen to the reactive surface. When metals are protected by oxide or inhibitor films, corrosion rates may be increased significantly by the mechanical removal of the film by large values of wall shear stress or by the impingement of solids and bubbles carried by the fluid stream. Erosion-corrosion combines the mechanical attrition of the metal surface and the electrochemical reaction with the aggressive environment.

The concept of critical shear, the minimum force required to remove a protective film, was used to compare the film persistency and efficacy of the different corrosion inhibitors. The shear stress at the electrode surface is proportional to the radial distance from the electrode centerline. The critical radial distance was inferred from the surface profiles of a corroded electrode surface to yield the critical wall shear stress, a major contributor to the enhanced corrosion at the periphery of the disk.

Two corrosion inhibitors were obtained from the Chemical and Metals Department of DOW Chemical, USA in purified form. The two pure compounds were amino ethyl heptadecyl imidazoline and 2–heptadecenyl–2–imidazoline. An additional single compound inhibitor, 1–octene–3–ol, and a fully formulated commercial inhibitor were also tested. The values obtained for critical shear stress were:

- 1–octene–3–ol: $\tau_{rs,crit} = 411 \pm 57$ dyne/cm^2 at -350 mV (SCE) and $\tau_{rs,crit} = 331 \pm 52$ dyne/cm^2 at -250 mV (SCE),
- amino ethyl heptadecyl imidazoline: $\tau_{rs,crit} = 718 \pm 160$ dyne/cm^2 polarized galvanostatically at 2.5 mA/cm^2 (corresponding to -485 mV (SEC)),
- 2–heptadecenyl–2–imidazoline: $\tau_{rs,crit} = 606 \pm 137$ dyne/cm^2 polarized galvanostatically at 2.5 mA/cm^2 (corresponding to -475 mV (SEC)), and
- Dow 36421–18: $\tau_{rs,crit} = 376 \pm 28$ dyne/cm^2 at -475 mV (SCE).

These results suggest that amino ethyl heptadecyl imidazoline may be a more effective inhibitor in high velocity acidic chloride solution than is 2–heptadecenyl–2–imidazoline and that both imidazoline compounds are have superior persistency as compared to 1-octene-3-ol and the formulated inhibitor in these solutions. These results are preliminary and more work is needed to identify the effect of potential, solution composition, and inhibitor composition on prevention of corrosion in high velocity environments.

A portion of this work was presented at Corrosion/87, the national meeting for the National Association of Corrosion Engineers and has been submitted for publication in *Corrosion*.[21,22] While this work demonstrated that inhibitor compounds can be removed by fluid shear and that the resistance to removal is a function of chemical composition and applied potential, the data obtained through profilometry after extended corrosion were very scattered. This work showed the need for a direct measure of erosion–corrosion effects through ellipsometry.

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