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THEORY AND APPLICATION OF THE STAINING ELECTRODE

DISSERTATION

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

By

Tomomi Murata, B.Met.Eng., M.S.

***

The Ohio State University
1971

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GENERAL INTRODUCTION

The straining electrode is significant because most metals, which are used as electrode substrates, are under some type of mechanical stress and locally surface dislocations are always moving slightly. One incentive to study the straining electrode is simply to better understand the substrate under which the electrode processes are occurring. Another incentive to study the straining electrode is that several important technological problems are related to the properties of the straining electrode, primarily these are stress corrosion cracking, pitting and hydrogen embrittlement. The straining electrode is also used by chemists and electrochemists to study the properties of clean metals since straining electrodes provides a continuous source of fresh metal to the electrolytes.
INTRODUCTION TO LITERATURE SURVEY

1. Information Obtained from the Straining Electrode

For a given electrode-environment system the straining electrode provides information on the following properties.

(1) Initial anodic current density measurements at freshly produced slip steps on both film-covered and film-free electrodes.

(2) Repassivation processes, from which the mechanism of film formation and film properties could be analysed, at freshly produced slip steps on film-covered electrodes.

(3) Anodic current decay processes, from which transient dissolution of surface atoms could be analysed, at freshly produced slip steps on film-free electrodes.

(4) Rate of area increase during straining, for a given strain rate, could be obtained for both film-free and film-covered electrodes. This information is useful especially for the calculation of current density at slip steps.

(5) Effect of elastic stress on electrode behavior for both film-covered and film-free electrodes.

The information described under (1), (2), (3), and (5) can be obtained in terms of overpotential, anion and cation concentrations, pH, temperature, concentration of oxygen, solution flow rate, strain, strain rate, chemical composition of the electrode, surface preparation, and
metallurgical conditions of the electrode such as grain size, dislocation density (annealed or cold worked), and presence of second phase. Probably, the most significant technological applications of straining electrode are concerned with understanding the mechanisms of metallic deterioration under any type of stress as in stress corrosion cracking, hydrogen embrittlement, and pitting, although the amount of the information obtained from the straining electrode is limited from the very fundamental point of view because of the complexity of the experiment.

2. Important Unit Processes which should be Considered in Straining Electrode Studies

The unit processes and important considerations in the metal and environment, i.e. the separable processes which can be treated individually on a semi-quantitative basis, are described and evaluated in the following paragraphs.

(1) Surface characteristics

The characteristics of the crystal surface can be described by the kink-ledge-terrace model shown in Figure 1 and proposed originally by Kossel and Stranski. Even though this is a crude description of the surface, a better picture of the surface is not yet available) this model predicts many surface properties on film free electrodes. In addition to these surface characteristics dislocations-emerged to the surface and grain boundaries-are present.

(2) Potential of Zero Charge

When a metal is immersed in an electrolyte, an electric double layer is formed at the interface causing an excess charge on the metal
Fig. 1.—Schematic view of vicinal surface showing low index terraces, monatomic height ledges, atoms at positions described as (a) in surface, (b) in ledge, (c) at kink, (d) at ledge, and (e) adsorbed, and impurity atoms (f) adsorbed, (g) at ledge, (h) at kink. Alternate description of atoms positions by the number of nearest neighbors adjoining a site (11,16), for a (111) fcc surface would correspond to (a) 9 site, (b) 7 site, (c) 6 site, (d) 5 site, and (e) 3 site.

(Hirth)
side of the interface and a net excess of one kind of ion on the electrolyte side of the double layer. Electroneutrality conditions are thus fulfilled.

For an ideally polarized electrode, i.e., an interface across which charge transfer does not occur, the Gibbs adsorption isotherm at constant temperature and pressure is given by

$$d\bar{\gamma} = -q^m dE + \sum Z_i^\gamma d\mu_i$$

(1)

where $\bar{\gamma}$ is the interfacial tension (or surface energy); $q^m$ is the charge on the metal per unit area; $E$ is the electrode potential; $F$ is the Faraday; $Z_i$ is the charge of the ionic specie $i$; $\gamma_i$ is the surface excess of specie in the double layer; and $\mu_i$ is the chemical potential of the specie $i$.

Hence the excess charge density on the metal is

$$\left(\frac{\partial \bar{\gamma}}{\partial E}\right)_{T,P}, \mu_i = -q^m$$

(2)

and the potential at which the metallic side of the double layer has no excess charge ($-q^m = 0$) is defined as the potential of zero charge.

While the potential of zero charge is not a unique property of a metal but a function of the kind and the concentration of ions in the electrolyte, it could be a rational scale of electrode potential. The potential on the rational scale is given by the deviation from the potential of zero charge and is indicative of an approximate charge on the electrode.
(3) Charging of the Double Layer

The current involved in charging the double layer of freshly formed surfaces will contribute to the total current of the straining electrode. This contribution has been discussed by Bockris et al, Beck, Barnartt and Johnson, and Gerisher. Essentially the current from this contribution can be calculated by knowing the differential capacity of a clean surface at the final potential of the reacting surface (where the strain event occurred) relative to the potential of zero charge. The total coulombs involved, \( Q \), then are

\[
Q = K_I (E_I - E_{pzc})
\]

(3)

where \( K_I \) is the integral capacity up to \( E_I \) starting from \( E_{pzc} \) and \( E_I \) is the potential on the reacting surface. An approximate maximum value for this contribution would be equivalent to dissolving one layer of atoms from the surface or 0.3 mc/cm² of a doubly charged species. This contribution at best is only very approximately calculable because of the geometrical problem shown in Figure 2 and because in most cases the surface is covered by a film and the double layer capacities here are known only approximately for a few cases.

(4) Clean vs. Film-Covered Surfaces

The transient current response of a straining electrode depends greatly on the initial condition with respect to being electrochemically clean, covered with an adsorbed layer or covered with a three dimensional film. In the work of Bockris the surfaces were clearly dissolving according to activated kinetics on film-free surfaces. Early in the work of Hoar with stainless steels in MgCl₂ and through the paper of reference
(20-26) he assumed an actively dissolving surface as the initial state; however, this has been shown by numerous authors to be an incorrect assumption. This also raises questions of applicability of the work by Howard and Pyle\textsuperscript{27,28} since they applied their ledge propagation to stress corrosion cracking but most SCC occurs on film covered metals. The works by Eyring and his associates are also incomplete since the electrode surfaces and potential transients were not well defined in the light of modern electrochemistry. Galvel\textsuperscript{29}, Slater\textsuperscript{30} and Humpries and Parkins\textsuperscript{31} have defined clearly that a prior film exists in the case of their studies on carbon steels and stainless steels.

(5) Charge Due to Film Formation

When the metal environment system is such as to form protective films, part of the current transient associated with straining will be associated with forming a new film. Assuming the film to be Fe\textsubscript{2}O\textsubscript{3} on iron, there would be 915 X 10\textsuperscript{-5} coulombs per A of thickness per cm\textsuperscript{2}. The details of kinetics of forming these films vary among metals but the Mott-Cabrera model is a good first approximation where

\[
\frac{1}{d} = A - B(\log)t
\]

Here \( d \) = film thickness
\( A, B \) = constants
\( t \) = time.

(6) Elastic Stress

Elastic stress is ideally defined as the stress under which no dislocations move, but practically, some dislocations starts moving under
a stress far below the elastic limit. This is especially true for engineering polycrystalline materials because of the complex state of local stresses and the presence of dislocation sources. Elastic stress which we discuss hereafter is the latter one. The effect of the elastic stress must be considered in terms of surface properties for any system in which an electrochemical variation occurs at the metal-liquid interface.

(7) The Slip Process

When a metal is deformed a disregistry occurs on the surface due to the movement of dislocations. This disregistry can essentially two shapes as shown in Figure 2. The actual situation is very complicated, since the mode of slip changes during deformation. In face centered cubic metals, the early stages of deformation tend to look like case I of Figure 2, whereas, at later stages of deformation the surface slip approaches the morphology of case II owing to cross slip and dislocation-dislocation interactions within the metal. This tendency for starting with case I is based on the restricted number of slip systems available (111) [110]. In bcc metals the initial stages of slip tend to look like case II because of the more complicated slip systems; and the slip becomes even more complex as deformation proceeds. Additionally, factors such as lowered stacking fault energy and ordering tendency to favor case I slip; whereas, as shown by Latanision and Staehle\textsuperscript{32}, the presence of a film promotes the more diffuse slip of case II. Further, workers studying the behavior of fcc materials, e.g. Mitchell and his co-workers\textsuperscript{33}, have shown that case I slip is not realistic but in
Fig. 2.—Slip modes.

The slip which really occurs is a combination of cases I and II. The height \( h_k \) and width \( d_k \) of the slip events are variable. The height of slip events is certainly much greater than one Burgers vector, \( b \), and may vary from \( 5b \) to \( 100b \); there is certainly no unit step height as suggested by Bockris et al.\(^{19}\). The complicated nature of slip plus the grain rotation at high strains undoubtedly accounts for the "roughness factor" invoked by Bockris. In fact, from a metallurgical point of view, it is difficult to separate reasonably the process into "roughness", "line ledges", and "high index planes" as Bockris et al. have done.

(8) Increasing the Ledge Density, Roughness and High Index Planes

In the paper by Bockris et al.\(^{19}\) an attempt is made to divide contributions from these respective ideas. This approach, while lacking metallurgical discrimination as described above, is certainly a reasonable one but it is useful only for active surfaces. In the case of film covered surfaces, it can be expected that the ledge propagation is stifled early by the formation of the film. Bockris points out that complex slip will produce effectively a high index plane and this will dissolve rapidly until a stable configuration is obtained in case of film free electrodes as shown in case I of Figure 2.

(9) Reactivity of Dislocations\(^{34,35}\)

Dislocations are energetically more reactive than the surrounding matrix because (a) lattice distortion and strain field of the dislocation which is the order of 5-8 eV per atom plane, (b) geometry of planes associated with a screw dislocation which is the reverse of crystal growth in case of dissolution (this will be described in detail
later); and (c) segregation of impurity atoms at the dislocation which changes the chemical composition around the dislocation.

Generally, the elastic energy of an edge dislocation per unit length is more than that of a screw dislocation and the core energy of the dislocation, which must be estimated because linear elasticity theory cannot be applied, is in the order of 0.5-1.5 eV for each atom plane threaded by the dislocation. Static dislocations are, in general, chemically more reactive than moving dislocations: the moving dislocations will not be decorated by impurity atoms if the dislocations move faster than the diffusion rate of the impurity atoms.

(10) Plasticity of Films

When a film-covered metal deforms there is no clear basis for defining the criteria for the actual breaking of the film and subsequent exposure of clear metal. If the film is sufficiently plastic, then substantial deformation will occur before the film ruptures, and the converse applies for brittle films. The relative plasticity of films has been studied by Vermilyea and Bubar

\[36,37\] as well as Leach and Neufeld

\[38,39\]. Depending on the interaction between the slip modes of Figure 2 and the film plasticity, the reaction current during straining will vary with the absolute strain and the strain rate.

Deformation of the film, which has an ionic character, tends to produce so called "exoelectron" emission\[40\] in proportion to strain rate. It is believed that trapped electrons at defect centers within the film are excited to the conduction band and give up their energy to nearby shallow surface centers from where electrons are emitted. This effect,
however, could be neglected in most electrochemical studies because the exoelectron emission contribution is only in the order of $10^{-14} \text{A/cm}^2$, which is several orders of magnitude smaller than any passive current density observed. Dislocations in ionic crystals will, in general, carry an electrical charge and produce charged point defects resulting in transient electrical effects. These effects could also be neglected because, whenever surface thin films are broken by the action of dislocations, bare matrix surface will be exposed to the electrolyte and will generally produce several orders of magnitude higher current density.

(11) Material Dissolved before Film Formation

In many film-covered surfaces where the film is first broken and then repaired, a certain amount of metal is dissolved before the film is repaired. The resulting morphology as illustrated in Figure 3 is based on film dissolution studies by Swann and Embury or Smith and Staehle where a thin metal foil has been exposed to the environment, stressed, and examined by electron transmission microscopy. The approximate number of coulombs, $Q$, dissolved from a trench such as the one in Figure 3, assuming linear penetration per unit area, is

$$Q = \int_{0}^{\infty} j_a^0 e^{-\beta t} dt = \frac{j_a^0}{\beta} = \frac{nF\rho x}{\mu}$$

where: $j_a^0 =$ current density at fresh surface

$\beta =$ decay constant

$F =$ Faraday constant
Fig. 3.—Schematic model for the local dissolution and repassivation at slip step.
n = Valence number of dissolving ions  
\( \rho \) = density of dissolving metal  
M = Gram molecular weight of dissolving metal  
X = penetration distance.

In summary (1) it is very difficult to be specific about slip morphology, (2) the initial surface must be clearly defined with respect to presence or absence of films and (3) the approximate number of coulombs involved in important unit processes are in the order of several hundreds of angstroms in the case of 18-8 stainless steel in sulfuric acid at room temperature. The most important contribution is that from metal dissolution before repassivation occurs. When this process operates high currents can be expected.

3. Phenomenological Description

A metal corroding at steady state in an electrolyte will have a polarization behavior described by Figure 4(a). Here the initial anodic and cathodic polarization curves are \( A^i \) and \( C^i \) and is the corrosion potential. These curves do not presuppose a particular type of kinetics (activated or film covered). If, upon straining at open circuit (see Figure 4(b)), the anodic kinetics are increased from \( A^i \) to \( A^s \) (s = straining), the corrosion potential (see Figure 4(c)) drops from \( E_{corr}^i \) to \( E_{corr}^s \). Here it has been assumed that the cathodic kinetics are unaffected. The corrosion potential will recover depending on how rapidly the transient introduced by straining is recovered. If the cathodic kinetics are influenced more than the anodic kinetics, a positive transient will be observed.
Fig. 4.—Phenomological description of open circuit strain transient.
If the specimen is strained at constant potential, a slightly different interpretation applies according to Figure 5. Here at potential $E^\circ$ (controlled potential) the steady state current is initially at b and increases to c when the specimen is strained. The current monitored decreases from c to b as $A^5 \rightarrow A^1$ as shown in Figure 5(c). Again the cathodic kinetics are assumed to change negligibly here.

Figures 4(c) and 5(c) were constructed from a strain pulse; however, if the straining were continuous the potential minimum or the current maximum would be sustained until the cessation of deformation, whereafter; these quantities would decay.

It is possible to construct a similar set of figures for galvanostatic control but the pattern would be the same as described in Figures 4 and 5.

4. Historical Aspect of Straining Electrode

Key experiments concerning straining electrode will be briefly cited here. The effect of elastic stress and cold work on electrode behavior, such as the change in rest potential (or corrosion potential) and anodic dissolution rate, has been of interest to numerous investigators since the accelerated anodic dissolution of metals in the presence of stress in acid solution was first reported by Osmond and Werth in 1885. Reported studies since then, however, have been inconclusive mainly due to the different surface preparations, i.e., film free or film present; the presence of a deformed surface layer during specimen preparation; impurity content of the electrode; and different sign conventions for the direction of potential change.
Fig. 5.—Phenomelogical description of the strain-induced current transient at fixed potential.
The straining electrode was suggested first by Hoar and Hines in 1956 as a tool for studying the stress corrosion cracking of metals. The essential rationalization for this suggestion was based on the fact that the metal at the base of an advancing stress corrosion crack can be thought of as straining locally at a relatively high strain rate. Therefore, it is reasonable, according to Hoar, to assume that any electrochemical analysis of crack velocity should be performed on straining material. On the basis of this hypothesis a number of papers were published by Hoar and his colleagues showing that there was good correlation between stress corrosion cracking and results from straining electrode studies. Hoar proposed a theoretical explanation for these straining electrode effects.

Straining electrode studies on film-free electrodes were recently conducted by Dockris and his colleagues, Devanathan and Fernando, and Winfeld in an attempt to understand the fundamental aspects of mechano-electrochemical dissolution. The most controversial problem is whether dynamic straining or cold work reduces the activation energy for anodic dissolution or increases the number of available sites for dissolution and this problem is still unresolved.

Straining electrode studies on film-covered surfaces have been conducted for the last ten years by numerous investigators including Parkings and Humphries, Hanie and Boyd, Hoar and his colleagues, Takano and Shimodaira, Graf and Spring, Leach and his coworkers, Venczel and Wranglin, Swann and Pickering and Murata and Staehle. Most of the above mentioned studies on film-
covered electrode are directly associated with the study of stress corrosion cracking of alloys.

The effect of sudden plastic deformation on the electrode potential decay was studied extensively by Eyring and his co-workers and Leidheizer and Kellerman at open circuit potential while Shibata and Staehle conducted their experiments potentiostatically. This type of experiment so called "strain electrometry" is equivalent to straining electrode experiments at extremely high strain rates. Recently proposed theoretical interpretations of the straining electrode in terms of Rayleigh waves have been published by Howard and Pyle. Thermodynamical analysis of a stressed solid was conducted by Yang, Horne and Pound and Li, Oriani and Darken. In addition to these studies irreversible thermodynamics of a yielding metal was proposed by Gutmen in 1967.

5. Techniques

The straining electrode is being employed by workers cited earlier using a number of techniques depending on the aim of the investigation.

(1) Direct Straining

Here the specimen is placed on an electrochemical cell and pulled in tension. The electrochemical measurement can be made potentiostatically (i.e. measure i at constant E), by measuring the potential transient at constant current, or by measuring the transient behavior of the open circuit potential. In this experiment the specimen should be sufficiently ductile for total strains of at least 10-20%. Such experiments have been performed by Hoar and co-workers, Parkins and Humphries, Bockris et al., and others.
(2) Strain Transient

In this case a small predetermined strain transient is imparted to a specimen as described by Eyring and his colleagues and Leidheizer and Kellerman. Electrochemical measurements are made as above. This approach provides a better defined surface area than for the continuously deformed straining specimen. Such a surface can be examined after the experiment using an appropriate physical technique.

(3) Rapidly Broken Brittle Specimen

Beck has studied the transient behavior of titanium specimens by rapidly loading to failure and monitoring the current at constant potential. The specimens were relatively brittle and the experiment provided initially clean surfaces of known overall area. By measuring the anodic and cathodic response, a series of time-dependant polarization curves were obtained. These data were applied to studying electrochemical reactions at a crack tip. This technique poses obvious problems of defining the newly formed surface area and the metallurgical state of the phenomenon to be explained especially for a ductile material.

(4) Scrape or Abrasion

Clean surfaces can be exposed by abrading or scratching the surface. This can be done under the same electrochemical conditions as for item (1) above. Such experiments have been performed by Russian workers using a corundum disk to study cathodic processes, anodic dissolution and passivation as well as the effect of adsorption of anions on the kinetics of electrode and corrosion processes and by Beck using rotating electrode scraped with sapphire cutter in 6M HCl.
(5) Rotating Electrode in Abrasive Slurry

A film covered metal can be kept activated by rotating in an abrasive slurry; when the rotation is sluggish, the film will form. Such studies have been conducted by Bartholf and Beck\textsuperscript{92} using commercial alloy electrodes in $\text{Al}_2\text{O}_3$ or $\text{SiO}_2$ containing solutions. Again the electrochemical measurements possible here are the same as for item (1) above. This technique has difficulties in the area of defining the exact time of differentiation between clean surface and start of film growth because of the momentum decay of the slurry.

(6) Potential transients

The straining electrode may be also approximated by a rapid transition of potentials between a condition where the surface is immune to a condition of activated dissolution or film formation. The resulting transient current may then be monitored as a function of appropriate variables. Such studies have been conducted by Barnartt\textsuperscript{93} studying the activation and diffusion parameters for the $\text{Fe}^{+2}/\text{Fe}^{+3}$ electrode and by Novakovski and Likhachev\textsuperscript{94} for passive films.

This is the first time that the entire subject of so called "mechano-electrochemical" area has been reviewed. The study of the effect of various stresses or strains on the electrode behavior involves very fundamental problems such as work function ($\varphi$) for an electron tunneling, surface energy, surface stress, surface defects, potential of zero charge and electric double layer as well as technological applications such as stress corrosion cracking and hydrogen embrittlement.
First the effect of elastic stress on the electrode behavior will be reviewed. This is followed by the effect of cold work, the effect of sudden plastic strain and finally the effect of dynamical straining on the electrode behavior will be reviewed and discussed. Each section involves substantial criticisms concerning the techniques and the theories developed.
I. ELECTRODE UNDER ELASTIC STRAIN

When a metal is strained elastically its internal energy is increased. This process is mechanically reversible below elastic limit. The change in free enthalpy under constant pressure and temperature may be given by

\[ \Delta H = \frac{\sigma^2}{2E} \quad (6) \]

where \( \sigma \) is applied stress and \( E \) is Young's modulus of elasticity. The volume change during straining is negligible and the internal energy is approximately equal to enthalpy. Numerous papers have stated that a metal having either elastic or residual strain energy could be assessed as a reversible electrode in a given environment using the relationship in equation (7) where the increase of internal energy of stressed solid is converted to the potential change at the interface.

\[ \frac{\sigma^2}{2E} = -n\Delta E F \quad (7) \]

Here \( n \) designates the valence number of reacting ions at the interface, \( E \) is the potential change (due to the applied stress in this case), and \( F \) is the Faraday. Equation (7), however, is not correct because of the following reasons: (a) a metal with elastic or residual strain energy cannot have a reversible electrode potential as pointed out by Clark. 

23
whereas; relation (7) holds only for the reversible reaction in equilibrium; (b) $\sigma^2/2E$ is a bulk property and, therefore, is not necessarily a surface property such as potential change ($\Delta E$) at the metal-electrolyte interface; (c) $\sigma^2/2E$ may not be the correct expression for the internal energy increase from a practical point of view because dislocations move at stresses well below the elastic limit, especially for polycrystalline materials.

In addition, the metal surface has to be film-free in order to discuss the effect of elastic stress from an equilibrium thermodynamical point of view.

There is substantial confusion concerning the study of the effect of stress on the electrode behavior since: (a) the electrochemical behavior of both cold worked and elastically strained electrodes have been discussed on the same basis; and (b) the electrochemical behavior of film-free and film-covered electrodes have not been clearly separated although they behave quite differently as briefly mentioned in the introduction. In this chapter the works on electrodes subjected to elastic strain will be reviewed and critisized and studies on cold worked electrodes will be treated in the next chapter.

Two types of potential change upon application of an elastic strain have been reported by Nobe and his co-workers$^{94-98}$, Giolotto$^{99}$ and Fryxell and Nachtrieb$^{100}$, Bockris et. al$^{101}$, Eyring and his colleagues$^{64}$, Richards and Behr$^{102}$ and Murata and Stachle$^{103}$: (1) transient potential changes which lasts only a few seconds; (2) rather permanent but reversible potential changes with elastic stress. Other works which could be
relevant to this subject, from an historical point of view, are those by Ramsey, Cohen, Ynovye and Euwen and Poulter and Ritchey.

1. Transient Potential Change (Open Circuit)

The transient potential change observed upon the application of elastic tensile stresses on film-free electrode was first reported by Nobe and his co-workers for Cu-CuSO₄, Cu-NaCl and Zn-ZnSO₄ systems. Typical data are shown in Figure 6 where the direction of the copper electrode potential change induced by tensile stress changes from negative to positive as the concentration of CuSO₄ decreases from 1N to 0.001N upon removal of the load the change is in the opposite direction. The concentration dependence of the direction and the magnitude of transient potential changes is shown in Figure 7.

The above investigators attributed the strain induced electrode potential, which was found to decay to almost that of a strain free electrode in a few seconds, to the alteration of the double layer capacitance at virtually fixed charge. Considering Stern's model of the electrical double layer at the metal-solution interface, there is a charge per unit area of the metal, and the corresponding charge in solution is composed of the charge \( q_1 \) in the adsorbed layer and the charge \( q_2 \) in diffuse layer.

\[
q_1 + q_2 = q_0
\]  

(8)

The electrostatic potential difference \( \psi_0 \) is also composed of \( \psi_1 \) of the adsorbed layer, and \( \psi_2 \) of the diffuse layer. Assuming the total charge
Fig. 6.—Potential response, strain is $3.42 \times 10^{-4}$.
(Nobe et al. 96)

Fig. 7.—Potential response amplitude vs. strain.
Dotted circle 1N CuSO$_4$; dotted square 0.1N CuSO$_4$; dotted triangle 0.01N Cu SO$_4$; dotted diamond 0.001N CuSO$_4$.
(Nobe et al. 96)
stays constant before and after elongation, \(qA = \text{constant}\)

\[
\frac{dq}{q} = -\frac{dA}{a} = -\left(\frac{dL}{L} + \frac{dr}{r}\right)
\]

(9)

where \(A\) is the surface area of the electrode.

Introducing poisson's ratio

\[
\frac{dq}{q} = -(1 - \mu) \frac{dL}{L}
\]

(10)

and therefore,

\[
\frac{d\psi}{dL} = -(1 - \mu) \frac{d\psi}{dq}
\]

(11)

since \(\psi_0 = \psi_1 + \psi_2\) the potential change is

\[
d\psi_0 = -(1 - \mu) \frac{dL}{L} \frac{d\psi_1}{dq} \frac{d\psi_2}{dq} + \frac{d\psi_2}{dq}
\]

(12)

The potential across the adsorbed layer is the same as that across a capacitor with charge density \((q_1)\) after elongation.

\[
\frac{d\psi_1}{q_{1dq_1}} = \psi_1
\]

(13)

The charge across the diffuse layer was calculated by Butler\(^{106}\) by balancing the effects of coulombic and diffusional forces within the double layer. In the case of dissolution and deposition of the same ion \(q_2\) is given by

\[
q_2 = 2\sqrt{\frac{DRTC}{2}} \sinh\left(\frac{Zeq_2}{2kT}\right)
\]

(14)
where D is the dielectric constant of the electrolyte; C is the electrolyte concentration in moles per cc; Z is the valence of positive and negative ions and e is the charge on an electron. Thus, from equation (14) we obtain

\[ \frac{d\psi_2}{q_{2dq_2}} = \frac{2kT}{Ze} \tanh\left(\frac{Ze\psi_2}{kT}\right) \]  

(15)

Substituting (13) and (15) into (12) and using the relation, \( \varepsilon = \frac{dL}{L} \), we obtain

\[ \Delta \psi_0 = -(1 - \mu) \varepsilon \psi_0 \text{ (for small } \frac{Ze\psi_2}{2kT} \text{)} \]  

(16)

\[ \Delta \psi_0 = -(1 - \mu) \varepsilon \left[ \psi_1 + \frac{ZkT}{Ze} \right] \text{ (for large } \frac{Ze\psi_2}{2kT} \text{)} \]  

(17)

This potential difference between stressed and unstressed electrodes will decay with time toward the equilibrium value which the authors defined, according to equation (7), as

\[ \Delta E = -\frac{Ma^2}{2EnpF} \]

where \( p \) is the density and \( M \) is the atomic weight of the metal.

Based on this model and experimental data for copper and Zinc in aqueous electrolytic solutions of their respective salts or salts of major metal constituents, Nobe and his colleagues concluded the following:
(1) The amplitude of the response is a linear function of strain within a order of $10^\text{4}$ $100$ $\mu V$ as predicted by the theory.

(2) The responses upon loading and unloading are equal but of opposite sign.

(3) Equilibrium potential change between stressed and unstressed electrodes are negligible ($\approx 1$ $\mu V$) in the case of Cu and Zn.

The above derivation for $\Delta \psi_0$ is correct but the definition is not because: First, they attributed the potential across the double layer to a potential determined from a Nernst relation in terms of concentration of ions, but this potential is arbitrarily defined with respect to the standard hydrogen electrode. If their expression for the potential change is right, all of the systems which have their equilibrium potentials more noble than that of the standard hydrogen electrode should negative change under elastic strain, and the systems which have their equilibrium potentials below that of the standard hydrogen electrode should show positive change. Second, as discussed above, the relation between internal energy induced by elastic stress and potential change at the electrode surface is not valid.

The first discrepancy could be corrected if the concept of potential of zero charge, $\psi_{\text{pzc}}$, is introduced. Then any potential deviation from potential of zero charge for a given system, $(E - \psi_{\text{pzc}})$, which is independent of reference potential scale, is a rational scale of surface charge and a function of ion concentration. According to their prediction $\Delta \psi_0$ should still be negative for $0.001$ $N$ CuSO$_4$ because the Nernst relation gives a positive value of $\psi_0$ and, as a consequence, the theory
is unable to explain the observed data shown in Figure 7. If, on the other hand, \( V_0 \) is defined as \( (E - E_{pzc}) \), equation (17), which is the appropriate expression for a small potential change across a diffusion zone, will be corrected by

\[
\Delta V_0 = -(1 - \mu) \varepsilon (E - E_{pzc}) \quad (17')
\]

If, \( E_{pzc} \), for this system is about 0.25 \( V_H \), then equation (17') predicts the direction of potential change whereas equation (17) does not.

The other type of transient phenomenon concerning the elastic stress was observed on film-covered electrodes. The film covered electrode, nickel, 18-8 stainless steel\(^{102} \), and titanium\(^{107} \), were plastically strained in the passive region potentiostatically. The new films were grown on freshly produced slip steps under elastic tension after cessation of plastic straining. The anodic passive current was observed to increase by several \( \mu A/cm^2 \) and decay within a minute after release of the applied stress, as shown in Figure 8. This current transient is always in the positive direction regardless of the metal-environment systems and not explainable by the charge redistribution in the double layer of the solution side. Equation (17') predicts the opposite direction in the current change when the potential is controlled in the passive region. Perhaps consideration should be given to effects such as redistribution of space charge and thermoelastic effect within the film. There is no satisfactory explanation as yet.
Nickel
1N H_2SO_4
800 mV_H (passive)
25°C

Pig. 8.—Transient current observed upon release of elastic tension on film-covered nickel in 1N H_2SO_4.
(Murata and Stachle)
2. Stable and Reversible Potential Change

It would be appropriate to review briefly the thermodynamical analysis of a stressed solid before introducing any experimental data. Yang, Horne and Pound\textsuperscript{72} and Li, Oriani and Darken\textsuperscript{73} made essentially the same thermodynamical calculation of the chemical potentials for both mobile and immobile components in a stressed, solid based on the Gibbs treatment\textsuperscript{113}.

(1) Chemical potential of immobile components
(Substitutional element)

For immobile components, the chemical potential can be considered only as a surface property because the addition or the removal of the component must take place at or from an external or internal surface of the body. If a rectangular parallelepiped of a pure substance is compressed in three mutually perpendicular directions by compressive stresses, $P_x$, $P_y$ and $P_z$ respectively, the chemical potential, at each of these three faces (in the case of one component system), is given by

$$
\mu_x = \mu^0 + \bar{W} + P_x \bar{V};
$$

$$
\mu_y = \mu^0 + \bar{W} + P_y \bar{V};
$$

$$
\mu_z = \mu^0 + \bar{W} + P_z \bar{V}.
$$

Where $\mu^0$ is the chemical potential of the unstressed substance, $\bar{W}$ is the molal strain energy in the stressed solid, and $\bar{V}$ is the molal volume. The normal stresses to the surface, $P_x$, $P_y$ and $P_z$, are performing external work isothermally during addition or removal of the component and the $P\bar{V}$ term must be the reversible work.
This is the so-called "accretion constraints" and it is applicable only for the reversible transport of substance to an elastically stressed solid. If the $PV$ term is neglected, the chemical potential of a surface atom will be increased by the molal strain energy which gives rise to a potential change of about $10^{-4}$ - $10^{-5}$ mV/1000 psi.

(2) Chemical potential of mobile components

(Interstitial element)

The system could be defined as reversible under stress if the homogeneous stresses are applied so slowly that the mobile component can diffuse uniformly. This depends on the state of stress and the fact that its surface concentration is not changed appreciably by the electrochemical exchange reaction. A typical example, discussed by both Yang et. al. and Li et. al., is the case where the mobile component is hydrogen dissolved in homogeneously stressed iron. The strain energy, $\bar{W}$, stored within the iron of relaxed volume, $V$, under uniaxial tensile stress $\sigma$ is:

$$\bar{W} = \frac{\sigma^2 V}{2E}. \quad (19)$$

Where $E$ is Young's modulus at the existing hydrogen concentration. The work, $W_H$, done on the system during the addition of $n_H$ to the bar of iron is:

$$W_H = \sigma A \frac{\Delta l}{\rho n_H}. \quad (20)$$

Where $\Delta l/\rho n_H$ is the change of length of the bar in the direction of $\sigma$ produced by the transfer of $\sigma n_H$ gram atom of hydrogen; $A$ is the cross-
sectional area normal to $\sigma$. Differentiating (19) with respect to $n_H$ at constant $n_{Fe}$:

$$\bar{\nu}_H = \left( \frac{\partial \bar{\nu}}{\partial n_H} \right)_{n_{Fe}} = \frac{3}{2E} \frac{\partial^2 \nu}{\partial n_H^2} - \frac{2\nu_{XFe}}{2E^2} \cdot \frac{\partial E}{\partial n_H} \cdot \left( \frac{2}{3} \right) . \quad (21)$$

Substituting the values of $\bar{\nu}_H$ and $\bar{\nu}_H$ into the general expression for chemical potential under stress we obtain:

$$\nu_H = \nu_H^o + \bar{\nu}_H - \bar{\nu}_k;$$

$$\nu_H = \nu_H^o + \frac{\partial \nu_H}{\partial n_H} \cdot \frac{\partial n_H}{\partial n_H} + \frac{\partial \nu_H}{\partial n_H} \cdot \frac{\partial n_H}{\partial n_H} - \sigma A \cdot \frac{\partial n_H}{\partial n_H} \cdot \left( \frac{2}{3} \right) . \quad (22)$$

Where $\nu_H^o$ is the chemical potential of the hydrogen in the unstressed iron with the same hydrogen concentration. If the dissolved hydrogen is assumed to expand the lattice isotropically regardless of the applied stress, then

$$\frac{\partial n_H}{\partial n_H} = \frac{1}{3n_H} \cdot \bar{\nu}_H = \frac{\bar{\nu}_H}{3n_H} . \quad (23)$$

If $\sigma/E$ is small, equation (22) can be simplified to

$$\nu_H = \nu_H^o - \sigma \kappa_H / 3 . \quad (24)$$

Thus, tension decreases the chemical potential while compression increases it.

For a triaxial stress system

$$\bar{\nu} = \frac{\sigma Z^2}{2E} + \frac{\sigma Y^2}{2E} + \frac{\sigma Z^2}{2E} \cdot \bar{\nu} ;$$
\[ \tilde{\nu}_H = \Sigma \sigma_x \cdot A_x \left( \delta \frac{1}{x} \tilde{\eta}_H \right) \]

Substitute the above relations and equation (23) into equation (22). The equation becomes:

\[ \nu_H = \nu_H^0 - \frac{\tilde{\nu}_H}{3} (\sigma_x + \sigma_y + \sigma_z) + \tilde{\nu}_H. \quad (25) \]

This is the adsorption constraints which is applicable for the reversible transport of interstitial solute atoms in an elastically stressed solid solution. It is clear that tension decreases the chemical potential while compression increases it. Thus tension increases the solubility and compression decreases it. If the strain energy term, \(\tilde{\nu}_H\), is small as calculated for the immobile case then the change in the chemical potential of hydrogen under uniaxial stress will be converted to the surface potential change from equation (7) for uniaxial tension:

\[ \nu_H = -\frac{\sigma_z \tilde{\nu}_H}{3} = -n\Delta EF; \]

and therefore:

\[ \Delta E = \frac{\sigma_z \tilde{\nu}_H}{3}. \quad (26) \]

However this equation contradicts the expression, \(\Delta E = \frac{P_z \tilde{\nu}_H}{3}\), obtained by Yang et al.\(^7\) in that \(P_z\) is a hydrostatic pressure and \(\sigma_z\) is the principal stress, \((P_z = -\sigma_z)\).

Yang et al.\(^7\) reviewed the previous works on the effects of elastic stress on the electrode potential of metals. In order to avoid substan-
tial confusion due to the surface condition and strain (elastic or plastic), the data in their table are reorganized in Table I and II including the recent results in terms of presumably film-free and film-covered electrodes and with elastic or plastic strain. It is not obvious that for film-free electrodes the potential shift is always in the noble direction. For film-covered electrode the potential shift is in the less noble direction, except for reference (111) where apparently a different sign convention was used because the potential became more noble for larger plastic strain. Plastic strain exposes fresh surface areas to the environment and therefore the potential should tend to be less noble.

Adsorption constraints (adsorption of interstitial atoms) predicts the direction of the potential shift according to equation (26):

\[ \Delta E \text{ more noble under tension,} \]
\[ \Delta E \text{ less noble under compression.} \]

The magnitude of the potential shift is not calculable unless the partial molal volume of an interstitial atom is known. Yang et al calculated \( \Delta E \) as 0.03 mV/1000 psi based on the assumption that the partial molal volume of hydrogen is 1 cc/mole. However, they predicted the polarity such that the electrode is anodic (-) under tension and cathodic (+) under compression. This is apparently opposite to their conclusions. There could be some confusion in sign convention. Thus, adsorption constraints predicts the direction of the potential shift for all of the cases. Unfortunately, the concept of a reversible system under stress may not be valid because mobile elements must diffuse so fast to or from the interface that the surface concentration does not deviate from that
<table>
<thead>
<tr>
<th>Reference</th>
<th>Metal</th>
<th>Solution</th>
<th>Reference Electrode</th>
<th>Stress</th>
<th>Potential Shift</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>Fe</td>
<td>0.1NH₂SO₄</td>
<td>Pt</td>
<td>Tension</td>
<td>noble</td>
<td>2* 2.4mV/3000Kg/cm²</td>
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<tr>
<td>96,97</td>
<td>Ag</td>
<td>1-0.001NaNO₃</td>
<td>Ag</td>
<td>Tension</td>
<td>noble</td>
<td>1* larger shift for</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>more dilute solution</td>
</tr>
<tr>
<td></td>
<td>Steel</td>
<td>1NH₂SO₄</td>
<td>Steel</td>
<td>Tension</td>
<td>noble</td>
<td>1*</td>
</tr>
<tr>
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<td>noble</td>
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</tr>
<tr>
<td>100</td>
<td>Au</td>
<td>0.06MHAuCl₄</td>
<td>Au</td>
<td>Tension</td>
<td>noble</td>
<td>3* 0.01mV/1000 psi</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>less noble</td>
<td>0.1mV/1000 psi</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Compression</td>
<td>less noble</td>
<td>0.1mV/1000 psi (Mechanically</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>polished)</td>
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<tr>
<td></td>
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<td></td>
<td>Compression</td>
<td>less noble</td>
<td>0.5mV/1000 psi (Electropolished)</td>
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<td>Calomel</td>
<td>Tension</td>
<td>noble</td>
<td>3*</td>
</tr>
<tr>
<td>111</td>
<td>Fe</td>
<td>FeSO₄</td>
<td>Calomel</td>
<td>Tension</td>
<td>noble</td>
<td>3* not always observed</td>
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<td>1NH₂SO₄</td>
<td>Calomel</td>
<td>Tension</td>
<td>noble</td>
<td>4*</td>
</tr>
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</table>

(Table Continued Next Page)
TABLE I. (Continued)

* Explanations by authors:
1. Surface charge redistribution model
2. Thermodynamical model (adsorption constraints)
3. Not explained clearly
4. Adsorption isotherm

** This experiment was conducted potentiostatically and the cathodic current was observed to increase, which is equivalent to noble potential shift at open circuit.
### TABLE II. Potential Shift (Film-Covered electrode)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Metal</th>
<th>Solution</th>
<th>Reference Electrode</th>
<th>Stress</th>
<th>Potential Shift</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>96,97</td>
<td>Brass</td>
<td>1-O.01NCuSO₄</td>
<td>Brass</td>
<td>Tension</td>
<td>noble</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>3.5% NaCl</td>
<td>Ag</td>
<td>Tension</td>
<td>less noble</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Brass</td>
<td>3.5% NaCl</td>
<td>Brass</td>
<td>Tension</td>
<td>less noble</td>
<td>1*, 2*, 6*</td>
</tr>
<tr>
<td></td>
<td>Steel</td>
<td>3.5% NaCl</td>
<td>Steel</td>
<td>Tension</td>
<td>less noble</td>
<td></td>
</tr>
<tr>
<td>108</td>
<td>Mild steel</td>
<td>KCL</td>
<td>Mild steel</td>
<td>Tension by bending</td>
<td>less noble</td>
<td>2* a few mV</td>
</tr>
<tr>
<td>109</td>
<td>Mild steel</td>
<td>KCL</td>
<td>Mild steel</td>
<td>Compression by bending</td>
<td>noble</td>
<td>3* a few mV</td>
</tr>
<tr>
<td>110**</td>
<td>Fe single crystal</td>
<td>FeSO₄</td>
<td>Fe single crystal</td>
<td>Tension (plastic strain)</td>
<td>less noble</td>
<td>4* 1 mV/1Kg</td>
</tr>
<tr>
<td>112**</td>
<td>Cu</td>
<td>CuSO₄</td>
<td>Cu</td>
<td>Tension (plastic strain)</td>
<td>noble</td>
<td>(different sign convention?)</td>
</tr>
</tbody>
</table>

* Explanations by authors:
1. Distribution of the excess charge at metal-film and film-electrolyte interfaces
2. Film rupture
3. Reduction of fissures' gap by compression
4. Not available or not explained
5. Surface charge redistribution
6. Deleterious effect of halid ions on the passive film

** Plastic deformation is involved upon loading.
of equilibrium. Deposited metal on a stressed electrode could be strain-free and the diffusivity of hydrogen in a metal, say nickel, is the order of $10^{-5} \text{cm}^2/\text{sec}$ at 400°C. If the extrapolation is permitted to room temperature, the diffusivity will be the order of $10^{-9} \text{cm}^2/\text{sec}$ which is a very slow rate. However, the experimental data shown in Figures 9-11 indicate that the potential shift is instantaneously completed. In addition, some systems in Table I have their equilibrium potential much more mole ($\text{Ag-AgNO}_3 + 0.7V_H$) than that of the standard hydrogen electrode. Therefore, hydrogen ad-atoms may not be present in such cases on metal surfaces.

The theory of surface charge redistribution can not explain the permanent potential change as Nobe et. al tried to do. As will be shown in the discussion, the adsorption isotherm, with the change of surface energy upon application of elastic stress, might explain the observed phenomena.

A second set of experimental data is listed in table II where, presumably, the electrode is covered by a film. The data obtained under plastic deformation are not listed except for references (101, 110-112) where apparently stresses over the elastic limit were applied. Because of the lack of consistent sign convention and the definition of the surface conditions some data are contradictory. It is of great interest to note that silver, brass and steel in 3.5% NaCl solution show quite different behaviors from those metals in their respective ions as shown in Figure 12 (a) and (b). Nobe and his colleagues attributed the potential shift, in the less noble direction upon loading, to perturbation of
Fig. 9(a).—Effect of tension on electrode potential of gold. (Electrolyte: 0.06M HAuCl₄).

Fig. 9(b).—Effect of compression on electrode potential of gold. (Electrolyte: 0.06M HAuCl₄).

(Rryxell and Nachtrieb)
Fig. 10.—Typical change of corrosion potential with time for iron "A" upon stressing in the elastic region. 0.1N H₂SO₄ solution. (Despic et al. 19)

Fig. 11.—Electromotive force of stressed silver electrodes. (Tan and Nobe 98)
Fig. 12(a).—Typical potential response, brass-3.5% NaCl cell. (Nobe and Tan)

Fig. 12(b).—EMF vs. stress, brass-3.5% NaCl cell. (Nobe and Tan)
the distribution of the excess charge carriers and lattice defects induced by strain at metal-film interface, in the film, or at the film-electrolyte interface. The unloading process was explained by some kind of anodic action caused by a slight amount of film rupture when the load was released. However, the latter explanation may not be probable since an oxide is generally stronger under compression than under tension. This unloading process is quite similar to the phenomenon shown in Figure 8. The brass-CuSO$_4$ system showed the combined character of transient and permanent potential change although it is in the less noble direction. Recall that the copper-CuSO$_4$ system shows the transient character. There is no consistent explanation for film covered electrodes but the following factors must be considered:

(a) the local film ruptures under tension which tends to change the open circuit potential in a less noble direction because of an accelerated anodic reaction,
(b) a space charge redistribution within a film under stress,
(c) the deleterious effect of halide ions on the passivity of metals,
(d) a charge redistribution on the film's surface,
(e) specific adsorption, and
(f) a thermoelastic effect and exoelectron emission whose contribution could be small.

In a summary of chapter II, it could be stated:

(a) there is no powerful theory to explain the phenomena as yet,
(b) the concept of the surface charge redistribution in the double
layer can be applied only to limited cases (transient potential change).  

(c) a thermodynamical explanation does not hold in predicting both the direction and the magnitude of the permanent potential shift,  

(d) the adsorption isotherm, in the case of film-free electrodes can be a useful consideration to explain the instantaneous potential change with an elastic strain, and  

(e) further investigations are required before establishing the rational explanation.
II. COLD WORKED ELECTRODE

When metals are deformed the dislocation density increases substantially; at times the concentration reaches \( \approx 10^{13}/\text{cm}^2 \). Each individual dislocation is a special case of an electrode under elastic strain. The corrosion behavior of heavily cold worked material is an important consideration in industrial technology. Many corrosion related studies have been conducted using cold worked materials. It is, therefore, appropriate to consider this area separately and to discuss this section in terms of phenomenological results where the surface or corrosion behavior is studied as a function of cold work.

First we will consider the dissolution behavior of individual dislocations. However, most research has been conducted in connection with ionic crystals because of interests in plastic flow properties. The possibility for identifying plastic flow properties by dislocation etch pitting methods exists after a certain amount of cold work has been done to one crystal. Secondly, we will consider the kinetics of anodic dissolution of cold worked metals with and without a surface film.

1. Dissolution at Dislocations

Johnston\(^3^4\) and Robinson\(^1^1^5\) reviewed local dissolution or etch pit formation at dislocations. Crystal dissolution and evaporation occur by the removal of atoms from monomolecular surface steps. Kossel\(^2\) introduced the concept of kinks on crystal surfaces as shown in Figure 1.
During dissolution atoms can more easily be removed from kinks because an atom on a kink site has six nearest neighbors and is less strongly bound than other surface atoms—except for an adatom which has three nearest neighbors. Frenkel pointed out that growth from a vapor phase need not be proceeded by direct motion of an atom from the vapor to a kink site. Instead, the atoms would first be adsorbed on the surface (for e in Figure 1), diffuse to a step (g) and move along the step to a kink. In evaporation or dissolution the reverse process would occur. When a dissolving step reaches the edge or terminates at a grain-boundaries this step will be eliminated. If it terminates at a screw dislocation, shown in Figure 13, a step can not be eliminated during dissolution because of the configuration of the screw dislocation: such a dislocation is a perpetual dissolution source. On a perfect area of a surface, away from existing steps, new steps can be formed only by two-dimensional nucleation with sufficiently large undersaturation.

The major factors contributing to dissolution in addition to undersaturation are: (a) configuration of screw dislocation; (b) strain energy and core energy of a dislocation; (c) chemical potential of a dislocation due to the segregation of impurity atoms; (d) surface energy.

(a) Configuration of a screw dislocation

As mentioned above a screw dislocation provides a perpetual source of steps which may consist of kink sites and adsorbed atoms as shown in Figures 1 and 13. Formation of screw dislocations will be discussed in this section. A schematic description of the motion of the surface dislocation loop is shown in Figure 14 where Burgers vector, $\mathbf{b}$,
Fig. 13.—Sketch of a spiral etch pit formed at the point of emergence of a screw dislocation. The step height of the spiral is equal to the component of the Burgers vector normal to the surface. (Johnston)
(a) Dislocation loop approaching surface.

(b) Creation of a surface step with two mixed dislocations at B.

(c) Creation of a surface step with two screw dislocations at C.

Fig. 14.—Dislocation motion at surface where A denotes edge character, B denotes mixed character and C denotes screw character.
is assumed to be normal to the surface. Accordingly, part A has an edge character, part C, where a dislocation is parallel to the Burgers vector, has a screw character, and part B has a mixed character. When the dislocation breaks through the surface it produces a tiny step shown in Figure 14(b) with two mixed dislocations emerging at the surface. As the dislocation loop proceeds it tends to be a pure screw dislocation with two screw dislocations emerging at the surface as shown in Figure 14(c). It is probable that most of the emerged dislocations have either mixed or screw character.

(b) Strain energy of a dislocation

In the core region a dislocation involves such a large displacement of atoms that linear elastic theory can not be applied but elastic strain calculations outside the core has been performed by numerous investigators\textsuperscript{117-119}.

The expression for the elastic strain energy per unit length, $W/L$, of a screw dislocation is:

$$\frac{W}{L} = \frac{\mu b^2}{4\pi} \log \frac{R}{r_o};$$

where $\mu$ is the elastic shear modulus of the crystal, $b$ is the Burger vector, $r_o$ is the radius of the core, and $R$ is the outer limit of the calculation. For an edge dislocation we have:

$$\frac{W}{L} = \frac{\mu b^2}{4\pi(1-\nu)} \log \frac{R}{r_o};$$

where $\nu$ is poisson's ratio. The only difference between magnitude of
these two kinds of dislocations is the factor \((1 - \nu)\): the energy is larger for a edge dislocation by a factor of \(1/(1 - \nu)^{\frac{3}{2}}\). Aluminum, for example, has about \(3.3\text{eV}^{118}\) per atomic length of strain energy for a screw dislocation, for which \(b = 2.9 \times 10^{-8}\text{cm}, \mu = 2.8 \times 10^{11}\) dynes/cm², and \(R\) is taken to be equal to the subgrain size, \(10^5\eta\). Usually the elastic energy of a dislocation lies in the range of \(5\text{~10eV}\).

The core energy contribution to the total self-energy is relatively small but not negligible. Bragg suggested\(^{120}\) that the core energy can not exceed the latent heat of fusion which is approximately \(1\text{eV}\); and a reasonable estimate for the core energy is \(\gamma \mu b^2/10\)-assuming \(\mu/30\) is the approximate stress level within the core.\(^{118}\)

(c) Chemical potential of a dislocation due to impurity segregation

Segregation of impurity atoms to dislocations was first suggested by Cottrell\(^{121}\) and Koehler and Seitz\(^{122}\). Large interstitial impurity atoms tend to be attracted at the tension side of an edge dislocation while small substitutional atoms tend to be attracted by the compression side. A distinction must be made between clean dislocations and dislocation which are decorated with impurity atmosphere. The presence of the impurity atoms slightly decreases the core energy and strain energy in the vicinity of the dislocation. But the presence of the impurity may produce a chemically active region. Suits and Low\(^{123}\) have shown that aging is necessary for the occurrence of etch pitting of dislocations in Fe-3%Si alloys and that carbon is the important segregating impurity. Pickering\(^{35}\) studied the reactivity of dislocations in Fe-3%Si alloys using transmission electron microscopy and found that
etch pits never formed at freshly introduced dislocations (shown in Figure 15) and that the decorated dislocations could not move easily from their impurity atmosphere. Pickering also found that both edge dislocations and screw dislocations are etch pitted but at different rates.

(d) Surface energy

The importance of surface energy will be discussed in the following section in connection with nucleation theory of two dimensional etch pits at a dislocation.

(e) Two dimensional nucleation at a dislocation

The first extensive theoretical treatment of the nucleation of etch pits at dislocations was given by Cabrera and Levine and Cabrera. Preferred dissolution at dislocations was postulated because of the reduction of free energy required for the nucleation of a cavity of unit depth by the strain energy associated with dislocations.

The free energy change associated with the formation of a nucleus at a dislocation involved a strain energy term in addition to the volume and surface energy terms and is given by:

$$\Delta G = \frac{r^2h}{\Omega} \Delta \mu_D + 2 rh \gamma - hE(r)$$

(volume term), (surface term), (strain energy term)

where $r$ and $h$ are the radius and depth of the nucleus, molecular volume, and $E(r)$ is the strain energy within cylinder of radius $r$, per unit length of dislocation line. The change in chemical $\Delta \mu_D$ potential as a
Fig. 15.—Preferential dissolution at dislocations decorated by impurity atoms in a 0.003C Fe-3% Si alloy.
molecule of crystal goes into solution is given by:

\[ \Delta u_0 = kT \log \frac{C}{C_0} ; \]  

(30)

where \( C_0 \) is the equilibrium concentration of the crystal in the solvent and \( C \) is the actual concentration. \( E(r) \) is expressed as the sum of the strain energy and the core energy, \( E_c \):

\[ E(r) = A \log \frac{r}{r_0} + E_c ; \]

where \( A = \mu b^2/\mu \) for a screw dislocation and \( \mu b^2/4 (1-\nu) \) for an edge dislocation respectively.

Cabrera et al. did not include a core energy term in their treatment; therefore:

\[ \Delta G = \frac{r_0^2}{\Omega} \Delta u_0 + 2 \pi \delta r_0^\lambda - A \log \frac{r}{r_0} . \]  

(31)

Differentiate equation (31) with respect to \( r \)

\[ \frac{d\Delta G}{dr} = \frac{2\pi \delta}{\Omega} \Delta u_0 + 2 \pi \delta r_0^\lambda - \frac{\pi b^2}{4 \pi \gamma} \lambda ; \]  

(32)

Equation (32) has two roots when \( d\Delta G/dr = 0 \), they are:

\[ r_1 = \frac{\rho_0}{2} [1 - (1 - 4 \mu \rho_0)^{1/2}] \]

\[ r_2 = \frac{\rho_2}{2} [1 + (1 - 4 \mu \rho_0)^{1/2}] \]  

(33)

where \( \rho_0 = \mu b^2/8 \) and \( \rho_c \) is the radius of a critical nucleus.
A schematic illustration of $\Delta G$ vs $r$ is shown in Figure 16 where curve-I is for pit formation on a perfect surface, (no dislocation) curve-II is for pit formation at a dislocation, and curve-III is for pit formation at a dislocation including the core energy and the fact that the curve must go through the origin as proposed by Johnston. It should be pointed out that the presence of a dislocation reduces $\Delta G$ appreciably, especially when the core energy is included in the consideration. Cabrera's model, has been criticized by Gilman on the ground that neither the elastic strain energy nor the configurational factor are necessary for the formation of a dislocation etch pit because the strain energy of a pure screw dislocation at the surface is zero and the reactivity of both an edge and a screw dislocations is the same. The core energy is more important than the strain energy because (a) the elastic strain energy of dislocations in metals is about the same for all materials including ionic crystals were the core energy is higher; (b) dislocations having quite different core structures in a given crystal etch at quite different rates.

Schaarwächter has modified Cabrera's model as suggested by Gilman and showed that Cabrera's model is not applicable for metals where the radius of a dislocation core, $r_c$, is smaller than the critical radius for nucleation. If a dislocation attracts impurity atoms near the core region the volume term in equation (29) may play the most important role.

2. Residual Strain.

When a metal is cold worked, most of the energy is expended in
Fig. 16.—Schematic representation of energy change, $\Delta G$, for the formation of a pit of monatomic depth as a function of pit radius, $r$. Curve I is for pit formation on a perfect surface. Curve II is for pit formation at a dislocation, taking into account the elastic energy (after Cabrera). Curve III is for pit formation at a dislocation, taking into account also the core energy, and the fact that the curve must pass through the origin.

(Johnston)
changing the shape and generating heat but a small proportion (~10%) remains stored in metal mainly in the form of elastic energy in the strain field of dislocations and point defects. Various calorimetric methods, such as differential calorimetry, have been used to measure the released energy upon beating the cold worked metal. Figure 17 is the data from the work of Gordon\(^{129}\) and shows that the stored energy of polycrystalline 99.999% pure copper increases with increasing deformation rather linearly and the fraction of energy stored decreases. Many attempts have been made\(^{126,128}\) to correlate the amount of stored strain energy induced by plastic deformation with the electrode potential. Lewis et. al\(^{128}\) studied the residual strain energy of cold worked copper wires using X-ray diffraction line broadening, equilibrium electrode potential measurements and anodic dissolution rates in 0.1M CuSO\(_4\) by the method of anodic polarography. They found that there is a fundamental discrepancy among the data obtained by different methods. Figure 18(a) shows the residual strain energy obtained by X-ray diffraction line broadening vs the relative change of free energy calculated from quasi-study state electrode potentials. The residual strain energy is one order of magnitude smaller than the free energy change, but in good correlation with Gordon's result. Figure 18(b) shows the logarithmic relation between the exchange current density vs the microstrain concentration obtained from X-ray diffraction line broadening. They explained the results in terms of heterogeneous distribution of strain as:

(a) X-ray measurements yield information on the volume strain while electrode potential measurements yield information on surface
Fig. 17.—Stored energy of cold-work and fraction of the total work of deformation remaining as stored energy for high purity copper plotted as functions of tensile elongation. (Gordon)
Fig. 18(a).—Relative change of free energy vs. residual strain energy (from X-ray measurement).

(Lewis et al.128)

Fig. 18(b).—\( i_0 \) vs. microstrain concentration.

(Lewis et al.128)
strain. Since the dislocation density is much higher near the surface, X-ray results could be underestimated.

(b) The electrode potential measurements are characteristic of high surface strains, such as dislocation cores that have emerged at the surface.

However, the above view is not correct, as criticized by Clark, in that a direct relationship between the strain energy and the equilibrium potential of the electrode does not exist because: (1) the electrode behavior of plastically deformed metals is an irreversible process; and (2) the increase in the internal energy is not only due to the elastic strain energy but it is also due to the increase in defects, such as vacancies and dislocations. The key consideration used to explain the discrepancy is the kinetic approach which will be discussed in the next section.

3. Dissolution under Activation Control

Consider the kinetic equation for the anodic current on a film-free electrode:

\[ i_a = K u \left( \frac{N_s}{N_o} \right) C_s \exp \left( - \frac{G \alpha}{RT} \right) \exp \left( - \frac{\beta \Delta E F}{RT} \right); \]

\[ = i_o \exp \left( - \frac{\beta \Delta E F}{RT} \right); \quad (34) \]

where \( K \) is a constant, \( N_s \) is the total number of surface lattice sites, \( N_o \) is Avogadro's number, \( \alpha \) is the proportion of total surface atoms constituting active sites, \( C_s \) is the concentration of reactants at the outer
Helmholtz layer, \( i_0 \) is the exchange current density and \( \beta, \Delta G_0^* \), \( R, \) \( T \), \( E \) and \( F \) have the usual meanings.

Assum that the increase in internal energy due to plastic deformation is \( \sigma^2/2E \), where \( \sigma \) is the uniaxial tension and \( E \) is Young's modulus. Then the exchange current density for a deformed metal can be written as:

\[
i_0 = K \alpha' \left( \frac{N_s}{N_0} \right) \exp \left( - \frac{\Delta G_0^* - \sigma^2/2E}{RT} \right);
\]

where \( \alpha' \) is \( \alpha \) for a deformed metal surface and dissolution is considered to occur at kink sites and ledges because of the lower bonding energy (fewer nearest neighbors). Therefore, as plastic deformation proceeds the number of dislocations emerging at the surface to form slip steps increases, as discussed in the previous section. These surface dislocations provide more sites favorable for dissolution. This is even truer for cold worked metals whose surface dislocations can be decorated by impurity atoms and thereby making them chemically more active than moving dislocations. Consequently, \( \alpha' \) is larger than that of an annealed metal and even \( \Delta G_0^* \) might be reduced. On the other hand, the \( \sigma^2/2E \) term contributes only a few cal/mole compared with \( \Delta G_0^* \) which has a value of 10-100 Kcal/mole. In addition the strain energy term may not be applicable because of stress relaxation due to impurity segregation.

Lewis et al.\(^{128}\) reported that \( i_0 \) increased exponentially with total plastic strain. This trend agrees with the results obtained by Green and Saltzman\(^ {131} \) for iron and steel in 1 N \( \text{H}_2\text{SO}_4 \). But Foroulis\(^ {132} \) did not find any significant effect of cold work on the exchange current of iron in various environments, such as deaerated HCl, \( \text{H}_2\text{SO}_4 \) and \( \text{HClO}_4 \) at
25°C. As Jenkins and Stiegle \cite{133} and Foroulis \cite{132} suggested, this might be due to the fact that at low current densities or at low overpotentials, anodic dissolution is controlled by the number of active sites on the surface of metals. At high current densities or high overpotentials, anodic dissolution is kinetically controlled by the charge transfer step. The discrepancy that Lewis et al. \cite{128} faced arose, first of all from the estimate of the bulk plastic strain, and secondly, an unsound thermodynamical treatment— as Clark pointed out. In addition, the rest potential they measured, as the equilibrium potential, was perhaps controlled by the increased anodic kinetics due to an increase in active surface sites rather than a strain energy contribution to the exponential term, as discussed above. Therefore, the free energy calculated from the rest potential change can not be compared with that calculated from the bulk strain.

4. Passive Region

Most of the anodic passive films are considered to be electronically conductive and a precipitation type film is considered as ionically conductive. In this section the first case will be briefly described and the relation to cold work will be discussed.

A steady state current density flowing through the passive film was derived for iron in H$_2$SO$_4$ by Sato \cite{127}. At steady state the possible film-electrolyte interface reactions are:

\begin{align}
\text{Fe}^{3+} \text{(oxide)} & \rightarrow \text{Fe}^{3+} \text{(aq)} ; \\
\text{H}_2\text{O} \text{(aq)} & \rightarrow \text{O}^{2-} \text{(oxide)} + 2\text{H}^+ \text{(aq)}. 
\end{align}

(36) 
(37)
Reaction (37) is considered to be in equilibrium since the thickness of the film is constant at steady state. The potential difference associated with reaction (37) is given by

$$\Delta E = \frac{1}{2F} (\mu_0^- + 2\mu_{H^+} - \mu_{H_2O}),$$

$$= \frac{\Delta \mu^o}{2F} + \frac{RT}{2F} \ln \left[ a_{O^2} \cdot a_{H^+}^2 \right];$$  \hspace{1cm} (38)

where $\Delta \mu^o =$ standard chemical potential change for the reaction,

$\mu_0^-$ = chemical potential of oxygen ion in the oxide,

$\mu_{H^+}$ = chemical potential of hydrogen ion in electrolyte,

$\mu_{H_2O}$ = chemical potential of water,

$a_{O^2} =$ activity of $O^2$,

$a_{H^+} =$ activity of $H^+$,

$R =$ gas constant,

$F =$ Faraday constant, and

$T =$ absolute temperature.

If $a_o$ is assumed to be constant $\Delta E$ is determined by the activity of $H^+$ (pH). The resultant potential difference, $\Delta E$, is considered to control reaction (36) therefore the anodic dissolution current, $i_k$ is given as

$$i_k = k a_{Fe^{3+}} \cdot \exp (3F \Delta E / RT),$$  \hspace{1cm} (39)

where $\alpha$ is an electrochemical transfer coefficient ($0 < \alpha < 1$). Combining equations (38) and (39) we obtain $i_k$ as
\[ i_k = K' \cdot a_{\text{Fe}^{3+}} \cdot a_{\text{O}^=}^{\frac{3\alpha}{2}} \cdot a_{\text{H}^+}^{3\alpha} \]  

(40)

where \( K' \) is \( K \cdot \exp\left(\frac{3\alpha \nu^0}{RT}\right) \).

If \( a_{\text{Fe}^{3+}} \) and \( a_{\text{O}^=} \) in the oxide are assumed to be constant at steady state, equation (40) can explain the empirical relation between \( i_k \) and pH given for iron\(^{138}\) and nickel\(^{139}\) respectively by:

\[ \log i_k = -4.26 - 0.87 \text{ pH (A/cm}^2\text{),} \]  

(Fe in \( \text{H}_2\text{SO}_4\))  

\[ \log i_k = -6.2 - 0.46 \text{ pH (A/cm}^2\text{).} \]  

(Ni in \( \text{H}_2\text{SO}_4\))

It should be recalled that there is no generalized theory for the current associated with film dissolution and the mechanisms are dependent on the systems.

It has been observed by France\(^{135}\) that the polarization curves are influenced by cold work as shown in Figure 19. Type 1008 steel was deformed by torsion in 0.6 \( \text{MN} \cdot \text{H}^2\text{NO}_3 \). This data indicates that the passivation potential is shifted in the noble direction as the number of twists (shown by 0X, 1X, etc. in Figure 19) increases prior to polarization measurements. Finley and Myers reported\(^{136}\) the same tendency of shifting passivation potential in the noble direction for cold worked (rolled) iron in \( \text{H}_2\text{SO}_4 \). It is more difficult to form passive films on cold worked materials than on annealed materials.

In the case of polycrystalline nickel in 0.5N \( \text{H}_2\text{SO}_4 \) the apparent activation energy for passive current was found\(^{63}\) to be reduced from
Fig. 19.—Potentiodynamic anodic polarization curves showing the effect of torsional deformation on Type 1008 steel in 0.6M NH₄NO₃ solution at 25 C. (France[^135])
18.8 Kcal/mole (annealed state) to 16.8 Kcal/mole (as received state). The passive current at room temperature was found to be slightly higher for the as-received nickel. These experimental facts indicate that, because of the surface strain field, the surface film on the cold worked metals could have either a higher concentration of defects in the film on localized defect structures. Defects in the film or local metal defects, i.e. grain boundaries, may cause higher ionic diffusion rates. In such a case the apparent activation energy may be reduced.

5. Corrosion of Cold worked Metals

France135 reviewed the studies conducted in the last 75 years on the effect of cold work on corrosion rate of metals. In Table III he pointed out that there are inconsistent results:

(a) plastic deformation increases corrosion rate,
(b) plastic deformation decreases corrosion rate, or
(c) plastic deformation does not effect corrosion rate.

The inconsistent results could be due to the lack of the control of many variables which, sometimes, mask the effect of deformation. Some examples are aeration or deaeration of the electrolyte; film-free or film covered electrodes (the potential should be controlled in order to define the surface clearly); the method of deformation such as rolling, drawing or extension and possible anodic and cathodic kinetics.

As a summary, the following statements may hold:

(a) Dissolution at a dislocation in the film-free metal surface is accelerated because the strain energy and the core energy of the dislocation can reduce the free energy for the nucleation, of an unit sized pit.
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<th>Investigator</th>
<th>Material</th>
<th>Environment</th>
<th>Corrosion Rates</th>
<th>Reference</th>
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<td>Andrews (1894)</td>
<td>Steel</td>
<td>NaCl</td>
<td>Strained &lt; Unstrained</td>
<td>140</td>
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<tr>
<td>Hambuchen (1900)</td>
<td>Steel</td>
<td>FeCl₃</td>
<td>Strained &gt; Unstrained</td>
<td>141</td>
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<tr>
<td>Walker &amp; Dill (1907)</td>
<td>Iron</td>
<td>FeSO₄</td>
<td>Strained ≤ Unstrained</td>
<td>111</td>
</tr>
<tr>
<td>Heyn &amp; Bauer (1909)</td>
<td>Steel</td>
<td>1% H₂SO₄</td>
<td>Strained &gt; Unstrained</td>
<td>142</td>
</tr>
<tr>
<td>Garre (1930)</td>
<td>Tin</td>
<td>HCl</td>
<td>Strained &lt; Unstrained</td>
<td>143</td>
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<td>Franks (1948)</td>
<td>18-8 Stainless Steel</td>
<td>65% HNO₃</td>
<td>Strained (30%) = Unstrained</td>
<td>144</td>
</tr>
<tr>
<td>Copson (1948)</td>
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<td>5.9% HCl</td>
<td>Strained = Unstrained</td>
<td>145</td>
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<td>Straumanis &amp; Wang (1956)</td>
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<td>1.0 N HF</td>
<td>Strained (90%) = Unstrained</td>
<td>146</td>
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<tr>
<td>Greene &amp; Saltzman (1964)</td>
<td>Zone-Refined Iron Steel</td>
<td>0.1 N HCl and 1.0 N H₂SO₄</td>
<td>Strained &gt; Unstrained</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1 N HCl and 1.0 N H₂SO₄</td>
<td>Strained &gt; Unstrained</td>
<td></td>
</tr>
<tr>
<td>Foroulis and Uhlig (1964)</td>
<td>Zone-Refined Iron Steel</td>
<td>0.12 N HCl</td>
<td>Strained (50%) = Unstrained</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.12 N HCl</td>
<td>Strained (50%) &gt; Unstrained</td>
<td></td>
</tr>
<tr>
<td>Tomashov and Ivanov (1965)</td>
<td>Titanium</td>
<td>3-40% H₂SO₄ and 5 and 10% HCl</td>
<td>Strained (20-95%) &lt; Unstrained</td>
<td>148</td>
</tr>
<tr>
<td>Trabanelli and Zucchi (1966)</td>
<td>Nickel</td>
<td>20 and 40% H₂SO₄</td>
<td>Strained (80%) = Unstrained</td>
<td>149</td>
</tr>
</tbody>
</table>
(b) From a practical point of view, the more determining factor for accelerated dissolution is (i) the segregation of impurity atoms along with the dislocation (thus, the static dislocation is more reactive than the moving dislocation); and (ii) the configuration of a screw dislocation and the orientation of the crystal.

(c) Preferential dissolution at energetically active sites, such as kink sites and corner atoms of ledges, could be identified only at low current densities on low overpotentials. At higher current densities or higher overpotentials dissolution would be kinetically controlled by the charge transfer step.

(d) Film on the cold worked metal may have a more conductive nature because of the presence of dislocations and their strain field at the metal-film interface. The surface stress should be relieved in the film.

(e) Corrosion tests on cold worked metals provided inconsistent results as to the effect of plastic deformation on the corrosion rate. This discrepancy is probably due to lack of control of many variable which may mask the effect of plastic deformation.
III. ELECTRODE UNDER SUDDEN PLASTIC STRAIN

Sudden plastic strain can be introduced by applying a certain dead load with or without controlling the strain. This may be compared to the extreme case of straining electrode at very high strain rates, to rapidly broken brittle metal, and scraping of metal surface with diamond through the use of a rotating device.

All of the classic works on the so called "strain potential" were conducted at open circuit potential by straining one electrode with a dead load while using a similar but unstrained electrode as a reference. Results, however, have been contradictory because of the following reasons.

1. Surface was not clearly defined (clean or filmed).
2. Potential that was measured was not a single electrode potential but was the difference of two mixed potentials as shown below as a function of time, t.
   \[ E(t) = E_m^O - E_m^S(t) \]
3. Specific adsorption of anion such as Cl\(^-\) on the strained electrode was not considered.
4. Conventional definition of polarity of the electrode potential was not clearly stated.

The so called "strain potential" will be discussed hereafter in terms of an (a) open circuit electrode or (b) a potentiostatically or
galvanostatically controlled electrode. Numerous studies have been reported by Nikitin, Gautam and Jha, Dudley et al., Eying et al., Leidheiser and Kellerman, and Shibata and Stachle. The obtained results are listed in Table IV with authors' explanations. It could be concluded from this table that (a) film-covered electrodes show negative (less noble) transient potential shifts; (b) film-covered electrodes in chloride ion containing electrolytes tend to show the opposite behavior; and (c) silver in AgNO₃ behaves like case (b). Film rupture and the resultant accelerated anodic dissolution followed by film repair model can explain case (a) but there is no conclusive explanation for cases (b) and (c) although anion adsorption is a probable mechanism. In the following, the theory developed by Eyring and his colleagues will be introduced and discussed, then useful data obtained by several investigators will be examined.

1. Theory of Strain Potential

Eyring and his colleagues first proposed the kinetic theory for the potential transient of electrodes after abrupt plastic deformation. Their works were intended to explain the fundamental aspects of corrosion processes such as dissolution and film repairing, and the behavior of inhibitors on freshly produced surface.

At the steady state electrode potential, anodic and cathodic processes transfer charges across the electrical double layer at the same rate. In the case of corroding metals in aerated aqueous solutions two reactions have been found adequate to explain most experimental data. These are the oxygen reduction reaction as the cathodic reaction and the
<table>
<thead>
<tr>
<th>Reference</th>
<th>Metal</th>
<th>Solution</th>
<th>Reference Electrode</th>
<th>Stress</th>
<th>Potential Shift</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>151</td>
<td>Cu</td>
<td>0.1NCuSO₄</td>
<td>Cu</td>
<td>Tension</td>
<td>less noble</td>
<td>3° 1+2 mV</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.1ZnSO₄</td>
<td>Zn</td>
<td>Tension</td>
<td>less noble</td>
<td>3° after cathodic treatment it became less noble</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>0.1FeSO₄</td>
<td>Fe</td>
<td>Tension</td>
<td>less noble</td>
<td>3°</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>0.1AgNO₃</td>
<td>Ag</td>
<td>Tension</td>
<td>noble</td>
<td>4°</td>
</tr>
<tr>
<td>152</td>
<td>Cu</td>
<td>0.5 0.0005NCuSO₄ (25 C 85 C) 0.0%NCuCl₂</td>
<td>Cu</td>
<td>Tension</td>
<td>less noble</td>
<td>1° ~5 mV (25 C) 3° ~30 mV (85 C) adsorption of Cl⁻</td>
</tr>
<tr>
<td>112</td>
<td>Cu</td>
<td>CuSO₄</td>
<td>Cu</td>
<td>Tension</td>
<td>noble</td>
<td>5° different sign convention</td>
</tr>
<tr>
<td>64,65</td>
<td>Cu</td>
<td>0.01MNH₄OH H₂O 1M CuSO₄ 1MNaCl 1M HCl</td>
<td>Cu</td>
<td>Tension</td>
<td>less noble</td>
<td>1° most elaborate work 1° initially small peak toward noble direction then less noble direction</td>
</tr>
<tr>
<td>66</td>
<td>Fe</td>
<td>H₂SO₄</td>
<td>Calomel</td>
<td>Tension</td>
<td>less noble</td>
<td>1°</td>
</tr>
</tbody>
</table>

(Table Continued Next Page)
TABLE IV. (Continued)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Metal</th>
<th>Solution</th>
<th>Reference</th>
<th>Electrode Stress</th>
<th>Potential Shift</th>
<th>Remarks</th>
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</thead>
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<tr>
<td>102**</td>
<td>18-8 Stainless steel</td>
<td>0.1NH₂SO₄</td>
<td>Calomel</td>
<td>Tension noble</td>
<td>2*</td>
<td>potentiostatic experiment</td>
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<tr>
<td></td>
<td></td>
<td>0.1MKCl</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>69</td>
<td>Ae</td>
<td>0.1MNaCl</td>
<td>Calomel</td>
<td>Tension less noble</td>
<td>1*</td>
<td>various conditions were used</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PH(3.5 7.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Explanations by authors:

1. rupture of oxide film
2. adsorption of anions
3. thermoelastic effect
4. not explained
5. not explained properly

** This experiment was conducted potentiostatically in active region, the current was observed to decrease. This is equivalent to potential shift to noble direction.
metal dissolution reaction as the anodic reaction as shown in Figure 20 along with other steady state potentials. Each anodic reaction has a velocity, \( v_i \) (number of reactions per second per unit area) and a charge transfer \( z_i e v_i \) (per second per unit area) from the electrode to the solution due to this reaction. The reverse of the anodic reaction is a cathodic reaction; proceeding with the velocity, \( v_i' \). The total charge transferred in a unit time per unit area is the sum of the charges transferred by each of these possible pairs, thus,

\[
Q = eZ_i (v_i - v_i')
\]  

(43)

where \( e \) is the electron charge and \( Z_i \) is the number of electron charges transported by a single ith process, irrespective of sign.

The reaction velocity is shown by

\[
v_i = v_{i0} \exp \left[ \frac{Z_i a_i eV}{kT} \right]
\]

(44)

\[
v_i' = v_{i0}' \exp \left[ -\frac{Z_i (1-a_i) eV}{kT} \right]
\]

(45)

where \( V \) is the potential difference between electrode and solution, and \( a_i \) is a fraction for a ith process.

From equation (43), (44) and (45) we have

\[
\frac{dQ}{dt} = eZ_i \left[ v_{i0} \exp \left( \frac{Z_i a_i eV}{kT} \right) - v_{i0}' \exp \left( -\frac{(1-a_i) eV}{kT} \right) \right]
\]

(46)

They assumed that the stationary electrode potential is fixed when the rates of competing anodic and cathodic reactions are equal, and the initial stage and the maximum potential stage are special cases at which
Fig. 20.—Schematic illustration of pair potentials and steady-state potentials. (Eyring et al. 64)
\[
\frac{dQ}{dt} = 0. \quad \text{In the particular case in which all } Z_i \text{ are equal, and all } \alpha_i \text{ equal } 1/2, \text{ the solution of equation (46) for } V \text{ is}
\]

\[
V \text{ (initial)} = \frac{KT}{Ze} \ln \frac{E_{\text{ui}}}{E_{\text{ui}_0}}
\]

The same treatment for the potential maximum will give rise to the theoretical maximum for the potential transient, \( \Delta V_m \).

\[
\Delta V_m = \frac{KT}{Ze} \ln \frac{E_{\text{ui}}}{E_{\text{ui}_0}} - \ln \frac{E_{\text{ui}}}{E_{\text{ui}_0}} = \frac{KT}{Ze} \ln \frac{E_{\text{ui}}}{E_{\text{ui}_0}} \frac{E_{\text{ui}}}{E_{\text{ui}_0}}
\]

where \( u_{i_0}, u_{i_0}' \) are constants for velocities at the maximum potential. Regardless of their expression for the reaction velocities, this equation contains fundamental errors as follows:

1. \( V \) is an experimentally unmeasurable quantity; (2) \( V \) is not applicable to film-covered electrode where the current is independent of the applied potential; (3) surface area factor is not considered.

3. Important Observations

Important observations will be reviewed in terms of various mechanical and electrochemical conditions such as strain, pH, anion concentration, aeration of the electrolyte, etc.

(a) Effect of Total Strain

Figure 21 shows the effect of the amount of strain on the potential transient behavior of 1100 aluminum alloy in air saturated 0.1M NaCl at pH 5.5. For larger strains the potential shift is larger.
Fig. 21.—Schematic illustration of the polarizability.
The magnitude of the potential change observed was compared with the results reported by Hagyand et. al\textsuperscript{152-154} who studied the reaction of freshly exposed aluminum in 1M KCl by using a high-speed abrasion wheel to cut through a plastic coated surface. The potential change, -1.91 V (vs SCE), at pH 3.5 gradually shifted to a potential of -1.54 V in 0.01 sec. The former potential was attributed to aluminum-aluminum ion potential (-1.94 V) and the latter was attributed to the corrosion potential with hydrogen ion reduction reaction as a cathodic reaction. Figure 22 shows the transient corrosion potential since only the part of the whole surface became film-free compared with the rotating electrode which could bring the whole surface near the film-free electrode potential.

Eyring et. al\textsuperscript{167} derived an equation for the relation between strain and $\Delta V_m$ assuming that only the anodic reaction velocity is changing in proportion to strain (relative elongation), $S$, and valence number of reacting ions are taken as an average one,

$$ -\Delta V_m = \frac{KT}{Ze} \ln (1 + \alpha S) $$  \hfill (49)

where $\alpha = g/\nu_{f0}$ and $g$ is the relative anodic rate of a clean surface. If $\alpha S$ is considerably larger than unity, equation (49) can be written as

$$ -\Delta V_m = \frac{ke}{Ze} [\ln \alpha + \ln S] $$  \hfill (50)

Figure 23 shows the results, $\Delta V_m$ plotted vs $\ln S$, and the average valences for metals. It is, however, questionable whether there is valuable meaning in the concept of average valences.
Fig. 22.—The effect of amount of strain on the potential-time behavior of 1100 aluminum alloy wires which had been heated in boiling water for 15 minutes. Experiments were carried out in air saturated 0.1M NaCl at 5.5.

(Leidheiser et al. 69)

Fig. 23.—Strain transients vs. \ln (strain). Distilled water at 25 °C.

(Eyring et al. 67)
(b) Effect of the Atmosphere

The presence of oxygen does not affect the rate of the initial potential change but it does affect the maximum change and the film repairing process shown in Figures 24 and 25. The amount of strain to yield the given change is not stated in the report.

(c) Effect of pH

The maximum change in potential and restoring behavior is primarily determined by the initial condition (mostly the film property) and the film repairing ability of the system. Both of these factors are definitely a function of pH.

Figure 26 shown the effect of pH on the amplitude of the transients. Except for acid solutions, a single peak was observed while at pH less than two (2) peaks were observed. At intermediate pH the potential change can be simply explainable by the film rapture model. The cathodic peak was considered to be due to the catalyzed hydrogen reduction reaction at active sties. The increase in the cathodic peak in proportion to the hydrogen ion concentration could be the evidence of this explanation. At high pH dissolution of the film occurs with the formation of the cupric ion. The amount of strain to obtain $\Delta V_m$ is not clear but is supposed to be a few %. Leidheizer et. al also found the same tendency as shown in Figure 27. Above pH 9 the aluminum becomes active and, therefore, the potential change will be smaller.

(d) Effect of Polarization

The experimental data shown in Figure 28 were obtained by Eyring et. al, by putting several wires in solution and at regular intervals pH, initial voltage, and strain transient were measured. The
Fig. 24. — The effects of $H_2$ and $O_2$ on the electrode strain transient of iron. (Eyring et al. 66)

Fig. 25. — The effect of atmosphere on the potential-time behavior of 1100 aluminum alloy wires strained 4.5% in 0.1M NaCl at pH 5.5. (Leidheizer et al. 69)
Fig. 26.—The pH dependence of transient amplitude.
(Eyring et al.)

Fig. 27.—The potential-time behavior of 1100 aluminum alloy wires strained 4.5% in air saturated 0.1M NaCl at pH of 3.5, 5.5, and 7.5.
(Leidheizer et al.)
Fig. 28.—The effects of polarization on iron wires in H$_2$SO$_4$. (Eyring et al. 66)
increases in pH and potential with time was attributed to reduction of oxygen and precipitation of Fe (OH)$_3$ in the pores, respectively. As a consequence the potential transient increased.

Galvanostatic polarization tests were conducted by Tomashov and Vershinina using the method of continuous mechanical scouring of the surface with a rotating corundum disk. The over voltage of ionization of metals similar to iron was considered to be determined essentially by the inhibition of the anodic process caused by adsorption of oxygen or anions such as $\text{SO}_4^{2-}$ rather than by a slow charge-transfer step. With continuous scouring they could remove the adsorbed layer almost completely for higher rotating speeds (>1000 rpm) and this action prevented significant polarization as shown in Figure 29, especially for metals such as nickel which have low exchange current densities. It was found, in the passive region of passivating metal as titanium and chromium, that scouring can not eliminate passivation even in an argon atmosphere (without molecular oxygen); accordingly, observed potential-current curves reached the steady state between two competitive reactions, dissolution and passivation as shown in Figure 30. It is interesting to note that iron and steel containing 13% Cr did not show any passivation in $1\text{NH}_2\text{SO}_4$ on scouring at 500 rpm and higher speed while nickel, chromium and titanium did.

(e) Effect of Anion

Anion concentration can also change the film properties. Figure 31 shows results for two solutions each containing cupric ion and chloride ion. Both curves show the same tendency. At higher concentrations, a considerable amount of cuprous chloride was observed to deposit
Fig. 29.—Overvoltage of metal ionization ($\eta_{me}$) as a function of log (current density) for Ni, Fe in 1N H$_2$SO$_4$ and Pb, Zn in 1N HCl without scouring (full curves) and with scouring (dotted curves) at 2000 rev/min.

(Tomashov et al. 79)

Fig. 30.—Anodic potentiostatic curves for Ti in 1N H$_2$SO$_4$, in air. 1, without scouring; 2, with scouring at 500 rev/min; 3, 1000 rev/min; 4, 2000 rev/min.

(Tomashov et al. 79)
Fig. 31. — Amplitude and decay time data in chloride and cupric ion solutions. (Eyring et al. 65)
as a white film on the electrode surface. It was assumed that the inhibitive properties of this film caused the amplitude to increase at higher concentrations. The reasons for the critical concentration at which the lowest amplitude was observed is not clear and again the amount of strain to produce the given results is not stated. Assumingly, a few % of each time is expected.

(f) Voltage Transient of Noble Metals

Perkins et al. introduced the method for determining the zero charge potential of solid electrodes such as Pt, Pd, Au, Cu and Ag in various \( \text{N}_2 \) saturated solutions by rapidly scraping or cutting off the existing surface with its charge and double layer.

The criteria to be satisfied in order to identify the observed maximum potential transient as zero charge potential are:

1. adsorption must approach equilibrium before appreciable reaction occurs to change the electrode charge. Therefore noble metal should be used;
2. experimental apparatus should be sensitive enough to separate adsorption and charge transfer reactions;
3. Sufficiently large number of scraping should be done in order to avoid possible charge redistribution from shavings onto the fresh surface.

They concluded that the peak potential change during straining corresponds to the zero charge potential through the following observations:

(a) \( V_{pk} \) is independent of initial electrode potential;
(b) \( V_{pk} \) comes to a limiting value with increased scraping speed;
(c) \( V_{pk} \) increasingly becomes more negative with anion variation in the order of \( F^- < \text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^- < \text{SCN}^- < I^- \);
(d) in a given solution (0.1N KCl) \( V_{pk} \) is more negative for metals with lower work functions\(^{155,156}\) i.e., \( V_{\text{pt}} > V_{\text{Au}} > V_{\text{Hg}} > V_{\text{Cu}} \).

But pH dependence of \( V_{pk} \) is a contradicting observation. This was explained by Perkins et al.\(^{69}\) to be due to the immediate discharge of nearby \( \text{H}_3\text{O}^+ \) and \( \text{H}_2\text{O} \) which drives the potential in the positive direction before \( V_{pk} \) is measured. Immediately following this, the reduction rate decreases rapidly since the rate controlling step changes from rapid discharge onto an empty surface to the slow H-atom desorption and slow mass transfer of \( \text{H}_3\text{O}^+ \) to the surface. Therefore \( V_{pk} \) tends to be more positive in acid solution than in basic solutions.

(g) Rapidly broken Electrode

Rapid brittle failure of mill annealed Ti 9-1-1 was made use of by Beck\(^8\) as a technique to obtain electrochemical kinetic data for newly generated surfaces in connection with stress corrosion cracking. This technique, according to Beck, was satisfactory to study the multilayer oxide formation, but it is not suitable to study monolayer formation such as adsorption because the observed current was too high for the potentiostat used and the recorder response was too slow.

These disadvantages, however, were overcome later by Beck\(^7\) when he controlled the amount of fracture to 2mm per hour and used an oscilloscope to record the response as shown in Figure 32. The initial,
Fig. 32.--Kinetic data for growth of oxide on Ti:8-1-1 alloy.  (Beck)
approximately horizontal, part of the curve corresponds to the formation of about a monolayer of oxide ions. Monolayer coverage of oxide ion gives $4.25 \times 10^{-4}$ cb/cm$^2$. 
The straining electrode was first suggested by Hoar and Hines in 1955 as a tool for studying the stress corrosion cracking of metals.

The essential rationalization for this suggestion was based on the fact that the metal at the base of an advancing stress corrosion crack can be thought of as straining locally at a relatively high strain rate. Therefore, it is reasonable, according to Hoar, that any electrochemical analysis of crack velocity should be performed on straining material. On the basis of this hypothesis a number of papers were published by Hoar and his colleagues showing that there is a good correlation between stress corrosion cracking and results from straining electrode studies. Hoar proposed a theoretical explanation for these straining electrode effects.

A second extensive set of studies on straining electrodes was conducted by Windfeldt aiming at explaining the effect of plastic flow on the anodic dissolution of active iron, nickel, and copper based on a model involving direct dissolution at kinks in crystal steps in the surface. The model for the accelerating dissolution of film-free metal electrodes during yielding was proposed by Bockis and his colleagues considering much larger mechano-electrochemical effects on high-index planes.

All of the theories mentioned above concern non-filmed electrodes; whereas the theory developed by Murata and Staehle is associated with
the quantitative analysis of straining film-covered metal electrodes. Numerous other studies relevant to understanding straining electrodes have been conducted by Humphries and Parkins\textsuperscript{31}, Takano and Shimodaira\textsuperscript{53-57}, Graf and Spring\textsuperscript{58}, Beck\textsuperscript{7}, Hanie and Boyd\textsuperscript{52}, Buban and Vermilia\textsuperscript{36,37}, and Leach and his co-workers\textsuperscript{38,39}.

In the next few sections the existing theories for mechano-electrochemical dissolution on film-free electrodes will be reviewed. Then, the theory on film-covered electrodes will be introduced.

1. **Effect of Dynamic Straining on Film-Free Electrodes**

There are several schools which presented different mechanisms for accelerated anodic dissolution of metals.

The following factors must be taken into consideration in analysing the experimental results regardless of the proposed mechanisms.

(1) Structural defects on the surface such as dislocation cores, steps (ledges), interstitial atoms at dislocations, Kinks, grain boundaries.

(2) Metallurgical factors controlling slip formation at the surface such as the number of slip systems; total strain, stacking fault energy, twin formation, phase transformation, grain size, grain boundary, and rotation of the crystal.

(3) Adsorption of polarized water molecules, cations, anions and gas molecules, especially specific adsorption of some ions such as halide ions.

(4) Possibility of precipitation type film formation.
(5) Vibrational frequency of loosely bound atoms on the surface.

(6) Potential deviation of the electrodes from equilibrium potential of single electrode in a given environment, or from zero charge potential.

(7) Kinetics of possible anodic and cathodic reactions.

(8) Possibility of the presence of diffusion controlled steps on solution side.

(9) Sensitivity of the recorder which is used in the experiments. Some of the above factors could be neglected depending on the given conditions.

(a) Simple continuum case for straining film-free electrode

The simplest case for a straining specimen is to assume that the new increment of current $\Delta i$ is due only to the new increment of surface as shown in Figure 33(a). Further, assume that the new surface is smeared out so that volume conservation applies at the specimen in a smooth plastic continuum of initial length $a$ and initial radius $r_0$.

Taking

$$ds = 2\pi(r dl + l dr) \tag{51}$$

$$dv = 0 \tag{52}$$

$$dr = -\frac{1}{2} r \frac{dl}{l} \tag{53}$$

Substituting (53) into (51)

$$ds = \pi r dl \tag{54}$$

Dividing by $dt$, substituting for $r$, letting
Fig. 33.—Schematic illustration of the simple continuum dissolution.
Using the following relation

where \( i = js \)

\( i = \) current

\( j = \) current density

\( s = \) instantaneous surface area

and integrating

\[ i = i_{\text{initial}} \exp \left( \frac{1}{2} \cdot \dot{e} t \right) \]  

(56)

Since strain will be on the order of 30\%, we can simplify (56) to obtain

\[ i = i_{\text{initial}} \left( 1 + \frac{1}{2} \dot{e} t \right) \]  

(57)

At low strains this suggests that the current should be linearly related to total strain or that current as a function of time will increase linearly with strain rate as shown in Figure 33(b) and the increased current, \( Ai \), is only a function of total strain. This assumes no contribution from double layer charging which would be very small relative to the current usually observed in activated kinetics.

(b) Transient dissolution plus simple continuum case

When there is a transient dissolution in addition to the area contribution at freshly produced slip steps as shown in Figure 34(a) the observed current will be strain rate dependent. Since transient dissolution lasts for a short time, very slow strain rate produces the simple
Fig. 34.—Schematic illustration of the transient dissolution.
continuum case. On the other hand, if the strain rate is fast enough to accumulate the transient phenomena as shown in Figure 34(b), the observed current at the cessation of straining is higher for higher strain rates. Mathematical treatment of transient dissolution will be shown in the discussion as an extension of the theory developed for film-covered electrodes.

(c) Simplest Continuum Case plus Specific Adsorption

Murata and Staehle observed that the anodic current decreased linearly at fixed potential during yielding of type 304L stainless steel in dilute sulfuric acid with 0.1 mole of KCl. This was interpreted as a specific adsorption of Cl\(^-\) onto newly exposed surface. The rate of decrease is a function of overpotential, concentration of Cl\(^-\), pH, strain rate, diffusivity of Cl\(^-\) and temperature. The predicted current change, without specific adsorption during straining, is denoted by \(P\) in Figure 35(a). This is calculated simply from the area increase. At high strain rate, however, the current was observed to start increasing after a certain time with the same slope as current when there is no chloride ions. This indicates that the diffusion of Cl\(^-\) onto the electrode surface is a possible rate determining step. On this assumption the steady state Cl\(^-\) concentration adsorbed on the new surface can be calculated as follows.

The number of adsorbed atoms, \(N\), per unit area at steady state could be approximately assessed. Assuming a constant diffusion zone at the electrode solution interface, the concentration variation with distance within the diffusion zone is assumed to be linear as schematically illustrated in Figure 36(a). This assumption is valid to the first order
Fig. 35.—Decrease in anodic current during straining due to adsorption of Cl⁻ (a) at low strain rate, (b) at higher strain rate.
Fig. 36.—Schematic illustration of the diffusion zone.
approximation in the presence of natural convection or artificial stirring.

The current due to adsorption per unit area, \( j_{ads} \) is given by the Nernst-Plank flux equation as

\[
    j_{ads} = -nFD \left( \frac{nF}{RT} \cdot C_b \frac{d\psi}{dx} + \frac{(C_b - C(t))}{\delta} \right)
\]

where
- \( n \) = valence number of adsorbing ion
- \( D \) = diffusion coefficient of an adsorbing ion
- \( C_b \) = bulk concentration of adsorbing ion
- \( C(t) \) = effective concentration of adsorbing ion at the interface at time \( t \)
- \( \delta \) = depth of diffusion zone
- \( \frac{d\psi}{dx} \) = strength of the electric field across the diffusion layer and double layer, but concentration overpotential across the diffusion zone in dilute solution is negligible compared with that of double layer.

This could be approximated by the double layer overpotential \( \psi_d \) divided by the depth of the diffusion zone.

\[
    \frac{d\psi}{dx} = \frac{\psi_d}{\delta}
\]

Concentration overpotential produced by adsorbing ions within the diffusion zone could be cancelled by that produced by dissolving ions of opposite sign. The time interval required to set up the diffusion layer varies with the current density and diffusion rate, but it is the order
of seconds compared with the $10^{-3}$ to $10^{-4}$ seconds needed to establish the electrical double layer. Therefore, $E_{zcp}$ is not considered here.

Boundary conditions in the equation (58) are

1. $C(t) = C_b$ at $t = 0$ (steady state),
2. $C(t) = 0$ at $t = t_c$ (at which concentration of adsorbing ions at newly exposed surface becomes zero).

Before straining $j_{ads} = 0$ at steady state. During straining the increase in net anodic current density in time $dt$ is shown as

$$
\frac{dj_a}{dt} = j_a \left( \frac{ds}{dx} \right)
$$

(60)

where $\left( \frac{ds}{dx} \right)$ is the rate of area increase and $j_a$ is the anodic current density.

After $t_c$ the number of moles transported across the diffusion zone in time $dt$ is equivalent to the number of moles adsorbed on the new surface in $dt$. This is clearly shown in Figure 36(b).

$$
-\frac{\delta}{2} \frac{dC(t)}{dt} = \frac{N}{N_a} \left( \frac{ds}{dt} \right)
$$

(61)

where $N =$ equilibrium number of adsorbed atoms per unit area

$N_a =$ Avogadro's number.

Combining (58), (59), (60) with (61), the rate of the observed current change is expressed as follows:
\[ \frac{d\Delta j}{dt} = \frac{dj_a}{dt} + \frac{dj_{ads}}{dt} \]

\[ = j_a \frac{ds}{dt} - \frac{d}{dt} \cdot nFD \left( \frac{nF}{RT} \cdot C_b \cdot \frac{nd}{\delta} + \frac{(C_b - C(t))}{\delta} \right) \]

\[ = j_a \frac{ds}{dt} + \frac{nFD}{\delta} \left( \frac{dc(t)}{dt} - \frac{nFC_b}{RT} \frac{d\delta}{dt} \right) \quad (62) \]

This equation is valid only at new surfaces, accordingly, \( \eta_{\text{double}} \) is safely assumed as a time independent term. As a consequence, we obtain

\[ \frac{d\Delta j}{dt} = j_a \frac{ds}{dt} + \frac{nFD}{\delta} \frac{dc(t)}{dt} \]

\[ = j_a \frac{ds}{dt} - \frac{nFD}{\delta} \frac{2}{\delta} \left( \frac{N}{Na} \right) \left( \frac{ds}{dt} \right) \quad (63) \]

When \( t = t_c \)

\[ \frac{d\Delta j}{dt} = 0 \]

\[ j_a = \frac{2nFD}{\delta^2} \left( \frac{N}{Na} \right) \quad (64) \]

The unknown value, \( D \), can be derived from the experimental results and the integration of equation (62). At \( t = t_c \), \( \Delta j \) will be obtained from the experimental data as shown schematically in Figure 37. The observed current decrease can be derived as follows.

\[ \Delta j = j_a \Delta S - \frac{nFD}{\delta} \left( \frac{nF}{RT} \cdot \eta_o \cdot C_b + C_b - C(t) \right) \quad (65) \]
Fig. 37.—Schematic analysis of the specific adsorption by Cl⁻.
Derive $C(t)$ from equation (61)

$$\frac{d(t)}{dt} = - \frac{2}{\delta} \left( \frac{N}{Na} \right) \frac{dS}{dt}$$

$$C(t) = - \frac{2}{\delta} \left( \frac{N}{Na} \right) \Delta S + \text{constant}$$

The boundary condition is

$$C(t) = C_b \quad \text{when} \quad S = 0$$

$$\therefore \quad C(t) = - \frac{2}{\delta} \left( \frac{N}{Na} \right) \Delta S + C_b \quad (66)$$

Substitute (66) into (65) we have

$$\Delta j = j_a \Delta S - \frac{nFD}{\delta} \left( \frac{nF}{RT} \cdot \eta_d \cdot C_b + \frac{2}{\delta} \left( \frac{N}{Na} \right) \Delta S \right) \quad (67)$$

Diffusion coefficient, $D$, is given from (67)

$$D = \frac{(j_a \Delta S - \Delta j)}{nF} \cdot \frac{nF}{RT} \cdot \eta_d \cdot C_b + \frac{2}{\delta} \left( \frac{N}{Na} \right) \Delta S \quad (68)$$

Substitute (68) into (64) for $(N/Na)$ we obtain

$$\frac{N}{(Na)} = \frac{j_a \sigma^2}{2nFD}$$

$$= \frac{j_a}{2(j_a \Delta S - \Delta j)} \cdot \left( \frac{nF}{RT} \cdot \eta_d \cdot C_b + \frac{2}{\delta} \left( \frac{N}{Na} \right) \Delta S \right)$$

Therefore we have for $(N/Na)$ as

$$\frac{N}{(Na)} = \frac{j_a \cdot C_b \sigma}{-2\Delta j} \cdot \frac{nF}{RT} \cdot \eta_d$$

$$= \frac{j_a}{2|\Delta j|} \cdot \frac{C_b \sigma}{\Delta j} \cdot \frac{nF}{RT} \cdot \eta_d \quad (69)$$
Equation (69) indicates that \( \frac{N}{Na} \) is linearly proportional to the overpotential to the first order approximation. An example of the application of equation (69) to the steady state adsorption of \( \text{Cl}^- \) on the active 304L stainless steel will be briefly discussed based on the data shown in Figure 35(b) at \( t = t_c \). Using the following values:

where \( \eta_d = -0.053 - (-0.410) = 0.357 \text{V} \)

\[
j_a = 6.4 \text{ mA/cm}^2
\]

\[
j = 0.1 \text{ mA/cm}^2
\]

\[
n = 1
\]

\[
\delta = 100 \mu
\]

\[
C_b = 3.9 \times 10^{-11} \text{M/cm}^2
\]

\[
\left( \frac{N}{Na} \right) \text{ (moles/cm}^2 \) \text{ is shown as}
\]

\[
\frac{N}{Na} = \frac{6.4 \times 10^{-3}}{2 \times 0.1 \times 10^{-3}} \times 10^{-2} \times 1.45 \times 10^{-11} \times \frac{0}{0.059}
\]

\[
= 7.8 \times 10^{-11} \eta_d \text{ (moles/cm}^2 \)
\]

The obtained relation is plotted in Figure 38 to find the critical concentrations for the onset of the local dissolution at mechanically produced new surfaces in the passive region.

The critical concentration for local dissolution can be calculated by substituting \( \eta_d \) by overpotential for the critical potential, \( E_c \), above which local dissolution becomes appreciable. The critical concentration for pits formation, \( E_p \), is also plotted in Figure 38.
$\left( \frac{N}{Na} \right) = 7.8 \times 10^{-11} \gamma_D$

\[ \text{mole/cm}^2 \]

\[ \times 10^{-11} \]

\[ -0.41 \quad -0.053 \quad 0.28 \quad 0.49 \]

$E_p^o \quad \text{Potential}(V_H) \quad E_c \quad E_p$

304 Stainless Steel
0.1N H$_2$SO$_4$
0.1M KCl
1.67%/min.
25°C aerated

... under dynamic yielding

... static

Fig. 38.—Schematic illustration for the steady state concentration of adsorbed atoms.
Surface concentration of the adsorbed anion would be higher than the bulk concentration when the migration term in equation dominates the mass transport process. This case is shown in Figure 39 as a "steady state". The initial state of freshly produced surface is illustrated as a "transient state". The surface concentration of adsorbed ions (anion in this case) tends to increase toward the steady state concentration, $C_s$. However, the concentration at newly exposed area may stay as zero if the rate of the surface area increase exceeds the rate of adsorbing ion supply onto the new surface.

(d) Accelerated dissolution at High Index Planes

Despic et. al investigated the effect of dynamic straining on the anodic dissolution kinetics of film-free electrodes such as iron and nickel in $0.1\text{NH}_2\text{SO}_4$, copper in $0.1\text{NI}_2\text{SO}_4$ plus $0.1\text{NCuSO}_4$, and molybdenum in INKOH. The study was undertaken in connection with the observations of Robertson and Bakish who found, in the study of stress corrosion cracking, preferential attack along the surface slip traces of deformed Cu, Au immersed in FeCl$_3$ solution. Raicheff et. al suggested that there may be a relation between the increase in velocity of dissolution of a metal and its tendency to develop high index planes at yielding.

The theory developed by Despic et. al will be reviewed followed by their experimental observations.

They assumed that the following effects should contribute to an increased current density upon plastic straining:

(1) Double layer charging on the new surface,
Fig. 39.—Schematic illustration for the surface concentration of chloride ions at slip steps.
(2) Increase of surface roughness,

(3) Increased activity for dissolution at the edge of the slip steps,

(4) Increased activity to dissolution at the high index planes,

The current due to the charging of the double layer is

$$i_{dl} = q^m \frac{ds}{dt} \quad (70)$$

where $q^m$ is the charge per unit area of the new surface necessary to bring it from the zero charge potential to the rest potential; $S$ is the newly created surface. Further,

$$q^m = K_{dl} (E - E_{zcp}) = L_{dl} \Delta E \quad (71)$$

where $K_{dl}$ is the integral double layer capacity. Now, the $ds/dt$ is

$$\frac{ds}{dt} = \left( \frac{\partial S}{\partial L} \right) \frac{dE}{dt} L_o \quad (72)$$

where $dE/dt$ is the strain rate and $L_o$ is the original length of the wire.

The current due to the dissolution of slip edges per unit area is

$$i_{ed} = \left( N_e \frac{Y_o L_o}{S_o} \right) i_e \quad (73)$$

where $Y_o$ is the average length of slip line, $N_e$ is the number of slip lines per unit length of the wire, $S_o$ is the original surface before straining, and $i_e$ is the current per unit edge length.

The surface roughness contribution is

$$i_r = \frac{i_{ns} L_o}{S_o} \frac{\partial S}{\partial L} \int \tau \quad (74)$$
where $i_{ns}$ is the current density at the newly formed surface and $F$ is the roughness factor.

Finally the current due to higher index planes is derived as follows. The plane ABCD in Figure 40 represents an initial configuration as $A'B'C'D'$ represents the intermediate state. The transient current is obtained as a function of $r$, and the steady state current is obtained when $r$ becomes zero leaving only low index planes in the surface.

Assuming a number $dx$ of individual h.i.p. are produced at any time interval $dt$, ie,

$$\frac{dx}{dt} = KL_0 \left( \frac{dE}{dt} \right)$$  \hspace{1cm} (75)

where $K$ is the frequency of occurrence of slips per unit elongation. The total current on the slip planes, $i_{sp}$, is a sum of the currents on these individual h.i.p. developed up to $t$:

$$i_{sp} = \int_0^x i_{sp} \, dx = \int_0^x i_{sp} \left( \frac{dx}{dt} \right) \, dt$$

$$= KL_0 \left( \frac{dE}{dt} \right) L_{sp} \, dt$$  \hspace{1cm} (76)

where $i_{sp}$ is a current transient at a single h.i.p. and obtained as

$$i_{sp} = B' - A't$$  \hspace{1cm} (77)

where $B'$ and $A'$ are constants.

One obtains for a constant $KL_0(dE/dt)$

$$i_{sp} = Bt - At^2$$  \hspace{1cm} (78)

where $B$ and $A$ are constants.
Fig. 40.—Model of dissolution of one high index plane site developed upon slipping along B, C.

(Despí 19)

Fig. 41.—Anodic-current-density (time) relationships for iron (0.1N H₂SO₄ solution, E = -0.290 V), molybdenum (1N KOH solution, E = -0.340 V), nickel (0.1N H₂SO₄ solution E = -0.060 V), and copper (0.1N H₂SO₄ + 0.1N CuSO₄ solution, E = +0.310 V). Strain rate 0.0167 (cm/cm) sec⁻¹, initial current density -15 10⁻² A cm⁻². B—Breaking point.

(Despí 19)
The total current density in the plastic region is a sum of (1) (2) (3) and (4)

\[ A_i = i_{de} + i_{ed} + i_r + i_{sp} \]

\[ = Q + (P + B)t - At^2 \quad (79) \]

where \( Q = \frac{Kde L_o \left( \frac{\partial S}{\partial L} \right)}{S_o} \frac{E}{dt} + \frac{N_e Y_0 L_o I_e}{S_o} \)

\[ P = \frac{ins L_o \left( \frac{\partial S}{\partial L} \right) f}{S_o} \frac{dE}{dt} \]

They tried to explain the asymptotic tendency of the current, \( i \), with increasing strain by using equation (79) and calculating the current at high index planes, \( i_{h.i.p.} \). Their model and discussion, however, contain the following uncertainties which should be corrected:

1. An asymptotic behavior of the observed current for B.C.C. metals (Fe, Mo) as shown in Figure 41 is similar to the transient dissolution in the early stage of the straining F.C.C. metals. As the deformation process of B.C.C. crystals is complexed because of numerous slip systems and high stacking fault energy, the frequency and the mode of a slip step formation change with the total strain and strain rate although the predominant slip system at ambient temperature is \((110)(111)\).

When a plastic instability, or a localized deformation starts, a drastic change in the rate of surface area increase, \( ds/dt \), occurs. As a consequence the maximum current, \( i_{max} \), and time \( t_{max} \) do not have significant physical meanings.
It is, therefore, more reasonable to ascribe the initial asymptotic behavior to the transient dissolution in the early stage of deformation before $t_s$ at which the transient dissolution and the decay will reach the steady state. If a constant appearance of the same type of the new surface is expected during yielding we would observe the linear relationship between the current increment and strain as a simple continuum case discussed in chapter IV-1-(a), but if the deformation mode and the frequency of the slip formation change with the total strain and strain rate the deviation from the linear relationship would be observed as shown in Figure 42. Bockris and his colleagues ascribed the deviation to the $-\alpha t^2$ term in equation (79): the transient dissolution of high index planes.

(2) Polycrystal specimens contain grains which may have high index planes at surfaces. If the rate of dissolution is 50 times larger for these high index planes compared with that of low index planes as they proposed, a static polycrystal electrode may yield rather high dissolution rates at high index planes. Consequently the effect of yielding would not contribute significantly to the total current since slip planes are predominantly low index planes.

Probably, the point that they should have made is not a homogeneous dissolution in the high index planes but the increase of kink sites and edges of slip steps due to complex slip modes. Because of a complex dislocation--dislocation interactions in the near surface region, due to numerous slip systems and rather high stacking fault energy, B.C.C. metals tend to have higher concentrations of energetically favorable sites for dissolution than F.C.C. and H.C.P. metals.
ideal case

accelerated dissolution due to surface defects

localized deformation

fracture

fracture

contribution from perpetual current at slip steps

Fig. 42.—Schematic analysis of a symptotic current-time curve under straining.
(3) In the calculation for the rate of dissolution at high index planes they assumed a constant frequency of occurrence of slips per unit elongation, $K$, throughout the deformation. This is obviously an incorrect assumption for B.C.C. metals where we tend to have a different mode and frequency depending on the total strain and strain rate. The significant observations by Despic et. al are:

(a) The maximum currents vs. strain rate are plotted in Figure 43; it is significant that $i_{\text{max}}$ for Cu (F.C.C.) is slightly dependent on the strain rate while $i_{\text{max}}$ for iron (B.C.C.) and molybdenum (B.C.C.) show a larger dependence on the strain rate. This is due primarily to the difference in deformation processes between F.C.C. metals and B.C.C. metals. Figure 44 shows the linear relation between maximum current, $i_{\text{max}}$, and strain rate for various potentials in active region. The slight change in the applied potential causes a drastic change in $i_{\text{max}}$ since it contributes to the current exponentially;

(b) Figure 45 shows the calculated dissolution current at a high index plane in terms of potential and normal polarization curve at the static electrode. Regardless of the model, it is of interest to note that the observed current due to the accelerated dissolution ($i_{\text{h.i.p.}}$ this time) is higher at lower overpotential. This observation agrees quite well with reported data$^{48,132,133}$ as partly discussed in chapter II.

(c) There is an asymptotic relation between the observed current and strain especially in B.C.C. metals where high index planes are expected during straining. Saturation current was observed in the case of F.C.C. metals where slip systems are mainly $(111)(110)$.
Fig. 43.---Maximum attained current density ($i_{\text{max}}$) as a function of strain rate for iron, molybdenum, and nickel. (Despic et al. \textsuperscript{19})
Fig. 44.—Maximum current density ($J_{\text{max}}$) as a function of strain rate at different potentials for iron. 
(Despic et al. 19)
Fig. 45.—Initial and h.i.p. dissolution of potential in the case of iron.  (Despic et al. 19)
(e) Thermodynamics of Mechanochemical Effect

Gutman\textsuperscript{76,75} developed the method of the thermodynamics of irreversible processes in order to analyse the mechanico-chemical and related effects based on certain simplifying assumptions and corresponding models.

The essential purpose of this theory is to describe quantitatively the relation between the mechanical phenomena of emergence of dislocation at the surface and electrochemical dissolution by introducing the concept of the chemical potential of dislocations. It was shown through the derivation that the deformation affects metal dissolution mainly by reducing the energy of sublimation of metal atoms. This is the similar concept as that of Hoar (next section) except that Gutman's theory is strictly limited to a thermodynamical approach where the results can predict only the change in the chemical potential of atoms in metals or ions in solutions.

(1) Linear phenomenological equation

The fundamental steps of the derivation of the equation will be shown. The deformation in the linear strain-hardening stage where no cross slip takes place is considered since the mechanico-chemical effect is maximized in this case. First of all the entropy production, $\sigma^I$, due to plastic deformation is derived as follows. The density of mobile dislocations generated in a deformed metal is related to plastic strain $\varepsilon$ by

$$N = \alpha (\varepsilon - \varepsilon_0) = \alpha \Delta \varepsilon$$

(80)
where $\alpha$ is a constant and $\epsilon_0$ is the strain corresponding to the elastic limit. Hence the strain for a single dislocation formation at constant temperature and stress $\tau$ is equal to $1/\alpha$: the work done, which is equivalent to the chemical potential $\mu_D$, is given by

$$\frac{\tau}{\alpha} = \mu_D \quad (81)$$

The chemical affinity, $A$, of a dislocation is given by the difference in the chemical potential between two stress states,

$$A = \Delta \mu_D = \frac{\Delta \tau}{\alpha} \quad (82)$$

and the flux density of generated dislocations, $n$, is defined as

$$n = NV \quad (83)$$

where $V$ is the rate of dislocation motion. Then the entropy production due to deformation is given by

$$\sigma^T = \frac{nA}{T} \quad (84)$$

Dislocation flux density, $\dot{n}$, could be expressed in terms of measurable quantities as

$$\dot{n} = \frac{\epsilon_p}{bA} \Delta \epsilon = L_{III} \quad (85)$$

where $\epsilon_p$ is the plastic deformation rate, $b$ is the Burgers vector, $A$ is a constant given by $\Delta \epsilon$ times free dislocation path, $a$ and $L_{II}$ is given by
where θ is a strain hardening coefficient. A is also obtained in terms of measurable quantities by

\[ A = \frac{\Delta \tau}{\alpha} = \frac{\theta \Delta \epsilon}{\alpha} \]  \hspace{1cm} (87)

Equation (84) becomes a quadratic form by substituting the expressions (86) and (87)

\[ T_0^I = L_{II}^2 = \frac{\epsilon_0^\theta}{\kappa \lambda \alpha} \Delta \epsilon^2 \]  \hspace{1cm} (88)

Secondly, the entropy production due to electrochemical reaction such as anodic dissolution is given by

\[ \sigma_{II} = \frac{I \eta}{T} \]  \hspace{1cm} (89)

where η is the overpotential and I is the corrosion current given by the following equation

\[ I = L_{22} \eta \]  \hspace{1cm} (90)

The coefficient \( L_{22} \) depends on the kinetics of the electrochemical reaction and is a measure of electrode polarizability. Here Gutman defined the linear relation between I and η based on the observed data that the polarizability during the propagation of a stress corrosion cracking is low and consequently \( L_{22} \) is equal to the reciprocal of the polarization resistance. When a metal electrode undergoes plastic deformation, the
overall entropy production is given by equation (84) and (90) and the
cross coefficients \( L_{12} \) and \( L_{21} \):

\[
T_0 = T(\sigma^I + \sigma^{II}) = \dot{n}A + I \mathcal{N}
\]  
(91)

where

\[
\dot{n} = L_{11}A + L_{12} \mathcal{N}
\]  
(92)

\[
I = L_{21}A + L_{22} \mathcal{N}
\]  
(93)

The coefficients \( L_{12} \) is equal to \( L_{21} \) by Onsager equation.

The physical meaning of \( L_{21} \), the quantitative mechanico-chemical
effect, can be elucidated and quantitatively studied on the basis of con­cepts of nonequilibrium electrochemistry, according to which the entropy
production in the absence of mechanical process is given by

\[
T_0^{II} = \frac{IA}{ZF}
\]  
(94)

where \( Z \) is the ionic valency of the metal, \( F \) the Faraday number, and the
electrochemical affinity \( \tilde{A} \) for the case of anodic dissolution is

\[
A = \Lambda \mu + ZF \Phi
\]  
(95)

where \( \Lambda \mu \) is the chemical potential difference between an ion in the metal
and the electrolyte, and \( \Phi \) is the electrical potential of the metal.

From equation (94)

\[
I = \frac{L_{22}A}{ZF}
\]
Substitute the following relations in (91)

\[ \eta = \phi - \phi_o \]

\[ \phi_o = -\frac{\Delta \mu}{ZF} \]

\[ I = \frac{L_{22}}{ZF} \frac{L_{21}}{L_{22}} ZF \frac{\Delta \tau}{\alpha} + \Delta \mu + ZF \phi \]  \quad (96)

The first term is the mechanical one, the second term is the chemical one, and the last one is the electrical work. Equation (96) shows that \( \Delta \tau \) increases the chemical potential of ions in the metals; in other words, deformation reduces the necessary work of sublimation.

The above discussion is limited to small deviation from the equilibrium of the system.

(2) Non-linear Phenomenological Equation

When the deviation from the equilibrium of the system is not small, kinetic relations for the principle flux and forces must be considered. Here only the final expression will be described. Dislocation flux is given by

\[ \dot{n} = L_{11} RT (e^{\frac{\Delta}{RT}} - 1) + L_{12} \eta \]  \quad (97)

and anodic current \( I \) is expressed as

\[ I = L_{21} A + L_{22} b (e^{\phi} - 1) \]  \quad (98)

where \( b = \) Burgers vector

\( \eta = \) overpotential \( (\phi - \phi_o) \)
A = Chemical potential change at dislocation;

\[ \mu_D - \mu_D^0 = \frac{\Delta \gamma}{a} \]

\[ k_2 = \text{rate constant for metal reduction} \]

\[ L_{22} = \frac{k_2}{2} \frac{Z_F L^n}{i^{+\mathcal{H}}} (\lambda_i \cdot C_i^o) V_i \]

\[ L_{11} L_{12} = L_{21}; \text{kinetic coefficients} \]

\[ \lambda_i \] = activity coefficient of specie i

\[ C_i^o \] = concentration of specie i

\[ V_i \] = stoichiometric coefficient

\[ l^{\text{nm}} \] = indices of starting components

Gutmen applied equations (96) and (98) to the case where he used a steel (08sv) - 7NH4SO4 system straining one wire at 345/min and using the other wire as a reference electrode. Figure 46 shows the experimental results. In the linear hardening range the observed current was also linear with total strain as predicted by equation (96) and in the no linear range equation (98) was used as an adequate description of the saturating current.

The chemical potential of a dislocation introduced here is defined only by the work done to move the dislocation. However, this concept includes only the strain energy term of a dislocation. The reactivity of the dislocation should be discussed in terms of impurity atmospheres along with the dislocations, core energy, and configuration in addition to strain energy as we discussed in chapter II. Because of the many assumptions and simplifications during derivation, the direct application of the obtained equation is questionable.
Fig. 46.—Tensile load $p$ (curve 1) and corrosion current, $I$ (curve 2) plotted against strain rate.

(Gutman)
(f) Accelerated Dissolution due to Rayleigh Waves

Rayleigh waves are elastic perturbations propagating near the free surface of the solid and decay with depth. It could be described schematically as Figure 47.

Howard and Pyle\textsuperscript{27,28} introduced the concept of Rayleigh waves to explain the relative reactivities of atoms at different sites on the metal surface and, consequently, the tendency to transgranular stress corrosion cracking. This model is based on Bass\textsuperscript{168} remarks that the physical position of an atom on the surface is not an overriding factor in determining the activation energy of the dissolution process and that the frequency of vibration of the atom at the surface determines whether or not the atom can become solvated by an electrolyte. It is the atoms which vibrate most slowly that are the active atoms on this model and, therefore, the activation energy varies continuously with the frequency of vibration of the atoms. It must be recalled that the stronger is the binding force, the higher is the vibrational frequency.

For a perfectly plane interface only the vibrations normal to the surface makes any contribution to the dissolution of the metal. Bass\textsuperscript{168} assumed that the frequency distribution of these vibrations is given by the Debye distribution. In addition Rayleigh waves contribute when the solid is subjected to any condition which causes an elastic perturbation. The key steps for the calculation of the dissolution rates are the following. Bass\textsuperscript{168} assumed that the presence of the electrolyte reduces the binding of the outermost ions to a value $1/\epsilon$ of that in vacuo and the activation energy required for an ion to be solvated becomes $V_0/\epsilon(w)$
Fig. 47.---Schematic illustration of Rayleigh waves.
where $V_0$ is the potential of the electrode and $\varepsilon(w)$ is the dielectric constant of the solution and chosen to be that corresponding to the frequency of the ionic vibrations as

$$
\varepsilon(w) = \varepsilon + \frac{\varepsilon_s - \varepsilon^\infty}{1 + \omega^2 \tau^2}
$$

(99)

where $\varepsilon_s$ is the static dielectric constant of the solution at the interface, is the relaxation time of the solution dipoles, $\varepsilon^\infty$ is the optical dielectric constant of the solution, and $\omega$ is the frequency of dissolving ions.

Now, the probability, $P(w)$, per unit time that an ion will surmount a barrier $V_0/\varepsilon(w)$ is:

$$
P(w) = \frac{1}{2\pi} \left[ 1 - \exp\left(-\frac{1}{\tau} \right) \right] \cdot \exp\left(-\frac{H}{\varepsilon(\omega)}\right)
$$

(100)

where $H = n_f \omega$. The total dissolution rate is then obtained by integrating this function over the whole range of the frequencies of vibration of the ions and is given by:

$$
R = \int_{0}^{W_g} P(w)dz
$$

(101)

where $dz$ is the number of vibrations of surface ions in a frequency range between $\omega + d\omega$ and $W_g$ is the maximum frequency. Since the calculation for $dz$ is complexed, it will not be shown in this review.

In this model the rates of dissolution depend strongly on two parameters: the frequency of vibration of the ions in the metals, which is associated with surface microtopography, and the relaxation time of
the solvent molecules which is dependent upon the temperature and composition of the solution. Dividing surface sites into two kinds; an atom sitting in the plane and an atom occupying the corner of a step on the surface, the rates of dissolution of these two kinds of sites, $R_p$ and $R_c$, are given by

$$R_p = \frac{3N_d a^3}{4MW^3} \cdot \frac{1}{14} \int_0^{x_{\text{max}}} \exp \left(-\frac{V_1}{\varepsilon_s KT} \cdot \frac{1 + x}{1 + \frac{\varepsilon_K x}{\varepsilon_s}}\right) x \, dx$$

(102)

$$R_c = R_p + \frac{1}{14} \left(\frac{3N_d a^3}{4MW^3}\right)^{2/3} \cdot \frac{\varepsilon_K}{\varepsilon_s} \frac{a^2}{W^2} \left(\frac{1 + x}{1 + \frac{\varepsilon_K x}{\varepsilon_s}}\right)^{1/3} \int_0^{x_{\text{max}}} \exp \left(-\frac{V_2}{\varepsilon_s KT} \cdot \frac{H\sqrt{x}}{1 + \frac{\varepsilon_K}{\varepsilon_s}}\right) x^{1/2} \, dx$$

(103)

where $M$ is the atomic weight of the metal, $\rho$ the density, $a$ the mean distance between two atoms, $x = (W_g^2)^{2/3}$, and $V_1$ and $V_2$ the real potentials of the ion at the surface and edge sites, respectively. The first term, $R_p$, represents the contribution made to the dissolution from the plane surface by vibration normal to the surface. The second term is the contribution of the Rayleigh waves to the dissolution rate which is considered to be effective at discontinuities in the surface. However, as the density of the proper modes of vibration of the Rayleigh waves is greater in the lower frequencies than that of Debye waves, the second term is about $10^4$ times greater than the first.
There is a limitation on the range of permissible frequency for the surface waves; generally, $\omega A = \text{constant}$ in particular, $\omega_{\text{max}} = 10^{13}/\text{sec}$ when $A_{\text{max}} = 2a$, where $a$ is the atomic diameter. The limiting frequency is given by

$$\omega = \frac{2a \times 10^{13}}{l} \quad (104)$$

where $l$ is the step separation. Since the probability of an ion becoming solvated decreases rapidly for frequency $\omega < 10^{11}/\text{sec}$ and the distribution of the modes of vibration is proportional to $\omega^2$, the optimum frequency is $\omega \approx 10^{10}/\text{sec}$. Substituting this value into equation (104) we obtain the critical step spacing, $\sqrt{5} \times 10^{-5}\text{cm}$.

Technological application of this concept was proposed by Howard and Pyle\textsuperscript{28} in connection with transgranular stress corrosion cracking and the ratio $R_c/R_p$. Figure 48 shows that the relation between $R_c/R_p$ and average slip step width. In spite of the agreement in the restricted cases such as stainless steels in boiling MgCl$_2$ and Cu-Zn alloy, there are several ambiguous in this theory as follows.

(1) This theory is based on the two big assumptions that the surface is free of oxide films and the vibrational frequency of surface atoms is the rate controlling factor in the dissolution of a metal. However, most of the metal-environment systems, where stress corrosion crackings have been found, show the existence of some kind of films. It is true that the lower the frequency of an atom the higher the tendency for dissolution of the atom, but generally the most favorable site for dissolution is a kink atom and not a corner atom of a step, and an
Fig. 4.8.—Change of reactivity with step length for atoms at step edges on the surface of copper alloys. For Cu-Zn alloys, \( \eta \approx 0.20 \). (Howard and Pyle\textsuperscript{28})
adsorption of a particular anion is also expected at a kink site preferentially in the process of dissolution.

(2) The part played by the solution is, according to the theory, to reduce the binding energy of outermost surface atoms by a factor of $1/e$ where $e$ is a dielectric constant of the static solution. The effect of $\text{Cl}^-$ is to increase the viscosity of the solution and the effect of raising the temperature is to reduce the viscosity thereby the critical spacing changes. However, the effect of $\text{Cl}^-$ is not clear at this time and all that we know is that it assists the break down of passivity and accelerates local dissolution. No experimental data are available to show the relation between concentration of $\text{Cl}^-$ and surface slip width in connection with stress corrosion cracking.

(3) The critical frequency $\sim 10^{10}$ is an approximate value and therefore the critical separation which is calculated using the critical frequency is also an approximate value. As a consequence it is not reasonable to explain the drastic change in the susceptibility of stainless steel to stress corrosion cracking because the slip separation is neither an sufficient nor a necessary condition for stress corrosion cracking.

(4) The part played by the overpotential term in an active dissolution is not discussed in the theory. If Rayleigh waves play an important role in the dissolution of metal under dynamical straining, it would be under the condition that the surface is totally clean, overpotential is small, and the concentrating of ions which chemically react with metal atoms is low so that the contribution would be appreciable compared with the total current density.
Therefore, the above theory is not generally applicable to the anodic dissolution of a metal and stress corrosion cracking.

(g) Accelerate Dissolution due to Kink Sites

This theory was developed by Windfeldt\textsuperscript{50,51} to explain the accelerated dissolution on film-free electrode based on the recent observation and proposal by Hurlen\textsuperscript{162} that the reaction of solid metal metal-ion electrodes occur directly at kinks in the surface steps. Therefore, dissolution should be proportional to the number of kink sites per step times the number of steps per unit area. This model differs from that by Devanathan et. al in that diffusion of surface ad-atoms to and from kink sites is neglected whereas, Devanathan et. al\textsuperscript{48} assumed a slow diffusion as the rate controlling process at low overpotential.

According to Hurlen\textsuperscript{162}, anodic current is directly proportional to surface property and thereby it is possible to express the concentration of the surface defects, $S$, at any potential in terms of overpotential, $n$, and the equilibrium concentration of the surface defect at equilibrium potential, $S_e$, as

$$S = S_e \exp \left( \frac{ZF\eta}{nRT} \right)$$  \hspace{1cm} (105)

Here kink density per step is assumed to be independent of overpotential for small $\eta$.

Windfeldt studied\textsuperscript{50,51} the effect of straining on the anodic dissolution of active iron and nickel in acid chloride solutions and active copper in acid cupric sulphate solutions. He measured the maximum
potential change under straining up to fracture at both open circuit potential and constant current densities which were externally controlled. The typical potential shift, $E$, vs. time relation for iron and nickel are shown in Figure 49.

An attempt was made to give a theoretical treatment of the effect of plastic flow in metals on their dissolution and deposition behavior. It was found that the effect was increased with the ratio of strain rate to dissolution rate (current) and disappeared shortly after deformation.

From equation (105) the ratio of current density at two different potential can be written as

$$\frac{i_1}{i_2} = \frac{S_1}{S_2} = \left(\frac{S_{e1}}{S_{e2}}\right) \exp\left(\frac{V_1 - V_2}{b}\right) \quad (106)$$

where $S$ is the dissolution rate at the potential $V$ and step density $S$, and $b$ is the Tafel slope. The numbers have corresponding meanings for different potentials, $V_1$ and $V_2$. It is also expected from equation (106) that the surface of dissolving solid metal has a density of self perpetuating steps that is proportional to the activation overvoltagage, $\eta$, when $\eta$ is small.

$$S = K (V - E) = K\eta \quad (107)$$

where $K$ is a nucleation constant and $E$ is equilibrium potential.

For a strained electrode there will be a number of non-perpetuating steps generated by the slip occurring in addition to self-perpetuating steps. The non-perpetuating steps could be assumed to form at a rate
Fig. 49.—Examples of potential-time curves. Stress started at A, wire fractured at B. Solid line Fe, dotted line Ni. (Windfeldt\textsuperscript{50})
proportional to the strain rate and disappear at a rate proportional to their density in the surface and to the dissolution rate.

Under steady state conditions, the total step density in the surface of simultaneously yielding and dissolving metal is given by

\[ S' = K\eta' + K'(r/i) \]  

(108)

where \( K' \) is a constant, \( r \) the strain rate. Equation (108) covers both a purely energetic term \( Kn' \) and a purely kinetic term \( K'(r/i) \), but the former effect is comparatively small and reduces to (107) at zero strain rate.

From equation (106), (107) and (108) Windfeldt derived the expression for the maximum potential change \( \Delta V = V' - V \) under galvanostatic conditions (\( i = i' \)).

\[ \Delta V = -\ln \left( 1 + \frac{\Delta V}{\eta'} + \frac{K'}{K} \left( \frac{r}{i'} \right) \right) \]  

(109)

with increasing \( (r/i) \) this approaches the following equation

\[ V = -\ln \left( \frac{K'}{K\eta'} \left( \frac{r}{i} \right) \right) \]  

(110)

It is assumed in this derivation that the energetic effect of the strain is negligible (i.e. \( \eta = \eta' \)) and that strain does not directly change the kink density in steps.

The observed data will be briefly reviewed. Pure iron and nickel wires were strained at given strain rates to fracture and the maximum change of the corrosion potential, or potential change under galvanostatic condition, were recorded. The electrolytes used were 0.01M HCl
+ 0.99M KCl for iron and 0.1M HCl and 0.9M KCl (pH 1.0) for nickel.

Figure 50 shows the maximum change of potential vs ratio of strain rate to dissolution rate (\(r/i\)). The potentials were produced at 2%/sec for iron and 3%/sec for nickel at various currents. As expected from equation (110) \(\Delta V/d\log(r/i)\) approaches the Tafel slope \(b\) for higher strain rates. For a small current, which is one of the condition to derive equation (110), the potential shift vs log \(i\) shows an approximately linear relationship as shown in Figure 51.

The potential shifts were found to be independent of pH in case of iron dissolution as shown in Figure 49. This observation does not agree with Hurlen\(^{163}\) who suggested the pH dependence of steady state step density for iron. Hurlen suggested that pH influences the steady state kink density in steps by hydroxyl ions taking part in the relatively few kink forming reactions.

Windfeldt\(^{51}\) conducted the same kinds of experiments on copper in acidified cupric sulphate solutions under galvanostatic conditions. Copper has a relatively high exchange current density. Therefore, a slight modification is needed in the derivation for \(\Delta V\). The obtained equations are the following;

for small \((r/i)\)

\[
\Delta V = -\frac{K'N}{S_0(r/i)} + \Delta E
\]

(111)

for large \((r/i)\)

\[
V = \gamma + \Delta E
\]

(112)
Fig. 50.—Maximum change of potential versus ratio of strain rate to dissolution rate (r/i). Solid (Ni) and dotted (Fe) curves calculated from equation (110). Closed circles (Ni) and open circles (Fe) show experimental points. (Windfeldt)
Fig. 51.—Maximum change of anode potential versus anodic current density. Strain rate: Fe 2%/s, Ni 3%/s, Fe in 0.01M HCl + 0.99M KCl, pH 2.0. Ni in 0.1M HCl + 0.9M KCl, pH 1.0.

(Windfeldt 50)
where $\Delta E = E' - E$ and it is purely a energetic effect of the plastic strain. The maximum change of potential vs. ratio of strain rate to dissolution rate $(r/i)$ is shown in Figure 52. It is clear that the maximum potential change actually approaches a limiting value at high values of this ratio as predicted by (112). This value is numerically equal to the activation overvoltage $(V-E)$ less the permanent potential change $(\Delta E)$ due to an increase of stored energy which is, however, the order of $10^{-6} \approx 10^{-5} \text{mV}$ and negligible.

His conclusions about the effect of continuous plastic flow on the anodic dissolution are as follows.

1. The maximum potential shift is proportional to $(r/i)$.
2. The effect is not lasting but disappears shortly after the deformation process is stopped.
3. For large $(r/i)$, $\Delta V$ vs. log $(r/i)$ shows a linear relationship as predicted in case of Fe and Ni in chloride solutions.
4. For large $(r/i)$, $V$ reaches the maximum value $-(V-E) + E$ in case of copper in copper sulphate solutions.
5. Thus the results are in accordance with a model involving direct dissolution at kinks in crystal steps in the surface.

The assumption for the linear relation between step density and overpotential, however, may not be required to explain the observed results.

Steady state step density may not increase linearly with the overpotential but the probability for dissolution of atoms is the steps increases exponentially with overpotential because of the increased driving
Fig. 52.—Maximum change of corrosion potential (open symbols) and anodic potential (closed symbols) of iron versus dissolution rate in solutions of various pH. Strain rate 2%/s.

pH 2.0, pH 1.0, pH 0.05.

(Windfeldt50)
Fig. 53.—Maximum change of potential vs. ratio of strain rate to dissolution rate (r/i). Dotted line calculated from equation (109), solid line calculated from equation (110). Open circles show experimental points.  

(Windfeldt51)
force for dissolution. It is, therefore, possible to derive the equation for $\Delta V$ using a constant step density at steady state instead of equation (107).

From equation (106) we have

$$\frac{i'}{i} = \frac{S'}{S} \exp \left(\frac{\Delta V}{b}\right)$$

Assuming that the step density increases by $K'(r/i)$ during straining, then

$$\frac{i'}{i} = \frac{S_o + K'(r/i)}{S_o} \exp \left(\frac{\Delta V}{b}\right) \quad (113)$$

where $S_o$ is the steady state step density.

For a galvanostatic condition we have $i = i'$ then $\Delta V$ is expressed as

$$\Delta V = -b \ln \left(1 + \frac{K'}{S_o} \left(\frac{\rho}{i}\right)\right) \quad (114)$$

when $\frac{K'}{S_o} \left(\frac{\rho}{i}\right) < 1$ we obtain

$$\Delta V = -b \frac{K'}{S_o} \left(\frac{\rho}{i}\right) \quad (115)$$

when $\frac{K'}{S_o} \left(\frac{\rho}{i}\right) > 1$ we have

$$\Delta V = -b \ln \left(\frac{\rho}{i}\right) + C \quad (116)$$

where $C = -b \ln \frac{K'}{S_o}$
Since this is a galvanostatic case the dissolution rate involves the overpotential term. Both equations (115) and (116) could replace equations (109) and (110).

Secondly, $\Delta V_{\text{max}}$ may not have much meaning from the metallurgical point of view: since it is the transient potential at which necking or localized deformation is occurring on the electrode when specimens are strained to fracture. The maximum potential shift, $V_{\text{max}}$, is also a function of crystal structure, or rather slip systems. It is more meaningful to stop straining before necking starts and to keep the total strain constant regardless of the strain rate, and compare the results. As it will be discussed in chapter VI, the quantitative analysis of either the transient potential at fixed current density or the transient current at fixed potential can be done this way. It is noted that the potential shift is approaching zero at high current density according to his observations the contribution of the transient dissolution to either current density or potential shift is significant only at smaller overpotentials or lower current densities.

(h) Anodic dissolution controlled by slow surface diffusion

Devamathan and Fernando investigated the dissolution of copper in CuSO$_4$ under strain at low overpotentials where dislocations may play a predominant role. Studies were carried out in the range 2.5-15mV with strain rate ranging from 0.047-0.9105 strain/min. in order to verify the kinetic model proposed by Mehl and Bockris and Lorenz for deposition and dissolution of metals. This model involves a surface diffusion of ad-atoms or ad-ions to and from kink sites as a rate controlling step.
at low overpotentials. First, their model for anodic dissolution under strain will be introduced and then the important observations will be discussed.

The dissolution and deposition of metals when surface diffusion is rate controlling at low overpotential has been studied by Kita, Bodris and Enyo and Bockris and Damajanovic. The expression for the dissolution current controlled by surface diffusion is

\[ i = ZF \left( k_1 - k_2 C_0 \right) \frac{D}{L^2k_2} \]

where

\[ k_1 = \frac{\dot{C}_0}{ZF} \exp \left( \frac{\alpha ZF}{RT} \right), \]

\[ k_2 = \frac{\dot{C}_0}{ZFC_0} \exp \left( (d-1) \cdot \frac{ZF\eta}{RT} \right), \]

\( C_0 \) is the equilibrium ad-atom concentration at the surface, \( D \) is diffusion constant, \( \alpha \) is the transfer coefficient and \( L \) is the average separation of dislocations.

For the direct kink sites dissolution model the current is given by

\[ i = \frac{\pi D'ZFC_0'}{L \ln(L/\alpha_0)} \cdot \frac{ZF\eta}{RT}, \]

where \( D' \) is the bulk diffusion constant, \( C_0 \) is the concentration of ion in the bulk and \( \alpha_0 \) is the lattice spacing. Devanathan and Fernando introduced the relationship among strain, strain rate and dislocation density into equations (117) and (118). They assumed that the relationship between density of dislocations, \( N_1 \) and the shear strain \( E_d \) developed for a single crystal by Young is applicable for copper polycrystal wires.
N = Ae \quad (119)

Since the separation between surface dislocations is related to dislocation density by the following equation developed by Kita et. al\textsuperscript{169}.

\[ L^2 = \frac{1}{4N} \quad (120) \]

From equations (117), (118), (119) and (120) we have the expression for the current controlled by the surface diffusion as

\[ i \propto \varepsilon^{1/2} \quad (121) \]

and for the current controlled by direct charge transfer at kink sites

\[ i \propto \frac{e^{1/2}}{\ln \varepsilon^{1/2} + C} \quad (122) \]

where C is a constant. If the simple assumptions expressed by equations (119) and (120) hold the current will be proportional to \( \varepsilon^{1/2} \) for the former case and a very complex function of \( \varepsilon \) for the latter case. The experimental data shown in Figure 54 supports the slow surface diffusion model. However, the transient dissolution where the surface diffusion is not a rate controlling step can also produce the linear dependence on \( \varepsilon^{1/2} \) in the beginning of straining. This will be discussed in chapter VI. The slow surface diffusion model should be examined carefully since it is based on the unknown surface factors such as the distribution of step width and step height as a function of strain and strain rate.
Fig. 54.—Net anodic cd vs. (corrected strain)$^{1/2}$, for different overpotentials. 0.1084 strain/min. (Devanathan$^{49}$)
2. Effect of Dynamic Straining on Film-Covered Electrode

Most of the straining electrode theories were intended for film-free electrodes. Hoar's "lattice disarray" theory was originally developed to explain the straining effects observed for 18-8 stainless steel in boiling magnesium chloride solution assuming the electrode surface is film-free. However, it was found later that 18-8 stainless steel has a surface film in this environment. Therefore, his theory will be discussed in this section together with their observations. Murata and Staehle developed the straining electrode theory for film-covered electrodes aiming at obtaining the initial current density at freshly produced slip steps and information on film repairing processes. Several other studies on film-covered electrodes have been conducted by Leach and Neufeld, Takano and Shimodaira, Hoar and Calvele, Slater and Hoar, Humphries and Perkins, Rainie and Boyed, Graf and Springe, Latanision and Staehle and Chen and Beck. Two existing theories will be discussed first and the relevant works will be briefly reviewed.

(a) Accelerated Dissolution due to Lattice Disarray

Yielding assisted anodic dissolution was studied by Hoar and West demonstrating that low strain rates considerably reduced the activation polarization required to dissolve 18-8 chromium-nickel steel anodically in hot concentrated magnesium chloride solution. Hoar and his colleagues continued this type of study, both galvanostatically and potentiostatically, assuming the electrode is free from film in the given condition. This assumption was questioned and
experimental evidence of the presence of the film was shown by many investigators including Graf\textsuperscript{58}, Slater\textsuperscript{30}, and Swann and Embury\textsuperscript{164}.

Hoar suggested\textsuperscript{21} a lattice disarray mechanism in order to explain the significant increase of anodic current under yielding in terms of the following:

(1) Thermodynamics of Disarrayed Lattice

Total extra energy by elastic deformation is no more than 10 cal/mole and the stored energy of plastically deformed metals, calculated from stress strain curves, is at most 100 cal/mole. Those elastic or stored energies are too small to explain what would happen at the surface of the electrode.

(2) Kinetics of Disarray

The significant difference in electrochemical behavior between cold worked and annealed metal can be related to the rate of anodic dissolution and potential by an equation,

\[
I_a = A n \exp \left( -\frac{\Delta G_a^*}{RT} \right) \exp \left( \frac{\alpha Z F e}{RT} \right)
\]  

(123)

where

\begin{align*}
A &= \text{a constant} \\
\alpha &= \text{transfer coefficient} \\
\Delta G_a^* &= \text{the standard free energy of activation of these sites at reversible potential} \\
e &= \text{electrode potential}
\end{align*}
The possible ways to increase $a$ on the clean surface are:

i) increase $n$

ii) decrease $\Delta G_a^*$

iii) both i) and ii).

The decrease of $\Delta G_a^*$ due to total strain energy stored in an electrode is not sufficient to explain the observed data. As a result, increase of $n$ is the most probable reason for that large increase of the current.

It is, however, reasonable to suggest an average energy for the severely disarrayed regions such as grain boundaries and dislocation cores in the range of 2-10 Kcal/mole, approximating in energy to that of the liquid state. This contribution may be still minor compared with the overall dissolution which depends mainly on self-perpetuating sites. The better solution for this problem could be obtained by considering film and transient dissolution upon break down of the film along with newly exposed areas. This concept will be discussed in detail in the following section.

(b) Theory of Straining Film-covered Electrodes

At present only a simplified phenomenological theory is possible. The essential basis for this development is the trench-like dissolution resulting from dislocation motion observed by Smith and Staehle and Swann and co-workers during corrosion studies of thin foils.

There are a number of current consuming processes which may possibly be included such as double layer changing, film repair, lattice disarray and rapidly dissolving high index surface. However, from the electron
metallographic studies of thin foils, the coulombs involved in metal
dissolution are much greater than consumed in these other processes;
therefore it is legitimate to consider only this single process.

The exact transient response during film breaking and subsequent
repassivation will not be clear until a more rigorous theory is developed.
Therefore, the development herein assumes an exponential decay during
repassivation which starts at \( t = 0 \) and an arbitrary initial amplitude
\( i_0^a \). Figure 3 relates a unit process of dissolution and a single slip
step with the associated single current transient. The three cases
illustrate the point that there may be a wide range of repassivation
rates. In a simple way the material dissolved per slip step event, \( \Delta m \)
can be calculated from equation 4 as

\[
\Delta m = K i_0^a \int_0^\infty e^{-\beta t} dt
\]

where \( K \) is a constant, \( i_0^a \) is the initial current amplitude and \( \beta \) is a
decay constant. Clearly the molecular details of the single slip step
dissolution event are complicated e.g. the local area and potential are
changing with time. However, the simple approach taken here will serve
a useful purpose.

There is no experimental way to determine uniquely the current as-
associated with a single transient. It is therefore necessary to utilize
an average experiment like the straining electrode where the current from
a large number of individual slip step events is obtained. The summation
of this slip step events to produce a total current in an external measur-
ing system is shown in Figure 55. Here the maximum steady state current
\( i_d(t) = i_a^0 e^{-\beta t} = j_a^0 \Delta s e^{-\beta t} \)

(a) **UNIT DECAY CURVE**

- \( i_{a}^{s,M} \): Maximum Saturation Current
- \( i_{a}^{s,a} \): Average Saturation Current

(b) **SUMMATION OF UNIT CURVES**

\[
\frac{i_{a}^{s,a}}{\Delta t} = \frac{i_{a}^{0}}{i_{a}^{s,a}} \sum_{i}^{k} \int_{(k-1)\Delta t}^{k\Delta t} e^{-\beta t} dt = \int_{0}^{t_s} e^{-\beta t} dt
\]

(c) **Analysis**

*Fig. 55.* Schematic illustration of the straining electrode theory.
occurs after a time $t_g$ when the first transient has decayed to an exponentially negligible value; the time for the current to decay upon cessation of straining is also $t_g$ from the same reason.

Implicit assumptions in the model depicted as in Figure 55 are the following:

1. Straining is conducted at constant potential and the local potential condition at an emergent step remains constant.

2. Each step height is the same under given strain rate regardless of condition of the film, but steps can be produced successively on the same plane or different plane.

3. Complications due to mass transfer and local potential shift may be neglected.

4. All slip steps have approximately the same angle of emergence with specimen surface within a certain amount of total deformation.

5. There is a uniform time interval between successive steps under given strain rate.

6. Decay of reaction current can be approximated by an exponential decay function $e^{-\beta t}$, where $\beta$ is the decay constant depending on the alloy, environmental condition and potential.

Continuing in this simplified view the extensive anodic current, $I_a^o$ is related to a current density by:

$$I_a^o = j_a^o \Delta S$$

(125)

where $j_a^o = \text{current density}$, $\Delta S$: slip step area.
The current of a single transient is then given

\[ I_a(t) = i_0 \exp (-\beta t) \]
\[ = J_0 \Delta S \exp (-\beta t) \tag{126} \]

The key parameters which need to be obtained are \( \beta, j_0^0 \) and \( \Delta S \). The straining electrode behavior will be evaluated for \( \beta \) and \( j_0^0 \) but \( \Delta S \) can not be uniquely obtained.

The straining electrode current density \( S_a(t) \) can be evaluated according to the following analysis. Following Figure 51(c) the peak of any current spike can be obtained by seeing the contribution of the decaying portion of previous transients with that of the maximum spike so that

\[ \Delta t \cdot I_a(t) = \int_{1}^{K} \sum_{k=1}^{K} e^{-\beta t} dt \tag{127} \]

Here the \( k \) index refers to previous transient events. Since it is desirable to eliminate this serration index, to simplify calculation, it can be observed that the summation of the individual elements in the left Figure 55(c) is exactly the equal of adding these elements together to obtain a single transient as in the right hand portion of Figure 55(c). In other words, from Figure 55(b) a series of prior transients contributes to the height of the cross hatched region when these elements are separated as shown in Figure 55(c) (left); the elements are combined in Figure 55(c) (right).
The number of coulombs in the cross hatched column of figure 51(b) is approximately \( \int_0^{\infty} e^{-\beta t} dt \). Thus,

\[
\int_{s,a}^d = \int_{a}^{\infty} (\Delta S) \int_0^{ts} e^{-\beta t} dt
\]

(128)

If we assume that the upper integration limit is \( t_s \) which can be taken at a small fraction of \( i_0 \), then

\[
\int_{s,a}^d = \int_{a}^{\infty} \frac{Q}{\beta} (1 - e^{-\beta t}) \left( \frac{\Delta S}{\Delta t} \right)
\]

(129)

We can obtain another useful expression from the decay curve. Assume that the current at any time after the cessation of straining is \( I_a(t) \). Then, the number of coulombs in any element \( \Delta t \) width is:

\[
I_a(t) \Delta t = \int_{\Delta S}^{0} e^{-\beta t} dt
\]

then

\[
= \int_{\Delta S}^{0} \frac{Q}{\beta} (e^{-\beta t} - e^{-\beta t_s})
\]

(130)

Experimentally we know \( t, I_a(t) \), and \( I_{s,a} \). We can take the ratio of equations (129) and (130) to obtain

\[
\frac{I_{s,a}}{I_a(t)} = \frac{1 - e^{-\beta t_s}}{e^{-\beta t} - e^{-\beta t_s}}
\]

(131)
If we take $t = \frac{t_s}{2}$ then

$$\frac{\dot{S}_a}{l_a(t_s/2)} = \frac{1 - (e^{-\beta t_s/2})^2}{e^{-\beta t_s/2} - (e^{-\beta t_s/2})^2}$$

This can be solved to obtain

$$\beta = -\frac{4.606}{t_s} \log \left( \frac{\frac{1}{\dot{S}_a} \left( \frac{\dot{S}_a}{l_a(t_s/2)} \right)}{\ddot{S}_a - \dot{S}_a} \right)$$

where the ratio $\frac{\Delta S}{\Delta t}$ need not be known.

If we wish to obtain $\frac{\Delta S}{\Delta t}$ then, assuming a straining cylinder at constant volume it is possible to obtain in relationship from the equation (9) assuming instantaneous area $S = S_o$, original surface area within small strain.

$$\frac{\Delta S}{\Delta t} = \frac{1}{2} \varepsilon S_o \delta$$

where $\frac{\Delta S}{\Delta t} = \text{area change of given specimen exposed to a given environment}$

$S_o = \text{original surface area exposed to a given environment}$

$\varepsilon = \text{strain rate}$

$\delta = \text{correction factor due to serrated surface: this can be obtained from the measurement of increase of passive current, } A_i, \text{ in a passivating system after stop of straining.}$
substituting (133) into (129) we obtain for \( j_0 \) as

\[
\int_{j_a}^{j_0} = \frac{F S_a}{S_0 e^\beta} (1 - e^{-\beta t_s})^{-1} \tag{134}
\]

Since we know \( \beta \) from (132) we can write

\[
j_0 = 4.606 \frac{\dot{S}_a}{S_0 e^\beta} \log \left[ \frac{\dot{S}_d - \dot{S}(ts/2)}{\dot{S}(ts/2)} \right] (1 - e^{-t_s})^{-1} \tag{135}
\]

From equation (132) and (135) it is now possible to obtain two of the required critical parameters. These two quantities can be used to give an extremely valuable result—an estimation of one dimensional time dependent penetration rate.

\[
\frac{dx}{dt} = \frac{M}{nFp} \frac{j_0}{\beta} \exp(-\beta t) \tag{136}
\]

Integration of (136) gives

\[
X = \left( \frac{M}{nFp} \right) \frac{j_0}{\beta} \tag{137}
\]

where \( X \) is the total penetration per event. Equation (138) shows the relationship among \( x \), \( j_0 \) and \( j_a \) for iron (\( f = 7.85 \), \( n = 2 \), \( A = 55.85 \))

\[
X = 2.71 \times 10^{-5} \frac{j_0}{\beta} \text{ (cm/event)} \tag{138}
\]

(c) Important Observation

The anodic behavior of 18-8 stainless steel while yielding in 42% aqueous \( \text{MgCl}_2 \) at 154 C was studied by Hoar and West\(^{23,24}\), who demonstrated marked yield assisted anodic dissolution. Hoar and Scully\(^{26}\) modified West's apparatus to overcome the objection by van Rooyen\(^{171}\)
concerning the reproducibility, and could show that 18-8 stainless steel would dissolve at $\approx 100 \text{mA/cm}^2$ at a potential of $-140 \text{mV}_H$ under the same conditions used by West.

Hoar and Galvele$^{29}$ studied the anodic behavior of mild steel during straining, at a constant potential in various hot nitrate solution in terms of pH, strain rate and potential. They found the large increase in anodic current as high as $2 \text{A/cm}^2$ upon yielding the oxide-covered steel. This increase is, however, almost independent of strain rate and is a linear function of total strain as shown in Figure 56. The rate of stress corrosion cracking observed at low strain rate was estimated as $\approx 0.25 \text{cm/hr}$, which is equivalent to an anodic dissolution of an advancing edge of the crack of up to $\approx 2 \text{A/cm}^2$. Thus they concluded that the purely electrochemical dissolution is a reasonable explanation of the crack propagation of this system.

Slater and Hoar$^{30}$, however, were unable to reproduce the high dissolution current during yielding using the same physical conditions as Hoar and West$^{23,24}$ and Hoar and Scully$^{26}$ demonstrated as shown in Figure 57. Slater and Hoar$^{36}$ clearly stated the presence of film in boiling MgCl$_2$ solutions. The presence of the film on 18-11 stainless steel in boiling MgCl$_2$ solution was also postulated by Graf and Springe$^{58}$ assuming that the high cathodic current masks the presence of passive region. They found that stress corrosion cracking is occurring only in this postulated passive region and stress corrosion cracking and pitting is exclusive each other. If the corrosion potential is in the range of active dissolution the corrosion will not be localized and if the
Fig. 56.—Variation of current density with % strain
4N Ca(NO₃)₂, pH 3.7 (at 25°C), 102°C, eH = -0.10V.
Strain rate: ●, 307%/min; ○, 154%/min; □, 31%/min; △, 8%/min
(Galvez29)
Fig. 57.—Potentiostatic cd vs. strain curves for Fe-Ni-Cr alloys in boiling MgCl$_2$ solution at various potentials. (Slater$^{30}$)
corrosion potential is in the range of pitting the localized dissolution leads to the subsequent ductile failure because of the reduction of the cross sectional area. Their observations were confirmed by Murata and Staehle\textsuperscript{63} in the study of straining effect on the film-covered 18-8 stainless steel in 0.1NH\textsubscript{2}SO\textsubscript{4} - 0.1NHKCl solution. They found the potential range in which the localized dissolution along with slip lines was observed during repassivation as shown in Figure 58. It is this potential range, (E\textsubscript{p} - E\textsubscript{c}), that Murata and Staehle found stress corrosion cracking. At potentials more noble than this potential range pitting was dominating and therefore a ductile fracture was observed while at potential less noble than the potential range localized dissolution was negligible and a consequence no stress corrosion cracking was found.

In the study of stress corrosion cracking of low carbon steels in both sodium hydroxide and sodium nitrate, Humphries and Parkins\textsuperscript{31} found a certain potential range where plastic straining of film-covered specimens result in a large increase in anodic current, the magnitude of which is considerably greater than would appear likely from consideration of the area of film-free metal exposed by the film rupture. They also found stress corrosion cracking in this potential region. In hydroxide the range of the potential agree reasonably will with that in which HFeO\textsubscript{2}\textsuperscript{−} is stable, while in nitrates formation of Fe\textsuperscript{2+} or Fe\textsuperscript{3+} is possible in this potential range as a soluble specie. Takano and Shimodaira\textsuperscript{55, 57} discussed the possible mechanism of stress corrosion cracking of brass and stainless steel in various environments in terms of observed stress strain curves in situ and surface film properties. Figure 59(a) is
Fig. 58.—Stationary state current density as a function of the electrode potential. (Murata and Staehle\textsuperscript{63})
Fig. 59(a).—Polarization curves of 18Cr-11Ni austenitic stainless steel in 42\% MgCl₂ aqueous solution; Curve 1, solution B, Curve 2, solution A.

Fig. 59(b).—(1): Stress-strain and current density-strain curves obtained in solution aerated MgCl₂ (42\%) at different applied potentials, (2): Enlargement of stress-strain-current density relation at the early stage in (1), (6*2.7*10⁻²sec⁻¹). (Takano and Shimodate)
polarization curves of 18-11 stainless steel in (1) 42% MgCl$_2$ aerated aqueous solution (145°C) and (2) the same solution but deaerated. Figure 59(b) shows the stress-strain curves at various potential in Figure 59(a) in the solution (1). It should be noted that straining accelerates the anodic dissolution at potential where presumably the surface film is present as postulated by Graf and Springe$^{58}$. 

Mechanical properties of the surface film is a measure of effectiveness in prevention of metal from corrosion. It is not possible to predict the mechanical properties of surface oxide films by extrapolating data on bulk oxides. Anodic alumina films stripped off of the metal surface were studied by Bradhurst and Leach$^{172}$ and anodic films on the metal were studied by Bradhurst and Leach$^{173}$ and Dubar and Vermilyea$^{36,37}$. The experimental evidence obtained by Leach and Neufeld$^{38,39}$ strongly suggests that the mechanical relaxation effect of aluminum shown in Figure 60 upon application of anodic field is due to enhanced oxide plasticity under these conditions. The most likely mechanism for oxide plasticity is diffusional similar to that proposed by Nabarro$^{174}$ and Herring$^{175}$. They demonstrated that the mechanical effects arising from temperature change and electrostatic forces or surface dissolution are too small to explain the observed data. The effect of anodic oxide layer on the mechanical properties was also studied by Latanision and Staehle$^{32}$ for nickel single crystal in H$_2$SO$_4$ solution. They found that the first stage can be masked by the presence of anodic film since the dislocation motion is stifled at metal oxide interface unless the stress is high enough, by pile up dislocations, to break the oxide film. They
Fig. 60.—Extension under 20g load of alminium wire anodized for 5min at 10mA/cm$^2$ in 15% H$_2$SO$_4$.

(Leach and Neufeld$^{39}$)
also found that the presence of the thin film tends to produce finer slip modes compared with the slip mode on film-free surface.
V. EXPERIMENTAL APPARATUS AND PROCEDURE

Introduction

The experimental program was arranged to produce the environmental and metallurgical parameters applicable to interpreting anodic dissolution kinetics of straining electrodes. The base electrolyte was H₂SO₄ in which the polarization behavior of nickel has been studied in detail. This system gives well defined regions of passivity, transpassivity and activated dissolution. Preliminary tests were conducted in order to confirm anodic polarization characteristics. Figures 61-67 shows the behavior of nickel in the pH range (0-14) and the temperature range (0-75°C). As pH increases the reactions tend to be more complex and less producible.

Anion (SO₄²⁻) concentration was kept constant to be 0.5 mole unless specially stated.

The following types of experiments were conducted:

(a) Anodic polarization curves were determined by the potential sweep method in order to obtain Tafel behavior.

(b) A few experiments were conducted in which potential decay was measured with time starting at passive potentials.

(c) Apparent activation energy in the passive region was determined on a static electrode by measuring the steady state current densities at various temperatures.
Fig. 61. Anodic polarization curves.
Fig. 62.—Anodic polarization curves.

0.2N H$_2$SO$_4$ (pH 1.2)
N$_2$ SATURATED
SCAN RATE 2V/hr.
Fig. 63.---Anodic polarization curves.
Fig. 64.—Anodic polarization curves.

- **PURITY Ni**
- 0.2 M $K_2SO_4$ (pH 6.2)
- $N_2$ SATURATED
- SCAN RATE 2 V/hr.

Temperature: 0°C, 25°C, 50°C, 75°C
Fig. 65.—Anodic polarization curves.
Fig. 66.—Anodic polarization curves.
Fig. 67.—Anodic polarization curves.
(d) Current-time behavior at constant potentials was determined in straining electrode experiments as follows.

(1) Straining was continued to fracture.

(2) Straining was continued until the slope indicated saturation. (For higher strain rates such as 50, and 100%/min saturated slopes were not obtained because of limited strain before fracture)

(3) Straining was continued for a given time, especially in the cathodic region, where the effective surface increased during straining was determined on film free surface.

(4) After straining current decay was recorded with and without elastic stress.

(5) Surfaces of the specimens were examined by scanning electron microscopy.

An important feature of this work involved an examination of the straining electrode response over the wide range of potential (including active, passive and cathodic regions). There is work reported on the quantitative analysis of straining electrodes except Bockris' work where he and his colleagues simply assumed that higher index planes dissolve much faster than low index planes. Their work was successful to explain the different anodic dissolution rate under straining between B.C.C. metals and F.C.C. metals. However, even F.C.C. metals show transient dissolution, which lasts a few seconds only, thereby non-linear dissolution behavior at high strain rate will be observed. Another feature of
this work is to determine the apparent activation energy for dissolution under straining. The role played by stress in stress corrosion cracking is not clarified as yet since, there is a controversial discussion as to whether plastic deformation decreases the activation energy for anodic dissolution or increases the number of dissolution sites.

1. Specimen Preparation

Commercially produced, 0.46mm diameter, nickel wires were chosen. Specimens 15cm. in length were enclosed in quartz capsules in an argon atmosphere and annealed at 760°C for one hour, then air cooled. The approximate grain size is 20-40µm. Specimens were decreased and then pickled in a 50-50 weight % solution of sulfuric acid and nitric acid for one minute, then washed in double distilled water. They were then coated at the ends with "microstop" for low strain rate and room temperature tests and with silicon sealant diluted with 2-butanon over "microstop" for high strain rate or high temperature tests since the silicon sealant has a good elastic property. Exposed area (center portion of specimens) was approximately 0.5cm².

2. Electrolyte

In most experiments 1 NH₂SO₄, 0.5 NH₂SO₄ + 0.25M K₂SO₄ and 0.2NH₂SO₄ + 0.4MK₂SO₄ were used. The solution was prepared from reagent grade sulfuric acid and double-distilled water. Most electrolytes were purged with nitrogen by passing purified and de-oxygenated through heated copper turnings.
3. The Polarization Cell

All electrochemical experiments were conducted in the 1000ml glass cell shown in Figure 68 which contains a verticle glass tube specimen chamber.

The centrally located specimen is surrounded by a platinum gauge working electrode. A fitted glass cylinder for bubbling nitrogen alternative and a reference electrode are introduced through openings in the cell. A slight nitrogen overpressure was maintained in the cell by admitting the gas through a water trap. The reference probe was constructed so that the capillary was about 1mm away from the specimen.

The external portion of the reference probe was placed in a container of saturated K\textsubscript{2}SO\textsubscript{4} solution, which was in turn connected to a saturated KCl solution which received the saturated calomel electrode (SCE) used as the reference electrode throughout the experiments. All potentials were plotted converted to the standard hydrogen scale by adding 242mV to the potential measured with respect to SCE.

4. The Constant Potential Apparatus

For polarization measurements a Model 66 TS 10 Wenking potentiostat was employed in conjunction with a motor potentiometer and an Esterline Angus Model E 1101S Speedservo recorder which has one-fifth second full scale response time. An attempt was made to employ an oscillograph in the above system for higher sensitivity but 60 cycle noise from the A.C. power source of the potentiostate disturbed the measurements. In order to avoid the noise problem a potentiostat was constructed using an operational amplifier as shown in Figure 69.
Fig. 68.—Glass cell.
Fig. 69.—Schematic diagram of potentiostatic circuit.
Dynamic straining was accomplished with an Instron tensile testing machine. Extension rates in the range of 0.05 to 10 cm/min were used.

5. Experimental Procedure

To begin a test each wire specimen, coated with "microstop" or additional "silicon sealant", was secured in the glass specimen chamber and the cell was filled with 800 ml of electrolyte. The thermometer, the pickled specimen, nitrogen gas inlet, and Luggin capillary were then introduced into the cell and nitrogen was purged through the system for two hours.

Current-time characteristics were measured at constant potentials during straining of the specimens. Potentials were chosen in cathodic, anodic (0.20 and 100 mV\textsubscript{H}) and stable passive (700-900 mV\textsubscript{H}) regions. Straining at a given potential was stopped when the total anodic current vs time curve reached the saturation value. This procedure was not followed at high strain rates where no saturation was observed before fracture.

Except for those experiments designed to show the effect of strain rate a strain rate of 1%/min was used. This strain rate was found to be most effective to separate non perpetual dissolution (transient dissolution) from rather perpetual dissolution at slip steps. The temperature of the system was controlled with water bath from 0°C to 75°C.

Change of the total surface area of the specimen during each test will be discussed in the next chapter.
6. Choice of Experimental Conditions

First, solutions in the range of pH 0-2 were chosen based on preliminary tests (Figures 61-67) because these solutions provide rather stable polarization characteristics. Temperatures were chosen in which the system yielded reproducible results. Above 60°C most of the systems do not show a reversible behavior, examples are shown in Figures 70 and 71. In measuring the activation energy for dissolution of static electrodes in the passive range a hysteresis was observed. This hysteresis is due to active patch formation or preferential dissolution at grain boundary at higher temperatures and repassivation at lower temperatures.
Fig. 70.—Hysteresis of passive current density.
Fig. 71.—Hysteresis of passive current density.
VI. RESULTS AND DISCUSSION

First, the activation energies of static electrodes will be discussed over the active and passive potential ranges. Then, the surface area determination for both film-free and film-covered electrodes will be demonstrated. Finally, the effect of straining on film-free and film-covered electrodes and corresponding activation energies will be discussed in detail based on the newly developed straining electrode theory.

1. Activation Energy Measurements at Static Electrodes

(a) Passive region

The activation energy for anodic dissolution in passive region has been discussed by Sato and Okamoto\textsuperscript{176} and Beck and his colleagues\textsuperscript{177}. The reported data were reproduced here in order to compare the activation energies in both the passive and active regions, with those obtained under straining.

Figures 72-76 show typical plots for steady state current densities the slope of which provides the activation energies. Figure 77 shows that the apparent activation energies in the stable passive region are independent of potentials. This is reasonable since the electric field is constant in this region. At more noble than 900mV\textsubscript{H}, the surface film becomes unstable (transpassive region). When anion concentration was not kept constant the activation energy was more pH dependent as shown in Figure 78. This is considered to be caused by the temperature
Fig. 72.—Activation energy measurement in passive region.

\[ \Delta H = 22.4 \text{ kcal/mol} \]

0.2 N H\textsubscript{2}SO\textsubscript{4}  
\( \text{pH 0.96 AT R.T.} \)  
700 mV\textsubscript{H}
Fig. 73.—Activation energy measurement in passive region.

$\Delta H = 20.9 \text{kcal/mol}$

$700 \text{ mV}$

$0.5 \text{ NH}_2\text{SO}_4$
Fig. 74. -- Activation energy measurement in passive region.

\[ \Delta H = 22.3 \text{ kcal/mol.} \]

\[ \Delta H = 18.4 \text{ kcal/mol.} \]

In H$_2$SO$_4$

700 mV$_H$
Fig. 75.—Activation energy measurement in passive region.

5N H$_2$SO$_4$
700mV$_H$
$\Delta H = 17.7$ kcal./mole
Fig. 76.—Activation energy measurement in passive region.
Fig. 77.--Apparent activation energies for various pH and potentials.
Fig. 78.—Anion concentration dependence of activation energies.
dependence of the disassociation of sulfuric acid. The predominant disassociation is given by (139).

\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^- \] (139)

\[ \text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{2-} \] (140)

It is, however, probable that the second disassociation (140) may change the effective concentration of \( \text{H}^+ \) in the solution at high temperature since the disassociation constant is a function of temperature. If the passive current, \( i_p \), is expressed simply as

\[ i_p = A [\text{H}^+] e^{-\frac{\Delta H}{RT}} \] (141)

where \( A \) is a constant, and \( H \) is an apparent activation energy as discussed in chapter II (section 4). The activity term of hydrogen ion can be deduced from Figure 78 as \( \frac{5.2}{RT} \) where \( [N] \) is the bulk concentration of sulfuric acid (in normal) and a constant, 5.2, is expressed in terms of Kcal.

For constant sulphate ion concentration the disassociation is stabilized and therefore much less temperature dependent.

2. Active Region

Unlike most reported works, there are double peaks in the active region for which there is no clear explanation. Two possible explanations are,

1) Preferential dissolution at grain boundaries.

2) Two kinetic steps.
It is not the author's purpose to study the above phenomenon and, therefore, further experiments were not conducted.

The activation energy was measured for different solutions (0.2N \( H_2SO_4 \) + 0.4M \( K_2SO_4 \) and 1N \( H_2SO_4 \)) from exchange current densities which were obtained from Tafel relationship as partly shown in Figure (79) and (80). The results are 19.5 Kcal/mole for both solutions. The precise anodic dissolution mechanism is not known yet.

3. Area Determination on Film Free Electrode Surface Under Straining

When the sample is strained in the cathodic potential region the cathodic current increases (negative direction), and the elastic and plastic deformation effects on the hydrogen reduction reaction can be clearly separated. The linear current change is a function of cathodic current (or cathodic overpotential) and strain rate as shown in Figures 81 and 82.

It should be noted that a cathodic current change due to 1% strain is a function of strain rate as shown in Figure 82.

The above observations could be explained by using the diagram illustrated in Figure 83. At potential \( E_1 \) the observed cathodic current is expressed as \( (C_1 - A_1) \) since the real anodic current is \( A_0 \) and the real cathodic current is \( C_1 \). Once the sample is strained each polarization curve is shifted to \( C_1^S \) and \( A_1^S \), then the net change due to the area increase is given by \( (C_1^S - A_1^S) S \). If the potential observed is close to the rest potential active dissolution may be observed and, if the active dissolution potential is more cathodic than the equilibrium potential of
Fig. 79.—Measurement of Tafel slope and the exchange current densities.
Fig. 80.—Measurement of Tafel slope and the exchange current densities.
Fig. 81.—Effect of potential on $i_{c}^{ob}$. 

$\Delta i_{c}^{ob}$ ($\mu$A/cm$^2$) vs. TIME (min) in 1 N $H_2SO_4$ at 25°C with $\dot{\epsilon} = 1$ and $\epsilon = 1$. 

1. -100 mV$_H$ 
   -40 $\mu$A/cm$^2$ 

2. -250 mV$_H$ 
   -180 $\mu$A/cm$^2$
EFFECT OF $\dot{\varepsilon}$ ON $\Delta i_{c}^{ob}$

IN $\text{H}_2\text{SO}_4$, 25°C

-100mV

-40$\mu$A/cm$^2$

Fig. 82.—Effect of strain rate, $\dot{\varepsilon}$, on $i_{c}^{ob}$. 
Fig. 83.—Schematic illustration of anodic and cathodic polarization curves with and without straining.
nickel the observed current will be a purely cathodic current. This is analysed schematically in Figure 84. Since it takes time to reach the steady state for adsorption and desorption (hydrogen gas formation), there is a cathodic transient as shown by B \rightarrow C in Figure 84. The change B \rightarrow C' is purely due to the area increase. The area discussed here is a kinetically defined area rather than geometrical one but it could be assumed as a geometrical one because (1) preferential chemisorption of hydrogen ions onto newly formed surface defects such as kink sites is not controlling the observed cathodic current (at steady state) but desorption of hydrogen molecules is; (2) surface topography, especially, slip band formation is a function of strain rate.

When the metal is strained near the rest potential where both cathodic and anodic reactions are present, both reactions are accelerated and the resulting current response is given by a summation of two currents as shown in Figure 85. Anodic current is featured at a peak in the beginning of plastic deformation, whereas; anodic current decay, when straining is stopped, is described as an accelerated cathodic current after C in the figure. Typical current-time curves for various potentials are shown in Figure 86. The standard equilibrium potential for nickel dissolution as a divalent ion is approximately -250 mV$_H$ and, therefore; the anodic dissolution could be neglected at more cathodic potential such as -400 mV in Figure 86.

The general expression for the current response under straining could be approached in the following way. The observed cathodic current for static electrodes, $i_{\text{obs}}^c$, is given by the summation of two opposing
Fig. 84.—Cathodic current change during straining.
Fig. 85. — Schematic analysis of current change, $\Delta i$, at high $\dot{\varepsilon}$. ($E \approx E_c$)
CURRENT CHANGE DURING STRAINING

IN H₂SO₄ 25°C
STRAIN RATE: 100% /min
i_c: μA/cm²

-100mV_H (i_c = -48.8)

-200mV_H (i_c = -492)

-400mV_H (i_c = 7500)

Fig. 86. — Current change during straining at various potentials.
currents as described by

\[ i_{c}^{\text{obs}} = j_c - j_a \]  

(142)

where \( j \) denotes current density and \( c \) and \( a \) denote cathodic and anodic currents, respectively. If the metal is strained the above equation will be replaced by

\[ i_{c}^{\text{obs}} = j_{c}^{s} - j_{a}^{s} \]

\[ = j_c (1 + K_a \frac{\Delta S}{S_0}) - j_a (1 + K_c \frac{\Delta S}{S_0}) \]

\[ = j_{c}^{\text{obs}} + (K_c - j_a \frac{\Delta S}{S_0}) \]  

(143)

where \( \frac{\Delta S}{S_0} \) is a ratio of surface area increase for a given condition, \( a \) and \( K_a \) and \( K_c \) are constants for anodic and cathodic reactions, respectively. If the overpotential for each reaction is lowered at freshly produced slip steps, \( K_a \) and \( K_c \) will be larger than unity. The observed current change, \( \Delta i_{c}^{\text{obs},s} \), during straining is described by the second term in equation (143). Substitute \( j_a \) by \( j_c - j_{c}^{\text{obs}} \) through equation (142) we obtain

\[ \Delta i_{c}^{\text{obs},s} = \left[ j_c K_c - j_a (j_c^{s} - j_c) \right] \frac{\Delta S}{S_0} \]

\[ = \left[ j_c (K_c - K_a) + j_{c}^{\text{obs},s} K_a \right] \frac{\Delta S}{S_0} \]  

(144)

therefore, the following equation is obtained:

\[ \frac{\Delta i_{c}^{\text{obs},s}}{i_{c}^{\text{obs}}} = \left[ \frac{j_c}{i_{c}^{\text{obs}}} (K_c - K_a) + K_a \right] \frac{\Delta S}{S_0} \]  

(145)

If \( i_{c}^{\text{obs}} \) could be assumed to be approximately equal to the real cathodic current density \( j_c \), we have
\[
\frac{\dot{A}_c \text{obs,}}{A_c \text{obs}} = K_c \frac{A_S}{S_0} \tag{146}
\]

If \(A_c \text{obs}\) is smaller than \(A_c\) or if the anodic current is too high to be neglected, we have higher values because of \(J_c / A_c \text{obs}\) term unless \(K_c = K_a\). Experimental data shown in Figure 87 shows the linear relationship between potentials and the ratio expressed in equation (146) at potential more cathodic than that of equilibrium of nickel and nickel divalent ions. If we could assume that \(K_c = 1\) at steady state where the desorption is rate controlling the rate of area increase can be quantitatively obtained. Logarithmic strain rate dependence of the area increase for 1% plastic strain indicate that the correction factor, for the area calculation discussed in chapter IV is now given experimentally from Figure 87 as

\[
\delta = 2 (3.5 + \log \dot{\varepsilon}) S_o \tag{147}
\]

therefore, the general expression of \(ds/dt\) on film-free electrodes is described as

\[
ds/dt = S_o \dot{\varepsilon} (3.5 + \log \dot{\varepsilon}) (\text{cm}^2/\text{min}) \tag{148}
\]

This is shown in Figure 88.

4. Area determination on Film-Covered Electrode Surface Under Straining

There is no direct method to calculate the rate of area increase during straining for film-covered electrode. It is, however, approximately calculable if we measure the increase of steady state passive current density, \(\Delta i_p\), after repassivation in terms of given strain and strain rate. The measurement of \(\Delta i_p\) should be conducted.
DETERMINATION OF $\Delta S / S_0$

$$\text{INH}_2\text{SO}_4 \ 25^\circ \text{C}$$

$$\dot{\epsilon} = \%/\text{min}$$

$$\frac{\Delta i_{c}^{ob}}{i_c^{ob}} = K_c \frac{\Delta S}{S_0}$$

$\dot{\epsilon} = 100$

$\dot{\epsilon} = 10$

$\dot{\epsilon} = 1$

Fig. 87.—Determination of $\Delta S / S_0$ from cathodic current measurement.
INH\(_2\)SO\(_4\) 25°C

\[
\frac{ds}{dt} = \dot{\varepsilon} (3.5 + \log \dot{\varepsilon}) S_0
\]

\((S_0 = \text{UNIT AREA}) \quad 1 \text{cm}^2\)

Fig. 88.—Experimentally determined \(\frac{ds}{dt}\) on the film-free surface of nickel.
under stress-free condition since the presence of elastic stress may cause different type of film formation at freshly produced slip steps.

Assume that $\Delta i_p$ corresponds to the increase of surface area, $\Delta S$, the following simple equation may hold.

$$\frac{\Delta i_p}{i_p} = \frac{\Delta S}{S_0}$$  \hspace{1cm} (149)

where $S_0$ is the original surface area and $i_p$ is the passive current density at steady state before straining. The obtained $\sigma$ through this method for film-covered electrode is plotted against strain rate in Figure 89 together with $\sigma$ for film-free electrode. It is obvious that the presence of the film reduces the value of $\sigma$ especially for small total strain and low strain rate in which thickness of the surface film could be comparable to slip height. The data shown in Figure 89 were obtained for 1% total strain.

5. Effect of Straining on Film-Covered Nickel Electrode

First, general features of current response upon yielding at 800 mV_{passive} will be discussed. Then, activation energy measurement for anodic dissolution at freshly produced slip step will be shown together with the developed theory.

(a) Effect of Strain Rate

Figure 90 shows the current increment during straining at various strain rate in 1M H_{2}SO_{4}. The same data are replotted against strain in Figure 91. The current increment is approximately linear with strain but it is a function of strain rate. This observation does not
Fig. 89.—Correction factor as a function of strain rate.
Fig. 90.—Effect of strain rate, $\dot{\varepsilon}$, on $\Delta i_a$. 

$1 \text{ N } H_2\text{SO}_4 \ 25^\circ C$

$800 \text{ mV}_H$
Ni
1 N H₂SO₄ 25°C
800 mVₜₜ
\( \varepsilon: \% / \text{min} \)

\[ \Delta i_0 (\text{mA/cm}^2) \]

\[ \varepsilon = 100 \]
\[ \varepsilon = 50 \]
\[ \varepsilon = 10 \]
\[ \varepsilon = 5 \]
\[ \varepsilon = 1 \]

STRAIN (%)
0 5 10

Fig. 91.—Effect of strain rate, \( \varepsilon \), on \( \Delta i_0 \) at 25°C.
agree with data reported by Hoar and Galvele where the current is only a function of total strain. Since the current increase on film-covered electrode (passive region) is associated with (1) coulombs involved in the film formation; and (2) coulombs involved in anodic dissolution, the observed current increase should be strain rate dependent. When the coulombs associated with film formation is predominant we should obtain the same tendency of current increment at high temperature. Figure 92 indicates little difference from Figure 91 and therefore the data supports the above assumption.

(b) Film Formation

In Figure 93 and 94, the decay current densities are recorded with time for both non-strained and strained nickel. The tendency for film formation on static nickel electrode is similar to that for iron in various electrolyte. Regardless of the temperature the total coulombs associated with film formation is found to be close. Therefore, the current increment of film-covered nickel upon straining is essentially the accumulation of the current for film formation. Scanning electron microscopic observations also indicated the no appreciable amount of dissolution at slip steps.

It is of great interest to note that the local film formation at slip steps on film-covered electrode is quite different in that the decay slope is one half of that of static electrode. The possible explanation is that the presence of local cathode (oxide film) next to film-free slip step and the elastic stress may bring the different film formation processes and, as a consequence, different film properties such as more ionic character.
Fig. 92.—Effect of strain rate, $\dot{\varepsilon}$, on $\Delta i_a$ at 50°C.
Fig. 93.—Current decay at 800 mV$_H$ in 1N H$_2$SO$_4$ at 25°C.
Fig. 94.—Current decay at 800 mV\textsubscript{H} in LN H\textsubscript{2}SO\textsubscript{4} at 50°C.
(c) Generalization of the Previous Theory

In the case of complete repassivation after straining such as stainless steel in oxidizing environment at ambient temperature, the theory developed by Murata and Staehle is applicable. However, if different film, which is more conductive, is formed at slip steps or if the experiment is conducted at rather high temperature the resultant increase in passive current, $\Delta i_p$ can not be neglected.

When the more conductive films such as precipitation film form on newly exposed surface during straining, unit current vs. time curve may look like one shown in Figure 95(a). The additional term compared with the previous model is a linear increment of background current with total strain.

Therefore, the total transient current, $i_a^{sa}$ is given at any time from zero to $t_s$ as follows (see Figure 95(b)).

$$0 < t \leq t_s$$

$$i_a^s(t) \Delta t = (j_a^o - j_f^o) AS \sum_{k=1}^{k} e^{-\beta t} dt + j_f t AS$$

$$= (j_a^o - j_f^o) AS \left( \frac{1-e^{-\beta t}}{\beta} \right) + j_f t AS$$

(150)

Thus,

$$i_a^s(t) = \left[ (j_a^o - j_f^o) \frac{1-e^{-\beta t}}{\beta} + j_f t \right] \left( \frac{\Delta S}{\Delta t} \right)$$

(151)

Here $j_f^o$ is the current density of newly formed anodic oxide film and the other parameters are defined same as in chapter IV. The unknown parameters in equation (151) are $\beta$, $j_a^o$ and $j_f^o$ but $\beta$ is calculated from equation (132).
Fig. 95.—Schematic illustration of the straining electrode theory for more conductive film formation at slip steps.
\[ \dot{j}_a^{sa}(t) = \left( (j_o^a - j_f) \frac{(1-e^{-\beta t})}{\beta} + j_f^t \right) A \]  

Equation (152) is derived based on the assumption that the transient current increase after \( t_s \) is merely due to contribution of current density from film repaired area, \( j_f^t \) as shown in Figure 95(a). It can be simplified as 

\[ \dot{j}_a^{sa}(t) = Bt + C \]  

where 

\[ B = A j_f \]  

\[ C = A(j_o^a - j_f) \frac{(1-e^{-\beta t_s})}{\beta} \]  

Knowing the slope of (152'), \( j_f^t \) is calculated 

\[ j_f^t = \frac{B}{A} \]  

Substituting (155) into (154) we obtain 

\[ j_o^a - j_f^t = \frac{\beta C}{A(1 - e^{-\beta t_s})} \]  

thus \( j_o^a \) is given by 

\[ j_o^a = \left[ \frac{\beta C}{(1 - e^{-\beta t_s})} - B \right] / A \]  

Schematically B and C are shown in Figure 96 indicating both values are easily obtained experimentally. The value of \( j_o^a \) can be checked
Fig. 96.—Schematic illustration of the experimentally measurable quantities.
by using equation (151) assuming that we know $\beta$, $A$ and $j_f$, $j_a^o$ is expressed as follows:

$$\dot{j}_a = Bt - De^\beta t + D \quad (157)$$

$$0 < t \leq t_s$$

where

$$B = A\dot{j}_f$$

$$D = A\frac{\beta}{\beta^o} (j_a^o - j_f)$$

Thus we obtain for $j_a^o$ as

$$j_a^o = \frac{\beta}{A} \left( \frac{i'_a(t) - Bt}{1 - e^{-\beta t}} \right) + j_f \quad (158)$$

(d) Activation energy measurement for anodic dissolution at freshly produced slip steps in passive region

In order to keep metallurgical factors constant during tests and also to meet the conditions for a saturation slope of the current-time (or strain) curve, low strain rate (1% min) and small total strain for each test (1-2%) were employed. The following electrolytes were used as main ones.

1. 0.2N $H_2SO_4 + 0.1M K_2SO_4$
2. 0.5N $H_2SO_4 + 0.25M K_2SO_4$
3. 1N $H_2SO_4$

The testing temperatures were chosen so that the surface film is stable under given conditions. Typical current-time curves during and after cessation of straining are shown in Figures 97, 98, 99 and 100.

The initial current density before repassivation starts is
Fig. 97.—Typical current-time curves under yielding in 0.2M H$_2$SO$_4$ + 0.4M K$_2$SO$_4$ at 25°C.
Fig. 98.—Typical current-time curves under yielding in 0.2N H₂SO₄ + 0.4N K₂SO₄ at 60°C.
Fig. 99.—Typical current-time curves under yielding in 1N H2SO4 at 25°C.
Fig. 100. - Typical current-time curves under yielding in 1 M HCl at 55°C.
generally found to be the order of a few mA/cm² and \( j_f^* \) to be a few times larger than normal passive current \( i \). The calculation was made for \( j_f^* \) and \( j_a^0 \) by using equation (152'), (153) and (154). The obtained for film-free electrodes.

6. Effect of Straining on Film-Free Electrode

In contrast to the film-covered electrode, where the essential contribution to the total current increase is the coulombs associated with film formation, the current increase during straining film-free electrodes is composed of (1) transient dissolution which vanish within ten seconds after cessation of straining; (2) increase in background current due to surface area increase. The first contribution should be recognized only at high strain rate.

(a) Effect of strain rate

Figure 101 demonstrate the effect of strain rate on the current response under straining. It is noticeable that the current becomes appreciably high only when high strain rates such as 50 and 100%/min are employed. It is also noted that at these high strain rate the initial current response takes the more asymptotic shape indicating larger transient dissolution is involved.

(b) Calculation for the transient current density and number of atoms-per unit area-dissolving in this manner

The concept of equations (152'), (153) and (154) are directly applicable to film-free electrode. The only correction to be made is nomenclatures involved. The passive current density at new slip
Fig. 101. — Effect of strain rate, ε, on Δia in active region.
steps $J_f$ is replaced by the anodic current density before straining. Therefore, transient current can be more noticeable at low current density or low overpotential.

The calculation for transient current density is possible only when saturated slope is observed as shown in Figure 102. The calculation for number of atoms associated with transient dissolution is simply made by assuming bivalent ion dissolution as approximately $5 \times 10^{-12}$ mole/cm$^2$ compared with the total surface atoms $2.5 \times 10^{-8}$ mole/cm$^2$.

Background current is considered to be due to the increase of perpetual dissolution during straining. The experimentally calculated $ds/dt$ is now superimposed in Figure 103 where the expected $ds/dt$ for film-free electrode is written in the dotted line. There is a good correlation between them except for very high strain rate at which no saturation slope was observed before fracture.

(c) Effect of overpotential and temperature

It is expected that at either high overpotential or high temperature, the area term predominantly contributes to the current increase during straining. Figure 104 shows the straightforward relation between strain and current increment. This is clearly shown in Figure 105 where 10%/min strain rate produces negligible amount of transient dissolution. Obviously transient dissolution vanish in a shorter time at either high overpotential or high temperature. Figure 106 and 107 indicate that the transient dissolution vanishes in ten seconds at room temperature while it vanishes in 4 ~ 5 seconds at 53 C. The activation energy for this transient dissolution at
Fig. 102.—Calculation of transient dissolution.
Fig. 103.—Calculation of \( \frac{ds}{dt} \) from the increase in perpetual current in active region.
Fig. 104. — Effect of $\dot{\varepsilon}$ on $\Delta i_a$ in active region.
Fig. 105.—Transient dissolution at higher overpotential.
Fig. 106. — Effect of $\dot{\varepsilon}$ on the decay of the transient dissolution in active region.

1N $\text{H}_2\text{SO}_4$, $25^\circ \text{C}$

$20 \text{ mV}_H$

$\dot{\varepsilon} = 6.5\%$

$\dot{\varepsilon} = 100\% \text{/ min}$

$T (\text{sec})$
Fig. 107. --- Effect of $\dot{\varepsilon}$ on the decay of the transient dissolution in active region.
0 mV, in 1N HSO\textsubscript{4} is calculated from \( j_0 \) at various temperatures as 12.4 Kcal/mole.

7. Discussion of the Obtained Activation Energies for both Film-Covered and Film-Free Electrodes

(a) Film-free electrode

It has been considered by numerous investigators\textsuperscript{169,170} that the anodic dissolution may be controlled by slow surface diffusion at very low overpotential or very small anodic (real) current density while it may be controlled by direct charge transfer process at kink sites when the overpotential for anodic reaction is appreciably high.

Since the equilibrium potential for nickel-nickel devalentions are approximately -250 mV\textsubscript{H}, anodic dissolution of nickel at 0\textasciitilde100 mV\textsubscript{H} is considered to be controlled by the charge transfer process.

From the temperature dependence of base current density after cessation of straining, the activation energy for the perpetual dissolution was calculated and found to be equal to those obtained through the temperature dependence of exchange current densities as shown in Figure 108. Considering that the perpetual dissolution is occurring at kink sites, where those sites have six nearest neighbour atoms, transient dissolution could be adatoms which have three nearest neighbour atoms because the experimentally obtained activation energies are 19.5 Kcal/mole for perpetual dissolution and 12.4 Kcal/mole for the transient dissolution.
Fig. 108.—Activation energy-potential diagram.
(b) Film-covered electrode

The activation energies for anodic dissolution at slip steps are independent of applied potentials in passive region and one half of the values for those at static electrode where anodic oxide film is reacting with cations, anions and water molecules. The precise mechanism for passive current is not known as yet.

If the initial anodic dissolution at freshly produced slip steps is activation controlled, the activation energies should be the order of 19 Kcal/mole.

It is, however, questionable if the measured current density is equal to the real one because (1) local cell (film-fresh surface), which is directly connected each other, may reduce the otherwise observable current density; (2) response of the recorder; (3) diffusion of reacting species is a rate controlling step.

Since the use of an oscillograph did not change the observed data and the potential shift method (active→passive) at static electrode produced much higher current at the same overpotential the reason, (1), is the probable explanation. This could be checked by employing a high strain rate reducing the contribution of the local cell to the total current.

The pH dependence of the activation energies shown in Figure 109 are also considered to be an indication of possibility (1) as discussed above because anodic dissolution of nickel should depend on OH⁻ ion concentration.
Fig. 109.—Activation energy for anodic dissolution at slip steps in passive region at 800 mV_H^+.
3. Temperature Dependence of the Effect of Elastic Stress

Nickel electrode was strained at 1%/min strain rate in 1N H₂SO₄ at -70 mV, where both anodic and cathodic reactions are operating. It should be noted that the current decay due to elastic tension is instantaneous and markedly increased at higher temperature with a little transient current upon release of the stress as shown in Figure 110. Non-linear current increase upon release of the stress is due to the response of Instron machine and not due to an electrochemical reaction.

As discussed in chapter I, thermodynamical explanation predicts the direction of the permanent current change but the theory does not have sound basis since the diffusivity of hydrogen atoms at room temperature (D = 10⁻³ ~ 10⁻⁹ cm²/sec for nickel) is not large enough to reach an equilibrium condition at interface rather instantaneously.

Alternative explanation is the preferential chemisorption of hydrogen ions to reduce the increased surface energy under tension. Further study is needed in order to discuss the problem in terms of work function for the electron transfer, surface energy, chemisorption etc.
Fig. 110.—Temperature dependence of the effect of elastic stress on the electrode behavior. (1N H$_2$SO$_4$, -70 mVH)
VII. SUMMARY AND CONCLUSIONS

1. Important aspects of straining electrode for metals, which have a limited number of slip systems, were clarified; also a technique was developed which may be useful to determine the new surface area formed during plastic deformation for either film free surface or filmed surface.

2. A technique was developed for determining the current density at freshly produced slip steps and decay constant, \( \beta \). This involves the solution of an analytical expression for either the saturation current density or the saturation slope of current-time curves during straining.

3. Important observations on the properties of straining nickel electrode are:
   
a) An interesting change in the current density in the active region was observed during straining, i.e. transient current, which was observed more at lower overpotential or higher strain rate, decay out within several seconds. This could be due to the dissolution of ad-atoms.

b) An apparent activation energy for the transient dissolution of nickel in 1N \( \text{H}_2\text{SO}_4 \) was 12.4Kcal/mole whereas the activation energy for perpetual dissolution in the same environment was 19.5Kcal/mole which is the same for the activation energy at static electrode.
c) An apparent activation energy for anodic dissolution at freshly produced slip steps of nickel in passive region was approximately 10 Kcal/mole regardless of pH. This may not be an activation energy for a single reaction step since the repassivation process is occurring simultaneously.

d) Repassivation process was slower on stressed electrode than that on stress free electrode. This could be an indication of different type of film formation, i.e. it is more conductive.
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