MASTER

Corrosion Research Center
of the
University of Minnesota

Progress Report
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Summary of Work

The investigative objective of the Corrosion Research Center is to do basic research on materials-degradation problems of technical importance to the energy posture of the nation. The approach is to involve as many as possible of the staff of the Institute of Technology of the University of Minnesota to develop interdisciplinary research strategies to address the basic phenomena underlying those problems. It is desired thereby to generate points of view and to apply techniques which are both useful and new to corrosion research, or at least to focus a variety of techniques on any one problem. At present, the research ranges from the quantum mechanics of the corrosion unit reactions, organic and inorganic coatings, surface reactions on polymers, metals and semiconductors to high-temperature chemistry of interest to solar-energy conversion. A second objective of the Center is to increase the utilization of corrosion data by the technical community through education and through the dissemination of appropriately formatted information. At present, two projects are in the planning stage for the near future. One is a pedagogical symposium on corrosion in microelectronic components and systems; the other is a series of lectures and videotapes, as well as a workshop on cathodic protection.

The administrative machinery of the Center is virtually fully established. With respect to the construction of a building to house the Corrosion Research Center, a proposal for space requirements and use of space, costs of construction, building schedule, manner of integration with other building plans on the campus, and location has been submitted to the University management and has received their approval. Negotiations are in progress to arrive at an equitable funding and repayment plan.

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TECHNICAL PROGRAM

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I. Research on Coatings

Principal investigators involved	Approximate effort months/calendar year	
	<u>Current funding period</u>	<u>'81-'82 fiscal year</u>
M. V. Tirrell	$\frac{1}{2}$	$\frac{1}{2}$
M. F. Evans	$\frac{1}{2}$	1
S. Prager	$\frac{1}{2}$	1
P. G. Gassman	$\frac{1}{2}$	-
E. Pfender	1	1
L. E. Toth	-	1

The work on polymeric coatings has reached the stage where virtually all of the experimental techniques and apparatus are developed. In addition, some important theoretical work has been accomplished, the predictions of which have been verified by preliminary experiments. Similarly, much of the equipment for the study of inorganic coatings has been assembled. The remainder of the present funding period and the next fiscal year should see the accumulation of a large amount of data.

Investigation of the Corrosion Resistance Imparted
To Metal Surfaces by Plasma Processed Polymer Films

M.V. Tirrell, Department of Chemical Engineering
and Material Science

J.F. Evans, Department of Chemistry

Introduction

The goals of this project as set forth in the original proposal are to compare the corrosion-inhibiting properties of plasma-processed polymer coatings to conventional polymer coatings (dip coated). Four types of processing using non-equilibrium plasma discharges are included. The first involves the deposition of a linear polymer (e.g. polystyrene, PS) from solution, followed by exposure to argon-plasma discharges sustained above the coated metal/PS film composite. A second approach is to synthesize the polymer film by plasma polymerization of the monomer (styrene) such that a polymer deposit is formed on the metal substrate surface (plasma polymerized PS, PPS). The third type of film under study is that produced by the second method, which is then further processed by inert-gas ion-beam bombardment (Ar^+ , 1KeV). Lastly, a method involving the exposure of condensed-phase monomer to inert-gas plasmas is being examined, in which polymer formation would be induced by the discharged, rather than initiated in the gaseous plasma (c.f. method 2). The reason behind the multiplicity of these procedures lies in the anticipated differences in permeability of the different film types to corrosive agents (e.g. Cl^- , aqueous; O_2) due to the different extents and depths of highly crosslinked polymer chains which can be anticipated from different processing approaches.

Success in achieving the stated goals relies upon the ability to carry

scopy and the corrosion of various samples has been evaluated by examining their cyclic voltametric responses in unbuffered aqueous chloride and oxygen-containing solutions.

The XPS (Fig. 2 and 3) results indicate that by employing low power/molecule ratios in the plasma-deposition reaction, polymer films which to a large extent retain the phenyl ring moiety of the monomer can be generated. The oxygen concentration at the surfaces of such preparations is on the order of the levels observed at the surface of conventionally prepared linear (dip-coated) films, from which it may be inferred that relatively hydrophobic surfaces can be generated by plasma techniques. Alternatively, when high power/molecule ratios are employed to generate PPS films on Ag, XPS analysis shows a loss of the phenyl ring structure and a concomittant increase in surface oxygen content. We interpret these results as indicating that the higher power discharges lead to more highly crosslinked polymer films, but that oxygen is more readily incorporated into this highly crosslinked material either during or following the deposition reaction. Therefore, although diffusion rates of corrosive agents are expected to be decreased due to increased crosslinking (loss of phenyl ring) the presence of higher concentrations of oxygen functional groups most likely renders the surface of this material to be more hydrophilic. (Hydrophilicity would be predicted to increase diffusion rates of aqueous solutes due to increased diffusion rates of aqueous solutes due to increased swelling of the polymer.) The net result of these effects in terms of transport of corrosive agents in the films generated by high power discharges cannot be assessed until the thickness of the polymer films is accurately measured, and it is established whether or not the oxygen-containing functional groups are present throughout the film or are incorporated only the surface and near-surface regions examined by XPS (0-100 ^o Å).

Fig. 1 Apparatus for Plasma Deposition Reactions.

TC = Thermocouple Gauge
 SR = Styrene reservoir
 M = Matching network
 PM = Power meter
 RF PS = Radio frequency power supply

Substrates may be placed at various axial positions along horizontal relative to coil and monomer inlet. Monomer inlet may be at position shown here or nozzle located in the middle of the reactor or at rightmost inlet.

APPARATUS FOR PLASMA POLYMER DEPOSITION

Fig. 2. Low resolution XPS spectrum of PPS deposited under low power/high pressure conditions. As the power is increased for a given pressure, the features attributable to surface oxygen species [O(A) and O(1s) peaks] are noted to increase in intensity by as much as a factor of ten.

Fig. 3 High resolution XPS spectra of PPS in the C(1s) region. Upper trace shows spectrum typical of depositions carried out at low power/high pressure, where the π - π shake-up at ca 292.5 eV BE indicates the presence of phenyl ring structure in the surface region. Lower trace is for high power/low pressure discharge conditions in which phenyl ring structure of monomer is completely destroyed.

The cyclic voltametric responses (aqueous 0.1 M KCl) for composites generated by plasma polymerization of PS from the gas phase (method 2, low power) are compared to those at bare silver foils in Figure 4. The anodic process corresponding to wave 1 is the step mechanism proposed by Katan et al. (1):

The cathodic wave (2) with peak potential at ca = 0.2v corresponds to the reverse process. It should be noted that not only is the charge passed for either process diminished by a factor of at least 4.5 for this sample with a ~8000 Å thick PPS overlayer, but also the anodic and cathodic processes show diffusion-controlled behavior. Presumably, the rate of deposition of AgCl or Ag is limited by transport of either Cl^- or $\text{AgCl}_n^{(n-1)-}$ in the plasma-deposited polymer film. It is stressed that the so-called silver reformation cycle (anodization followed by cathodization) is particularly demanding of the polymer overlayer, in that nodular deposits of AgCl and Ag grow and recede during the cycle (see refs. 1, 2). That is, during the reformation cycle, rather severe microscale mechanical transformation of the silver surface is known to occur. Even though the polymer/metal interface undergoes such mechanical rearrangement during these processes, the performance of the corrosion-inhibiting PPS film is not substantially degraded by multiple reformation cycles as shown in Fig. 4C.

The electrochemistry for the reduction of oxygen at bare and PPS-coated

electrodes was also examined briefly. The motivation here was to semiquantitatively assess the transport rates for molecular oxygen through PPS films, since it is known that dissolved molecular oxygen will cause surface oxidation of Ag to AgCl in aqueous solutions (2). The electrochemical results show a threefold decrease in diffusion rates of O_2 for the PPS-coated electrode. Preliminary XPS results indicate that the reduction products ($O_2^{\cdot-}$, $O_2H^{\cdot}$, H_2O_2) react with the PPS film to increase the oxygen concentration in these polymer films. The exact nature of these reactions is not presently understood, and will be one of the subjects pursued in future studies.

Future experiments will evaluate the corrosion inhibition imparted to more reactive metals (e.g. Fe, Ni, etc.) by plasma-processed polymer films vs the dip-coated linear polymer films derived from the same monomer. These evaluations will be normalized to film thickness and correlated with the surface and bulk film compositions as determined by XPS and FTIR, respectively.

Design and Fabrication of a Versatile Plasma Reactor

In the results described above for the PPS/Ag system, a relatively crude reactor was used to carry out what must be viewed as exploratory experiments. The critical limitations of this reactor (Fig. 1) are: 1) poor vacuum integrity (base pressure limit was 10^{-3} Torr), 2) inability to properly measure total gas pressure, 3) inability to reproducibly control flow rate of discharge gases, 4) inability to measure monomer flow rate during deposition, 5) inability to measure deposition rate, 6) inability to control reactor and/or substrate temperature and 7) relatively limited sample size. To overcome these limitations, a larger and more sophisticated reactor was designed and fabricated which employs differential pumping to achieve base pressures of 10^{-7} Torr or less. This reactor is depicted schematically in Fig. 5. It has not, as yet, been tested due to delays in delivery of the flow elements and diffusion pump stock; it is however virtually completely constructed.

Fig. 4 Cyclic voltammetry observed for bare and PPS-coated silver foils in 0.1 M KCl (aqueous). Scan rate was $10 \text{ mV}\cdot\text{s}^{-1}$ in all cases with potentials referenced to 0.1 M Ag/AgCl. Electrode areas were 0.24 cm^2 in all cases. Curve A: voltammogram for mechanically abraded pure silver foil. Curve B: Voltammogram recorded for ca 8000 Å PPS deposited under low power/high pressure conditions. Curve C: Same sample as curve B, after four reformation cycles.

Fig. 5 Schematic of New Plasma Reactor and Gas Handling System

1,2: Monomer reservoirs	18: Capacitance manometer
3,4: Differential capacitance manometers	19: Throttling valve
5,6: Flow element	20-22: Shutoff valves
7-9: Leak valves	23: Thermal conductivity gauge
10-12: Shutoff valves	24: Ion gauge
13: Diluent gas reservoirs	25: Liquid nitrogen trap
14: Substrate mount	26: Diffusion pump
15: Sample (substrate probe)	27: Molecular sieve trap
16: Differentially pumped chamber ($P \sim 1 \times 10^{-3}$ Torr)	28: Mechanical pump
17: Bottom flange	29: Glass tube ($P \leq 1 \times 10^{-7}$ Torr)

(Fourth gas inlet not shown)

PLASMA REACTOR SCHEMATIC

In this system not only will base pressures be improved, but proper pressure and flow measurement capability have been incorporated. Up to four gases may be fed into the reactor under either static or differentially pumped discharge conditions. Flow control will be substantially improved by using micrometer-fitted, bellows-sealed metering valves for condensable gases and leak valves for high-vapor-pressure materials. Sample position may be readily varied within the 2-foot high by 4-inch diameter discharge volume since the substrates are mounted on a double o-ring sealed probe of cylindrical symmetry incorporating differential pumping across the o-rings. Eventually, the entire reactor will be placed in a thermally insulated housing so that temperature control may be achieved via convective or radiative heating with concomittant temperature measurement.

Because of the use of a removable probe, a probe will be constructed to allow for substrate heating/cooling, as well as one which will accomodate the mounting of a quartz-crystal microbalance for the measurement of deposition rates as a function of discharge conditions (power, gas composition, position in the reactor, etc.). Modest funding for the cost of these probes is included in the renewal budget request.

Development of Expertise in the Measurement of Thin Film Thickness

A considerable effort has been expended in acquiring expertise in the use of ellipsometry and profilometry for the determination of polymer film thicknesses. The data analysis program of McCracken (3) has been implemented and debugged on a NOVA 2 minicomputer system. It has been utilized to reduce data acquired from a Gaertner ellipsometer (He-Ne laser at 70° to sample normal) on plasma-polymerized vinylferrocene films (4). The use of profilometry for analysis of thick (>5000 Å) PPS films on silver has been examined briefly, and the results indicate that this approach may provide a promising complement

to ellipsometric capability. That is, where ellipsometric measurements become complicated by variation in refractive index as a function of depth into the thin film (such as may be expected for plasma-treated or ion-bombarded linear polymers) thickness information may be obtained more straightforwardly using the profilometric technique. However, scanning electron microscopy of samples which have been profiled in this fashion will have to be carried out to determine the extent of stylus damage imparted to the polymer surface as a consequence of the measurement.

Determination of Bulk Film Structure by FTIR Spectroscopy

We have found that single-crystal silicon samples can be readily used as infrared-transparent substrates for plasma-deposition reactions, and offer advantages over alkali halide substrates for infrared spectroscopic studies of plasma-processed polymer films. The primary advantages offered by silicon are increased vacuum compatibility (less adsorbed water) and improved stability in the plasma discharge (experiments conducted on KCl substrates showed via XPS the incorporation of chloride on the surfaces of thick plasma-deposited films).

Because of the fact that we are interested in films which may be as thin as 200-500 Å, the sensitivity afforded by FTIR is essential. Preliminary results on thin (ca 5000 Å) linear polystyrene films (dip-coated onto Si wafers) have shown that background due to the silicon substrate (Si-O, SiOH) can be readily subtracted giving high-quality PS vibrational spectra which could not be obtained using a dispersive spectrometer. This capability provides a means of analyzing the effects of various plasma-processing parameters on the bulk structure of the polymer films. Therefore, experiments are planned in which a silica substrate will be mounted along with the metal of interest during a plasma reaction, so that FTIR spectral information may be correlated with electrochemical and surface analytical studies on the metal/polymer composite.

Contemplated Technical Publications

1. "Nonequilibrium Plasma Polymerization of Styrene at Low Power: Evidence for Retention of the Phenyl Ring Moiety", Erik D. Johnson and John F. Evans, in preparation.
2. "Effects of Plasma Polymerized Thin Film Overlayers on the Electrochemical Reformation of Silver", George W. Prohaska, Erik D. Johnson and John F. Evans, in preparation.

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1. T. Katan, S. Szpak and D.N. Bennion, J. Electrochem. Soc., 121, 757 (1974).
2. J.F. Evans, M.G. Albrecht, D.M. Ulllevig and R.M. Hexter, J. Electroanal. Chem., 106, 209 (1980).
3. F. L. McCracken, NBS Technical Note 479, April 1969.
4. M. R. Ross, M.F. Dautartas and J.F. Evans, in preparation.

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The Healing Process at Polymer-Polymer Interfaces

Stephen Prager, Department of Chemistry
Matthew Tirrell, Department of Chemical Engineering
and Materials Science

Abstract

The purpose of this work is to develop some fundamental information, both theoretical and experimental, about the processes of fusing separate pieces of polymer. This is a central question in producing corrosion-resistant films of organic polymers. Most such films are applied as dispersions of separate polymer particles which must weld themselves together to form the sealed coating. The present work is directly applicable to choosing optimal polymers and optimal curing conditions for such coatings.

Thus far, theoretical analysis for the early stages of the healing or curing process has been completed. It shows that the extent of curing as measured by the number of chains per unit area crossing the original interface at any specified (early) time will depend upon (molecular weight)^{-3/4}. Extensions of this analysis to long times, polydisperse distributions of molecular weight and effects of diluents (as are present in coating applications) are in progress. Aside from these immediate practical implications for corrosion protection, this analysis suggests a new experimental approach to the difficult problem of measuring the self-diffusion coefficient in a pure bulk polymer, by measuring the extent of healing of a polymer-polymer interface through measuring the stress required to break the interface. Our prediction of $t^{1/4}$ dependence of the early strength development is exactly borne out by some recent preliminary data of Kausch and coworkers.

We have, in these eight months, developed our own experimental technique for studying the healing process, which we will ultimately use to study the effects of parameters such as molecular weight using polymers of well-defined narrow distributions. Three separate techniques have been studied and we have now settled on one which gives us the best reproducibility of strength measurement. Our own preliminary measurements also clearly support our $t^{1/4}$ prediction of the time dependence of curing by coalescence.

Introduction

The purpose of this project is to develop both theoretical insight and experimental information about the interdiffusion which takes place when two pieces of polymeric material are brought together. This work has many practical applications (mechanical properties of multiphase polymer blends, measurement of diffusivity in bulk polymers, healing of weldlines in polymer processing) but the primary application we are concerning ourselves with here are those related to the corrosion protection afforded to metallic surfaces by organic polymer coatings. Most such coatings are applied in a two-stage process where, in the first stage, a dispersion of organic polymer particles is applied to the surface and then the film is cured, that is subjected to heat, so that interdiffusion between the particles takes place and the particles merge into a uniform pinhole-free coating. This process is illustrated in Figure 1. The two-stage process employing a suspension of polymer particles is used so that a large amount of polymer (and consequently a small amount of toxic or expensive dispersant) per unit volume of coating fluid can be applied to the surface without having to deal with the high viscosities which would be encountered if the polymer were dissolved in the coating fluid. Thus, the disappearance of fluid-fluid interface when two particles of the same fluid are put into contact is the key process in curing of dispersed polymer coatings.

This progress report is divided into two major sections. The first describes the theoretical work, which thus far has treated the situation of planar interfaces. We have shown what we expect the time and molecular weight dependence of the curing process to be. This type of information can be used in coating design and optimization. The second section describes our experimental work which has been directed toward testing our theoretical

Figure 1

Molecular model of healing in polymers according to Voyutskii⁽¹⁾.

Self-diffusion (a) and healing (b) in polymer systems.

Figure 2

predictions. We have some preliminary data and have developed a very reproducible experimental technique. We conclude with a discussion of the contributions of personnel to the project and a summary of presentations and publications resulting from this work.

Theoretical

When two samples of the same amorphous polymer are brought into contact at a temperature above the glass transition, the junction surface gradually develops increasing mechanical strength until, at very long contact times, the full fracture strength of the bulk polymer is reached. At this point the junction surface has in all respects become indistinguishable from any other surface that might be located within the bulk material: we say the junction has "healed". Such healing is important in many areas of polymer processing, most obviously of course when one wishes to produce a polymer-polymer weld, but also whenever polymer pellets are to be extruded and molded into a larger casting, or when individual resin particles from a polymer dispersion must merge to form a continuous protective film.

The earliest systematic studies of healing in polymers appear to have been undertaken by S. S. Voyutskii and his group (1) in the Soviet Union, and it is to Voyutskii that we owe the molecular interpretation shown in Figure 1. Before contact is made, the situation is as shown on the left, with the polymer chains being prevented by energetic considerations from extending isolated tendrils through the polymer-air surface. This is also the case immediately after contact, before significant configurational relaxation has had a chance to occur, as shown in the center diagram of Figure 1: although the density of polymer segments is now the same near the junction surface as in the bulk, the configurational distribution of the polymer

molecules certainly is not, since each chain is still required to lie entirely to one side of the junction. In time, of course, configurational relaxation does occur, leading to an increasing number of intersections of polymer chains with the junction surface (left-hand diagram), which is reflected macroscopically by the growing mechanical strength of the joint. In what follows we shall in fact assume that the fracture stress at any given time after contact is proportional to this crossing density.

The molecular interpenetration process just described is clearly related to the phenomenon of self-diffusion measurement, we see the polymer coils moving over distances many times their mean diameter (Figure 2a), whereas healing is essentially complete in the time it takes a polymer molecule initially next to the junction surface to move halfway across it (Figure 2b). The characteristic time for healing should thus be comparable to the configurational relaxation time T_c of a typical polymer coil. Indeed, we shall focus our attention on the early stages of healing, that is on times small compared to T_c (depending on the polymer, its molecular weight, and the temperature T_c (depending on the polymer, its molecular weight, and the temperature, T_c may run to minutes, hours, or even days).

As our model for configurational relaxation in the bulk polymer we shall use the simplest version of the "reptation" model proposed by DeGennes (3). Each polymer chain is considered to be confined to a tube (see Figure 3), along the length of which it executes a random back-and-forth motion. In time, this motion will cause the chain to slip out of a section of tube at one end or the other, and when this occurs all memory of that portion of the initial tube is lost, while at the opposite end an equal length of new tube is being added. The configurations of the new sections of tube are totally uncorrelated with the initial tube configuration, except that they must start from either end of the remaining portion of the initial tube. Eventually the initial

Three stages in configurational relaxation by the DeGennes model of polymer reptation (current configuration: ———, initial configuration: remaining portion of initial tube: =====).

Figure 3

Random walk representation of tube decay (chain in remaining portion of initial tube: $N-n$, "new" chain: Δ)

Figure 4

tube will have decayed to one final segment containing one of the chain ends; when that end leaves, the initial configuration will have been "forgotten", i.e. the first relaxation interval will be complete. The chain now finds itself in a new tube, which will in turn be forgotten (the second relaxation interval), and so forth. These successive relaxations form the steps of a Markov process representing the reptational motion of a polymer chain. As already stated, we will be primarily concerned with events occurring during the first relaxation intervals.

The Crossing Density at $t \ll T_c$

We consider a homopolymer whose chains consist of N freely jointed segments, each of length l . Within its tube a chain moves forward or back by one segment with a frequency ν which one would expect to be inversely proportioned to the molecular weight, i.e. $\nu = \nu_0 / N$. The motion of the chain in its tube can be characterized by a single progress variable, the net number of segments s by which the chain has been displaced down the tube: the time evolution of s is a one-dimensional diffusion process with a "diffusion coefficient" $\nu/2$ (Figure 4).

What is the probability $P(n, \Delta, t) d\Delta$ that at time t between n and $n + dn < N$ segments from say, the left hand end of the initial tube will have been lost and replaced by between Δ and $\Delta + d\Delta < N$ segments of new chain protruding from the left end of the remaining portion of initial tube? In other words, what is the probability that at time t the net displacement s is in the range $n - \Delta$ to $n - (\Delta + d\Delta)$, that during the entire period 0 to t the displacement has never left the range $-(N - n - dn) \leq s \leq n$ but that at some time during the period $s \geq n$? The probability $\bar{P}(n, \Delta, t) d\Delta$ that at time t the displacement has reached a value between $n - \Delta$ and $n - \Delta - d\Delta$ without ever going out of the range $-(N - n) \leq s \leq n$ is just the familiar first passage time problem (4)

of the Brownian particle which starts out from the origin and must proceed vt steps of unit of unit length without encountering either of two absorbing barriers at $-(N-n)$ and n . For small times and large N (specifically, for $t \ll N^2/v$), the left hand barrier can be ignored, and $\bar{P}$ is just the superposition of two Gaussian contributions, one centered at the origin and the other at the image point $(n+\Delta)$:

$$\bar{P} = \frac{1}{\sqrt{2\pi vt}} (e^{-\Delta^2/2vt} + e^{-(n+\Delta)^2/2vt}) \quad (1)$$

The probability P is simply minus the derivative of $\bar{P}$ with respect to n , i.e.

$$P(n, \Delta, t) = \frac{(n+\Delta)}{\sqrt{2\pi}(vt)^{3/2}} e^{-(n+\Delta)^2/2vt} \quad (vt \ll N^2) \quad (2)$$

All crossings of the junction surface by a polymer chain must be contributed by segments lying outside the undestroyed portion of the original tube, since the latter does not traverse the junction at all (Figure 5). The average number $C(z, \Delta)$ of intersection to be expected from a chain fragment of Δ segments starting out at a distance z from the junction surface can also be obtained as the solution to a random walk problem, but the random walk now refers to the laying out of the chain, in steps of length, in a three dimensional space, with Δ replacing the time variable vt , and z the displacement s ; also, because the walk occurs in three dimensions (even) though we are interested only in the component normal to the junction plane) the "diffusion" coefficient $v/2$ becomes $1/6\ell^2$ (not $1/2\ell^2$). The probability that the m th segment of a chain lies within a distance ℓ of the junction if the first segment is located at z is

$$\frac{1}{\sqrt{(2/3)\pi m \ell^2}} e^{-3z^2/2\ell^2 m} \cdot 2\ell,$$

and the probability that the m th segment will then cross the junction is $\sqrt{2/3\pi} *$. The average number of times a Δ -segment chain fragment starting

*This takes the individual segment lengths to be themselves distributed in a Gaussian manner with rms length ℓ .

Typical configuration of partially relaxed chain near junction surface
(remaining portion of initial tube: ---)

Figure 5

at z should intersect the junction plane is thus

$$C(z, \Delta) = \frac{1}{\pi} \int_0^\Delta m^{-1/2} e^{-3z^2/2\ell^2 m} dm = \frac{2}{\sqrt{\pi}} \sqrt{\Delta} \left[\frac{1}{\sqrt{\pi}} e^{-\zeta^2/\Delta} - \frac{\zeta}{\sqrt{\Delta}} \operatorname{erfc}\left(\frac{\zeta}{\sqrt{\Delta}}\right) \right] \left[\zeta \equiv \sqrt{3/2} z/\ell \right] \quad (3)$$

Finally, we must recognize that the initial zero-crossing constraint leads to a preference for conformations that favor segments near the ends of the chain over center segments at the junction surface⁽⁵⁾. To see this, we count the number of zero-crossing configurations $\Omega(z, n)$ open to an N -segment chain whose n th segment lies at z . If the total number of configurations available to the unrestricted chain is $\Omega_T(0)$, then $\Omega/\Omega_T^{(0)}$ is the probability that an unrestricted chain whose n th segment is at z will not cross the junction:*

$$\Omega(\zeta, n) = \Omega_T^{(0)} \operatorname{erf} \frac{\zeta}{\sqrt{n}} \operatorname{erf} \frac{\zeta}{\sqrt{N-n}}, \quad (4)$$

The total number of configurations open to a chain which is known to have one of its segments located at z and to have no intersections with the junction surface is

$$\Omega_T(\zeta) = \int_0^N \Omega(\zeta, n) dn, \quad (5)$$

and the probability $F(\zeta, n)$ that a segment located at z is the n th segment of its chain is therefore

$$F(\zeta, n) = \frac{\Omega}{\Omega_T} = \frac{1}{N} \left[\operatorname{erf} \frac{\zeta}{\sqrt{n}} \operatorname{erf} \frac{\zeta}{\sqrt{N-n}} \right] \left[1 - 2 \left(1 + 2 \frac{\zeta^2}{N} \right) \operatorname{erfc} \frac{\zeta}{\sqrt{N}} + \left(1 + 8 \frac{\zeta^2}{N} \right) \operatorname{erfc} \frac{2\zeta}{\sqrt{N}} + \frac{4\zeta}{\sqrt{\pi N}} \left(e^{-\zeta^2/N} - e^{-4\zeta^2/N} \right) \right]^{-1}$$

$$\left| \begin{array}{l} \xrightarrow{\zeta \ll \sqrt{N}} \\ n \ll N \end{array} \right. \frac{1}{2\zeta\sqrt{\pi N}} \operatorname{erf} \frac{\zeta}{\sqrt{n}} \quad (6)$$

The approximation to $F(\zeta, n)$ given in equation (6) for small n may be used in the early stages of healing ($vt \ll N^2$).

*The probability that an n -segment fragment starting at z does not cross the plane at $z=0$ is $\operatorname{erf} \zeta/\sqrt{n}$. The second error function factor in (4) is the probability the remaining $(N-n)$ segments do not produce any crossings either.

We are now ready to assemble the foregoing results into an expression for the crossing density $\sigma(t)$. The probability that a junction surface is the site of an entrance to an unforgotten section of initial tube from which between Δ and $\Delta+d\Delta$ segments of "new" chain have emerged is

$$\int_0^N F(\zeta, n) P(n, \Delta, t) dn,$$

and the contribution of such sites to $\sigma(t)$ is

$$\int_0^N F(\zeta, n) P(n, \Delta, t) dn \cdot C(\Delta, \zeta) \cdot \rho d\zeta$$

The total crossing density from all chains still in their first relaxation interval at time t is therefore

$$\sigma_1(t) = 2\rho \int_0^\infty \int_0^N \int_0^N F(\zeta, n) P(n, \Delta, t) C(\Delta, \zeta) dn d\Delta d\zeta \quad (7)$$

At small times P may be approximated by equation (2), and the small n limit may be used for F ; in this early portion of the healing process, equation (7) becomes

$$\sigma(t) \rightarrow \sigma_1(t) \rightarrow A \frac{\rho l}{\sqrt{N}} (vt)^{1/4} = A (v_0 t)^{1/4} N^{-3/4} \quad (8)$$

$$(t \ll N^2/v = N^3/v_0)$$

where A is a numerical constant whose value is given by the integral

$$A = \frac{4}{\sqrt{3\pi^3}} \int_0^\infty \int_0^\infty \int_0^\infty \frac{1}{\xi} \operatorname{erf} \frac{\xi}{\sqrt{\lambda}} \cdot (\lambda + \gamma) e^{-(\lambda + \gamma)^2} \cdot \gamma^{1/2} \left(\frac{1}{\sqrt{\pi}} e^{-\frac{\xi^2}{\gamma}} - \frac{\xi}{\sqrt{\gamma}} \operatorname{erfc} \frac{\xi}{\sqrt{\gamma}} \right) d\xi d\lambda d\gamma$$

Equation (8) contains the necessary information for understanding the important variables of the coating curing process.

At later time we would expect σ_1 to vanish, since ultimately every chain will have forgotten its initial configuration, and the contribution $\sigma_2(t)$ made to σ by chains which have passed through one or more relaxation intervals

to dominate (Figure 6). That $\sigma_2(t)$ does not however compete with $\sigma_1(t)$ at small times can be inferred from the small-time behavior of the probability $P_0(t)$ that a chain has undergone its first relaxation by time t :

$$P_0(t) \xrightarrow{vt \ll N^2} 4 \left(\frac{2vt}{\pi N^2} \right)^{1/2} e^{-\frac{N^2}{2vt}}$$

As t goes to zero, P_0 vanishes much more rapidly than σ_1 .

Comparison with Experiment

Kausch⁽²⁾ has obtained remarkably reproducible data on the healing of PMMA samples through the use of a crack propagation method. A sample is notched and put under tension until a crack begins to initiate at the tip of the notch and allowed to propagate until it has reached a certain length. The tension is removed and the sample heated above its glass transition T_g for a measured length of time, following which it is cooled again below T_g and once more placed under tension. The tension is increased until the partially healed crack is reinitiated.

Plots of the initial stress intensity factor (which is proportional to the applied stress for a crack of a given length) against $t^{1/4}$ (Figure 7) do indeed appear as straight lines, in agreement with equation (8), but Kausch's explanation of this fact is quite different from ours. Kausch also uses a diffusion-reptation model, but argues that the crossing density σ should be proportional to the rms displacement of a polymer coil, which would give $\sigma \sim t^{1/2}$. He then applies the Griffith theory of failure, according to which the crack will initiate when the release of stored elastic energy per unit increase of crack area matches the energy required per unit area of fresh surface exposed. In a material which behaves elastically up to failure, the former goes as the square of the applied stress, and one would

Time dependence of the crossing density (σ : total, σ_1 : contribution from chains still in their first relaxation interval, σ_2 : contribution from remaining chains).

Figure 6

Reduced fracture strength (bulk material = 1) vs. time for PMMA (MW 120000) at 117°C
(Taken from a preprint kindly supplied by Professor Kausch).

Effect of duration of contact, τ , on peeling strength, P , and autohesion, Au .

Effect of molecular weight on healing rates for polyisobutylene: (1: MW = 20000, 2: 100000, 3: 150000, 4: 200000)

Figure 8

expect the latter to be proportioned to σ , so that the critical stress should go as $\sigma^{1/2}$, or $t^{1/4}$.

The difficulty with the arguments of the preceding paragraph is two-fold: the crossing density goes as $t^{1/4}$, not $t^{1/2}$, as we have seen, and the Griffith theory as used by Kausch is intended for a crack propagating into virgin material. For a material with a planar fault, as a crack in the early stages of healing, the stored elastic energy will be concentrated in the fault itself, rather than in the bulk material, and on this basis one arrives at a critical stress which is proportional to σ instead of $\sigma^{1/2}$. The end result of course is once again the experimentally observed $\sigma \sim t^{1/4}$.

The molecular weight dependence of σ offers a second test of our calculations, according to which at fixed t ($\ll N^3/v_0$). The crossing density should go as $N^{-3/4}$, but then unfortunately data of high quality are lacking at this time. Some measurements by Voyutskii and his collaborator do show qualitative agreement with our expectations: a healing rate which decreases with increasing molecular weight, even though up to a point higher molecular weights ultimately produce greater fracture strengths (Figure 8). However, our theory was developed for a homopolymer, whereas available measurements were made on commercial polymers with very wide molecular weight distributions. One would expect the initial time dependence of the healing process to be relatively insensitive to the heterogeneity of the polymer, but of course the same cannot be true of the molecular weight dependence.

Experimental

Healing experiments must be done with polymers which are above their glass transition temperature. We could therefore either do experiments

with polymers having T_g below room temperature or with polymers have T_g above room temperature provided we heat the latter materials above T_g during the interdiffusion process. We explored both approaches. For any type of material the general experimental approach is to bring two flat surfaces of the same material together above T_g , allow them to interdiffuse for some period of time, then pull them apart and measure the stress required to break the healing interface.

In the first, we employed polyisobutylene (PIB) which has a T_g of -80°C . PIB is thus rather fluid and tacky at room temperature. In order to pull a PIB-PIB interface apart it is necessary to back the PIB with something stiffer. This was in fact the technique used by Voyutskii and coworkers, who backed the PIB with stiffer plastic and then did a peel-type test to separate the welding surfaces, while measuring the stress for a constant rate of peel. In our experiments this summer, we found this to be a totally unreliable experimental procedure. First of all, it is very difficult to find a material to which PIB sticks more tenaciously than it does to itself. Consequently, the PIB often peeled away from the backing instead of at the healing interface, much like what happens when two sticky sides of Scotch tape are put together. Secondly, the peel test is not as well-defined as mechanical experiment as we would like. We ultimately want to relate the macroscopic mechanics of the interface disruption to the detailed macromolecular mechanics. We hope to understand things like whether polymer chains pull out of the bulk on the other side of the healing interface or rupture. This is very difficult to do with the peel test as the geometry of the disengaging is not well-defined. Additionally, we found the peel test very difficult to do reproducibly. These factors combined to lead us to abandon the peel test, and therefore experiments with polymers above T_g at room temperature, after about one month of exploratory work.

Our emphasis shifted to polymers which are glassy at room temperature. Poly(methylmethacrylate) (PMMA, $T_g \cong 105^\circ\text{C}$) was selected since it is abundantly available in all sorts of shapes convenient for mechanical testing. Our first set of experiments was done with the most straightforward approach possible. Two short (~2") of 1" diam. PMMA were butted together and heated to the temperature of interest, typically 110°C to 130°C . At set points in time the samples were cooled back to room temperature effectively quenching the interdiffusion. Later (sometimes days later) the vitrified, partially-healed interface was pulled apart and the stress required to fracture it measured. This type of experiment has some advantages. First, the interdiffusion is thermal activated and easily quenched at room temperature which is experimentally convenient. Second, the geometry is perfect for analyzing the mechanics of the stress fracture event. The technique is pitted with subtle difficulties, however. Most relate to the difficulty of getting reproducible interfacial contact initially. After much "scouting" experimentation we settled on the following optimal experimental procedure for this particular technique. The 1" rod material to be used was annealed at 130°C for 48 hrs. in order to relax all stresses and produce an homogeneous isotropic distribution of molecular orientations throughout the sample. The contact surface was machine faced on a lathe and then surface finished using $3\mu\text{m}$ silicon carbide lapping film with water. This produces a mirror-like smoothness at the contact interface. One piece of each pair of pieces to be joined was machined down so that only an annular contact area remained protruding as shown below:

It was found that this gave more reproducible results than abutting two identical surfaces, presumably since errors in gross amount of surface contact area were eliminated. This produced a contact area of 0.294in^2 . In order to minimize the effects of small scale surface roughness; the sample surfaces were placed in contact and brought up to the desired temperature under a compressive stress of 1220 psi. The samples welded for the desired time, were quenched, and subsequently stress in tension until interfacial fracture.

The interdiffusion process is quite slow under these conditions at temperatures of 120°C or less, requiring in excess of 24 hrs. to produce any measurable strength at the interface. The lack of very good reproducibility, (demonstrated below) even with this optimized technique, requires many repetitions to obtain statistically significant data. Thus, the only extensive set of data we have is at 132°C and is presented in Table 1 and in Figure 9.

Table 1
Data at 132°C

<u>Time (min)</u>	<u>Force (at break, lbf)</u>	<u>Std. Dev.</u>	<u># of rep. samples</u>
60	610	350	20
90	741	295	16
120	1100	441	8
210	1497	471	5

We see that the error is in some cases in excess of 50% of the mean value and in no case less than 30%. Better results are (understandably) obtained with stronger joints, that is longer times. The trend is in the right direction, but the force in this time range is increasing roughly with $t^{1/2}$ not the $t^{1/4}$ predicted by our analysis described earlier. However, we do not expect our analysis to be applicable to any but the earliest stage of the healing process and (it seems almost too obvious to state) very little

Figure 9.

reliance on the power law extracted from Figure 9 is warranted.

The reproducibility of these data being what it is we continued our investigation of alternative techniques. Since the difficulties with the straight butt weld are certainly tracable directly to the lack of good reproducible surface contact, we decided to look at rehealing of crack surfaces reunited where we can get near perfect topographical fits. The technique is similar to that of Kausch and coworkers. Of course, we must develop it and improve on it ourselves if we are to use it to study all the aspects of the healing process we would like (molecular weight dependence, etc.) and which Kausch (a fracture man) has not pursued.

We have found we get the best results with the type of sample sketched below:

Figure 10 shows the rate of regrowth of strength with time. Also plotted is the same ratio of crack initiation stresses vs $t^{1/4}$. Our experience thus far with this technique is that it is reproducible to within about $\pm 10\%$, a great improvement over the straight butt weld. In this connection we note that while the interface was always visible in butt welding even at long times due to incomplete contact, the interface becomes invisible to the naked eye after about 2 hrs. at 130°C in crack rehealing. Even more encouraging is the good fit obtained with these preliminary data to our theoretical

Ratio of stress to crack healing sample to stress to
crack virgin sample vs. time
(crack rehealing technique)

132°C

Figure 10a)

Ratio of stress to crack healing sample to stress to
crack virgin sample vs. $(\text{time})^{1/4}$
(crack rehealing technique)

132°C

Figure 10 b)

prediction of a $t^{1/4}$ dependence of the healing process. We are in the midst of a thorough continuation of this area of our experiments.

Summary

Theoretical analysis of polymer welding, applicable in many areas including coalescence (curing) of particles in organics coatings for corrosion protection is well under way. Predictions have been made of the time and molecular weight dependence of the curing process; we can begin to use these equations for optimization of latex coating, formulation and curing. Considerable investment of time has been made to find the best experimental techniques for studying the healing process under idealized conditions. We have developed a crack-rehealing technique which, in our hands, yields data of $\pm 10\%$ precision and, so far, supports our theoretical analysis very strongly. We are now ready (and beginning) to generate a large amount of data to accurately map out the time, molecular weight and temperature dependences of polymer-polymer interdiffusion. We are also in a good position to extend our work to coalescence of particles, the prime area of application of this work to corrosion.

Personnel

Since the funds for this work became available too late to attract a graduate research assistant, three undergraduate research assistants have carried out the experimental side of our program thus far. Dan Morin and Paul Loudas did most of the "scouting" experimentation, working from late April until the summer. Most recently Tom Wood has replaced Loudas and is spending about 20 hours/week along with Morin on the crack rehealing. Graduate student Jaye Magda did supervise the work of the undergraduate students for 1 quarter.

Several new graduate students have expressed interest in this work this fall and we expect to engage one shortly.

Presentations and Publications of This Work

M. Tirrell and S. Prager, "Healing of Polymer-Polymer Interfaces", presented at Aug. 1980 ACS meeting, Las Vegas, Nev.

S. Prager, "Healing of Polymer-Polymer Interfaces", invited seminar, November 7, 1980, Polymer Division, National Bureau of Standards, Gaithersburg, MD.

S. Prager and M. Tirrell, "The Healing Process at Polymer-Polymer Interfaces", J. Chem. Phys., to be submitted (1980).

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Spontaneous (Air) Oxidation of Polymer Surfaces

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During the period covered by this report, considerable progress has been made in our study of the air penetration and air oxidation of both linear and crosslinked polymer films. We believe that our findings will prove useful in terms of having a better understanding of the factors which influence the oxidation of organic coatings (thin films).

Much of the initial work on this project has been involved with the development of the techniques necessary for a detailed analysis of transformations which occur in polymer films. Of particular concern to us was the use of both ESCA and infrared spectroscopic methods for the measurement of rate profiles for oxidative processes. In order to be able to contrast film exposed to atmospheric oxygen with film which was not oxidized, we required the construction of an inert atmosphere (dry) box on the entrance port to an Auger-ESCA-SIMS Spectrometer. Mr. Steve Willging, the graduate student who is involved in this project, has now completed the construction of such a set-up on the Chemistry Department's Auger-ESCA-SIMS Spectrometer.

Our recent efforts have been devoted to exploring the rate of oxygen penetration of both linear and crosslinked polystyrene films. In order to have a "tag" which will permit definitive measurements, we have attached easily oxidized labels to the phenyl groups of the polystyrene films. Utilizing ESCA spectroscopy, we have been able to follow the surface oxidation of these films to a depth of 50-75 angstroms. Since we are using films which are approximately 20 microns thick, the complete oxidative process can be followed by transmission infrared spectroscopy.

Our initial efforts involved the use of phosphines as detectors. It is known that phosphines of general formula, $\text{P}(\text{R})_3$, can be air oxidized to phosphine oxides of formula $\text{P}(\text{R})_3\text{O}$. In order to make use of this oxidation, polystyrene film in which some of the aryl groups had been con-

verted to triphenylphosphine was necessary. These films were prepared

by two different synthetic approaches. The first approach involved the synthesis of both crosslinked and non-crosslinked 4-bromostyrene - styrene copolymers. The synthetic approach to the monomeric species is de-

scribed above. Since the ultimate goal was the polymeric phosphine, an alternate path which involved the synthesis of the monomeric phos-

phine derivative, 4, was carried out. This synthetic path is described

in flowsheet form above. With the monomers in hand, we could prepare both linear and crosslinked films. Polymerization of **3** with an equivalent of styrene and 3.5% of divinylbenzene (DVB) in the presence of azobisisobutyronitrile (ABIN) gave the crosslinked polymer **6**. Similar polymerization in the absence of divinylbenzene gave the linear polymer **7**. Treatment of the crosslinked film, **6**, with *n*-butyllithium to give a

metal-exchange reaction followed by treatment with chlorodiphenylphosphine, gave the crosslinked phosphine substituted polystyrene **8**. Interestingly, similar treatment of the linear polymer, **7**, under the same conditions also gave the crosslinked polymer. It would appear that this occurs through radical coupling which results from electron transfer reactions of **7** with the *n*-butyllithium and the possible eventual formation of a crosslinking as depicted in **9**, where biphenyl type linkages exist.

Utilizing **4** as the starting monomer, similar polymerization pro-

cesses could be accomplished to produce the "clean" polymers 8 and 10. The polymer 8 prepared from 6 had a lower phosphine content than the polymer formed from 4.

With both 8 and 10 available, we were able to study the oxygen penetration in terms of the chemical reaction of oxygen with the phosphine to yield a phosphine oxide. This reaction was readily followed by ESCA spectroscopy. Figure 1 shows a series of ESCA spectra taken at 0, 4, 8.5, and 26 hr relative to time of exposure to air for polymer 10 (linear polymer made from 4). A similar study for 8 showed similar behavior. As can be seen from the figure, the phosphine phosphorus appears at 130.5 ± 0.3 eV. On this same scale the phosphine oxide appears at 132.2 ± 0.3 eV. Clearly, in 26 hr the surface is almost completely oxidized. In terms of complete oxidation of the film (20 micron thick), infrared spectral analysis showed only 5% oxidation after seven months exposure to air. This is for nonswollen polymer. When the polymer is swollen with benzene 15% total oxidation is noted after seven days.

In contrast to the oxidation observed with polymer formed from 4, the polymer formed from 3 via 6 and 7 exhibited much more rapid oxidation. In this case the surface (50Å) was completely oxidized after 24 hr and about 5% total oxidation was observed for the whole film after seven days. The cause of the major difference is not understood at this point. Hypothetically, it could be argued that trace amounts

Figure 1. ESCA spectra of the phosphorous region of the polymer film 10 after exposure to air for (a) 0, (b) 4, (c) 8.5, and (d) 26 hr.

of oxygen are reacting with the intermediate organolithium species to generate hydroperoxides which are then acting as catalysts which promote oxidation. In support of this hypothesis, we know that there is incorporation of trace amounts of oxygen into the film in a chemically bound manner in the steps leading to phosphine formation. The nature of this incorporation is not understood at this time.

In view of the differences observed with the phosphine-substituted polystyrene films, we decided to explore the use of another "oxidation label." For this purpose the dihydropyridylpyridine label was used which was synthesized as shown below. The polymer $\lambda\lambda$ is dark purple

and on oxidation to the bipyridyl derivative $\lambda\lambda$ gives a light yellow film. Much to our surprise, this polymer film (20 micron thickness) was completely oxidized to $\lambda\lambda$ in 45 min on exposure to atmospheric oxygen. In contrast to this behavior on exposure to air, the film remains purple ($\lambda\lambda$) for relatively prolonged periods in an inert atmosphere. At the present time we lack an adequate explanation for these observations.

We are continuing to investigate this problem.

Corrosion of Alloys and Plasma-Sprayed Coatings
in Coal Gasification Environments

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1. Introduction

This report covers the progress on two research grants initiated in April of 1980. The first project is an award made to Professor Toth to study the effects of coal gasification environments on metals and alloys. The second project is an award to Professors Pfender and Toth to develop plasma-sprayed coatings, both metallic and non-metallic, suitable for coal gasification environments. Shortly after receiving the awards, Professor Toth agreed to accept a rotator's position as associate program director at the National Science Foundation. Because of this development, Professor Pfender agreed to monitor and co-direct the research on metal alloys in addition to the work on coatings. For this reason it is appropriate to consider the research as one integral unit.

There are also sound scientific reasons for doing so. In the original thinking about the problem and in reading the existing literature, it was realized that because of the massive size of these coal

gasification units and the very large amounts of metals required in their construction, that it would not be economical to utilize expensive materials. Besides, many of the candidate materials such as cobalt are not only expensive but in short supply. Therefore, in many of the proposed units, the corrosion resistant materials will be coatings. We initially thought that the best way of approaching the overall problem is to mount a concerted effort on both corrosion of alloys and coatings in these environments. It was furthermore realized that plasma spraying is one of the most effective methods of depositing coatings. Stressing this aspect of the research would tie in well with the expertise Professors Pfender and Toth have developed on plasma processing of materials.

There is still another reason for combining the two projects. To take Professor Toth's place during his absence, Dr. T.T. Huang of the University of Pittsburg has been hired as an assistant professor. Dr. Huang is eminently qualified to carry on this research as it is similar to his Ph.D. thesis research. While Dr. Huang has not been able to join the group until January of 1981, he has been contributing to the scientific decisions on both projects. He has also contributed to the write-up of this document and for some of the research contained therein. Both Professor Pfender and Toth recommend strongly to the reviewing committee that Professor Huang be made a co-principal investigator on this project.

2. Part 1. Corrosion of alloys in coal gasification environments

2.1 Summary of original research goals and research plan

One of the most important problems in coal gasification is corrosion of the containment vessels, primarily due to the presence of

sulfur in the coal. Sulfur combines with the metal surface to form metallic sulfides. The rate of growth of these layers is usually much more rapid than that of the oxides. Furthermore, protective or self-limiting layers are usually not formed as is the case in oxide formation. Another complication is that some of the sulfides are liquid at the temperature of interest.

Another complicating problem is that the coal gasification atmosphere is really a mixture of corrosive species. Thus, one has a competition between sulfidization, oxidation and carburization. Each of these reactions proceeds at a separate rate. In some cases, one mechanism will overwhelm the other chemical reactions, but in general, the reactions occur simultaneously and the net result is difficult to predict on the basis of a straight thermodynamic analysis. Numerous sequential chemical reactions are known to occur in selective systems even when the corrosive gas is maintained at a fixed chemical composition. In reality, the gas composition does not remain constant due to the inhomogeneous nature of the overall gasification reaction. Still another complication is the erosion due to the presence of particulate matter. Finally, one has to consider the effects of thermal cycling the gasifier.

Our goals in this phase of the research are as follows:

1. To identify the types of atmospheres appropriate to the various gasification procedures,
2. To identify alloys most suitable for these environments,
3. To simulate these environments in the laboratory,
4. To conduct corrosion studies on these alloys in which we identify the mechanisms by which the corrosion occurs, and
5. Use the above information to develop more corrosion-resistant alloys.

In the initial stages of this research we are deliberately not considering the very important effects of erosion caused by particulate matter and also the effects of thermal cycling. Such effects should be considered in a later stage of the research.

To accomplish the previously mentioned goals, we have devised the following plan consisting of:

1. Literature survey of atmospheres in coal gasifiers and identification of candidate materials with particular emphasis on thermodynamic data,
2. Literature survey of known kinetic effects with an emphasis of how such effects might alter the thermodynamic considerations,
3. Identification and implementation of experiments which will lead to a better understanding of the mechanism of corrosion.

More details are provided in the attached full progress report.

2.2 Research plan and progress during the reporting period

The objective of this program is to study the attack on nickel, cobalt, and iron alloys containing chromium and aluminum, by gases containing a second oxidant (such as sulfur and carbon) at temperatures up to 2000°F. The emphasis of the experimental techniques is to use Auger electron spectroscopy and high-resolution electron microscopy to identify the chemical reactions which occur near the surface, and to study the mechanisms responsible for the failure of these alloys and coatings in coal-gasification environments. This study is being done as a function of the type of oxide formed at the surface (Al_2O_3 or Cr_2O_3), alloy composition, and environmental conditions that are representative of a wide range of coal gasification processes. The goal of this study is, first, to provide a basic understanding of surface chemistries

and atomic mechanism of high temperature corrosion in coal-gasification environments, second, to determine the behavior of different commercial alloys in a wide range of coal gasification environments, and, third, to develop or select alloys and coatings suitable for different coal gasification processes.

The program is being conducted in three consecutive tasks as follows:

Task 1: Materials and testing equipment

(see full report for more details)

The choice of certain alloys should allow answers to the following questions:

1. What is the best base element (Ni, Fe, or Co) for alloys or coatings to use in coal gasification environments?
2. What is the optimum Cr/Al ratio in alloys and coatings?
3. Which is the best oxide scale (Al_2O_3 or Cr_2O_3) in coal-gasification environments?
4. What is the effect of nickel additions to the corrosion behavior of Fe-Cr alloys?
5. What is the effect of various additives such as Y or Hf to the corrosion behavior?

Tests are being conducted in both vertical and horizontal furnaces. The weight change of the specimen is being recorded by a Cahn 1000 microbalance in a controlled atmosphere. Gas mixtures are blended and regulated with precision flow meters. All exposures are conducted in the equilibrium gas mixture, which is achieved by passing the gas flow through the catalyst (honey-comb type Pt-coated Al_2O_3) near the hot zone of the furnace.

Progress: Task 1

Sixteen high-purity alloys have been tungsten-arc melted under an argon atmosphere, remelted several times and drop-cast into a water-cooled copper chill.

The furnace and microbalance have been assembled and are ready for use.

Thermodynamic stability diagrams have been calculated for a set of alloys which will be used in an initial set of studies. These alloys are Ni-30Cr, Ni-50Cr, and Fe-31Cr-28Ni.

Task 2: Corrosion in multicomponent oxidizing environments

Model alloys and commercial alloys will be exposed to four different types of test atmospheres under constant temperature and gas composition. The atmospheres will contain more than one oxidant including (a) H_2 - H_2S - H_2O , sulfidizing-oxidizing, (b) H_2 - H_2S - CH_4 , sulfidizing-carburizing, (c) H_2 - CH_4 - H_2O , carburizing-oxidizing, (d) H_2 - H_2S - CH_4 - H_2O , sulfidizing-carburizing-oxidizing. Most of the work will concentrate on the sulfidizing-oxidizing condition. The surface chemistry of the specimens developed under these conditions will be carefully studied.

Progress: Task 2

An understanding of sulfidation-oxidation mechanisms of the alloys requires first an understanding of the oxidation behavior of these alloys. Preliminary tests on some of these alloys have been conducted in air at $950^\circ C$ by Dr. T.T. Huang at the University of Pittsburgh and also by Penny Peck at the University of Minnesota. At this temperature, Ni-18Cr-6Al and Ni-18Cr-6Al-1.0Hf alloys form a Al_2O_3 scale. The presence of Hf improves

the adhesion of the Al_2O_3 scale, but localized breakdown of this scale in Hf-containing alloys is still evident. The growth rate of this scale is relatively small. For Co-18Cr-6Al and Co-18Cr-6Al-1.0Hf alloys oxidized at this temperature, a significant amount of transient oxide (Co, Cr)-rich oxide forms. This scale then blocks the inward diffusion of oxygen flux and allows an Al_2O_3 scale to form. The ease of formation of Al_2O_3 scale in Ni-based alloys compared to Co-based alloys can be rationalized as follows:

1. the growth rate of NiO is slower than that for CoO, and
2. the outward diffusion of Al in Ni-based alloys is faster than in cobalt based alloys.

An Al_2O_3 scale is, therefore, relatively easier to form in Ni-based alloys compared to cobalt-based alloys.

Task 3: Corrosion in real coal gasification atmosphere

In the coming year, some of the model alloys and commercial alloys will be exposed to real coal-gasification environments. The interaction of alloys with this complicated environment will result in oxidation, sulfidation and carburization under different conditions. Unfortunately, a detailed thermodynamic analysis of this multicomponent gas-alloy interaction is presently too complicated to be attempted and also there is a lack of thermodynamic data. A detailed surface-chemistry study of the scales formed under these conditions, however, will enable us to identify the mechanisms by which the specific alloys failed in a CGA environment. These studies will serve as a guideline for the selection and modification of the potential alloys for use in CGA environments. In these studies, kinetic effects, as well as thermodynamic considerations, will be emphasized.

3. Part II Plasma sprayed coatings suitable for coal gasification atmospheres

3.1 Introduction

In April, 1980, Professors Pfender and Toth received an award for research on plasma-sprayed coatings suitable for coal-gasification atmospheres. In the original proposal emphasis was placed on the deposition of multilayered/multipurpose coatings. It was proposed to first deposit a dense, corrosion-resistant metallic layer and then a porous ceramic layer. This latter layer was to act as a thermal barrier to protect the metallic layer. The ceramic layer was to be porous for adequate thermal shock resistance.

As the research on this project was initiated, it was realized that the "science" of plasma spraying is somewhat primitive. For example, commercial plasma guns are of the same design as 20 years ago. With such guns, it is difficult to achieve fully dense coatings, although there are some proprietary designs using supersonic velocities that can achieve nearly full densities. Most plasma sprayed coatings are either heat treated or shot-peened to improve the properties of the coatings. Nevertheless, the rejection rate for coatings in industry is often quoted to be about 50%.

By attending a number of workshops and conferences on plasma chemistry, we learned of some preliminary results on plasma spraying by European scientists that might enable one to control porosity and, thus, improve the quality of coatings. Such efforts require highly sophisticated theoretical calculations of the interaction of particulate matter with a plasma, measurements of the temperature and velocity distribution of the plasma jet, as well as of the sprayed particles, and the use of the above knowledge to improve gun design.

Basically, the problem with present-day technology of gun-design is that the injected particles possess different velocities, trajectory-paths and temperatures. A plasma is viscous and because of this viscosity, the plasma resists the injection of cold gases and entrained particulate matter. In plasma spraying some of the injected particles fully melt, but others remain solid or only partially melted. The coating is made up of a deposition of both solid and liquid particles. The particles deposited as a solid contribute to the porosity of the coating.

To decrease the porosity (or to control the porosity) it is necessary to control the velocity distribution and temperatures of the sprayed particles. Ideally, one needs nearly monoenergetic particles. The achievement of such is, of course, far ahead of commercial technology and even laboratory research.

In the sections which follow we outline results of computer calculations and experiments which appear very promising in achieving the desired results. We regard this as an exciting research opportunity. Not only does it now appear possible to improve coatings for corrosion resistance, but also for other applications such as wear resistant coatings.

3.2 Work Performed During the Reporting Period

A type 7M plasma flame spray system has been purchased from Metco Inc.

Two types of substrates were chosen for the initial experiments:

- 1) Cyclinders of 25 mm dia, and 2) 2.5 cm x 7.5 cm plates 0.3 cm thick. Both types of samples are made of mild or stainless steel.

During the spraying process the cyclindrical substrates are rotated and the plates are mounted stationary while the gun traverses back and

forth to produce a multilayered coating. A denser coating can be achieved by applying a greater number of thin layers as opposed to a lesser number of thick layers. Therefore, layers greater than 75 μm per pass should be avoided. Remelting a previously deposited layer before the next one is applied may reduce porosity and increase bond strength.

Using a separate gas stream such as Ar blowing over the workpiece aids in reducing the formation of oxides. Surface preparation has included cleaning with a solvent such as acetone. Since the bond is largely of a mechanical nature, increasing the surface area is essential. Therefore, gritblasting at 30 psig with a coarse iron grit is necessary. Baking the substrate prior to spraying in an inert or reducing atmosphere in order to drive off any contaminants needs to be considered.

An optimum powder particle size exists for each alloy. The region of highest temperature in the plasma lies along its axis, and particles injected perpendicular to the direction of flow should reach this region to insure complete melting. Particles with excessive momentum (i.e. too large) tend to pass through the jet leaving insufficient dwell time for complete melting whereas particles without sufficient momentum tend to float on the fringes of the jet and also remain unmelted. Hence, it is important that both average powder particle size and injection velocity are considered.

Selection of mechanical testing methods

In addition to the corrosion analysis, the mechanical properties of coated samples will be investigated. Density, thermal cycle cracking, stress rupture, tensile properties, erosion resistance, and bond strength are among the prime candidates under investigation.

Development of a spectroscopic facility

In the process of plasma spraying, particles are injected into the plasma jet emanating from a plasma torch. The molten particles impinging on the substrate form a coating. The quality of this coating depends on the uniformity of size and velocity of the particles and on their temperature (completely molten, but not superheated particles are desirable). Therefore, knowledge of the temperature distribution in the plasma jet is crucial for injection and controlled heating of the particles. Because of the temperature level in the plasma ($\leq 20,000$ K), spectrometric methods are particularly useful for measuring the temperature distribution.

In general, spectrometric methods are tedious and time-consuming. Considering the fact that any variation of the operating parameters of the plasma torch (current, mass flow rate and gas composition) will give rise to variations of the temperature distribution, the time required for such measurements and the associated data evaluation becomes prohibitive. For this reason a semi-automatic spectroscopic facility is under development which can be directly connected to a minicomputer for data evaluation. Since this facility will also be used for another research project supported by NSF, there are no charges for personnel against this project.

Laser Doppler equipment

A complete Laser Doppler Anemometer (LDA) is available from another research project for measuring particle velocities in a d.c. plasma torch. As a measuring method LDA has been chosen in dual-beam mode. The LDA equipment consists of a 2W argon-ion laser, frequency stabilized by an etalon, a TSI beamsplitter, a photomultiplier, and a TSI Counter (Model 1990). The data

transfer from the counter to the mini-computer (PDP 11) and the control of the equipment will be done by means of a HP microprocessor. The PDP 11 is used for data storage and data reduction.

The optical set-up has been completed and a cold air flow system seeded either with water droplets or with solid particles serves as the test medium. Experiments are in progress to check the data transfer and the response of the electronic system to changes in the measuring point. A program for data transfer and data reduction is in preparation.

Initially, particle velocities will be measured in a commercial plasma spray gun manufactured by Metco. Later on the program will be extended to measurements in torches built in our shop. Provisions have been made for mounting the torches on a x, y, z drive which permits axial as well as lateral scanning.

Modelling of particle injection and particle motion in a plasma

Computer modelling of the heating environment (plasma) of the particles and of the particle behavior in the plasma jet has been initiated in conjunction with the previously described experimental studies. It is felt that the results of this modelling work will establish guidelines for the proper choice of particle size and injection velocities for a given plasma jet. Since the modelling work is based on the same geometry and on actual operating parameters of the plasma torch (arc current and mass flow rates) direct comparisons between predictions and experimental results should be feasible.

II. Surface Reactions and Modifications

<u>Principal investigators involved</u>	<u>Effort, Months/Calendar Year</u>	
	<u>Current Funding Period</u>	<u>'81-'82 Fiscal Year</u>
W.G. Miller	½	1
L.D. Schmidt	-	1
G.L. Griffin	1	1
P.I. Cohen	-	1
R.J. Collins	1	1

Two techniques are being applied for the first time to reactions at surfaces. The adhesion of the first monolayer of polymer and how it is affected by environmental agents can now be evaluated; this is something which has not been accomplished by any other technique. Development of apparatus is well in hand for the study of the initiation of oxidation and of corrosion of a semiconductor surface. Preliminary experiments appear to show that a vitrified surface of iron has improved resistance to corrosion, but verification of various aspects is needed.

The Interaction of Polymeric Films with Surfaces at the Molecular and Submolecular Level

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A large number of experiments have been performed on the adhesion of poly(vinyl acetate) and polystyrene to oxides of aluminum, titanium and silicon, of varying morphologies, as a function of temperature, presence or absence of environmental agents such as water or hydrocarbon, and conditions of polymer deposition. The report which follows is built around these studies for which figures have been drawn up. It is not exhaustive, but representative of the type of studies which have been done. Four manuscripts describing this work are in various states of preparation.

Basis of Principal Experimental Technique

Through use of a chemically and thermally stable nitroxide spin label,

the dynamics of polymeric segmental motion may be nondestructively assessed through analysis of the spectral line shape using electron spin resonance spectroscopy (ESR). Using lightly labeled polymer, typically 1 label per 1000 monomer units, the ESR spectrum of labeled poly(vinyl acetate), PVAc, is shown in Figure 1 as a function of concentration when in solution, in Figure 2 as a function of temperature in the bulk polymer, in Figure 3 when adsorbed at a solid-liquid interface, and in Figure 4 as a function of temperature when thinly coated (less than monolayer coverage) on an oxide surface. A companion temperature study of bulk polystyrene and polystyrene thinly coated on an oxide surface is shown in Figure 5. From Figures 1 and 3 one can conclude that the segmental dynamics of adsorbed trains and dangling loops can be differentiated easily. By proper comparison to theoretical simulation, as, for example, shown in Figure 6, the percentage of loops and trains as well as their motion may be determined. Comparisons of Figures 2, 4 and 5 show convincingly that the effect of adhesion to a solid surface can be easily assessed, as well as differences in adhesion between different types of monomeric units. In the examples shown vinyl acetate is seen to adhere more strongly to the SiO_2 surface than styrene. In fact, PVAc must be at about 200°C before it no longer adheres to the solid surface.

The Range of the Effect of the Solid Surface on Polymer Motion

The effect of the oxide as one moves laterally away from the surface was deduced. From temperature dependence studies as a function of film thickness, as

for example, shown in Figure 7, one can deduce that the surface affects local segmental motion only a few angstroms above an oxide surface. Even in a monolayer, corresponding to a film thickness of less than $10\text{\AA}$, the segmental motion of many loops is unaffected by the adherence of other units of the same chain to the surface. Further studies using differential scanning calorimetry (DSC) are shown in Figure 8. At monolayer coverage (11% PVAc) a glass transition (T_g) is not observable. At a mean depth of about $40\text{\AA}$ (50% PVAc) a broad T_g is observed while at a mean depth of $350\text{\AA}$ (90% PVAc) a normal T_g is observed. Inasmuch as T_g measures the cooperative motion of many chain atoms whereas the spin-label technique measures local segmental motion extending only over a few (4-6) chain atoms, the difference in the two types of measurements is understandable. These conclusions are quite in contrast to those previously published (C. A. Kumins, J. Coating Technology, 52, 39 (1980)). A detailed comparison will be given in a paper in the process of being written. Our conclusions are further strengthened by modulus measurements, an example of which is shown in Figure 9.

In contrast to SiO_2 surfaces, Al_2O_3 surfaces were found by the spin-labeling technique to bind PVAc to much higher temperatures, and a thicker polymer film was necessary before a glass transition was observed by calorimetry, Figure 10. Therefore the range of interaction clearly depends on the nature of the surface.

Diffusion of Bound Polymer From an Oxide Surface

In preparation for solvent displacement studies, it became of importance as well as of intrinsic interest to determine how fast a polymer molecule bound to a surface would diffuse into the surrounding polymer matrix. An experiment was designed, as shown in Figure 11. A monolayer or less of a spin-labeled polymer is deposited on an oxide surface, and overcoated with unlabeled polymer. The temperature is suddenly raised and the spectral line

shape followed as a function of time. By reference to previous studies, for example, Figures 2 and 4, the time necessary for the adsorbed polymer to diffuse off the surface and into the surrounding unlabeled polymer can be determined. Some results are shown in Figures 12 and 13, representing extremes. With PVAc on SiO_2 , Figure 12, the labeled polymer had diffused off the surface before the first measurement could be made (ca. 4 minutes). With PVAc on Al_2O_3 , Figure 13, the labeled polymer had not diffused off the surface in two days (the maximum lifetime of the label at this temperature).

Effect of Environmental Diluents on Polymer-Surface Delamination

Two examples were studied: 1) water, an everpresent chemical, and 2) decane, taken as a model hydrocarbon. Three types of test conditions were set up in order to measure the effect of the environmental diluent on:

1) the bulk labeled polymer, 2) the labeled polymer deposited as a monolayer on the surface of interest, and 3) the labeled polymer on a surface but overcoated with unlabeled polymer. Some typical results are shown in Figures 14-17. With PVAc on SiO_2 water effectively displaces the polymer at room temperature whereas decane is moderately effective at higher temperatures only. On Al_2O_3 neither water nor decane displaces the polymer at ambient or at higher temperatures, even after several days. These results are rather dramatic.

Additional types of studies have been made where a labeled PVAc is adsorbed on a surface and overcoated with unlabeled polystyrene, an incompatible polymer. Again the delamination is followed as a function of environmental solvent and temperature. Large differences are observed.

Spin Label Perturbations of Segmental Motion

Using a labeling technique always makes one vulnerable to the criticism that the label perturbs the system. To address this question a comparison was made using ^{13}C nuclear magnetic resonance spectroscopy (nmr). Some results are shown in Figure 18. Without going into details, we have shown that the

two measurements, one using a label, give not only similar but nearly quantitatively identical results. However, the nmr experiment takes roughly 100 times as long so we plan to stay with the spin label technique.

Figure 1. ESR spectrum at 25°C as a function of concentration of PVAc(61,000), randomly labeled. Polymer concentration (wt.%) in CHCl_3 is A, 1%; B, 44%; C, 61%; D, 72%; E, 100% (bulk).

Figure 2. Temperature dependence of bulk PVAc. The glass transition is $\sim 30^\circ\text{C}$. Temperatures are in $^\circ\text{C}$.

Figure 3. The spectra of PVAc(61,000) adsorbed at the solid-liquid (CHCl_3) interface at saturation surface coverage. A, no solvent or surface; B, Al_2O_3 ; C, TiO_2 ; D, glass (3-8 μ); E, SiO_2 (Cab-O-Sil M5).

Figure 4. Temperature dependence of PVAc(6x10⁵) in the bulk state, and when adsorbed onto SiO₂ (obtained by drying a sample adsorbed from CCl₄ at 50% surface coverage).

Figure 5. Temperature dependence of polystyrene in the bulk state, and when adsorbed onto SiO₂ (obtained by drying a sample adsorbed from CCl₄). The glass transition for bulk polystyrene is ~100°C.

Figure 6. Simulated composite spectra consisting of 4% of the nitroxides undergoing motional narrowing (isotropic, homogeneous broadening of 1G) with rotational correlation times as indicated.

Figure 7. Temperature dependence of PVAc(6x10⁵) on SiO₂ when adsorbed from CCl₄ to 50% of saturation coverage (LOW) before drying, or at saturation coverage (HIGH) before drying.

Figure 8

Figure 9

Figure 10

ΔT ↓ time

Figure 11

Figure 12 Diffusion of PVAc from SiO₂ surface into bulk polymer

POLY(VINYL ACETATE) 145°C

Figure 13

Figure 14

Figure 15

POLY(VINYL ACETATE)

Figure 16

POLY(VINYL ACETATE)

Figure 17

POLY(VINYL ACETATE)
80°C

POLY(VINYL ACETATE)
IN
DECANE

Figure 18

CHARACTERIZATION OF ELECTRODE SURFACES

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Two graduate students and a part-time undergraduate have been working on this project. They have been working on the following topics:

- (1) Construction of ultrahigh-vacuum environmental chambers for surface characterization without contamination.
- (2) Development of techniques for cyclic voltammetry of electrodes.
- (3) Surface analysis of electrodes and of Pt-Rh alloys using x-ray photoelectron spectrometry (XPS).
- (4) Crystallographic anisotropies in chemical and electrochemical etching of Pt.

The first three projects are in construction and preliminary data-gathering phases. We have been fairly successful in using XPS and sputter depth profiling to determine monolayer and multilayer films on electrodes and alloys, but results are still tentative.

Therefore, in this report we shall describe in detail only the fourth project as results for it are approaching completion.

CRYSTALLOGRAPHIC ANISOTROPIES IN CHEMICAL AND ELECTROCHEMICAL ETCHING OF PLATINUM

Erosion and corrosion compete as major material degradation processes, erosion being the removal of the material into a liquid or vapor phase and corrosion being formation of compound layers of inferior properties. The anisotropy of these processes is a major cause of their pernicious consequences because they seldom proceed simply as uniform alterations of layers near the original surface. Attack is usually anisotropic and proceeds preferentially along grain boundaries, dislocations, regions of stress, etc. This anisotropy results from different rates of attack caused by different stabilities of the material because of 1) stresses and 2) crystallographic anisotropies. The latter determines the direction and rate of attack at grain boundaries and other stressed regions, but geometric structures in many situations obscure crystallographic anisotropies and will, in fact, control morphologies and rates of attack.

The objective of this research is to determine crystallographic anisotropies in erosion rates in the absence of stresses by using defect-free single crystal microspheres. Platinum is an ideal candidate for these prototype studies because it does not form stable bulk compounds and therefore will erode rather than corrode in attacking environments.

The use of a single-crystal spheres to examine crystallographic anisotropies was first reported by Gwathmy and coworkers who studied the thickness of oxide films on Cu spheres ~ 1 cm in diameter and to study faceting Cu and Ni produced by oxidation. We have used smaller spheres because surface tension produces a spherical shape upon melting and small spheres are usually single crystals. Spheres less than 0.1 cm in diameter are also convenient for scanning electron microscopic (SEM) characterization

because on a single micrograph both facet structure and orientation variations can be displayed.

Experimental

Specimens were prepared by melting the ends of .0025 or .0075-cm diameter high-purity Pt wires in a $\text{CH}_4\text{-O}_2$ torch to form spheres 0.01 to 0.05 cm in diameter. Short segments of wire had been spotwelded to a larger wire so that an array of eight spheres could be examined simultaneously. This was useful because some spheres exhibited grain boundaries and some were damaged. By examining several spheres for the same treatment conditions, it could also be ascertained that behavior was characteristic of all specimens.

Boiling aqua regia (3 parts HCl to 1 part HNO_3) was used for chemical etching, and specimen were submerged for times from several seconds to 30 minutes. Electrochemical etching was done in 3-molar HCl saturated with KCl. Approximately 5 volts were applied at 60 Hz between the Pt and a carbon reference electrode. In preliminary experiments direct current was observed to give much less extensive etching patterns even though vigorous bubbling occurred. No attempts have been made thus far to examine other solvents or etching conditions.

Specimens were examined by SEM in JEOL JEM 100 electron microscope. Effects of time of etching were studied both on a single specimen which was etched repeatedly, and on different specimens. All results shown here represent typical behavior observed in several different experiments.

Electrochemical Etching

Figure 1 shows a specimen after electrochemical etching. The original spheres exhibited smooth surfaces of constant radius except for small flat

(111) faces. However, after etching, the sphere is transformed into the shape of a cube with the corners cut off. Symmetry shows that the square faces are (100) and the triangular faces at the corners are (111). The flat faces are slightly rounded, so that the flat regions deviate up to 10° from the (100) direction. These regions are completely smooth except for regions of shallow pyramids with curved caps near (100). The regions of (111) orientation are not smooth but are completely faceted into triangular pits which also expose predominantly (100) planes.

A shorter time of etching (Figure 1e) produces a surface in which the region near (100) has become etched but the region around (111) and near (110) remains smooth. The edges of the cubes have not yet appeared.

The effects of grain boundaries on etching patterns is shown in Figures 1f and 1g where a grain boundary is evident near the center of the micrograph. Two (100) poles oriented at $\sim 30^{\circ}$ from each other index the geometry of the grain boundary. Figure 1g shows that the walls of the grain boundary form flat (100) planes. Little evidence for preferential attack to open up the grain boundary has been observed in any grain boundaries.

Chemical Etching

Figure 2 shows spheres after etching in aqua regia. Extensive etching also transforms the sphere into roughly a cubic shape, just as with electrolytic etching. However, the (100) orientation does not remain smooth as with chemical etching but instead exhibits extensive faceting. Figure 2b shows a region which includes (100) and (110) orientations. Careful examination reveals that facets $\sim 3\text{-}5\mu$ across cover the entire surface and that most planes formed have (110) regions which are flat and smooth. The (111) orientation remains smooth and is attacked from the edge of the large flat plane which

(a)

(b)

(c)

(p)

(e)

(f)

Figure 1

Figure 2

exists initially. Eventually the (111) plane shrinks and disappears completely. The (100) plane also appears to be attacked from its edge.

Initial stages of attack, Figure 2

is even more anisotropic than for electrochemical etching. Facets begin to form near the (210) orientation (forming (110) planes), and the regions attacked spread until the entire sphere is eventually faceted. The "wall" around the (100) poles is fairly large and smooth and it consists of the relevant (110) plane. The original (110) orientation is not attacked initially, nor are any orientations near it or around (111). These only become etched as the "front", originating from (210), spreads to finally envelope them.

Discussion

This is obviously a complicated process, and the unexpected morphologies and rates of attack suggest additional complexities. We shall only attempt to summarize some of the general features at this stage.

Both chemical and electrochemical erosion probably involve attack of chlorine atoms to form the soluble and stable chloroplatinate ion. In aqua regia Cl⁺ is generated homogeneously by oxidation of Cl⁻

while electrolysis produces Cl atoms at the surface

Adsorbed Cl then probably combines with H₂O to yield the chloroplatinate anion. Thus, it is interesting that very similar processes are occurring in both chemical and electrochemical etching, one requiring diffusion of Cl to the surface for adsorption and the other generating it directly.

We suggest that this may explain the larger anisotropy of attack in chemical etching compared to electrochemical etching because adsorption of Cl may be rate limiting and should exhibit large crystallographic anisotropies (it is observed to be slowest on (111) and fairly slow on (100)).

Table I

<u>Etching Mode</u>	<u>Planes Formed</u>	<u>Orientation Eroded Most Rapidly</u>	<u>Orientation of Initial Attack</u>
Electrochemical	Within 10^0 of (100)	All, (100) fastest	Near (100)
Chemical	(110)	(100)	(210)

Contrast of general behavior is summarized in Table I. Erosion is fastest near the (100) orientation because spheres are transformed into cubes by both etching processes. However, electrochemical etching produces large, smooth surfaces near (100) while chemical etching produces small facets whose orientation is predominantly (110).

Initial chemical attack is very specific to the (210) orientation, while electrochemical attack occurs generally over all regions near (100). The (111) plane is inert to chemical attack except from the edge of the large (111) planes which eventually shrink and disappear.

Summary

The single-sphere microsphere is an ideal specimen with which to examine anisotropies in erosion processes, and platinum is an ideal metal in that no oxide films compete with erosion processes. We have only begun to explore these processes, however, and many further experiments would be necessary to determine the influence of other variables. Factors such as impurities, temperature, and overvoltage could affect the nature and type of etching processes.

We are planning these experiments on platinum. Similar studies of metallurgically interesting metals such as Fe, Ni, and alloys require development of methods for preparation of single-crystal microsphere in situations where oxide growth can be avoided.

We shall also use scanning Auger microanalysis (SAM) to probe chemical composition of individual facets as soon as this instrument is operational. Sputter profiling should permit determination of monolayer and multilayer films on single crystal planes.

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Temperature Programmed Desorption of H_2 as a Chemical Probe of the
Partial Oxidation of Zn(0001) Surfaces

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Abstract

We have commenced an experimental program to measure the initial oxidation rates of clean Zn(0001) surfaces, and to characterize the adsorption properties of these initial oxide films using-temperature programmed desorption (TPD) of simple adsorbate molecules that might be found in a corrosive environment. For the present study, we have chosen H_2 as the adsorbate. An apparatus is described for performing TPD studies on H_2 adsorption on Zn(0001) surfaces that have been exposed to controlled amounts of O_2 . Separate results for H_2 adsorption on bulk ZnO are also presented.

Introduction

Zinc and Zn-based coatings are employed in a wide variety of commercial and technological applications, including the cathodic protection of steel surfaces (1), as anodes in conventional alkaline batteries and new high-energy density storage batteries (2), and in high strength Al-Zn-Mg alloys (3). In all of these applications, the self corrosion of Zn or related processes result in a degradation of product performance and lifetime.

In aqueous environments, Zn is passivated by a thick oxide layer which presents a diffusional barrier to corrosive attack. Factors which determine the protective capacity of this layer include its transport properties and its strength of adhesion to the Zn surface. Both of these properties are strongly influenced by the chemical composition of the layer and of the metal/oxide interface, which in turn are at least initially determined by the chemistry of the initial oxidation step.

In recent years there have been several studies of the initial oxidation rates of Zn surfaces (4-8). These studies have used Auger electron spectroscopy (AES) and ultraviolet and X-ray photoelectron spectroscopies (UPS and XPS) to determine the composition and electronic properties of the oxide layer. However, there have been no experiments reported which measure the chemical properties (other than composition) of the growing oxide layer. One such property of relevance in corrosion research is the binding energy of adsorbed molecules which might be present in the corrosive environment. Temperature programmed desorption (TPD) can be used to measure desorption energies of simple adsorbates, and thus represents a "chemical" probe of surface properties related to corrosion behavior.

With support from the Corrosion Research Center, the author has begun an experimental program to measure the initial oxidation rates of metal surfaces and to characterize the chemical properties of initial oxide layers using TPD of simple adsorbate molecules, in order to complement the information that is provided by the electron spectroscopies. In this progress report we describe the status of the first year's effort, an investigation of the initial oxidation rate of clean Zn(0001) surfaces using TPD measurements of adsorbed H_2 as a chemical probe. In a separate proposal we describe plans for future oxidation studies of Zn(0001) surfaces that have been pre-coated with sub-monolayer amounts of corrosion inhibitors or accelerators (e.g., Cr or Cl) (9).

Present Status

During the period covered by this progress report, the apparatus for performing a TPD investigation of the adsorption properties of the initial oxide film on Zn was designed, and the primary components for the apparatus were ordered (e.g., mass spectrometer, sputter gun, ion pump, etc.). The apparatus is presently being assembled, and a graduate student is being selected to assist with the project. Additional studies of H_2 adsorption on ZnO were completed by the author while at the National Bureau of Standards, prior to his arrival at the University of Minnesota in September, 1980. These are discussed below.

A schematic of the apparatus is shown in Figure 1. The sample chamber consists of a SS six-way cross. The system is pumped with a 20 ℓ /sec ion pump, which can be isolated from the sample chamber by closing a high conductance right angle valve. This allows the sample to be exposed to large doses of H_2 (see below) without overloading the pump. The isolation feature is also useful for minimizing the Ar pumping load during sputtering. A second valve is present to isolate the sample chamber from the sorption pump used for roughing. The apparatus also includes a sputter gun for cleaning the crystal, a nude ionization gauge, and the quadrupole mass spectrometer for TPD experiments.

The cut and polished Zn crystal is mounted at the mid-point of the sample chamber. The sample holder can be cooled to < 100 K with liquid nitrogen, and the crystal can be resistively heated. The thermocouple is attached directly to the back face of the Zn crystal. The edges and back face of the crystal can be covered with an evaporated Au layer if necessary, to eliminate desorption from these surfaces. The front face of the crystal can be cleaned by Ar^+ ion sputtering, followed by annealing at ≤ 425 K (5,6).

The partial oxide layer is grown by admitting O_2 into the sample chamber through a variable leak valve. An O_2 pressure of 10^{-7} torr is convenient for producing exposures of the order 0-100 L in reasonable times; such exposures are sufficient to accomplish the first stage of oxidation. For the present studies, we will estimate the oxygen coverage using Unertl's coverage vs. exposure results. In future work, the sample holder may be modified to permit sample transfer in vacuo to an analysis chamber for AES measurements of oxygen coverage.

The TPD experiments are performed as follows: Following the oxidation step, the crystal is cooled to below 200 K, which is well below the temperature at which desorption of Type 2 H_2 occurs on ZnO (see below). The crystal is then dosed with adsorbate by admitting H_2 into the sample chamber. For exposures greater than 100 L, the sample chamber can be isolated from the ion pump and QMS by closing the isolation valve. During H_2 exposure, the ionization gauge will be turned off to minimize atomic H production. The isolation

FIGURE 1: APPARATUS FOR TPD STUDIES
OF OXIDIZED METAL SURFACES

valve between the sample chamber and the QMS and ion pump also minimizes H atom production from those sources. Following the desired exposure, the H₂ is pumped off and the TPD experiment is begun. The crystal is warmed up at a linear heating rate, and the QMS is used to monitor the amount of H₂ desorbing as a function of temperature. The desorption energy E_d of the H₂ is then given by the Redhead equation:

$$2 \ln T_m - \ln \beta = E_d/RT_m + \ln(E_d/Rv_o) \quad (1)$$

where T_m is the temperature at which the maximum desorption rate is observed, β is the heating rate and v_o is the pre-exponential factor in the desorption rate constant.

While at NBS, the author completed a TPD study of Type I H₂ adsorption on bulk ZnO (10). These results will be useful for comparison with the anticipated results from the ZnO layers formed in the present study. A summary of the bulk ZnO results follows:

Type I H₂ adsorption is dissociative, and takes place on "pair sites" made up of Zn and O atoms. Although the adsorption process is dissociative, H₂ - D₂ exchange does not occur, which indicates that the Zn-O pair sites are spatially discrete.

A set of TPD spectra for H₂ adsorbed at 100 K and various pressures are shown in Figure 2. The main adsorption state has a maximum at ~ 240 K; less populated states are observed with maxima at 270 K and 300 K. There is an activation energy for adsorption, which means that the sticking coefficient for H₂ is quite small (e.g., 10⁻⁴ at 200K). Because of this low sticking coefficient, we are providing for high H₂ dosages in the present experiments by including the isolation valve between the sample chamber and the ion pump.

More detailed studies also completed at NBS suggest that the Zn-O pair sites for Type I adsorption are located on the Zn(10 $\bar{1}$ 0) crystal plane. This surface is corrugated, and is made up of ridges and troughs of Zn-O atom pairs, with the axis of each atom pair being perpendicular to the direction of the ridges. In the present study of the initial stages of oxidation of Zn(0001), we would expect (10 $\bar{1}$ 0) oxide sites to be formed around the perimeter of the epitaxial ZnO(0001) islands. If it turns out that H₂ is indeed preferentially adsorbed at the perimeter of surface ZnO islands, then the amount of H₂ adsorbed will not only provide an independent measurement of the extent of oxidation, but in conjunction with Auger or UPS measurements of oxygen coverage, it will provide a measurement of island size as well.

In the coming months, assembly of the apparatus will be completed, and the measurements of H₂ adsorption as a function of oxygen coverage will be performed. As noted above, plans are also being considered for modification of the sample holder to permit transfer of the crystal to an analysis chamber with AES and UPS capabilities. This would allow direct measurement of the oxygen coverage, for comparison with Unertl's coverage vs. exposure results. In addition, we would be able to search for changes in the oxide film valence electron structure as a function of H₂ coverage.

FIGURE 2: Thermal Desorption of H_2/ZnO
Dosage: Cooled in H_2 to 100 K
Then Evacuated

Summary

We have attempted to demonstrate the importance of the initial oxidation step in determining the outcome of subsequent corrosion processes. We have described an experimental procedure which uses TPD of H_2 to measure the adsorption properties of the initial oxide film on $Zn(0001)^2$ surfaces, as a function of the extent of oxide formation. This procedure is expected to provide chemical information about the initial layer which will complement the information provided by electron spectroscopic techniques, and which will increase our understanding of the interactions between oxide surfaces and corrosive environments.

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LASER SURFACE MODIFICATION

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I. INTRODUCTION

The corrosion resistance of amorphous or glassy metals has been recognized since the early work of the Cal-Tech group [1]. In these experiments the glassy structure was created through the use of rapid cooling from the liquid state. In most cases, the cooling rates have been of the order of $\sim 10^5$ degrees per second. More recently, surface treatment of metals with scanning lasers has been studied [2,3] and the technique has been used to generate different surface phases of materials. In general, the scanning laser was a carbon dioxide laser operating at $10\ \mu$ and melting was not produced. Within the last few years, work to induce surface modification of metals with short pulses (less than 10^{-6} seconds) of radiation has been reported [3]. In this technique, melting and resolidification is induced. The largest fraction of the work has involved semiconductors when the induced melting phase has been used to restore a crystal after destruction by ion implantation. Additional work on recrystallization of polysilicon has also been reported. While the results in semiconductors indicate recrystallization occurs and produces crystals of high quality, a preliminary report of work on resolidified layers in metals suggests a large number of defects occur [4].

In related work [5] the Naval Research Laboratory has used pulsed lasers to melt coatings. The combination of plasma-sprayed coatings with subsequent laser melting has been shown to produce ductile corrosion-resistant coatings on steels.

II. RESULTS

In the Spring of 1980 a program was begun to study the possible modification of the surface character using pulsed lasers. The first set of experiments were performed on iron, using a ruby laser at the University of Minnesota, a glass laser operating at 1.06μ and a frequency-doubled Nd YAG laser operating at $.53 \mu$ at the Air Force Laser Laboratory, Kirtland, NM and a CO_2 laser at the University of Southern California Center for Laser Studies.

The samples irradiated were then examined after returning to campus. The initial results showed that to be effective in modifying the corrosion resistance the heating pulse length had to be less 10^{-7} seconds, and further that as expected surface melting had to occur. These results are suggestive that a glassy phase may have been produced.

The essential aspect of reaching the glassy phase from a liquid appears to be the cooling rate. In the most general case, the cooling rate of the surface liquid layer is set by the thermal conductivity of the media and the thermal gradients that result. For the ideal case of a uniform temperature in a region near the surface with material parameters similar to iron, and assumed to be temperature independent, simple calculations have been carried out. For traditional splat-cooling techniques a liquid thickness of approximately $100\text{--}500 \mu\text{m}$ is normal, while for optically induced melting layers of $.1 \mu$ can be produced. In the simple calculation carried out to date, the complications of the latent heat have been ignored. For a layer whose thickness is

controlled by heating with an optical beam, the cooling rate is significantly higher than with splat cooling. This higher rate of cooling has led several groups (4,6) to study the process. In our analysis, cooling rates of $\sim 10^8$ °/sec were found.

The initial experiments used iron samples, which later showed modified corrosion properties. These samples have shown evidence of surface melting and were irradiated with powers of 10^7 watts/cm and 20×10^{-9} sec pulses. When the molten region was shallow (less than 1 micron) the irradiated regions exhibited lower corrosion than the unirradiated portions of the same material.

In a similar set of experiments [6] have reported that in single-crystal samples, irradiated with short pulses, the recrystallized layers do not achieve the high crystal state characteristic of the experience with semiconductors. This group did not report on the corrosion properties. However, in related experiments on the Cu-Al-Fe system, a statement was made that a metastable phase with no microscopic evidence of precipitation was observed and that corrosion resistance increased.

The work now in progress is to continue the current line of research and extend to study the resolidified layers in iron samples, to determine the power, time, conditions, optimum for inducing corrosion resistance surfaces, to identify the mechanisms inhibiting the corrosion. Overlapping the present and proposed extension will be experiments to introduce impurities into surface layers by melting and diffusion in the liquid phase to produce mixing.

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DEFECT-ENHANCED ELECTRODE DECOMPOSITION

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Corrosion of electrodes is the most serious problem standing in the way of useful electrolytic solar cells. The purpose of this project is to study the role of surface defects in this photoelectrolytic decomposition.

Nature of the Project:

A GaAs surface was to be prepared with a particular defect distribution. Electron diffraction and Auger spectroscopy would be used to characterize the surface before and after electrolytic reaction. As originally envisioned this project had four major components:

1. GROWTH OF PERFECT AND IMPERFECT GAAS SURFACES

GaAs surfaces were to be grown in the molecular beam epitaxy (MBE) facility of the Surface Analysis Center of the University of Minnesota. Although more complicated than elemental semiconductors its growth by MBE is the most highly developed and was the material to be studied by other users of the facility. Further, unlike Si or Ge, it is a direct bandgap material whose absorption is well matched to the solar spectrum and is used in the most efficient liquid junction solar cell so far constructed.¹ MBE is essential to this project since it allows us to prepare a clean undamaged semiconductor surface to which reactivity measurements can be compared.

2. DEFECT CHARACTERIZATION

We proposed to build a low-energy electron diffraction (LEED) apparatus to measure step densities, step directions, and type of step distribution. We also intended to use high-energy electron diffraction (HEED) to examine the surfaces during growth. We did not anticipate its use for defect characterization since it is a more complicated technique and poorly understood.

3. ELECTROLYTIC DECOMPOSITION

We proposed to attach an electrolytic cell to the MBE apparatus so that electrochemical reactions could be performed without exposing the surface to contamination from the atmosphere. The reactivity of different step distributions would be determined from current versus voltage measurements.

4. REEVALUATION OF THE SURFACE

After electrochemical treatment the sample's surface morphology would be reexamined with electron diffraction.

Research Progress:

High quality GaAs films have been obtained, as indicated by HEED measurements during growth and by Auger spectroscopy and mobility measurements afterwards. A LEED apparatus has been constructed and diffraction from a freshly grown GaAs surface observed. The utility of HEED for the study of defects during growth has been explored theoretically and preliminary Debye-Waller measurements performed. Details are given below.

1. The MBE facility is in operation and we are able to grow high-quality, uncontaminated films--the last film grown had a liquid nitrogen mobility of $83,000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, which after only a few months of experience is the second best (versus $\mu = 100,000$) film ever reported. (This particular film was grown by the machine operator F. O. Williamson and mobility measurements made by Prof. G. Y. Robinson's group.)

2. A low-energy electron diffractometer was constructed and is shown in figure 1. The apparatus consists of an electron gun that can focus a beam of 40-1000 eV electrons at a current of 0.5 μ A into a 1 mm spot on the sample. The electrons pass through a drift tube that insures a field-free region and can be electrostatically deflected in either of two independent directions across the sample. The sample can be translated across the beam or tilted in one direction. The diffracted electrons pass through a series of four spherical grids and the pattern is observed on a fluorescent screen. The grids are biased to repel unwanted inelastically scattered electrons; but because of the radial symmetry, do not disturb the trajectories of elastic

Fig. 1. Schematic of the LEED apparatus installed on the MBE system. A moveable Faraday cup will be placed between the spherical grids and sample. A channelplate behind the grids will be used to intensify the diffraction pattern.

electrons. The entire apparatus is surrounded by a cylinder of μ -metal to reduce the effect of the earth's field.

A LEED pattern was observed on a freshly grown GaAs(100) surface. The diffracted beams were observed visually to be $1/2^\circ$ wide, or as sharp as the incident beam. Unfortunately, the pattern is weak relative to the background caused by stray electrons which are not scattered from the sample but which manage to bypass the grids and reach the fluorescent screen. This problem is straightforward to solve by additional shielding of the screen assembly.

There is also a rotary feedthru and extra electrical feedthrus so that we can install a channelplate to enhance the diffraction pattern and a Faraday cup to measure the angular profile of the diffracted beam. (The angular width of the beam is a measure of the long-range order of the surface. The width of the beam as a function of energy is a measure of the step distribution on the surface. The diffuse intensity away from the main beam contains information on the disorder scattering.) A Faraday cup has not yet been installed.

3. An electrochemical cell which attaches to the MBE in which reactions can be performed without exposure of the sample to atmosphere is still being designed. It may, however, become apparent that a more sensible approach is to design an interlock/transfer mechanism to move the sample into the electrochemical system being constructed by Prof. L. Schmidt.

4. A stepped crystal (GaAs (100) cut 5° towards the (110)) has recently arrived from Crystal Specialities. We have yet to examine its diffraction pattern.

5. Analysis of HEED:

The scattering geometry of reflection, high-energy electron diffraction (HEED or RHEED or RED or MEED for medium-energy) is shown in figure 2. Electrons in a well collimated beam impinge

Fig. 2. HEED apparatus schematic. A portion of the incident electron beam misses the sample as shown. The diffracted part gives rise to a pattern of streaks on the phosphor screen.

upon the sample at near-grazing incidence with a kinetic energy of about 10 keV. Because of the low angle of incidence a long, narrow stripe on the sample contributes to the diffraction. Further, because of this low angle the diffraction is quite surface sensitive even though the inelastic mean free path of such highly energetic electrons is roughly 200 Å. The diffraction pattern from a smooth surface is a series of streaks

perpendicular to the sample surface. Two complications arise from this long path length: (1) the electrons can penetrate any roughness of dimensions ~ 200 Å in the surface stripe and give a diffraction pattern characteristic of the bulk material; and (2) multiple scattering will be quite important. Because of the difficulty of preparing smooth surfaces and of analyzing diffracted intensities with large multiple scattering components, this technique has seldom been used to study surfaces. In fact it currently is only used in epitaxial growth, where smooth surfaces are routinely obtained, as a monitor of whether the deposited layer is ordered.

Using the analysis of Park² I have estimated the limiting dimensions of the region on the surface over which HEED can detect long-range order--the so called coherence length or transfer width--and find it to be of the order of 2000 Å (compared to 200 Å for LEED.) The extent of long-range order in the sample is contained in the length of the streaks in the diffraction pattern and in the number of streaks that appear. If it is true that HEED can detect correlations over much larger distances than LEED then it would be exceedingly useful for studies of island growth in the formation of overlayers and for understanding the apparent repulsion of defects on surfaces.³

To check our understanding of the diffraction we have made measurements of the temperature dependence of the beams. This is also important in determining streak dimensions since different parts of the same streak are expected to have different temperature dependencies. The intensity should vary according to

$I = I_0 e^{-s^2 \langle u_{11}^2 \rangle}$ where I is the diffracted intensity,

$\vec{s} = \vec{k}_{\text{final}} - \vec{k}_{\text{initial}}$ is the momentum transfer with $k = 2\pi/\lambda$, and $\langle u_{11}^2 \rangle$ is the atomic mean square vibrational amplitude parallel to $\vec{s}$. Along the streak $\vec{s}$ changes, and hence so does the Debye-Waller factor $s^2 \langle u_{11}^2 \rangle$. Figure 3

Fig. 3. Debye-Waller plot of the intensity of a bulk diffraction beam versus temperature. The momentum transfer was chosen to be as large as possible to maximize the slope for convenient measurement. For HEED beams with lower s the decrease is unobservable.

shows the temperature dependence of a bulk diffraction beam (originating from diffraction from a rough surface) with large $\vec{s}$. Beams with incident and final $\vec{k}$ closer to grazing (small $\vec{s}$) had no measurable temperature dependence. In order to extract the length of a streak from high-temperature data, this temperature dependence must be known.

Summary:

Film growth and electron diffraction studies to prepare and characterize perfect and imperfect GaAs surfaces are well underway. Electrochemical studies have not yet begun.

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III.. Embrittlement Research

<u>Principal Investigators</u>	<u>Effort Involved, Months/ Calendar Year</u>	
	<u>Current Funding Period</u>	<u>'81-'82 Fiscal Year</u>
W. W. Gerberich	1	1
C. L. Jensen	1	1
J. P. Wallace	1	1
S. T. Wellinghoff	1/4	1

The corrosion resistance and the absence of hydride formation even at large hydrogen contents make β -Ti-30 Mo alloy a good candidate material for use in canisters for the disposal of nuclear wastes. This provides one impetus for the ongoing investigation of the cyclic fatigue properties and of the phase transformations of this alloy. Eddy-current monitoring has been successful in detecting carbide formation, but not in monitoring solidification after welding and work in this area is being discontinued. The x-ray diffraction and IR-reflection spectroscopy of hydrogen-charged iron give promise of yielding important information on the development of internal stresses by absorbed hydrogen. The work on spinodally decomposed, two-phase polymer system represents a wholly new approach towards combatting the pervasive environmental crazing problem of high polymers, and the large variety of techniques being applied is also unique.

"A basic study of environmental effects on cyclic fatigue in BCC Alloy systems"

W. W. Gerberich

Department of Chemical Engineering and Materials Science

1.0 Introduction

The aim of this program is a relatively broad theoretical and practical understanding of those variables which are important to corrosion fatigue processes in BCC alloys (1-4). At the same time, we are defining in a fairly

narrow sense a few experimental systems which we believe to be both important and resolveable. This limits the experimental base to a few Fe and Ti (BCC) systems evaluated via fracture mechanics techniques. The external variables are temperatures ranging from 72 to 363 K, external hydrogen fugacity or internal concentration and applied stress intensity range, K. The work is proceeding in four phases:

- Phase I -- Single crystal studies of Fe and Ti base systems.
- Phase II -- Polycrystalline studies of Fe and Ti base systems.
- Phase III -- Polycrystalline studies of Fe and Ti base systems in H_2S .
- Phase IV -- Theoretical studies of time dependent embrittlement.

This program involves four Ph.D. students, Cathy Asgian, Khlefa Esaklul, Kumar Jatavallabuhla and Andrew Wright, under the direction of Professor Gerberich. One of these, Kumar Jatavallabuhla, will graduate this year. As two of these students are relatively new, Cathy Asgian and Andrew Wright, they are just initiating their research programs. A visiting Professor or Post-Doctoral Fellow will be interfacing with these students before June, 1981.

1.1 Phase I -- Single Crystal Studies of Fe and Ti base systems by Cathy Asgian and William W. Gerberich

This phase is being headed by a first year graduate student (Masters Degree, Civil Engineering) who is just getting the literature review completed as preparation to the ordering of single crystals. Some preliminary use of polycrystalline samples for defining mechanical testing techniques will be accomplished by the end of this first year. The compositions to be ordered are Fe, Fe-0.1 Ti, Fe-1Ni, Fe-4Ni, Fe-1Si, Fe-4Si and Ti-30Mo. Depending on the relative cost of these and the availability of Ti-30 Mo, only several of these may be ordered this year.

The extra Fe-0.1Ti system is important to ascertain any effect of Ti (C, N) on the cyclic cleavage process. It is known that these particles have little or no effect on the flow properties⁽¹⁾ but are the nucleating event,⁽²⁾ in conjunction with twinning or slip band formation, for brittle fracture. At much lower stress intensities near threshold these may not be a favored nucleation site. In addition, the particles are about 4 μm in diameter with an average spacing of about 24 μm . This makes a chance encounter of a cyclic cleavage plane with one of these relatively infrequent unless the particle nucleates cyclic cleavage in advance of the macroscopic crack front. Previous results^(3, 4) for polycrystalline samples at ΔK ranging from about 12 to 30 $\text{MPa}\cdot\text{m}^{1/2}$ did not indicate this to be a large problem. Where particles were found, they were generally associated with other fracture modes such as ductile or intergranular or there was not a pronounced deviation in the cyclic cleavage striation spacing.

1.2 Phase II -- Polycrystalline Studies of Fe and Ti-base systems

by Khlefa Esaklul, Kumar Jatavallabuhla and William W. Gerberich

Considerable progress in this phase has consisted of obtaining polycrystalline materials, running preliminary cathodic and gas-phase charging experiments and determining the effect of internal hydrogen on the fatigue behavior of Ti-30Mo.

1.2.1 Materials

The composition of the Fe-binary alloys[†] are listed in Table 1. The first eight compositions are 50 pound (23 kg) laboratory heats prepared by vacuum-induction melting. All alloys except the HSLA steel were then mechanically processed by forging to 44 mm by 140 mm slabs at 1230^o C and then hot rolling at 1200^o C to about 12 mm thick. The HSLA steel is seen to have a similar composition except that the carbon level is about three times as

[†]We would like to acknowledge Robert Ault of the Republic Steel Corporation Research Center, Independence, Ohio, who provided these special alloy heats.

large and the Nb plus Ti is about four times smaller. The result is that the yield strength in the as-received, 10 μm grain size ferritic structure is nearly double the other Fe-binary alloys⁽¹⁾ with grain sizes of 25-50 μm . Although the yield strength is substantially higher, the ultimate strength of this HSLA steel is about the same as the medium grained Fe-1%Ni and Fe-1%Si alloys of a previous study.⁽¹⁾

Table 1: Compositions (wt. %) of Fe-base alloys

<u>Heat No.</u>	<u>C</u>	<u>Mn</u>	<u>Si</u>	<u>P</u>	<u>S</u>	<u>Ni</u>	<u>Ti</u>	<u>Al</u>	<u>Cr</u>	<u>Nb</u>
Y920	.007	.01	.01	.005	.005	--	.08	.02	--	--
Y921	.02	.01	.01	.005	.005	1.08	.10	.02	--	--
Y922	.02	.01	.01	.005	.005	2.50	.09	.02	--	--
Y923	.013	.01	.01	.005	.005	4.05	.10	.021	--	--
Y924	.011	.01	.45	.005	.005	--	.09	.021	--	--
Y925	.009	.01	1.20	.005	.005	--	.10	.017	--	--
Y926	.02	.01	1.90	.005	.005	--	.12	.018	--	--
Y927	.008	--	--	--	--	--	--	.017	--	--
HSLA	0.07	.51	.03	<.005	.005	.01	<.005	--	.01	.014

1.2.2 Cathodic and gas-phase charging

As was indicated in the last progress report, considerable success has been achieved in gas-phase charging of Ti-30Mo, a BCC alloy. Mechanical properties associated with hydrogen levels from 20 to 1200 ppm (wt.) are discussed in section 1.2.3. Similar success with gas-phase charging of HSLA steel has not been achieved to date. Charging for long times in 1 atm. of hydrogen at 500° C did produce variations in the range of 0.5 to 1.5 ppm hydrogen. Further exploration of gas-phase charging near 700° C will be completed by the end of this reporting period.

Because of the accuracy needed to evaluate such hydrogen levels, we have utilized a hot-silicone oil extraction technique as described by Nippes.⁽⁵⁾ This consists of a high temperature stability silicone oil saturated with hydrogen, receiving a charged sample in an inverted glass funnel with a calibrated burette and a stand of hydrogen gas at the top. The hydrogen evolution from the sample extracted at 100° C can be accurately measured. This technique has proven particularly successful for measuring diffusable hydrogen levels as produced by cathodic charging. The change in volume in the burette, Δv , may be converted to ppm extracted hydrogen by

$$H_{\text{ppm (wt)}} = \Delta v \left(\frac{273}{T} \right) \left(\frac{P}{760} \right) \left(\frac{90}{W} \right) \quad (1)$$

where W is the weight of the sample in grams and T, P are temperature and pressure in kelvin and mm of mercury.

Trial runs using cathodic charging have been accomplished using a sulphuric acid electrolyte (several percent H_2SO_4) with a poison. It was of interest to compare this to previous results from charging 4340 steel, where Barth and Steigerwald had found,⁽⁶⁾

$$\text{ppm}_{(\text{wt.})} = 4.7 + 2.7 \log I \quad (2)$$

with I the current density in amps/m (SI units). According to this, one might expect about 10.9 ppm hydrogen if the sample were allowed to come to equilibrium. However, taking a typical trapped diffusivity of $2 \times 10^{-11} \text{ m}^2/\text{sec}$ and six hours, the largest distance hydrogen could diffuse in is about 0.0013 m. Considering the hydrogen concentration profile and the volume of material being charged, one approximately calculates a value of 1.9 ppm. This is reasonably close to the 1.6 ppm (wt.) hydrogen extracted at 100°C according to Eq. (1) from this 20.5 gram sample.

1.2.3 Hydrogen-fatigue interactions in Ti-30Mo

Considerable progress in the study of Ti-30Mo in the vacuum annealed condition (92 μm grain size) has been made. The impetus for this work comes from two sources. In a complementary fatigue study,⁽⁷⁾ we have found evidence of cyclic cleavage in the temperature range of 120-300K. This is in the absence of environmental or internal hydrogen effects. Typical fractography in Figs. 1 (a) - 1 (b) indicate a standard type of cyclic cleavage pattern in Fig. 1 (a) for 123 K data and a much less defined cyclic cleavage process in Fig. 1 (b) for a 123 K and 189 K test. The steps along the secondary river lines in Fig. 1 (a) have been identified previously with cyclic fatigue markings wherein each step represents a cycle of growth.^(3, 4) Although we do not presently understand the difference in origin of these two cyclic processes, it is significant that the average microscopic growth rate from SEM measurements is of the same order as those observed macroscopically from crack-opening displacement gage measurements. If statistical sampling shows this to be the general case for both vacuum annealed and high-hydrogen

Fig. 1(a): Vacuum Annealed Ti-30Mo; Test Temp. 123 K

$$\Delta K = 26 \text{ MPa-m}^{\frac{1}{2}}; \left. \frac{da}{dN} \right|_{\text{micro}}^{\text{SEM}} \approx 7.5 \times 10^{-7} \text{ m/cycle}; \left. \frac{da}{dN} \right|_{\text{macro}}^{\text{gage}} = 4 \times 10^{-7} \text{ m/cycle}$$

Fig. 1(b): Vacuum Annealed Ti-30Mo; Test Temp. 123 K

$$\Delta K = 19.6 \text{ MPa-m}^{\frac{1}{2}}; \left. \frac{da}{dN} \right|_{\text{micro}}^{\text{SEM}} \approx 3.7 \times 10^{-7} \text{ m/cycle}; \left. \frac{da}{dN} \right|_{\text{macro}}^{\text{gage}} = 1.43 \times 10^{-7} \text{ m/cycle}$$

conditions, this will be an excellent model material for evaluating a basic corrosion-fatigue process.

The second reason for the promising potential of this material system evolved out of a hydrogen embrittlement study of slow crack growth.⁽⁸⁾ In that work, details of how internal hydrogen, as provided by cathodic charging, affect plastic flow and fracture properties are presented. For example, it was shown that as little as 200 ppm hydrogen addition raised the ductile-brittle transition temperature (DBTT) by 100°C and lowered the fracture stress by 240 MPa. The cleavage fracture stress, as determined by standard notch-bend techniques, was given by⁽⁸⁾

$$\sigma_f^* = \sigma_{fo}^* - \alpha_o' C_H \quad \text{Electrolytically charged} \quad (3)$$

where σ_{fo}^* was 1926 MPa and α_o' was 1.18 MPa·ppm⁻¹. Because these coarse-grained samples exhibited cleavage due to hydrogen effects, it appeared as though the evaluation of hydrogen on cyclic cleavage would be possible. As a first step, it was essential to determine the effect of gas-phase charging on properties since the large specimens involved in compact-tension fatigue testing made cathodic charging tedious and slow. Therefore, the cleavage fracture stress measurements were repeated in the present study using hydrogen as provided by gas-phase charging at 800°C. The general yield loads as determined from tensile tests and the fracture loads as determined from slow notch bend testing are indicated in Fig. 2. The crossover points give the cleavage fracture stress knowing the plastic constraint factor for the specimen configuration. The astonishing finding was that the response to internal hydrogen was now completely different.

A similar 200 ppm hydrogen addition now only raised the ductile-brittle transition by 33°C. From the four hydrogen levels evaluated in Fig. 2, the cleavage fracture stress is now given by

$$\sigma_f^* = \sigma_{fo}^* - \alpha_o C_H^{1/2} \quad \text{Gas Phase Charged} \quad (4)$$

where σ_{fo}^* is 1960 MPa and α_o is 10 MPa - ppm^{-1/2}. This is a good fit to the data since regressing on $C_H^{1/2}$ gives a correlation coefficient of -0.97. It is significant that both the magnitude of the effect and the functional dependence on hydrogen content are now substantially different.

Fig. 2: Effect of test temperature on notch-bend fracture, P_F , and general yield, P_{GY} , loads as a function of hydrogen content.

Further evaluation of gas-phase charged material has involved fatigue crack growth studies. Preliminary data at 190 K are shown in Fig. 3. Here, it is seen that the crack growth rates are relatively independent of hydrogen content at $\Delta K > 10 \text{ MPa-m}^{1/2}$ but that at lower values approaching threshold, growth rate increased with increasing hydrogen levels. It is seen that the threshold value is about 50 percent higher for the lowest hydrogen content compared to 1200 ppm (wt.). Similar data near threshold have been determined at other test temperatures, the threshold results being reported in Fig. 4. For all levels of hydrogen, the threshold remained the same at 340 K. For 22 ppm material, a maximum in the fatigue threshold is found at 190 K. A similar trend was found for the higher hydrogen levels except the maxima are shifted to higher temperatures. For 250 ppm, a transition in the threshold is observed between 190 and 230 K. At 1200 ppm, the transition occurs between 300 and 340 K. Since these data exhibit a shift in fracture resistance with increasing hydrogen content, it is important to compare these to the ductile-brittle transition shifts observed in Fig. 2. This comparison is shown in Table 3.

Table 3: Ductile-brittle and fatigue transitions as affected by hydrogen

C_H gas phase ppm(wt.)	T_{DBTT} K	$T_{\Delta K_{th}}$ K	σ_f^* MPa	$\Delta K_{th}(123K)$ $\text{MPa-m}^{1/2}$	$K_{th}(123K)$ $\text{MPa-m}^{1/2}$
22	252	160^{+10}	1890	5.5	62
250	285	210^{+10}	1835	4.7	53
640	354	—	1735	—	
1200	375	320^{+10}	1585	3.9	42

First, it is seen that as T_{DBTT} increases by 123 K, the fatigue transition increases by about 160 K. These are sufficiently close to suspect that the same mechanism is involved.

Fig. 3: Fatigue crack growth rate as a function of ΔK at 190 K for Ti-30 Mo containing various hydrogen levels.

Fig. 4: Threshold fatigue stress intensity as a function of temperature for Ti-30 Mo containing various hydrogen levels.

1.3 Phase III - Polycrystalline studies of Fe and Ti base systems in H_2S
by Cathy Asgian, Andrew Wright and William W. Gerberich

Outside of having the materials available, little progress has been made in Phase III since this awaits the findings of Phase I and II as well as the experimental facilities. With regards to the later, considerable progress has been made in acquiring two hydraulic, feed-back control mechanical test facilities, one for UHV testing and one for environmental testing. These should be available within 90 days.

1.4 Phase IV - Theoretical Studies of Time-dependent Embrittlement
by Andrew Wright and William W. Gerberich

Radical differences in incubation time data⁽¹⁰⁾ for initiation of hydrogen embrittlement in 4340 steel suggests that external and internal hydrogen must be treated very differently. This poses some interesting questions. Are concentration gradient induced lattice stresses sufficient to override any considerations of the applied stress tensor influence on both hydrogen concentration and the fracture stress? Is it realistic to run slow strain-rate tests to establish threshold stress intensities if incubation time is independent of the local maximum stress? Such questions are prompted by the following analysis.

Compact-tension samples with varying notch root radii of 0.21, 0.95 and 2.6 mm were machined such that any crack nucleation would be in a plane perpendicular to the rolling direction. The 4340 samples were austenitised for two hours at 843°C, oil quenched and tempered at 500°C for one hour. This resulted in a tempered martensite with a yield strength of 1310 Mpa. Half the samples were electrolytically charged at 21 amps/m², cadmium plated and baked at 150°C so that the total uniform hydrogen concentration was 3 ppm(wt.). The other half of the samples were tested with 1 ml of H_2SO_4 per

1000 ml of distilled water (pH 1.84) added to the notch. Both sets of samples were rapidly loaded to $54.9 \text{ MPa-m}^{\frac{1}{2}}$ and the time to the first acoustic emission was recorded as crack nucleation. After about 10 to 20 acoustic events the samples were unloaded and metallographic sectioning was conducted to locate the source of initiation. In the case of the internal hydrogen, the nucleation site was proportional to the elastic-plastic boundary as roughly calculated from the intersection of the elastic and plastic stress tensors.⁽¹¹⁾ Although this did not include strain hardening, it should be a good indication of the maximum stress tensor since the strain-hardening exponent was extremely small, $n=0.023$. The result shown in Fig. 5 is seen to represent the nucleation site very well. On the other hand, the nucleation site for hydrogen introduced externally from a corrosion reaction was independent of the notch root radius.

Since it is generally accepted that aqueous stress-corrosion, external hydrogen gas, and internal hydrogen from pre-charged specimens are all the same embrittlement mechanism, it was somewhat surprising to see such a different response of the crack nucleation site for external versus internal hydrogen. This difference was further emphasized by the differences in incubation times to crack nucleation shown in Fig. 6 whereas the incubation time increased linearly with increased notch root radii for the internal hydrogen case, it was independent of notch root radii for the stress-corrosion case. This does not necessarily mean that the local failure mechanism is different since detailed fractography suggests they are the same. It does suggest that the equations governing the time-dependency of the process and the location of microcracking events in relationship to the macroscopic crack front are dependent on the hydrogen source. Understanding both of these are crucial to any corrosion fatigue model where hydrogen is a potential embrittling agent.

INTERNAL HYDROGEN

Figure 5.

Figure 6.

As will be discussed in the renewal proposal, a number of other models could be invoked to explain such results. Since corrosion fatigue in steam-power generation applications, sour gas oil well drilling, or nuclear waste disposal will encounter multiple hydrogen sources, it is extremely important to resolve what mechanism and boundary-value solution approach is correct for each situation.

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HYDROGEN TRAPPING IN TITANIUM

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Introduction

The proposed program of research for the investigation of hydrogen trapping by interstitial elements, substitutional elements and second-phase particles was based on the assumption that Ti-30w/oMo would provide a stable matrix in which hydrogen trapping could be studied. As the trapping investigation proceeded, it soon became clear that Ti-30Mo-H alloys are seldom single phase. The original β phase was found to decompose into Mo-rich and Mo-lean regions at elevated temperatures. At low temperatures the α'' or ω phase was often found. Hydrogen was found to have an effect on each of these transformations.

Early in the research program we were faced with the choice of finding a new host in which we could study hydrogen trapping or to study the phase transformations which had observed in Ti-30Mo. We chose to base our research on the latter. This decision was based on several factors. The β -phase decomposition appears to occur at a temperature where the equilibrium phase diagram predicts that β should be stable. It certainly would be very important to determine if the Ti-Mo phase diagram is in error. Secondly, α'' and ω are known to greatly affect the mechanical properties of the sample in which they are found. Most notably, α'' and ω decrease ductility. Because these transformations are diffusionless, they can occur whenever the sample is cooled sufficiently. Thus, to prevent unexpected failure of titanium structures, it is necessary to develop a general understanding of how hydrogen content and thermal treatment can change the microstructure of β -phase titanium alloys. Finally, β -phase Ti alloys appear to be a very promising candidate for nuclear waste storage canisters. The β -alloys should have the corrosion resistance exhibited by α alloys without the problem of hydride formation experienced by the α alloys. However, it is very important to understand the effect of hydrogen, thermal treatment and state of stress on the formation of metastable phases which can form in β alloys if these alloys are to be considered for canister materials.

The following progress report is based on our observations concerning phase transformations in Ti-30 Mo.

Techniques

X-ray Diffraction

A Siemens D-500 diffractometer was used to measure interplanar spacings of the β matrix and to detect the presence of additional phases. The primary phases which have been identified in this investigation are the original β matrix containing 30w/oMo, two β phases which are richer in Mo and leaner in Mo than the original matrix, the orthorhombic α'' phase and the hexagonal athermal ω phase. The α'' and ω phases form athermally and hence their symmetry is not greatly different than that of the original β matrix. This presents some difficulty for positive phase identification by x-ray diffraction since many peaks may be buried in the peaks from the original β

matrix. (1-3) To illustrate this problem, Figure 1 schematically represents the angular position and qualitative intensity and width of diffraction peaks from the various phases observed in this study.

Electrical resistance

Measurements of electrical resistance as a function of temperature have been used to determine the temperature at which phase transformations occur. Figure 2 shows typical resistance-temperature data. We have taken the temperature at which a change in slope of the resistance-temperature plot occurs to be the temperature at which a new phase begins to precipitate. There is some evidence, however, that there may not be a definite precipitation temperature for the athermal phases. (4) The hysteresis between the heating and cooling data in Figure 1 indicates that the phase transformation is irreversible in a thermodynamic sense. Resistance data has been generally taken during continuous cooling or heating at a rate near 1 K/min. Several experiments have been done where isothermal conditions have been maintained for approximately 15 minutes before the resistance was measured. These experiments did not produce results significantly different from the continuous cooling measurements.

Results

High Temperature Transformations

It has been found that during vacuum annealing or during gas-phase hydrogen charging that Ti-30Mo may decompose into a Mo-rich and a Mo-lean β phase. Evidence for this transformation comes from x-ray diffraction experiments which show splitting of the β -matrix diffraction peaks. This is illustrated in Figure 3. As was discussed in connection with Figure 1, some ambiguity can exist in the identification of phases in Ti alloys. The splitting of the peaks shown in Figure 3 is taken as evidence of the formation of Mo-rich and Mo-lean zones rather than of ω -phase formation for two reasons. Similar decomposition has been observed in other β -Ti alloys. (5,6) Secondly, no new diffraction lines were found other than those formed by the splitting of the β -matrix reflections. The β -phase decomposition in other Ti alloys is thought to take the form of small solute-lean coherent particles surrounded by the zones which are rich in β stabilizers. (7) This should lead to a rather broad diffraction peak from the rich zone. However, the diffraction peaks corresponding to the Mo-rich zones (high-angle peak) are relatively sharp in Figure 3. We do not understand this at the present time.

The (211) interplanar spacing, d_{211} , is shown in Figure 4 as a function of hydrogen concentration for those gas-phase-charged specimens whose β peaks remained unsplit and for electrolytically charged samples. The slope of the data in Figure 4 represents only the expansion of the β matrix resulting from hydrogen addition and does not reflect changes caused by β decomposition. At this point, it should be mentioned that we have chosen to plot interplanar spacing rather than lattice parameter as it is impossible to locate enough diffraction peaks in back reflection such that a valid error analysis can be made to obtain one true lattice parameter. Hydrogen broadens the peaks sufficiently to make it impossible to locate the angular position of maximum intensity in back reflection.

Although hydrogen is not a necessary condition for β decomposition, hydrogen appears to influence the formation of Mo-rich and Mo-lean zones. Figures 5, 6 and 7 show the spacings of the (211), (220) and (310) planes as a function of hydrogen content. The addition of Mo to β Ti results in a decrease in lattice parameter⁽⁸⁾ and thus the Mo-lean β phase has slightly greater interplanar spacings than the matrix or the Mo-rich β phase. Figures 5 and 7 show that the interplanar spacing of the Mo-lean phase increases much more rapidly than that of the matrix or Mo-rich phase as the hydrogen content is increased. Figure 6 does not show this behavior. We do not know if the hydrogen effect is most pronounced along the [211] and [310] directions or if experimental error in the determination of d220 hides the hydrogen effect in Figure 6.

The procedure represented by the flow chart in Figure 8 was used to calculate the volume fraction of the Mo-lean and matrix phases as well as the Mo content of the Mo-lean phase. These results are shown as a function of hydrogen concentration in Figures 9 and 10. The method used to calculate the data in Figures 9 and 10 relies on intensity data, data from Figure 4 and the lattice parameter data of Rao and Houska.⁽⁸⁾ The data in Figures 5, 6 and 7. Thus, the unexpected decrease in Mo content of the Mo-lean phase as the hydrogen content is increased to 0.08 H/M does support the data in Figures 5 and 7 which show the interplanar spacing of the Mo-lean phase expanding more rapidly than that of the matrix or Mo-rich phase as the hydrogen content is increased to 0.08H/M.

An estimate of the coherency stress at the interface between the Mo-rich and Mo-lean regions indicates that at 0.08 H/M this stress may be near the yield strength of the material.⁽⁹⁾ This stress may be sufficient to cause incoherency or perhaps stress-assisted nucleation of α ." At this concentration, a rapid decrease in diffracted line width occurs indicating stress relief. Also, the α " phase is first detected near this hydrogen concentration, H/M = 0.11. When the interfacial stress is relieved, hydrogen appears to expand the Mo-lean, matrix and Mo-rich phases at the same rate as shown by the data for H/M > 0.10 in Figures 5 and 7. This proposed explanation for the observed data in Figures 5 through 10 is tentative at this time. We hope to find solutions to several questions which are unanswered. For example, we do not know how to control the amount of β decomposition with or without hydrogen. Also, we do not understand why hydrogen should affect the amount and composition of the Mo-lean phase to the extent that is shown in Figures 9 and 10. We are hoping to answer these questions by using transmission electron microscopy to directly observe the β decomposition and coherency strains and to find any possible orientation relationship between the Mo-lean and matrix phase.

Low Temperature Transformations

As was previously discussed, electrical resistance measurements have been used to detect the temperature at which athermal ω or α " precipitation occurs. In Figure 11, this transformation temperature is plotted as a function of hydrogen concentration for gas-phase-charged and electrolytically charged specimens. The precipitation temperature increases with increasing hydrogen content for both electrolytic and gas-phase charging. However, at any given hydrogen concentration the transformation temperature for the gas-

phase-charged specimens is greater than for the electrolytically charged samples. We interpret the data in Figure 11 to indicate that the formation of ω or α'' can occur at a higher temperature in alloys which contain Mo-lean zones. The electrolytically charged samples have not undergone β decomposition and hence must be cooled to a lower temperature to form α'' or ω . We have made a short study of Ti-Mo alloys containing less than 30% Mo. Our primary interest was to obtain an x-ray diffraction pattern for the athermal ω phase. During these experiments we learned that ω will form at temperatures above 300K when the Mo content is decreased below ~ 20% Mo. As the data in Figure 10 indicate the Mo content of the Mo-lean phase is decreased sufficiently to allow the precipitation of ω at much higher temperatures than would be observed in an alloy which has not decomposed to Mo-rich and Mo-lean zones.

At the present time, we have been unable to make positive x-ray identification of the phase which precipitates at low temperatures. We have not been able to produce this phase in sufficient volume fraction to allow us to distinguish between α'' and ω . We have ruled out the possibility of hydride phase precipitation on the basis that the incomplete x-ray diffraction pattern is not characteristic of TiH_x and also the general shape of the electrical resistance-temperature data is quite different than is observed in classic hydride-forming systems. (10)

We hope to learn to control the β decomposition such that a very large volume fraction of Mo-lean β can be produced. Upon cooling, these samples should form a sufficient volume fraction of the low-temperature phase to permit positive identification by x-ray diffraction or electron microscopy.

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Figure 1: Qualitative representation of the angular position, intensity and width of diffraction peaks corresponding to the β , α'' and ω phases.

Figure 2: Electrical resistance as a function of temperature for a gas phase charged specimen containing H/M. Arrow indicate heating and cooling data.

Figure 3: Diffraction peaks for a gas phase charged sample showing decomposition to Mo-rich and Mo-lean zones.

Figure 4: (211) interplanar spacing, d_{211} , as a function of hydrogen content for gas phase charged samples with unsplit β peaks and for electrolytically charged samples.

Figure 5: (211) interplanar spacing for the Mo-lean, matrix and Mo-rich β phases as a function of hydrogen content.

Figure 6: (220) interplanar spacing for the Mo-lean, matrix, and Mo-rich β phases as a function of hydrogen content.

Figure 7: (310) interplanar spacing for the Mo-lean, matrix, and Mo-rich β phases as a function of hydrogen content.

Figure 8

Figure 9: Volume fraction of Mo-lean and matrix β phases as a function of hydrogen content.

Figure 10: Mo content of the Mo-lean phase as a function of hydrogen content.

Figure 11: Precipitation temperature for α'' or ω as a function of hydrogen content for gas phase charging or electrolytic charging.

HYDROGEN IN STRUCTURAL WELDMENTS

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Summary of Work Performed

In this program we have completed a restricted set of experiments of those which were proposed because of experimental difficulties encountered in the welding evaluation and the x-ray measurements of lattice plane spacing. The eddy-current monitoring of welding was restricted to a continuous-cooling study of 304 and 316 stainless steel. This work is described in detail in the Addendum as a draft of a paper that will be submitted to the Journal of Non-destructive Evaluation. It will be presented as a Master's thesis by Edgar T. Armacanqui. It is reported in that document that it is possible to detect sensitization in real time by separating the eddy-current contribution of the precipitating Cr_{23}C_6 and the ferromagnetic transformation of the delta ferrite. This work will be completed within the month, when the chemistries of the samples are measured, along with the temperature dependence of the electrical resistivity of Cr_{23}C_6 . These data, along with the eddy-current equipment calibration, will allow a quantitative discussion to be written for the amounts of Cr_{23}C_6 and delta ferrite at specific times in particular samples. This will end the work on eddy-current monitoring of weldments as they are being fabricated.

The remainder of the work completed this year involves the detection of the presence of hydrogen in iron-based alloys (Fe & Fe 2%W) using x-ray diffraction measurement of lattice-plane spacing. The in situ detection of hydrogen in an iron-based material is difficult because of the small quantity of soluble hydrogen which can be introduced into the metal. It was found previously that pure iron specimens charged with hydrogen exhibit lattice parameter changes

and stresses close to the yield stress of the metal with little evidence of plastic deformation.¹ We have had these experiments verified by C. Briant of the GE Research Laboratory. In order to evaluate this technique, one must determine what is being monitored: A) the macroscopic strain of dissolved hydrogen in a large, inhomogeneously charged specimen, B) microvoid formation and growth or C) hydrogen forming a separate phase, such as an ordering on the interstitial lattice. The characteristics which one can look for in a typical measurement of x-ray-detected lattice plane spacing are: 1) the rate at which lattice plane spacings are altered, 2) the distribution of plane spacing changes in a statistical set of grains in a polycrystalline sample, 3) the sign of the lattice parameter change, 4) the line broadening, 5) the residual strain after discharging and 6) the effect of temperature on the plane spacing in charged specimens. Small changes in x-ray peak position (.01 degrees of arc and less) require well-defined and narrow Bragg reflections. To develop the technique we used high-purity polycrystalline iron from two sources. These were annealed in 1 atmosphere of H₂ at 800 C for 4 hours. A typical 110-Bragg reflection is shown in Figure I. To hydrogen-charge the specimens we constructed a fluid jet charging cell shown in Figure II. Charging the specimen from the rear was necessary to remove bubbles by the flow of electrolyte. The critical dimension is the position of the front surface with respect to the calibrated diffraction plane of the diffractometer. The positioning is accomplished by pressing the specimen against the front surface ring with an o-ring in compression. Thus, despite any dimensional changes perpendicular to the surface of the specimen, the position of the diffracting surface will remain stationary.

Electrolytic charging from the rear at .1 amps/cm² produced the shifts detected in Figure IIIa and front-surface charging on a different specimen produced the response in Figure IIIb. There was a delay of approximately 40 minutes before any change in the lattice parameter was detected in either

FIGURE I

FIGURE II HYDROGEN CHARGING CELL

HYDROGEN INDUCED ELASTIC STRAIN VS. CHARGING TIME

NORMAL STRAIN MEASURED FROM A (110) PEAK

FIGURE III

3/8" diameter by 1/8" thick disks of Fe and Fe 2%W. The front-surface-charged specimen shows that an equivalent compressive stress on the sampled grain of 40KSI would be needed to produce the measured strain. Also, not indicated in the Figures is that the peak intensity of the 110-Bragg peak decreased to 20% of its initial value at the maximum change in plane spacing. When the charging was halted, the peak intensity returned within seconds as the specimen discharged. With no measureable changes in line broadening, this intensity variation is indicative of grain rotation. Such effects have been detected earlier by Bastien and his coworkers.² Something else that must be considered is that the specimens in Figure III are in different states of residual stress. This is indicative of plastic damage somewhere in the specimen, or of residual hydrogen which gives rise to these strains. The major difficulty in these charging studies is that less than 5% of the observations on charging produced measureable lattice plane shifts. We verified that those charged specimens which showed no detectable charges did indeed contain significant amounts of hydrogen. In order to determine whether the effects are localized to a small area fraction or are dependent on other variables such as grain size, observation of charging specimens will be made in an interference microscope which will detect changes in relief to .1 micrometers. Surface holograms at 1X have been insufficient as yet to detect any changes in surface strains. Mr. Y. L. Chang is carrying out this portion of the work; it will be continued to establish the nature of these x-ray measurements.

The final portion of our studies is being taken by Mr. E. T. Armacanqui starting January 1, 1981. This work is to evaluate the utility of IR-reflection spectroscopy to monitor the presence of hydrogen in iron and steel. The x-ray measurements are limited to single and polycrystalline materials free of large internal strains so that small plane spacing changes can be measured out.

The IR measurements³ should be able to measure the effects of hydrogen on iron-based alloys with high internal strains which arise from martensite and dense dislocation substructure. We have assembled the necessary equipment for this work. Also under construction is a hydrogen analysis unit for iron and steel specimens to make rapid quantitative effusion measurements. When these two measurement techniques for the in site study of hydrogen in iron and steel are available we will then apply them to ferritic weldments.

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Stress Corrosion Resistance of Polymer Glasses Containing a Rubber-Reinforced Ductile Phase

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I. CRAZING IN MICROCRYSTALLINE POLYSTYRENE FILMS

Introduction

Recent work has shown that the gelation and simultaneous crystallization of both IPS and 2,6 dimethyl polyphenylene oxide, 2MPP0, in a wide variety of solvents is a consequence of spinodal decomposition at an upper critical solution temperature. Since the fracture resistance of the polychlorostyrene-2MPP0 blends we are making depends in part upon spinodal decomposition to form an interconnected ductile 2MPP0 phase (see last year's proposal), we hoped that we could model this phase microstructure with glassy IPS and 2MPP0 films cast from a gelled solution for the purpose of practicing the requisite microbeam electron diffraction on the crazed material of the simpler systems.

We decided to start with oriented IPS films, deformed both parallel and perpendicular to the orientation direction in the expectation of determining whether the small microcrystallites would maintain their integrity within the craze, consequently giving rise to a possible mechanism to retard solvent plasticization in the craze during exposure to environmental stress crazing.

Results

Figure 1 shows gel glass, formed after evaporation of solvent from an oriented gel of IPS in decalin, that has been deformed 50% at 100%/min. One immediately sees, especially in phase contrast at slight defocus, that lamellae-like structures $80\text{\AA}$ thick and $200\text{--}1000\text{\AA}$ long are oriented with the long axis perpendicular to the deformation direction. Some voids form between the lamellae but are usually isolated. A few crazes form but do not grow very large; in some cases lamellae are included within the craze, but in most cases, they

disappear. We attempted to obtain microbeam diffraction from within these crazes but were initially unsuccessful because of the small craze size.

Wide-area diffraction patterns, both from undeformed and deformed films (Figure 2) reveals a highly oriented fiber pattern with only the ordinary hexagonal crystal form present.

Figure 3 shows the craze morphology from a film deformed 50% at 100%/min perpendicular to the orientation direction. Crazing is quite profuse and gold decoration prior to deformation shows that a rather large deformation is present within the craze. In this sample, microbeam (ca. 100Å) diffraction was obtained both inside (Figure 4a) and outside a craze (Figure 4b). The position of the beam was checked by observing the location of the contamination spot that developed after a few minutes of STEM beam exposure. Although in most cases there is no change in either the orientation or d-spacing upon crossing the craze boundary, Figure 4b shows a craze pattern with two orientations, undoubtedly reflecting the complicated microstructural orientations that can occur during craze growth. The important thing to notice, however, is that craze voiding occurs relatively easily between crystalline bundles, thus enabling a significant number of microcrystals to survive when drawn into the highly deformed craze.

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Figure 1. Highly oriented IPS microcrystalline film deformed in the orientation direction. A craze has developed and is growing perpendicular to the orientation direction.

130,000X

Figure 2 Electron diffraction pattern obtained from a film similar to that in Figure 1. Line connecting (220) reflections perpendicular to the orientation direction.

Figure 3 Part of a long craze formed by deforming the highly oriented IPS microcrystalline film perpendicular to the orientation direction. The film was gold decorated prior to deformation to define the local strain

Figure 4 a) Microdiffraction pattern obtained from outside the craze in a film similar to that in Figure 3 except no gold decoration.
b) Same as a except inside a craze.

II. HIGH STRAIN DYNAMIC MECHANICAL BEHAVIOR OF POLYMER BLENDS

Introduction

One of the goals of polymer rheology has been to predict the ultimate properties of polymer glasses, such as yielding and fracture, from low-strain viscoelastic measurements. Backbone motions are required for delocalized yielding while relaxations involving side chain motions have little or no effect on ductility^{1,2}. Recently, through their design of a forced-torsion oscillator that operates in the non-linear, stress-activated regime, Davis and Macosko,³ have been able to rapidly determine the contribution of backbone motion to yield, by measurement of non-linear loss modulus, G_3'' , and storage modulus, G_3' . Both are related to the apparent loss modulus, G_a'' , and, G_a' , the apparent storage modulus by

$$G_a' = G_1' + \gamma^2 G_3'$$

$$G_a'' = G_1'' + \gamma^2 G_3''$$

where G_1' and G_1'' are storage and loss modulus for shear strain, γ , equal to zero. Peaks in G_3'' and G_1'' over the same temperature range were thought to identify this temperature span as one containing backbone motions, as opposed to side chain motions. Low-strain dynamic mechanical measurements demonstrate that about 15% polystyrene, PS, a brittle polymer, can completely suppress the backbone β relaxation of a ductile polymer 2, 6 dimethyl polyphenylene oxide, 2MPP0, at -50°C . However, surprisingly, ductility was maintained even in 50/50 compatible blends of these two polymers for temperatures above -50°C .

In this work we attempted to see if the 2MPP0 backbone motions, frozen out at low stresses by blending with PS, can be activated by higher stresses. The ultimate objective of this work is to sufficiently identify the relaxation processes in the more well studied one-phase PS-2MPP0 system so that experience will be available to study the similar, complicated polychlorostyrene-2MPP0

system. It is of special importance to be able to determine whether sub- T_g backbone motions can be adequately determined in blends by high-strain dynamic mechanical measurements.

Results

Figure 1 shows as an example the plot of apparent loss and storage modulus vs. strain percent squared for 2MPP0, the data having been obtained on a computerized Rheometrics dynamic spectrometer. As a first approximation, the first 5-7 data points (below 1% = γ) were fit to least-squares line (solid line in Figure 1). G_3'' was calculated from this line's slope and is plotted vs. temperature for all the blends in Figure 2. A shallow peak is observed for 2MPP0 and all blends at about -40°C ; APS shows a constantly rising G_3'' . The presence of a shallow peak at -40°C is expected since the β relaxation is suspected of being a main-chain motion responsible for ductility. What is surprising is the absolute magnitude of G_3'' , which after an initial decrease with 15% APS increases continuously up to 50 APS. At present we do not yet know how to interpret this effect. But it should be noted that Davis and Macosko² showed that polymethylmethacrylate's G_3'' remained level at -2.3×10^{11} dyn/cm² (at 25°C) through its β relaxation while polycarbonate's G_3'' increased to a maximum of 9.0×10^{11} (at -110°C) and fell to 3.7×10^{10} (at 30°C) as its β peak was traversed indicating that the level of G_3'' is not as important as the mere presence of a peak in determining ductility since PMMA is brittle at room temperature while PC is ductile.

In the high-temperature region above 25°C 50/50 and 85/15 show rapid rises in G_3'' ; however, no peaks are observed. Blends 70/30 and 2MPP0 are relatively flat in this temperature range. Unfortunately, we are unable to offer an explanation at this time. If an enhanced intermediate relaxation induced by blending² occurs here, why doesn't 85/15 show a similar increase in G_3'' ?

The G_3' plots (Figure 3) are relatively featureless except for a general increase at the low-temperature tail of the T_g , unlike PMMA and PC which show G_3' , G_3'' , and G_1'' peaks at the same temperature.²

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1a

1b

1c

1d

Figure 1a,b,c,d: The observed storage & loss moduli of PPO sample as a function of $(\gamma\%)^2$ at 1 Hz, -60°C (fig a,b) & 0°C (figc,d)

Figure 2

Figure 3

III. EFFECT OF SMALL ORGANIC MOLECULES ON CRAZE GROWTH

Introduction

The goal of this project is to characterize craze growth and equilibrium in the presence of various organic environments. Experimental data are being collected by monitoring craze growth and eventual equilibrium conditions. These results are then used in models developed from fracture mechanics to determine the parameters which control craze initiation, growth and equilibrium.

Craze growth is being monitored in compact tension specimens which are immersed in a temperature-controlled bath of organic solvent. After inserting a small razor blade precrack, each specimen is subjected to a predetermined stress intensity and the growing craze length recorded at regular intervals with a traveling microscope. Eventually, the craze stops growing and an equilibrium situation is established.

A test program has been developed where a matrix of six stress intensities by four test temperatures will be investigated for each organic crazing agent. An analysis of this information will yield information on the parameters controlling craze initiation, growth and equilibrium. The following sections will briefly discuss these parameters and, if possible, their determination from the experimental work which has been completed at this time.

Effects of Solubility Parameter and Hydrogen Bonding Parameter on Craze Growth

Craze growth tests of the type discussed above are being run in a series of low-molecular-weight primary alcohols and a series of linear alkanes. Each of these solvents exhibits a different solubility parameter, S , and hydrogen bonding parameter as shown in Table 1.

Table 1.

Solvent/Polymer	3-d Solubility Parameter, $\delta(\text{cal/cm}^3)^{1/2}$ [1,2]	Hydrogen Bonding Parameter [3,4]
PMMA	9.88	—
Methanol	14.28	19.8
Ethanol	12.92	17.7
N-pentanol	10.61	11.0
N-pentane	7.05	0
n-hexane	7.27	0
n-octane	7.54	0

Such a test program will indicate whether the proximity of the solvents solubility parameter to that of the polymer will have any effect on craze growth and equilibrium. As this difference $|S_{\text{solvent}} - S_{\text{polymer}}|$ decreases, the degree of plasticization and rate of relaxation will increase. It follows that if the solubility parameters were the only factor governing craze growth, the solvent with the smallest difference $|S_{\text{solvent}} - S_{\text{polymer}}|$ should produce the greatest craze growth rate. Experimental results shown in Figure 1, indicate exactly the opposite behavior. Therefore, it is probable that the process controlling craze growth is either transport of the solvent through the porous craze material or into the uncavitated process zone at the tip of the craze.

Williams et. al. [5-10] have modeled fluid flow through the porous craze material using D'Arcy's law. They have concluded that for low-stress-intensity situations such as we are dealing with, craze growth is controlled by solvent transport through the length of the craze. These conclusions are quite different from those which we have obtained from preliminary experimental results [11]. Here, it was shown that for crazes approaching a quasi-equilibrium condition, methanol transport into the plastic zone at the tip of

the craze is the process governing craze growth. It must be noted, however, that these calculations were made on the assumption that methanol transport in PMMA exhibits classical Fickian diffusion. This assumption is not correct, over the range of temperatures used in this test program the methanol-PMMA combination is known to exhibit anomalous or Case-II transport characteristics [12]. Although the occurrence of this type of transport is well documented for many solvent-polymer combinations, there is still some question on the exact shape of the concentration profile [13]. Furthermore, without knowing the cause, attempts to theoretically model this type of transport have little justification. We have therefore initiated a research program aimed specifically at characterizing methanol transport in PMMA. The goals and techniques of this program will be discussed in the research proposal.

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Figure 1

IV. Projects Not Otherwise Grouped

<u>Principal Investigators</u>	<u>Effort, Months/Calendar Year</u>	
	<u>Current Funding</u>	<u>'81-82 Fiscal Year</u>
J. W. Halley	1	1
E. A. Fletcher	0	$\frac{1}{2}$

The quantum-mechanical investigation of the corrosion reactions has succeeded in obtaining the energy-distance functional for ionized hydrogen approaching the excess electron in the metal, approximated by the jellium model. This is the first time that exchange, correlation and coulomb interactions, and the zero-point energy of the electron gas have been considered in such a calculation. The solar furnace construction, pushed forward by much dedication and input of moneys from other sources envisions studies of refractory materials at high temperatures in a variety of relevant environments. Such data are notable for their scarcity, and will be important for the development of future energy technologies. The Addendum presents one example of the energy relevance of such studies (J. E. Noring et al).

Theoretical Studies of the Microscopic Theory of Corrosion

J. W. Halley
Department of Physics

1. Introduction.

In this project we are studying the basic chemical reactions involved in corrosion using modern techniques of many-body theory to treat the quantum mechanics of the electronic processes in corrosion correctly. To do this, we need at the beginning to use somewhat oversimplified models which will be refined to be more realistic as the program progresses. At present, we are considering models of corrosion of a metal by an acid in which the metal is modeled as semi-infinite "jellium" (an electron gas and a uniform positive background) and the part^{1*} of the corrosion reaction $M + 2H^+ \rightleftharpoons M^{2+} + H_2$

*
References are in section 4 of this report.

which is represented by the partial reaction $H^+ + e^- \rightleftharpoons H$

in the presence of the metal surface is being studied. As described in our original proposal, we had two preliminary objectives in this work. First, we wished to calculate the energy of the jellium + proton system in its ground and excited (ionized) state as a function of the distance z of the proton from the surface of the metal. The ground state was expected (for z large away from the jellium) to describe the state H in the reaction

was to describe the state $H^+ + e^-$. Second, we wished to develop a phenomenology which would permit us to find characteristics of the corrosion process, given the values of the ground and excited state energies. Below, we describe progress on these two objectives. Briefly we have succeeded in obtaining preliminary results for the excited state energies representing the $H^+ + e^-$ state using the density-functional methods which include exchange, correlation and coulomb interactions as well as quantum mechanical zero-point energy of the electron gas for the first time. This work is described in the 2nd part of this report. We have also made some progress in the phenomenological development, particularly with regard to the model called the diffusion-limited case in our original proposal. This progress is described in the third part of the present report.

The project has succeeded in engaging the efforts of two excellent people in addition to the principal investigator. David Dahl, an assistant professor at St. Olaf college is consulting on this theoretical work one and one-half days per week. Dr. Dahl was trained at Stanford and the University of California at San Diego in many body theory of the electron gas and is extremely well qualified for this work. A curriculum vita of Dr. Dahl is attached in section 5 of this report. Bradford Johnson is working as undergraduate assistant for this project. He is among our most outstanding

undergraduate physics majors at Minnesota and has been making extremely effective and devoted efforts in the computer aspects of the microscopic calculations in this program. The principal investigator visited the University of Michigan physics department in Ann Arbor in September 1980 for a week in order to consult with H. Shore, L. Sander and J. Rose of that department about the application of density functional methods. H. Shore also visited Minnesota in October to give a talk and to further consult on this work. We are very grateful to these physicists for their generosity with their time and for the permission of them and their colleague, E. Zaremba, to use a computer program which has proved indispensable in the progress reported in part 2 of this report.

The principal investigator and Dr. Dahl plan to attend the "March" (solid state) meeting of the American Physical Society in Phoenix in Spring 1981 to present the results described in this progress report. A copy of the abstract which will be published in the American Physical Society Bulletin is attached as section 6 of this report. The principal investigator is also planning to attend a Gordon conference on electro-chemistry in January in order to discuss this work.

2. Microscopic Electronic Level Calculations.

As described in the introduction the problem was to calculate the ground and excited states of the proton-jellium system as a function of distance z from the metal-fluid interface, using the density functional variational technique first described by Hohenberg and Kohn.² A similar calculation had been done for the ground state only by Ying, Smith and Kohn.³ We discovered that a simpler approximation technique, due to Norskov and Lang⁴ was available which reproduced the results of Ying, Smith and Kohn³ to within a fraction of an ev. We have used this technique called an

effective medium approximation, together with a solution to the homogeneous jellium plus proton problem to generate new results for the ionized state (H^+ + metal) as well as to check the results for Norskov and Lang for the ground state. Very briefly, the procedure is as follows. One approximates the energy $E_{g,e}(z)$ of the ground or excited state when the proton is a distance z from the jellium surface as $E_{g,e}^{hom}(n(z))$ where $n(z)$ is the electron density at a distance z from a semi-infinite jellium surface (as calculated, for example by Lang and Kohn⁵) and where $E_{g,e}^{hom}(n)$ is the energy of the ground or excited state of a proton in infinite (not semi-infinite) jellium. As noted by Norskov and Lang,⁴ this approximation works well for the ground state and we were encouraged by our consultants to try it for the excited state. To do so, we needed to compute the ground and excited energies of the proton in infinite jellium using density-functional methods. For this purpose we used a modification of a particular form of the density variational technique which was originally due to Kohn and Sham⁶ and which had been applied by E. Zaremba et al.⁷ to the problem of a proton in infinite jellium. The Kohn-Sham method is as follows: One can show that the original Hohenberg-Kohn method summarized in the first proposal on this work can be reformulated as a eigenvalue problem

$$\left(\frac{-\hbar^2}{2m} \nabla^2 + V(n) \right) \psi_\lambda(r) = \epsilon_\lambda \psi_\lambda(r) \quad (2-1)$$

$$n(r) = \sum_{\lambda, occ} |\psi_\lambda(r)|^2 \quad (2-2)$$

where

$$V(n) = \phi(r) + \frac{\delta E_{xc}(r)}{\delta n} \quad (2-3)$$

and $\phi(r)$ is the electrostatic potential due to the electron density as well as to the protonic charge and the uniform positive background of the jellium.

$E_{xc}(n(r))$ is the exchange and correlation energy which is a functional of the electron density $n(r)$. Equations (2-1) - (2-3) must be solved self-consistently. The energy of the entire system in the variational state (expressed as the change ΔE in energy due to the introduction of the proton) is then

$$\Delta E = \Delta T_s + \Delta E_{es} + \Delta E_{xc} \quad (2-4)$$

where

$$\begin{aligned} \Delta T_s = & 2 \sum_{b=1}^B \epsilon_b + Z \epsilon_F \\ & - \frac{Z}{\pi} \sum_l (2l+1) \int_{\mu-\epsilon_F}^{\mu} d\epsilon \delta_l(\epsilon) \end{aligned} \quad (2-5)$$

$$- 4\pi \int_0^{\infty} dr \, r^2 n(r) V(r)$$

$$\Delta E_{es} = 4\pi \int_0^{\infty} dr \, r \, \Delta n(r) [Q(r) - Z] \quad (2-6)$$

$$\Delta E_{xc} = 4\pi \int_0^{\infty} dr \, r^2 [n(r) \epsilon_{xc}(n(r)) - \bar{n} \epsilon_{xc}(\bar{n})] \quad (2-7)$$

are the changes in kinetic, electrostatic and exchange and correlation energies due to the introduction of the proton. Here $\Delta n(r) = n(r) - \bar{n}$ where $\bar{n}$ is the jellium electron density

$$Q(r) = 4\pi \int_0^r dr' \, r'^2 n(r')$$

Figure 1: Preliminary results on the energy of the ground (E_0) excited (E_+) states of a proton near the surface of a jellium surface as a function of the distance z of the proton from the jellium surface. We have taken $r_s = 2$ in this calculation. See the text for further details.

and $\epsilon_{xc}(n)$ is an approximate form of the exchange and correlation energy per particle due to Hedin and Lundquist. $\delta_e(\epsilon)$ are the phase shifts due to scattering of a single electron in the potential $V(n)$ and ϵ_b are the energies of bound states of electrons in this potential.

E. Zaremba et al. supplied us with a program which solved equations (2-1) - (2-3) inclusive self-consistently and computed ΔE for the ground state. For jellium with $r_s \geq 2$ one finds 1 (or more) bound states in the self-consistent potential. We first mastered the details of this program for the ground state and got it running on the U of M computer (a matter of several months). We then modified it to compute an approximate excited state as follows: We solved equations (2-1) - (2-3) again, but computed $\chi(\epsilon)$ (equation (2-2)) with the bound state omitted and 2 more electrons in the continuum. The results are shown in Figure 1. The ground state is essentially identical to that found by Norskov and Lang. (This is encouraging because these authors solved the infinite jellium problem by a different technique.) The new, excited state results has essentially all of the qualitative features conjectured to obtain in the original proposal: The energy of the excited state falls as the proton gets closer to the metal and is bound closer to the metal than the ground state. We believe that the results described in Figure 1 represent a major step forward in our original program and open the way to rapid progress toward more realistic models as described in the accompanying new proposal.

3. Phenomenology.

A corrosion situation such as iron in sulfuric acid⁸ always involves at least two reactions (oxidation and reduction) which occur in a preferential

direction even in the absence of an applied current.⁹ For example,

resulting in the corrosion of iron with production of hydrogen gas. With no applied current ($i_a = i_{ca}$) the rates must balance each other at a value of i_c (the corrosion current) and a potential E_c (the corrosion potential), measured w.r.t. the standard Hydrogen Electrode. Typical values are $E_c = -515$ mV and $i_c = 5 \times 10^{-4}$ amps/cm² for iron in .52N H₂SO₄.

Application of an applied current $i_{ap} = i_{ca} - i_a$ can alter this dynamic equilibrium and force it in either direction, with a corresponding change in the cell potential $\epsilon = E_c - E_i$ (E_i = potential with current flowing).

Experimentally we observe

$$i_a = i_c e^{\epsilon/\beta_a} \quad ; \quad i_{ca} = i_c e^{-\epsilon/\beta_{ca}}$$

with characteristic slopes $\beta_a \approx 60$ mV, $\beta_{ca} \approx 105$ mV.

Near the corrosion potential ($\epsilon \approx 0$) the applied current becomes linear in the overvoltage ϵ with slope related to β_a, β_{ca} and i_c .¹ The purpose of our work is to theoretically predict i_c, E_c, β_a and β_{ca} from the two models discussed in the initial proposal: the diffusion-limited model and the rate-limited model.

A. Diffusion Limited Model.

Here we describe the model for the partial reaction $\text{H}^+ + e^- \rightleftharpoons \text{H}$

To determine the corrosion potential and current we will also need to make

a similar model for the second, anodic reaction. Possible procedures for treating this second reaction are discussed in the new proposal. The starting point for both the diffusion-limited and rate-limited models are then energy curves $E_+(z)$ (bare proton plus metal) and $E_0(z)$ (H atom plus metal) whose calculation was described in the previous section. In the diffusion-limited model we assume that the drift rate of protons toward the metal under the action of the force $-dE_+/dz$ is slow enough and the transition rate to the state $E_0(z)$ is fast enough so that the transition occurs immediately at the cross-over point as sketched below.

The rate-limited model described in section 3.B makes the opposite assumption that the transition rate is slow and the drift rate is fast so that the proton drifts into the minimum in the $E_+(z)$ curve. In

both models we need to consider the coulombic interactions between the ions in order to make a complete theory and will need to include an account of the negative ions in the acid (SO_4^{-2} for sulphuric acid).

Usually these negative ions play no role in the chemistry and we can assume that there are no currents associated with them. For simplicity we will suppose these negative ions to have one unit of electronic charge. (The generalization to arbitrary charge is trivial). The currents can be written as

$$j_+ = -\mu_+ \left[k_B T \frac{dn_+}{dz} + e \frac{d\phi}{dz} n_+ + \frac{dE_+}{dz} n_+ \right]$$

$$j_- = -\mu_- \left[k_B T \frac{dn_-}{dz} - e \frac{d\phi}{dz} n_- + \frac{dE_-}{dz} n_- \right]$$

(3-1)

Mass conservation requires a counter current of H atoms equal and opposite to j_+ but this plays no role in this model (while, in contrast, the curve $E_-(z)$ does play a key role in the rate-limited model.) In equations (3-1), ϕ is the electrostatic potential due to the + and - ion interactions with Poisson equation

$$\frac{d^2}{dz^2} \phi = \frac{-4\pi e(n_+ - n_-)}{\epsilon} \quad (3-2)$$

We are taking $e > 0$. $E_-(z)$ the potential of the negative ions in the presence of the metal surface. Its calculation requires a separate quantum chemical calculation which we will defer. Here we set $E_-(z) = 0$, for purposes of illustrating the basic features of the model and will consider $E_-(z)$ in the new proposal. As discussed, we must set $j_- = 0$. The second of equations (3-1) then has solution

$$n_-(z) = \text{constant} \times e^{e\phi(z)/k_B T} \quad (3-3)$$

Writing $j_+ = j$ we have from the first of equations (3-1)

$$\frac{dn_+}{dz} + \frac{n_+}{k_B T} \left(\frac{dE_+}{dz} + e \frac{d\phi}{dz} \right) + \frac{j}{\mu_+ k_B T} = 0$$

Defining the variable $S(z)$ through the equation $n_+(z) = S(z) e^{-1/k_B T (E_+ + e\phi)}$ this equation can be formally solved (using the fact that j is independent of z in steady state) to give

$$n_+(z) = \left[\frac{j}{\mu_+ k_B T} \int_z^L e^{\frac{1}{k_B T} (E_+(z') + e\phi(z'))} dz' + n_+(L) \right] \times e^{-\frac{1}{k_B T} (E_+(z) + e\phi(z))} \quad (3-4)$$

Here we have chosen the zero of energy so that $E_+(L) + e\phi(L) = 0$.

Then (3-3) becomes

$$n_+(z) = n_+(L) e^{(E_+(L) + e\phi(z))/k_B T} \quad (3-5)$$

Equations (3-2), (3-4), and (3-5) can be written as a closed, one dimensional integro-differential equation for $\phi(z)$ which can be integrated numerically.

The procedure is to take L large enough so that

$$\left. \frac{dn_+}{dz} \right|_L \approx 0, \quad \left. \frac{dE_+}{dz} \right|_L \approx 0$$

Then

$$\left. \frac{d\phi}{dz} \right|_L = \frac{-j k_B T}{e n_+(L) \mu_+}$$

$n_+(L)$ is given by the acid concentration and $\phi(L) = -E_+(L)/e$. Thus the initial conditions for a numerical integration starting at L are known. Choosing a j , we integrate from $z = L$ to $z = 0$ thus obtaining the potential drop $V = e[\phi(L) - \phi(0)] + E_+(L) - E_+(0)$ across the interface. Repeating, we obtain j versus V for the values of $k_B T$, acid concentration and metallic density (as reflected in $E_+(z)$) chosen. Thus we can obtain the polarization curve for the partial reaction $H^+ + e^- \rightleftharpoons H$ (as quoted by Steigerwald¹ for example). The form of (3-4) makes it plausible that j will have the observed exponential form in V and the slope β_a of $\ln j$ versus V can be determined. Proposed applications and extensions of this theory are discussed in the new proposal.

B. Rate-Limited Model.

This model assumes the proton H^+ moves in rapidly enough to reach the minimum of $E_+(z)$. Oscillations of frequency ω_+ (typically 100 mV) take place in the "well" with a barrier B separating the proton from the more stable atomic configuration $E_0(z)$. Escape is a thermally activated process with time constant (rate)

$$\frac{1}{\tau_+} = \omega_+ e^{-B/k_B T}$$

with B determined by the intersection of the E_+ , E_0 curves. The imposition of an external potential (current) will again alter the barrier height $B(V)$ allowing us to find β_a and explain the observed $1/T$ temperature dependence.

The curves calculated as described in section 2 will, when obtained with sufficient resolution, permit a calculation of both β and ω_+ and thus permit a comparison of the rate limited and diffusion limited models with experiment. Proposed applications and further development of the rate-limited model are discussed in the new proposal. In this model, the equations (3-2), and (3-5) still hold but equation (3-4) acquires a new term $= \tau_+ j \delta(z)$. The resulting set can again be solved for ϕ and $n_+(z)$ as a function of V , T , v_s etc..

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STUDIES OF HIGH TEMPERATURE SOLAR PROCESSES

E. A. Fletcher
Department of Mechanical Engineering

Introduction

For several years we have been doing basic research in thermochemical solar energy storage. Except for a few exploratory experiments on materials, the studies have all been analytical. We are interested in high temperatures because high temperature is an essential characteristic of high efficiency thermal processes.

As we conducted our studies, we became aware that very little is known about the chemistry, in the range 2-3000 K, of many systems which will one day be of great interest. A few examples are:

1. Chemical attack on refractory oxides and nitrides in the presence of high intensity solar radiation and fluid flow.
2. Chemical attack on refractory metals such as iridium, tungsten, molybdenum, and tantalum under similar conditions.
3. Evaporation and erosion rates of these substances in various chemical environments.
4. The behavior of laminated, plated, and composite materials made from these substances and of structures in which relatively unreactive but structurally weak ceramic materials are supported by underlying structures of more reactive but strong refractory metals.
5. Permeabilities of nonporous materials to various gases at high temperatures.

It may be anticipated that, as energy technology advances, useful processes using highly concentrated solar flux into what are essentially black-body receiver cavities will emerge, because such cavities can provide higher temperatures, cleanly, than can be achieved by ordinary combustion processes.

Accordingly, we proposed that a small, versatile solar furnace be constructed here. Our broad objectives are to:

1. Assemble a small group about the nucleus which we now have to design and construct a small solar furnace, guided by the experience which has been obtained at the French Solar Furnace at Odeillo-Font Remeu.
2. Assemble a greater-than-critical sized group of individuals who will, hopefully, become a nucleus for a growing research and teaching effort at the University of Minnesota in this field.
3. Conduct small-scale and exploratory experiments of the nature of those which have been described above.
4. Conduct systematic research which is aimed at solving many different kinds of problems of the high-temperature thermochemical storage of solar energy and thermochemical processing.

Our objective during the period ending June 30, 1981, is to design and get well along in the construction of the furnace. In subsequent years we shall assemble and construct the apparatus and conduct the experimental work which is suggested by our analytical and theoretical studies.

WHAT WE'VE DONE SO FAR

The solar furnace, located on the roof of Akerman Hall, is now under-

going construction. We have had a great deal of help from student volunteers, and in the form of contributions from individuals, industrial organizations, and the Mechanical Engineering Department. The furnace will have the following attributes:

1. The concentrator diameter will be 4.2 meters.
2. It will be capable of year-round use.
3. It will have a stationary point of focus.
4. It will have an actual concentration ratio of 5-9000, and thus will be capable of achieving temperatures in excess of 3000K.

The facility consists of five major components:

1. The heliostat
2. The concentrator
3. The concentrator cavity housing
4. The tracking system
5. The receiver cavity and test stand,

A brief description of each of the components and our progress to date follows:

The Heliostat

The heliostat is a large array of flat mirrors capable of tracking the sun on two axes. Located north of the concentrator, its function is to reflect the direct solar flux into the stationary concentrator mirror array and thus maintain a fixed point of focus. The heliostat under construction will contain a planar array of 20 - 1.07 X 1.52 meter mirrors. Its total area is thus 32.5 m^2 . Thus far, the heliostat frame, including the main support base, azimuth and elevation bearings and

drive systems, the mirror support rack, and mirror support backings have been completed. The only major task that remains is the attachment and alignment of the mirrors and mirror backing assemblies to the main frame. The recently-completed elevation drive system and a tiedown system remain to be installed. We have been helped in staying within our budget limitation by Professor Don Olson, UMD Physics Department, who located for us an old military radar, some of whose components we have modified and adapted to our needs. The heliostat is now 85% complete.

The Concentrator

The concentrator will consist of 312 spherically curved mirrors, hexagonal in plan form, arranged into a close-packed hexagonal spherical surface. We have purchased the mirrors. The major support structure has been completed. The devices which will be used to support and adjust the individual mirrors have been designed and the necessary components obtained.

Fabrication of one of the components of the support structure is being furnished to us free of charge by the Bermo Company, a local manufacturer whose owner is intrigued by the idea. The remaining tasks are to assemble the mirror support components and to focus the mirrors. Focusing the mirrors will be time consuming, but we estimate that the concentrator is 60% complete.

Concentrator and Cavity Housing

The concentrator and cavity housing is a 226 m^3 structure which encloses the concentrator and provides protection from the elements. In addition, it provides a comfortable work space and makes year-round operation possible. The basic enclosure has, for the most part, been completed.

We made use of standard building construction techniques, including adequate insulation. The structure and its anchorage have been approved by an independent engineering firm, Meyer, Borgman and Johnson, Inc. We are in the process of installing the electrical service.

Fluorescent lighting for the structure was donated by the Lynes Electric Company. This component is 90% completed.

Tracking System

The tracking system senses the position of the sun and directs the heliostat. The motors and their controls have been acquired and adapted to the heliostat drive systems. The sun sensor and the associated controls have been made, have undergone preliminary testing, and all that remains to be done is their installation.

Many of the electrical components were scrounged from the military radar pedestal. This component is 90% complete.

Receiver Cavity and Test Stand

The receiver cavity will sit at the focus of the concentrator atop a test stand. As of now, construction of this component has not yet begun. Our first receiver will be made from graphite. It will be used to calibrate our radiation pyrometer. We are looking into obtaining a used milling machine for use as a test stand. The cavity is now in the planning stage. It is thus 0% completed.

Construction of the high-temperature solar facility has proceeded on schedule. We anticipate that we will not request additional funding for this fiscal year in spite of the fact that our grant was somewhat

below our initial request. We have used some personal funds to get us through rough spots. We have received a substantial amount of help from our department. Professor Springer has been especially helpful. Moreover, we have sought and received contributions from private concerns to the project of time and materials. We have also used some funds from a related project, as well as funds which the principal investigator received from the assignment of a patent to the University, to support three paid graduate students and two paid undergraduates who worked on the project. We also substituted less expensive flat mirrors for those we originally intended using, with, we hope, very little deterioration of the optical quality of the device.

V. Instrumentation Projects

<u>Principal Investigators</u>	<u>Effort, Months/Calendar Year</u>	
	<u>Current Funding</u>	<u>'81-'82 Fiscal Year</u>
L. D. Schmidt	0	-
J. F. Evans	0	-
R. M. Hexter	1	1

The Automatic Scanning Ellipsometer

R. M. Hexter
Department of Chemistry

Significant progress in the construction of a wavelength-scanning ellipsometer has been impeded by the extended absence due to surgery of the Senior Scientist assigned to this project. Fortunately, prior to his departure he was able to spend several months studying ellipsometer design and he then formulated a provisional list of components. The process of obtaining a definitive medical determination that our Senior Scientist could not continue with the work and the task of identifying a replacement have been difficult, and we have lost about a half-year of progress. We believe, however, that we have a highly qualified replacement, and we fully expect to achieve our original design goal.

The Scanning Auger Microprobe

R. M. Hexter and L. D. Schmidt

This instrument, Physical Electronics Model 595, was purchased cooperatively with the NSF-funded Regional Instrumentation Facility in Surface Analysis. The Corrosion Research Center specifically has purchased the following portions, which are identified as CRC property:

Cylindrical mirror assembly

Scanning system control

Electron gun control

TV monitor

The scanning Auger microprobe is slated for use at present by eight investigators on Corrosion Center projects. In addition, the other facilities of the Regional Instrumentation Facility are being heavily used in our projects.

A MULTIPLE USER ULTRAHIGH VACUUM SYSTEM FOR CORROSION STUDIES

AN INSTRUMENTATION PROJECT

L. D. SCHMIDT

The following items have been purchased for this system using Corrosion Center funds:

Stainless steel bell jar with approximately 12 ports on two levels for multiple technique capabilities.

Mass spectrometer

High precision sample manipulator

Auger electron spectrometer (partial)

The following components will be available from other funds:

Ultraviolet photoelectron spectrometer

Low energy electron diffraction

The entire system should be operational in early 1981. It is also planned to construct transfer capabilities so that specimens may be transferred between this chamber and the X-ray photoelectron spectrometer for XPS and sputter depth profile analysis. Use of this facility, described in the proposal for 1980-81, are summarized below:

Analytical Instrument Development

The system will provide vacuum and analytical capabilities to prepare and maintain well-defined surfaces to use in developing new techniques for surface analysis. These include ellipsometry, energy electron energy loss

spectrometry (EELS), and optical properties of surfaces. Ellipsometry is being constructed by R. M. Hexter, and this instrument will provide the vacuum conditions for well-defined surface experiments. L. D. Schmidt and W. T. Peria are independently designing and building EELS instruments for vibrational spectroscopy of adsorbates, and these will be housed in this system when they are operational. There are many optical techniques (infrared reflectance, fluorescence, laser excitation of surfaces) which are promising candidates to study engineering surfaces, and this instrument can be used to develop techniques for using these methods.

Single Crystal Analysis

The Surface Analysis Center (SAC) does not have capabilities to include several techniques specifically designed for characterization of single crystal surfaces because 1) the three vacuum systems being acquired in SAC cannot accommodate them, 2) single crystal experiments require dedicated usage, and 3) the general analysis systems will probably not have adequate vacuum for single crystal experiments. The techniques needed are low energy electron diffraction (LEED) and ultraviolet photoelectron spectroscopy (UPS). Both require perfect, clean single crystal surfaces, but both give unique information about geometric and electronic structures of surfaces.

Characterization of Corrosion Surfaces

The AES and QMS capabilities of this instrument provide techniques for initial studies of corrosion surfaces prepared in environmental chambers described in other projects. This system would allow us to do dedicated experiments which would "tie up" analytical instruments for periods longer than is compatible with the three SAC systems.

All of the electrochemistry equipment ordered on budget 0630-5522-06/-02 has been delivered. The following list details equipment received:

- A. 2 Princeton Applied Research model 173 Potentiostat/Galvanostats.
- B. 1 model 376 Log Current Convertor Plug-in for model 173.
- C. 1 model 179 Coulometer Plug-in for model 173.
- D. 1 model 175 Waveform Programmer.
- E. 2 X-Y Recorders (11" x 17" format).
- F. 2 Tabletop Relay Racks for mounting above hardware.
- G. Cabling for interconnection of various pieces of equipment.
- H. 1 Princeton Applied Research Corrosion Cell Kit.

The general concept here is to establish two work stations, each consisting of a waveform programmer, a potentiostat/galvanostat and X-Y recorder. One of these units will be heavily used in our work (CRC budget: 0630-5520-). It is anticipated that the other will either circulate among groups requiring its use, or remain in a given laboratory where it can be accessed by all investigators requiring use of the second work station.

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TECHNOLOGY TRANSFER FUNCTION

Although there has been insufficient time in the half-year of the current funding period to embark fully upon activities in the technology transfer area, we do have two which are in the active planning stage:

1. Conference on the Corrosion of Microelectronic Components and Assembles - Planned for June 1981 as a pedagogical/informational/state of the art symposium for engineering personnel in the electronics industry. It will explore the corrosion problems associated with electronics both in manufacture and service. A working committee composed of interested technical people in the Twin Cities area has been established and has met several times.
2. Seminars and workshop on cathodic protection - Negotiations have taken place with John H. Morgan, well-known expert on cathodic protection, and author of a book on that subject, to have him present at the University a series of seminars for industrial people who wish to learn more about cathodic protection. These seminars would be videotaped for distribution by the National Association of Corrosion Engineers. Mr. Morgan would also organize a nationally advertised workshop.

ADMINISTRATION OF THE CORROSION RESEARCH CENTER

The administrative apparatus of the Center is almost at steady state. A formal statement of policy and of operation has been drawn up and adopted by vote of the Management Committee of the Center.

An External Advisory Panel has been established and almost fully staffed. The purpose of this body is to advise the Director on policy, operations and research problems. The people who have agreed to serve, each for three-year terms, are:

J. C. Danko, Electric Power Research Institute

B. R. T. Frost, Argonne National Laboratory

E. W. Haycock, Shell Development Co.

J. Kruger, National Bureau of Standards

In addition, Dr. Z. A. Foroulis, Esso Research and Engineering, has also been asked, but has not yet replied.

A Peer Review Panel has been set up to review research proposals and to counsel the Director as to their scientific quality and technical relevance. Grateful thanks are due to the panelists for their recent labor in connection with the proposals for the '81-'82 fiscal year. Selection of proposals was aided by an ad hoc group of experts from outside the University, chosen by the Director for their knowledge of the subject.