

# **Microfabrication Methods Applied to the Development of Rigorously Defined Occluded Region Corrosion Samples**

## **Project Summary**

We propose to use microfabrication methods developed for microelectromechanical systems (MEMS) manufacturing to create crevice samples with rigorously controlled critical dimensions on the appropriate size scale. With such samples, current obstacles to direct comparisons between measurements and modeling of crevice corrosion will be surmounted. Crevice corrosion occurs as a result of the development of aggressive conditions inside extremely small occluded regions on metal surfaces. One of the primary stumbling blocks to the comparison of modeling and experimental results in crevice corrosion has been the extraordinary difficulty involved in experimentally producing a crevice sample that is directly equivalent to a geometry that is amenable to computational modeling. Generally modeling work has assumed that a crevice consists of a one-dimensional metal and a crevice former separated by a uniform gap. To date, it has been impossible to make crevices that have truly uniform gaps on the order of actual crevices (*i.e.*, 0.1-10  $\mu\text{m}$ ). Instead, either the crevice geometry is scaled up or an “average” crevice gap is used which ignores the effects of subcrevices where surface asperities of the crevice former and metal are in intimate or near-intimate contact. The proposed scaling laws have not been experimentally verified on a size scale of relevance to practical instances of crevice corrosion. Thus, comparisons between experiment and computation are plagued by uncertainty.

In the proposed work, both sides of the crevice will be made on Si wafer substrates. The metal side of the crevice will be formed by patterning, etching, and oxidizing the Si before deposition of the metal. A highly planar surface will be produced. The metal surface will be segmented to allow measurement of current distribution within the crevice. The crevice former side of the crevice (formed by patterning and depositing  $\text{SiO}_2$ ) will contain precisely grown spacers that will control the gap between the crevice former surface and the metal electrode to a uniform level selected by the experimenter. The crevice former will also contain microsensors for pH, chloride concentration, and electrochemical potential. Using these types of samples, measurements will be made that will be directly relatable to the computational results from our recently developed 2-D occluded region mass transport model. In this way, the phenomena controlling crevice corrosion initiation and propagation will be directly probed. For example, the nature of subcrevices can be investigated with a specially patterned crevice former.

The proposed work will investigate some of the principal technical issues with which the field of corrosion science has struggled for many years and which have prevented the development of effective crevice corrosion mitigation strategies as well as life prediction methodologies. It will also have impact on other forms of corrosion because the critical structures and processes that control many types of corrosion operate on the micron to sub-mm size scale. For example, the chemistry and electrochemistry associated with corrosion due to inclusions in stainless steel, constituent particles in Al alloys, droplets in atmospheric corrosion, defects in organic coatings, as well as stress-corrosion and corrosion fatigue cracks all occur on the 1  $\mu\text{m}$  to several mm size scale. The size scale and dimensionality of the controlling structures have made both experimental and computational studies very challenging, requiring compromises and approximations in order to make the problem tractable. The effects of these concessions on the results and conclusions have not been assessed to date. This new approach will allow the importance of these concessions to be quantitatively determined.

## PROJECT DESCRIPTION

### Background

Corrosion in occluded regions (crevice corrosion) is one of the most damaging forms of material degradation. Not only is such attack difficult to detect or mitigate prior to component failure, but also our lack of understanding of the contributions of the processes involved generally prevents the prediction of its occurrence except from painful experience. Engineering structures as diverse as lap joints in aircraft, flanged pipes in chemical processing plants, metal surfaces under (initially) protective coatings, and environment-assisted cracks in metallic materials all have an occluded solution. This similitude was originally pointed out by Brown [1], and has gained general acceptance [2] due to the striking similarities in the chemical composition and behavior of occluded regions such as crevices, pits, cracks, and exfoliation sites. Thus, one can consider a crevice as a generic occluded system.

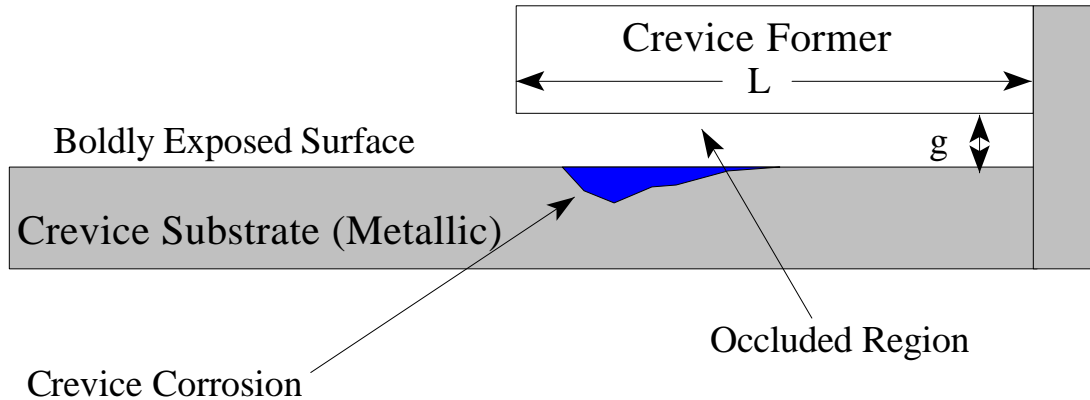


Figure 1: Schematic cross-section of crevice. Not to scale.

Figure 1 defines the important geometric aspects of a crevice (with one end closed). The crevice *substrate* is the metallic material of interest. The crevice *former* is the material that defines the *occluded region* of solution. The *boldly exposed surface* of the substrate is that portion of the substrate outside the occluded region that is in direct contact with the bulk solution. The gap ( $g$ ) between the crevice former and substrate is generally in the range of 0.1 to 10  $\mu\text{m}$  whereas the length of the crevice ( $L$ ) is usually on the order of millimeters.

The occluded region solution has restricted communication with the bulk environment to which the structure is exposed due to the tight geometry of the crevice. Limitations on mass transport trap the products of electrochemical and chemical reactions occurring within the occluded region. These reaction products (*e.g.*,  $\text{H}^+$ ) increase the aggressiveness of the local solution to the point where the occluded chemistry controls the progress of corrosion. In addition to the huge costs caused by such swift, localized attack, the safety of structures, including the airworthiness of aircraft, are at risk from this type of corrosion.

The general description of the evolution of aggressive occluded environments has its basis in the acid-hydrolysis theory of Hoar [3]. Later work by Fontana and Greene [4] gave a qualitative description of the initiation of stainless steel crevice corrosion. The crevice substrate

initially dissolves at a low rate due to the presence of a protective film (*i.e.*, it is passive). Within the occluded solution, the metal cations produced by this passive dissolution cannot be transported out of the occluded region at a sufficient rate to prevent an increase in their local concentration due to the geometric restrictions to mass transport. Hydrolysis of the metal cations occurs, altering the occluded pH. Anions in the bulk environment migrate into the occluded region in order to maintain electroneutrality. The altered environment becomes more aggressive due to the increased concentration of the hydrolysis products and the anions (often chloride due to its high mobility). This occluded solution leads to higher rates of corrosion within the crevice which leads to more hydrolysis and anion migration. The autocatalytic process eventually reaches a steady state defined by the ability of the (restricted) mass transport to remove aggressive species from the crevice, or by changes in the electrochemical behavior of the material (*e.g.*, formation of a salt film).

Although this broad picture of occluded chemistry is widely accepted and has been codified by Oldfield and Sutton [5,6] among others, it is insufficient to explain many important aspects of crevice corrosion phenomenology. For example, it does not adequately describe the location and intensity of the corrosion that occurs. The most severe corrosion attack is usually observed not at the mouth of the crevice, but at some distance into the occluded region as shown in Figure 1 (typically 0.1 to 1 mm). Nor does it account for the potential dependence of crevice corrosion initiation, as pointed out by Sridhar and Dunn [7]. It also does not allow the effects of alloying elements, subcrevices, or microstructural heterogeneities on the initiation and propagation of crevice corrosion to be quantitatively understood.

All crevice corrosion is controlled by the potential and chemical composition gradients within the occluded region and their interaction with the electrochemical behavior of the substrate material. Understanding these interactions is required to develop both predictive capabilities (including life prediction methodologies) as well as mitigation strategies. The Fontana and Green framework alone does not provide a means to gain such understanding. The development and maintenance of the potential and chemical composition gradients within an occluded region are influenced by a wide range of chemical, metallurgical, and electrochemical factors. Our recent efforts to address some of these factors in the case of austenitic stainless steels are discussed in the next section on *Results from Prior NSF Support*.

During that work, two critical hurdles in the understanding of crevice corrosion became apparent. Comparisons between mass transport models and experimental studies have generally failed because of the great differences in the geometries and boundary conditions considered in the modeling versus those imposed by experimental considerations. The processes of importance must be probed on the appropriate spatial scale in order to connect laboratory measurements to practical instances of crevice corrosion. This proposal describes a new approach to crevice corrosion sample construction that will allow both of these hurdles to be cleared.

## **RESULTS FROM PRIOR NSF SUPPORT**

My research group has recently focused much of its effort on the determination and understanding of occluded region chemistry on a variety of materials and types of corrosion. With NSF support (DMR-9505760), Sean Brossia (Ph.D., 1997) and I recently completed a study on the effects of alloying elements on the crevice corrosion behavior of Type 304 stainless steel (Type 304SS). The controlling effects of alloy sulfur were of particular interest as these are not explicitly addressed in the Fontana and Greene framework. Alloy sulfur effects in the localized corrosion of austenitic stainless steels have long been known to be manifested through

the behavior of MnS inclusions (due to the very low solubility of sulfur in austenite). There has been great controversy concerning the mechanism by which these inclusions control localized corrosion initiation. We attacked the problem with a coordinated experimental program involving crevice solution analysis with capillary electrophoresis (CE), electrochemical measurements in bulk analogues of the occluded solutions, surface analysis with small-spot XPS, and micrometallurgical examinations of inclusions with high-resolution TEM/EDS.

The fundamental origin of the controversy has been the identity of the specific reaction path and products of MnS inclusion dissolution. One can rationalize a wide range of possible pathways and products due to the complexity of the chemistry and electrochemistry of sulfur. Virtually all valence states of sulfur, from sulfide (-2) to sulfate (+6) have been implicated as causative in crevice corrosion initiation [8-12]. The main obstacle to understanding the phenomenon was the absence of direct measurements of occluded solution composition.

We were able to use CE to analyze the ionic content of crevice solutions just after the initiation of crevice corrosion as a function of alloy sulfur content and bulk solution composition. The **only** sulfur species detected within the Type 304SS crevices at initiation was sulfide, in contrast to the proposals and measurements of others who had used MnS powder electrodes as analogues for MnS inclusions [9,12]. We have also shown [13,14] that although the initiation time for crevice corrosion decreases with increasing alloy sulfur content, the composition of the occluded region is independent of the alloy sulfur content.

The CE measurements not only gave new insights into the crevice solution composition, but also enabled these solutions to be reproduced in bulk form. Electrochemical measurements of material behavior were then made in these bulk analogues to delineate the role of the various ionic species present. We were able to demonstrate that the presence of sulfide in solution is critical to rationalize the observed crevice dissolution rates. A solution of low pH, even when combined with a high [Cl<sup>-</sup>], was not able to reproduce the dissolution rates observed within the crevice. The IR model of crevice corrosion [15,16] was not applicable, as no active/passive transitions were observed for these materials in the occluded solution.

Five papers and a thesis have resulted or will result from this work. In addition, Sean Brossia's Ph.D. was selected as the most outstanding Ph.D. dissertation in 1996-97 in the physical sciences and engineering at UVa and received the Allan Talbott Gwathmey Award.

Additionally, the same NSF grant has provided partial support for Kevin Stewart (Ph.D. expected May, 1998). His work has focused on the development of a two-dimensional computational framework and computer code for modeling mass transport within occluded regions. This work stemmed from my frustration at the general unavailability of occluded region modeling codes that were sufficiently flexible to handle a range of occluded region phenomena. In corrosion science, too often the basic modeling work has been repeated by each investigator. Either the results of the labors of earlier investigators are not available or the details of the problem (*e.g.*, geometry, material composition, electrochemical behavior, etc.) under consideration were integrated into the program, making it unusable for any other geometry or boundary condition situation.

Kevin has developed a code that can model the spatiotemporal chemical and potential fields in two spatial dimensions. The availability of two spatial dimensions allows many important problems to be addressed, such as the effects of localized corrosion (*e.g.*, pits) within occluded regions as well as the effects of fracture mechanics specimen geometry on the distribution of potential and chemistry within a crack. Both diffusion and migration mass transport modes are taken into account. It can handle virtually any 2-D geometry that can be

meshed with a commercial meshing program (e.g., ANSYS). The model's object-oriented structure makes it modular, allowing it to evolve as our understanding of the occluded corrosion process increases. New factors can be incorporated into the modeling process without forcing a complete rewrite of the code.

An example of the results of such calculations is shown in Figure 2 in which effects of an active pit inside an occluded region on the current distribution inside the crevice are shown. All of the material in the occluded region has the electrochemical behavior shown in Figure 2a, except for the pit, which is actively dissolving at  $1 \text{ A/cm}^2$ . The solution composition in this case is the same at all points, representing a case of IR-controlled crevice corrosion [15,16]. The

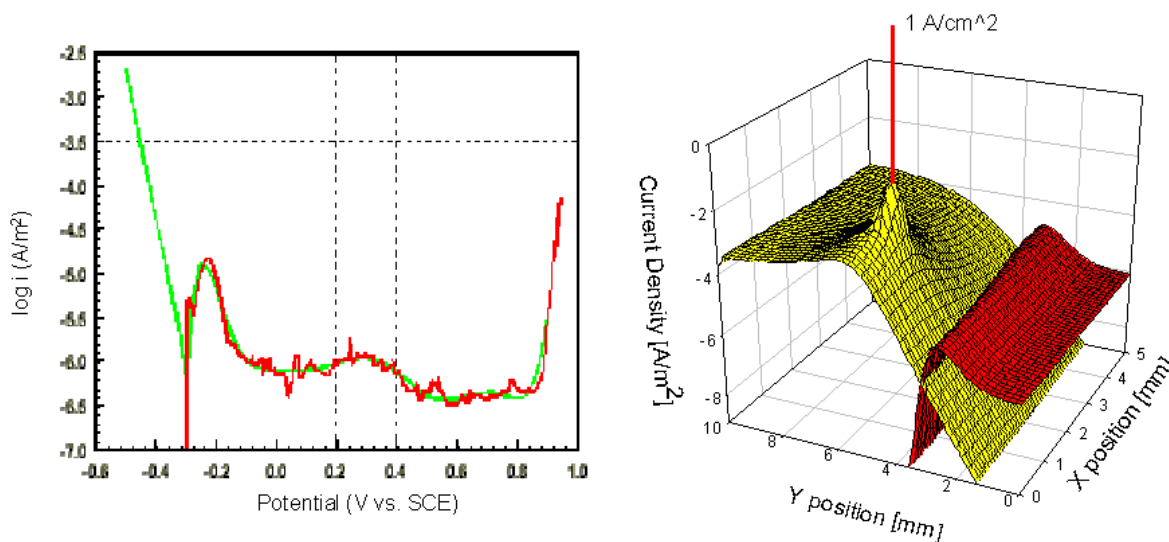


Figure 2: (a) Polarization behavior for material in crevice except for one site which is actively dissolving at  $1 \text{ A/m}^2$ . Both actual polarization data and polynomial fit are shown, (b) Calculated current distribution in crevice due to combination of active/passive transition (IR\*) and active pit site. Yellow = cathodic current, red = anodic current.

dramatic effects on the distribution of current surrounding the site are apparent. This example demonstrates the capability of the code to handle complex electrochemical boundary conditions (i.e., the simultaneous presence of an active/passive transition and a potential-independent dissolution site). The flexibility of the code allows the effects of the position of the active site, or the presence of one or more additional active sites, on the potential and current distributions to be determined without resorting to a rewriting of substantial portions of the program.

Although we feel that our current and past NSF programs have been successful, the work has pointed to a major obstacle to understanding crevice corrosion: the inability to rigorously compare models of occluded region behavior with experimental measurements on the relevant size scale. The alloy sulfur work analyzed the solution rinsed from the entire occluded region to determine the nature and relative concentrations of the species present. We then used estimates of the affected volume of solution (e.g., based on Faraday's Second Law and diffusion calculations) to develop starting points for our electrochemical measurements in bulk analogues. Although such measurements were critical in establishing the importance of solution phase sulfide in the crevice corrosion process, they are not directly comparable to results from our mass transport modeling work for several reasons. The experimental concentrations were average

concentrations based on nominal crevice volumes. The effects of subcrevices within the main crevice could not be extracted. In addition, no data were collected concerning local variations in the chemical concentrations and electrochemical potential. These are exactly the type of data that is predicted by mass transport models. As described below, similar difficulties have plagued others because the difficulties inherent in making such measurements on conventionally manufactured crevice samples are daunting. Thus we feel there is a need to attack the problem differently by making the crevice samples more directly modelable. After reviewing past work in the field, the remainder of this proposal presents a description of a means to accomplish such comparisons.

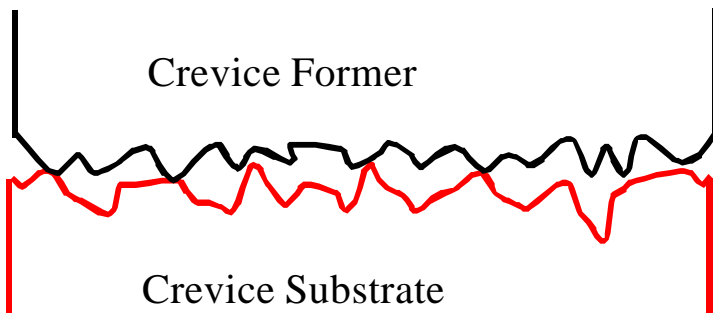
**Publications to date from the NSF-supported Work (DMR-9505760)**

1. R.G. Kelly, C.S. Brossia, K.R. Cooper, J. Krol, "Analysis of Disparate Levels of Anions of Relevance to Corrosion Processes", *Journal of Chromatography A*, Vol. 739, pp. 191-198 (1996).
2. C.S. Brossia, R.G. Kelly, "Influence of Alloy Sulfur Content and Bulk Electrolyte Content on Crevice Corrosion Initiation of Type 304SS", *Corrosion*, in press (1998).
3. C.S. Brossia, R.G. Kelly, "Alloy Sulfur Content and Its Influence on the Crevice Corrosion Behavior of Type 304SS", *Corrosion Science*, submitted (1997).
4. C.S. Brossia, R.G. Kelly, A.W. Wilson, J.M. Howe, "Characterization of Sulfide Inclusions and Inclusion/ Interfaces in Type 304SS and Their Relation to Corrosion", *Metallurgical Transactions*, in preparation (1997).
5. C.S. Brossia, R.G. Kelly, "On the Role of Alloy Sulfur in the Initiation of Crevice Corrosion in Stainless Steel", in *Critical Factors in Localized Corrosion - II*, P. Natishan, R. G. Kelly, G. S. Frankel, R.C. Newman, *Electrochemical Society Proceedings Volume 95-15*, pp. 201-217 (1996).

**PREVIOUS WORK IN THE FIELD**

Hurdles for Experimental Studies

The challenges in probing small, occluded areas make experimental studies of local variations in potential and chemical composition within occluded regions very difficult. The crevice in Figure 1 is an idealized schematic of a real crevice. The gaps in real crevices are highly variable throughout the occluded region because they are defined by the meeting of asperities on the two surfaces as shown in Figure 3. An actual crevice has a highly distributed geometry. Conventional methods of preparing occluded geometry samples, such as by pressing serrated poly-(tetrafluoroethylene) (PTFE) washers onto polished metal surfaces, do not allow rigorously defined crevices to be made. Conventional polishing does not make truly flat surfaces,



but a series of ridges and asperities. Pressing the PTFE washer onto the polished metal surface forms an occluded region with a wide range of crevice gaps including small areas of intimate contact. Although the *total crevice volume* and *nominal crevice gap* of the occluded region can be determined with

Figure 3: Schematic cross-section of a real crevice in which surface asperities cause variations in local gap.

appropriate experiments [9,13,14], the local conditions within the occluded region will vary based on the surface finishes and relative hardness of the contacting surfaces, time (due to creep of the PTFE), etc. Thus, most measurements in true crevices have either averaged the concentrations over the entire crevice volume [9] or used an estimate of the affected crevice volume, which may only be bounded by an order of magnitude [13,14]. The variations in the crevice geometry caused by the method of crevice formation are the likely root of much of the scatter often observed in crevice testing and engineering performance. More importantly, this lack of rigorously defined experimental conditions makes it impossible to directly compare the results obtained to those predicted by any model because models use rigorously defined, uniform crevice geometries in their calculations.

In order to better assess local occluded conditions, workers have often tried to use commercially available microelectrodes to probe the chemical and potential gradients [17-20]. Unfortunately, commercially available “micro” -electrodes are actually 1 mm in diameter [17,21]. Their size makes them somewhat insensitive to changes that occur on the size scales of interest because they sense an even wider area. In addition, the introduction of such large electrodes into a standard crevice geometry, in which nominal gaps range from 0.1 to 10  $\mu\text{m}$ , can greatly distort the exact conditions one wants to study.

For example, Sridhar and Dunn did careful *in-situ* measurements of pH and chloride concentration inside crevices during their work on crevice corrosion of Type 304SS and Alloy 825 [17]. They used commercial microelectrodes for pH,  $[\text{Cl}^-]$ , and potential, each of which was 1 mm in diameter. Sets of these electrodes were secured into ports in the crevice former near the mouth and near the tip of an experimental simulation of a 1-D rectangular slot. The alloys were polarized in chloride solutions to a potential between the breakdown and repassivation potentials. Changes in the pH,  $[\text{Cl}^-]$ , and potential during crevice corrosion were successfully measured. However, post-test examination of the surfaces showed that in some cases, the presence of the electrodes influenced the location of the crevice corrosion. In addition, the size of the electrodes only allowed two regions of the crevice to be sensed. As discussed below, Sridhar and Dunn concluded subcrevices due to surface asperities were controlling. The diameters of the microelectrodes were each several times the period of the asperities, complicating the interpretation of the measurements. Siitari and Alkire [22] used segmented electrodes of Al and steel to study the current distribution during crevice corrosion. However, they were unable to measure pH and potential under identical conditions due to the size of the probes needed for those measurements.

To overcome these difficulties, researchers have attempted to scale up localized corrosion sites to allow the use of such measuring devices [15, 20, 23, 24]. Pickering [15] has had success in his studies using this approach, but those studies represent a special case of crevice corrosion in which the controlling mechanism (IR drop) was assumed and the experimental conditions were selected to ensure the dominance of that mechanism. Unfortunately, the scaling laws to use for a more general case are generally based on computational model results and have not been verified experimentally on samples of the relevant size scale. For example, it is unclear whether all of the modes of mass transport would follow the same scaling laws [22]. In fact, it would be expected that natural convection would become increasingly more dominant as the scale of the occluded region increased. However in practical crevices, natural convection can be ignored due to their small gaps [25]. Thus, although the work of Pickering has focused needed attention of the importance of ohmic drop in crevice corrosion stabilization, extrapolation of the results to other systems or geometries is not straightforward.

### Hurdles for Computational Studies

Many of the fundamental characteristics of occluded regions make computational studies of their behavior difficult. In most occluded regions, both diffusion and migration of species must be considered as contributing to mass transport. These processes take place on very different time scales and the coupling of the equations leads to a set of mathematically stiff, simultaneous, differential equations that must be solved. Both temporal and spatial stability criteria must be met. Ideally, small time steps and a fine spatial mesh should be used, but these both lead to long computation times.

To avoid uncomfortably long calculation times, computational codes dealing with occluded region conditions have been limited in scope and generally inflexible with respect to boundary conditions, including geometry. The most common restriction of the scope is the number of physical dimensions considered. The vast majority of cases have considered 1-D occluded regions [16, 22, 26-28], although some have considered pseudo-2-D cases (*i.e.*, the second dimension depends on the first in a regular way) [29,30]. The types of geometries considered have also been restricted, with rectangular slots enjoying the greatest popularity. Another restriction of the scope of the models developed to date is the use of simplistic boundary conditions. Most often, only one region or site has been considered to be electrochemically active, and it has usually been set at a constant flux independent of potential or solution composition changes (and often located only at the base of an occluded region). Sometimes the site has had constant (often passive) kinetics [26,27], and in rare cases, active/passive behavior has been taken into account [28].

Although these restrictions have been driven by the limitations on computational power available, progress in the field has been additionally limited by the inability of future workers to build on the achievements. Historically, successive researchers have had only limited access the computer codes that have been developed. At best, they have been discussed in archival journal articles where detailed descriptions of the actual code are severely limited. In some cases, the source code has been available for other workers [22,30] although only in hard-copy format. Finally, even in cases where the code has been available, many of the assumptions and chosen restrictions have been integrated into the program, making it of limited utility for other problems.

### Barriers to Comparisons of Experiment and Theory

Comparisons between experimental and computational studies of occluded regions have had limited success due in large part to the hurdles discussed above. Essentially, the problem involves trying to compare computational results from models which use rigorously defined geometries and boundary conditions to results from experiments which use much more poorly defined geometries and boundary conditions.

Some of the most successful comparisons to date have been those of Pickering [15,16]. He and his students have worked with large (0.5 mm wide, several mm deep) crevices of Ni and Fe in order to better understand the effects of ohmic drop on the stabilization of crevice corrosion of materials with active-passive transitions. When other workers have attempted comparisons in practical crevices, the results have been much less encouraging [17, 24, 32].

For example, Sridhar and Dunn [17] compared the initiation conditions predicted by mass transport models to those observed for their experimental simulation of 1-D rectangular slots of Type 304SS and Alloy 825. The model predicted that initiation would occur after a local decrease in pH and increase in [Cl<sup>-</sup>]. Not only did the model results give poor predictions of

initiation time, but also the time course for the pH and [Cl<sup>-</sup>] showed something unexpected. For both alloys, the applied current increased (indicating the initiation of crevice corrosion) *before* pH decrease was detected in the crevice contrary to the predictions of the Fontana and Greene framework. The observed lag times ranged from 10<sup>4</sup> to 10<sup>5</sup> sec, well outside what would have been required for diffusion to carry aggressive solution from an initiation site within the crevice but remote from the microelectrodes to their sensing sphere. Sridhar and Dunn concluded that this observation (similar to that of Wang and Bradford using similarly instrumented crevices [18]) was due to the presence of subcrevices caused by physical asperities on the mating surfaces of their crevice former and substrate. The models, which used perfectly parallel, rectangular slots, could not predict the effects of the subcrevices. Sridhar and Dunn proposed that these subcrevices actually initiated corrosion first, and increased in size with time. After a certain amount of growth, their effects on the solution were large enough for the electrodes to sense. Connolly observed that the crevice corrosion initiation sites on AA3104-H19 were spatially matched to machining marks on the polymethyl methacrylate crevice former [33], again indicating the importance of subcrevices.

Siitari and Alkire compared their measurements on Al [22] to computational results [34]. Although some qualitative agreement was found (*i.e.*, the shape of the current distribution and relative ordering of the initiation at the segmented electrodes were quite similar), there were major discrepancies. For example, the theoretical time for breakdown was one-half that observed, the calculated critical pH was 1.6 units lower than that observed, and the calculated effect of crevice radius (analogous to length in a Cartesian system) was opposite that observed. Whereas it is likely that the fundamentals of the model used by Siitari and Alkire did correctly represent the physical processes, it is not surprising that important areas of disagreement emerged. In order to calculate the current distributions, a uniform crevice gap was assumed and migration effects were ignored. It is likely that effects similar to those seen by Connolly [33] and Sridhar and Dunn [17] were responsible.

Because of our inability to overcome this fundamental challenge of the scientific method, the direct comparison of measurement and theory, progress in the field has been stifled. The accuracy of the various models proposed for crevice corrosion have not been rigorously tested. The relative contributions of chemical and potential gradients in the initiation and propagation of crevice corrosion have not been determined, the role of subcrevices have not been elucidated, and the effects of pitting within occluded regions have not been understood. In addition, the compromises and approximations needed to make experimental and computational studies possible have never been closely scrutinized. The effects of these compromises on the results obtained have been debated, but rigorous and fair comparisons of experiment and model have been lacking.

## **A Proposed Path**

Recent advances in the fields of microelectronics, computation, and sensors offer exciting opportunities for corrosion science researchers to make crevice corrosion test samples with precisely controlled dimensions that are extensively instrumented in an integrated fashion. Microelectronics fabrication techniques are capable of making precise physical structures from a wide variety of materials on the sub-micron to mm scale in all three physical dimensions. These methods are increasingly available at shared facilities at universities and through a national infrastructure.

The historical tradeoff between speed and cost in computation is rapidly becoming an anachronism. Computation speed available to scientific researchers has increased several orders of magnitude in the last two decades. This spectacular increase in computation capability has allowed problems to be attacked that have been identified for many years, but whose computational load has always led workers to accept compromises in the physical description of the problem to allow the calculations to be finished in a reasonable time. Now, more rigorous calculations are less intimidating, and the promise of increased speeds in the future allows a new outlook on the tractability of certain problems. In addition, the Internet allows the sharing of information and computer codes easily, overcoming another of the obstacles to continuous development of accurate models of occluded conditions.

Finally, improvements in sensors capable of quantitatively measuring the concentrations of ionic species have often involved making these sensors compatible with microelectronics fabrication methods. This compatibility has been required for such sensors to be made reproducibly and cheaply enough to be disposable for the mass market (*e.g.*, for medical applications of blood analysis [35]).

By taking advantage of these advances through a coordinated experimental and computational program, a new approach to the investigation of crevice corrosion will be used that will overcome many of the barriers to progress delineated above. Using microfabrication methods, we will produce crevice corrosion samples for experimentation that have precisely defined geometries. The crevice formers will also have sensors for pH, potential, and chemical species incorporated into them. Therefore, experimental results from these samples will be able to be directly compared to the results predicted by the computational code developed at UVA considering identical geometries. The relative contributions of the various possible controlling factors in crevice corrosion will then be evaluated. The code will be made available on the Internet as freeware. In addition, steps will be made to couple this work with that of S. H. Jones in the Department of Electrical Engineering who (with a grant from IBM) is making EE device simulations available through Java-applets on the World Wide Web (see attached letter).

## **GENERAL APPROACH**

### Microfabrication of Precisely Defined Occluded Regions

For rapid corrosion to occur at any given point within a crevice, specific local conditions (*i.e.*, potential and chemical composition) must be met. These local conditions are controlled in large part by geometric considerations. The geometric considerations of importance are those dimensions that control the length and tortuosity of the path from the point under consideration within the crevice to the outer, boldly exposed surface and solution. These dimensions impact both mass transport and electrical potential. Historically, this path has been defined for computational models as gap and length, and in experimental work as *nominal* gap and length (in 1-D). Unfortunately, the inherent mismatch between the dimensions used in computational and experimental studies has prevented rigorous comparisons between model and experiment.

In the proposed study, we will construct rigorously defined occluded regions using microfabrication techniques. First, the substrate will be constructed as a pattern of electrodes with precisely controlled dimensions. Starting with a single crystal silicon wafer with a thin insulating coating of silicon nitride, a pattern of metal electrodes will be defined. Each electrode

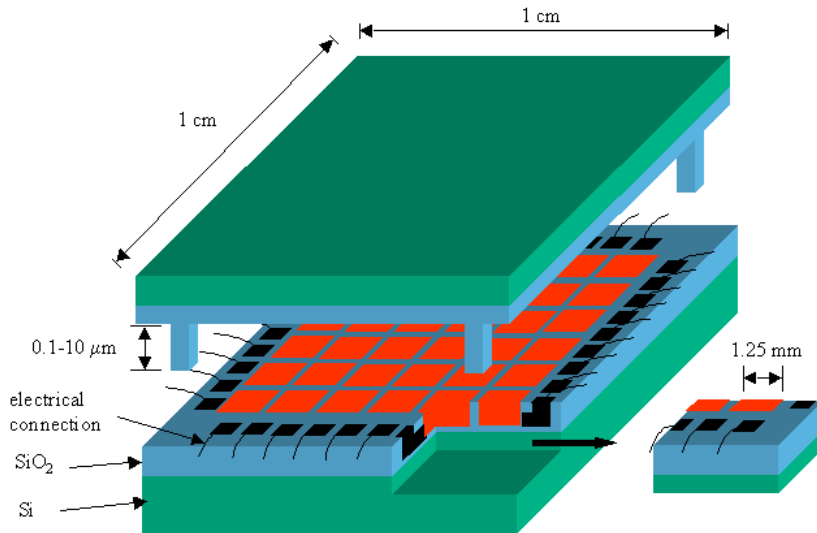


Figure 4: Schematic of a microfabricated crevice sample with crevice former separated above crevice substrate to allow viewing of substrate.

will be separated from its neighbors by a coplanar layer of insulator (e.g.,  $\text{SiO}_2$ ) with each part of the pattern having a separate electrical connection. For

example, consider an overall die size of 1 cm x 1 cm. In Figure 4 the red portions represent individual metal or alloy electrodes deposited by evaporation, electroless or electrodeposition, or sputtering [36]. In this illustration, each electrode is 1.25 mm on a side, although

electrodes as small as 1  $\mu\text{m}$  are easily manufactured. The electrodes are electrically insulated from one another, but the surfaces are coplanar. This geometry can be microfabricated by using a variety of techniques, such as lift-off processing, chemical-mechanical polishing, or selective deposition. Each electrode has an individual, insulated electrical connection (not shown for clarity) which extends to the edge of the die. The hatched areas are  $\text{SiO}_2$  deposited by chemical vapor deposition or reactive sputtering. The lateral separation between electrodes is 20  $\mu\text{m}$ . The result will be a flat, segmented crevice substrate with an array of electrodes which can be individually addressed electrically.

Although others have used segmented electrodes in crevice testing [22], the flexibility of the microfabrication design and fabrication tools will allow the pattern to have any arbitrary arrangement that suits the goals of a particular experiment. For example, not all of the electrodes need be the same size, or in a regular arrangement, or be made of the same material. This capability and the accuracy of the dimensions represent the keys to answering many of the critical questions concerned with occluded corrosion regions.

The crevice former will be made in a similar manner from a separate Si wafer. Small diameter  $\text{SiO}_2$  spacing posts will be fabricated in order to rigorously define the crevice gap. The  $\text{SiO}_2$  posts can be tailored to the experiment and will be in the range from 0.1 to 10  $\mu\text{m}$  in height. Once assembled, the posts will rest on insulator pads on the crevice substrate. The segmented metal electrodes will be connected via zero resistance ammeters (ZRA) which will allow the contributions each makes to the overall current to be accurately measured. Only light pressure will be needed to hold the two pieces of Si together. The result of this construction will be a

crevice with an identical, rigorously defined gap everywhere within the crevice. This configuration represents a key new tool for crevice corrosion studies. In addition, the ability to follow the currents from the individual electrode segments will allow the current distribution within the crevice to be determined at any time. As discussed below, the crevice former can also be processed to include an array of sensors for specific ions as well as reference electrodes to measure the potential gradient throughout the crevice. Testing will commence after electrolyte is introduced into the crevice. The flexibility inherent in the processing allows this simple approach to open doors to numerous paths that combine experimental and computational tasks to address a large number of the fundamental questions concerning occluded region conditions.

## **SPECIFIC PROJECT PLAN**

During the work proposed here, two questions will be addressed in detail:

1. What are the fundamental characteristics of subcrevices that are important in crevice corrosion?
2. What are the fundamental characteristics of pits that are enhanced within crevices that lead to the pitting-induced crevice corrosion often seen?

### Subcrevices:

Subcrevices exist in virtually all practical crevices and in most laboratory crevice corrosion samples, but their influence has not been quantitatively considered. They form when a rough substrate and crevice former are pressed together as shown above in Figure 3. The surface asperities interact to form an irregular array of occluded regions within the main occluded region.

Subcrevices can affect the local conditions in two primary ways. They can lead to higher local solution resistance (and hence increased IR drop). Subcrevices can also act as additional mass transport barriers to that of the overall crevice, making the development and maintenance of critical chemical conditions easier locally. Using the microfabrication approach described above, specimens can be made to separately study these effects by using a range of subcrevice geometries in conjunction with different experimental systems. Subcrevice geometry will be controlled by the fabrication of the crevice former via changes in the patterning and deposition processes. The initiation time and location as well as the current distribution can be determined as a function of the frequency of the subcrevices, their shapes and positions, as well as the nature of the substrate material and bulk environment.

For many years, the effect of surface finish on crevice corrosion has been known, although the extent to which intimate contact of surface asperities controls behavior as opposed to the curling over of metal during the polishing process is unknown. Sridhar and Dunn [17] have proposed that subcrevices dominated the crevice corrosion behavior of Type 304SS and Alloy 825. This question can be answered by the direct comparison of the effect of true crevice gap and nominal crevice gap for Ni and Al. These metals represent two different types of crevice electrochemical behavior. Nickel is generally thought to develop an active-passive transition in occluded environments [15, 37, 38], whereas Al does not [39]. Microfabricated samples will be creviced either with standard PTFE crevice formers at different nominal crevice gaps (as determined by crevice volume) or with micromachined crevice formers with rigorously defined crevice gaps with or without subcrevices. The micromachined crevice formers with subcrevices will have the same total crevice volume as the PTFE crevices, but will vary in the subcrevice dimensions. One example is shown in Figure 5. The period of the subcrevices, their

tightest gap, and aspect ratio will be varied. The range of the dimensions to be covered will be determined by profilometry studies of metal surfaces polished to different extents (60 grit to 0.5

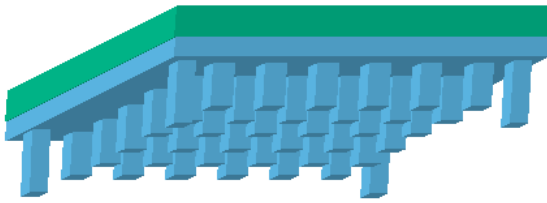


Figure 5: Schematic microfabricated crevice former with regular, rectangular subcrevices.

$\mu\text{m}$ ). The effects of these geometric parameters on the incubation time,  $\tau$ , the location of the initial attack,  $x_{\text{crit}}$ , and the current distribution will be determined and compared to the results from computations on the same geometry. In this manner, the relative importance of local versus global crevice conditions (e.g., length:gap) can be determined for the two types of material behavior. The effect of subcrevice shape can also be explored via the patterning and

anisotropic etching of the Si crevice former.

To determine the effect of subcrevices on potential distributions, experiments will be performed which extend the work of Pickering on IR-drop controlled crevice corrosion to two spatial dimensions and include the effects of non-uniform geometry. Nickel in sulfuric acid will be used as the experimental system with experimental conditions set to prevent alteration of the occluded chemistry [15,16]. By using this system, the effects of local geometric perturbations on the current (and therefore the potential distribution) can be determined without the complicating effects of occluded solution compositional changes. These experimental results can be directly compared to our 2-D FEM model of crevice conditions by either varying the heights of the FEM elements or by designing the subcrevices to be grooves to reduce the problem to two spatial dimensions.

The crevice gaps initially used will be based upon the scaling laws proposed by Pickering [40] for 1-D crevices. By using the information from the ZRAs of the individually instrumented electrodes, the current distribution within the crevice will be determined directly. By modifying the crevice former, the system can be made 1-D, allowing direct comparison the results of Pickering *et al.* to those measured here in order to determine the effect of absolute size scales on scaling laws. Afterwards, the distribution of the attack will be documented with the confocal laser scanning microscope (CLSM) recently acquired at UVa. To determine the effect of subcrevices on chemically driven crevice corrosion, Al in chloride solution will be used. Siitari and Alkire [22] used instrumented, segmented electrodes in a crevice on the mm-to-cm scale to probe the current distribution. Our results will be compared to theirs to quantify the effects of subcrevices.

One extension of the microfabricated crevice sample approach is the inclusion of ion-sensitive electrodes or conductivity sensors as part of the crevice former. Glab *et al.* [41] has shown that Ir/IrO<sub>2</sub> electrodes can operate as pH-sensitive interfaces with open circuit potentials that vary linearly with the solution pH. We have constructed micro-pH electrodes based on this chemistry in our laboratory and have had success in analyzing the pH inside coating blisters. One approach to including such electrodes in the crevice former is shown in Figure 6. A pattern of Ag/AgCl reference electrodes (with agar salt bridges) and Ir/IrO<sub>2</sub> pH electrodes can be incorporated into the patterning of the crevice former to allow compositional changes to be followed within the occluded region. The dimensions of the electrodes could be on the order of

20  $\mu\text{m}$  on a side. Alternatively, a pattern of independent, four-pin conductivity sensors could be incorporated to allow the local solution conductivity to be followed.

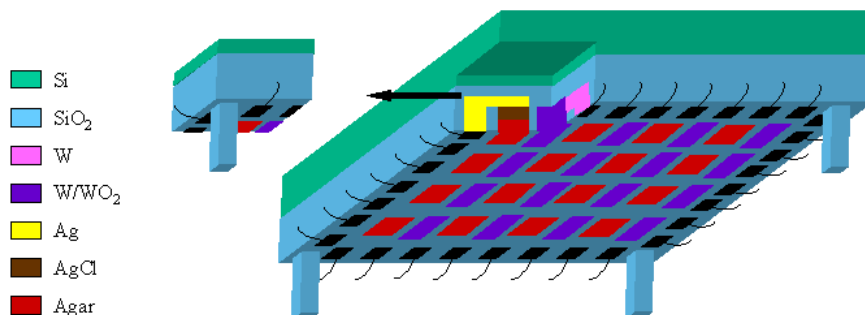


Figure 6: Schematic of instrumented crevice former with an array of microelectrodes to monitor potential, pH, and chloride concentration.

### Pitting within Crevices:

In some alloy systems, crevice corrosion is thought to start by the formation of micropits [42,43]. The additional mass transport barrier provided by the crevice increases the likelihood that these metastable pits will stabilize than if they were formed on a boldly exposed surface. Aspects of metastable pits that could be of importance include location relative to the crevice mouth, dissolution kinetics of the pit, as well as the number and relative position of other pits.

The effect of metastable pits within crevices will be studied by alterations in the basic design of the crevice substrate. By a combination of deposition of different materials within the crevice and applying current to only certain electrodes within the crevice, the relative importance of these effects can be assessed. The pits can formed either by depositing a more active material (*e.g.*, sputter depositing S-contaminated Ni) or applying a high current to only these electrodes via a bipotentiostat, one of which is operating in galvanostatic mode. Alternatively, the effects of local cathodes within crevices could be studied by making the a portion of the electrode array a more noble material.

Again, the flexibility offered by the microfabrication tools will allow the important parameters to be investigated. Changing the location, number, and relative positions of the pits would be accomplished by changing the pattern used in manufacture of the crevice substrates. The dissolution rates of each pit could be controlled by use of multipotentiostats. Nickel and Al would again be used as the model systems in order to determine the relative importance of potential drop and chemical changes in these two systems.

Eventually, the types of materials investigated will be expanded to include other pure metals as well as alloys. The only limitation on the type of material studied is the existence of a method by which the material can be deposited onto the Si substrate.

### **Design and Preparation of Samples**

Access to the design and fabrication tools needed for the proposed work will be accomplished in two ways. The UVa Applied Electrophysics Laboratory (AEpL) offers several well-equipped laboratories for the design, fabrication, and testing of microsystems. One of the

resources within the AEPL is the Semiconductor Device Laboratory (SDL) which operates a 4,500 ft<sup>2</sup> clean room for microfabrication. This lab includes all the basic equipment needed to fabricate novel solid state devices using new and traditional processing techniques. The primary equipment available within the SDL includes molecular beam epitaxy, reactive ion etching, high-vacuum sputtering, electron-beam evaporation, photolithography, wet chemistry stations, and oxidation and annealing equipment. A number of characterization tools are also available including SEM, optical microscopes, surface profilers, and electronic device test equipment. These tools are available on a user fee basis. Prof. Michael Reed, an expert in micromachining metallic structures, has recently joined the EE faculty at UVa and will assist in the design and preparation of the crevice structures.

A second means of accessing these tools is the national micromachining infrastructure which exists via the coordination efforts of MCNC (Research Triangle Park, NC). The MUMPs program (Multi-User MEMS Processes) allows researchers at U.S. universities to submit computer-aided designs of structures which are then fabricated using a specific series of deposition, patterning, and etching steps.

These two sources will be used as needed. Although the MUMPs program gives access to state-of-the-art facilities, its design rules are quite strict and will, in some cases, be limiting. The greater flexibility of the UVa AEPL will allow post-processing of the dies, including the deposition of metal and alloy electrodes and the formation of the crevice formers.

## **SUMMARY**

The proposed work will address some of the critical questions in crevice corrosion that have broad fundamental scientific and practical engineering significance. We will gain insights into the processes which control crevice corrosion by implementing advances in the capabilities and accessibility of microfabrication methods, sensors, and computational modeling. For the first time, it will be possible to directly compare the results of computational models to experimental results on the same size scale in two spatial dimensions using identical, rigorously defined geometries. One direct impact of this work will be in the development of accurate life prediction codes for a wide range of engineering structures. These require computational frameworks which have been experimentally verified on a fundamental level.

The effects of subcrevices will be quantified for the first time, and the controlling aspects of the subcrevice geometry will be determined. This understanding will be useful in the design of structures by providing guidance on what types of subcrevices should be avoided. For example, a finding of geometric limitations to crevice corrosion would have substantial implications in designing around crevice corrosion.

The relative contributions of ohmic drop and local chemical changes will be assessed for two experimental systems in order to gain insights into the importance of and scaling laws for each in crevice corrosion on the size scale relevant to practical crevices. Mitigation strategies for the two types of control are substantially different. Understanding the relative contributions of these processes will allow more effective mitigation strategies to be developed. The important characteristics of pits that form within crevices on some materials and lead to crevice corrosion will be also delineated. Finally, the protocols, test geometries, and computational codes developed for occluded corrosion testing will be directly transferrable to other researchers interested in these phenomena via the Internet.

The proposed work builds on the past work on crevice corrosion in this laboratory and elsewhere by identifying and understanding some of the principal technical issues that the field

has faced for many years and which have prevented the development of effective corrosion mitigation strategies and life prediction methodologies.

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## Biographical Sketch of **Robert G. Kelly**

### **EDUCATION**

Ph.D. The Johns Hopkins University, January 1989  
M.S.E. The Johns Hopkins University, May 1986  
B.E.S. The Johns Hopkins University, May 1984  
(satisfied the requirements for both Biomedical and Materials Science & Engineering, graduated with departmental and general honors)

### **PROFESSIONAL EXPERIENCE**

Associate Professor, Dept. of Materials Science and Engineering, School of Engineering and Applied Science, University of Virginia, Charlottesville, VA - 8/97 - present

Assistant Professor, Dept. of Materials Science and Engineering, School of Engineering and Applied Science, University of Virginia, Charlottesville, VA - 9/94 - 8/97

Center Assistant Director, Center for Electrochemical Sciences and Engineering, University of Virginia, Charlottesville, VA - 7/90 - present

Research Assistant Professor, Dept. of Materials Science and Engineering, University of Virginia, Charlottesville, VA - 7/90 to 9/94

Visiting Research Fellow, Corrosion and Protection Centre, University of Manchester Institute of Science & Technology, Manchester, United Kingdom - 9/88 to 7/90

Ph.D. Candidate, Dept. of Materials Science and Engineering, The Johns Hopkins University, Baltimore, MD - 5/86 to 9/88

M.S.E. Candidate, Dept. of Materials Science and Engineering, The Johns Hopkins University, Baltimore, MD - 5/84 to 5/86

### **HONORS AND AWARDS**

A. B. Campbell Award for Best Paper by Young Author in *Corrosion* journal - 1997  
1996-7 University Teaching Fellow  
Rodman Scholars Award for Excellence in Teaching - 1996  
NSF/NATO Post-Doctoral Fellowship - 1989-90  
Fulbright Scholarship - 1988-89 Academic Year  
Sigma Xi Scientific Research Honor Society - elected 1988  
NSF Graduate Fellowship - 1984-86  
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ASM Undergraduate Fellow - 1983-84 Academic Year

### **TEN RECENT RELEVANT REFEREED PUBLICATIONS**

1. B. K. Nash, R. G. Kelly, "Applications of Ion Chromatography to Corrosion Studies," *J. Chromatography*, 605, pp. 135-140 (1992).

2. L. A. Pawlick, R. G. Kelly, "An Electrochemical Investigation of the Corrosion Behavior of AA5052 in Methanolic Solutions," *J. Corrosion Sci. & Engr.*, **1**, No. 4, pp. 1-12 (1995).
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4. B. K. Nash, R. G. Kelly, "Applications of Ion Chromatography to Corrosion Studies," *J. Chromatography*, **605**, pp. 135-140 (1992).
5. J. F. Dante, R. G. Kelly, "The Evolution of the Adsorbed Solution Layer During Atmospheric Corrosion and Its Effects on the Corrosion Rate of Copper," *J. Electrochemical Society*, **140**, pp. 1890-1897 (1993).
6. S. Kannan, R. G. Kelly, "The Role of Dihydroxybenzenes in the Corrosion of Steel in Black Liquor," *Corrosion Science*, **38**, pp. 1051-1069 (1996).
7. P. D. Bastek, R. C. Newman, R. G. Kelly, "Experimental Determination of the Effects of the Surrounding Passive Film on Scratched Electrode Behavior," *J. Electrochemical Society*, **140**, pp. 1884-1889, (1993).
8. B. K. Nash, R. G. Kelly, "The Characterization of the Crevice Solution Chemistry in 304 Stainless Steel," *Corrosion Science*, **35**, pp. 817-825 (1993) (*invited paper*)
9. R. P. Gangloff, R. G. Kelly, "Microbe Enhanced Fatigue Crack Propagation in HY 130 Steel", *Corrosion*, **50**, pp. 345-354 (1994).
10. H. S. Scully, L. Brumback, R. G. Kelly, "Chromatographic Studies of Localized Corrosion Sites," *J. Chromatography*, **640**, pp. 345-350 (1993).

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Current: Dr. Jiangnan Yuan (96-present), Jennifer Grandle (Ph.D., exptd. 1998), Kevin Stewart (Ph.D, exptd. 1998), Kevin Cooper (Ph.D., exptd 1999), Christopher Weyant (M.S., exptd 1998), Karen Lewis (M.S. exptd. 1998), Lisa DeJong (M.S. exptd 1999)

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Patrick J. Moran, US Naval Academy (M.S. and Ph.D.), Jerome Kruger, Johns Hopkins Univ. (Ph.D.), Eliezer Gileadi, Tel Aviv Univ. (Ph.D.), Roger Newman, Univ. of Manchester Inst. of Sci. & Tech. (Post-doctoral)

**Current and Pending Support for R. G. Kelly**

**"Determination of the Role of Molybdenum and Nitrogen on the Conditions Inside Occluded Corrosion Sites in Stainless Steels"**

Sponsor: National Science Foundation Division of Materials Research

P.I. and all Co-PI's: R. G. Kelly

Amount: \$ 214,008/3 years

Dates of Contract: July 1, 1995 - June 30, 1998

No. of Graduate (Undergraduate) Students Supported: 1

**"Mitigation of Atmospheric Corrosion by Surface Active Papers"**

Sponsor: 3M

P.I. and all Co-PI's: R. G. Kelly, G. E. Stoner

Amount: \$ 110,000/2 years

Dates of Contract: June 1, 1996 - May 31, 1998

No. of Graduate (Undergraduate) Students Supported: 1

**"The Role of Coating and Substrate Heterogeneities in the Long-Term Performance of Painted Aluminum Alloys"**

Sponsor: Air Force Office of Sponsored Research

P.I. and all Co-PI's: S. R. Taylor, R. G. Kelly, J. R. Scully

Amount: \$ 655,371/3 years

Dates of Contract: May 1, 1996 - May 31, 1998

No. of Graduate (Undergraduate) Students Supported: 3

**Measurement of the Chemical Composition of Solutions Inside Aircraft Lap-Splice Joints Developed During Service**

Sponsor: NASA Langley Research Center

P.I. and all Co-PI's: R. G. Kelly

Amount: \$ 180,000/3 years

Dates of Contract: June 1, 1996 - May 30, 1999

No. of Graduate (Undergraduate) Students Supported: 1

**Development of an Embeddable Microinstrument for Measurements of Rebar Corrosion in Reinforced Concrete**

Sponsor: Va. Transportation Research Council

P.I. and all Co-P.I.'s: R. G. Kelly, S. H. Jones, A. P. Batson

Dates of Contract: July 1, 1996- June 30, 1998

Amount: \$166,053/2 years

No. of Graduate (Undergraduate) Students Supported: 2

**Pending**

**"Microfabrication Methods Applied to the Development of Rigorously Defined  
Occluded Region Corrosion Samples"**

Sponsor: National Science Foundation Division of Materials Research

P.I. and all Co-PI's: R. G. Kelly, M. Reed

Amount: \$ 360,000/3 years

No. of Graduate (Undergraduate) Students Supported: 2

Status: this proposal

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### Employment

1997 - present Associate Professor of Electrical Engineering, University of Virginia  
1996 Visiting Professor, Physical Electronics Laboratory, ETH Zürich, Switzerland  
1993 - 1997 Associate Professor of Electrical and Computer Engineering, Carnegie-Mellon University  
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1983 - 1987 Research Assistant, Integrated Circuits Laboratory, Stanford University  
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### Professional

Member of: Institute of Electrical and Electronics Engineers, American Physical Society, Materials Research Society, Tau Beta Pi, Eta Kappa Nu  
Editorial Board of *Journal of Micromechanics and Microengineering*, 1991 - present  
Editor, MRS Proceedings on *Materials for Mechanical and Optical Microsystems*, 1996  
Associate Editor (North America), *Sensors and Materials*, 1996 - present  
Technical Program Committee, Micro Electro Mechanical Systems Workshop, 1991 - 1997  
Micro Machine and Human Science Symposium Steering Committee, 1994 - present  
Technical Co-Chairman, 1995 IEEE Micro Electro Mechanical Systems Workshop  
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Organizer, 1996 MRS Symposium on Materials in Microsystems  
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### Honors and Awards

1989 NSF Presidential Young Investigator  
1989 IBM Faculty Development Award  
1988 Hertz Foundation Doctoral Thesis Prize  
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**Research:** Professor Reed is the author of approximately 50 research articles and books, and has 5 issued and 9 pending patents, in microfabrication technologies. His recent work is concentrated on applications of microelectromechanical systems, especially for microelectronic and biomedical uses.

### **Five Publications Relevant to Proposed Research:**

- M. L. Reed, T. E. Schlesinger, "Wavelength Tunable Electronic and Electrooptical Semiconductor Devices," United States Patent 4,935,935, issued June 19, 1990.
- C.-Y. Hung, T. E. Schlesinger, M. L. Reed, "Piezoelectrically Induced Stress Tuning of Electrooptic Devices," *Applied Physics Letters* **59**(27), 3598 - 3600, 1991
- G. K. Fedder, S. Santhanam, M. L. Reed, S. C. Eagle, D. F. Guillou, M. S.-C. Lu, L. R. Carley, "Laminated High-Aspect-Ratio Microstructures Fabricated in a Conventional CMOS Process," *Sensors and Actuators A* **57**, 103 - 110, 1996.
- T. Abe, M. L. Reed, "Low-Strain Sputtered Polysilicon for Micromechanical Structures," Proceedings of the Ninth International IEEE Workshop on Micro Electro Mechanical Systems (MEMS-96), San Diego, February 1996, pages 258 - 262.
- M. L. Reed, G. K. Fedder, "Photolithographic Microfabrication," Chapter 2 of *Micro Mechanical Systems and Technology*, T. Fukuda and W. Menz, editors, Elsevier Science B.V., Amsterdam, 1997.

### **Five Other Publications:**

- H. Han, L. E. Weiss, M. L. Reed, "Micromechanical Velcro," *IEEE Journal of Microelectromechanical Systems* **1**(1), 37 - 43, 1992.
- S. Hashmi, P. Ling, G. Hashmi, M. L. Reed, R. Gaugler, W. Trimmer, "Genetic Transformation of Nematodes Using Arrays of Micromechanical Piercing Structures," *BioTechniques* **19**(5), 766 - 770, 1995.
- T. Abe, M. L. Reed, "Control of Liquid Bridging Induced Stiction of Micromechanical Structures," *Journal of Micromechanics and Microengineering* **6**(2), 213 - 217, 1996.
- S. Tan, M. L. Reed, H. Han, R. Boudreau, "Mechanisms of Etch Hillock Formation," *IEEE Journal of Microelectromechanical Systems* **5**(1), 66 - 72, 1996.
- M. L. Reed, T. Abe, "Method to Prevent Adhesion of Micromechanical Structures," United States Patent 5,658,636, issued August 19, 1997.

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C.C. Wu, University of Pittsburgh;

### **Recent Students and Postdocs (of 20):**

A. Nadeem, University of Pittsburgh; M. Mescher, CMU; B. Brunett, CMU; S. Eagle, CMU; J. Ebel, CMU; T. Abe, Tokyo Gas; K. Rebello, Intel; J. Kneller, University of Pittsburgh; C.-Y. Hung, CMU

### **Graduate Advisors**

Robert L. Hickok, Rensselaer Polytechnic Institute  
James D. Plummer, Stanford University



## Current and Pending Support

**See GPG Section II.D.8 for guidance on information to include on this form.)**

The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal.

|  |   |
|--|---|
| Investigator: Michael L. Reed  | Other agencies (including NSF) to which this proposal has been/will be submitted: |
| Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support |   |
| Project/Proposal Title:  |   |
| <b>Acquisition of a Flexible High Rate Thin Film Sputter Deposition System for Multidisciplinary Microfabrication Research</b>   |   |
| Source of Support: NSF   |   |
| Total Award Amount: \$371,760                      Total Award Period Covered: 9/98 – 8/00   |   |
| Location of Project: University of Virginia  |   |
| Person-Months Per Year Committed to the Project.                      Cal: 0                      Acad: 0                      Sumr: 0   |   |
| Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support |   |
| Project/Proposal Title:  |   |
| <b>Microfabrication Methods Applied to the Development of Rigorously Defined Occluded Region Corrosion Samples</b>   |   |
| Source of Support: NSF   |   |
| Total Award Amount: \$360,000                      Total Award Period Covered: 8/98 - 7/01   |   |
| Location of Project: University of Virginia  |   |
| Person-Months Per Year Committed to the Project.                      Cal:                      Acad: 0                      Sumr: 1   |   |
| Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support |   |
| Project/Proposal Title:  |   |
| <b>Development of a New Intracoronary Gene Stent</b>   |   |
| Source of Support: University of Pittsburgh Division of Cardiology   |   |
| Total Award Amount: \$30,000                      Total Award Period Covered: 6/96 – 5/98  |   |
| Location of Project: University of Pittsburgh  |   |
| Person-Months Per Year Committed to the Project.                      Cal:                      Acad: 0                      Sumr: 0   |   |
| Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support |   |

