De-alloying and Stress-Corrosion Cracking

Final Report

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Introduction

This research program has had two major areas of focus that are related: (1) alloy corrosion and (2) the role of selective dissolution in the stress corrosion cracking of alloy systems. These interrelated issues were examined using model systems such as Ag-Au and Cu-Au by conventional electrochemical techniques, *in situ* scanning tunneling microscopy (STM), *in situ* small angle neutron scattering (SANS), ultrahigh speed digital photography of fracture events, and computer simulations. The STM and SANS work were specifically aimed at addressing a "roughening" transition known to occur in alloy systems undergoing corrosion at electrochemical potentials greater than the so-called "critical potential". Analytical models of de-alloying processes including the roughening transition were developed that specifically include curvature effects that are important in alloy corrosion processes. Stress-corrosion experiments were performed on the same model systems using rapid optical and electrochemical techniques on 50 μm - 250 μm thick sheets and small diameter wires. The magnitude of the individual single-shot brittle events was examined as a function of various controlling parameters including the de-alloyed layer thickness, electrolyte, and alloy composition. The primary goal of this work was to develop a fundamental understanding of the corrosion and electrochemistry of alloys and the stress-corrosion cracking processes these alloys undergo. Computer simulations and analytical work identified *surface stress* and an important parameter in environmentally assisted fracture. The major results of our research on this program since the summer of 1993 are briefly summarized below.

Curvature effects in alloy dissolution

We developed a thermodynamic and kinetic analysis using a "mean-field" approach that accounts for curvature effects in alloy dissolution [1]. The phenomenon of the critical potential for macroscopic selective dissolution was analyzed in terms of a surface roughening transition. This transition results from a competition between curvature dependent dissolution and surface diffusion. The following expression for the critical potential as a function of alloy composition was developed [1]:

$$V_{crit} = 4 \frac{\gamma \Omega}{nqa} \left(\frac{p}{2-p} \right) + \frac{2k_B T}{nq} \sinh^{-1} \left[\frac{32\pi^2 N_s D_s}{a^2 J_o} \left(\frac{p}{2-p} \right)^2 \right]$$

Here V_{crit} is the critical potential, γ is the solid/electrolyte interfacial free energy, Ω is the mean atomic volume of the binary alloy, n is the number of electrons transferred in the dissolution process, q is the elementary charge, a is the nearest neighbor distance in the alloy, p is the atom fraction of the more-noble constituent (Au in the example below), k_B is Boltzmann's constant, T is the absolute temperature, N_s is the number of atoms per unit area, D_s is the surface diffusivity and J_o is the atom flux corresponding to the exchange current density.

Recently we began some experiments to test the predictions of the curvature analysis [2].

Figure 1 shows results for the critical potential as a function of composition for Ag-Au alloys.

Figure 1. Experimentally determined values (data points) of the critical potential of Ag-Au alloys in 0.1 M HClO₄ + Ag⁺ as a function of the Au concentration in at%. The solid curves through the data are the theoretical fits using the equation for V_{crit} above. Fitting parameters are shown in Table I.

The experimental results were fit to the expression for the critical potential using two adjustable constants; *constant 1* determines γ , and *constant 2* determines the ratio $D_s J_o^{-1}$. Table I shows the results for these parameters as a function of the Ag⁺ concentration in the electrolyte. We were able to determine D_s (see Table I) by using some known data [3] for the exchange current density at Ag⁺ concentrations of 10⁻³ M and 10⁻¹ M. The values of γ and D_s in Table I are consistent with those obtained from other measurements of D_s [4] and first principles calculations of γ for Au(111) surfaces [5]. These experimental results provide an important validation of the critical potential analysis.

De-alloying below the critical potential

Conventionally, the critical potential represents the potential marking the onset of bulk de-alloying. The current density below the critical potential is only weakly dependent on potential and the physical processes responsible for this passive - like behavior have been poorly understood.

Table I. Parameters used to fit the theoretical equation for the critical potential to the experimental data shown in Figure 1. The constants in the table were defined by the

following form: $V_{crit} = 14609\gamma \left(\frac{p}{2-p} \right) + 0.051 \sinh^{-1} \left[7.6 \cdot 10^{32} \frac{D_s}{J_o} \left(\frac{p}{2-p} \right)^2 \right]$, where

$const1=14609\gamma$, and, $const2=7.6 \cdot 10^{32} D_s / J_o$.

[Ag ⁺] [M]	Const1 [V]	γ [J m ⁻²]	Const2	$D_s J_o^{-1}$ [cm ⁴]	D_s [cm ² s ⁻¹]
0.0001	1.37	0.93	123 538	1.63 10 ⁻²⁸	
0.001	1.32	0.90	40 328	5.31 10 ⁻²⁹	5 10 ⁻¹¹
0.01	1.27	0.87	17 842	2.35 10 ⁻²⁹	
0.1	1.22	0.84	8 925	1.17 10 ⁻²⁹	3 10 ⁻¹⁰
1	1.19	0.81	4 337	5.71 10 ⁻³⁰	

In situ STM [6] was used to study the nature of the surface morphology which develops at potentials less than the critical potential. At fixed potential, the time dependent evolution of the surface morphology was correlated with the observed current decay. This allowed us to identify and model the physical processes that control the current decay. We found two general regimes of power - law behavior in the current decay which corresponded to exhaustion of an activation controlled dissolution process (t^{-1}) and the operation of one of three mechanisms of surface mass transport control ($t^{-5/8}$, $t^{-1/2}$, and $t^{-1/4}$). Potential pulsing experiments were performed in order to examine the effect of a "blocking" noble - metal layer on the nucleation and growth of the porous structure associated with bulk de-alloying. These results were analyzed using a Johnson - Mehl - Avrami analysis. The Avrami exponents found were fractional and in the range of 1.25 - 1.8. The fractional exponents were interpreted in terms of the fractal dimension characterizing the initial stages of porosity formation during bulk de-alloying .

Alloy dissolution and underpotential deposition

We used *in situ* STM to study de-alloying of Ag from "dilute" (Ag concentrations < 20 at %) Ag-Au alloys in order to determine the voltage required to strip monolayer levels of Ag clusters from the alloy surface [7]. During our measurements we noted that in this composition regime the stripping of Ag from the surface had many similarities to stripping of an underpotentially deposited (upd) monolayer of Ag on Au. In particular, upd and stripping is directly associated with the manner in which the electrochemical activity of one component is affected by the presence of atoms of the other component. We examined the upd and stripping behavior of Ag in 1M HClO₄ on both pure Au and Ag-Au alloy electrodes. These experiments [7] were the first that we know of where upd behavior on alloy substrates was examined. Ag-Au electrodes were prepared using thin film techniques. The results characterizing the electrode behavior roughly fall into the

category of either Au-like or Ag-like and this behavior parallels the known dissolution behavior of Ag from Ag-Au alloys. The break in the alloy dissolution behavior occurs at roughly 65 at% Ag and the break in the upd behavior occurred at 30 at% Ag. This quantitative difference was expected since on average a Ag atom in the superficial upd overlayer is coordinated differently with respect to neighbor identity than a Ag atom on the surface of the alloy.

Surface morphology evolution

We examined various aspects of Ag/Au(111) upd process, with the additional aim of developing a better understanding of kinetic processes controlling the dynamic evolution of a surface undergoing dissolution or growth. We performed experiments [8] and computer simulations [9]. In the experiments, we examined the electrochemical growth of Ag on Au (111) [8]. These results were compared to surface evolution growth models [7]. In situ STM was also used to observe the morphological details of the transition from layer-by-layer growth to 3-dimensional island growth during the potentiostatic deposition of Ag onto Au (111) substrates in 0.1 M HClO₄ + 10⁻⁴ M Ag⁺. Island growth began after the completion of 2 close-packed Ag monolayers that formed so-called wetting layers. Immediately following the completion of the 2nd monolayer, nucleation and growth of 3D islands were observed. The 3D or Stranski-Krastinov growth began when 2D nuclei for the incipient 3rd ad-layer reached a critical size of order 20 - 50 nm. Our observations and analysis [8] suggest that this growth mode transition was kinetically controlled by ad-atom migration over descending steps. We examined these Schwoebel barrier issues using computer simulations [10].

In situ Small Angle Neutron Scattering (SANS)

We used SANS to investigate the morphological evolution of a silver gold alloy undergoing bulk de-alloying [11,12]. The experiments were performed at the Cold Neutron Research Facility at NIST in Gaithersburg, MD. The behavior of Ag_{0.8}Au_{0.2} alloy foils, 250 μ m thick, was examined in a special electrochemical cell designed for the SANS experiments. This was the first time that an in situ investigation employing SANS has been used to follow the evolution of corrosion morphology. Figure 2 which shows the data for the scattering intensity vs. wave vector indicates the emergence of a well defined peak indicative of the length scale associated with the bi-continuous morphology of the corroded structure. We used a model developed by Berk [13] for scattering in random bi-continuous structures to interpret our data and generate representative images of the corrosion morphology as it evolved in time as shown in Figure 3. Using this data we have been able to determine the distribution of the ligament size of the porous gold morphology as a function of time. Figure 4 shows that ambient temperature coarsening of the de-alloyed morphology followed $t^{1/4}$ kinetics.

Figure 2. In-situ scattering data of $\text{Ag}_{0.7}\text{Au}_{0.3}$ in $1\text{ M HClO}_4 + 1\text{ mM Ag}^+$ at 700 and 450 mV vs. Ag/Ag^+ . A very broad peak with weak intensity was observed after 18.7 hours of dealloying at 700 mV. After 18.7 hrs. of dealloying at 700 mV, the applied potential was changed to 450 mV (below the critical potential).

Figure 3: Simulated TEM images (768 nm x 768 nm) calculated from fits to the scattering data after (A) 1.7 hours and (B) 20 hours at 450 mV. The average ligament width calculated from the images is (A) 7.8 nm and (B) 15.0 nm.

Figure 4: The calculated average ligament width versus time at 450 mV.

Stress-corrosion cracking (SCC)

The primary objectives of this portion of our research are summarized below:

- Measurement of the crack penetration depth (during rapid brittle crack propagation) as a function of the de-alloyed layer thickness.
- Relating the de-alloyed layer pore size distribution as a function of de-alloying potential and aging time to the film induced fracture process.
- Examine the possibility that film-induced intergranular separation (intergranular SCC) results from selective anodic grain boundary dissolution.

Experimental work on de-alloyed layer induced brittle fracture was performed using the so-called "single shot" method. Here a small diameter alloy wire or thin alloy sheet of order 100 μm (diameter or thickness) is de-alloyed to a prescribed layer thickness. The layer thickness is estimated from the accumulated charge density during the de-alloying process. Following de-alloying the sample is rapidly strained (at strain rates ~ 10) and the fracture mode and layer thickness was determined by scanning electron microscopy (SEM).

Single shot SCC tests were performed on Ag - Au alloys in the form of 50 μm - 250 μm diameter wires and sheets (thickness) in perchloric acid electrolytes [14,15]. These tests were done using a solenoid actuated tensile machine specially constructed for this purpose. De-alloyed layers were grown to thicknesses ranging from 150 nm to 50 μm at a potential above the critical potential and then the potential was reduced to a value below the critical potential where no significant corrosion occurs. Samples were rapidly fractured and immediately removed from the electrochemical cell and rinsed with purified water. The tests demonstrated that a 150 nm de-alloyed layer produced a 10 μm brittle fracture. Furthermore, the extent of the brittle fracture event scaled approximately linearly with the film thickness for films up to $\sim 3 \mu\text{m}$ in thickness. We observed that a de-alloyed layer 3 μm in thickness could induce 100% brittle intergranular fracture across a 250 μm diameter wire. There was no film-induced brittle fracture observed for

films of greater than $\sim 3 \mu\text{m}$ in thickness owing to the time required to grow these thicker layers. Figures 5 and 6 show typical results for intergranular brittle crack penetration distance as a function of the de-alloyed layer thickness for Ag-Au samples de-alloyed at the indicated potentials. The FIC/Ductile line is drawn with a slope of 1 strictly defining the boundary between a film-induced cracking and a fracture event that stops at the film/substrate interface. The slope, m , of the other line in these figures, was used as a measure of susceptibility to the film-induced brittle fracture event for the prescribed de-alloying condition. Increasing m corresponded to a higher degree of susceptibility. The growth time associated with thick ($> \sim 3 \mu\text{m}$) layers allowed for ambient temperature coarsening of the de-alloyed microstructure and this resulted in a ductile de-alloyed layer which did not trigger brittle cracking. In these cases the fracture was arrested at the de-alloyed layer/substrate interface.

Figure 5. Results of rapid fracture tests on a $\text{Ag}_{0.8}\text{Au}_{0.2}$ alloy in 1.0 M HClO_4 dealloyed at 0.975 V (SCE). Sample thickness 60 μm .

Figure 6. Results of rapid fracture tests on a $\text{Ag}_{0.7}\text{Au}_{0.3}$ alloy in 1.0 M HClO_4 dealloyed at 1.1 V (SCE). Sample thickness 60 μm .

Even in the case of a thin ($< \sim 3 \mu\text{m}$) de-alloyed layer, we found that the ability of the layer to trigger a brittle event could be reversed by going to an open circuit condition, and allowing the bi-continuous dealloyed structure (at fixed layer thickness) to coarsen. This result was in agreement with previous work on the brittle-ductile transition in porous gold [16] and the SANS results described above.

High-speed optical techniques were used to determine the instantaneous crack velocity in these single shot experiments. This portion of the work was done in collaboration with R.C. Newman's group at Manchester [17]. An Imacon ultra high speed imaging system was used for this work. The results showed that the instantaneous crack velocity in the film-induced cleavage experiments was at least $\sim 2 \text{ m.s}^{-1}$.

Special experiments were conducted to determine the extent of preferential grain boundary dissolution in Ag-Au alloys that are susceptible to SCC [15]. While this can be performed by simple SEM examination of cross-sections of samples, there is always the concern that the extent of corrosion penetration down a boundary may not be resolved using this technique. Instead, we used an electrochemical technique. A two compartment cell was used to de-alloy one side of an alloy sheet

while on the back-side the solution was 18.1 MΩ doubly-distilled and de-ionized water. The first compartment was filled with 1.0 M HClO₄, and this side of the foil was polarized to a potential greater than the critical potential. The solution conductivity in the rear compartment was continuously monitored using an AC technique [15]. When the specimen perforates due to selective dissolution the conductivity in this compartment necessarily rises. By noting the amount of charge passes prior to the rise in conductivity, the difference between the calculated thickness of the dealloyed layer and the actual depth of penetration was determined. This difference was a direct measure of the amount of preferential grain boundary attack. The system was sensitive to changes in conductance of order 2×10^{-8} S, which for our electrochemical system corresponded to ~ 1.6 ppb change in solution concentration. As shown in Figure 7, (which represents the most severe grain-boundary attack we observed) the results are plotted as the solution conductance versus the calculated film thickness. The dealloyed layer thickness, calculated from the accumulated charge, required to perforate a 60 μm thick Ag_{0.8}Au_{0.2} sheet was found to be 21 μm . The actual dealloying was ~ 3 times deeper than that calculated assuming a uniform planar front. From measurements of this sort we concluded that grain-boundary penetration rates are at most a factor of three times the average de-alloying rate assuming a planar front. This result taken together with the observation that the ability of the layer to trigger a brittle event could be reversed provides strong evidence for the existence of a purely mechanical component of cracking in the SCC process.

Figure 7. Perforation test result on a 60 μm Ag_{0.8}Au_{0.2} alloy sheet showing that breakthrough occurs when the mean film thickness is 23 μm .

Surface Stress Effects on Dislocation Nucleation Processes

Recently Rice [18] introduced a new formalism for dislocation emission from a crack tip based on the Peierls model of a dislocation in a crystalline solid. He defined a new solid state parameter, γ_{us} , equal to the work per unit area required for the bulk block-on-block sliding process of slip. Rice termed this new parameter the *unstable stacking energy*. The model developed by Rice is an exact analysis for dislocation emission for a crack loaded in mode II. In his original paper, Rice also examined the situation for dislocation emission from a mode I crack, however, this analysis was not exact. In this analysis, he defined an effective mode II stress intensity equal to $K_{II}^{eff} = K_I \cos^2(t/2) \sin(t/2)$, where t was the angle between a crack and slip plane. Rice assumed

that emission would occur in mode I when this effective value of mode II equaled the critical K value at emission under pure mode II loading. This analysis did not include the energy associated with ledge creation, which may need to be accounted for if the nucleated dislocation has a component of its Burgers vector perpendicular to the crack plane.

Sieradzki and Cammarata [19] suggested that a proper thermodynamic approach to the issue associated with dislocation emission at a crack surface would involve the excess work per unit area associated with elastic stretching of the crack tip surface during the dislocation nucleation event. The effects of surface stress on intrinsic crack tip emission processes were examined using Molecular Dynamic Simulations that employed realistic Embedded Atom Methods potentials [20]. Both two-dimensional (2D) triangular lattices and three-dimensional (3D) fcc lattices were investigated. The measured mode II results were within 10% of Rice's predictions for all the materials investigated. The mode I results in 3D were in disagreement with Rice's approximate mode I analysis for dislocation emission. Surface stress corrections to Rice's approximate analysis were able to accurately predict the mode I simulation results for the critical K_I for all the fcc materials which we investigated.

The physical properties of fcc solids, such as gold, nickel or copper, are reasonably well described by existing EAM potentials. Moreover, this crystalline structure provides a substantial number of slip systems available for dislocation emission and motion. In fcc crystals the most important slip system is along a partial Shockley route, owing to the, relatively small value of the unstable stacking energy. Here, we summarize the results of 3D simulations of dislocation emission from a crack tip for the fcc solids: copper, silver, gold, nickel, palladium and platinum. The simulations were focused on verifying the accuracy of the dislocation nucleation criterion of Rice [18] and investigating the magnitude of effects on the emission process due to surface stress.

The following set of physical properties of the fcc solids was computed:

- the elastic constants C_{11} , C_{12} and C_{44} in the coordinate system with axes parallel to the cube axes,
- the surface stress in the $\{111\}$ -plane, f_{111} ,
- the unstable stacking energy along a Shockley partial route, γ_{us} ,
- the stacking fault energy, γ_{sf} .

The results are summarized in Table 2.

Table 2. The material properties of Johnson EAM Solid.

Metal	C_{11} [GPa]	C_{12} [GPa]	C_{44} [GPa]	f_{111} [J/m ²]	γ_{us} [J/m ²]	γ_{sf} [J/m ²]
Cu	184	115	69	1.1076	0.06778	0.0
Ag	131	89	43	1.0364	0.05002	0.0
Au	187	148	39	1.7124	0.04843	0.0
Ni	260	141	119	0.8164	0.14254	0.0
Pd	240	172	68	1.9683	0.07472	0.0
Pt	303	256	81	2.7583	0.11379	0.0

For crack-tip dislocation emission simulations, a block of an fcc crystal was oriented so, that its sides coincided with $\{112\}$, $\{110\}$ and $\{111\}$ crystalline faces. The size of the sample was characterized by three parameters: N_x , N_y and N_z , that were related to the linear dimension of the sample: l_x , l_y and l_z , by means of the following relations

$$l_x = 3 N_x / 2 d_{112}, l_y = N_y d_{110}, l_z = N_z d_{111}, d_{ijk} \text{ is the appropriate inter-planar spacing.}$$

Figure 8. Sample configuration.

A crack was introduced into the solid by cutting interatomic bonds between two consecutive $\{111\}$ planes located at $z_1 = (N_z/2 - 1) d_{111}$ and $z_2 = N_z/2 d_{111}$. The length of the crack was always equal to $l_x/2$. The crack front was oriented along $\langle 110 \rangle$ direction, with the crack plane with normal in $\{111\}$ direction. The bonds broken in the process of creating the crack were not allowed to reform during the entire simulation.

The sample was subdivided into three distinct regions, interior, boundary, and crack surfaces.

The interior atoms were entirely free to move and to minimize the energy of the crystal. The boundary atoms (blue circles in Figure 9) had their x and z coordinates fixed, with no restraints placed on their y locations. They were placed in the positions corresponding to the plane strain linear elastic displacement field for a cracked anisotropic solid. The boundary atoms were supplied with the electron density contributions from missing atoms to simulate atoms located in a bulk crystal. While the interior atoms were free to move in all three directions, periodic boundary conditions were employed in the y direction such that $u_y(x, y, z) = u_y(x, y + d_r, z)$ where $d_r = N_y d_{110}$ is the lattice repeat distance parallel to the y -axis.

Figure 9. Sample configuration for $N_x=20$, $N_y=3$ and $N_z=24$. Yellow circles represent atoms at crack surfaces, blue circles correspond to atoms located at boundary.

Sieradzki and Cammarata [19] suggested that to account for surface stress effects, a correction term of order $f e$, (where f is the value of surface stress and e is the strain in the segment of a free surface at the tip) should be added to γ_{us} in the emission criterion of Rice [18]. Our simulations were aimed at testing this general idea. We measured the critical value of the stress intensity factor for dislocation emission in mode I, K_I^e , and pure mode II, K_{II}^e . The mode I results of the simulations are presented in Table 2, where K_I^e is the critical value of K_I measured for dislocation emission, K_I^{Rice} is the value of critical K_I predicted by Rice's criterion, and e_{111} is the value of strain measured in the $\{111\}$ segment at the tip.

Table 3. The results of 3D simulations of dislocation emission in mode I.

Metal	K_I^e [MPa m ^{1/2}]	K_I^{Rice} [MPa m ^{1/2}]	e_{111}
Cu	0.708	0.276	0.193
Ag	0.439	0.190	0.182
Au	0.313	0.186	0.149
Ni	1.096	0.510	0.220
Pd	0.650	0.298	0.168
Pt	0.625	0.407	0.146

In mode I, we did not observe a significant departure from the dislocation emission scenario assumed in continuum models, except that the dislocation became unstable when the relative shear displacement of atoms at the crack surface was *less than* $b/2$ (b is the magnitude of Burgers vector for a fully formed dislocation). The crack tip region just prior to emission for gold is shown in Figure 10.

Figure 10. Dislocation-core configuration just prior to the instability in Au. Dashed line indicates the inclined slip plane.

Figure 11. Crack tip configuration just after dislocation emission in Au.

There was only one mechanism of dislocation nucleation observed in mode I, i.e., the emission of a single Shockley partial dislocation on an inclined slip plane. The vicinity of the crack tip just following emission is shown in Figure 11.

As described above Rice defined an effective mode II stress intensity for Mode I loading as $K_{II}^{eff} = K_I \cos^2(t/2) \sin(t/2)$, and assumed that a dislocation would be emitted in mode I when K_{II}^{eff} equaled the value of the stress intensity for dislocation emission in pure mode II, i.e., $K_{II}^{eff} / K_{II}^e = 1$. We calculated the values of this ratio on the basis of our 3D simulations. The results are presented in Table 4, where C_1 and C_2 are the first and second order surface stress correction terms [19] in mode I, and are defined by, $C_1 = (1 + f_{111} e_{111} / \gamma_{us})^{1/2}$, and $C_2 = (1 + f_{111} e_{111} / \gamma_{us} + f_{111}^2 e_{111}^2 / 2 \gamma_{us})^{1/2}$.

Table 4. Measured values of K_{II}^{eff} / K_{II}^e in the simulation along with values of this ratio predicted by surface stress correction terms to the Rice emission criterion. We note that the Rice estimate is $K_{II}^{eff} / K_{II}^e = 1$ for all materials.

Metal	K_{II}^{eff} / K_{II}^e	C_1	C_2
Cu	2.12	2.03	1.97
Ag	1.98	2.18	2.03
Au	1.79	2.51	2.30
Ni	2.11	1.50	1.62
Pd	1.89	2.33	2.14
Pt	1.39	2.13	1.98

As demonstrated by the results in Table 4, introduction of the first order correction term, C_1 , greatly improves the agreement between the continuum predictions and simulations for all materials with the exception of Pt. Changes due to higher order effects in strain are not large, but bring the Rice model values closer to the ones measured.

There are a number of reasons why the modified Rice model fails to predict the critical value of the stress intensity factor in mode I accurately. The original Rice treatment of the emission process on an inclined slip plane does not take into account the creation of a ledge left at a surface, when a dislocation nucleates [18]. From a continuum viewpoint, the effects of a ledge on an incipient dislocation in the vicinity of a stressed crack tip can be viewed as a line force

acting on the incipient dislocation. In general, the ledge creation energy contains two terms, one accounting for broken bonds, and one accounting for the deformation of the crack surface where the ledge emerges. In our simulations the bond breaking effects are not present, since the number of bonds prior and after the dislocation emission remains unchanged. Still, some ledge creation energy due to surface stress is present, and this is an important factor affecting the K_I^e values.

Journal Publications, Reviewed Conference Proceedings, and Invited Presentations Resulting from this work since 1993. (This includes the first six months of the program while K. Sieradzki was at Johns Hopkins University)

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REVIEWED CONFERENCE PROCEEDINGS

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4. K. Sieradzki, S.R. Brankovic, and N. Dimitrov, "Silver Deposition and Dissolution at Low Overpotentials, " proceeding of the symposium on Electrochemical Synthesis and Modification of Materials, MRS Fall Meeting, Boston, MA 1996.
5. K. Sieradzki and K. Wagner, "Selective Dissolution of Ag-Au and Cu-Au Alloys Below The Critical Potential, " proceeding of the symposium on Electrochemical Synthesis and Modification of Materials, MRS Fall Meeting, Boston, MA 1996.
6. S.G. Corcoran and K. Sieradzki, "In Situ Small Angle Neutron Scattering of the Formation of Nanoporous Gold By Electrochemical Dissolution," proceeding of the symposium on Electrochemical Synthesis and Modification of Materials, MRS. Fall Meeting, Boston, MA 1996.

INVITED PRESENTATIONS

1. K. Sieradzki, Curvature Effects In Alloy Dissolution, National Association of Corrosion Engineers (NACE), March 1993, New Orleans, LA.
2. K. Sieradzki, New Developments in Alloy Corrosion, 1994 Gordon Conference on Corrosion, Colby Sawyer College, NH.
3. K. Sieradzki, Curvature Effects In Alloy Dissolution, Brian Ives Symposium on Dissolution and Corrosion, Fall 1994 TMS/ASM Meeting, Rosemont, Illinois.
4. S.G. Corcoran, D.G. Wiesler, and K. Sieradzki, *Small Angle Neutron Scattering of Alloy Corrosion*, National Association of Corrosion Engineers, Spring Meeting, March, 1995, Orlando, Florida.
5. S. G. Corcoran, D.G. Wiesler, and K. Sieradzki, *An In-situ Small Angle Neutron Scattering Investigation of AgAu Dealloying*, The Electrochemical Society, Spring Meeting, May, 1995, Reno, Nevada.
6. K. Sieradzki, *Curvature Effects in Alloy Dissolution*, Electrochem '95, University of Wales, September, 1995, Bangor, Wales.
7. K. Sieradzki, "Stress Effects in Stranski-Krastanov Thin Film Growth Transitions", Symposium on Stress Effects in Electronic Material Nanostructures, 1995 Fall Materials Research Society Meeting, Boston, MA., 1995.

8. K. Sieradzki and J. Knap, "Molecular Dynamic Simulation of Dislocation Nucleation on Vicinal Surfaces", Symposium on Fracture-Instability Dynamics, Scaling and Ductile/Brittle Behavior, 1995 Fall Materials Research Society Meeting, Boston, MA., 1995.
9. K. Sieradzki, K. Wagner, S.R. Bankovic, and N. Dimitrov, "De-alloying Below The Critical Potential", Annual Meeting of the National Association of Corrosion Engineers (NACE), New Orleans, LA, March 13, 1997.

Ph.D's awarded through research on this program since July 1993.

Jaroslav Knap, Ph.D. Arizona State University, December 1997, "Surface stress effects on dislocation nucleation process."

Sean Gerald Corcoran, Ph.D, The Johns Hopkins University, March 1994, "In situ scanning tunneling microscopy of deposition processes."

Fritz, Friedersdorf, Ph.D, The Johns Hopkins University, October 1993, "Stress corrosion cracking of binary noble metal alloys."