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DE-ALLOYING AND STRESS CORROSION CRACKING

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*K. Sieradzki

Department of Materials Science and Engineering
The Johns Hopkins University
Baltimore, Maryland 21218

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*Now at Arizona State University
Department of Mechanical and Aerospace Engineering
Arizona State University
Tempe, Arizona 85287-6106

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1. INTRODUCTION

The major aim of this research program is the study of the physical and chemical processes responsible for corrosion in alloy systems and the effect of these processes on fracture. We have identified several key areas of this problem as unresolved: (1) the mechanical properties of porous de-alloyed structures and dynamic fracture, (2) morphological changes associated with the initial stages of de-alloying - the kinetic surface roughening phenomena and the so-called critical potential and (3) the kinetics of de-alloying processes. In the last 21/2 years there has been considerable progress in each of these areas both by our own research group and other workers.

According to the film-induced cleavage model of stress-corrosion cracking (SCC) the selective corrosion process produces a brittle nano-porous layer which serves to nucleate a high speed crack that penetrates into the underlying ductile substrate. The model was originally formulated to explain the discontinuous nature of the transgranular SCC process in face-centered cubic (fcc) metals [1,2]. Recently a number of groups [3-6] have demonstrated that very thin porous de-alloyed layers can also trigger *intergranular* SCC. The extent of a brittle intergranular cracking event ($\sim 100 \mu\text{m}$) is an order of magnitude larger than the corresponding transgranular event and this has made the intergranular process easier to study experimentally. A sound theoretical understanding for the relative prominence of intergranular or transgranular cracking under different experimental conditions is still lacking.

Our own work in this area has focused on the use of thin foils (10-250 μm thick) which allows for the isolation of a single brittle cracking event. Typically a de-alloyed film of the order of several microns in thickness is used to nucleate a crack which passes entirely through the thin foil. Newman et al. [6] have shown that a de-alloyed layer of less than 0.1 μm gave rise to several microns of transgranular cleavage in α -brass foils. Kelly et al. [7] and Saito et al. [8] have investigated the effect of pore coarsening of de-alloyed layers on film-induced intergranular fracture of Ag-Au foils in 1M HClO_4 . Their work showed that aging of de-alloyed films at

potentials above 550 mV (SCE) quickly destroyed the ability of the film to nucleate brittle cracks owing to pore coarsening. At lower potentials brittle behavior persisted for up to two hours. Chloride ions accelerated the coarsening and pyridine retarded it. Devine has recently demonstrated brittle intergranular behavior of thin Cu-Au alloy sheets in 0.6 M NaCl solution [3]. Ricker et al. showed evidence for film-induced fracture in Rh-electroplated Ni [9].

The results of our own work on the fracture properties of porous de-alloyed gold structures (section 2.3) indicates that this material undergoes a brittle-ductile transition as the size scale of the porosity increases [10]. Similar transitions have been predicted in theoretical work of Duxbury [11] and Kahng et al. [12] and their work provides a framework within which the brittle behavior of porous gold has been understood. The results of the fracture experiments on de-alloyed porous materials are in good agreement with the studies described above where it was found that the ability of the film to induce brittle cracking of thin foils decreased as pore coarsening occurred. High resolution scanning electron microscopy indicates that the individual ligaments fail by a shear process in porous gold regardless of the ligament size. As discussed by Li and Sieradzki [10], the macroscopic brittle behavior of this material results from a localization of the fracture process which develops in the very fine porosity material. On microscopic scales (individual ligament size) the fracture is ductile. The crack which moves through the porous material may nucleate as a high speed ductile crack. In materials with coarser microstructures ligament damage is distributed throughout the volume of material and no fast brittle fracture develops.

Presently, our level of understanding of the fracture related aspects of the SCC process exceeds our knowledge of the electrochemical conditions and the physical processes which allow for the formation of the porous microstructure. Figure 1 shows the generic polarization behavior of a binary alloy. The potential labeled E_c is the so-called critical potential in that it signals the onset of the development of the de-alloyed microstructure which leads to SCC. Sieradzki and Newman [1] have argued that the porous morphology results from a competition of two processes: (1) dissolution of the less noble constituent which causes the surface to roughen on length scales defined by the alloy microstructure and (2) diffusion of the remaining constituent which tends to smoothen the dissolution induced roughness. The critical potential defines the point at which the

smoothing process can no longer keep up with the dissolution induced roughening. A quantitative analysis of this kinetically induced roughening is not possible owing to fundamental difficulties. The basic problem is that we have no framework for understanding corrosion in alloy systems, i.e., how does one define the overpotential for dissolution of the less noble component from an alloy? Does it depend on the composition of the alloy? A simple experimental measurement is complicated by the kinetic coupling of the dissolution of the less noble constituent to the diffusion of the more noble constituent. Ideally, we would like to be able to measure the potential required to dissolve the more active component from just the top surface layer as a function of alloy composition. Some aspects of the work reported on and proposed herein address fundamental issues related corrosion in alloy systems.

2. PREVIOUS WORK

2.1 Morphological Aspects of De-alloying

We performed in-situ scanning tunneling microscopy (STM) experiments aimed at understanding surface morphological changes accompanying selective dissolution in binary alloys [13]. The following questions related to surface diffusivity and porosity coarsening were examined: (i) To what extent does the surface diffusion of metal atoms of one type augment or retard dissolution of atoms of the other type? (ii) How is surface diffusion affected by the electrochemical potential and the nature of the electrolyte? and (iii) What is the role of defect interactions in the diffusion process which controls the annealing and/or coarsening of the de-alloyed surface morphology? The studies were performed on Ag-Au alloy thin films with exclusively [111] texture prepared by the simultaneous sputtering Ag and Au onto heated mica substrates. The Ag-Au system was chosen for this study for the experimental convenience of having air-stable surfaces. The selective dissolution of Ag from alloy films containing from 5 - 65 at% Ag was examined in perchloric acid.

Dissolution of Ag from the low content Ag alloy films resulted in the injection of mainly monovacancy pits into the surface. Measurements on the 5 at% Ag alloy have allowed us to estimate a surface self-diffusivity of $\approx 2 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ (at the de-alloying potential) for a disordered gold surface in the electrolyte. This determination was made by direct measurement of the recession velocity of a ledge of monatomic height owing to the annihilation of vacancies and vacancy clusters at that ledge. We have also examined the process of self-diffusion under conditions where the main diffusive flux is carried by vacancy clusters of 2-20 nm in diameter. These studies focused on the nature of vacancy cluster motion, i.e., do they move owing to purely entropic effects or do interactions bias the random walk process? Using the STM, vacancy cluster motion was easily followed on a terrace. Our results indicate that vacancy clusters on {111} gold surfaces move in an unbiased manner until they are in close proximity to other defects. The in-situ observations indicate that near a step edge vacancy cluster motion stopped for what was often a prolonged period of time. Finally, after times as long as 60 minutes the vacancy cluster moved to the step edge where it was annihilated. The distance from the step edge at which motion halts seems to scale with the diameter of the cluster although observations are not detailed enough at present to make definitive quantitative statements. A portion of this work has been done in collaboration with C.E.D. Chidsey and D.J. Trevor of the AT&T Laboratories.

We performed molecular dynamic (MD) simulations in order to examine substrate mediated elastic interactions between vacancies and between a vacancy and a ledge on a (111) Au surface [14]. This investigation was motivated by the STM investigations described above. The simulations were performed on a 7-layer thick (111) oriented Au slab containing approximately 2500 atoms using periodic boundary conditions in the x-y plane with free surfaces in the z direction. An embedded atom method potential for Au was used. The system was equilibrated using MD and a modified form of the Parinello-Rahman Lagrangian. Figure 2 shows the result for the strain field decay near a surface vacancy. This decay was fit to the algebraic form, $\epsilon \sim r^{-n}$, where r is the radial distance from the vacancy and the best fit for n was -2 . The dilatational strain and the pressure were found to undergo a rapid oscillatory decay to zero at a distance of 1 nm from the vacancy which suggests that there is no long range interaction between vacancies on this

surface. The results of calculations shown in Figure 3 indicate that the elastic interaction between a vacancy and a monatomic step becomes significant only at separations of less than $\sim 1\text{nm}$. The interaction is determined by a mixing of the oscillatory pressure and dilational fields of the step and the vacancy. A vacancy on the upper terrace of a step has to overcome an energy barrier of $\sim 0.1\text{ eV}$ in order for vacancy annihilation to occur at the step edge. A vacancy on the lower terrace of a step is trapped near the edge. These calculations are in accord with the STM observations and have been very useful in helping us interpret some of those results.

It is worth mentioning that we were somewhat surprised to see Ag atoms removed from terrace sites on the surface of this alloy. The reason relates to the magnitude of the de-alloying threshold in the Ag-Au system and our understanding of the processes controlling this behavior. Sieradzki et al. [15] have argued that there should be a clustering of de-alloying thresholds near the 2D and 3D site percolation thresholds. For alloy systems containing elements with a relatively small difference in the equilibrium metal/metal ion electrode potentials (such as Ag-Au) dissolution should only occur from sites with low coordination i.e., ledge and kink sites. In effect dissolution was believed to occur by a layer by layer process which has the requirement that the electrochemically active component percolate in each layer. The STM results described above indicate that these ideas are probably not entirely correct and leave open the possibility that the high de-alloying thresholds observed in some binary alloy systems have a kinetic origin.

A fundamental issue in alloy dissolution which controls compositional aspects of corrosion relating to kinetics and morphology is the manner in which the electrochemical activity of one component is affected by the presence of neighboring atoms of the other component. We have been exploring this using insitu electrochemical STM. The experiments are performed by starting with a virgin alloy surface in ultra pure 1M perchloric acid and slowly raising the electrode potential (10 mV/s) until the Ag atoms on the surface have been removed. A starting composition is chosen ($\sim 5\text{ at\% Ag}$) so that most of the silver atoms which dissolve originate primarily from the surface layer and have predominantly gold atoms as near neighbors. Holding the voltage at the stripping potential allows for the monovacancies to agglomerate into vacancy clusters. Next the potential is reduced to a point allowing the Ag atoms now in solution to plate back on to the

surface. This occurs at a potential significantly below the potential (≈ 0.5 V) required to plate Ag on to a silver substrate. The plated silver atoms fill in the vacancy cluster sites produced in the first stripping wave. On the next stripping cycle we measure the electrode potential associated with removing Ag atoms from clusters with a well defined size distribution as determined from the STM measurements. The size of the vacancy clusters produced is altered simply by changing the holding time at the stripping potential. This process is repeated and for each cycle we measure stripping potentials associated with removing Ag atoms from clusters of successively larger size. Using this technique, we have been able to correlate the stripping potential of Ag to the Ag cluster size. Some results of this work are shown in Figure 4.

Recently, we identified a new experimental approach which we believe is very promising with respect to providing a general understanding of dissolution potentials in alloy systems. The approach involves the general phenomenon of underpotential deposition (upd) and the identification that this process is related to some of the issues important to alloy dissolution discussed above. 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 have been examining the upd and stripping behavior of Ag in 1M HClO₄ on both pure Au and Ag-Au alloy electrodes. Our experiments are the first which we know of where upd behavior on *alloy* substrates has been examined. Ag-Au electrodes were prepared using the same thin film techniques as those described above. Figure 5 shows that upd of Ag occurs on the alloy substrates and that the potential of the upd wave and the stripping wave depends on the composition of the substrate. The results characterizing the electrode behavior roughly falls into the category of either Au-like or Ag-like and this behavior parallels the known dissolution behavior of Ag from Ag-Au alloys [16]. The break in the alloy dissolution behavior occurs at roughly 65 at% Ag and the break in the upd behavior occurs at roughly 30 at% Ag. This quantitative difference is to be 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.

In situ STM of the upd process indicates that point defects on the surface of the electrode play an important role in the electro-adsorption process. We found that monatomic steps were not

strong preferential adsorption sites even at low overpotentials for upd. The monolayer was observed to nucleate at multiple sites on terraces which we associate with point defects. The density of these defects is of the order of a few percent of a monolayer. The stripping process is reversible in that the last spots on the surface to fill in are the first to be removed.

We have made two trips to the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) to perform specular and nonspecular x-ray reflectivity measurements on de-alloyed surfaces. This work is being performed in collaboration with S. K. Sinha (Exxon Corporate Research), K.G. Huang (Argonne Nat. Lab.) and B.M. Ocko (BNL) on the X-22C beam line. Roughening of the de-alloyed Ag-Au surface was detected in both specular and diffuse specular scan modes. Initial results shown in Figure 6 indicate the development of a peak at $q_z = 0.04$ nm corresponding to a global microstructural length scale of about 1.5-2.0 nm for the porosity. This is consistent with our STM results. We are currently fitting the scattering data to a model developed by Sinha for reflectivity from self-affine surfaces. The eventual aim of this work is to obtain a real time global characterization of the roughening and subsequent annealing process using *in situ* x-ray techniques.

2.2 Chaotic Aspects of De-alloying Kinetics

De-alloying kinetics determine the rate of porosity formation and the rate of stress-corrosion crack advance. Experiments in our laboratory designed to measure de-alloying rates on bulk alloys over the last few years indicated that transport processes on the solution side of the interface was rate limiting under some circumstances. The major result of these experiments which caught our attention related to the eventual development of complicated oscillatory behavior or "noise" in the dissolution current-time behavior of a selective dissolution process. As a simple experimental model of the complicated de-alloyed tunnel microstructure, we decided to examine the dissolution behavior of a one dimensional artificial pit electrode [17]. The artificial pit configuration is a silver wire embedded in epoxy in a manner similar to lead in a pencil. In the experiment the silver wire is dissolved back at a constant applied electrochemical potential and the

silver dissolution current is monitored during the process. The term one dimensional relates to the *macroscopic* one dimensional transport fields maintained by the geometry. The results of these experiments have been fascinating. We observe *chaotic* electrochemical oscillations associated with the silver dissolution process. An interesting aspect of this work is that the oscillations lead to the development of real *microscopic* pits of varying sizes on the surface of the artificial macroscopic pit. The oscillations result directly from a process associated with a metastable salt film which forms owing to mass transport limitations intrinsic to "pitting dissolution". We analyzed the oscillatory behavior by determining phase space plots, attractor dimensions, and the Lyapunov exponents characterizing the chaotic system.

We have modeled the pitting dissolution process using finite difference numerical methods to integrate the partial differential equations describing the process in order to elucidate the mechanism of the oscillatory chaotic behavior. The following processes were taken into account in the model: (1) metal dissolution under low field and/or high field conditions, (2) iR and concentration polarization effects resulting from diffusion and electromigration transport (3) moving boundary effects (4) salt film precipitation at a critical level of supersaturation and (5) chemical dissolution of the salt film. As shown in Figure 7, at a constant level of applied dc voltage, our model of the single pit only undergoes regular periodic oscillations. We have not been able to drive single pits into chaotic behavior. Figure 8 shows the behavior of 2 pits that have been resistively coupled simulating the behavior of microscopic pits on the surface of the macroscopic artificial pit. As a function of the applied dc voltage the oscillations become more complex until chaotic behavior is observed. The embedding dimension for the attractor was found to be less than 5 and the positive Lyapunov exponent was 2.2. An electrical analogue of the electrochemically coupled pits is a system of two resistively coupled diode relaxation oscillators. The behavior of this electrical system was examined some time ago by Gollub, Brunner, and Danly [18].

2.3 Fracture of Porous De-alloyed Structures, Dynamic Fracture, and SCC

We have already mentioned that the oscillations lead to the development of microscopic surface porosity. Owing to some of our general ideas regarding the role of porosity in SCC, we decided to attempt to stress corrode silver under conditions simulating the electrochemical conditions responsible for the oscillations and concomitant porosity development. We examined the SCC behavior of Ag wire electrodes under conditions for which salt film instabilities occur [19]. The electrolyte was 1M HClO₄ saturated with Ag⁺ ions added as Ag₂O. Constant extension rate tests were conducted in this electrolyte at a displacement rate of 1.3×10^{-5} cm/s with the overpotential set to maintain a current density of ≈ 1 mA/cm². A special cell made of high density graphite was used for these tests. The cell served as the counter electrode and its cylindrical symmetry assured uniform dissolution of the wire. A summary of the SCC test results is shown in Table I. These results demonstrate that under appropriate electrochemical and mechanical conditions SCC can occur even in a system undergoing active dissolution. This behavior is counter to the widely held belief that global passivity is a requirement for occurrence of SCC. It is also important to point out that we are not suggesting that all corrosion induced porosity leads to SCC. The size scale of the porosity, the thickness of the porous layer, and the "disorder" in the porosity are all parameters which determine the ability of such layers to induce SCC. For example α -brass becomes porous owing to de-alloying in sea water, yet it is well known that α -brass does not undergo SCC in aqueous chloride environments.

Another system which we identified that displays porosity induced SCC during active dissolution is Cu in non-tarnishing cupric ammonia solutions. Oriented copper single crystals tested at high strain rates in this electrolyte were observed to undergo severe stress-corrosion cracking [21]. A porous surface morphology and concomitant cracking develops in these samples when there is a balance between the rate of corrosive attack which is manifested as etch pitting and the imposed dynamic strain rate. At too low a strain rate the relatively high lateral velocity of etch pit walls prevents distinguishable etch pits of sub-micron size from forming. At too high a strain rate failure occurs by normal ductile processes. Using a simple model, we developed general quantitative arguments describing the onset of porosity formation in this system by considering the statistics of etch pit nucleation. We assumed etch pit nucleation to result from thermally activated

localized desorption of an ion or breakdown of the air-formed film in the neighborhood of a dislocation core. Our analysis demonstrates that dynamic straining collapses the width of the distribution of etch pit nucleation times which results in the development of a homogeneous microporous morphology leading to the cleavage like stress-corrosion cracking observed in this system.

We completed work on the fracture properties of random porous gold [10]. The focus of this aspect of the program has been to understand the intrinsic fracture behavior of the de-alloyed material which trigger film-induced cleavage events. Porous Au was produced from $\text{Ag}_{0.74}\text{Au}_{0.26}$ alloy beams by selectively leaching out the Ag and giving the resultant porous structure treatments at various temperatures for fixed duration in order to obtain geometrically similar microstructures at different length scales. The microstructure is that of an interpenetrating two-phase solid, similar to porous vycor glass. The length scales obtained ranged from 10-1000 nm. Digital image analysis was used to characterize the pore size and ligament size distributions. Load-displacement curves were obtained for the samples in 3-point bending. The results of the mechanical tests showed that porous Au undergoes a microstructurally controlled brittle/ductile transition as shown in Figure 9. High resolution scanning electron microscopy of the fractured samples indicated that there was no change in the microscopic fracture mode of the individual ligaments in the different samples. The fractured ligaments in all samples displayed both slant and flat surfaces which we interpret as mainly ductile. The brittle behavior resulted when the microstructure allowed for a localization of the fracture process, i.e., the number of fractured ligaments in the failed sample was approximately equal to the number of ligaments contained in a cross section of the beam. For samples containing larger pores and ligaments the ligament fractures were distributed throughout the sample volume and this resulted in ductile sample failure. Our interpretation of these results has been greatly influenced by theoretical and numerical work by Duxbury [11] and Kahng et al [12].

A fundamental question for the film-induced cleavage model of SCC relates to the dynamics of the cracking process, i.e., how fast is the crack moving at the instant it leaves the de-alloyed layer and penetrates the normal metal? We have been doing experimental and computer simulation work in order to better understand this issue. New molecular dynamic (MD) investigations were performed to follow up on some of our earlier work on dynamic fracture [21].

The major conclusions in the earlier MD work on the 2D triangular Johnson solid were that the terminal velocity of a crack was found to be only about half of that predicted by continuum theory and that the crack achieved terminal velocity much more rapidly than described by the continuum crack tip equation of motion [22-24]. The aim of the present simulations was to evaluate the effect of the non-linear force law which we had previously employed. Figure 10 shows our recent MD results for 2D triangular linear elastic (Hookean) and Johnson solids. The sample configurations used were identical to those examined earlier. Our results demonstrate that non-linearity in the force-displacement law reduces the magnitude of the crack terminal velocity to about 63% of the value of that in a linear elastic solid. Additionally, the value for the crack tip terminal velocity which we obtain for the Hookean solid is still only 64% of the long wavelength Rayleigh velocity. In Hookean solids or Johnson solids artificially cut off at small strains, cracks traveled at a terminal velocity defined by the *phase velocity* of the shortest wavelength Rayleigh wave. This result is in agreement with earlier work of Ashurst and Hoover [25].

Considerable progress was made in developing high speed pulsed holographic recording to "freeze" the image of cracks propagating in glass [26]. These techniques were perfected using thin glass slides and could be used in the future for crack velocity determination during a film-induced cleavage event. Preliminary studies used a pulsed Nd-YAG laser with a nine nanosecond pulse duration to holographically record the position of crack fronts in glass. A variable length optical delay line permitted two holographic exposures to be made in rapid succession varying from about 50 to nearly 500 nanoseconds. The initial studies demonstrated the potential of this technique for recording crack position and shape, the fact that the crack position was recorded at only two instants in time permitted only a single average velocity determination during crack propagation. The inability to precisely determine the time at which propagation initiated in any test did not allow us to reliably link data from several tests employing different delay times to produce a single composite crack history curve. In order to permit consecutive measurements of crack velocity for a single fracture event the holographic system was modified. Using custom manufactured optical components a new technique was developed so that a single pulse from the recording laser could be split into 10 optical beams each of which could be separated in time over intervals in the range

of 28-160 nanoseconds. On a single holographic plate 10 holographic images were recorded in sequence to produce a set of images describing the crack position. The holographic reconstruction of each of the images could be examined microscopically to facilitate accurate measurement of crack length. In addition a loading frame was constructed which permitted pre-loading of a pre-cracked specimen. A provision has been made to permit an explosive charge to be used for rapid loading of the specimen to induce crack growth. In addition, an experimental procedure was developed using intense pulsed laser illumination to generate sharp stable pre-cracks in the glass specimen to be loaded in the test frame.

Our greatest disappointment in the last 2 1/2 years of this work is that we have not been able to make a crack velocity measurement during a film-induced brittle fracture event. The optical techniques which we developed suffer from a triggering problem which is the reason for using explosive charges to load the glass specimens. With the present laser equipment available to us it does not seem that the optical approach will be successful and we plan on developing other techniques.

Finally, de-alloyed film induce brittle fracture experiments are being performed on Ag-Au and Cu-Au alloys in the form of thin sheets in the range of 10-250 μm in thickness. The major focus of this work has been the following: (1) determination of the functional relationship between de-alloyed film thickness and crack penetration depth (2) identification of the selection mechanism determining the intergranular or transgranular nature of the fracture, and (3) direct measurement of the crack velocity during the fracture event.

We are developing an indirect potential drop technique to measure dynamic crack motion. Owing to the high conductivity of the typical sheet sample used in film-induced cleavage experiments, there is only a small variation in the potential drop (under application of a constant current) as crack propagation proceeds through the thickness of the sample. Recent work of Fineberg et al. [27] has given us some new ideas for employing this technique in our research. We intend to overcome the high conductivity difficulty by coating the edge of the sample with an insulating layer and then covering the insulating layer with about 50 nm of gold. The 50 nm gold

layer should be resistive enough to provide a large gain in sensitivity to crack length changes. Microelectronic thin film techniques will be employed for the production of these samples.

We are performing preliminary work in order to determine the optimum conditions for the film thickness-crack penetration experiments. The parameters being examined are electrolyte composition, alloy composition, de-alloying potential, and holding potential. These experiments are performed on thin sheet tensile samples by (a) forming a de-alloyed layer of prescribed thickness under zero applied load, (b) shifting to another potential (holding potential) in order to "freeze in" the microstructure and (c) load (or displacement) pulsing the sample. The aim of the recipe is to allow us to grow de-alloyed layers with with the same microstructure over a range of thickness. Experimental difficulties relate to porosity coarsening which can occur in step (a). This coarsening is known to modify and/or destroy the ability of the film to induce a brittle cracking event [7]. We have made good progress in identifying the appropriate test conditions. The first set of complete experiments will be performed on $\text{Cu}_{0.70}\text{Au}_{0.30}$ alloy sheets in 1M HCl. Preliminary experiments indicate that at appropriate potentials we can hold for times as long as 30 minutes without measurably affecting the ability of a 2 μm de-alloyed layer to induce brittle fracture in 60 μm sheets.

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FIGURE CAPTIONS

Figure 1. Schematic illustration of the anodic polarization curve for a binary A-B alloy. The curves for the individual elements are shown. E_c is the critical potential for selective dissolution in the alloy.

Figure 2. The strain field of a vacancy on a (111) Au surface. ϵ_r is the radial strain, ϵ_θ is the tangential strain, and ϵ_z is the strain perpendicular to the surface.

Figure 3. The vacancy (and trivacancy) energy as a function of position from a step on a (111) Au surface. Negative distances correspond to positions on the lower side of the step and positive distances correspond to positions on the upper side of the step.

Figure 4. Cyclic voltammetry of underpotential stripping and plating for a 7% Ag, Ag-Au alloy in 1M HClO₄. The arrows indicate the position of the major upd waves. T_2 is the hold time in seconds at 650 mV and T_1 is the hold time at 100 mV. All potentials are measured with respect to the potential of bulk Ag equilibrated with 10^{-3} M Ag⁺ ions. The hold time T_1 allows for the diffusion limited plating of the de-alloyed Ag to the electrode surface. The hold time T_2 allows for vacancy cluster growth on the de-alloyed surface. Both (a) and (b) contain three consecutive curves (marked 1, 2, and 3) for the indicated hold times. Note the shift in the upd and stripping waves as T_2 increases.

Figure 5. Under potential deposition and stripping on Ag-Au alloy substrates.

Figure 6. Specular and diffuse scans from a Ag₅₀Au₅₀ alloy film surface. (a) before de-alloying (b) after de-alloying. Note that the 1° off diffuse scan falls off faster for the smooth surface (a) in the region of $0.35 \text{ \AA}^{-1} < q_z < 1.0 \text{ \AA}^{-1}$. Also note the bump on the specular scan at about $q_z = 0.4 \text{ \AA}^{-1}$.

Figure 7. Model results of the single pit showing oscillatory behavior. The overpotential for dissolution determined at the metal/solution interface is 25 mV.

Figure 8. Model results of the coupled pit behavior. The pits are slightly different in diameter and consequently oscillate at slightly different voltages and frequencies. (a) At 26 mV the second pit is just activated and simply perturbs the oscillatory behavior of the first pit. (b) 30 mV (c) At 45 mV chaotic behavior occurred.

Figure 9. (a) Scaled fracture displacement Δ_f and (b) fracture strain ϵ_f vs the sample size L , as measured in units corresponding to the natural length scale in each of the structures. Note the rapid decrease in the fractures strain with increasing L indicative of the ductile-brittle transitional behavior.

Figure 10. Normalized crack-velocity-crack-length results for Hooke's law and Johnson 2D solids showing the response of a crack in a sample loaded to just above the critical Griffith load. ϵ_f is the fracture strain, l_0 is the initial crack length, and V_c/V_L is the crack velocity normalized by the longitudinal sound velocity of the material.

Figure 1. Schematic illustration of the anodic polarization curve for a binary A-B alloy. The curves for the individual elements are shown. E_c is the critical potential for selective dissolution in the alloy. p^* is the de-alloying threshold which is related to what is often termed the "parting limit" of the alloy.

Figure 2. The strain field of a vacancy on a (111) Au surface. ϵ_r is the radial strain, ϵ_θ is the tangential strain, and ϵ_z is the strain perpendicular to the surface.

Figure 3. The vacancy (and trivacancy) energy as a function of position from a step on a (111) Au surface. Negative distances correspond to positions on the lower side of the step and positive distances correspond to positions on the upper side of the step.

Figure 4. Cyclic voltammetry of underpotential stripping and plating for a 7% Ag Ag-Au alloy in 1M HClO_4 . The arrows indicate the position of the major upd waves. T_2 is the hold time in seconds at 650 mV and T_1 is the hold time at 100 mV. All potentials are measured with respect to the potential of bulk Ag equilibrated with 10^{-3} M Ag^+ ions. The hold time T_1 allows for the diffusion limited plating of the de-alloyed Ag to the electrode surface. The hold time T_2 allows for vacancy cluster growth on the de-alloyed surface. Both (a) and (b) contain three consecutive curves (marked 1, 2, and 3) for the indicated hold times. Note the shift in the upd and stripping waves as T_2 increases.

Figure 5. Under potential deposition and stripping on Ag-Au alloy substrates. The surface concentrations have been corrected for segregation.

Figure 6. Specular and diffuse scans from a $\text{Ag}_{50}\text{Au}_{50}$ alloy film surface. (a) before de-alloying (b) after de-alloying. Note that the 1° off diffuse scan falls off faster for the smooth surface (a) in the region of $0.35 \text{ \AA}^{-1} < q_z < 1.0 \text{ \AA}^{-1}$. Also note the bump on the specular scan at about $q_z = 0.4 \text{ \AA}^{-1}$.

Figure 7. Model results of the single pit showing the current vs time oscillatory behavior. The overpotential for dissolution determined at the metal/solution interface is 25 mV.

(a)

(b)

(c)

Figure 8. Model results for current vs time of the coupled pit behavior. The pits are slightly different in diameter and consequently oscillate at slightly different voltages and frequencies. (a) At 26 mV the second pit is just activated and simply perturbs the oscillatory behavior of the first pit. (b) 30 mV (c) At 45 mV chaotic behavior occurred.

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