

DOE/ER/45421--2

DE92 009086

RECEIVED BY USIA
MAY 1 8 1992

Critical Issues in De-alloying and Transcrystalline Stress-Corrosion Cracking

Progress Report

for Period March 1, 1991 - February 28, 1992

K. Sieradzki and J.W. Wagner
Department of Materials Science and Engineering
The Johns Hopkins University
Baltimore, Maryland 21218

March 1992

Prepared for

The Office of Basic Energy Sciences of the U.S. Department of Energy
Agreement No. DE-FG02-90ER45421

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This report describes our progress since the last reporting period (March 1991) and details the third year research plans on the program, "Critical Issues in De-alloying and Transcrystalline Stress-Corrosion Cracking" (G/C No: DE-FG02-90ER5421) which was funded in July 1990 by the Office of Basic Energy Sciences of The United States Department of Energy. The three major components of the program relate to (1) kinetic aspects of the selective dissolution in alloys and the coarsening of de-alloyed layers, (2) measurements of crack dynamics during film induced cleavage processes, and (3) mechanical properties of the intrinsic de-alloyed layers responsible for film-induced cleavage events. We discuss progress in each of these areas below.

During May and June of 1991 we set up our own electrochemical scanning tunneling microscope (STM) and atomic force microscope (AFM) at Hopkins. Insitu experiments were performed examining the following aspects of de-alloying in Ag-Au alloys:

(a) Site selectivity - A fundamental issue in alloy dissolution which controls compositional aspects of corrosion relating to kinetics and morphology is the manner in which different types of sites on a crystal surface (terrace, step, kink, and etc.) contribute to the corrosion current at a prescribed value of the electrochemical potential. We have been exploring this using insitu scanning tunneling microscopy. 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 (~ 10 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. 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 (≈ 0.5 V) the potential required to plate Ag on to a silver substrate (underpotential deposition). 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. 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 to site selectivity in terms of number and identity of nearest neighbors. A publication on this topic is currently in preparation.

(b) Surface mobility issues - Insitu STM observations of vacancy cluster development and motion following a de-alloying cycle support earlier indications that cluster-ledge interactions control the later stages of surface annealing. Vacancy cluster motion was easily followed on a terrace. 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 and has recently appeared in *Science Magazine*. We have performed molecular dynamic simulations of vacancy-vacancy and vacancy-step interactions on (111) Au surfaces and the results have been very helpful in understanding these STM observations. These simulations are discussed later in this report.

(c) Porosity formation - Insitu STM selective dissolution experiments have been performed in order to examine the role of composition in determining de-alloyed morphologies. We found that no porosity formation (on length scales of 0.5 nm or greater) occurred for alloys with less than c.a. 65 at% Ag in a 1M perchloric acid electrolyte. This composition corresponds to the well known "parting limit" in this alloy system. For alloys containing greater than 65 at% Ag, porosity formation occurred above a threshold

electrochemical potential known as the critical potential. Our observations clearly indicate that this potential is a kinetically controlled process. Furthermore, the porosity formation developed homogeneously over the alloy surface and seems to be related to a spinodal decomposition mechanism rather than one involving nucleation and growth. This interesting new issue is currently under investigation.

We have performed molecular dynamic investigations aimed at examining the nature of surface vacancy interactions with one another and ledges on a (111) Au surface. This investigation was motivated by our recent insitu STM investigations of de-alloying of (111) oriented Ag-Au alloy surfaces. Analysis of resultant vacancy cluster size distributions and observation of vacancy cluster motion following the stripping of Ag from the surface of a Ag-Au alloy indicated that diffusion of vacancies and vacancy clusters was not occurring by unbiased random walk processes. The purpose of our study was to examine substrate mediated elastic interactions between vacancies and between a vacancy and a ledge. We found that near a surface vacancy the strain field decays as r^{-n} with $n \sim 2$ and the dilatational strain undergoes a rapid oscillatory decay to zero at a distance of 1 nm from the vacancy. This result suggests that there is no direct long range elastic interaction between vacancies on this surface. The elastic interaction between a vacancy and a step only becomes significant at separations of less than ~ 1 nm and is controlled by a mixing of the oscillatory pressure field of the step with the dilatational field of the vacancy. Our calculations indicate that a vacancy on the upper portion of a terrace associated with a step has to overcome an energy barrier of ~ 0.1 eV in order for vacancy annihilation to occur at the step edge. These calculations have been very useful in helping us interpret some of our STM results.

A number of investigators have recently demonstrated that both intergranular and transgranular stress-corrosion cracking can result from a film-induced cleavage process. During the past year our own work has focused on the relationship between the de-alloyed film morphology and extent of the fast fracture event. Electrochemical double-layer capacity measurements are being used to characterize the porosity in the de-alloyed layer just prior to the cleavage event and the scanning electron microscope is used to examine the extent to which the brittle fracture penetrates into the uncorroded substrate. Additionally we are investigating the use of electric potential drop techniques (direct and indirect) in addition to pulsed holographic recording (described below) for measuring the instantaneous crack velocity during cleavage.

Considerable progress has been made in developing high speed pulsed holographic recording to "freeze" the image of cracks propagating in glass. These techniques are being perfected using thin glass slides and will be used in the future for crack velocity determination during a film-induced cleavage event. Recall that preliminary studies during the first year 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. While these early 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 during this program year. 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, therefore, 10 holographic images could be recorded in sequence to produce a set of images describing the crack position. The holographic reconstruction of each of the 10 images can be examined microscopically to facilitate accurate

measurement of crack length. In addition a loading frame has been constructed which permits 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.

We have made two trips to the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) to perform 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-alloy Ag-Au surface was detected in both specular and a diffuse specular scan modes. Initial results show 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. We are currently fitting the scattering data to a model developed by Sinha for reflectivity from self-affine surfaces. One additional trip is planned

Anticipated Progress During 3rd Year Funding (July 2, 1992-June 30, 1993)

Crack dynamics during film-induced cleavage processes

In the final months of the current program year crack propagation studies in glass using the high speed holographic cinematography system will be completed. During the next program year minor modifications will be made to the system which will permit the study of thin Ag-Au alloy sheets under film-induced cleavage conditions.

Additionally, an indirect potential drop technique will be used 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 J. Fineberg at The University of Texas has given us some new ideas and hope 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 ~ 50 nm of gold. The 50 nm gold layer will be resistive enough to give us a huge gain in sensitivity to crack length changes. Microelectronic thin film techniques will be employed for the production of these samples.

Kinetics of de-alloying and coarsening of de-alloyed layers

In situ STM work will focus on identifying the kinetic factors which determine the length scale of the porous structure which forms during selective dissolution. The effect of different anions on the critical potential and the coarsening process will be examined and linked to film-induced cleavage behavior. In particular, we will try to determine what effect the chloride ion has on the vacancy size distribution which develops on de-alloying. We will compare the behavior of the Ag-Au system to Cu-Au system at equal compositions of solute in an effort aimed at sorting out the role of the dissolved atom in setting the length scale of the porous gold which develops on de-alloying.

Further work will continue examining the role of site selectivity in the dissolution process using the cluster technique which we developed during the last year. Alloy compositions up to about the parting limit (65 at% Ag) will be tested and this information should be very useful in helping us sort out kinetic and thermodynamic issues related to the critical potential. We will continue to study the surface mobility of vacancy clusters and compare our observations with molecular dynamic and Monte Carlo calculations.

In the next year we will develop a cell which will be used for insitu x-ray reflectivity measurements at the NSLS. We hope to examine the time evolution of de-alloyed porous structures in these experiments for two different Ag-Au alloy compositions in an ultra-pure and a chloride containing perchloric acid electrolyte.

Mechanical Properties of de-alloyed layers

We will continue with our study examining the morphology of de-alloyed layers and the extent of the fast fracture event. Electrochemical double layer capacity measurements will be used to characterize the porosity in the de-alloyed layer just prior to the fast fracture event. This work will be performed on Ag-Au and Cu-Au alloys under conditions similar to the conditions examined in the insitu STM experiments.

We also plan a new study examining the mechanical properties of porous gold structures produced from de-alloying Cu-Au alloys. This study will be similar to a recent study of porous gold produced from Ag-Au alloys which we recently published in *Physical Review Letters*. Based upon some work of T. Devine (U.C. Berkley) we have reason to believe that the size scale of the porosity produced during the de-alloying of Cu-Au alloys is considerably larger than that found for the Ag-Au system. Consequently experiments along these lines should provide us with exciting new information on the ductile/brittle transition which we discovered in porous gold. This has obvious implications regarding understanding of stress-corrosion cracking phenomena in these systems.

Students supported by this program:

Sean Corcoran - full time support: Sean is involved with all aspects of this work except for the dynamic crack velocity measurements
enrolled 9/90 in graduate school
expected graduation, 4/95

Scott Steckenrider - support 1/4 time (3 months): Scott is working on the dynamic crack propagation measurements
enrolled 9/88 in graduate school
expected graduation, 1/93

Papers

Rong Li and K. Sieradzki, *Ductile/Brittle Transition in Random Porous Au*, Phys. Rev. Letters, Vol. 68, pp. 1168-1171 (1992)

I. Oppenheim, D. Trevor, C. Chidsey and K. Sieradzki, *In-Situ STM Observation of Corrosion of Silver-Gold Alloys*, Science, Vol. 254, 687 (1991)

K. Sieradzki and Rong Li, "Comment on New Dynamical Equation for Cracks" Phys. Rev. Letters, Vol. 67, 3042 (1991)

K. Sieradzki, and F.A. Streitz, *The Mobility of Surface Vacancies on Au (111) Surfaces*, Phys. Rev. B, in press

S.G. Corcoran and K. Sieradzki, *Chaos During The Growth of An Artificial Pit*, J. Electrochemical Soc. in press

S.G. Corcoran and K. Sieradzki, *Porosity Induced SCC of Ag*, Scripta Metallurgica, Vol. 26, pp. 633-637 (1992)

K. Sieradzki and J.S. Kim, *Etch Pitting and Stress Corrosion Cracking of Copper*, Acta Metall., in press.

M.J. Ehrlich and J.W. Wagner, *Nanosecond Scale Optical Pulse Separations in Double Exposure Holographic Interferometry or Investigation of Transient Events*, Appl. Physics Lett. Vol. 58, pp. 2883-2885 (1991)

J.S. Steckinrider, M.J. Ehrlich, and J.W. Wagner, *Pulsed Holographic Recording of Very High Speed Transient Events*, SPIE Proceedings, (F.P. Chiang, editor), Vol. 1554B, SPIE Bellingham, WA., pp. 106-112 (1991)

Presentations

S. G. Corcoran, P. Searson and K. Sieradzki, *Current Oscillations During the Growth of a Silver One-Dimensional Artificial Pit*, The Electrochemical Society Meeting, Phoenix, Arizona, 1991. (invited)

D.J. Trevor, C.E.D. Chidsey, P.L. Trevor, I. Oppenheim and K. Sieradzki, *In-Situ Scanning Tunneling Microscopy of Corrosion in Silver Gold Alloys*, The Electrochemical Society Meeting, Phoenix, Arizona, 1991. (invited)

K. Sieradzki, *Ductile-Brittle Behavior of Porous Metals and Stress-Corrosion Cracking*, The Metallurgical Society, Fall Meeting, Cincinnati, Ohio, 1991. (invited)

K. Sieradzki, *Etch Pitting and Stress-Corrosion Cracking of Copper Single Crystals*, The Metallurgical Society, Fall Meeting, Cincinnati, Ohio, 1991. (invited)

R.C. Newman and K. Sieradzki, *Film-Induced Cleavage*, The Metallurgical Fall Meeting, Cincinnati, Ohio, 1991. (invited)

K. Sieradzki, *Brittle Behavior of Ductile Metals During Stress-Corrosion Cracking*, American Physical Society (APS) March, 1992 Indianapolis, Indiana (invited)

K. Sieradzki, S.G. Corcoran, L. Sperling and P. Searson, *De-alloying and Deposition Processes*, National Association of Corrosion Engineers (NACE), April 1992, Nashville TN (invited)

S.G. Corcoran and K. Sieradzki, *Characterization of Chaotic Dissolution in Metals and Alloys*, National Association of Corrosion Engineers (NACE), April 1992, Nashville TN (invited)

K. Sieradzki, *Physics of Corrosion in Alloys*, Conference on Advances in Corrosion and Protection, July, 1992, UMIST, Manchester, U.K. (invited)

K. Sieradzki, *In-Situ STM and AFM Studies of Alloy Corrosion*, Faraday Division of the Royal Society of Chemistry, General Discussion on "The Solid Liquid Interface at High Resolution" (invited)

K. Sieradzki, *In-situ Scanning Tunneling Microscopy of Corrosion in Ag-Au Alloys*, 1992 Gordon Conference on Corrosion (invited)

K. Sieradzki, Invitation to participate in collaborative research on the Dynamics of Fracture and Growth Processes, Theoretical Physics Institute, University of Santa Barbara, Sept-Oct. 1992

END

DATE
FILMED
4 12 81 92

