A STUDY OF GRAIN BOUNDARY SEGREGATION USING THE AUGER ELECTRON EMISSION TECHNIQUE

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ABSTRACT

Studies of admiralty brass stress corrosion in copper sulfate and copper nitrate have provided information on environmental contributions to SCC in acid systems. SCC susceptibility is a function of bulk corrosion rate, and is maximized when conditions favor localized attack. At a given pH and stress, solution composition determines crack initiation rates, but the crack crevice environment is not characteristic of the bulk salt solution. Crack propagation appears to be strongly related to anodic dissolution; however, contributions from thin film rupture and hydrogen embrittlement must be considered. The brittle tarnish rupture mechanism is not operative during the stress corrosion of the copper alloys in any of a wide variety of environments.

Theoretical models have been developed that are providing a basic understanding of segregation to grain boundaries. The statistical thermodynamic approach using a distribution of energy sites at the grain boundary has extended the McLean model and the results are consistent with sulfur segregation in Ni_3Al and $Ni_3(Al,Ti)$. A model based on the interatomic potentials of Cu-Cu, Cu-Bi, and Bi-Bi shows the segregation of Bi should occur at grain boundaries and that the segregation should be more extensive at asymmetrical grain boundaries. This is in agreement with earlier measurements made in this program.

Grain boundary diffusion experiments continue. The Mo-S-Cr system is still the most desirable one for this purpose but difficulty has been encountered in controlling the sulfur additions and keeping the Cr plate on the surface. A new closed system has been designed that appears to have solved the problem. Experiments using the Cu-Bi-Ni system have been successful so it is clear that the general approach to studying grain boundary diffusion and the effect of impurity segregation on this diffusion will be successful.

I. INTRODUCTION

This report summarizes the work performed under Contract E(11-1)-2166 for the year 1976. The program has been directed toward the utilization of Auger Electron Spectroscopy (AES) to study segregation of impurities to grain boundaries that result in a deterioration in the properties of materials. Included in the properties of interest are grain boundary fracture, stress corrosion cracking, and grain boundary mobility during annealing and sintering operations. The past year has seen a greater effort on the development of theoretical approaches to develop a broader understanding of the mechanism of segregation and its relation to embrittlement.

Several papers (see attached list) have been published or prepared for publication in the past year.

II. RESEARCH PROGRESS (1976)

A. Stress Corrosion

We previously reported that admiralty brass (1Cu-28Zn-1Sn alloy) is susceptible to stress corrosion in acidic sulfate environments. The fracture surface is transgranular, characterized by cleavage facets and by a thin Sn-rich layer at the leading edge of the crack. The fact that Sn is an effective poison for hydrogen recombination suggested that hydrogen embrittlement may play a role in the stress corrosion mechanism. Further environmental studies on this system have been completed.

1. Corrosion Rate and Stress Corrosion Kinetics

Intermediate corrosion rates tend to maximize SCC susceptibility by enhancing the tendency for sustained localized corrosion. General exterior corrosion rates may not influence crack tip propagation events, but they can play a major role in crack initiation. If the corroding solution is highly oxidizing, gross surface dissolution will occur. In weak solutions dissolved copper will precipitate as a thick protective Cu_2O layer, retarding further attack. Solutions of intermediate concentration should provide the critical combination of dissolution rate and tarnish solubility that may produce local surface heterogeneities or allow pre-existing heterogeneities to function as crack initiation sites. This premise was tested by exposing admiralty tube specimens to several concentrations of copper sulfate solution. Specimen surface conditions and crack growth were monitored with time. Crack growth was measured with the nondestructive eddy current technique. This method detects flaws in materials by measuring current variations resulting from changes in the medium conductivity. A defect of any given character must be standardized and current signals must be calibrated in terms of the physical dimensions of the flaw. In the admiralty tubing all stress corrosion cracks were tight longitudinal fissures initiating on the outside diameter surface. Eddy current signals were correlated with crack depths by metallographic examination in preliminary tests. For crack growth studies, samples were tested in the eddy current jig and returned to solution for additional exposure. Results for admiralty in copper sulfate are shown in Figure 1. No SCC was observed in dilute solutions which produced a thick surface tarnish, or concentrated solutions that roughened and dulled the specimen surface. SCC was produced at intermediate solution concentrations. Specimen surfaces exhibited a semi-continuous or patchy tarnish product.

2. Specific Ion Effects

Specific ion effects of similar electrolytes were also examined. It is unlikely that specific adsorption of ions from an aqueous solution would accelerate crack propagation rates in admiralty or any single phase brass. For ductile materials the Griffith equation should

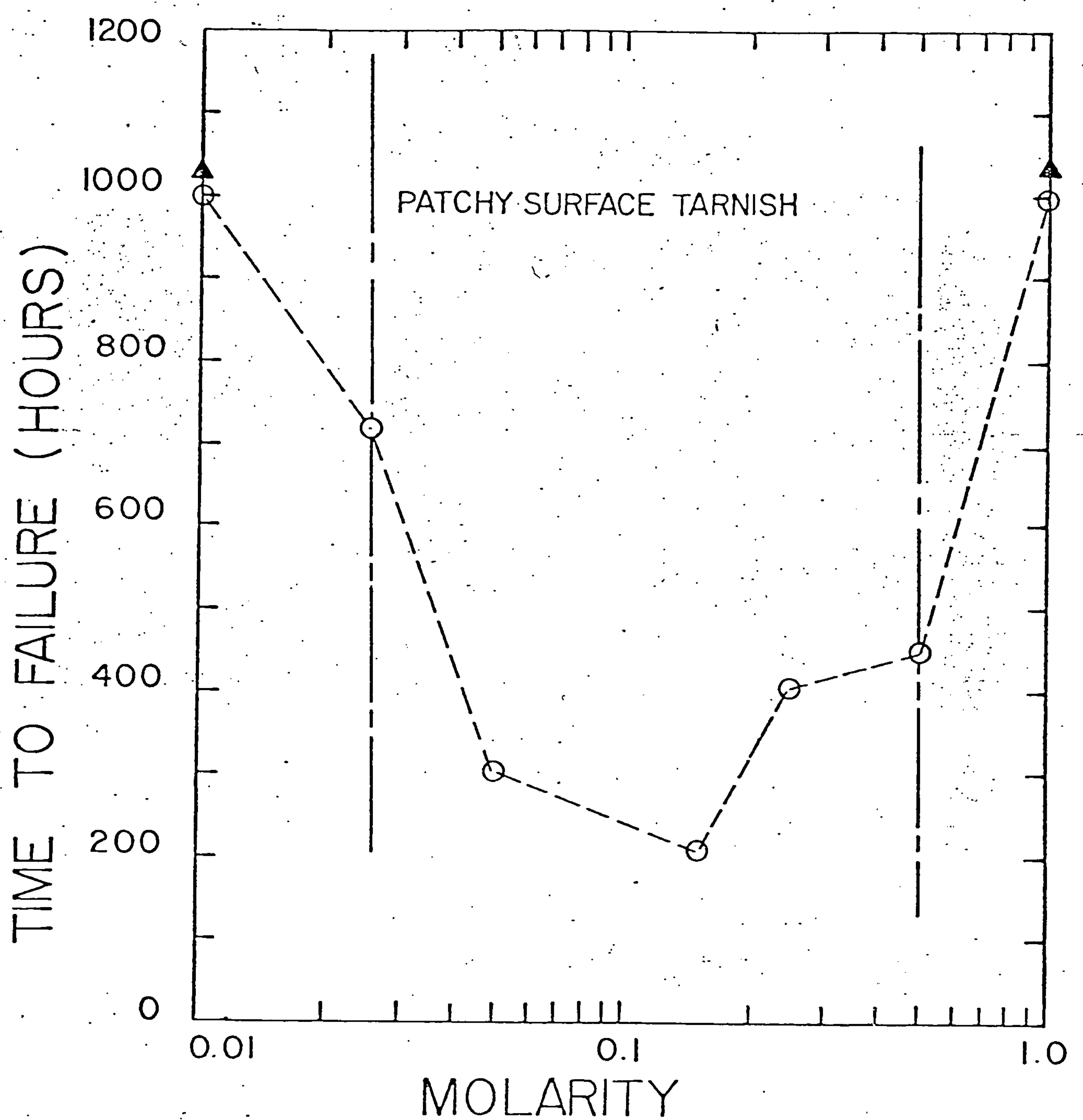


Fig. 1. Stress corrosion crack susceptibility of admiralty brass in aqueous copper sulfate.

be written to include the work associated with plastic deformation at the crack tip:[1]

$$\sigma_F = [\frac{E(\gamma_s + \gamma_p)}{a}]^{1/2}$$

where: σ_F = fracture stress

E = modulus of elasticity

γ_s = surface energy

γ_p = work for plastic strain

a = atom spacing

In a low flow stress material such as copper, γ_p would be expected to be much greater than γ_s. Any effect adsorption may have on the surface energy would produce negligible reductions in fracture stress. It has been suggested that corrosive attack may lower γ_p,[2] but this has not been demonstrated. Specific ions in the environment may affect SCC initiation in a number of ways. Surface adsorption may alter anode or cathode reaction kinetics, or localize corrosive attack by direct surface coverage or compound formation. Reynolds and Pement[3] have reported transgranular SCC in admiralty exposed to aqueous cupric nitrate. This was confirmed at our laboratory. It was also found that 0.15 molar solutions of $Cu\ SO_4 \cdot 5\ H_2O$ and $Cu\ (NO_3)_2 \cdot 3\ H_2O$ had values of pH very close to 4. To examine specific ion effects, admiralty tubes were exposed to each environment. Surface condition and crack growth were monitored with time. Figure 2 shows the crack penetration as a function of time for both environments. Crack propagation rates were nearly the same, but initiation time was significantly shorter in the nitrate environment. Specimens from both environments had a reddish-brown exterior surface tarnish and nontarnished SCC walls. X-ray diffraction of tarnish scraped from exterior surfaces

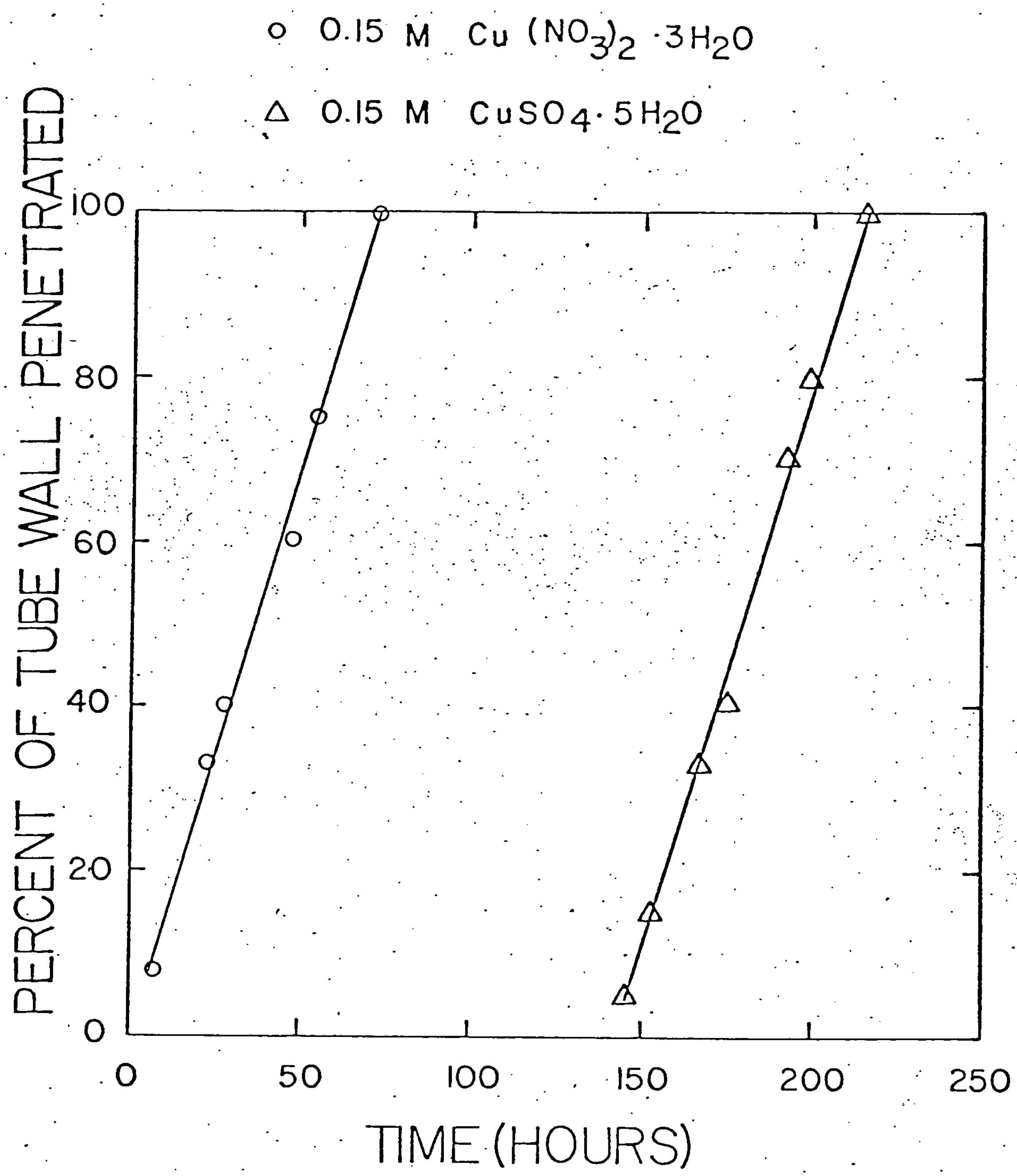


Fig. 2. Stress corrosion crack initiation and propagation rates in admiralty brass.

identified Cu_2O in all samples and $PbSnO_3$ in the copper nitrate tarnish. Auger analysis of stress corrosion fracture surfaces revealed thin Sn rich layers at the leading edge of sulfate cracks and Sn-Pb rich films on nitrate fractures. The presence of Pb in the nitrate crack crevices did not appear to accelerate SCC propagation, but a Pb compound was present in the exterior tarnish of the fastest cracking system.

3. Anodic Dissolution

The feasibility of SCC propagation resulting from selective anodic dissolution at the crack tip was examined. Since propagation rates were constant and nearly equal in the copper sulfate and copper nitrate solutions, a chemically controlled mechanism appears possible. If one assumes that crack extension is caused only by metal dissolution, the necessary anodic current density required for such a process can be calculated from Faraday's Law for any crack growth rate. The crack propagation rate of admiralty was about 4×10^{-7} cm/sec. This corresponds to a crack tip anodic current density on the order of 10 mA/cm^2. A current density of this magnitude is reasonable for propagation by crack tip dissolution. The kinetic requirement, a measurable rate of local attack that will not blunt the crack tip chemically, could be satisfied.

4. Crack Wall Composition and Morphology

Since the crack walls in admiralty samples were non-tarnished and the exterior surfaces were tarnished, determinations of the nature of the crack wall and the crevice environment were necessary to characterize additional processes active in the SCC propagation. Fracture surfaces produced in sulfate and nitrate environments appeared brittle and exhibited cleavage-like features, Figure 3. Auger analysis of these surfaces detected enough oxygen for the Sn rich and Pb-Sn rich films to be oxidized, Figure 4.

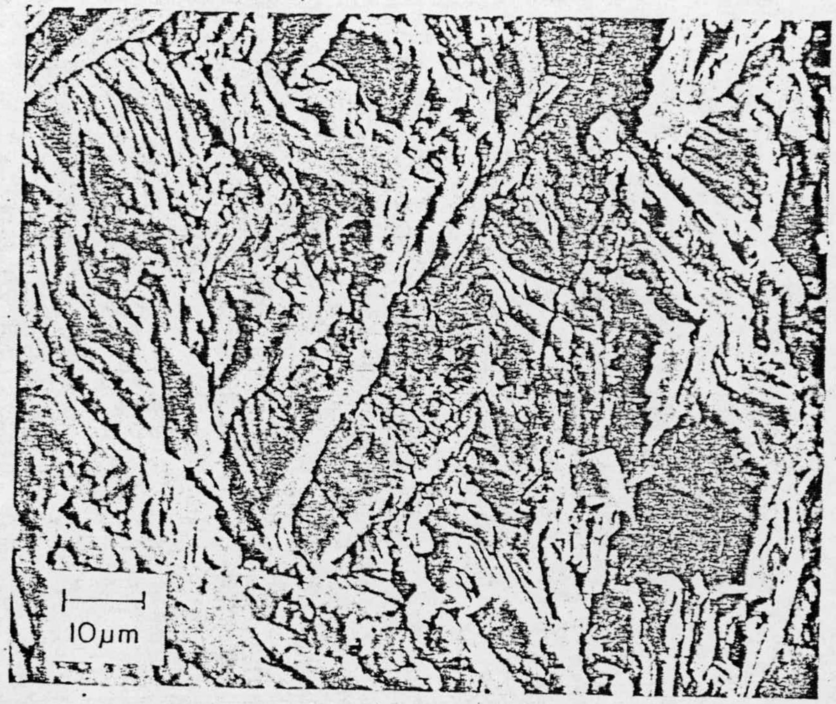


Fig. 3. SEM fractograph of an admiralty stress corrosion crack wall.

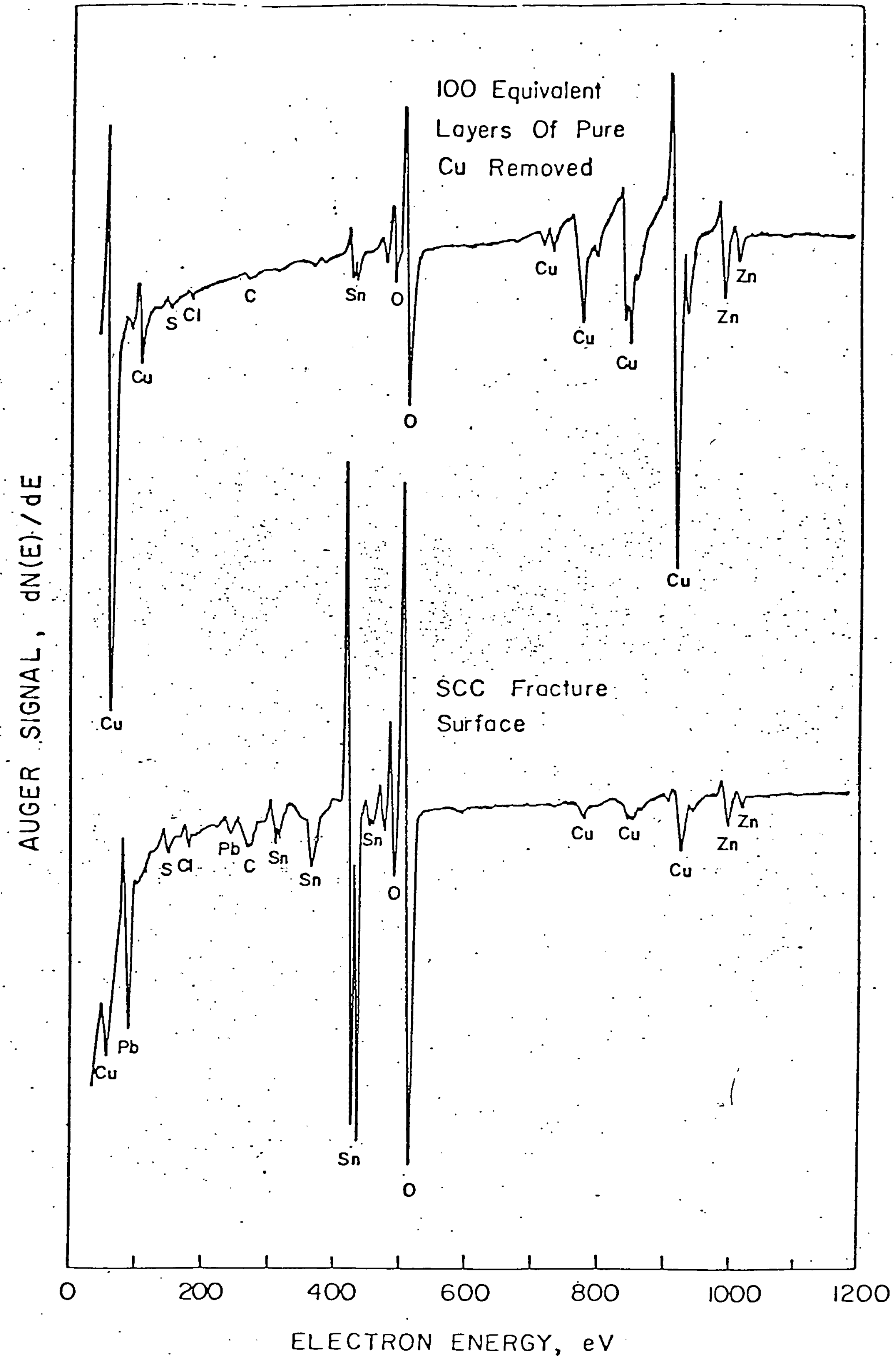


Fig. 4. Auger analysis of an admiralty stress corrosion crack-wall produced in nitrate solution.

Inert gas ion sputtering revealed the oxygen to be strongly bonded to the crack walls. Sputtering the equivalent of 100 layers of pure copper on a nitrate fracture surface completely removed the Pb and reduced Sn to its bulk alloy level.

The origin of the high Sn and Pb concentrations on the admiralty fracture surfaces was investigated. Pb was only observed on cracks generated in copper nitrate solution, which was concluded to be the source of Pb. Reagent grade Cu nitrate contains significant quantities of Pb (10-30 ppm), while reagent grade copper sulfate contains very little Pb, since lead sulfate is quite insoluble. In addition, inert gas ion sputtering easily removed all Pb from the fracture surfaces. Sn was detected on both sulfate and nitrate fractures. To determine the possibility of an environmental source for the fracture surface Sn, copper sulfate test solutions were analyzed by atomic adsorption. No tin was found with an instrument detectability of 250 ppb. In addition, annealed admiralty samples immersed in a pH 4 $SnSO_4$ solution did not crack during a 500 hour test. Exposure of annealed cartridge brass at stresses below the yield point to copper sulfate and copper nitrate solutions produced no cracking in 500 hours. These results indicate the alloy addition of Sn in admiralty was the source of the high Sn concentrations on the fracture surfaces.

Non-tarnished crack walls may result from the freshly created fracture surface being tarnish resistant[4] or from local environmental variations at the crack tip. To determine which effect controls crack wall conditions in admiralty a series of immersion studies was performed. Tubes that had been cracked in copper nitrate solution were radially compressed to expose SCC walls. Coupons about 7 mm square were cut from the tube, exposing the untarnished SCC fracture surfaces. These samples were washed and then immersed in 0.15M $Cu(NO_3)_2 \cdot 3H_2O$, the same environment that had caused SCC. Thick, adherent reddish-brown tarnish layers completely covered the SCC fracture surfaces after 40 hours exposure - the surfaces were clearly not tarnish-resistant in the bulk SCC environment. To determine the stability of this tarnish on the fracture surfaces, several of these coupons were exposed to solutions of cupric nitrate ranging in pH from 1-5. Fracture surface tarnish remained intact for all pH values during a 200 hour test. This result thus indicates a stable tarnish on SCC walls in solutions of copper nitrate below pH 5. Since this does not occur during SCC, the crevice environment near the SCC leading edge must not have the same characteristics as the bulk copper nitrate solution.

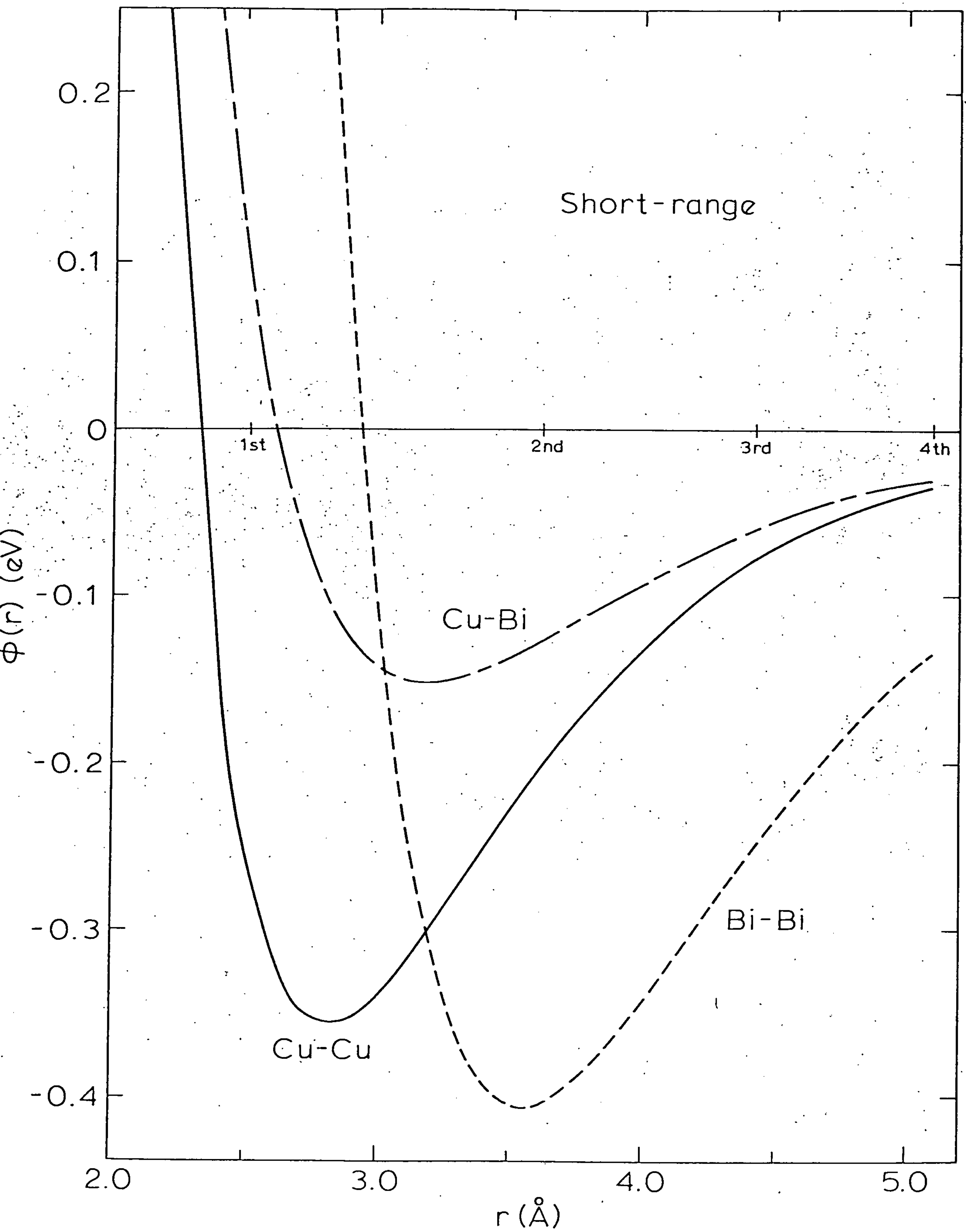
5. Summary

Studies of annealed admiralty tube in copper sulfate and copper nitrate provided much information on environmental contributions to SCC in acid systems. SCC susceptibility is a function of bulk corrosion rate, and is maximized when conditions favor localized attack. At a given pH and stress, solution composition determines crack initiation rates, but the crack crevice environment is not characteristic of the bulk salt solution. Crack propagation appears to be strongly related to anodic dissolution; however, contributions from thin film rupture and hydrogen embrittlement must be considered.

B. Theoretical Study on the Effect of Bismuth on Grain Boundaries in Copper

The objective of this portion of the program was to understand theoretically the effect of bismuth on the grain boundary structure in copper. Since interatomic potential functions are essential in describing the structure of a grain boundary, effort was first focused on developing the interatomic potential functions of Cu-Cu, Bi-Bi and Cu-Bi. However, the difficulties in developing the interatomic potentials of Cu-Bi and Bi-Bi arise from two facts; the first is that the structure of bismuth is not highly symmetric (rhombohedral) and the second is that the Cu-Bi system has a very limited solid solubility and thus there are no available thermochemical and mechanical property data which can be used to develop the Cu-Bi interatomic potential. Thus, following Girifalco and Weizer[5], Morse potentials were developed for the Cu-Cu, Bi-Bi and Cu-Bi interatomic interactions, as shown in Figure 5. A quasichemical approach and the Lorentz-Berthelot combining rules were used to determine the Cu-Bi Morse potential parameters.

With these potentials, equilibrium configurations of pure copper 36° 52' [100] symmetrical and asymmetrical tilt grain boundaries were obtained at absolute zero through the quasidynamic method and are found to be the same as those given by Hasson _et al._[6] Bismuth atoms are then distributed uniformly in the grain boundary regions. After a complete random mixing at a high temperature, the equilibrium segregation configuration of the bismuth-doped grain boundary regions were simulated through the Monte Carlo method. Figure 6 shows the bismuth concentration profile for three different normalized temperatures ($T^* = T/2646°K$) in the 36° 52' [100] _symmetrical_ grain boundary region, while Figure 7 presents the results for the 36° 52' [100] _asymmetrical_ grain boundary region. The layer "i" indicates the i^{th} atomic plane from the central atomic plane which is designated "o". The cross-hatched portion means a bulk-like region where the bismuth concentration was kept constant (11.11% in all the simulations) during the entire Monte Carlo calculation.



Short-range
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
1st
2nd
3rd
4th
Cu-Bi
Bi-Bi
Cu-Cu
φ(r) (eV)
2.0
3.0
4.0
5.0
r (Å)

Fig. 5

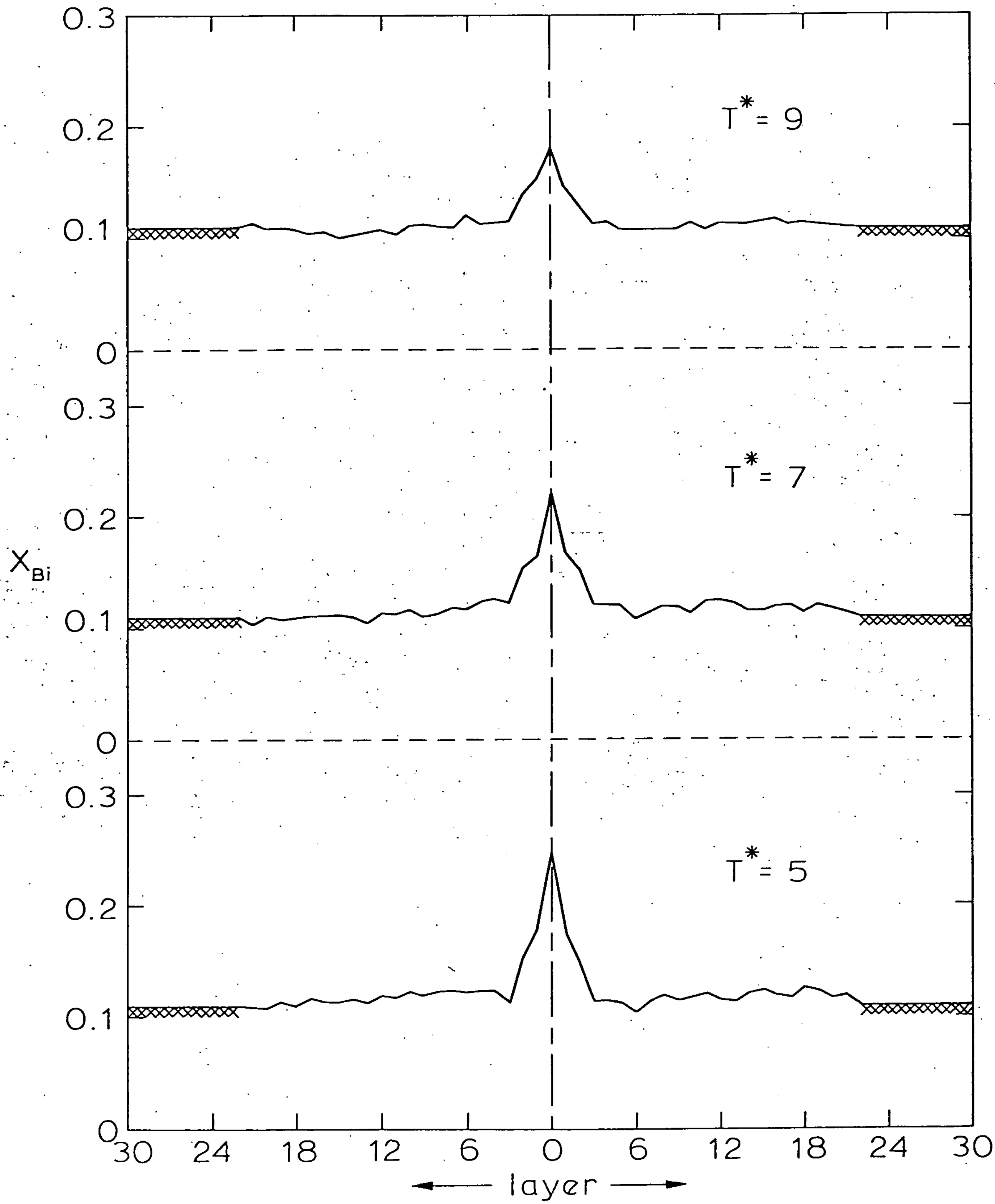

0.3
0.2
0.1
0
0.3
0.2
0.1
0
0.3
0.2
0.1
0
$T^{*}= 9$
$T^{*}= 7$
$T^{*}= 5$
X_{Bi}
30
24
18
12
6
0
6
12
18
24
30
layer

Fig. 6.

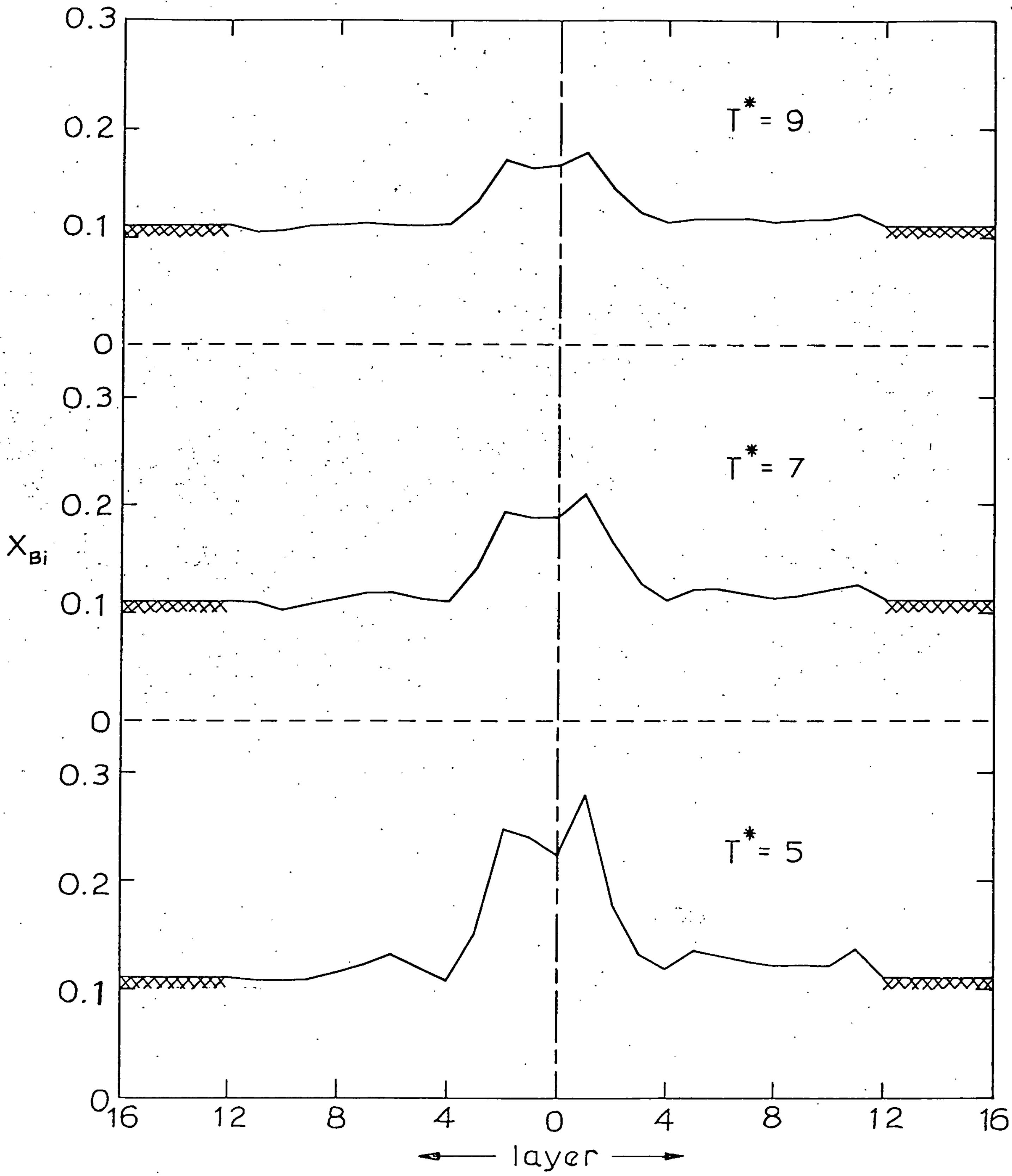


Fig. 7.

The results for both the symmetrical and the asymmetrical grain boundaries show an increase in bismuth concentration with decrease in temperature. However, while the concentration profile in the symmetrical grain boundary is symmetrical with respect to the central atomic plane (layer "o"), the concentration profile is no longer symmetrical in the asymmetrical grain boundary. Due to the limited theoretical model which was adopted in this study, i.e., a model in which only about one thousand atoms were simulated (1134 for symmetrical and 1266 for asymmetrical) and simple Morse potentials were represented as atomic interactions, no simulation at a realistic temperature (i.e., $T^* < 1$) was attempted. Nevertheless, these results show the segregation behavior of bismuth at pure copper grain boundaries, long-predicted by the Gibbsian thermodynamics and experimentally observed through an Auger electron microscope. It was also found that the amount of bismuth segregation at the asymmetrical grain boundary was larger than that of the symmetrical grain boundary and the difference increased with a decrease in temperature. This is consistent with the recent findings by Powell and Woodruff,[7] in which an anisotropy in the segregation of bismuth to the copper grain boundary fracture surface was observed.

Finally, using McLean's one-parameter equilibrium segregation equation, the binding energies of bismuth atoms to the copper grain boundaries were obtained, 0.98 eV for the symmetrical grain boundary and 1.19 eV for the asymmetrical grain boundary. The results of this study are being analyzed and prepared for publication. As a next step, a refined theoretical model which can simulate a realistic temperature range is being sought.

C. Statistical Thermodynamic Treatment of Segregation

Collaboration has continued with Dr. C. L. White of the Oak Ridge National Laboratory on a statistical thermodynamic approach to grain boundary segreation and two joint (White and Stein) papers were prepared for publication. The first was described in last year's progress report and this paper, "Sulfur Segregation to Grain Boundaries in Ni_3Al and $Ni_3(Al,Ti)$ Alloys," has been submitted to Metallurgical Transactions for publication. The second paper, "On the Upper Limits to Equilibrium Segregation at a Grain Boundary," re-examines the requirements for the validity of the upper limit of equilibrium segregation as formulated by Cahn and Hilliard.[8] It is shown that the requirement of Henrian behavior for the solute-solvent system can be relaxed to include a class of negative deviation from Henry's Law. However, for positive deviation from Henry's Law it is clear that the expression,

$$\Gamma_{B(A)}(X_O) < \frac{\gamma(O)}{RT(1 + \ln\frac{X_\ell}{X_O})}$$

where: $\Gamma_{B(A)}(X_B) = \Gamma_B - (\frac{X_B}{1-X_B})\ \Gamma_A$

Γ_A, Γ_B = the excess quantity of compounds A and B per unit area of interface;

$\gamma(O)$ = grain boundary tension of the pure solvent, A;

X_B = mole fraction of solute, B, in the alloy;

X_O = value of X_B at which the upper limit is desired;

X_ℓ = solubility limit of B in A.

is not the proper upper bound limiting the extent of segregation. It appears that substantial deviation can occur and that segregation could be easily twice the level predicted and possibly ten times.

D. Grain Boundary Fragility

Grain boundaries are usually stronger than expected since one would expect poor cohesion across this imperfectly packed interface, but cleavage fracture is more common than grain boundary fracture.

This is probably related to the interrelation between the maximum force to produce separation and the amount of plastic deformation at the crack tip. Figure 8 taken from Hahn and Gilbert[9] provides a basis for understanding the interrelation. σ^* is defined as the stress necessary to part the atoms, σ_y is the yield stress, and σ_{nom} is the applied stress. When the stress at the crack tip exceeds the yield stress, plastic deformation occurs and when it exceeds the fracture stress, separation occurs. If one considers a crack approaching a volume element dV its stress and strain history can be described as shown in Figure 8. From dislocation measurements it is observed that the dislocation velocity is a power function of stress represented by the empirical function,

$$v = A\tau^m$$

where v = dislocation velocity

A = constant

τ = shear stress

m = dislocation velocity exponent

Since m is between 10-40 for most engineering materials, a small increase results in a major increase in dislocation velocity (plastic deformation). Therefore a small decrease in the cohesive stress will result in a large decrease in the amount of plastic deformation.

In addition, Ayres and Stein and Tyson, Ayres and Stein[10,11] have shown that this plastic deformation will be anisotropic with respect to the plane on which fracture is occurring. For instance they showed that the (100) fracture plane in BCC metals is favored for cleavage even though the (110) plane usually has the lowest surface energy. This model is being extended by considering a grain boundary to be a series of micro-cleavage planes of all possible orientations. The stress fields have been calculated

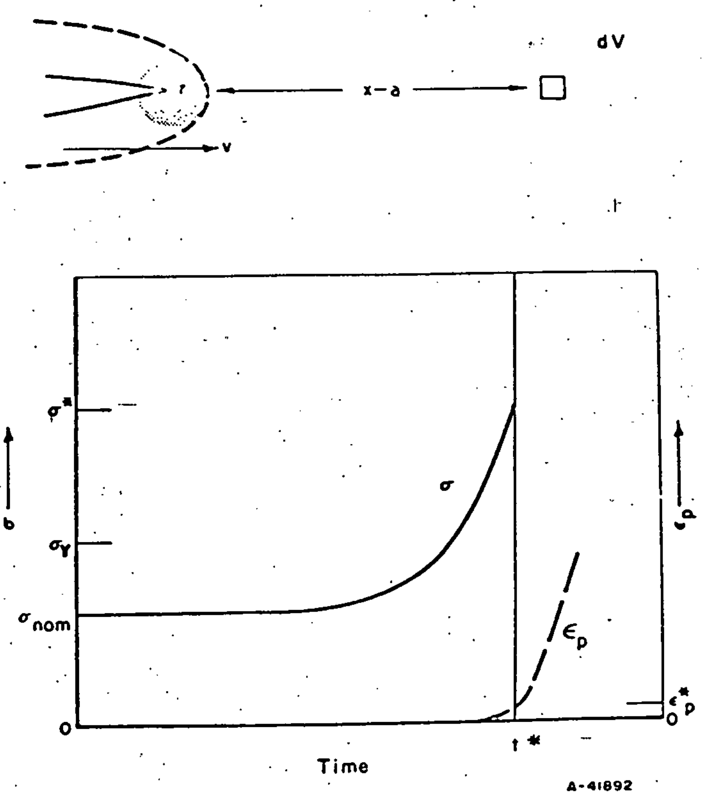


Fig. 8.

and related to dislocation motion and it was found that a variation of more than 20% occurs in the extent of the plastic zone size. The model is now being further developed to consider the change in plastic work absorbed at the crack tip as a function of crack orientation and direction and to consider the effect of changes in the true fracturing stress.

E. Grain Boundary Diffusion and Segregation Effects

Progress continues to be made in the experimental program to measure grain diffusion and determines how it is affected by a segregated species at the grain boundary. The original system chosen for study was the Mo-S-Cr ternary in which sulfur was to be segregated to grain boundaries and its effect on the diffusion of Cr measured. However, the flowing gas system for introducing the sulfur described in last year's report has not worked well and it has been necessary to redesign a closed system to try to solve the problems. The initial experiments appear to be working and therefore we are hopeful that we will achieve control of the Mo-S-Cr system in the coming year.

An alternate system, the Cu-Bi-Ni has been studied in the past year with success. This system was chosen since we have extensive experience in preparing alloys that will fracture along grain boundaries with controlled amounts of Bi segregation. Grain boundary diffusion of Ni has been measured in the Cu-Bi system and it is clear that a strong interaction between the Ni and Bi occurs. The Bi concentration at the grain boundary decreases as the Ni concentration increases, but more data needs to be gathered before the detailed analysis can be made. It is clear that the experimental program to measure the dependency of grain boundary diffusion on segregation is a viable experiment.

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III. PUBLICATIONS AND PRESENTATIONS ASSOCIATED WITH CONTRACT

Reprints & Preprints Removed

A. Publications

1. Additive and Impurity Distributions at Grain Boundaries in Sintered Alumina, W. C. Johnson and D. F. Stein, Journal of the American Ceramic Society, Vol. 58, No. 11-12, Nov.-Dec., 1975.

2. Study of Grain Boundary Segregation Using Auger Electron Spectroscopy, D. F. Stein, W. C. Johson and C. L. White, Chapter 9 in book, Grain Boundary Structure and Properties, Academic Press, 1976.

3. The Effect of Fe Additions on the Embrittlement of Cu-Bi Alloys, W. C. Johnson, A. Joshi and D. F. Stein, Met. Trans. A, Vol. 7A, July, 1976.

4. Stress Corrosion Cracking of Alpha Brass in a Non-tarnishing Ammoniacal Environment: Fractography and Chemical Analysis, T. R. Pinchback, S. P. Clough and L. A. Heldt, Met. Trans. A, Vol. 7A, August 1976.

5. Preparation of Oriented Molybdenum Twist Boundaries by Electron-Beam Zone Melting, S. P. Clough, S. J. Vonk and D. F. Stein, Journal of the Less Common Metals, 50, 1976.

B. Accepted for Publication

1. Reversible Temper Embrittlement - A Review, D. F. Stein, Annual Review of Materials Science.

2. Application of Fractography and Surface Chemical Analysis in the Study of Stress Corrosion Cracking, T. R. Pinchback, S. P. Clough, R. R. Binoniemi, and L. A. Heldt, ASM: Stress Corrosion Cracking, Testing and Phenomena.

3. Stress Corrosion Cracking of Admiralty Brass in Aqueous Copper Sulfate, T. R. Pinchback, S. P. Clough and L. A. Heldt, Corrosion.

C. Submitted for Publication

Sulfur Segregation to Grain Boundaries in Ni_3Al and $Ni_3(Al,Ti)$ Alloys, C. L. White and D. F. Stein, Met. Trans.

D. Prepared for Publication

On the Upper Limit to Equilibrium Segregation at a Grain Boundary, C. L. White and D. F. Stein, Scripta Met.

E. Invited Presentations

1. Grain Boundary Segregation and Environmental Interactions, L. A. Heldt, Symposium on Fundamentals of Grain Boundary Segregation, TMS-AIME, Niagara Falls, New York, Sept. 1976.

2. Stress Corrosion Cracking of Cartridge and Admiralty Brasses, T. R. Pinchback and L. A. Heldt, Symposium on Stress Corrosion of Copper Alloys, TMS-AIME, Niagara Falls, New York, Sept. 1976.

3. Segregation Induced Embrittlement of Metals, D. F. Stein, Northwestern University, Feb. 1976, and University of Wisconsin, March 1976.

4. New Surface Chemical Analysis Techniques for Metallurgical Analysis, and Effects of Impurity, D. F. Stein, Lehigh University, March, 1976.

5. How Metals Fail, D. F. Stein, West Virginia Tech., Nov. 1976.