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ASPECTS OF STRESS CORROSION

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The rate of formation of a surface notch in a single crystal material has been theoretically evaluated using first order perturbation theory and shown to depend upon the eighth power of the macroscopic stress for both surface diffusion, volume diffusion and dissolution mechanisms. This computation neglected coupled electrostatic potential effects which must be incorporated for a fully accurate assessment. By similarity reasoning, one can show that at a well developed crack front (a negative dendrite) can propagate at velocities [illegible] times that of a surface wave or ~ 0.1 to $10^{[illegible]}$ cm/sec for simple atomic migration

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mechanisms of crack propagation.

An experimental study of S.C.C. of austenitic stainless steels in hot halide evironments has revealed the presence of martensite on the fracture surfaces whereas it does not form in the bulk at that temperature. This suggests that martensite assists in the kinetics of crack propagation in these environments. The fracture seems to be caused by (a) higher dissolution rates along select low index planes, (b) hydrogen embrittlement of the solid immediately ahead of the crack tip and (c) formation and brittle rupture of a new phase.

The change of work function of copper single crystals by both elastic and plastic compressive strain has been determined. Although the sign of the elastic strain is consistent with basic theory, its magnitude is two orders of magnitude too large (thought to be associated with surface adsorption effects). The plastic strain effect is not consistent with theory.

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FINAL REPORT

Aspects of Stress Corrosion

Grant AFOSR 72-2206

A. Original Objectives

The objective of this research was to develop a new approach to stress corrosion and the attendant cracking that accompanies it. Further, the objective was to theoretically analyze, in a quantiative way, the responses of a surface to stress and environment changes and to experimentally determine the actual interface response in well-defined and well-controlled situations. It was designed to acquire basic information about the important processes involved in the complex phenomenon of stress corrosion and, by correlating theory and experiment, to build a structure of understanding that would allow quantitative predictions to be made of stress corrosion cracking expectations for the majority of materials and environments that one wishes to utilize.

B. General Accomplishments

From these initial studies, we have been able to postulate that it is the inhomogeneous stress distribution rather than a homogeneous stress distribution which sets the stress corrosion cracking process into operation. Inhomogeneous stresses in the solid lead to the development of inhomogeneous electrostatic potential fields both within the solid and along the envelope of a surface notch. This, in turn, sets in motion certain electrochemical relaxation processes both on the surface and in the adjoining media which result in either propagation or annihilation of the surface notch. Focusing on the notch growth problem, there appear to be four main contributions to the surface electrostatic potential, ϕ_S, given by

$$\phi_S = \phi_{\nu^*} + \phi_O + \phi_D + \phi_A \quad ,$$

where ϕ_{ν^*} is that associated with electron flow into the tip of the notch on the solid side because of the inhomogeneous tensile strain located there, ϕ_O is that associated with changes of work function (or contact potential) due to the elastic strain at the notch surface, ϕ_D is that associated with dislocation intersections with the notch surface and ϕ_A is that associated with chemical adsorption at the notch surface. It appears that from the sign and magnitude of ϕ_S changes along the notch surface, one can predict the likelihood of propagation of stress corrosion cracks.

This postulation needs more experimental and theoretical proof before a major new stress corrosion cracking effort should be mounted. However, it seems that the approach followed under this AFOSR support has laid a key foundation stone in the structure that will eventually determine a predictive approach to the very difficult stress corrosion cracking problem.

A very tangible result has been some 28 publications of which over half are already in print and the remainder are still in manuscript stage or are awaiting publication. Another important consequence of this work has been the support and scientific development of 4 Ph.D. students (1 overlapping from the previous "Energetics and Topography of Interface Phenomena" grant).

C. Significant Accomplishments

1. The rate of formation of a surface notch in single crystal material has been theoretically evaluated using first order perturbation theory and shown to depend upon the eighth power of the macroscopic stress for both surface diffusion, volume diffusion and dissolution mechanisms. This computation neglected coupled electrostatic potential effects which must be incorporated for a fully accurate assessment. By similarity reasoning, one can show that at a well developed crack front (a negative dendrite) can propagate at velocities $\sim 10^8$ times that of a surface wave or ~ 0.1 to 10^3 cm/sec for simple atomic migration mechanisms of crack propagation.

2. An experimental study of S.C.C. of austenitic stainless steels in hot halide environments has revealed the presence of martensite on the fracture surfaces whereas it does not form in the bulk at that temperature. This suggests that martensite assists in the kinetics of crack propagation in these environments. The fracture seems to be caused by (a) higher dissolution rates along select low index planes, (b) hydrogen embrittlement of the solid immediately ahead of the crack tip and (c) formation and brittle rupture of a new phase. The clear identification of a stress assisted and hydrogen-charging assisted phase transformation in the crack tip region is of great scientific and technological significance to the S.C.C. field.

3. The change of work function of copper single crystals by both elastic and plastic compressive strain has been determined. Although the sign of the elastic strain is consistent with basic theory, its magnitude is two orders of magnitude too large (thought to be associated with surface adsorption

effects). The plastic strain effect is not consistent with theory. This technique allows one to obtain most of the data for the evaluation of ϕ_S and thus to assess the S.C.C. potential of a particular material.

D. Professional Personnel Associated with this Grant

Professor William A. Tiller, Principal Investigator
Dr. B. K. Jindal, Research Associate
Mr. C. F. Jako, Research Associate
Dr. S. Ciraci, Research Associate
Mr. R. J. Asaro, Research Assistant
Mr. D. G. Boyers, Research Assistant
Mr. B. H. Johnston, Research Assistant
Mr. K. Majumder, Research Assistant
Mr. D. Nason, Research Assistant
Mr. K. Norton, Research Assistant
Mr. M. V. Rao, Research Assistant
Mr. J. Schumacher, Research Assistant

Thesis Titles

The Structure of Solid-Liquid Interface; D. Nason, Ph.D., January 1971.

Thermochemical Analysis of Phase Equilibrium in Alloy Systems; M. V. Rao, Ph.D., January 1972.

On Stress Corrosion Cracking; R. Asaro, Ph.D., June 1972

Stress Induced Changes in the Electronic Properties of Metals; J. Schumacher, Ph.D., June 1973.

E. Publications

(a) Published papers:

1. Tarnish Films and Stress Corrosion Cracking of α-brass, R. J. Asaro, Phil. Mag. 26, 425 (1972).

2. Interface Morphology Development during Stress Corrosion Cracking, Part I: Via Surface Diffusion, R. J. Asaro and W. A. Tiller, Met. Trans. 3, 1783 (1972).

3. On Surface Creation during Phase Transformations, W. A. Tiller and B. K. Jindal, Acta Met. 20, 543 (1972).

4. The Systems In-Ga: Thermodynamics and Computed Phase Equilibria, M. Vikram Rao and W. A. Tiller, J. Mater. Sci. 7, 14 (1972).

5. Computed Low Temprature Phase Equilibria in the System Fe-Cr, M. Vikram Rao and W. A. Tiller, Scripta Met. 6, 417 (1962).

6. Forces on Internal Stress Sources in Terms of Elastic Chemical Potentials, R. J. Asaro, Scripta Met. 6, 547 (1972).

7. Thermochemistry of Non-Regular Multicomponent Metallic Solutions: The System Fe-Cr-Ni, M. Vikram Rao and W. A. Tiller, J. Mater. Sci. & Engrg. 11, 61 (1973).

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13. On the Thermochemistry of Solid-Nickel Chromium Alloys, M. Vikram Rao and E. Flores-Magon, Met. Trans. 4, 2471 (1973).

14. Heats of Mixing in Liquid Solutions of Group V Elements in Indium and Gallium, M. Vikram Rao, Scripta Met. 7, 1165 (1973).

15. The Systems Fe-Cr and Fe-Ni: Thermochemistry and Phase Equilibria, M. Vikram Rao and W. A. Tiller, J. Mater. Sci. & Engrg. 14, 47 (1974).

16. The System Fe-Mn: Thermochemistry and Phase Equilibria, M. Vikram Rao and W. A. Tiller, J. Mater. Sci. & Engrg. 15, 87 (1974).

17. The Hydrogen Pump Model Revisited, W. A. Tiller, Scripta Met. 8, 487 (1974).

18. Impurity Striations in Czochralski Grown Al Doped Si Single Crystals, B. K. Jindal, V. Karelin and W. A. Tiller, J. of Electrochem Soc. 120, 101 (1973).

(b) Papers accepted for publication:

1. Interface Morphology Development during Stress Corrosion Cracking, Part II: Via Volume Diffusion, P. Vasudev, A. J. Asaro and W. A. Tiller, Acta Met.

2. Some Applications of the Bond Orbital Model, S. Ciraci and W. A. Tiller, Physica Status Solidi Schnftlietung.

3. Bond Orbital Model Calculation for Mixed Semiconducting Compounds, S. Ciraci, P. Vasudev and W. A. Tiller, J. of Physics and Chem. of Solids.

(c) Papers submitted for publication:

1. The Orientation Dependence of the Solid / Liquid Interfacial Free Energy in Binary Systems, D. Nason and W. A. Tiller, Surface Science.

2. A Study of Hydrogen Chemisorption in the Stress Corrosion Cracking, S. Ciraci and W. A. Tiller, Solid State Communications

(d) Papers in preparation for publication:

1. Comments on the Stress Corrosion Cracking of α-Brass, R. J. Asaro and W. A. Tiller.

2. Alteration of Cu Work Function by Compressive Stress, J. Schumacher, W. Spicer and W. A. Tiller.

(e) Publications - Grant AFOSR-68-1360

1. Interface Morphology Development during Stress Corrosion Cracking, Part I: Via Surface Diffusion, R. J. Asaro and W. A. Tiller, Met. Trans. 3, 1789 (1972).

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