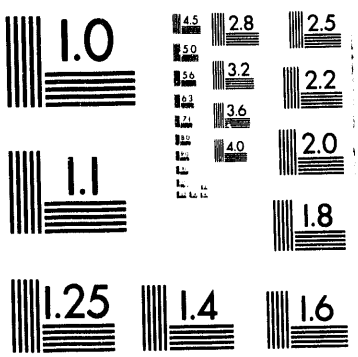
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ANNUAL
Performance Report

on

METAL INDUCED EMBRITTLEMENT

A Program Conducted Under
DOE Grant DE-FG06-87ER45287

by

Richard G. Hoagland
Principal Investigator

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Dept of Mechanical and Materials Engineering
Washington State University
Pullman, Washington 99164-2920

METAL INDUCED EMBRITTLEMENT

A Final Summary Report

Introduction

This program has been directed at the nature and cause of the severe embrittlement and loss of load carrying capability that occurs in certain solid metals when they come into contact with some liquid metals. This three year program began March 1, 1987, and, during its course, has involved a set of fracture mechanics experiments to explore the response of several alloy/liquid metal systems coupled with a more theoretical study consisting of atomic simulation of the crack tip separation process. Some of the information generated in this study is contained in papers published or submitted for publication and accompanying this report. This report is an overview of information contained in these papers as well as information currently in preparation for publication. While this is a Final Report, it is being prepared approximately seven months prior to the end of the program in order to apply for renewal, and, therefore, some of the information presented here derives from ongoing research.

Background

The motivation for this research is two-fold. First, there is extensive evidence for metal-induced-embrittlement, MIE, (1-3) and it has long been known that some solid metals, particularly high strength aluminum alloys, suffer profound loss in load carrying ability when exposed to certain liquid metals, for example, mercury and gallium, because these liquids induce slow crack growth at very low loads. Nevertheless, much of the quantitative data that characterizes the embrittlement are lacking. In particular, few MIE results derive from fracture mechanics experiments that examine the response to an embrittler in terms of the relation between applied stress, crack length, and the resulting crack velocity. Therefore, as part of this program, a number of experiments are being conducted to characterize the applied crack driving force, J, or equivalently, K, vs crack velocity relation and to use this information to assess the MIE dependence on a number of important factors including microstructure, embrittling species, temperature, and fracture mode.

This information also provides a potential linkage from the macroscopic response to the microscopic mechanisms occurring at a crack tip involving the interaction between the atoms of the liquid metal and those of the solid. Indeed, such information helps provide access to the source or cause of the embrittlement, which is the second motivating factor in this study. In this regard, MIE mechanisms have been the subject of speculation and some controversy with views ranging from suggestions of enhanced shear failure (4) to enhanced cleavage (2). Simple thermodynamic statements (5) relating the surface and interfacial energies of a liquid/solid metal system neither provide much insight into the nature of the interaction leading to embrittlement nor may be sufficient conditions for embrittlement to occur. Therefore, an additional issue of importance to this program is the clarification of the nature of the interactions that occur at a crack tip on an atomic scale causing crack advance. A major part of accomplishing this task is simply identifying the way in which the crack tip evolves as load is applied in the absence of an active environment.

Experimental Program

Overview

The focus of the experimental work has been on the Al/Hg and Al/Ga systems. The aluminum reported here is a high strength alloy, 7075 supplied as rolled 0.5in. plate and received in the T651 condition. Currently, tests on other alloys, 2024 and commercially pure aluminum, 1100, are underway, but no results from these alloys are available at this time. Fracture tests have employed a double cantilever beam specimen design in which the embrittling liquid is supplied to the crack tip from a reservoir at the tip of the initial slot. The loads applied to the specimens, and their resulting displacements, are monitored and digitally recorded at a high rate, typically 5-10 Hz, from which considerable detail of the K - crack velocity relation becomes available. These experiments have been conducted under several conditions:

- crack extension under fixed grip conditions in which K decreases as the crack grows.
- crack extension under fixed load or extending grip conditions in which K increases as the crack extends.
- different strength levels of the solid.
- different cracking orientations relative to the plate texture.

After fracture, the surfaces are examined and characterized by SEM including EDX analysis of the surfaces and, to a lesser extent, by Auger.

Results

The results so far derived from this experimental study have a number of implications concerning important issues and characteristics of MIE. In the following, the salient features of the results are reported within several different categories based on these essential characteristics

- Transient and Intermittent Crack Growth A characteristic property of the cracking behavior of the high strength aluminum alloy in both mercury and gallium is that

the crack velocity varies in a stochastic fashion as the crack extends, displays hysteresis in K - da/dt, and is otherwise not uniquely related to the applied K. Indeed, occasionally the crack is observed to halt momentarily before proceeding onward at some velocity in the range of 10^{-6} m/s to 10^{-2} m/s. This behavior is generally observed over a range of applied stress intensity levels from about 5 to 15 MPa$\sqrt{m}$ in Hg (6), and from about 0.5 to 8 MPa$\sqrt{m}$ in Ga. (For comparison, the K_{Ic} of this material is about 26 MPa$\sqrt{m}$.) The distances over which the velocity varies are not directly related to key microstructural features such as grain size and intermetallic particle spacing although, as pointed out below, there are microstructural elements responsible. This MIE behavior contrasts other types of slow crack growth behavior such as SCC in aqueous environments and fatigue in which da/dt or da/dN is observed to sensibly depend on the applied K to the extent that reasonable engineering predictions of life are possible. In our experiments, however, the da/dt is at best only weakly dependent on the applied K which implies that a stress-crack size failure envelope is not definable in these environments.

From an examination of the fracture surfaces, we have obtained a relatively clear indication that the source of this intermittent behavior is the stochastic production of unbroken ligaments of about one to two grains in extent and left behind the crack tip as it propagates. The formation and eventual rupture of these ligaments causes the crack tip to unload and load, respectively, as it extends. Thus, even though a unique relation between crack velocity may exist on a local scale, the variable screening effects from ligaments introduce a corresponding variability in the applied K - da/dt results.

- Effect of Strength Level Based on tests in mercury, the peak aged material suffers a greater degree of embrittlement than in the case of lower strength levels. The evidence for this is relatively recent test results on 7075 which has been overaged to lower strengths. As the strength decreases, the K-range within which the crack propagates increases as shown in Figure 1. While there is a distinct influence of strength on the active K range, no effect on maximum crack velocity is observed. These and additional test results are currently being prepared for publication.

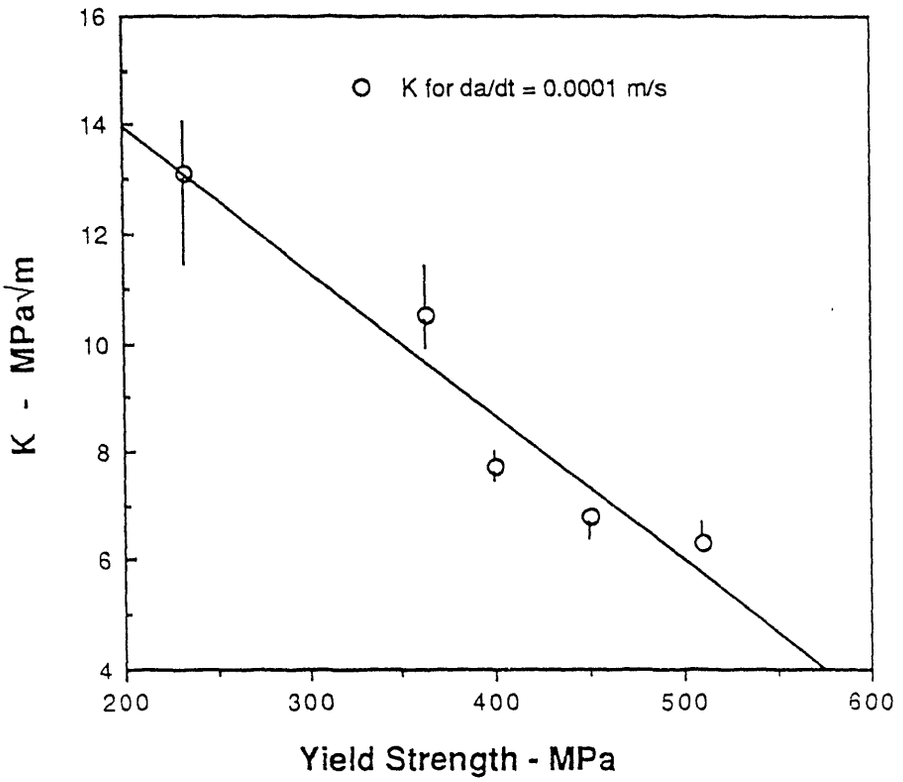

Figure 1. Effect of Flow Strength on the Stress Intensity Needed to Achieve a Crack Velocity of $1x10^{-4}$ m/s. The highest yield strength corresponds to the peak aged T651 condition.

The explanation for this strength dependence remains uncertain at this time. However, some ideas which have been advanced in regard to MIE are definitely inconsistent with these observations. For example, since the CTOD is inversely proportional to flow strength and proportional to K^2, in these results there is a dramatic increase in CTOD with falling strength. Consequently, arguments that infer that the crack velocity is limited by the transport rates of liquid to the crack tip, which, in turn, depends on CTOD, would predict an increasing velocity with lower flow strength. Additionally, we do not expect the precipitate distribution and morphology accompanying overaging to be associated with any significant changes in Hg/Al interfacial energy relative to Al/Air surface energy. This runs counter, therefore, to explanations of MIE based solely on low Liq/Solid interfacial energies.

Two explanations for the strength dependence which are being examined at this time are (1) a plastic wake effect in which the local K is decreased due to a screening by the residual stresses in the plastic wake of the extending crack, and (2) the influence of dislocation emission stress on the local tensile stresses at the exposed crack tip. The first explanation is primarily a continuum model while the second relies on results provided by the atomic simulation studies described below.

- Fracture Mode and Texture Effects When fractured under monotonic loading conditions in benign environments, such as air, aluminum and nearly all of its alloys separate by a ductile void nucleation and coalescence mechanism. The fracture toughness associated with such failures is sensitive to crack plane orientation and cracking direction in wrought products primarily because of nonuniform distributions in void nucleating particles and, to a lesser degree, anisotropy in flow strength. In the case of rolled plate, for example, cracks parallel to the plane plane of the plate tend to exhibit lower toughness because of the preponderance of particle sheets parallel to this plane.

In the presence of liquid mercury or gallium the failure mode is distinctly different. The easiest fracture path becomes the grain boundary and intergranular fracture becomes an important fracture mode. Because of the flattened grain morphology in our 7075 plate, delamination of the plate along relatively flat and continuous grain boundary sheets is strongly favored. In S-L specimens (oriented such that the crack plane is parallel to the short transverse plane) cracks grow at very low K levels, particularly in Ga, as Figure 2 shows. These results demonstrate that significant crack growth rates occur at stress intensity levels below 1 MPa$\sqrt{m}$, a level which is approaching the K-level for reversible crack extension (the Griffith toughness defined by the surface free energy) which we estimate to be on the order of 0.4 MPa$\sqrt{m}$.

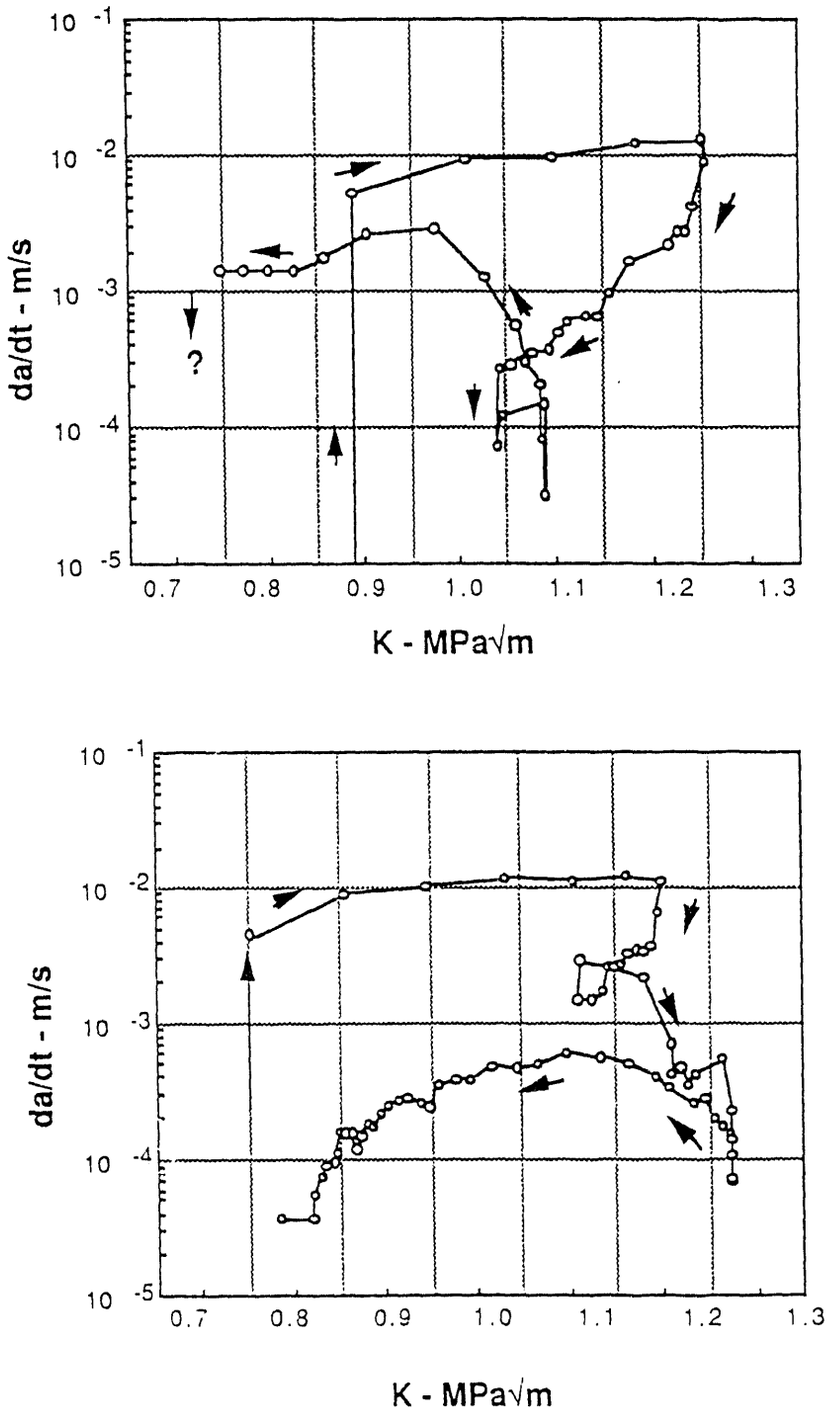

Figure 2. Two Examples Showing Crack Velocity as a Function of Applied K for 7075-T651 in Gallium. The specimens in these examples have an S-L orientation, i.e. the crack plane is parallel to the plane of the plate.

In addition to intergranular fracture, cleavage and ductile fracture modes are also observed. Evidence for cleavage is clear and dramatic, particularly in Ga, with occasional grains displaying three mutually perpendicular cleavage facets which indicates cleavage along {100} planes. This is significant in view of the fact that, with very rare exception, fcc metals do not cleave and, further, that cleavage vs. ductile fracture modes in crystalline solids are viewed (7-11) to be a consequence of competition between the shear stresses required in dislocation emission vs the tensile stresses needed for atomic separation. Therefore, embrittlement derives not only from the enhanced grain boundary separation but also mechanisms which tilt the balance in favor of tensile separation. The regions of ductile fracture which we observe are related to shear walls (6).

An additional interesting observation is that the maximum crack velocities, typically about 0.01 m/s, are relatively independent of strength, orientation, and embrittling liquid. This is of interest because it suggests that there may indeed be a transport mechanism controlling the rate of crack extension. One possibility which we are examining, is the very short range diffusion of Ga or Hg atoms into the solid. Another, possibility is the transport of dissolved Al from the crack tip via interdiffusion in the liquid. In this regard, at very low K levels, the CTOD becomes of the order of atomic dimensions and, therefore, of order of the mean free path in the liquid. Under such conditions the physical properties of the liquid within the confines of the crack should be substantially different than bulk. This is also a topic of current examination.

- Summary The results derived from this part of the program create a clearer picture concerning the properties and features of MIE. This is one of the principal goals of the program. We continue, however, to seek a quantitative description of the mechanism(s) directly responsible for the embrittlement.

Atomic Simulation Studies

Overview

This part of the program is concerned with characterizing the events that occur on an atomic scale at the tip of a crack as load is applied. These computer simulations allow one to watch the evolution of the atomic arrangements at a crack tip that lead either to dislocation

emission from the tip (blunting), and, therefore, tough behavior, or to separation on crystallographic planes (cleavage), and relatively brittle behavior. One of the principal concerns is that this evolutionary process may be strongly influenced by the presence of other types of atoms in the vicinity of the crack tip. Consequently, the atomic simulations provide the opportunity of observing the crack tip in a way not possible by physical means, e.g. microscopy, and for exploring the consequences of altering the environment.

The principal focus of this part of the program so far has been in the development and application of a computer code in which a wide variety of different crack models can be examined. Much of the first year of this particular part of the program was consumed in development of the computer code. In its current state of evolution, the code known as DRN3 can be used to explore a variety of problems concerning the atomic structure of both pure metals and alloys. The code itself is fairly small and quite transportable as it has been run on an IBM 3090 and both a Cray and a CDC supercomputer. Benchmark comparison with a molecular dynamics code called DYNAMO developed at Sandia, Livermore, was quite favorable as DRN3 was slightly faster. Of course, the quality of the results are intimately dependent on the description of the forces between atoms in the models, i.e. on the accuracy or realism of the interatomic potentials. Our models have employed embedded atom method (EAM) potentials for Al, and, in this regard, interaction with the group at Sandia, Livermore, namely Mike Baskes, Murray Daw, and Steve Foiles, has been helpful, particularly concerning the assistance they provided in developing EAM potentials for aluminum, benchmark checks of DRN3, and access to supercomputing facilities. EAM potentials are about as computationally convenient as pair potentials but possess a distinct advantage of incorporating some many body effects. The success of the Sandia group in applying EAM in simulations of a spectrum of physical properties, particularly those which concern surfaces in pure metals and alloys, lends strong support to at least the qualitative significance of our application of EAM potentials to fracture.

The majority of the results obtained in this part of the program are described in detail in Ref. 11. Highlights of the results contained in that paper are as follows.

- A small degree of lattice trapping is evident, i.e. a sharp crack is stable over a small range of K that spans the Griffith K.

- For a sharp crack the highly strained region in the vicinity of the crack tip behaves in an elastically nonlinear fashion, but, to first order, the altered field has a $r^{-1/2}$

singularity with a smaller K and an origin shifted approximately 10 to 15 Angstroms behind the physical crack tip.

- The effective elastic constants are about 15% smaller in the nonlinear near field region of an atomically sharp crack.

- Dislocation emission begins at slightly above the Griffith K and progresses by the sequential emission of partials.

- The emission of partials creates non plane strain displacements. Such displacements are interesting because they are not present in the conventional elastic field solutions.

- From a simple elastic-plastic fracture mechanics relation between the CTOD and J, namely $\delta = \lambda J/\sigma_f$, where λ is a dimensionless number of order unity and σ_f is an operative flow strength, the results indicate that the operative flow strength for dislocation emission from the crack tip is of the order of the theoretical strength of the solid, consistent with other theoretical arguments (7-10).

- The shape of the blunted crack tip provides a strong indication that dislocation emission causes the crack tip to evolve into two corner defects which separate in a direction perpendicular to the crack plane as load is increased. Accompanying this is a reduction in stress in the region initially confronted by the crack tip, which favors the continued glide of the corner defects, i.e. blunting. These observations also indicate that anything that interferes with the continued glide of the corner defects should reload the crack plane tipping the balance in favor of cleavage.

Although these results have direct bearing on how a crack in pure aluminum behaves in the absence of an active environment, they also provide insight as to how the material might be embrittled through environmental effects that reduce the tensile stress to cleave or increase the resistance to dislocation emission. In this regard, we have examined the possibility of conducting simulations of the Al/Hg and Al/Ga systems as a more explicit examination of the embrittling mechanisms. However, we have been unable to find the thermodynamic data needed to construct the dissimilar metal interaction, i.e. the part of the EAM potential that describes the interaction between the Al-Hg and/or Al-Ga atoms. Specifically, we need information concerning free energy of mixing in dilute solutions and the experimental effort

needed to acquire that information is beyond the scope of this program. An alternative approach that considers a spectrum of such interactions is being proposed as one of the research topics in a renewal program.

Another aspect pertinent to embrittlement which we are currently exploring concerns the effect which the distortions around a physically adsorbed atom may have on the crack tip field. The interest in this problem derives from the fact that when an atom is physically adsorbed a localized rearrangement in the substrate atoms occurs. If the adsorption site is near a crack tip, the crack field interacts with this adsorption field. We are interested in the nature of this interaction, e.g. the effect it may have on the resistance to dislocation emission and cleavage. This ongoing activity is currently limited to pure aluminum.

Personnel

This study has supported two graduate students. Mr. Yi Liu began working on this program in March, 1987. He completed his MS degree in December, 1988, and has begun work toward a PhD which is expected to be completed in the fall of 1991. Mr. Bradley Benson began working on the program in January of 1988 and is expected to complete his MS degree by the end of 1989. As principal investigator, Dr. R. G. Hoagland has been responsible for directing the experimental work and for the atomic modeling.

Publications and Presentations

1. Y. Liu and R. G. Hoagland, "Chaotic Crack Growth Behavior During LME of Aluminum", presented at the 1988 Fall Meeting of TMS, Chicago, IL., Sept. 26, 1988.

2. R. G. Hoagland, "Atomic Simulation of Crack Tips in Aluminum Using an Embedded Atom Potential", ibid.

3. R. G. Hoagland, "Designing Advanced Materials", presented at WEST '88, Seattle, WA, Oct. 17,1988.

4. Y. Liu and R. G. Hoagland, " Transient and Intermittent Crack Growth During Embrittlement of 7075-T651 Aluminum by Mercury", Scripta Met., 23, (1989) pp. 339-344.

5. R. G. Hoagland, M. I. Baskes, M. S. Daw, and S. M. Foiles, "An Atomic Model of Crack Tip Deformation in Aluminum Using an Embedded Atom Potential", submitted to J. Mat. Res.

6. B. Benson and R. G. Hoagland, "Crack Growth Behavior in Aluminum Embrittled by Liquid Gallium", presented at the Annual Meeting of TMS, Feb., 1989.

7. B. Benson and R. G. Hoagland, " Crack Growth Behavior in a High Strength Aluminum Alloy During LME by Liquid Gallium", submitted to Scripta Met.

8. Y. Liu and R. G. Hoagland, "On the Dependence of Embrittlement on Strength During LME of Aluminum in Mercury", to be submitted to Scripta Met.

9. Y. Liu, "Crack Growth Behavior During LME of High Strength Aluminum Alloy by Mercury", MS Thesis, Dec. 1988.

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