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## **STRESS INTENSITY INCUBATION PERIODS FOR THE AL-HG COUPLE SUBJECTED TO LME**

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### **ABSTRACT**

When in the presence of liquid metal environments, structural materials can potentially lose the ability to deform and plastically flow. In the case of a ductile material, the result of this reduction in flow ability is a transition from ductile to brittle behavior, resulting in a brittle-like failure. This phenomenon is known as liquid metal embrittlement (LME) and is a subset of the more commonly known family of environmentally assisted cracking (EAC). Both EAC and LME have a significant negative impact on structural materials that are designed to behave elastically. Previous research in all facets of EAC, including stress corrosion cracking (SCC), corrosion fatigue (CF) and LME, has revealed that structural materials subjected to loading will generate and propagate cracks at stresses and stress intensities well below the critical values for that material. Additionally, crack tip velocities have been predicted and observed to be orders of magnitude greater than in ambient environments, with velocities in the range of tens to hundreds of centimeters per second. A variety of experimental routines have been used to characterize the interaction and develop microstructural failure mechanism in LME; however, uncertainty still surrounds the true failure mechanism. In a novel experimental approach, the dependence of the stress intensity factor (SIF) on crack propagation in the presence of a liquid metal was observed. Fracture mechanics specimens machined from Al7075-T651 in the S-L orientation were fatigue pre-cracked and incubated under load while submerged in liquid mercury. The result was the observation of rupture times over a range of stress intensity factors. It was noted that any stress concentration could provide the necessary criterion for crack initiation and propagation, regardless of the presence of a crack. Critical stresses and critical microstructural orientations dictated rupture paths more so than a pre-formed fatigue crack. Further experimentation, involving original and novel methods, has been conducted to determine the relationship between the stress intensity factor, stress concentration and microstructural orientation. Ultimately, the

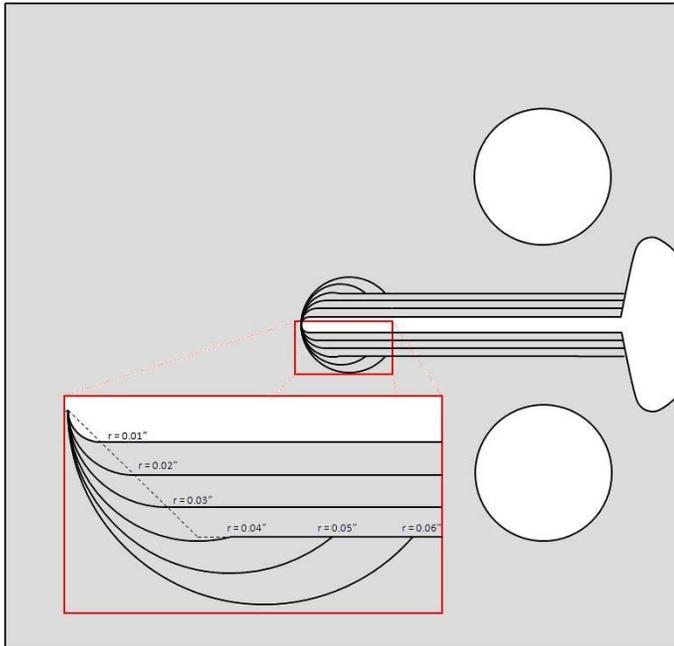
goal to confirm, extend or reject current microstructural failure mechanisms can be achieved through continued experimental routines.

### **INTRODUCTION**

The susceptibility of metals to attack by the surrounding environment has been observed to significantly affect the load carrying capability of the metal component. Through a chemical reaction, a reduction in the strength of structural components occurs, with the possibility of premature failure. Cracks that initiate and propagate in components subjected to various environments fall under the umbrella of phenomena known as environmentally assisted cracking (EAC). Environmentally assisted cracking includes several subsets, including: hydrogen embrittlement (HE), corrosion fatigue (CF), stress corrosion cracking (SCC) and liquid metal embrittlement (LME).

Liquid metal embrittlement, although not as prevalent as other branches, has led to the failure of several components in service [1-3]. Consequences are severe and catastrophic, with the loss of life a real possibility. A prime example was that of an ethylene plant, located in Texas, that experienced a failure in an aluminum pipe weld due to exposure to liquid mercury in 1987 [4]. It was noted that mercury does not wet aluminum well as a result of oxide formation, but in the event of corrosion, fatigue and other events, wetting can occur. Additional examples of failures have been previously discussed and provide thorough detail on the failure modes.

Of particular importance has been the underlying microstructural failure mechanism that drives cracks in the presence of liquid metals. Understanding the mechanisms behind LME could provide engineers, designers and technicians adequate knowledge needed at all phases in the life of a component. Acknowledging the presence of liquid metals, either present in the design, by the liquefaction of a solid metal or generation of liquid metals through chemical reactions, there



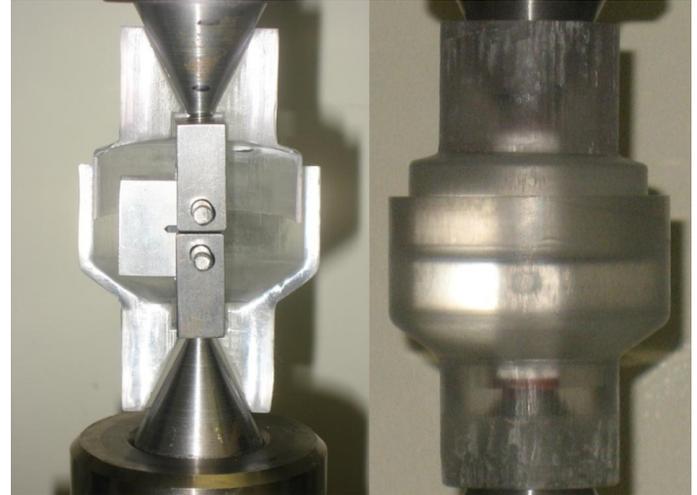
**Figure 1:** C(T) and blunt notch specimen, with various notch root radii, varying from a sharp notch to a large key hole.

exists a need for a comprehensive understanding of the microstructural failure mechanisms.

Several theories have been presented that attempt to define the driving mechanism of LME; however, only a select few have not rejected through experimental findings. Of particular interest are four key models that were developed: the Decohesion model [5-6], Stress Assisted Dissolution model [7-8], Grain Boundary Diffusion model [9] and the Adsorption Induced Dislocation Emission (AIDE) model [10]. Each model provided experimental results to substantiate the theory; however, even among these four, some are more commonly accepted than others.

Of the most widely accepted models is the Decohesion model that was proposed by both Stoloff and Johnston (1963) and Westwood and Kamdar (1963). Primarily, these two research groups built upon the previous work of Nichols and Rostoker [11]. In dealing with the surface energy of the liquid-solid couple, the embrittling liquid would ultimately lower the cohesive strength of the solid metal, allowing for failure at a lower tensile stress. The theory does not account for any ductility, as the failure would be completely brittle. Evidence of any ductility on the fracture surface would strongly oppose this theory.

The AIDE model, proposed by Lynch (1977), allows for some plasticity ahead of the crack tip. Working along the lines of the Decohesion model, fracture surfaces of specimens were viewed under SEM and concluded that there was some plastic flow ahead of the crack tip, albeit reduced when compared to fractures in air. Through adsorption of the liquid metal, nucleation and egression of dislocations at the surface is facilitated, microvoids in the solid would be generated and



**Figure 2:** Cutaway view of C(T) specimen loaded in environmental chamber (left) and the fully assembled chamber with specimen loaded (right).

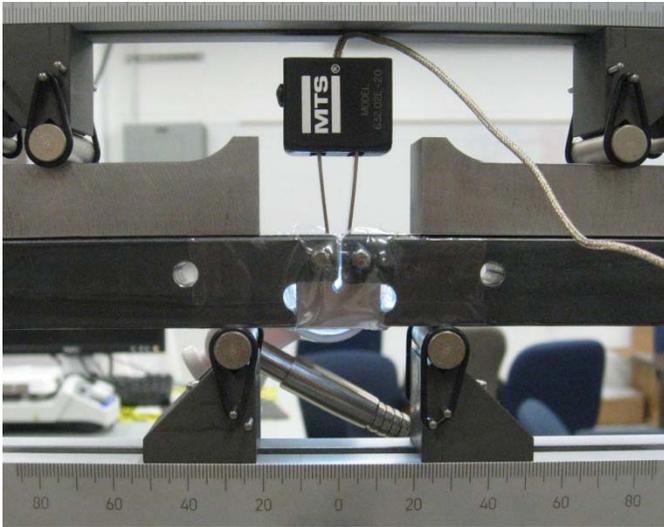
coalesce to propagate the crack. The liquid environment would thus enable plastic flow through shearing of the atomic bonds, opposing the notion of the Decohesion Model that no plastic flow was exhibited. Lack of ductile dimples on fractured surfaces would presumably provide contradictory evidence of this theory.

The two remaining theories, the Stress Assisted Dissolution and the Grain Boundary Diffusion, are viable LME mechanisms; however, are not suitable for all solid-liquid couples. The Stress Assisted Dissolution model supports the notion that the liquid metal is merely a transport and removes solid metal atoms from the body. Diffusion of liquid metals into solids [2] provides evidence that this theory is not capable of describing all couples.

The Grain Boundary Diffusion model provides evidence for the diffusion of liquid metals along the grain boundaries of solid metals. Through a reduction in strength of along the grain boundaries, components would fail intergranularly, i.e. decohesion of grain boundaries. Transgranular and cleavage-like fractures provide support that this model does not accurately describe all solid-liquid couples [12].

A variety of methods have been used to the effects of LME [12-20]. These tests include standard tensile, delayed fracture, slow strain rate and fracture mechanics experiments. These experiments have provided a wealth of knowledge; particularly that periods of incubation precede crack growth and propagation, crack growth rates can be on the order of centimeters per second and fracture surfaces reveal mostly brittle-like fractures.

Liquid metal embrittlement tests rely on intimate contact between the liquid and solid metals. Possible competition between oxides and liquid metals can prevent LME conditions from being achieved, as noted in [20]. To overcome this obstacle, acids are employed to remove any oxide layer, allowing for proper wetting of specimens, ensuring LME



**Figure 4:** Four-point bend apparatus that uses a C(T) specimen with special steel attachments to allow for loading and use of a clip gage.



**Figure 3:** Blunt notch specimen with sleeve used in containing liquid at the notch/crack tip.

conditions are present; however, results fail to disclose whether or not liquid metals were traced at all portions on the fracture surface. If the few drops of liquid metal applied are not sufficient enough to wet the entire surface, LME conditions may not be met. Additionally, the acid used could potentially weaken the solid, providing complex failure modes that are inconclusive.

In order to address the concerns presented, as well as to extend or reject the current microstructural failure mechanisms, a new experimental routine was developed to examine LME.

## EXPERIMENTAL METHOD

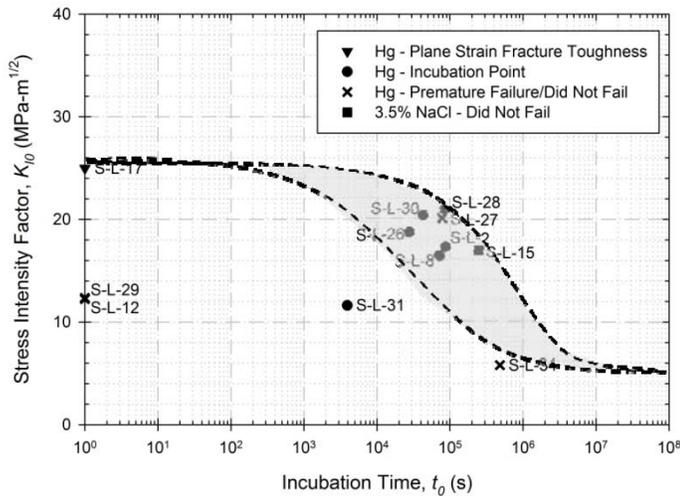
Compact tension, C(T), fracture and blunt notch specimens were machined out of Al 7075-T651 sheet in the S-L orientation, Fig. 1. This particular orientation was chosen as it allows for crack initiation and propagation through the center of the plate, avoiding edge effects that result from material processing. Additionally, data is not as readily available for this orientation as it is for others; namely T-L and L-T.

The embrittler used was commercially available, 99.999% pure mercury (Hg). The solubility parameter difference between aluminum and mercury is sufficiently high to ensure that the mercury will not readily diffuse into the aluminum. This allows for the adsorption of Hg over the surface of newly created surfaces and eliminates LME effects due to diffusion, which is not the case when other embrittlers, e.g. Ga, are used. Oxides present on the aluminum prevents adequate wetting; however, when new surfaces are formed, i.e. crack initiation and propagation, the oxide layer is nonexistent and adequate wetting is achieved.

Specimens were tested in two separate experimental setups. A traditional uniaxial plane strain fixture was employed for the first series of tests that incorporated both plane strain fracture testing, as well as delayed incubation/fracture experiments. An environmental chamber was developed capable of submersing the specimen in a liquid during pre-cracking and fracture tests, Fig. 2. During crack initiation and propagation, only mercury was present, eliminating any competition between LME and oxidation, providing adequate wetting. As this design did not incorporate a clip gage, approximations between crosshead displacement and crack mouth opening displacement (CMOD) were made, allowing for the approximation of the crack length while the specimen was submersed.

Additional experiments were conducted in a modified four point bend apparatus, Fig. 3. Advantages of the modified setup include the incorporation of a clip gage, a clear view of the notch and eliminated the reuse of embrittling liquid, as the required volume was drastically reduced. Blunt notch specimens were surrounded in a sleeve that confined the mercury to only the crack tip and were subsequently loaded at a constant load until failure, Fig. 4. Crack mouth opening displacements were used to determine crack initiation, as well as approximate crack lengths. Incubation periods were observed under constant load until rupture of the specimen.

Upon rupture of specimens in both methods, fracture surfaces were viewed under a scanning electron microscope (SEM). The mode of fracture and the crack initiation location, whether in a grain or grain boundary, was the focus during the fractography.



**Figure 5:** Incubation data obtained using conventional  $C(T)$  specimens in axial loading.

## RESULTS AND DISCUSSION

Results for both experimental setups reveal a large susceptibility of Al 7075-T651 to LME. Reduced plasticity, in the form of shear lips, were no longer present and the fracture surfaces were severely more discolored than their counterparts in air.

Incubation experiments conducted in liquid mercury revealed interesting behaviors. Initial tests resulted in specimens experiencing crack initiation and propagation at locations other than the starter notch. Ruptures were seen to occur at positions along the knife edge and through the load pin hole. These common occurrences led to the application of the rubberized coating around the bottom half of the  $C(T)$  specimen. Upon coating, ruptures occurred at the starter notch, as expected and incubation data was obtained.

Incubation data obtained via conventional  $C(T)$  testing is provided, Fig. 5. Several specimens failed prior to incubation times, as noted by a dot on the  $K_{I0}$ -axis at  $t_0 = 10^0$  s. Specimens typically failed during the pre-cracking routine; all of which failed at the EDM starter notch, as the rubberized coating solution was successful. Several other specimens lasted the full pre-cracking regime and were allowed to incubate until failure. Displacements and loads remained nearly constant up until complete fracture of the specimen occurred. Fractures of the specimens were observed to lead to complete rupture in less than 0.1 s. Crack growth data was not able to be extrapolated, as the sampling frequency was 10 Hz. The crack was able to extend through the width of the specimen before a subsequent data point was captured.

In Fig. 5, error bands have been added to address the scatter in the experimental data. These error bands are expected to be highly dependent on the metal couple used and are merely representative for the Al-Hg couple. Different couples that have a solubility parameter difference less or greater than that of Al and Hg might display a more confined or



**Figure 6:** Fracture surface of specimen fractured in mercury with extensive cracking and burn markings (S-L-10).

scattered relationship. It is also highly dependent on the subcritical crack growth, if any at all.

Analyzing the incubation points, it is shown that several experiments were conducted with varying results. Some specimens, e.g. S-L-26, S-L-30, were able to maintain an initial SIF and rupture as expected, while other specimens either fractured upon load application, as mentioned previously, or were interrupted/stopped, e.g. S-L-27. It is proposed that the reason the experiments contain as much variation as they do is directly related to the severity of macro-cracks at the starter notch. Depending on the surface roughness or a small flaw in the material, several cracks can initiate. If these cracks are sufficiently close to one another, the complex state of stress at each tip could overlap, creating a more severe state of stress; however, if the cracks are far enough apart, this will not happen. Overlapping stress fields will result in crack propagation at lower SIFs, while a single crack will behave significantly different.

Cracks were observed to occur at various locations along the starter notch. Provided the specimen orientation, approximately 45 grain boundaries were available in the S direction along the starter notch. No specific trends were observed in specimens that had crack initiation in locations other than the vertex of the starter notch. With this high concentration of grain boundaries along the notch, it provides evidence that LME could potentially be grain boundary-dependent and the orientation provides for multiple locations that provide favorable crack initiation conditions.

Fracture surfaces of specimens ruptured during SIF incubation experiments displayed a similar failure mode as the plane-strain fracture toughness specimens submerged in liquid Hg. Cracks were initiated in several locations and the “delamination flakes” were observed; several of which were observed to float in the liquid mercury upon completion of the test. The flakes exhibited similar fracture surfaces as the rest of the specimens, including dark regions that signify corrosion. Dark regions with several crack initiation sites were present,

which denoted a strong reaction between the aluminum and mercury. All experiments displayed these burn marks, as the time the aluminum was exposed to the mercury was significant in comparison to fracture toughness test specimens.

Significant features included burn markings, multiple layers of cracking and transgranular-like cleavage. Unlike previous specimens fractured in air, no macroscopic plastic deformation in the form of shear lips was observed. This particular alloy exhibits about 11% elongation in uniaxial tension tests, signifying that the mercury had a significant effect on the ductility. Completely brittle-like failures were common throughout all specimens tested in liquid mercury.

Specimen S-L-10 exhibited severe burn marks along the multiple crack initiation sites, as did others, Fig. 6. The fracture surface itself included several dark regions, anywhere from 30-90% of the total surface of specimens fractured in liquid mercury. The discoloration is attributed to the attack by liquid mercury by means of corrosion. Darker areas were observed to have several crack initiation sites, while areas of lighter or no discoloration appeared to behave normally.

Experiments utilizing the four point fixture have recently begun. Initial experiments have been conducted with the purpose of correlating relationships between the two experimental routines. Fracture toughness tests conducted on C(T) specimens that were pre-cracked and fractured in liquid Hg were nearly identical. Additionally, fracture surfaces were comparable in appearance to those fractured via the traditional axial-tensile test outlined by ASTM standards. Incubation experiments involving the blunt notch specimens are poised to provide a similar image to that of Fig. 6. With the applied stress, incubation periods are to be analyzed and crack initiation and propagation phenomena will be observed, as well as a critical stress that leads to rupture. Coupled with incubation periods for varying  $K_I$  values, the life of an aluminum component subjected to a stress in the presence of liquid mercury will be able to be predicted.

The results from this study thus far have particular implications in regards to the microstructural failure mechanisms discussed previously. It was observed that the failure of specimens, whether during the fatigue pre-cracking routine or after an extended period of time incubating, was dependent on a variety of factors. Ultimately, the rupture of specimens was both load- and microstructural orientation-based. A critical stress coupled with a favorable microstructural orientation can possibly provide the necessary conditions for crack initiation and propagation. None of the theories account for this dependency.

Both the Stress Assisted Dissolution Model (Robertson, 1966 and Glickman, 1977) and the Grain Boundary Diffusion Model (Krishtal, et al. 1973) were not observed to contribute to the results obtained in this study. The Stress Assisted Dissolution Model, which states that the liquid is merely a transport for the solid metal atoms, was not applicable for this couple, as the solubility of the aluminum in liquid mercury is negligible. The Grain Boundary Diffusion Model, where the fracture of specimens occurs along grain boundaries, is not

valid as both previous and current research provides evidence of transgranular fracture. Significant intergranular fracture was observed in specimens fractured in liquid Hg; however, on several surfaces river marks, which are a form of cleavage and transgranular fracture, were observed. For the Al-Hg couple, these two theories do not lend much support to the failure of specimens submerged in a liquid metal.

The remaining two theories, the Decohesion Model (Stoloff and Johnston, 1963 and Westwood and Kamdar, 1963) and the Adsorption Induced Dislocation Emission Model (Lynch, 1977), seem to account for failures observed in the Al-Hg couple. On the fast fracture surface of S-L-11, regions of localized plastic deformation (in favor of the AIDE Model) and regions of no ductile failure (in favor of the Decohesion Model) were observed. Both of the theories applied to different portions of the fast fracture surface and a combination of the two could be attributed to a dependency that was not included in either model.

The dependency on load and the microstructural orientation could provide for this combination of failures. Provided a favorable microstructural orientation, cracks could initiate and propagate in a manner that favors microvoid coalescence and localized regions of plasticity. Likewise, if a different orientation is provided, possibly in which several inclusion particles are located, very brittle fractures could be observed without any significant flow of material. Inclusion particles were observed to fail in a transgranular fashion; therefore, if an abundance of these inclusions are concentrated at the surface, it is likely that cracks could initiate and propagate with no plastic deformation. Coupled with a critical stress, a combination of the two theories could be applicable for this solid-liquid system.

Crack initiation is the major component missing from the failure theories provided. All of the theories study the effect of liquid metals on the propagation of existing cracks. It can be argued that the more important aspect to this research is in the study of a critical stress and a critical and/or favorable microstructural orientation. Understanding why a crack will initiate in the presence of liquid metal will provide engineers valuable information when designing components to resist EAC. In the presence of liquid metals, crack velocities are known to be extremely high, on the order of centimeters per second and higher; therefore, failure can be expected once a crack is initiated. It is the suggestion that more information regarding a critical stress and microstructural orientation favoring crack initiation be investigated to further extend the microstructural failure mechanisms of LME.

## CONCLUSIONS

The high strength aluminum alloy, Al 7075-T651, has shown its susceptibility to LME. In particular, crack growth rates in aluminum intimately exposed to a liquid metal environment have been shown to have crack velocities on the order of centimeters per second. The transferability of LME, namely when mercury is the liquid metal, can be extended to

hydrogen embrittlement (HE); a very real concern in all materials and materials processes. Methods have been developed to study the effects of LME and HE, but recent interest in both have generated the need for new methods to be developed.

Two novel methods of subjecting fracture mechanics specimens to liquid environments have been developed. An environmental chamber capable of housing both liquids at room temperature and fracture specimens was utilized in a variety of experiments in an effort to characterize the effects of LME on a high strength aluminum alloy. Similarly, a four-point bend setup was used to characterize the critical stress required for crack initiation in the presence of liquid mercury. Future studies can be conducted utilizing the current experimental configuration that makes use of solid-liquid metal couples that do not readily oxidize to further investigations in stress corrosion cracking and LME.

Mechanisms leading to failure were observed to be a result of an externally applied load and favorable microstructural orientation. Once a critical stress was achieved at a location with a potentially critical microstructural orientation, cracks can be expected to initiate and propagate. Failures were more dependent on crack initiation, as no significant amount of subcritical crack growth was observed. Specimens failed immediately at the onset of propagation, therefore the initiation conditions are more dominant in the role of rupture of specimens in liquid metal.

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