

ENVIRONMENT-ASSISTED CRACKING: CRITICAL UNRESOLVED ISSUES

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Introduction

Significant progress has been made in understanding environment-assisted cracking (EAC). Alloy-environment combinations prone to EAC and “windows of susceptibility” have been defined in terms of metallurgical, mechanical, and electrochemical parameters. EAC mechanisms have emerged ranging from anodic dissolution and film-induced cleavage to H-promoted local plasticity, decohesion, and phase-induced cracking.

Models have emerged that predict crack growth rate and thresholds in electrochemical potential, stress, stress intensity factor, temperature, alloy composition and microstructure, as well as environment composition. However, sharp thresholds may not exist, as supported by high resolution crack growth data, the lack of theoretical basis supporting abrupt transitions in many mechanisms, and the probability of encountering worst-case defects within large at-risk volumes of material. Moreover, prediction in new alloy-environments remains uncertain and modern alloys continue to suffer severe EAC.

Accurate prediction of crack growth rate and threshold properties based on atom or continuum-scale approaches remains elusive due to critical uncertainties. Barriers to advancement stem from shortcomings in two broad areas: (i) local crack tip reaction and transport phenomena, and (ii) crack tip mechanics and process zone damage phenomena. The large gradients in stress, strain, concentration, and electrochemical potential field at a crack tip hinder progress. These shortcomings are generic to many alloy-environment systems and block successful modeling. For instance, growth rate predictions based on anodic dissolution by slip/film rupture/repassivation are jeopardized by uncertain crack tip strain rates, crack tip film properties, and depassivated metal dissolution kinetics in the pertinent crack tip solution. Hydrogen environment embrittlement (HEE) models, under conditions favoring local crack tip H uptake, are flawed by uncertainties over the crack tip surface, lattice, and diffusible H concentrations, C_H , and the pertinent H transport rate. Even during internal H embrittlement (IHE), where a controlled concentration of H is introduced *uniformly*, uncertainties over crack tip mechanics including the local stress distribution, H repartitioning between varying-strength trap states, and the critical distance over which damage occurs plague accurate crack growth predictions.

This review addresses critical issues associated with EAC likely governed by H. The emphasis is on recent progress in understanding local crack tip reaction rates and H entry, local crack tip H concentration-depth profiles, as well as micro- and continuum mechanics unique to a sharp environment-assisted crack tip. Understanding these issues enables better definition of the relative roles of crack tip dissolution and H production in EAC.

Crack Tip Reaction and H Entry

The dependencies of threshold K and crack growth rates on bulk-diffusible and total-trapped H concentration are well established. However, local H concentrations remain elusive when crack tip H uptake is dominant. Near-surface C_H levels within crack tips and pits elude quantification due to local accumulation and gradients on length scales smaller than the resolution of experimental

probes. Early attempts to quantify C_H at crack tips focused on permeation experiments in bulk analogs of crack tip solutions at assumed crack-tip potentials. Relationships between H production and diffusible C_H are jeopardized by uncertain inventory of transient dissolution and H production kinetics at crack tips, uncertainty concerning local crack solution compositions as well as surface films, near-surface trap states and densities, and near-surface alloy compositions. These issues hinder quantification of C_H at crack tips, crevices and pits. Analysis is particularly thwarted if a passive film that forms on crack flanks act as an H permeation barrier.

Several approaches including thermal desorption and neutron activation analysis of cracks quantify local H production and uptake, and shed new light on HEE. Local crack tip H concentrations are found to be very high in the vicinity of Al and Ti crack tips even when anodically polarized. Locally high C_H are expected based on qualitative hydrolysis considerations, IR drop and H overpotential, but are difficult to measure with probes that lack spatial and depth resolution. Steep C_H gradients are seen at crack tips. Moving line source analysis of H transport at of non-stationary cracks supports steep H concentration gradients ahead of crack tips.

Crack Tip Mechanics and Process Zone Phenomena

Limitations in predicting HEE and IHE are traced to the lack of understanding of the time-dependent interaction of H with stress, plastic strain, and microstructural traps within the crack tip fracture process zone. Understanding is hindered by the complexity of such processes and the very small length scale relevant to the crack tip. The location of FPZ, hence the kinetics of cracking, depend on crack-surface H production for HEE and the distribution of H-trapping sites for IHE. The crack tip stress distribution, determined by opening shape, superposes to affect the location of fracture sites. Considering HEE, the FPZ is located within 1 μm of the crack tip for a wide variety of complex alloys. Analyses of the kinetics of HEE cracking, in the form of da/dt and the dK/dt dependence of K_{TH} , support this conclusion. Rates are directly proportional to trap-modified H diffusivity, provided that the diffusion distance is 1 μm or less ahead of the crack tip.

Further support for a very near-tip FPZ is provided by the ultra-high levels of H that are measured within 1 μm of the surface of crack wakes, as well as observed crack tips that are substantially sharper than predicted by a continuum blunting model. Crack sharpness is pronounced for growth along an interface or grain boundary, and may be governed by the mechanics of elastically and plastically dissimilar grains and dislocation hardening unique to a sharp strain gradient. This sharpness and strain gradient plasticity provide a basis for ultra-high crack tip stresses within a very-near tip FPZ. Considering IHE, cracking kinetics are governed by redistribution of H, from homogeneously distributed low to moderate strength trap sites to the crack tip stress field and contained traps. This diffusion distance can be short, of order 1-5 μm .

In spite of these and other advances over the past decade, mechanism-based modeling of EAC, dominated by either anodic or cathodic processes at the crack tip, remains semi-quantitative.

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