NEW FRACTURE MECHANICS APPROACH TO CHARACTERIZE INTERNAL HYDROGEN EMBRITTLEMENT OF STEEL FOR FITNESS-FOR-SERVICE MODELING

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ABSTRACT

A new experimental method was developed to characterize the threshold stress intensity and kinetics of internal hydrogen embrittlement under a known-constant amount of hydrogen about the crack tip. This is accomplished using a fracture mechanics specimen, with H charged electrochemically through symmetric slots, but not contacting crack surfaces. Elastic-plastic finite element modeling provided solutions for stress intensity (K), compliance, and *J*-integral. A three-dimensional H diffusion model established the time, temperature and K dependencies of H about the stressed crack tip in slotted and standard-H_2 precharged CT specimens. Experiments calibrated slot-H uptake *vs.* electrochemical charging conditions for 2¼Cr-1Mo weld metal, and established that the slotted specimen produces significant H-embrittlement for both slow-rising K and fixed crack mouth opening displacement loading. The slotted case provides higher levels of H than the standard case for long time or elevated temperature experiments, but is limited by the amount of H produced electrochemically. The effect of such H concentration differences is understood through diffusion modeling of H trapped at the stressed crack tip. The slotted technique can establish the temperature dependence of subcritical cracking; H loss precludes accurate results from precharged-standard specimens.

1 INTRODUCTION

1.1 Technological and Scientific Needs

Thick-section steel pressure vessels in petrochemical applications are exposed to high temperature-high pressure H_2 environments that dissolve up to 5 wppm of atomic H in the steel during service. At issue is the risk of subcritical internal hydrogen embrittlement (IHE) during shutdown and startup near-ambient temperature where such H promotes subcritical crack growth [1-6]. IHE in weld metal and the deleterious effect of long-term temper-embrittlement are of particular concern [1,5-6]. Fracture mechanics methods can predict the fitness-for-service (FFS) of such components, including the deleterious effects of H and temper-embrittlement for various dissolved H concentrations, but such efforts are limited by a lack of material property data as well as basic understanding of the H damage mechanism at the crack tip.

The IHE resistance of steel is governed by critical variables including dissolved H concentration (trapped and total), temperature, loading form and rate, constraint, yield strength, bainitic microstructure, and degree of temper-embrittlement [1,4-12]. Extensive laboratory experiments, using fracture mechanics specimens precharged with H then stressed in moist air, define the dependencies of H-cracking threshold and kinetics on these variables. Cracking data and mechanism-based modeling using elastic fracture mechanics are well established for high strength steels, but less so for yield strengths less than 750 MPa [13].

As illustrated in Fig. 1 for bainitic Cr-Mo base metal tested for IHE at 25°C, the threshold stress intensity factor (K_{TH}) for crack arrest at fixed crack mouth opening displacement (CMOD) decreases with increasing strength [1]. Notably, very low threshold stress intensity for the onset of subcritical crack growth (K_{IH}) is produced by slow-rate rising CMOD loading for lower strengths [1]. The K_{TH} and K_{IH} for IHE rise with decreasing dissolved H and increasing temperature, such that brittle cracking may be eliminated at critical levels for each variable [1,13]. Subcritical crack growth rates (da/dt) depend similarly on these variables.

Fracture mechanics experiments were compromised by H loss from the bulk specimen and crack tip, particularly for materials with high H diffusivity ($D_H \approx 10^{-6}$ cm^2/s at 25°C) such as low to moderate strength C-Mn and Cr-Mo steels. For 25 mm thick CT specimens of 2¼Cr-1Mo base steel (σ_{UTS} = 580-650 MPa), 20-40% of the initial-total dissolved H content remained after 85-100 h exposure at 25^{o}C [1]. Only 15-20% of the initial H remained after 3-6 h experiments at 60-100°C. These measurements demonstrate substantial H loss from the bulk, but are not relevant to the crack tip process zone where H content is governed by loss through tip surfaces, as well as hydrostatic stress and plasticity trapping. It is necessary to develop a new method to guarantee that dissolved H is retained about the crack tip at a known level, while maintaining IHE instead of hydrogen environment embrittlement (HEE), relevant to a thick-steel component. The issues of crack tip hydrogen production and uptake that constitute HEE are ill defined and not necessarily relevant to the IHE problem [7,13].

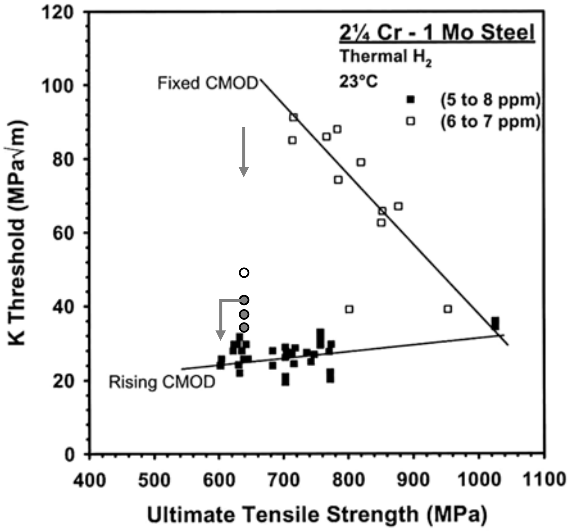

Figure 1: Stress intensity threshold from H_2-precharged standard specimens of bainitic Cr-Mo base steel at ambient [4]. Threshold data from slotted specimens during slow-rate rising CMOD (●) and fixed CMOD (o) for lower strength Cr-Mo weld metal are shown for comparison. The slotted CT was under electrochemical charging using thiosulfate that produced total H of 3.0 wppm on slot surface.

1.2 Objective

The objective of this research is to design, implement and validate a new experimental method to quantitatively characterize the threshold and kinetics of IHE under a known-constant amount of H about the crack tip process zone. The resulting data will be input to fitness-for-service modeling and interpreted to understand H concentration, temperature, and loading rate dependent IHE in Cr-Mo steel.

2 APPROACH AND PROCEDURES

The experimental method uses the slotted CT specimen in Fig. 2. Hydrogen is charged from an electrolyte pumped through the slots before and during a fracture experiment. The specimen and cell are mounted in a tensile machine coupled with a chamber for heating or cooling. The specimen is instrumented to measure load, CMOD and crack length, and the machine is automated to control these loading parameters. Output is the H-sensitive threshold for subcritical cracking, as well as growth rates, for IHE under both rising CMOD-rising K and fixed CMOD-falling K loading using elastic-plastic fracture mechanics [4,14].

Implementation and validation of this approach requires several steps. Finite element analysis (FEA) is performed to quantify the effect of the slot on fracture mechanics parameters necessary for data analysis. Second, mechanical experiments verify the FEA modeling and provide the relationship for crack length monitoring by the direct-current potential difference (dcPD) method. Third, FEA is used to model the time evolution to steady state of the H distribution in the CT specimen *vs.* temperature and K, focusing on the crack tip region. Fourth, electrochemical experiments are employed to determine a safe-manageable electrolyte for H charging, and to

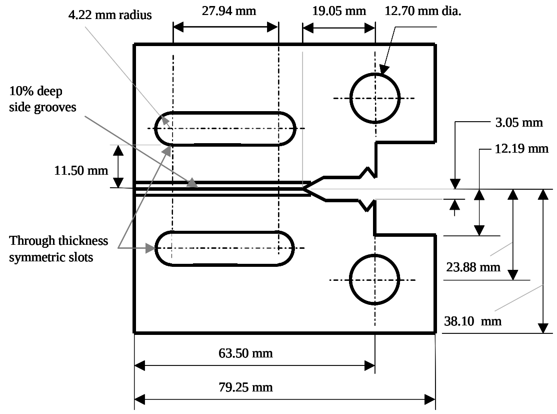

Figure 2: The modified CT specimen used for IHE experiments. The 25.4 mm thick specimen with 10% deep side grooves has through thickness symmetric slots at 11.50 mm from the crack plane.

establish the calibration relationship between diffusible and total hydrogen concentrations *vs.* current density and temperature. Finally, it is necessary to demonstrate that the slotted specimen method produces IHE and fracture mechanics data useful in quantitative FFS modeling. The details of these procedures are reported elsewhere [4].

2¼Cr-1Mo weld metal was studied. The material was supplied in the as post-weld heat treated and step-cooled condition to produce constant temper embrittlement. The microstructure is tempered bainite, yield strength (σ_{YS}) is 508 MPa, ultimate tensile strength (σ_{UTS}) is 639 MPa, and Charpy fracture appearance transition temperature (FATT) is 45°C suggesting substantial temper embrittlement. The plane strain initiation fracture toughness (K_{JICi}) of this weld metal, measured at 25°C without H addition, varied from 102 to 133 MPa√m, typical of the transition regime fracture behavior of temper-embrittled Cr-Mo steel

3 RESULTS

3.1 Fracture Mechanics

A two-dimensional finite element model using ABAQUS demonstrated that slots above and below the crack plane of the CT specimen do not diminish crack tip stresses from standard CT specimen constraint and *J*-dominance, and provided solutions for K, compliance, and elastic-plastic *J*-integral [4,15]. The crack tip stress and plastic strain distributions are used in diffusion modeling.

3.2 Hydrogen Diffusion Modeling

Hydrogen distributions about the crack tip were modeled in 3D using ABAQUS [16] and as a function of time, temperature, K and dK/dt. An apparent H diffusivity ($D_{H\text{-}app}$) that varied with H content, temperature and plastic strain, was used to approximate the effect of reversible trapping on H transport and diffusible H concentration. Hydrostatic stress and equivalent plastic strain distributions were obtained from the fracture mechanics model. The slot surface diffusible H content, $C_{H\text{-diff-slot (t)}}$, and the initial-bulk diffusible H for the H_2 precharged case, $C_{H\text{-diff-bulk (t=0)}}$, were set at 1.0 wppm to facilitate comparison. Results are shown in Fig. 3. Predicted times for slot

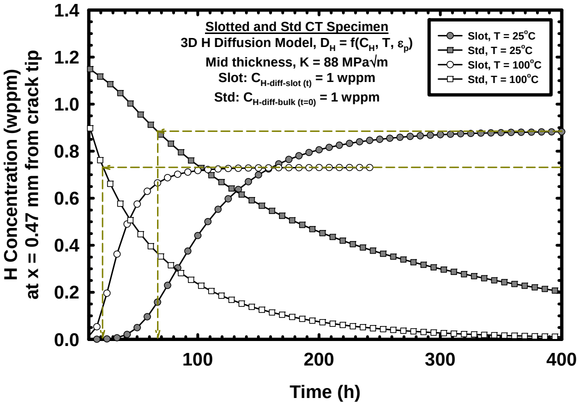

Figure 3: Time history of diffusible H concentration near the crack tip at mid thickness for both slotted and standard specimens of Cr-Mo weld metal at K = 88 MPa√m and two temperatures.

precharging to steady state at K = 0 were 278 h (25°C) and 91 h (100°C). The standard CT has a higher predicted diffusible H content just (0.47 mm) ahead of the crack tip than the slot case during rising-K at 25°C and 100°C, for dK/dt = 7 x 10^{-3} MPa√m/s. This H level in the standard specimen drops to below that of the slotted case after 67 h (25°C) and 22 h (100°C) at K = 88 MPa√m.

3.3 Hydrogen Uptake

Hydrogen uptake into steel increases with increasing trap site density and increasing H-trap binding energy; typically encountered in higher strength martensitic and carbide precipitate hardened microstructures [4,13]. Hydrogen uptake into the relatively low strength Cr-Mo weld metal from electrolytes at 25-100°C is hindered by the modest H trapping. This behavior limits application of the new slotted-CT specimen to characterize IHE from higher total H contents (3-5 wppm) typical of high temperature-pressure H_2 charging [1]. Less corrosive and safe alkaline-hydroxide solutions provide less diffusible H (0.5-1.0 wppm), with a 2.0-2.5 wppm diffusible H level achievable with toxic arsenic addition and acidification that produces steel surface damage [4]. The optimum diffusible and total H absorbed by low to moderate strength Cr-Mo steel are 2.0 and 3.0 wppm, respectively, when using sulfuric acid plus thiosulfate solution at 25°C, or with addition of an inhibitor at 60°C [4]. This environment was used for the IHE experiments.

3.4 IHE Experiments

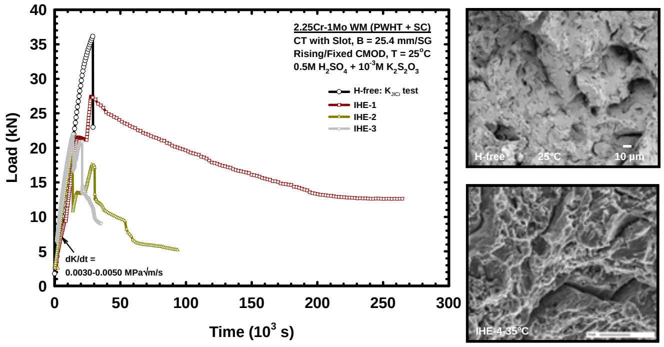

Figure 4: Load *vs.* time data for three 2.25Cr-1Mo weld metal slotted CT specimens tested under rising and fixed CMOD. The specimens were charged with 0.5M H_2SO_4 + 10^{-3}M $K_2S_2O_3$ at 25°C. Included for reference is a H-free fracture toughness test at 25°C. H-embrittlement produced a fracture mode change as evidenced by the SEM images of H-free (top) *vs.* H-charged (bottom) specimens.

Slotted specimens of Cr-Mo weld metal, charged with 0.5M H_2SO_4 + 10^{-3}M $K_2S_2O_3$ at 25°C and 5 mA/cm^2, developed IHE when stressed at 25°C. Fig. 4 shows load *vs.* time for replicate H charged specimens subjected to rising and fixed CMOD, and compared to a H-free specimen. The H-free case exhibited unstable crack growth, without prior-stable tearing, at a load of 36 kN for K_{JICi} = 121 MPa√m. The loading curves establish that each of the H charged specimens exhibited substantial H-cracking during both rising and fixed CMOD at K below K_{JICi} (102-133 MPa√m) [4].

IHE-1 exhibited subcritical H-cracking during rising and fixed CMOD segments, with growth of 1.1 mm (Δa_{RISE}) and 3.7 mm (Δa_{HOLD}). The K_{IH} was 41 MPa√m. During rising CMOD, loading stopped due to equipment malfunction; after 2 h at stalled CMOD, load again rose to the programmed hold. Growth rates slowed immediately then accelerated, responding to these changes in loading. Subcritical H cracking continued at fixed CMOD, with $K_{INITIAL}$ and K_{TH} of 90 MPa√m and 48 MPa√m, respectively. A 5th order polynomial was fit to a(t) data and da/dt *vs.* K results were calculated; Fig. 5. Growth rate relationships depend on loading format. For IHE-1, da/dt of 3 x 10^{-4} mm/s at the end of rising CMOD at K = 90 MPa√m dropped almost instantaneously to 5 x 10^{-5} mm/s when CMOD was fixed. Crack growth rate during rising CMOD decreased to that of fixed CMOD cracking when the load stopped rising due to the malfunction.

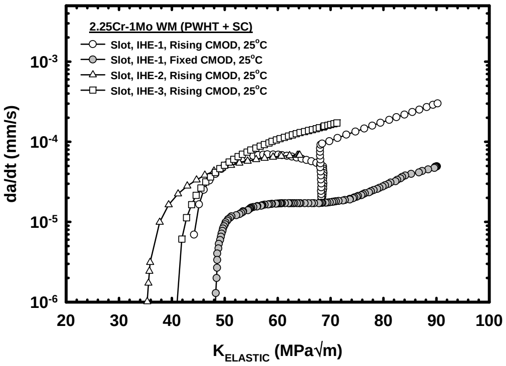

Figure 5: da/dt *vs.* $K_{ELASTIC}$ for 2.25Cr-1Mo weld metal under rising and fixed CMOD from slotted specimens charged using sulfuric acid + thiosulfate at 25°C.

The K_{TH} (48 MPa√m) for crack arrest is greater than K_{IH} (41 MPa√m) for the onset of subcritical crack growth under rising K.

Replicate experiments with weld metal at 25°C (IHE-2 and IHE-3) confirmed H-enhanced cracking and yielded similar IHE properties. The K_{IH} from IHE-2 and IHE-3 were 35 and 38 MPa√m. Although applied dK/dt in the three experiments varied somewhat (0.003-0.005 MPa√m/s before crack initiation), the da/dt for stable cracking upon rising CMOD at K of 50 MPa√m were almost equal (5-5.1 x 10^{-5} mm/s in Fig. 5). Specimens, IHE-2 and IHE-3 exhibited stable H-cracking on rising K, followed by mixed stable and very rapid H-crack growth segments during both rising and falling K segments. Crack growth during rising CMOD was substantially longer for IHE-2 and IHE-3. (IHE-2: Δa_{RISE} = 12.4 mm and Δa_{HOLD} = 7.1 mm; IHE-3: Δa_{RISE} = 12.7 mm and Δa_{HOLD} =1.3 mm). Cracking over such large distances deviated toward the slot due to the higher H concentration and/or high T bending stress.

4 DISCUSSION

The slotted CT method is validated as a tool to produce fracture mechanics data on IHE, relevant to fitness-for-service modeling of thick-wall reactors. Necessary fracture mechanics formulations and electrochemical conditions are established [4]. The slotted specimen produced severe IHE in temper embrittled Cr-Mo weld metal during both rising and falling K loading. The amount of H introduced electrochemically in low strength steel is limited compared to elevated temperature H_2 charging. As illustrated in Fig. 1, K_{IH} from the slotted specimen (35-41 MPa√m) is higher than the large body of data from H_2-precharged standard specimens (20-32 MPa√m). This is due to the lower dissolved H at steady state and proximate to the crack tip process zone in the slotted CT with slot surface total H of 3.0 wppm. For the standard CT, initial total H from H_2 can be controlled between 0.5 and 5-6 wppm. Diffusion modeling, including the effects of crack tip stress and H trapping at dislocations from plastic strain, uniquely correlates measured K_{IH} from the standard and slotted CT specimens with the level of H enriched in the crack tip process zone.

The K_{TH} from the slotted specimen (48 MPa√m) under slowly falling K is lower than that expected from the standard specimen (≈ 80-100 MPa√m) at the same strength level. This is due to both differing degrees of temper embrittlement between the present weld metal and data for base plate in Fig. 1, as well as H loss from the standard CT during 400-600 h loading at ambient. The results from the standard specimen at fixed CMOD are non-conservative and not useful for fitness modeling. The K_{TH} measured from the slotted specimen is higher than K_{IH}, establishing that this difference is not an artifact of H loss from the standard specimen, but rather results from an undefined H-plasticity interaction in the crack tip process zone.

The slotted specimen is ideally suited for characterizing the temperature dependence of IHE, a central issue in fitness modeling. Results in Fig. 3 establish the significant and variable H loss from the standard H_2 precharged CT specimen stressed at 50^{o}C-150^{o}C. The slotted specimen results in Figs. 1 through 5 were obtained at 25^{o}C, but the method was extended to measure K_{IH}/K_{TH} and da/dt for IHE at temperatures up to 65^{o}C [4]. Issues of temperature dependent H uptake and corrosion of steel in sulfuric acid/thiosulfate electrolyte are significant, but solvable.

5 CONCLUSIONS

(1) A new slotted CT specimen approach delivers sufficient H to the crack tip in Cr-Mo steel to cause internal H embrittlement at 25°C, with the advantage that dissolved H is constant and not lost. This method characterizes effects of variables to enable fitness-for-service modeling.

(2) A 3-D finite element diffusion model predicts H distribution about the stressed crack tip, including trapping. The slot case provides higher-constant H for long test times. If slot surface H is two-fold higher than uniform H from H_2, then the slot method is always superior.

(3) H from sulfuric acid-thiosulfate charged slots embrittles 2¼Cr-1Mo weld metal, with the onset of subcritical cracking threshold under rising CMOD ($K_{IH} \approx 35\text{-}41$ MPa√m) less than the crack arrest threshold at fixed CMOD ($K_{TH} \approx 48$ MPa√m). Subcritical crack growth rates are higher for rising *vs.* fixed CMOD loading; suggesting a role of crack tip plasticity.

(4) Enriched crack tip H concentration governs H-embrittlement. Higher K_{IH} from the sulfuric acid-thiosulfate charged slotted specimen, compared to thresholds form H_2-precharged specimens, correlates with reduced crack tip H estimated from the H diffusion model.

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6 REFERENCES

[1] Gangloff RP. Laboratory studies of hydrogen embrittlement in aging Cr-Mo steel for thick-wall reactors. Joint Industry Program on Hydroprocessing Reactors, Chevron Research and Technology Co., Richmond, CA, 2001.

[2] Sakai T, Takahashi T, Yamada M, Nose S, Katsumata M. Effect of hydrogen on MPT and de-hydrogenation during shut down in hydroprocessing reactors. In: High Pressure Technology, ASME'97, PVP-344, p. 79-89, 1997.

[3] Prescott GR. Temper embrittlement and crack growth in vintage hydroprocessing reactors. Report No. 7, Joint Industry Program on Hydroprocessing Reactors, Chevron Research and Technology Co., Richmond, CA, 1998.

[4] Al-Rumaih AM. Measurement and modeling of temperature dependent hydrogen embrittlement of Cr-Mo steel to enable fitness-for-service life prediction. PhD Dissertation, University of Virginia, Charlottesville, VA, 2004.

[5] Bagdasarian AJ, Bereczky EL, Ishiguro T, Ishizuka T, Tahara T. Investigation of 26 year old hydroprocessing reactors. Paper No. 629, Corrosion'93, NACE, Houston, TX, 1993.

[6] Al-Rumaih AM. Aging hydroprocessing reactors. CSD Technology Report No. SAER 5743, Saudi Aramco, 2000.

[7] Gao M, Wei RP. A hydrogen partitioning model for hydrogen assisted crack growth. Metall. Trans. A, 1985; 16A: 2039-50.

[8] Gerberich, WW, Livne T, Chen XF, Kaczorowski M. Crack growth from internal hydrogen-Temperature and microstructural effects in 4340 steel. Metall Trans A, 1988; 19A: 1319-34.

[9] Moody NR, Baskes MI, Robinson SL, Perra MW. Temperature effects on hydrogen-induced crack growth susceptibility of iron-based superalloys. Engng Fract Mech, 2001; 68: 731-50.

[10] Gangloff RP. Fracture mechanics characterization of hydrogen embrittlement in Cr-Mo steel. In: Present Situation on Steels for Hydrogen Pressure Vessels, CLI, Burgundy, France, 1998.

[11] Yamakawa K, Sakai O. Critical hydrogen content on hydrogen embrittlement of high strength steel. In: Int Congress on Metallic Corrosion, National Research Council, Toronto, Canada, 1984. p. 254-61.

[12] Kobayashi J, Ouchi H, Takeshi Y, Takeda T. Evaluation of threshold stress intensity of 2.25Cr-1Mo steels in hydrogen charging environment. In: Conf Proceed Pressure Vessel Technology, Germany, 1992.

[13] Gangloff RP. Hydrogen assisted cracking of high strength alloys. In: Comprehensive Structural Integrity, V6, Milne I, Ritchie RO, Karihaloo B, Eds., Elsevier Science, New York, NY, p. 31-101, 2003.

[14] Standard test method for measurements of fracture toughness. 1999 Annual Book of ASTM, 03.01, E1820-99a, West Conshohocken, PA.

[15] Vargas PM. Unpublished Research. ChevronTexaco, Richmond, CA. 2001.

[16] ABAQUS std user's manual: Volume I-III. Version 6.1, Hibbitt, Karlsson & Sorensen, Inc., Pawtucket, RI 12860.