

# Literature Review of Fracture Mechanics–based Experimental Data for Internal Hydrogen-assisted Cracking of Vanadium-modified 2¼Cr-1Mo Steel

API TECHNICAL REPORT 934-F, PART 2  
FIRST EDITION, AUGUST 2017



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# Literature Review of Fracture Mechanics–based Experimental Data for Internal Hydrogen-assisted Cracking of Vanadium-modified 2¼Cr-1Mo Steel

**Downstream Segment**

API TECHNICAL REPORT 934-F, PART 1  
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## Executive Summary

Literature data collectively suggest that V-modified 2¼Cr-1Mo base plate and weld metal each exhibit improved resistance to Internal Hydrogen-assisted Cracking (IHAC) compared to modern 2¼Cr-1Mo steel, where each steel is typified by modern-low J-factor or low  $X_B$ , and thus minimal temper embrittlement. IHAC in petrochemical applications typically involves H charging of the steel during elevated temperature exposure in high-pressure  $H_2$ , followed by stressing at near-ambient temperatures. For V-modified Cr-Mo, the slow-rising-displacement threshold stress intensity ( $K_{IH}$ ) is a significant fraction of the H-free plane strain fracture toughness; however, V-modified steels are immune to IHAC for this conservatively aggressive loading mode. This good IHAC resistance is attributed to beneficial H interaction with nano-scale vanadium carbide trap sites, but the details of this complex trapping behavior are neither quantified nor fully understood.

No single study of IHAC in 2¼Cr-1Mo-0.25V base plate or weld metal is sufficiently comprehensive and quantitative to support fracture-mechanics modeling of pressure vessel fitness for service or a minimum pressurization temperature. Uncertainties in the existing data base are associated with:

- a) the challenge in detecting  $K_{IH}$  in the midst of substantial crack tip plastic deformation;
- b) slow crack growth rates typical of reversible H-trap interaction;
- c) the lack of experimental results for very slow loading rates, weld metal, and stressing temperatures from -25 °C to 200 °C;
- d) demonstration of H retention during an IHAC experiment;
- e) lack of understanding of the fundamental mechanism by which H trapping at  $V_xC_y$  precipitates reduces susceptibility to IHAC; and
- f) the effect of low-temperature H charging.

All  $K_{IH}$  data for conventional and V-modified Cr-Mo steel reflect H charging followed by rising-displacement loading in moist air. A novel-deleterious interaction of IHAC and Hydrogen Environment-assisted Cracking (HEAC) for stressing of H precharged specimens in  $H_2$  may occur, but is not supported by sufficient published data for Cr-Mo and Cr-Mo-V steels. H precharging, with stressing in moist air, or stressing in high-pressure  $H_2$ , without H precharging, are both capable of producing substantial H embrittlement in conventional Cr-Mo steel. Preliminary data show that V-modified Cr-Mo (without H precharging) is susceptible to HEAC in high-pressure  $H_2$ , conforming with the behavior of other low-to moderate-strength alloy steels, and apparently less affected by H trapping at vanadium carbides.  $K_{IH}$  values for uncharged 2¼Cr-1Mo-0.25V base plate stressed in high-pressure  $H_2$  are substantially less than the thresholds typical of IHAC. The HEAC susceptibility of V-modified Cr-Mo should be considered in pressure vessel fitness-for-service modeling.

The ongoing laboratory study, commissioned by API Task Group 934F on Heavy Wall Pressure Vessel MPT, is addressing these uncertainties for 2¼Cr-1Mo-0.25V weld metal and base plate. Literature results obtained after about 2002 are sufficiently accurate and detailed to provide important comparisons with these newly emerging laboratory data. The result will be a strong characterization of the IHAC susceptibility of V-modified Cr-Mo steels.

# Literature Review of Fracture Mechanics–based Experimental Data for Internal Hydrogen-assisted Cracking of Vanadium-modified 2<sup>1</sup>/<sub>4</sub>Cr-1Mo Steel

## 1 Background

Between 1980 and 1990, researchers in Japan, France, and the United States determined that bainitic 2<sup>1</sup>/<sub>4</sub>Cr-1Mo steels (UNS K21590) exhibited unexpectedly low-threshold  $K_{IH}$  for the onset of Internal Hydrogen Assisted Cracking (IHAC). Much of this work was sponsored by the American Petroleum Institute and the Materials Properties Council (MPC). Such cracking was observed for compact tension specimens that were fatigue precracked, precharged with atomic hydrogen (H) through elevated temperature exposure in high pressure H<sub>2</sub>, and stressed under slow-rising crack mouth opening displacement (CMOD). The threshold for IHAC under static displacement loading was very high, as is expected for this moderate-strength steel.

While this class of Cr-Mo pressure vessel steels is clearly susceptible to significant IHAC under these conditions, initial data were uncertain for several reasons:

- lack of a standardized experimental method;
- detection of the onset of crack growth during rising CMOD was not rigorous;
- plasticity during loading complicated crack-growth detection and elastic stress intensity factor analysis;
- variables including actual loading rate in terms of  $dK/dt$  and H loss during testing were either not controlled or not reported;
- high variability in  $K_{IH}$  measurement both for a single laboratory and across groups;
- the mechanism for the deleterious effect of rising CMOD on IHAC was not elucidated; and
- much of this work was presented as hard copy associated with API-MPC committee presentations, or in conference proceedings, and was not published in peer-reviewed journals.

Between 1994 and 2000, a joint industry program (JIP) was conducted, including five laboratories in Japan, France, and the United States, to develop a rigorous-standard test method for measurement of  $K_{IH}$ , as well as crack-growth rate ( $da/dN$ ) versus elastic-plastic stress intensity ( $K_J$ ) and the threshold for the arrest of IHAC ( $K_{TH}$ ) [1,2]. This method was then applied to develop a strong data base for IHAC of 12 heats of 2<sup>1</sup>/<sub>4</sub>Cr-1Mo base plate and weld metal, with impurity composition (and degree of temper embrittlement) being a primary variable, as well as retained H concentration and applied  $dK/dt$  [2]. Figure 1 provides a collection of results from this work, plotted as  $K_{IH}$  versus total-dissolved H concentration for several low-impurity (J-factor < 100 wt pct) and thus low-Fracture Appearance Transition Temperature (FATT) (FATT < -28°C) heats of 2<sup>1</sup>/<sub>4</sub>Cr-1Mo base plate and weld metal [3]. All experiments were conducted at 23 °C, with 25.4 mm thick standard compact tension specimens precharged in H<sub>2</sub> at several combinations of elevated temperature and H<sub>2</sub> pressure. Results for the high-purity Phase I steels are shown by filled diamonds with the associated trend line [3]. Open and filled circles and triangles represent older literature data for a 2<sup>1</sup>/<sub>4</sub>Cr-1Mo base plate that was not temper embrittled (J and FATT were not published, but are very likely low). The ultimate tensile strength of these steels was between 585 MPa and 605 MPa. The solid-to-dashed line shows the Phase I REACT software algorithm used to describe the H concentration dependence of  $K_{IH}$  for high-purity/low-FATT steels [2].

The severity of IHAC for this class of Cr-Mo steels is apparent in Figure 1, considering that the plane strain fracture toughness for this class of steels is of order 300 MPa√m at 23 °C. From 2002 through 2008, Phase II of this JIP centered on measurement and modeling of the effect of temperature on IHAC in 2<sup>1</sup>/<sub>4</sub>Cr-1Mo base plate and weld metal, and a fracture mechanics–based method was developed to predict the

minimum pressurization temperature based on IHAC under rising displacement [3,4]. This analysis augments determination of MPT governed by other important failure modes, including H-sensitive unstable fracture [5-7].

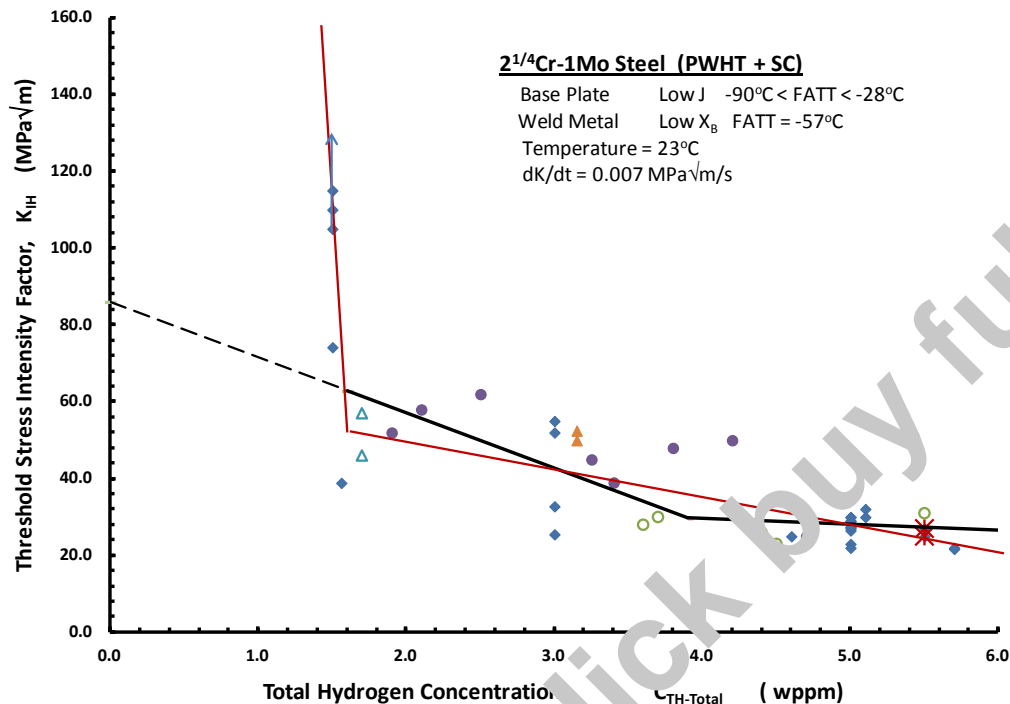


Figure 1 (after Chang [3])

In the early 1980s, in parallel with this focus on IHAC of Cr-Mo, vanadium-modified Cr-Mo steels were developed for heavy wall hydrocracking reactor applications [8,9]. The microstructure was almost always bainitic. The presence of homogeneously precipitated, nano-scale vanadium carbides ( $VC$  and  $V_4C_3$ ) was hypothesized to greatly reduce the mobility of H through strong-reversible or even irreversible trapping, with the result being reduced susceptibility to IHAC. Fracture mechanics-based data were presented to characterize the IHAC performance of two primary compositions:  $2\frac{1}{4}Cr-1Mo-0.25V-0.035Nb-0.13C$  (UNS K31835, minimum yield strength ( $\sigma_{YS}$ ) = 415 MPa, and minimum ultimate tensile strength ( $\sigma_{UTS}$ ) = 585 MPa) and  $3Cr-1Mo-0.25V-0.035Nb-0.13C-(Ti,B)$  (UNS K31830, minimum  $\sigma_{YS}$  = 415 MPa and minimum  $\sigma_{UTS}$  = 585 MPa).

These V-modified steels exhibited better resistance to IHAC under slow-rising CMOD compared to conventional Cr-Mo steels. However, these data are not sufficient to quantify the IHAC resistance of these steels because:

- the issues noted above for  $2\frac{1}{4}Cr-1Mo$  are equally relevant to V-modified steels;
- reduced H mobility likely reduces  $da/dt$ , which further complicates time-dependent experimental measurements relevant to long-term IHAC behavior;
- the temperature dependence of IHAC depends on H trapping and may differ for the V-modified grades, and was not reported; and
- small laboratory heats were used for a portion of the early laboratory experiments.

Given these uncertainties, API Task Group 934-F on Heavy Wall Pressure Vessel MPT commissioned a laboratory study of the IHAC resistance of modern  $2\frac{1}{4}Cr-1Mo-0.25V-0.035Nb-0.13C$ . The objective of this program is to employ the JIP-developed standard method to quantify the IHAC resistance of precracked specimens of modern  $2\frac{1}{4}Cr-1Mo-\frac{1}{4}V$  base plate and weld metal. Particular emphasis is placed on