

Subcritical Cracking of Modern 2¹/₄Cr-1Mo-¹/₄V Steel Due to Dissolved Internal Hydrogen and H₂ Environment, Research Report

API TECHNICAL REPORT 934-F, PART 3
FIRST EDITION, DECEMBER 2017



AMERICAN PETROLEUM INSTITUTE

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Contents

	Page
Executive Summary	xiv
Background	1
Literature Review of Hydrogen Cracking in Cr-Mo-V Steel	3
Research Objectives	4
Abbreviations	4
Experimental Procedures	4
Results	17
Discussion	93
Conclusions	136
Annex A—Cr-Mo-V Base Plate Specifications	139
Annex B—Cr-Mo-V Weld Metal Specifications	140
Bibliography	142

Figures

1	The effect of predissolved bulk total H concentration on K_{IH} for IHAC of several heats of modern low-impurity Cr-Mo base plate and weld metal stressed under slow-rising K at 23 °C	2
2	Welded test block of 2¼Cr-1Mo-0.27V steel	6
3	Welded test block geometry	7
4	Autoclave assembly used for elevated-temperature H charging in a high-pressure H ₂ environment ...	8
5	The temperature dependence of the Sievert's law solubility coefficient for Cr-Mo and Cr-Mo-V steels	10
6	The temperature dependence of the H diffusivity for Cr-Mo and Cr-Mo-V steels	11
7	Results of an error analysis relating the concentration of dissolved H (top axis, in wppm) and the mass of the steel specimen analyzed (vertical axis, gm) to the error index	13
8	C(T) specimen orientation in the welded blocks of 2¼Cr-1Mo-¼V steel	14
9	Instrumentation elements of the IHAC test method	15
10	Compact tension specimen and associated probes for IHAC testing	16
11	Apparatus used for high-pressure H ₂ testing of compact tension specimens	18
12	Time-dependent H loss during isothermal exposure of 2¼Cr-1Mo-0.30V base metal in moist air at 23 °C and 100 °C	22
13	Time-dependent H loss during isothermal exposure of 2¼Cr-1Mo-0.27V weld metal in moist air at 23 °C and 100 °C	22
14	The temperature dependence of trap-sensitive effective H diffusivity (D_{H-Eff}) for weld metal and base plate of the 2¼Cr-1Mo-0.3V steel used in this API study of IHAC.	23
15	R-curve based fracture toughness for step-cooled 2¼Cr-1Mo-0.3V base plate and weld metal at two loading temperatures.	24

Contents

Page

16	(Top) Load and DCPD vs CMOD, and (bottom) definition of the onset of stable crack propagation based on amplified DCPD vs CMOD	25
17	Scanning electron fractographs showing ductile fracture in 2¼Cr-1Mo-0.3V base metal at 23 °C	26
18	Crack extension vs applied K_I for C(T) specimens of 2¼Cr-1Mo-0.3V base metal, with and without precharged H	27
19	(Top left) DCPD vs CMOD and (bottom right) DCPD vs the J-integral to define the onset of crack extension at the indicated value of K_{IH} for specimen BM8A of 2¼Cr-1Mo-0.3V containing precharged H	28
20	(Top) Stretch zone in 2¼Cr-1Mo-0.3V base metal without H (BM2A), (bottom left) stretch zone appearance in a base metal specimen with precharged H (BM8A), and (bottom right) stretch zone in a H-precharged specimen of weld metal (WMA4)	29
21	The slope of DCPD vs CMOD, prior to the onset of organized crack extension, is parallel for noncharged base metal, noncharged weld metal, and H-precharged base metal at 26 °C and 40 °C	30
22	Measured DCPD vs CMOD (top) and calculated crack length from Johnson's equation vs CMOD (bottom), using the first deviation in DCPD–CMOD linearity as the onset of crack extension for specimen BM6A	32
23	Measured DCPD vs CMOD (top) and calculated crack length from Johnson's equation vs CMOD (bottom), using the first deviation in DCPD–CMOD linearity as the onset of crack extension for specimen BM10A	33
24	SEM fractographs of the zones of stretch and stable cracking ahead of the fatigue precrack shown in the bottom half of each image for: (top) BM6A and (bottom) BM10A	34
25	Measured DCPD vs CMOD (top) and calculated crack length from Johnson's equation vs CMOD (bottom), using the first deviation in DCPD–CMOD linearity as the onset of crack extension for specimen BM4A	36
26	SEM fractograph of the zones of fatigue precrack (bottom arrow), stretch/H cracking (middle arrow), and post-test cleavage (top arrow) specimen BM4A	37
27	Measured DCPD vs CMOD (top) and SEM fractograph for specimen BM11A	38
28	Measured DCPD vs CMOD (top) and SEM fractograph for weld metal specimen WMC4.	40
29	Measured DCPD vs CMOD (top) and calculated crack length from Johnson's equation vs CMOD (bottom), using the indicated deviation in DCPD–CMOD linearity as the onset of crack extension for specimen WMD3	41
30	SEM fractograph of the three zones of cracking observed in the interrupted loading experiment with H-precharged weld metal specimen WMD3.	42
31	Macrophotographs of the fracture surfaces for interrupted specimens of Cr-Mo-V steel	42
32	Measured DCPD vs CMOD (top) and calculated crack length from Johnson's equation vs CMOD (bottom)	43
33	Composite SEM fractographs of the fracture surface from specimen BM12-3	44

Contents

Page

34	Macrophotographs of 2¼Cr-1Mo-0.30V base metal compact tension specimens that were fatigue precracked, H-precharged, stressed under slow-rising K in moist air, unloaded, and fractured in liquid nitrogen	48
35	(Top) Load and DCPD vs CMOD. (Middle) Amplified definition of the onset of crack propagation using the defined departure in linear DCPD vs CMOD at the resulting value of K_{IH} . (Bottom) Crack growth resistance curve, given as the amount of stable crack growth vs applied elastic-plastic K	49–50
36	Crack growth resistance curves, plotted as the elastic-plastic stress intensity factor vs crack extension from DCPD, for H-precharged 2¼Cr-1Mo-0.3V base metal stressed under slow-rising K at 26 °C.	51
37	Macrophotograph of the fracture surface of 2¼Cr-1Mo-0.3V base metal specimen BM8A, showing the fatigue precrack (bottom flat region), IHAC region (middle roughened features), and liquid nitrogen cleavage region (top)	52
38	Scanning electron fractographs for (top) ductile fracture in H-free 2¼Cr-1Mo-0.3V BM and (bottom) IHAC in H-precharged BM, each stressed under slow-rising K in moist air at 26 °C.	52
39	Scanning electron fractographs for (top left) ductile fracture in H-free 2¼Cr-1Mo-0.3V BM and (top right and bottom) IHAC in H-precharged BM, each stressed under slow-rising K in moist air at 26 °C	53
40	The loading rate dependence of K_{IH} for IHAC in 2¼Cr-1Mo-0.3V BM at 26 °C compared to values measured for 2¼Cr-1Mo BM and WM at 23 °C to 26 °C using the conservatively aggressive slow-rising K test method.	54
41	Crack growth resistance curves, plotted as crack extension vs the elastic-plastic stress intensity factor, for 2¼Cr-1Mo-0.30V base metal, both as-received and after H charging, for slow-rising K loading at a 23 °C and 100 °C	55
42	Crack growth resistance curves, plotted as the elastic-plastic stress intensity factor vs crack extension from DCPD, for H-precharged 2¼Cr-1Mo-0.3V base metal stressed under slow-rising K at a variety of temperatures	55
43	Crack growth resistance curves, plotted as the elastic-plastic stress intensity factor vs crack extension from DCPD, for H-precharged 2¼Cr-1Mo-0.3V base metal stressed under slow-rising K at a variety of temperatures	56
44	The temperature dependence of K_{IH} for IHAC in 2¼Cr-1Mo-0.3V BM for the specific slow-rising dK/dt and total remaining H concentration conditions listed in Table 9	56
45	The temperature dependencies of K_{IH} (○,● from Figure 44) and K_{JIH} (▲) for IHAC in 2¼Cr-1Mo-0.30V BM for the specific slow-rising dK/dt and total remaining H concentration conditions listed in Table 9	57
46	Crack growth resistance curve and C(T) specimen temperature vs crack extension for the H-precharged 2¼Cr-1Mo-0.30V BM specimen stressed under slow-rising K at –10 °C	58
47	Macrophotographs of fatigue precracked, H-precharged, and fractured specimens of 2¼Cr-1Mo-0.27V weld metal. (top) WMA4 and (bottom) WMA1.	59

Contents

Page

48	(Top) Load and DCPD vs CMOD. (Middle) Amplified definition of the onset of crack propagation using the defined departure in linear DCPD vs CMOD at the resulting value of K_{IH} . (Bottom) Crack growth resistance curve, given as the amount of stable crack growth vs applied elastic-plastic K	59–60
49	Applied elastic-plastic K_J vs stable crack extension for 2¼Cr-1Mo-0.27V weld metal subjected to slow-rising displacement loading at 26 °C, with and without H precharging to a total dissolved H concentration of between 7.5 wppm and 7.8 wppm remaining in the C(T) specimen after fracture testing.	61
50	SEM fractographs of the IHAC morphology in 2¼Cr-1Mo-0.27V weld metal (specimen WMA4: 26 °C, 7.8 wppm remaining H content, 18 MPa√m/h) showing the region just after the fatigue precrack, with H-assisted crack propagation from bottom to top.	63
51	SEM fractographs of the IHAC morphology in 2¼Cr-1Mo-0.27V weld metal (specimen WMA4: 26 °C, 7.8 wppm remaining H content, 18 MPa√m/h) showing the region substantially ahead of the fatigue precrack, with H-assisted crack propagation from bottom to top . .	64
52	SEM fractographs of the IHAC morphology in 2¼Cr-1Mo-0.27V weld metal (specimen WMA4: 26 °C, 7.8 wppm remaining H content, 18 MPa√m/h) showing the region substantially ahead of the fatigue precrack, with H-assisted crack propagation from bottom to top . . .	65
53	SEM fractographs of transgranular IHAC morphologies in 2¼Cr-1Mo-0.3V weld metal (left images: specimen WMA4: 26 °C, 7.8 wppm remaining H content, 18 MPa√m/h) and base metal (right images: specimen BM8A 25 °C, 9.5 wppm remaining H content, 2 MPa√m/h) comparing various regions ahead of the fatigue precrack, with H-assisted crack propagation from bottom to top	66
54	Applied elastic-plastic K_J vs stable crack extension for 2¼Cr-1Mo-0.27V weld metal subjected to slow-rising displacement loading at 26 °C and 100 °C, with and without H precharging to a total dissolved H concentration of between 7.5 wppm and 7.8 wppm for 26 °C and 6.6 wppm for the 100 °C specimen	67
55	Crack growth resistance curves, plotted as the elastic-plastic stress intensity factor vs crack extension from DCPD, for H-precharged 2¼Cr-1Mo-0.27V weld metal stressed under slow-rising K at a variety of temperatures	67
56	The temperature dependence of K_{IH} for IHAC in 2¼Cr-1Mo-0.27V WM for the specific slow-rising dK/dt and total remaining H concentration conditions listed in Table 9	68
57	The temperature dependence of K_{JIH} for IHAC in 2¼Cr-1Mo-0.27V WM for the specific slow-rising dK/dt and total remaining H concentration conditions listed in Table 9	69
58	Applied elastic-plastic K_J vs stable crack extension for 2¼Cr-1Mo-0.3V base metal and weld metal, each subjected to slow-rising displacement loading at 26 °C and 100 °C, with and without precharging to the indicated total dissolved H concentrations.	70
59	Crack growth resistance for the API lot of 2¼Cr-1Mo-0.3V BM tested in high-pressure H_2 (25 °C) at Sandia National Laboratory in Livermore, CA, compared to the behavior of H-free and H-precharged specimens tested at Hy-Performance Materials Testing	71
60	(Top) Load and DCPD vs CMOD. (Middle) Amplified definition of the onset of crack propagation using the defined departure in linear DCPD vs CMOD at the resulting value of K_{IH} . (Bottom) Crack growth resistance curve, given as the amount of stable crack growth vs applied elastic-plastic K	72–73

Contents

Page

61	Elastic-plastic K_J vs Δa resistance curve for as-received 2¼Cr-1Mo-0.30V base metal stressed under slow-rising K in high-pressure H_2 at 25 °C and various P_{H_2} levels	74
62	Elastic-plastic K_J vs a resistance curve for as-received 2¼Cr-1Mo-0.30V base metal stressed under slow-rising K in high-pressure H_2 at 25 °C and various P_{H_2} levels, compared to the IHAC behavior of this base metal containing 9.5 wppm H-precharged H and stressed in moist air	75
63	Scanning electron fractographs of crack surfaces produced in 2¼Cr-1Mo-0.30V base metal stressed under slow-rising K in: (top left) moist air without H precharging, (b) moist air after H precharging, (c) high-purity low-pressure H_2 without H precharging, and (d) high-pressure H_2 without H precharging; each at 25 °C	76
64	Scanning electron fractographs of crack surfaces produced in 2¼Cr-1Mo-0.30V base metal stressed under slow-rising K in: (top left) moist air without H precharging, (b) moist air after H precharging, (c) high-purity, low-pressure H_2 without H precharging, and (d) high-pressure H_2 without H precharging; each at 25 °C	77
65	H_2 pressure dependence of K_{IH} for slow-rising K stressing of as-received 2¼Cr-1Mo-0.3V base metal and weld metal for a variety of environmental conditions discussed in the text. The H-free K_{JICi} is arbitrarily plotted at P_{H_2} of 0.001 MPa, and the regression equation is shown based on the data for BM in pure H_2 at 25 °C (●), without K_{JICi} (top) and with K_{JICi} (bottom) . .	78
66	H_2 pressure dependence of K_{JIH} for slow-rising K stressing of as-received 2¼Cr-1Mo-0.3V base metal and weld metal for a variety of environmental conditions discussed in the text. The H-free K_{JIC} is plotted at 0.001 MPa, and the regression equation is shown based on the data for BM in pure H_2 at 25 °C (●) with K_{JIC}	79
67	Elastic-plastic K_J vs Δa resistance curve for as-received 2¼Cr-1Mo-0.30V base metal stressed under slow-rising K in high-pressure H_2 , and in O_2 -contaminated H_2 , each at 25 °C and P_{H_2} of 13.8 MPa	80
68	Elastic-plastic K_J vs Δa resistance curves for as-received (0 wppm H) and H-precharged (9.3 wppm to 9.4 wppm H) 2¼Cr-1Mo-0.30V base metal stressed under slow-rising K in high-pressure H_2 (P_{H_2} of 4.8 MPa or 13.8 MPa), compared to the behavior of as-received as well as H-precharged (9.5 wppm) BM stressed in moist air, each at 25 °C	81
69	Elastic-plastic K_J vs Δa resistance curves for as-received (0 wppm H) and H-precharged (7.2 wppm to 7.8 wppm H) 2¼Cr-1Mo-0.27V weld metal stressed under slow-rising K in either moist air or 13.8 MPa H_2 , each at 25 °C	82
70	Elastic-plastic K_J vs Δa resistance curves for as-received (0 wppm H) 2¼Cr-1Mo-0.3V weld metal and base metal stressed under slow-rising K in moist air compared to results for H-precharged (7.2 wppm or 9.4 wppm H) WM and BM stressed in high-pressure H_2 (P_{H_2} of 13.8 MPa), each at 25 °C	83
71	H_2 pressure dependence of K_{IH} for slow-rising K stressing of as-received and H-precharged 2¼Cr-1Mo-0.3V base metal and weld metal for a variety of environmental conditions discussed in the text. The H-free K_{JICi} is arbitrarily plotted at P_{H_2} of 0.001 MPa, and the regression equation is shown based on the data for BM in pure H_2 at 25 °C (●), without K_{JICi} (top) and with K_{JICi} (bottom)	84

Contents

Page

72	H ₂ pressure dependence of K_{JH} for slow-rising K stressing of as-received and H-precharged 2¼Cr-1Mo-0.3V base metal and weld metal for a variety of environmental conditions discussed in the text. The H-free K_{JIC} is plotted at 0.001 MPa and the regression equation is shown based on the data for BM in pure H ₂ at 25 °C (●) with K_{JIC}	85
73	Effect of loading format on the IHAC growth rate vs stress intensity factor relationship for a modern-pure 2¼ Cr-1Mo base plate containing 5 wppm predissolved H ($C_{H-Total}$) and stressed at 23 °C	86
74	Crack length vs time for a 2¼Cr-1Mo-0.30V base metal compact tension specimen, precharged with H and stressed in moist air under slow-rising CMOD to induce stable-subcritical IHAC at 25 °C, followed by application of a CMOD hold period starting at 84 h and ending at 90.7 h	87
75	Crack growth rate vs elastic-plastic stress intensity factor, analyzed using the data in Figure 74 for a 2¼Cr-1Mo-0.30V base metal compact tension specimen, precharged with H and stressed in moist air under slow-rising CMOD to induce stable-subcritical IHAC at 25 °C, followed by application of a CMOD hold period starting at 84 h	88
76	Crack length vs time for a 2¼Cr-1Mo-0.30V base metal compact tension specimen, precharged with H and stressed in moist air under slow-rising CMOD to induce stable-subcritical IHAC at 100 °C, followed by application of a CMOD hold period starting at 61.4 h and ending at 65.4 h.	89
77	Crack length vs time for a 2¼Cr-1Mo-0.27V weld metal compact tension specimen, precharged with H and stressed in moist air under slow-rising CMOD to induce stable-subcritical IHAC at 26 °C, followed by application of a CMOD hold period starting at 26.8 h and ending at 34.1 h.	90
78	Crack length vs time for a 2¼Cr-1Mo-0.27V weld metal compact tension specimen, precharged with H and stressed in moist air under slow-rising CMOD to induce stable-subcritical IHAC at 100 °C, followed by application of a CMOD hold period starting at 26.5 h and ending at 35.1 h.	91
79	Crack length vs time for a 2¼Cr-1Mo-0.30V base metal compact tension specimen, stressed under slow-rising CMOD in 13.8 MPa H ₂ without H precharging to induce stable-subcritical HEAC at 25 °C, followed by application of a CMOD hold period starting at 15.4 h and ending at 18 h	92
80	Crack length vs time for a 2¼Cr-1Mo-0.30V base metal compact tension specimen, precharged with H and stressed under slow-rising CMOD in 13.8 MPa H ₂ to induce table-subcritical HEAC at 25 °C, followed by application of a CMOD hold period starting at 15.3 h and ending at 18.3 h	93
81	The loading rate dependence of K_{IH} for IHAC in 2¼Cr-1Mo-0.3V BM at 26 °C compared to values measured for 2¼Cr-1Mo BM and WM at 23 °C to 26 °C using the conservatively aggressive slow-rising K test method	95
82	The total bulk-dissolved H concentration dependence of K_{IH} for IHAC in modern low J-factor 2¼Cr-1Mo BM and WM, compared to that for 2¼Cr-1Mo-0.30V base metal from the present study. Each K_{IH} was measured using the slow-rising K test protocol. Test temperature was 23 °C for Cr-Mo and between -10 °C and 122 °C for Cr-Mo-V base metal, with specific test conditions and results given in Table 9.	96

Contents

Page

83	The total bulk-dissolved H concentration dependence of K_{IH} for IHAC in modern low J-factor 2¼Cr-1Mo BM and WM, compared to that for 2¼Cr-1Mo-0.27V weld metal from the present study. Each K_{IH} was measured using the slow-rising K test protocol. Test temperature was 23 °C for Cr-Mo and between -10 °C and 140 °C for Cr-Mo-V, with specific test conditions and results given in Table 9	96
84	Scanning electron fractographs showing: (top left) microvoid-based ductile fracture in specimen BM2A that was fractured in moist air without H precharging, (top right) transgranular IHAC in specimen BM8A, and (bottom left and right) transgranular IHAC in WM4A	97
85	The effect of test temperature on K_{IH} for the onset of IHAC under rising CMOD ($dK/dt = 0.007 \text{ MPa}\sqrt{\text{m}}$) for 2¼Cr-1Mo base plate and weld metal of moderate-purity and a single $C_{H\text{-Total}}$ of 5 wppm	98
86	The temperature dependence of K_{IH} for IHAC in 2¼Cr-1Mo-0.3V base plate and weld metal for the specific slow-rising dK/dt and total remaining H concentration conditions listed in Table 9.	99
87	The temperature dependence of K_{JIH} for IHAC in 2¼Cr-1Mo-0.3V base plate and weld metal for the specific slow-rising dK/dt and total remaining H concentration conditions listed in Table 9.	100
88	The temperature dependence of K_{IH} for IHAC in 2¼Cr-1Mo base metal from Figure 85, compared to K_{IH} for 2¼Cr-1Mo-0.30V BM for the slow-rising dK/dt and total remaining H concentration conditions listed in Table 9	101
89	The temperature dependence of K_{IH} for IHAC in 2¼Cr-1Mo base metal from Figure 85, compared to K_{IH} and the 0.2 mm blunting line offset K_{JIH} for 2¼Cr-1Mo-0.30V BM for the slow-rising dK/dt and total remaining H concentration conditions listed in Table 9	102
90	The temperature dependence of K_{IH} for IHAC in 2¼Cr-1Mo weld metal from Figure 85, compared to K_{IH} for 2¼Cr-1Mo-0.27V WM for the slow-rising dK/dt and total remaining H concentration conditions listed in Table 9	103
91	The temperature dependence of K_{IH} for IHAC in 2¼Cr-1Mo weld metal from Figure 85, compared to K_{IH} and the 0.2 mm blunting line offset K_{JIH} for 2¼Cr-1Mo-0.27V WM for the slow-rising dK/dt and total remaining H concentration conditions listed in Table 9	104
92	The temperature dependence of K_{IH} for IHAC in 2¼Cr-1Mo base metal and weld metal from Figure 85, compared to K_{IH} for 2¼Cr-1Mo-0.3V BM and WM for the slow-rising dK/dt and total remaining H concentration conditions listed in Table 9	105
93	H_2 pressure dependence of K_{IH} for slow-rising K stressing of as-received 2¼Cr-1Mo-0.30V base metal for a variety of high-pressure H_2 environmental conditions. The K_{JIC} for a H-free C(T) specimen is arbitrarily plotted at P_{H_2} of 0.001 MPa, and the regression is shown based on the three data points for BM in pure H_2 at 25 °C (●)	106
94	The H_2 pressure dependence of the threshold stress intensity for HEAC of alloy and C-Mn steels stressed at 25 °C	107
95	The temperature dependence of the threshold stress intensity for HEAC in several high and ultra-high strength martensitic steels tested in purified H_2 at either constant or rising load ..	108

Contents

	Page
96 The loading rate dependence of the threshold stress intensity for IHAC (O) and HEAC (●, Δ) in H-precharged (4.4 wppm) Cr-Mo base metal stressed under slow-rising K in either moist air or high-pressure H ₂	109
97 The H ₂ pressure dependence of the threshold stress intensity for HEAC of alloy and C-Mn steels stressed at 25 °C	110
98 H ₂ pressure dependence of K _{IH} for slow-rising K stressing of as-received and H-precharged 2¼Cr-1Mo-0.3V base metal and weld metal	111
99 The H ₂ pressure dependence of the threshold stress intensity for HEAC of alloy and C-Mn steels stressed at 25 °C. Literature data for alloy steels (O) were obtained for quasi-static loading to yield a crack arrest threshold, while literature data for C-Mn steel (*, X; σ _{YS} = ~300 MPa) were obtained using the slow-rising K crack growth resistance curve method.	112
100 H ₂ pressure dependence of K _{JIH} for slow-rising K stressing of as-received and H-precharged 2¼Cr-1Mo-0.3V base metal and weld metal for a variety of environmental conditions discussed in the text	113
101 The H ₂ pressure dependence of the threshold stress intensity for HEAC of low alloy and C-Mn steels stressed at 25 °C. Literature data are described in the caption of Figure 99	114
102 The calculated effects of H ₂ pressure and H-trap binding energy on the fractional occupancy of H trap sites for isothermal exposure at 25 °C	116
103 <i>Open-system H Trapping.</i> The estimated exposure-temperature dependence of lattice-soluble H concentration (C _L) and reversibly trapped H concentration (C _T) for a single trap state described by a trap binding energy of 35 kJ/mole.	117
104 <i>Closed-system H Trapping.</i> The estimated cooling temperature dependence of lattice-soluble H concentration (C _L , ■ for high trap density and ● for low trap density) and reversibly trapped H concentration (C _T , solid lines) for a single trap state described by a trap binding energy of 35 kJ/mole	119
105 Model predictions of H partitioning among lattice sites and four trap site types for equilibrium exposure of 2¼Cr-1Mo steel to 18 MPa H ₂ at 450 °C	120
106 Model predictions of H partitioning among lattice sites and four trap site types for equilibrium exposure of 2¼Cr-1Mo and 2¼Cr-1Mo-0.3V steels to 18 MPa H ₂ at 450 °C, followed by cooling to 25 °C	121
107 The dependence of K _{IH} on crack tip C _{Tσ} , defined by Equation (1) at a location 9 μm ahead of the crack tip surface for: (top) moderate-purity/moderate-FATT Cr-Mo steel, and (bottom) high-purity/low-FATT Cr-Mo steel.	122
108 The effect of total dissolved H concentration (C _{H-Total-OP}), present during reactor operation, and crack tip diffusible H concentration (C _{H-Diff 470 μm}), localized at the reference point of δ _{470 μm} ahead of the crack tip, on the predicted critical temperature for elimination of IHAC in a cracked section fabricated from (top) moderate-purity/moderate 2¼Cr-1Mo steel and (bottom) high-purity/low-FATT 2¼Cr-1Mo steel, as a function of total H concentration in the bulk of the vessel wall during elevated temperature exposure in high-pressure H ₂	125
109 Potential effects of Cr-Mo-V characteristics on the critical temperature for the onset of slow-stable IHAC in V-modified Cr-Mo steel, as defined by Equation (2)	129

Contents

Page

110	(Top) The total bulk-dissolved H concentration dependence of K_{IH} for IHAC in modern low J-factor 2¼Cr-1Mo BM and WM, compared to that for high-purity 2¼Cr-1Mo-0.3V base metal from the present study. (Bottom) The dependence of measured K_{IH} on crack tip H concentration defined by Equation (1) at a location 9 µm ahead of the crack tip surface high-purity/low-FATT Cr-Mo steel.	131
111	The effect of crack tip diffusible H concentration ($C_{H-Diff\ 470\ m}$), localized at the reference point of $\delta_{470\ m}$ ahead of the crack tip, on the predicted critical temperature for elimination of IHAC in a cracked section fabricated from high-purity 2¼Cr-1Mo ($\sigma_{YS} = 500\ MPa$) and 2¼Cr-1Mo-0.3V ($\sigma_{YS} = 575\ MPa$) steels following Equation (2) with $W_B = 38\ kJ/mol$, as a function of total H concentration dissolved in the bulk of the vessel wall during elevated temperature exposure in high-pressure H_2	132
112	The effect of crack tip diffusible H concentration ($C_{H-Diff\ 470\ m}$), localized at the reference point of $\delta_{470\ \mu m}$ ahead of the crack tip, on the predicted critical temperature for elimination of IHAC in a cracked section fabricated from high-purity 2¼Cr-1Mo ($\sigma_{YS} = 500\ MPa$) and 2¼Cr-1Mo-0.3V ($\sigma_{YS} = 575\ MPa$) steels following Equation (2) with $E_B = 38\ kJ/mol$, as a function of total H concentration in the bulk of the vessel wall during elevated temperature exposure in high-pressure H_2	133
113	The total bulk-dissolved H concentration dependence of K_{IH} for IHAC in modern low J-factor 2¼Cr-1Mo BM and WM [4,5], compared to that for 2¼Cr-1Mo-0.27V weld metal from the present study	134
114	The H_2 pressure dependence of the threshold stress intensity for HEAC of alloy and C-Mn steels stressed at 25 °C	135
115	The effect of applied dK/dt , during rising CMOD, on the crack growth rate for IHAC in H-charged weld metal and base plate of 2¼Cr-1Mo steel, precharged with 5 wppm H and stressed at 25 °C	136

Tables

1	Modern Fracture Mechanics Characterization of the Rising-CMOD Threshold Stress Intensity for IHAC in Conventional and V-modified Cr-Mo Steel	3
2	Steel Composition	7
3	Steel Heat Treatment and Mechanical Properties	8
4	Sievert's Law Parameters for H Solubility in Cr-Mo and Cr-Mo-V Steels	9
5	Relationship Between Figure 7 Index, H Concentration, and Relative Error for Hot-extraction Measurements of H	12
6	Measurements of Total Dissolved Hydrogen Concentration in 2¼Cr-1Mo-0.3V Base Metal and Weld Metal	19
7	Measured H Concentrations After Isothermal Outgassing of 2¼Cr-1Mo-0.3V for the Indicated Time-Temperature Conditions	21
8	Interrupted IHAC Experiments	31
9	Fracture Experiment Results for 2¼Cr-1Mo-0.3V Base Plate and Weld Metal	45

EXECUTIVE SUMMARY

A literature review demonstrates the need for an improved laboratory database, as well as basic understanding, to quantitatively characterize the hydrogen-assisted cracking (HAC) resistance of modern $2\frac{1}{4}\text{Cr-1Mo-}\frac{1}{4}\text{V}$ base plate, weld metal, and the weld heat-affected zone. The objectives of this API-sponsored research are to: (a) quantitatively characterize the internal hydrogen-assisted cracking (IHAC) resistance of modern $2\frac{1}{4}\text{Cr-1Mo-}\frac{1}{4}\text{V}$ steel, in both base metal and weld metal product forms and including the effect of stressing temperature, (b) scope the hydrogen environment assisted cracking (HEAC) resistance of $2\frac{1}{4}\text{Cr-1Mo-}\frac{1}{4}\text{V}$ base metal, (c) understand the mechanism(s) for the IHAC and HEAC behaviors of Cr-Mo and Cr-Mo-V steels, centered on hydrogen (H) interactions with microstructure-scale trap sites, and (d) assess application of data and understanding of IHAC and HEAC to determine the role of subcritical H-assisted cracking on a minimum pressurization temperature (MPT) estimate relevant to thick-wall hydrotreating reactor vessels.

This work focused on slow-stable subcritical H cracking and did not examine the effect of H on the fracture toughness for unstable cracking. The temperature dependencies of IHAC of $2\frac{1}{4}\text{Cr-1Mo-0.3V}$ base plate and weld metal were characterized using slow-rising displacement loading and elastic-plastic fracture mechanics analysis of crack growth measured through direct current potential difference (DCPD). This test method provides a conservative measure of susceptibility of alloy steels to HAC.

Specific conclusions of this research are as follows.

- 1) Compared to conventional $2\frac{1}{4}\text{Cr-1Mo}$ steel, and consistent with the literature, the solubility of H dissolved in $2\frac{1}{4}\text{Cr-1Mo-0.3V}$ base and weld metals increases two-fold due to VC precipitate trapping of H and when exposed to high-pressure H_2 at elevated temperature relevant to thick-wall reactor applications. Consistent with the reversible nature of H trapping at precipitate interfaces, the diffusivity of H in $2\frac{1}{4}\text{Cr-1Mo-0.3V}$ decreases by about 100 times compared to H mobility in conventional $2\frac{1}{4}\text{Cr-1Mo}$ steel.
- 2) Without predissolved H, the fracture resistance of high-purity (step-cooled) $2\frac{1}{4}\text{Cr-1Mo-0.3V}$ base and weld metals is high at 25 °C and 100 °C, characteristic of upper shelf behavior and a fracture appearance transition temperature (FATT) well below room temperature.
- 3) Quantitative characterization of IHAC and HEAC in low- to moderate-strength steels is challenged by substantial crack tip plasticity. For $2\frac{1}{4}\text{Cr-1Mo-0.3V}$, the DCPD method, coupled with J-integral elastic-plastic fracture mechanics, effectively characterizes slow-stable H-assisted crack growth during slow-rising stress intensity factor loading. Measurement of the threshold for such cracking, K_{IH} , and the associated crack growth resistance curve as K_I vs Δa , are demonstrated to be conservative when based on DCPD vs crack mouth opening displacement (CMOD) analysis, rather than DCPD vs elastic-plastic J. A validated test protocol is now available at a commercial testing laboratory for use in fitness-for-service and MPT analyses where reactor-steel-specific H cracking properties are required.
- 4) Cr-Mo-V base and weld metals containing a high concentration of predissolved H, $C_{H\text{-Total}}$ of 6 wppm to 11 wppm from elevated temperature exposure in high-pressure H_2 , significantly resist slow-stable IHAC compared to susceptible low-FATT (high-purity) Cr-Mo steel. Nonetheless, $2\frac{1}{4}\text{Cr-1Mo-0.3V}$ is susceptible to slow-stable IHAC propagation for severe slow-rising displacement loading in moist air (see Figure 36).
- 5) $2\frac{1}{4}\text{Cr-1Mo-0.3V}$ base metal (BM) and weld metal (WM) compact tension [C(T)] specimens exhibit stable crack extension that yields a rising R-curve, without evidence of the onset of H-stimulated premature fast fracture at K levels below K_{JIC} for H-free specimens. No evidence was obtained to demonstrate that H promotes premature fast fracture in these V-modified steels for the dissolved H concentration, loading rate, and temperatures examined. These results suggest that the H-stimulated fast fracture mechanism may not be operative in V-modified steel with a low FATT. This form of H degradation was reported in the literature to occur in Cr-Mo steel.

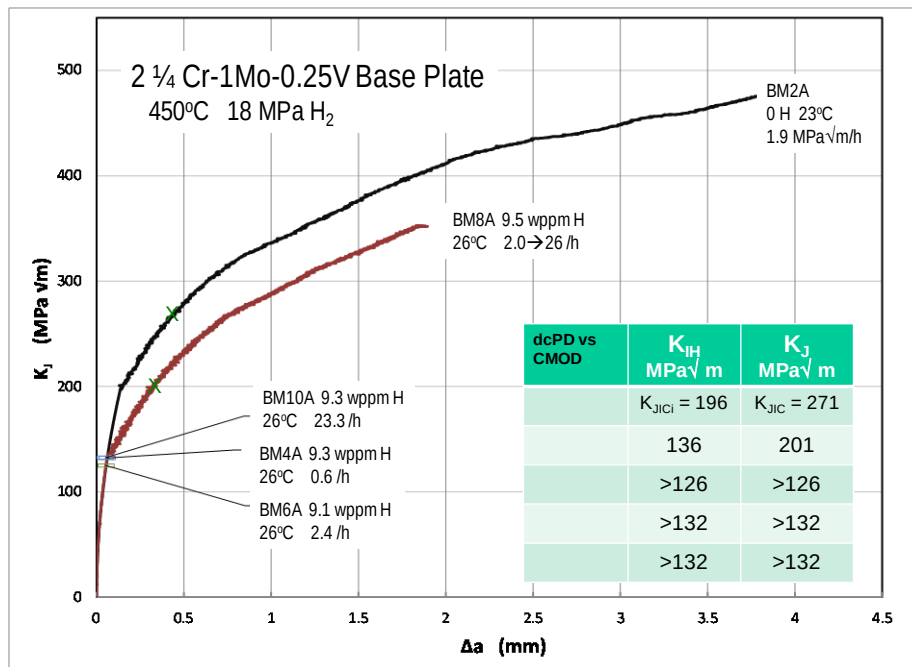


Figure 36—Crack growth resistance curves, plotted as the elastic-plastic stress intensity factor vs crack extension from DCPD, for H-precharged 2¼Cr-1Mo-0.3V base metal stressed under slow-rising K at 26 °C. Values of the 0.2 mm offset K_{JIH} and K_{JIC} are indicated by “X” on each resistance curve.

- 6) 2¼Cr-1Mo-0.27V weld metal is more susceptible to IHAC than 2¼Cr-1Mo-0.30V base metal, with the potential for variability in K_{IH} and K_J - Δa (see Figure 81, as well as Figures 82 and 83).

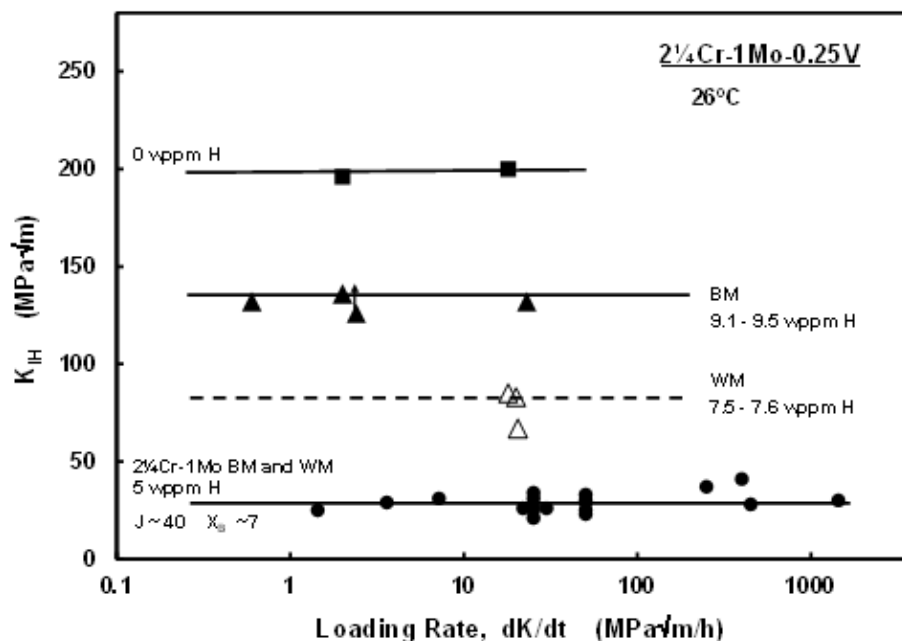


Figure 81—The loading rate dependence of K_{IH} for IHAC in 2¼Cr-1Mo-0.3V BM at 26 °C compared to values measured for 2¼Cr-1Mo BM and WM at 23 °C to 26 °C using the conservatively aggressive slow-rising K test method [2,4,5]. The conditions for the Cr-Mo steel experiments are reported in Bibliographic Item [2]. The dK/dt is the value of elastic K increase up to K_{IH} , above which this rate rises due to the onset of stable crack growth and/or plasticity.

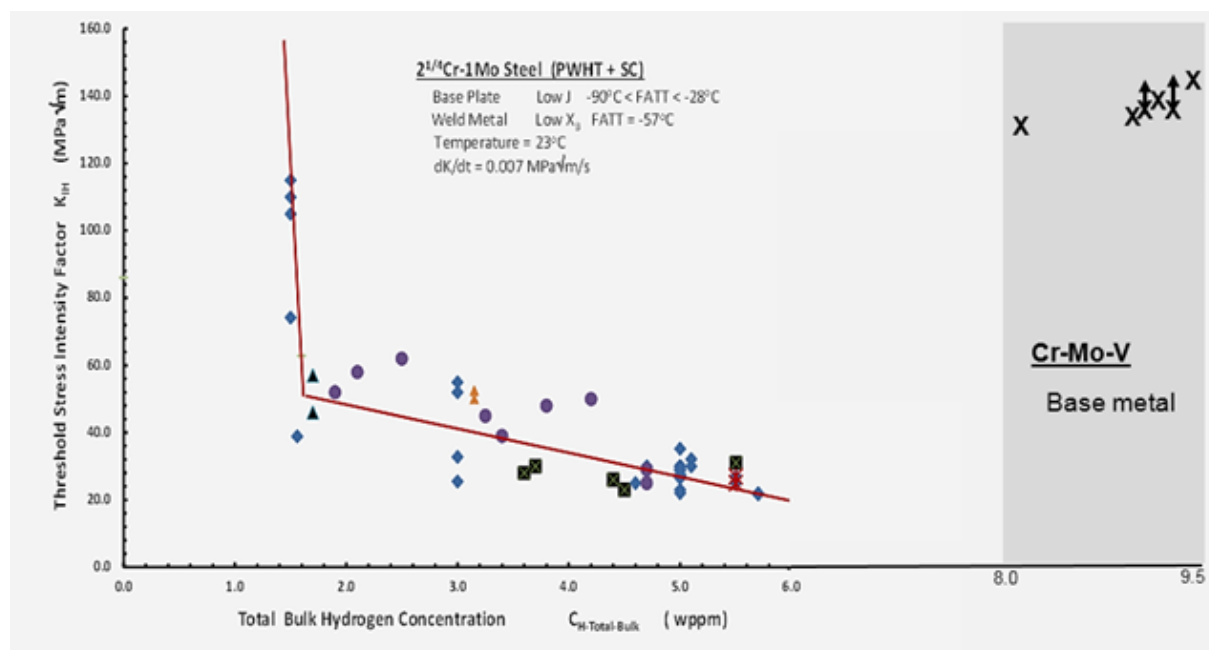


Figure 82—The total bulk-dissolved H concentration dependence of K_{IH} for IHAC in modern low J-factor 2 1/4Cr-1Mo BM and WM ^[2,4,5], compared to that for 2 1/4Cr-1Mo-0.30V base metal from the present study. Each K_{IH} was measured using the slow-rising K test protocol ^[1,2]. Test temperature was 23 °C for Cr-Mo and between -10 °C and 122 °C for Cr-Mo-V base metal, with specific test conditions and results given in Table 9.

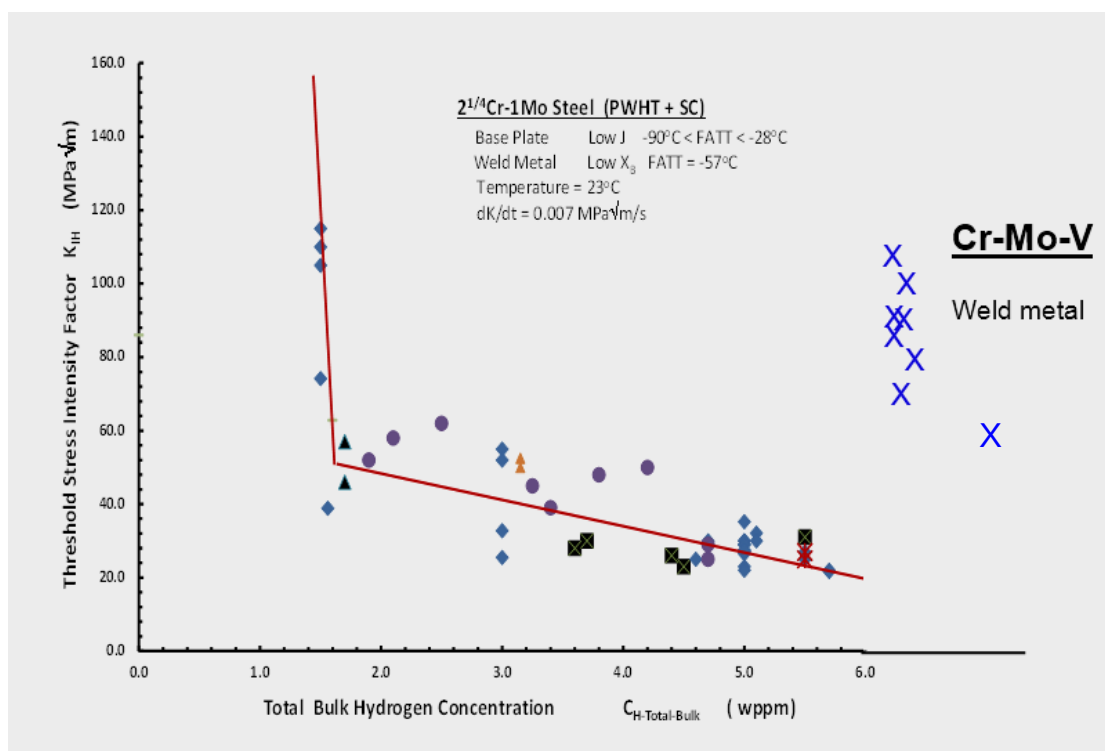


Figure 83—The total bulk-dissolved H concentration dependence of K_{IH} for IHAC in modern low J-factor 2 1/4Cr-1Mo BM and WM ^[2,4,5], compared to that for 2 1/4Cr-1Mo-0.27V weld metal from the present study. Each K_{IH} was measured using the slow-rising K test protocol ^[1,2]. Test temperature was 23 °C for Cr-Mo and between -10 °C and 140 °C for Cr-Mo-V, with specific test conditions and results given in Table 9.

- 7) Predissolved H causes a microscopic fracture mode and path transition in both base and weld metals of 2¼Cr-1Mo-0.3V steel. Without dissolved H, fracture is by microvoid processes at 25 °C to 100 °C, consistent with the low ductile-to-brittle transition temperature of this high-purity steel. In contrast, the presence of H results in several unique appearances of transgranular cracking, without evidence of intergranular cracking. These H-assisted modes appear to include altered microvoid formation/growth/coalescence, as well as transgranular cracking associated with bainite lath and packet interfaces.
- 8) Increasing stressing temperature from –10 °C to +140 °C has a nil to mild beneficial effect on K_{IH} and the overall K_J vs Δa resistance curve for IHAC in 2¼Cr-1Mo-0.3V base and weld metals, respectively. Abnormal K_{IH} reduction was not observed for any temperature within this range (see Figure 92).
- 9) Dissolved H is retained in 2¼Cr-1Mo-0.3V for all slow-loading rate and elevated temperature conditions, as demonstrated by direct measurement of total hydrogen concentration in specimens taken from all fractured compact tension specimens.
- 10) 2¼Cr-1Mo-0.3V base metal is susceptible to HEAC during slow-rising K loading in high-pressure H_2 . This susceptibility to HEAC exceeds the severity of IHAC for Cr-Mo-V and is similar to the HEAC behavior of conventional 2¼Cr-1Mo steel as well as other low alloy and C-Mn steels (see Figure 93).
- 11) H_2 environment chemistry critically affects the susceptibility of Cr-Mo steels to HEAC. K_{IH} and K_J vs Δa strongly depend on H_2 pressure, particularly in the relatively low pressure regime below about 1 MPa (150 psi) for 2¼Cr-1Mo-0.30V base metal. Based on limited experiments, HEAC is similarly produced in 2¼Cr-1Mo-0.30V base metal at 25 °C and 60 °C. Such cracking is retarded by the presence of O_2 contamination in the otherwise pure H_2 environment. Specific H_2 pressure and gas composition should be considered when interpreting laboratory data for HEAC and when assessing the impact of H_2 HEAC on MPT or fitness-for-service of a reactor pressure vessel.

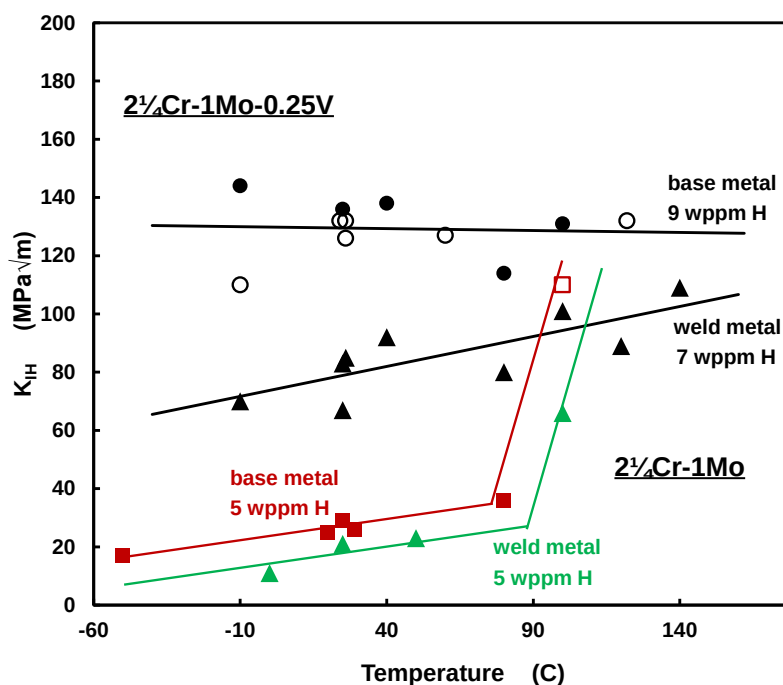


Figure 92—The temperature dependence of K_{IH} for IHAC in 2¼Cr-1Mo base metal and weld metal from Figure 85 ^[2], compared to K_{IH} for 2¼Cr-1Mo-0.3V BM and WM for the slow-rising dK/dt and total remaining H concentration conditions listed in Table 9. Open circles indicate experiments that were terminated prior to DCPD detection of the onset of stable crack growth.

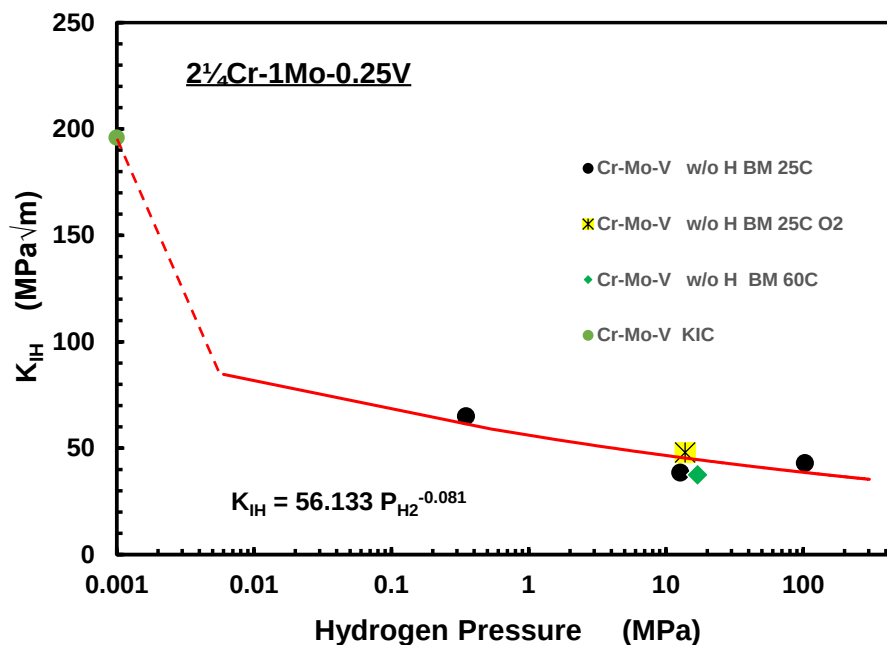


Figure 93—H₂ pressure dependence of K_{IH} for slow-rising K stressing of as-received 2 $\frac{1}{4}$ Cr-1Mo-0.30V base metal for a variety of high-pressure H₂ environmental conditions.

The K_{JIC} for a H-free C(T) specimen is arbitrarily plotted at P_{H_2} of 0.001 MPa, and the regression equation is shown based on the three data points for BM in pure H₂ at 25 °C (●).

- 12) A high concentration of predissolved H from elevated temperature exposure in H₂ has no resolvable effect on the quasi-equilibrium K_{IH} and K_{JH} for the onset of HEAC in either 2 $\frac{1}{4}$ Cr-1Mo-0.3V or 2 $\frac{1}{4}$ Cr-1Mo steels stressed in gaseous hydrogen at 25 °C. HEAC can exacerbate the rate of IHAC growth above K_{IH} for situations where the crack tip deformation rate is significant (see Figure 99).
- 13) 2 $\frac{1}{4}$ Cr-1Mo-0.3V base metal and weld metal do not exhibit resolvable-stable crack growth when stressed at fixed CMOD for IHAC, HEAC or combined HEAC–IHAC conditions and very high applied K levels after rising CMOD H cracking. DCPD measurements demonstrate that load decrease during fixed CMOD is likely due to creep and cannot be used as an elastic compliance indicator to quantify or infer the occurrence of H cracking.
- 14) The high IHAC resistance of Cr-Mo-V is understood based on closed-system H trapping from a high number of strong trap sites. Specifically, the lattice H concentration is markedly reduced due to reversible H trapping at VC precipitates, for Cr-Mo-V, but not for Cr-Mo steel that does not contain nanoscale precipitates. Hydrogen is therefore shielded from accumulating at crack tip process zone damage sites; such trapping is protective to about 20 wppm H.

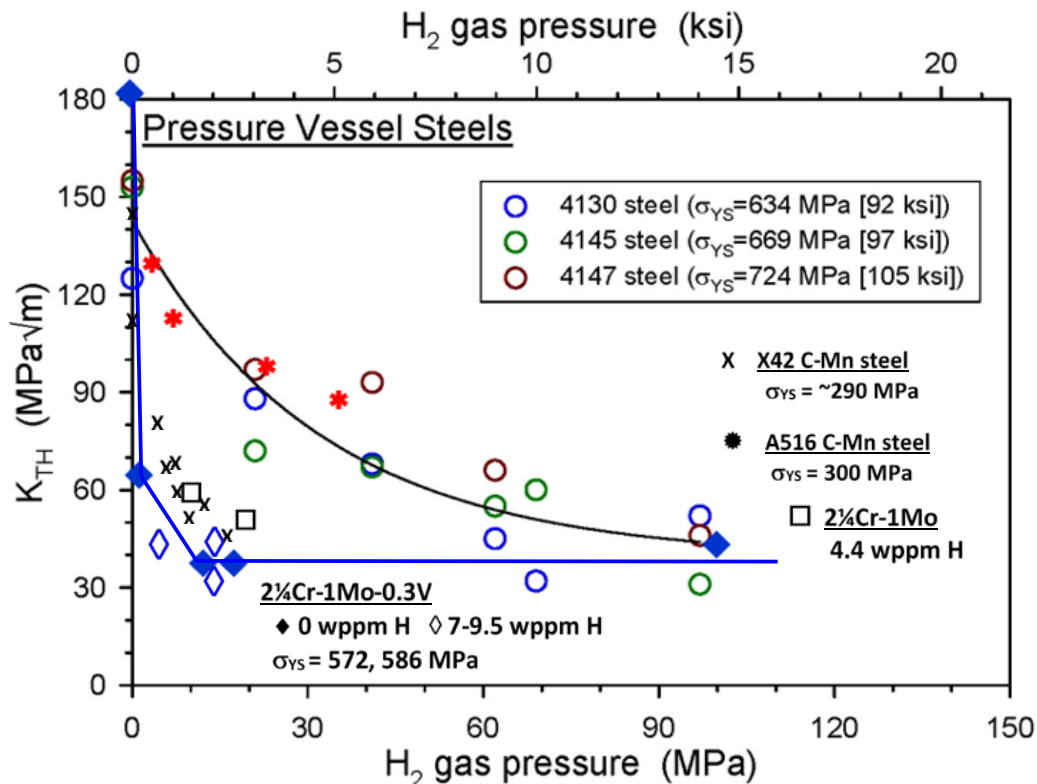


Figure 99—The H_2 pressure dependence of the threshold stress intensity for HEAC of alloy and C-Mn steels stressed at 25 °C. Literature data for alloy steels (O) were obtained for quasi-static loading to yield a crack arrest threshold^[41], while literature data for C-Mn steel (*, X; $\sigma_{YS} \approx 300$ MPa) were obtained using the slow-rising K crack growth resistance curve method^[42,43]. Literature data for H-precharged $2\frac{1}{4}\text{Cr-1Mo}$ steel ($\square$, $J = 60$, $\sigma_{UTS} = 758$ MPa, total predissolved H concentration = 4.4 wppm to 4.8 wppm) were obtained using the slow-rising K method^[10]. Filled diamonds were obtained during the current study for as-received $2\frac{1}{4}\text{Cr-1Mo-0.30V}$ base metal ($\sigma_{YS} = 572$ MPa) at 25 °C and 60 °C and open diamonds represent K_{IH} for H-precharged $2\frac{1}{4}\text{Cr-1Mo-0.3V}$ BM and WM stressed at 25 °C.

- 15) The HEAC susceptibility of Cr-Mo-V and Cr-Mo is understood based on open-system H trapping, where crack surface H in equilibrium with the H_2 environment fills all traps to the fractional-site H coverage dictated by P_{H_2} , temperature, and H-trap binding energy. VC trapping does not affect the level of lattice H, relevant to K_{IH} , and only reduces the kinetics (da/dt) of H cracking.
- 16) The critical temperature to cause IHAC in $2\frac{1}{4}\text{Cr-1Mo-0.3V}$ weld metal and base plate is well below 25 °C, suggesting very low MPT from the perspective of mitigating slow-stable H-assisted crack growth during shutdown and start-up, following the quantitative framework validated for Cr-Mo steel. Modest uncertainties are associated with Cr-Mo-V reactor applications involving very high stress intensity levels (above 130 $\text{MPa}\sqrt{\text{m}}$), weld metal property variability, differences in weld metal and heat-affected zone tempering temperatures, and the role of HEAC due to residual-pure H_2 (see Figure 112).

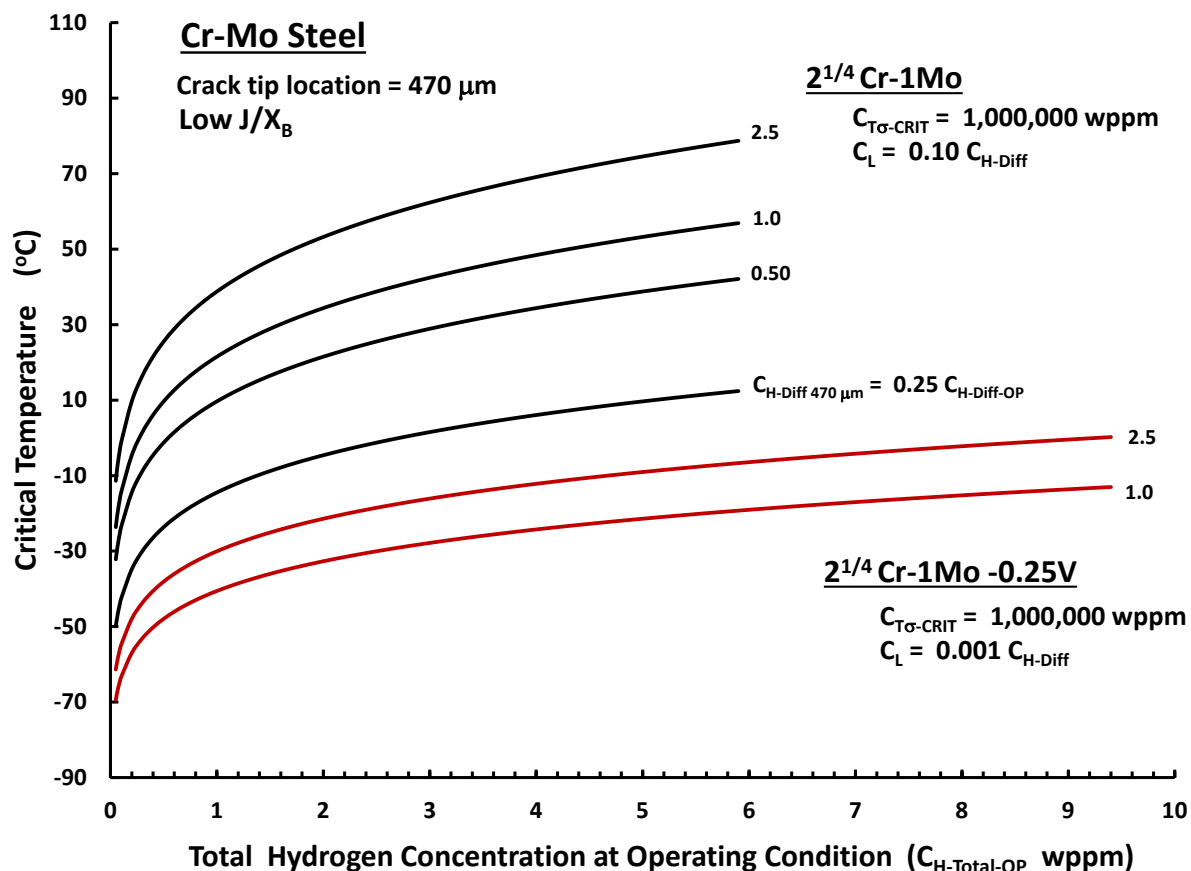


Figure 112—The effect of crack tip diffusible H concentration ($C_{H\text{-Diff } 470 \mu\text{m}}$), localized at the reference point of $\delta_{470 \mu\text{m}}$ ahead of the crack tip, on the predicted critical temperature for elimination of IHAC in a cracked section fabricated from high-purity 2^{1/4}Cr-1Mo ($\sigma_{YS} = 500 \text{ MPa}$) and 2^{1/4}Cr-1Mo-0.3V ($\sigma_{YS} = 575 \text{ MPa}$) steels following Equation (2) with $E_B = 38 \text{ kJ/mol}$; as a function of total H concentration in the bulk of the vessel wall during elevated temperature exposure in high-pressure H_2 . In Equation (3), $C_{T\sigma\text{-Crit}}$ is not changed, but the $C_{L\text{-FPZ}}$ is decreased by 100 times for Cr-Mo-V compared to modern Cr-Mo steel.

Subcritical Cracking of Modern 2¼Cr-1Mo-¼V Steel Due to Dissolved Internal Hydrogen and H₂ Environment, Research Report

BACKGROUND

Between 1980 and 1990, researchers in Japan, France, and the United States determined that bainitic 2¼Cr-1Mo steels (UNS K21590) exhibited unexpectedly low threshold K_{IH} stress intensity levels for the onset of slow-stable internal hydrogen-assisted cracking (IHAC). This significant and unexpected IHAC was observed for compact tension specimens that were fatigue precracked, precharged with atomic hydrogen (H) through elevated temperature exposure in high-pressure H₂, then stressed under slow-rising crack mouth opening displacement (CMOD). In contrast, the threshold for IHAC under static displacement loading was high, as expected for this moderate-strength steel. Much of this early work was sponsored by the American Petroleum Institute (API) and Materials Properties Council (MPC).

While this class of Cr-Mo pressure vessel steels is clearly susceptible to significant IHAC, initial data were uncertain for several reasons: (a) lack of a standardized quantitative experimental method, (b) poor detection of the onset of crack growth during rising CMOD, (c) steel plasticity during loading complicated crack growth detection and elastic stress intensity factor analysis, (d) variables including loading rate expressed as dK/dt and H loss during testing were typically not controlled or reported, (e) variability in K_{IH} measurement both for a single laboratory and across groups, (f) the mechanism for the deleterious effect of rising CMOD on IHAC was not elucidated, and (g) much of this work was presented at API/MPC committee meetings or in conference proceedings, but 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, with the goal of developing a rigorous fracture mechanics test method for measurement of K_{IH} , crack extension (Δa), and crack growth rate (da/dt) vs elastic-plastic stress intensity (K_I), and the threshold for the arrest of IHAC (K_{TH}) under static displacement loading^[1,2]. Focus was placed on retention of H during long-time loading of precharged specimens. This method was applied to develop an extensive database for IHAC of 12 heats of 2¼Cr-1Mo base metal and weld metal, with impurity composition [and degree of temper embrittlement judged based on the fracture appearance transition temperature (FATT)] 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} vs total dissolved H concentration ($C_{H-Total}$) for several low-impurity (J-factor < 100 wt%) and thus low FATT heats (FATT < -28 °C) of 2¼Cr-1Mo base metal and weld metal^[2,3]. All experiments were conducted at 23 °C with 25.4-mm-thick standard compact tension specimens precharged in H₂ at several combinations of elevated temperature and H₂ pressure. Results for the high-purity Phase I steels are shown by filled diamonds with the associated trend line^[2,4]. Open and filled circles and triangles represent older literature data for a 2¼Cr-1Mo base plate that was not temper embrittled (J and FATT were not published, but are likely low). The ultimate tensile strength of these steels was between 585 MPa and 605 MPa. The dashed-to-solid line in Figure 1 shows the Phase I REACT software algorithm used to describe the H concentration dependence of K_{IH} for high-purity/low-FATT Cr-Mo steels^[2]. Details of the REACT modeling approach can be obtained from Dr. Ted L. Anderson (TL Anderson Consulting, Boulder, CO; www.fracturemechanics.com) The severity of IHAC for this class of steel is apparent in Figure 1, considering that the plane strain fracture toughness 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 2¼Cr-1Mo base and weld metals^[3-5]. A fracture-mechanics-based method was developed to predict the minimum pressurization temperature (MPT) based on IHAC under rising displacement^[4]. This analysis augments determination of MPT governed by additional-important failure modes, including temper embrittlement and H-sensitive unstable fracture governed by H-shifted ductile-to-brittle transition behavior^[6-8].

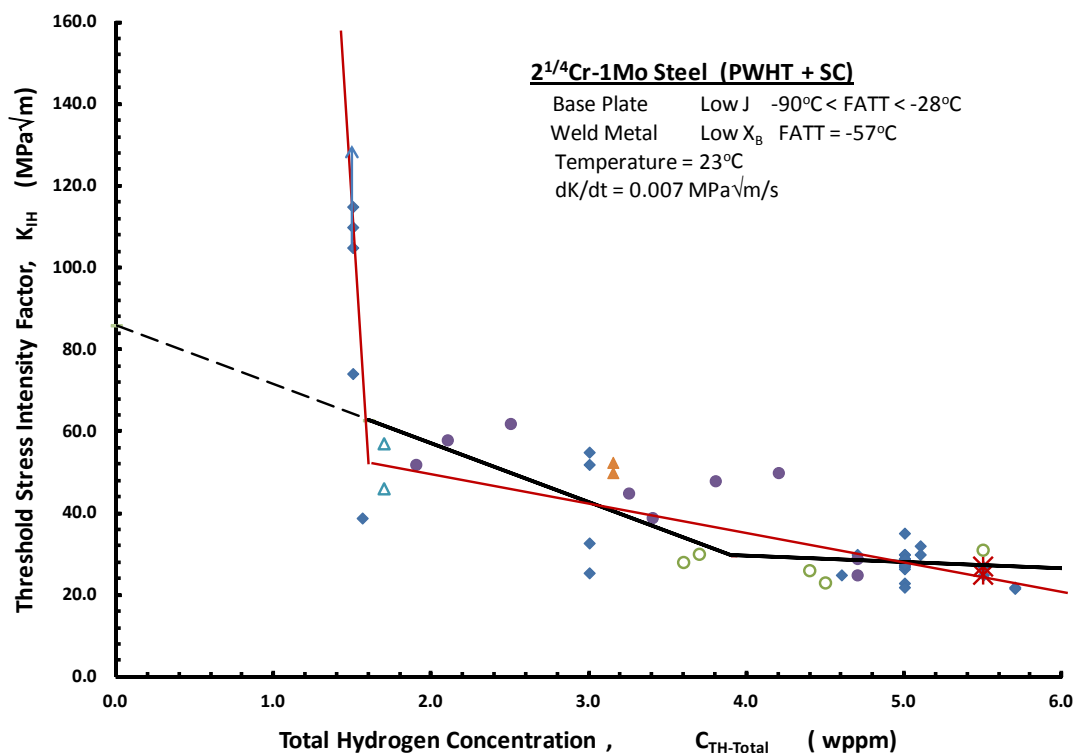


Figure 1—The effect of predissolved bulk total H concentration on K_{IH} for IHAC of several heats of modern low-impurity Cr-Mo base plate and weld metal stressed under slow-rising K at 23 °C^[4]. The dashed-to-solid line in Figure 1 shows the REACT software algorithm used to describe the H concentration dependence of K_{IH} for high-purity/low-FATT steels^[2].

In the early 1980s, vanadium modified Cr-Mo steels were developed for heavy wall hydrocracking reactor applications^[9–13]. The microstructure was typically bainitic, with V levels less than about 0.4 wt%. The presence of homogeneously precipitated, nanoscale vanadium carbides (VC and V_4C_3) was hypothesized to greatly reduce the mobility of H through strong reversible trapping, with the expected result being reduced susceptibility to IHAC. Fracture-mechanics-based data were presented to characterize the IHAC performance of two primary compositions; $2\frac{1}{4}\text{Cr}-1\text{Mo}-0.25\text{V}-0.035\text{Nb}-0.13\text{C}$ [UNS K31835, minimum yield strength (σ_{YS}) = 415 MPa and minimum ultimate tensile strength (σ_{UTS}) = 585 MPa] and $3\text{Cr}-1\text{Mo}-0.25\text{V}-0.035\text{Nb}-0.13\text{C}-(\text{Ti},\text{B})$ (UNS K31830, minimum σ_{YS} = 415 MPa and minimum σ_{UTS} = 585 MPa). These V-modified steels exhibited better resistance to IHAC under slow-rising CMOD compared to conventional Cr-Mo steel. However, early data were not sufficient to quantify the IHAC resistance of these steels because: (a) the issues noted above for $2\frac{1}{4}\text{Cr}-1\text{Mo}$ are relevant to V-modified steels, (b) reduced H mobility likely reduces da/dt , which further complicates experimental measurements of time-dependent cracking relevant to long-term IHAC, (c) the temperature dependence of IHAC depends on H trapping and may differ for the various V-modified grades and heat treatments, and such behavior was not reported, and (d) small laboratory heats were used for a portion of the early laboratory experiments.

Given these uncertainties, the API Task Group 934-F on Heavy Wall Pressure Vessel MPT commissioned a laboratory study of the IHAC resistance of modern $2\frac{1}{4}\text{Cr}-1\text{Mo}-\frac{1}{4}\text{V}$ steel. The objective of this API program was to employ the JIP-developed standard method^[2] to quantify the IHAC resistance of precracked specimens of modern $2\frac{1}{4}\text{Cr}-1\text{Mo}-\frac{1}{4}\text{V}$ base plate and weld metal. Particular emphasis was placed on detection of the onset of crack growth and state-of-the art elastic-plastic analysis of K_J , as well as the primary variables of temperature and loading rate. The technical plan for this work was detailed in a report to the Task Group^[14], which approved the investigation that was then carried out under API contracts with Prof. Richard Gangloff as a consultant, Dr. Kevin Nibur as a consultant and owner of Hy-Performance Materials Testing where all IHAC experimentation was performed, and Dr. Sylvain Pillot as a lead engineer at the Le Creusot Research Center of ArcelorMittal where all H charging and analyses were performed.

LITERATURE REVIEW OF HYDROGEN CRACKING IN Cr-Mo-V STEEL

At the Task Group's direction, the literature on H cracking of Cr-Mo-V was critically reviewed to provide a basis for designing and interpreting the current experiments carried out under sponsorship of the API. The complete literature analysis is presented in API 934-F, Part 2. This review is chronologically organized to cover initial and more modern works, as justified by improvement in test execution, data analysis, and reporting, as well as the evolution from laboratory- to commercial-scale heats of Cr-Mo-V. Since modern Cr-Mo-V steels are of relatively high purity, and retain a low FATT after laboratory simulation of in-service temper embrittlement, the database for 2¼Cr-1Mo shown in Figure 1 provides a context for assessment of the IHAC performance of V-modified grades. Hydrogen cracking of less pure V-modified Cr-Mo steels was not considered in this review. The highlights of the literature review in API 934-F, Part 2 are summarized as follows.

Literature data summarized in Table 1 collectively suggest that V-modified 2¼Cr-1Mo base metal and weld metal each exhibit improved resistance to IHAC compared to modern 2¼Cr-1Mo, where each steel is typified by a low J-factor or low X_B . For Cr-Mo-V, 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 not immune to IHAC for this conservatively aggressive loading mode. This good IHAC resistance is attributed to beneficial H interaction with nanoscale vanadium carbide trap sites, but the details of this H trapping behavior are neither quantified nor fully understood in the literature.

While the data summarized in Table 1 are significant, no single study of IHAC in 2¼Cr-1Mo-¼V base metal or weld metal is sufficiently comprehensive and quantitative to support fracture mechanics modeling of pressure vessel fitness-for-service or a MPT. Uncertainties in the existing database 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 slow loading rates, for weld metal, and for elevated 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 reduces susceptibility to IHAC, and (f) the effect of low temperature on H cracking.

Table 1—Modern Fracture Mechanics Characterization of the Rising-CMOD Threshold Stress Intensity for IHAC in Conventional and V-modified Cr-Mo Steel

Stressing Temperature °C	C _H -Total Initial-Final wppm	Product Final Heat Treatment ^a	σ_{UTS} MPa	FATT °C	dK/dt MPa√m/h	K_{IH} MPa√m	Source	Published
2¼Cr-1Mo								
23 °C	2–?	BP WM	582 to 649	–28 to –90	25	50	JIP Gangloff	2011 ^[4]
23 °C	6–?	BP WM	582 to 649	–28 to –90	25	22	JIP Gangloff	2011 ^[4]
2¼Cr-1Mo-0.25V								
23 °C	12–9	BP 705 °C 8 h	663	–78	18	115	Wada et al.	2002 ^[15]
100 °C	12–?	BP 705 °C 8 h	663	–78	18	170	Wada et al.	2002 ^[15]
23 °C	13.5–9	WM 705 °C 8 h	688	–28 (40 ft-lb)	18	88	Wada et al.	2006 ^[16]
23 °C	5.6–8.4	BP	716	–62	18	224 to 228	Shimazu et al.	2013 ^[17–19]
^a BP = base plate; WM = weld metal.								

All K_{IH} data for conventional and V-modified Cr-Mo steel (Table 1) reflect H charging followed by rising displacement loading in moist air. A hypothesized deleterious interaction of IHAC and HEAC for stressing of H-precharged specimens in H₂ is not supported by published data for Cr-Mo and Cr-Mo-V steels. Either H precharging, with stressing in moist air for IHAC, or stressing in high-pressure H₂, without H precharging for HEAC, is each 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 H₂, conforming with the behavior of other low- to moderate-strength alloy steels and apparently less

trapping at vanadium carbides. K_{IH} values for uncharged $2\frac{1}{4}\text{Cr}-1\text{Mo}-\frac{1}{4}\text{V}$ 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 laboratory study, commissioned by API Task Group 934-F on Heavy Wall Pressure Vessel MPT, addresses these uncertainties for modern industrial lots of $2\frac{1}{4}\text{Cr}-1\text{Mo}-\frac{1}{4}\text{V}$ weld metal and base metal ^[14]. Literature results obtained after about 2002 (see Table 1) provide important comparisons with the results of the present work, as detailed in the Discussion. The outcome of this work is a strong and relevant characterization of the IHAC susceptibility of modern V-modified Cr-Mo steels. Initial findings were recently published ^[20], and the complete results of the work are provided in this final report to the API.

RESEARCH OBJECTIVES

The objectives of the present API investigation of the H cracking resistance of Cr-Mo-V steel are to employ cutting-edge fracture mechanics experimental methods and theoretical understanding to:

- quantitatively characterize the IHAC resistance of modern $2\frac{1}{4}\text{Cr}-1\text{Mo}-\frac{1}{4}\text{V}$ steel in both base metal and weld metal product forms;
- quantitatively establish the effect of stressing temperature on IHAC for $2\frac{1}{4}\text{Cr}-1\text{Mo}-\frac{1}{4}\text{V}$ base metal and weld metal;
- provide an initial characterization of the HEAC susceptibility of $2\frac{1}{4}\text{Cr}-1\text{Mo}-\frac{1}{4}\text{V}$ steel and the importance of interaction between IHAC and HEAC. This goal was added midway through the program ^[14], in response to questions raised during progress reporting to the API 934-F Task Group. Initial experiments with rising K stressing in high-pressure gaseous hydrogen were enabled through a collaboration with Dr. Brian P. Somerday at the Sandia National Laboratory in Livermore, CA;
- qualitatively understand the mechanism(s) for differences in the IHAC and HEAC behaviors of Cr-Mo and Cr-Mo-V steels, centered on H interactions with microstructure-scale trap sites.
- assess application of data and understanding of IHAC and HEAC to determine the role of subcritical H-assisted cracking on MPT and more general fracture mechanics fitness-for-service analysis relevant to thick-wall hydrotreating reactor vessels.

The specific statement of work is as follows.

- Measure the fracture mechanics properties necessary to project the fitness-for-service of hydrogen-charged base metal and weld metal of modern $2\frac{1}{4}\text{Cr}-1\text{Mo}-\frac{1}{4}\text{V}$.
- Establish the effect of temperature on the hydrogen cracking resistance of base plate and weld metal of modern $2\frac{1}{4}\text{Cr}-1\text{Mo}-\frac{1}{4}\text{V}$ steel, necessary to predict the effect of hydrogen embrittlement on MPT.

ABBREVIATIONS

For the purposes of this document, the following definitions apply.

BM	base metal
CD	constant displacement
CMOD	crack mouth opening displacement
C(T)	compact tension
DCPD	direct current potential difference

FATT	fracture appearance transition temperature
FPZ	fracture process zone
HAC	hydrogen-assisted cracking
HEAC	hydrogen environment assisted cracking
IHAC	internal hydrogen-assisted cracking
JIP	joint industry program
LN ₂	liquid nitrogen
MPT	minimum pressurization temperature
PRHIC	plasticity related hydrogen induced cracking
SAW	submerged arc weld
SEM	scanning electron microscopy
WM	weld metal

EXPERIMENTAL PROCEDURES

Material

API Task Group 934-F obtained BM of 2¼Cr-1Mo-¼V steel from ArcelorMittal (provided by Cedric Chauvy and Lionel Coudreuse), specifically in the form of a 1.0 m × 1.0 m × 6.8 cm to 7.5 cm thick rolled plate. This steel is characterized as follows, with full specifications provided in Annex A. In particular, note that the V content is reported to equal 0.30 wt% and the steel was tempered at 705 °C for 6 h.

Fe-2.25Cr-1.05Mo-0.57Mn-0.30V-0.14C-0.034Nb-0.0009Ti-0.001S-0.004P-0.003Sn-0.001Sb-0.004As (wt%)

J-factor = 46 wt%

Austenitize 920 °C for 50 minutes, water quench, temper 705 °C for 6 h

σ_{ys} = 572 MPa, σ_{uts} = 689 MPa

No additional postweld heat treatment (PWHT) was applied to this plate, and this plate was not laboratory step cooled in the condition provided for this research

FATT = unknown

CVN = 289 J at -18 °C with 100 % shear area

A submerged arc weld (SAW) of 2¼Cr-1Mo-0.25V was obtained from Larsen and Toubro Limited (provided by Manas Ghosh and Milan Raskapoorwala) in the form of two welded blocks, each sized as: 10 cm (long) × 25 cm (wide) × 15.3 cm (thick). One block (stamped MIN PWHT) was subjected to a minimum PWHT of 705 °C for 8 h. The second block [stamped MIN PWHT + SC (step cool)] was given the same PWHT, then step cooled presumably according to the industry standard time–temperature protocol with a total heating time of about 225 h. One of these welded blocks is shown in Figure 2, with the longitudinal welding direction along the narrow (10 cm) direction.

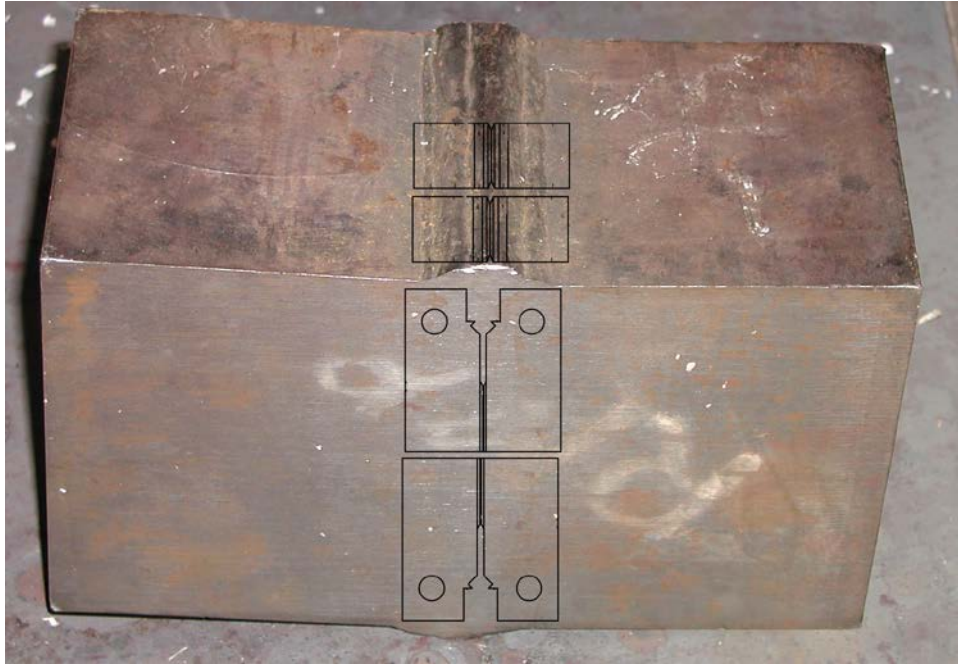


Figure 2—Welded test block of 2¼Cr-1Mo-0.27V steel provided by Larsen and Toubro Limited. The location and orientation of compact tension specimens is shown.

This WM was characterized as follows, and full specifications are provided in Annex B.

The wire electrode composition is:

Fe-2.38Cr-0.98Mo-0.95Mn-0.27V-0.079C-0.005Nb-0.002Ti-0.004S-0.004P-0.001Sn-0.001Sb-0.002As (wt%)

Diffusible H = 4 ml/100 gm Fe

$X_B = 6.1$ wppm

The SAW metal chemical composition is:

Fe-2.31Cr-0.98Mo-0.91Mn-0.27V-0.080C-0.002Nb-0.001Ti-0.002S-0.006P-0.002Sn-0.003Sb-0.002As (wt%)

H content = 0.84 wppm

$X_B = 8.5$ wppm

PWHT at 705 °C for 8 h

$\sigma_{ys} = 586$ MPa, $\sigma_{uts} = 641$ MPa for the as-PWHT condition

CVN = 170 J at -20 °C with 58 % shear area (as-PWHT)

CVN = 223 J at 25 °C with 64 % shear area (as-PWHT)

CVN = 133 J at -20 °C with 48 % shear area (PWHT + step cool)

CVN = 208 J at 25 °C with 70 % shear area (PWHT + step cool)

FATT = -58 °C (as-PWHT) FATT = -52 °C (PWHT + step cool)

In particular, note that the V content is reported to equal 0.27 wt% and the steel was tempered at 705 °C for 8 h.

Larsen and Toubro provided the sketch of the weld geometry shown in Figure 3, where T is assumed to be the thickness of the SAW deposit from the thicker side of the weld. That is, the original weld-root land appears to have been machined at $\frac{3}{4}$ of the plate thickness such that $T = 11.4$ cm.

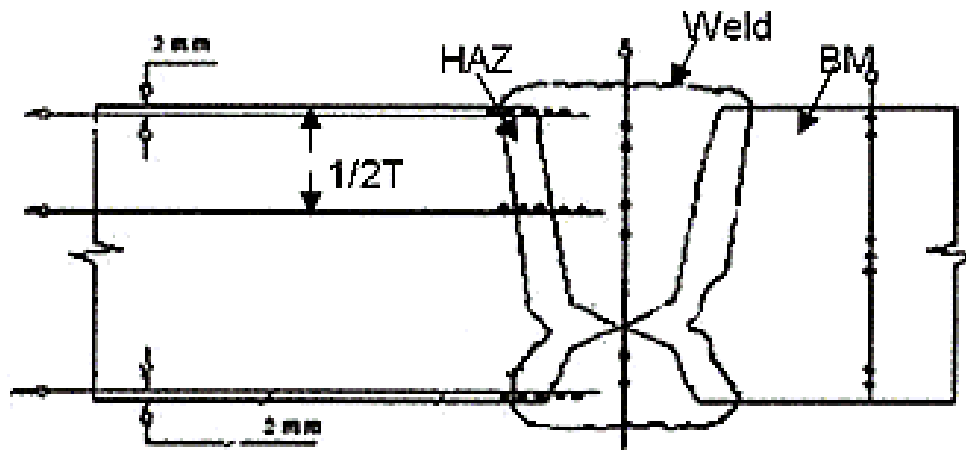


Figure 3—Welded test block geometry.

Both welded test blocks were subjected to the Larsen and Toubro reported minimum PWHT of 8 h at 705 °C, and one of the blocks was provided with a step cool treatment according to [API 934-A](#) that is intended to replicate temper embrittlement conditions expected to occur during normal operation. In contrast, base plate was received in the quenched and tempered condition (6 h at 705 °C), without PWHT. While temper embrittlement is known to exacerbate hydrogen embrittlement of legacy Cr-Mo steels^[2], this variable is judged to be less important for modern Cr-Mo and Cr-Mo-V compositions of either low J or low X_B . Nonetheless, as a matter of credible simulation of reactor service and for conservative worst-case characterization, a piece of the base plate and both weld blocks were subjected to the standard step-cooling heat treatment outlined in [API 934-A](#) (May 2008). This treatment was carried out the University of Virginia, prior to specimen machining for the hydrogen cracking experiments. Weld metal specimen identifiers starting with WMA and WMB received the duplicate step-cool treatment, while specimens starting with WMC and WMD received a single step-cool treatment.

The as-received composition and mechanical properties of the Cr-Mo-V steels are summarized in tabular form in Tables 2 and 3.

Table 2—Steel Composition

wt %	C	Mn	Si	Ni	Cr	Mo	Cu	Al	S	P	Sn
Base plate	0.139	0.57	0.08	0.088	2.25	1.05	0.05	0.015	0.001	0.004	
Weld metal	0.080	0.91	—	—	2.31	0.98	—	—	0.002	0.006	
	V	Nb	Ti	As	N	B (ppm)	Sb	O	H (ppm)	J	X-bar
Base plate	0.297	0.034	0.009	0.004	0.006	10	0.001	0.019	—	46	6
Weld metal	0.270	0.002	0.001	0.002	—	—	0.003	—	0.84	—	8.5

Table 3—Steel Heat Treatment and Mechanical Properties

	Base Metal	Weld Metal
Heat treatment	920 °C for 50 min, water quench, temper 705 °C for 6 h	PWHT 705 °C for 8 h
Tensile properties at 23 °C	Yield strength = 572 MPa Ultimate strength = 689 MPa	Yield strength = 586 MPa Ultimate strength = 641 MPa
Charpy V-notch properties	289 J at -18 °C FATT not reported FATT not reported (SC)	170 J at -20 °C FATT = -58 °C (PWHT) FATT = -52 °C (PWHT + SC)

Hydrogen Charging

Discussions among the leadership of API Task Group 934-F established the following H₂ exposure condition and expected concentration of total dissolved hydrogen.

Hydrogen pressure = 20.7 MPa

Exposure temperature = 440 °C

Exposure time = 48 h

Target total dissolved H concentration = 6.6 wppm

Specimens used in the present study were hydrogen charged by means of a high-pressure high-temperature autoclave able to reproduce actual service conditions of refining pressure vessels. This work was carried out at the Le Creusot Research Center of ArcelorMittal. The autoclave used is illustrated in Figure 4.

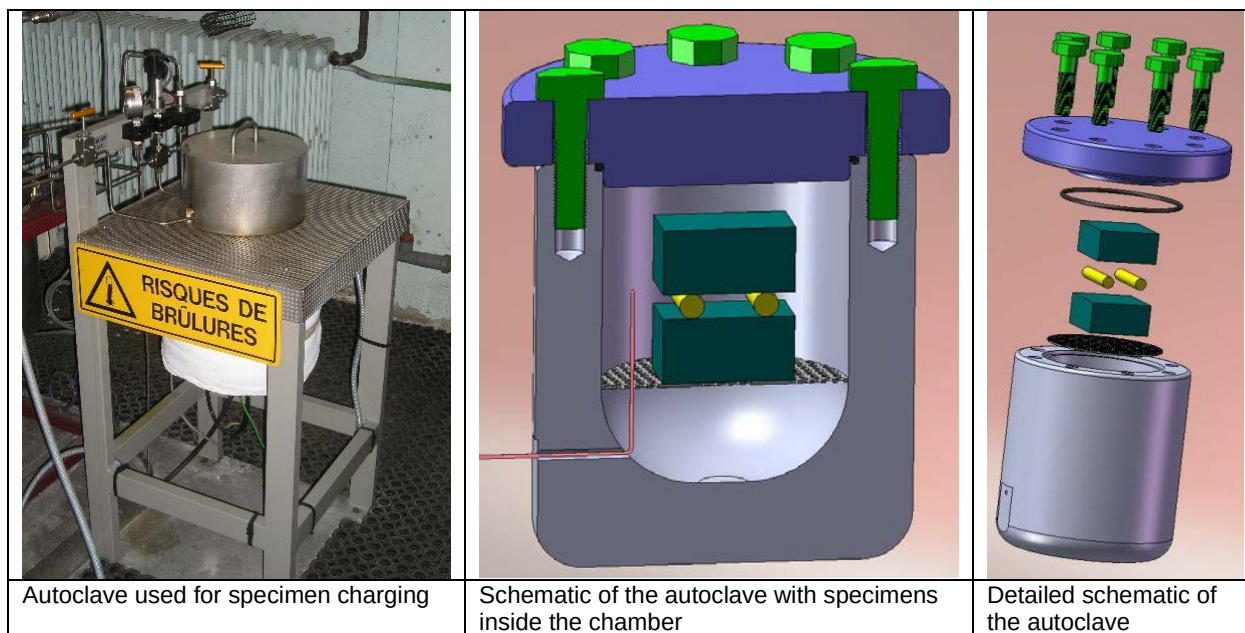


Figure 4—Autoclave assembly used for elevated-temperature H charging in a high-pressure H₂ environment at the Le Creusot Research Center.

Thermal charging introduces an accurate content of hydrogen in the alloy provided that the hydrogen solubility is known. Dissolved atomic hydrogen (H), which is equilibrium with a given H₂ pressure and temperature, is given by Sievert's law as expressed by the following relationship ^[21–24].

$$C_o = S(T)\sqrt{P} \quad (1)$$

where

$S(T)$ is hydrogen solubility, which is temperature (T) and material dependent (mole H/m³ Pa^{1/2});

P is H₂ partial pressure (Pa = 10⁻⁵ bar);

C_o is H concentration (mole H/m³ = 0.128 wppm).

The hydrogen solubility as a function of temperature is given by a classical Arrhenius law:

$$S(T) = S_o e^{-\frac{\Delta H}{R \cdot T}} \quad (2)$$

where

S_o is Sievert's law solubility coefficient (mole H/m³ Pa^{1/2});

ΔH is dissolution enthalpy (J/mole).

Both S_o and ΔH are fitting parameters based on experimental analysis of H solubility for a given steel composition and heat treatment. For Cr-Mo and Cr-Mo-V steels, the literature yields the parameters given in Table 4 and Figure 5, which were used to guide selection of charging temperature and H₂ pressure conditions.

Table 4—Sievert's Law Parameters for H Solubility in Cr-Mo and Cr-Mo-V Steels

Materials	S_o (mole H/m ³ Pa ^{1/2})	ΔH (J/mole)	Reference
2¼Cr1Mo	0.592	27,079	R. Koers, 1996 ^[21,22]
	0.814	27,710	Smitt and Ivens, 1993 ^[23]
	0.469	26,568	S. Pillot et al., 2012 ^{[24] a}
2¼Cr1MoV	0.036	6,943	S. Pillot et al., 2012 ^{[24] a}
3Cr1MoV	0.026	6,182	R. Koers, 1996 ^[21]
^a Base plate.			

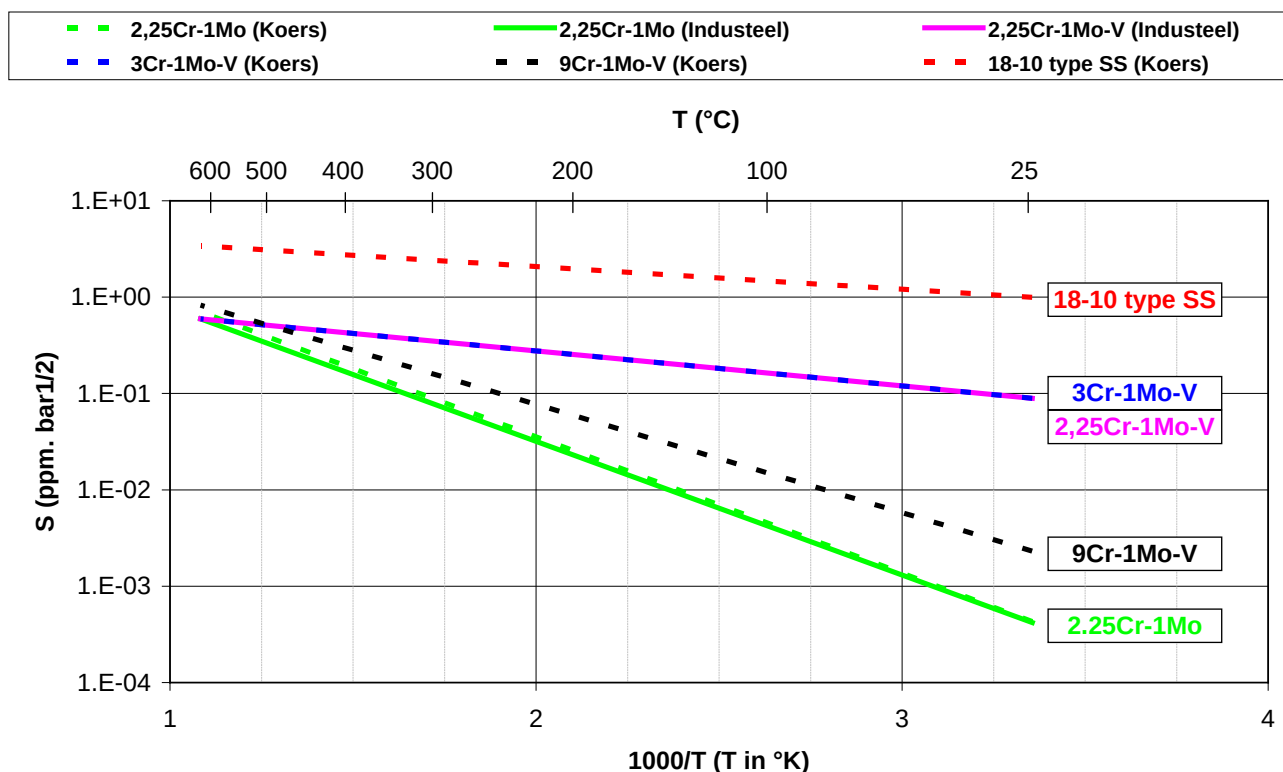


Figure 5—The temperature dependence of the Sievert's law solubility coefficient for Cr-Mo and Cr-Mo-V steels. The Cr-Mo-V steels were base plate microstructures, and the V content of the 2¼Cr-1Mo-¼V composition was 0.27 wt%.

Several batches of 2¼Cr-1Mo-0.3V BM and WM were charged with a high content of total H. Specimen batches consisted of sets of 25-mm-thick C(T) specimens plus reference cylinders [20 mm diameter and 22 mm height (54 gm) for BM, and 15 mm diameter and 22 mm height (28 gm) for WM] used to measure the total H-content introduced in the C(T) specimens during charging.

Reference cylinders and compact tension specimens were cleaned using acetone and alcohol in order to remove all traces of pollution and grease at surfaces that may change H adsorption during charging. The same operation was done on the autoclave walls in order to remove all traces of pollution and grease. All specimens were attached together using a metallic wire in order to ease and shorten the duration of the hot-removing operation. The batch was then put in the autoclave. The autoclave was initially full of air, and a vacuum at room temperature was achieved using a molecular pump. After reaching a sufficient vacuum level (about 0.1 torr), hydrogen was introduced inside the autoclave at room temperature. Vacuum was then obtained a second time. When a sufficient vacuum level was achieved, H₂ was again put under pressure inside the autoclave. The initial target pressure of H₂ at the charging temperature was estimated using $PV = nRT$. Even if not exactly true, this equation permits progressively heating the autoclave and specimen under hydrogen without significant contamination by oxygen and without exceeding the target H₂ pressure at temperature. Pressure was adjusted by addition of H₂ at high temperature. This is particularly true for materials with high hydrogen solubility such as 2¼Cr-1Mo-V that absorb large quantities of H. Heating was then initiated to the target temperature; temperature (and H₂ pressure) slowly increased. When temperature was close to the target, H₂ pressure in the autoclave was adjusted to the target value. When pressure and temperature were at the required level (in general heating lasted about 5 h to 6 h), soaking time started to produce a uniform distribution of hydrogen within the thickness of the specimens. Hydrogen pressure was manually adjusted to compensate for loss of pressure in the autoclave due to absorption of H in the metal. When soaking exceeded 48 h and pressure was stable (meaning no more absorption of hydrogen), an equilibrium state was considered to be reached and the hot removal procedure was started.

The hot removal procedure has been developed at the Le Creusot Research Center to minimize the time spent at high temperature in the absence of sufficient hydrogen pressure in the autoclave to maintain an

equilibrium H concentration on the steel surface and maintain a constant hydrogen profile within the thickness of the specimen. Slow cooling after H charging would result in a strong degassing of the specimens. The hot removal procedure consisted of minimizing the time spent to open the autoclave in the absence of H₂ and to cool the specimens to a temperature at which H degassing is very slow. In order to achieve this condition, H₂ pressure is purged from the autoclave and compressed air is blasted inside the autoclave. This later operation limits the heat brought to the specimens, but does not avoid degassing. It is then required to run concurrently the hot extraction procedure consisting of opening the autoclave at high temperature and removing the specimens. In order to do that, autoclave closing screws were rapidly removed and the specimen batch was rapidly taken to be quenched in cold water. Due to the small size of the specimens, the cooling procedure is quick and shortens the time spent in water. The autoclave opening and quenching operations have been timed. Opening operation lasts about 2 min to 3 min and quenching operation about 3 min to 4 min. From the very beginning of the operation (removal of the hydrogen pressure) to the storage in liquid nitrogen, the elapsed time is less than 15 min. This H charging technique is commonly used at ArcelorMittal to develop H degassing laws. A comparison of the H diffusivity data achieved for conventional 2¼Cr-1Mo steel from the literature^[21], with prior results from the ArcelorMittal technique, shows excellent agreement (Figure 6). The H charging method used for the present API study is thus validated. Hydrogen concentration data presented in the Results further establish the accuracy and reproducibility of this high-temperature H charging procedure.

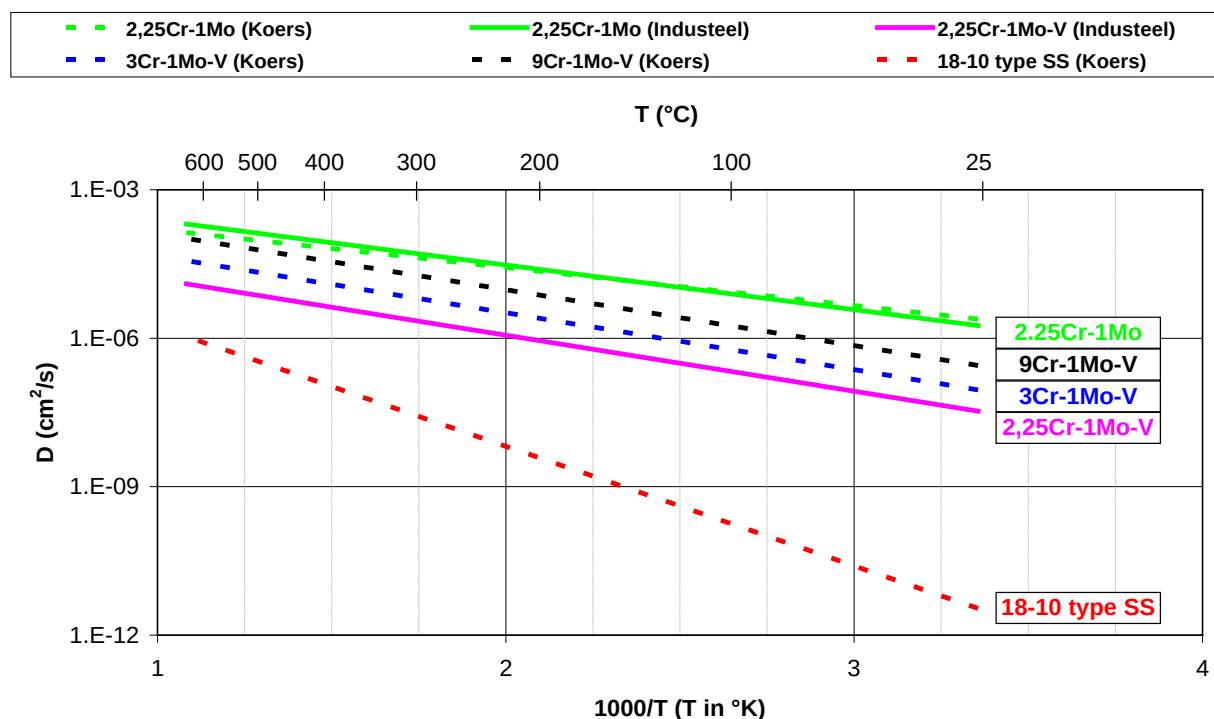


Figure 6—The temperature dependence of the H diffusivity for Cr-Mo and Cr-Mo-V steels. Results labeled “Industeel” were obtained using the elevated-temperature, high-pressure H₂ procedure at ArcelorMittal, as implemented for the present API research.

After removal from the autoclave, specimens were dried and stored in liquid nitrogen to fix the H concentration, avoiding loss prior to H measurement or fracture testing. Specifically, compact tension and select witness cylinder specimens were stored in liquid nitrogen until either expedited shipment to Hy-Performance Materials Testing in Bend, OR or hot extraction H measurement at ArcelorMittal. All specimens received at Hy-Performance Materials Testing were stored in liquid nitrogen until the IHAC experiment was conducted. Upon express shipping return to the Le Creusot Research Center, cylinders were stored in liquid nitrogen to avoid outgassing prior to H concentration measurement.

Total Hydrogen Content Measurement

Hydrogen content was measured using cylindrical specimens that were either charged in the autoclave alongside C(T) specimens or machined from C(T) specimens after fracture. Prior to H measurement, the specimen was removed from liquid nitrogen, sand blasted to remove surface oxide, and degreased in formaldehyde at room temperature for a few minutes to remove surface grease or oil. These operations are mandatory to ensure good reproducibility and accuracy of the H concentration measurement, as the quantities of hydrogen measured during these experiments are a few $\mu\text{g H}_2/\text{g}$ of steel. Just before measurement, specimens were removed from the degreasing solution and dried.

The hydrogen content measurement is based on a hot extraction technique coupled to a thermal conductivity detector. The device used to perform total hydrogen content measurement is a JUWE H-Mat 221 (former name of the BRUCKER G4 Phoenix). This instrument uses the carrier gas hot extraction method and enables a rapid and automatic determination of diffusible hydrogen in a wide variety of metallic matrices. The evolved hydrogen is detected by a sensitive and long-term stable thermal conductivity detector. The analyzer is equipped with a rapid heating (infrared heated) clamshell furnace capable of reaching 900 °C. The quartz tube diameter of 30 mm enables analysis of large samples. In the present study, hot extraction was performed at 650 °C to remove the majority of lattice diffusible, reversibly trapped, and strongly trapped H from the steel.

The testing procedure consists of heating the specimen in a quartz tube with a continuous passage of carrier gas (99.999 % purity N_2). Diffusible H, degassed from the heated specimen, recombines to form H_2 and is mixed with the N_2 carrier gas that flows through a thermal conductivity detector. The thermal conductivity of the $\text{H}_2 + \text{N}_2$ carrier gas mixture is compared to that of standard mixtures. From this comparison, the flux of hydrogen is measured and integrated for the test duration to capture the total diffusible hydrogen content in the specimen prior to outgassing. In the case of ferritic steels, as no permanent trapping occurs at 650 °C, this measured hydrogen content corresponds to the total hydrogen content in the bulk of the material. The accuracy of this technique is very good as large specimens are used. Accuracy has been estimated on the basis of a sensitivity analysis and is about 4.5 % to 5 % of the measured value. A guideline was defined by the Le Creusot Research Center to define the minimum cylinder mass and size-fit with the high accuracy range of the device ^[25]. Table 5 and Figure 7 give, respectively, the relative error measured during this study and the correspondence (for cylindrical specimens) between specimen mass and expected hydrogen content with the index of the calibration. Indices 1 and 2 in Figure 7 should be avoided to increase accuracy of the measurement. The large specimen size (54 gm for BM and 28 gm for WM) plus high hydrogen content (7 wppm to 10 wppm) measured for H-charged Cr-Mo-V always lead to a calibration index greater than 10 in Figure 7, meaning from Table 7 that the H concentrations were determined with a very high degree of accuracy in this study.

Table 5—Relationship Between Figure 7 Index, H Concentration, and Relative Error for Hot-extraction Measurements of H at the Le Creusot Research Center

	Hydrogen Volume				
Volume # (index in Figure 7)	V1	V2	V3	V4	V5 and above
H_2 (ml)	0.04096	0.0941	0.1735	0.25717	0.34823
H_2 (μg)	3.6	8.3	15.4	22.9	31
Maximum relative error (%)	31.9 %	10.5 %	4.8 %	4.8 %	4.8 %

Fracture Mechanics Experiments

Compact tension fracture mechanics specimens with width, W , of 50.8 mm and total thickness, B , of 22.86 mm were extracted from the base plate and weld metal. Base metal specimens were machined in the T-S orientation, as defined by [ASTM E1823](#), such that the loading axis is parallel to the transverse direction of the plate and the crack growth direction is through the plate thickness. Specimens from the welded blocks were extracted such that the crack plane was entirely within the fusion zone of the weld. The specimens were oriented with the crack growth direction from the outer surface toward the center of the weld, as shown in Figure 8. All specimens were machined with side grooves that reduced B to a net thickness, B_N , of 18.29 mm (80 % of B).

C(T) specimens were precracked by fatigue cycling in ambient laboratory air at room temperature and a minimum load-to-maximum load ratio of 0.10. Fatigue cracks were propagated under decreasing ΔK ($K_{\max} - K_{\min}$) conditions with final $K_{\max}$ values between 15 MPa $\sqrt{\text{m}}$ and 22 MPa $\sqrt{\text{m}}$. Initially, specimens were precracked to a final crack length equal to $0.55W$ and $K_{\max}$ equal to 15 MPa $\sqrt{\text{m}}$. Test results for Cr-Mo-V base metal C(T) specimens indicated large values of fracture toughness and associated high loads; as such, the final fatigue crack length was increased to $0.65W$ to facilitate smaller loads, and the final value of $K_{\max}$ was increased to 22 MPa $\sqrt{\text{m}}$ to facilitate efficient precracking.



Figure 8—C(T) specimen orientation in the welded blocks of 2½Cr-1Mo-¼V steel.

IHAC K_{IH} Procedures

After precracking, C(T) specimens were precharged with hydrogen via exposure to 18 MPa hydrogen gas at 450 °C for 48 h. Specimens, stored in liquid nitrogen prior to IHAC testing, were warmed to room temperature in dry N_2 to minimize frost and condensation on the specimen and critically to avoid condensed moisture at the crack tip.

Elastic-plastic fracture toughness tests were conducted in a servo-hydraulic test system operated in displacement control at a constant rate; a clip-on gage measuring load-line displacement provided the control signal. During the experiment load, CMOD and DCPD were recorded as a function of time by the system computer. Following each test, the linear-elastic stress intensity factor, K , was plotted as a function of time. A linear fit was applied to the initial portion of this plot. The slope of this fit, with units of $\text{MPa}\sqrt{\text{m}}/\text{h}$, was specified as the loading rate rather than the applied displacement rate so as to provide values that are independent of specimen geometry. Elements of this experimental method are shown in Figures 9 and 10.

Crack extension was monitored during each experiment using the DCPD method. (The specimen was not unloaded during IHAC testing, and unloading compliance was not used to determine either crack length or the plastic part of the J-integral.) A constant current of 8.00 amps was applied to the test specimen in series with a second specimen serving as a reference probe. Voltage was measured across the crack mouth in both the active and reference specimens. Current and voltage lead locations were as directed in [ASTM E1737-98](#), which employs Johnson's equation to relate measured voltage to crack length. Current direction was reversed periodically using relays. Recorded measurement values were averaged for the forward and reverse current separately, and a single data point resulted as one-half of the difference between the forward and reversed voltage measurements. This procedure eliminated spurious thermally induced voltages that obscure the DCPD associated with the crack.

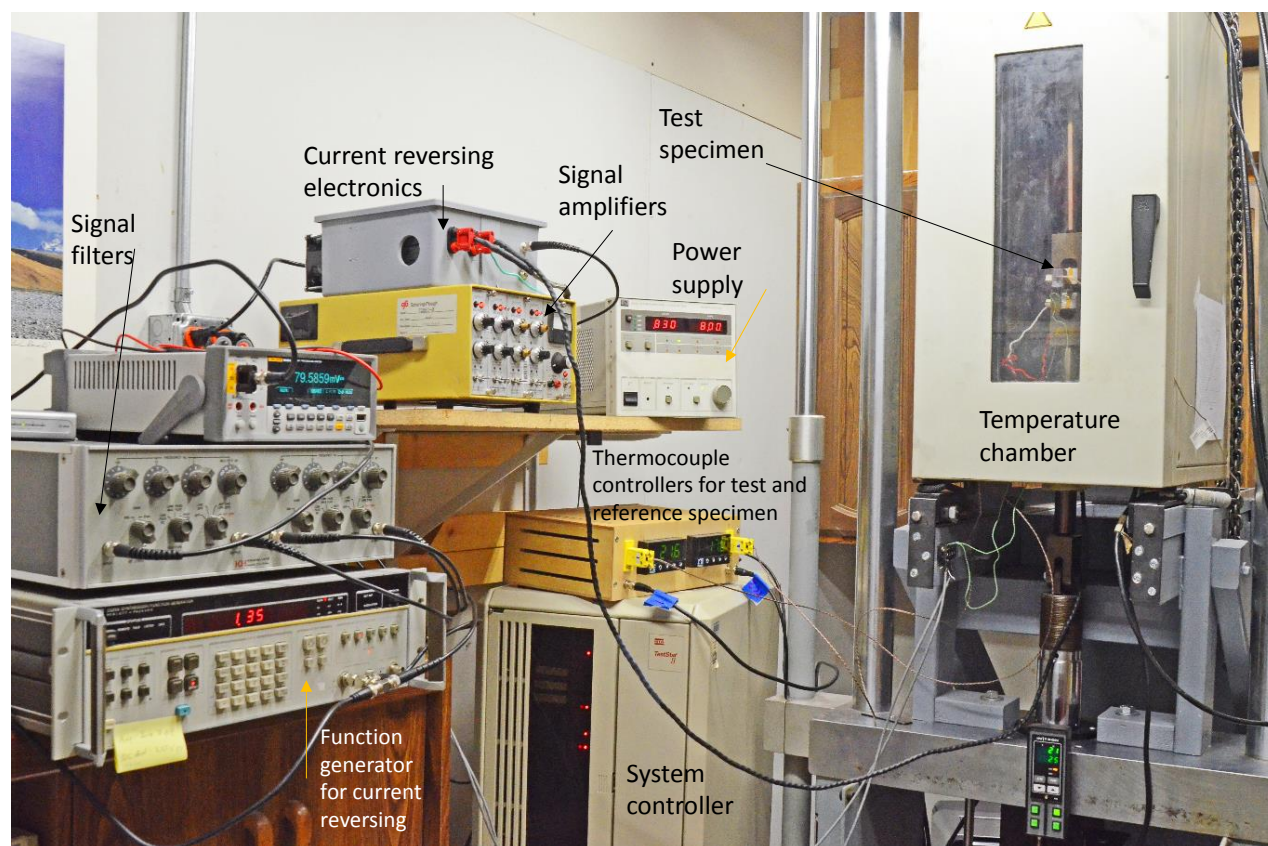


Figure 9—Instrumentation elements of the IHAC test method implemented at Hy-Performance Materials Testing in Bend, OR.

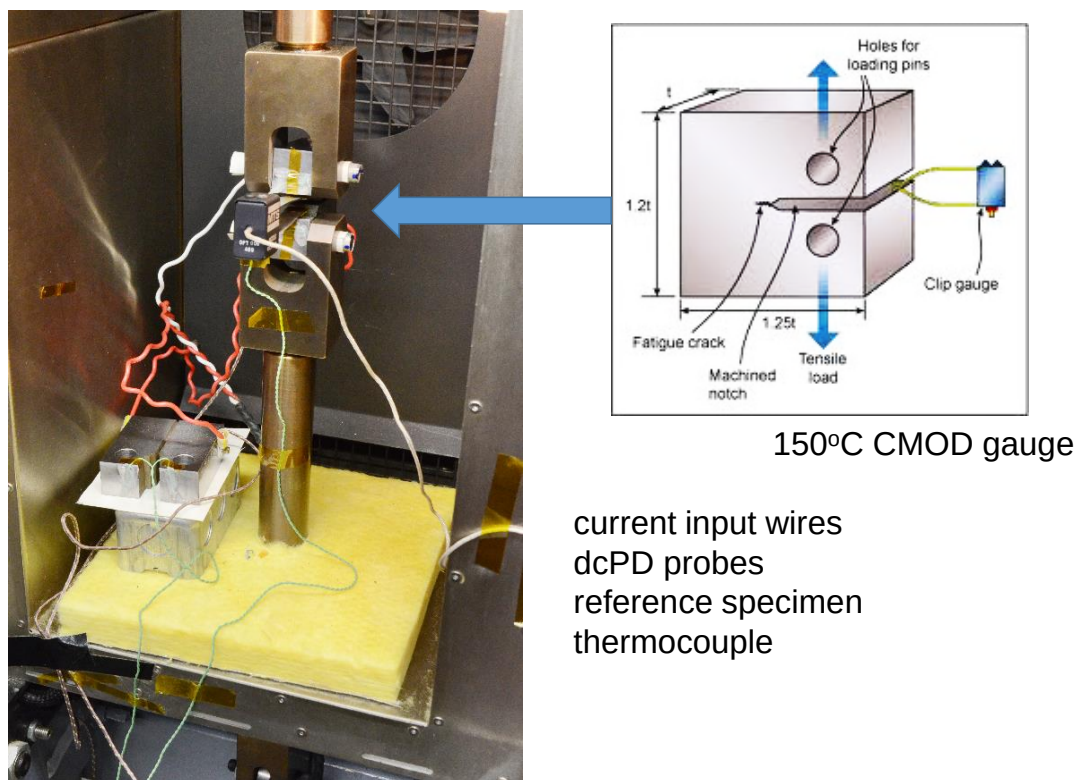


Figure 10—Compact tension specimen and associated probes for IHAC testing at Hy-Performance Materials Testing in Bend, OR.

Specimen temperature was carefully controlled (usually within 1 °C) by conducting all tests in a temperature chamber (see Figure 9) with PID temperature control and the ambient laboratory temperature was maintained within 1 °C to 2 °C. As such, the measurements from the reference specimen were unnecessary and often not used. The decision of whether to normalize data with the reference probe was made on a test-by-test basis in order to achieve the best data quality for each experiment.

For tests with nominal loading rates less than 20 MPa/m/h, the dK/dt was increased to 20 MPa/m/h once DCPD data clearly indicated that crack extension had commenced. Each test finished with a constant CMOD hold at the final CMOD value. This hold time was typically 8 h, which was sufficient to allow for nearly complete load relaxation. Crack extension during the hold was monitored with DCPD measurement; however, these data were not reported, as such cracking is outside the scope of the API work statement.

After the IHAC experiment was completed, the specimen was chilled in liquid nitrogen to promote brittle cleavage fracture, which revealed the fatigue precrack and hydrogen-assisted crack surfaces. One-half of each specimen was retained for fracture surface observations, while small cylinders were extracted from the other half of the broken C(T) specimen to measure hydrogen concentration at the Le Creusot Research Center. A hollow drill bit was used to cut a 9.6-mm-diameter cylindrical core from the C(T) specimen just below the location of the crack tip. Approximately 5 mm was removed from each end of the cylinder; the remaining 12.7-mm-long core was entirely from within the specimen and contained none of the specimen-free surfaces. This size of specimen was selected to yield accurate H concentration, following the results in Figure 7 and Table 5. The high levels of H concentration measured in cored specimens, expeditiously shipped to the Le Creusot Research Center, demonstrated that this machining and shipping procedure resulted in minimal H loss. Critically, this procedure provided an accurate measurement of the concentration of dissolved H present in each C(T) specimen after testing.

Precrack and final crack lengths were measured at nine locations across the thickness of the specimen, using a microscope and as described in [ASTM E1820](#). DCPD measurements were converted to crack length values using the procedures of [ASTM E1737-98](#). A linear correction was applied to the calculated crack lengths to

force a match with the physical measurements, though this difference was always quite small. J-integral values were calculated according to [ASTM E1820-11](#). The procedure used to determine the elastic-plastic K (K_J) vs crack extension (Δa) R-curve, and several versions of operationally defined threshold for the onset of stable H-assisted cracking (K_{IH}), are detailed in the Results.

HEAC K_{IH} Procedures

Fracture testing in high-pressure gaseous hydrogen was conducted using procedures similar to those described above for IHAC characterization. Compact tension specimen size was reduced such that $W = 44.5$ mm and $B = 12.7$ mm. Side grooves reduced the net thickness (B_N) to 80 % of B . Fatigue precracking was performed in ambient laboratory air with a final K_{max} of 22 MPa/m. A constant current of 5.00 amperes was used for DCPD measurements.

Testing was conducted at Hy-Performance Materials Testing using a custom designed environmental test chamber to contain high-pressure H₂, including specimen temperature control with DCPD monitoring of crack growth and servo-hydraulic system loading. The apparatus is shown in Figure 11. Load and load-line displacement were monitored using specially designed transducers placed inside the autoclave to eliminate measurement uncertainties. Care was taken to remove residual air from the chamber and to ensure that very high purity H₂ was used during testing. Prior to each experiment, the chamber was purged by pressurizing several times to about 1.8 MPa with 99.999 % He gas. The chamber was then evacuated to approximately 0.02 torr and held under vacuum for 1 h to 2 h to extract adsorbed water from internal surfaces. The chamber was then purged several times with 99.999 % pure H₂ and filled to the final test pressure. The hydrogen gas was certified by the supplier to contain less than 1 vppm O₂. Trace oxygen content in the test chamber was monitored throughout the purging process using a calibrated electrochemical sensor to ensure complete removal of oxygen. Trace oxygen levels were again measured at the completion of each experiment to ensure that purity was maintained for the duration of the test. Hydrogen gas used for all experiments was verified to contain less than 1 vppm oxygen. Due to the practical challenges of calibrating a sensor to 0 ppm O₂, measurements cannot be verified below 1 vppm O₂; however, actual O₂ values are likely less than 0.5 vppm.

Two additional compact tension specimens ($W = 26.4$ mm and $B = 12.7$ mm) were tested at Sandia National Laboratory in 0.35 MPa and 103 MPa H₂. Experimental procedures for these experiments were generally consistent with those described above. Further details regarding the experimental procedures are given elsewhere ^[26].

RESULTS

Hydrogen Concentration Measurements

Total dissolved hydrogen concentration measurements were obtained from Cr-Mo-V cylinders that were either: (a) H charged as part of each autoclave batch of compact tension specimens, cooled and stored in liquid nitrogen prior to hot extraction measurement, or (b) machined from tested C(T) specimens in Bend, OR, express shipped to France, and stored in liquid nitrogen prior to hot extraction measurements. The results of all ArcelorMittal measurements of total dissolved hydrogen concentration are presented in Table 6. The following findings are significant.

Witness cylinders of 2¼Cr-1Mo-0.3V BM and WM showed that each autoclave charging batch successfully produced the targeted H concentration of 6.6 wppm or higher. Specifically:

Batch 1	2¼Cr-1Mo-0.30V base plate	7.2 wppm H	7.5 wppm H
Batch 2	2¼Cr-1Mo-0.27V weld metal	6.6 wppm H	
Batch 3	2¼Cr-1Mo-0.30V base plate	8.5 wppm H	
	2¼Cr-1Mo-0.27V weld metal	7.1 wppm H	
Batch 4	2¼Cr-1Mo-0.27V weld metal	6.5 wppm H	6.2 wppm H
Batch 5	Not measured		

H₂ testing at HPMT

- H₂ gas pressure >2000 psi
- Temperature -100°C to > 60°C

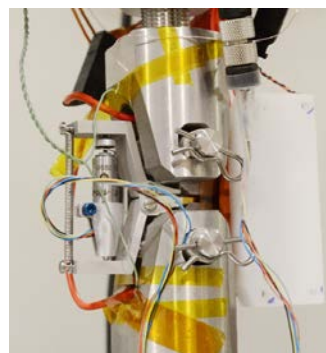
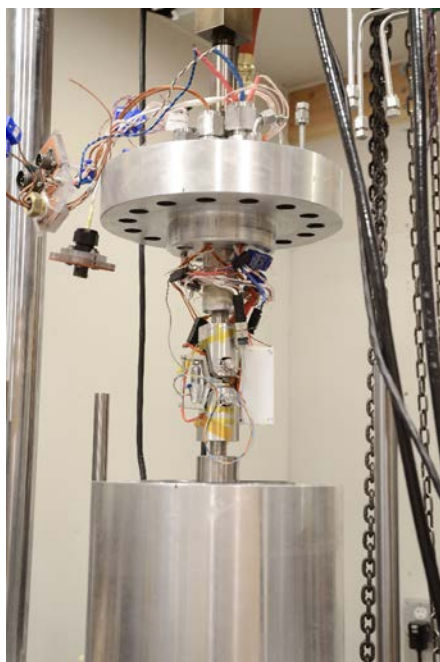


Figure 11—Apparatus used for high-pressure H₂ testing of compact tension specimens at Hy-Performance Materials Testing.

The base plate of 2¼Cr-1Mo-0.30V generally exhibited higher H solubility compared to the 2¼Cr-1Mo-0.27V weld metal—7.2 wppm to 8.5 wppm H compared to 6.5 wppm to 7.1 wppm H—as specifically illustrated by the two cylinders equally exposed in Batch 3. The higher H solubility of the 2¼Cr-1Mo-0.30V base plate was confirmed by the measured H concentrations of the compact tension specimens, presented in ensuing sections.

Experiments demonstrated that hydrogen was not lost during shipment of precharged Cr-Mo-V steel C(T) specimens to and from Bend, OR. From Table 6, a Batch 2 witness cylinder of weld metal contained 6.6 wppm after removal from the autoclave and storage in liquid nitrogen at the Le Creusot Research Center until H measurement. The H concentration was 6.1 wppm for a cylinder exposed with the same autoclave charging and liquid nitrogen storage protocol, with a 1-week outgassing exposure to laboratory air at ambient temperature added. Shipments at ambient temperature always required less than 1 week. This minimal loss of H is consistent with prior outgassing experiments conducted at ArcelorMittal, as well as with longer-term H outgassing experiments conducted during this API program and discussed in an ensuing section.

Table 6—Measurements of Total Dissolved Hydrogen Concentration in 2¼Cr-1Mo-0.3V Base Metal and Weld Metal

Specimen Label	Nature of Material	Type of Specimen	Batch	Storage	Comment/Remark	Hydrogen Content (ppm)
BM3A	Base material	C(T)	1	23 °C (2–3 days) + LN ₂	Machined from CT25 Batch 1 (from HPMT)	9.3
BM6A	Base material	C(T)	1			9.1
BM10A	Base material	C(T)	1			9.3
BM1	Base material	Cylinder	1	LN ₂	At end of autoclave charging Batch 1	7.5
BM2	Base material	Cylinder	1			7.2
BM3	Base material	Cylinder	1	23 °C (1 week) + LN ₂	At end of autoclave charging Batch 1	Stored in LN ₂
BM4	Base material	Cylinder	1			Stored in LN ₂
BM1A	Base material	C(T)	1	LN ₂	Machined from CT25 Batch 2 (from HPMT)	9.6
BM8A	Base material	C(T)	1			9.5
A1	Weld material	Cylinder	2	23 °C (1 week) + LN ₂	1 week at 23 °C after charging Batch 2	6.05
B1	Weld material	Cylinder	2	LN ₂	At end of autoclave charging Batch 2	6.6
BM5	Base material	Cylinder	2			5.4 (+ 5 min at 400 °C)
WMA1	Weld material	C(T)	2	LN ₂ at reception (2-day delay)	Machined from CT25 Batch 2 (from HPMT)	6.16
WMA2	Weld material	C(T)	2			6.33
WMA3	Weld material	C(T)	2			6.55
WMA4	Weld material	C(T)	2			7.84
WMB1	Weld material	C(T)	2	LN ₂ at reception (2-day delay)	Machined from CT25 Batch 2 (from HPMT)	7.48
WMB3	Weld material	C(T)	2			7.92
WMC1	Weld material	C(T)	2	LN ₂ at reception (2-day delay)	Machined from CT25 Batch 2 (from HPMT)	7.62
WMC2	Weld material	C(T)	2			7.53
BM4A	Base material	C(T)	1	LN ₂ at reception (2-day delay)	Machined from CT25 Batch 2 (from HPMT)	9.3
BM9A	Base material	C(T)	1			8.27
BM7A	Base material	C(T)	1			8.87
WMA2	Weld material	Cylinder	3	LN ₂	At end of autoclave charging Batch 3	7.06
BM6A	Base material	Cylinder	3			8.47
MB1	Weld material	Cylinder	4	LN ₂	At end of autoclave charging Batch 4	6.46
MB2	Weld material	Cylinder	4			6.22
WMD1	Weld material	C(T)	3	LN ₂ at reception (2-day delay)	Machined from CT25 Batch 3 (from HPMT)	7.1
WMD2	Weld material	C(T)	3			8.1
WMD4	Weld material	C(T)	4	LN ₂ at reception (2-day delay)	Machined from CT25 Batch 4 (from HPMT)	7.7
BM1B	Base material	C(T)	3	LN ₂ at reception (2-day delay)	Machined from CT25 Batch 3 (from HPMT)	10
BM3B	Base material	C(T)	3			10.7
BM4B	Base material	C(T)	3			10.7
BM6B	Base material	C(T)	4	LN ₂ at reception (2-day delay)	Machined from CT25 Batch 4 (from HPMT)	9.2
BM8C	Base material	C(T)	5	LN ₂ at reception (2-day delay)	Machined from CT25 Batch 5 (from HPMT)	9.4
BM8BT	Base material	C(T)	5			9.3
WM3C	Weld material	C(T)	5			7.2

NOTE HPMT = Hy-Performance Materials Testing

Cylinders of 2¼Cr-1Mo-0.3V BM and WM, machined from C(T) specimens in Bend, OR after the IHAC test and shipped to France for analysis, are as follows:

Batch 1	2¼Cr-1Mo-0.30V base plate	9.3, 9.1, 9.3, 9.5, 9.6, 9.3, 8.3, 8.9 wppm H
Batch 2	2¼Cr-1Mo-0.27V weld metal	6.2, 6.3, 6.6, 7.8, 7.5, 7.9, 7.6, 7.5 wppm H
Batch 3	2¼Cr-1Mo-0.30V base plate	10.0, 10.7, 10.7 wppm H
	2¼Cr-1Mo-0.27V weld metal	7.1, 8.1 wppm H
Batch 4	2¼Cr-1Mo-0.30V base metal	9.2 wppm H
	2¼Cr-1Mo-0.27V weld metal	7.7 wppm H
Batch 5	2¼Cr-1Mo-0.30V base metal	9.3, 9.4 wppm H
	2¼Cr-1Mo-0.27V weld metal	7.2 wppm H

All weld metal C(T) specimens contain between 6.2 wppm and 8.1 wppm H, with an average value of 7.3 wppm, while all base plate C(T) specimens contain between 8.3 wppm and 10.7 wppm H with an average value of 9.5 wppm. Several points are notable. First, the H concentration in 24 of the 26 2¼Cr-1Mo-0.3V C(T) specimens exceeds the Task Group target level of 6.6 wppm H, and the 2 lower levels (6.2 wppm and 6.3 wppm H) essentially equal this target. These H concentrations were directly measured for each C(T) specimen, after IHAC testing. Clearly, sufficient H was retained during the fracture mechanics experiment at each temperature considered. As such, the goals of this research program are accessible by the designed fracture mechanics experiment. Second, Equation (1) and the parameters in Table 4 predict that the dissolved H concentration in 2¼Cr-1Mo-0.3V should be 6.5 wppm for the standard 48 h exposure in 20.7 MPa H₂ at 440 °C; this H concentration is lower than that measured for the C(T) specimens in the current study. This difference was noted in other ArcelorMittal studies and is attributed to increased V content from about 0.25 wt% around the year 2000 to 0.30 wt% at present^[27]. The V contents of the BM and WM used in the current study are 0.30 wt% and 0.27 wt% (Table 2), respectively, consistent with this chronological increase in V content and presumably associated H solubility. Increased V content could result in an increase in the volume fraction of nanoscale V_xC_y precipitate sites for reversible H trapping. Third, the H solubility of base metal exceeds that of the weld metal, with this difference consistent with the higher V content of BM compared to WM. Fourth, the H concentrations typical of the C(T) specimens exceed the values measured for the witness cylinders charged in the same autoclave batch. For example, the averages for Batch 1 charging of witness cylinders and C(T) specimens are 7.4 wppm and 9.2 wppm H, respectively. This difference is most likely due to finite H loss from the smaller witness cylinders, in spite of the rapid removal from the elevated temperature autoclave. Finally, the H concentrations noted above, and in Table 6, may reflect small amounts of H loss during fracture mechanics IHAC experiments, with the amount dependent on test temperature and duration. As such, the variability shown above and in Table 6 is an upper limit. Specific values of H concentration, measured from the cores machined from the C(T) specimens, will be considered in conjunction with interpretations of the IHAC data.

Hydrogen Diffusivity Measurements

Cylinders were machined from the Cr-Mo-V BM and WM, then cleaned and stored to avoid surface oxidation. Materials were charged with gaseous hydrogen in the autoclave at high temperature and high pressure, following the procedures and conditions outlined in the Experimental Procedure. After H charging, specimens were quickly removed from the autoclave, rapidly quenched in water to fix hydrogen concentration, dried, and stored in liquid nitrogen.

Two specimens were extracted from the set and their total hydrogen contents were measured by high-temperature outgassing to determine the average initial content of hydrogen (C₀) in the set of all specimens. The remaining specimens were split into equivalent subsets, and each subset was put in a furnace equipped with accurate temperature control to promote isothermal diffusion. Specimens of each

subset were removed at different times from the furnace, cooled using the same procedure as after autoclave charging, and stored in liquid nitrogen. Then total hydrogen content was measured for each specimen. Using this procedure, H diffusion was characterized at room temperature ($23\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$) and at $100\text{ }^{\circ}\text{C}$ for both BM and WM, with the results summarized in Table 7. Data are plotted in Figures 12 (BM) and 13 (WM), and compared to results obtained during the ELIXIR program, as reported previously^[24,28].

These experiments demonstrate that reversible H trapping is substantial in 2¼Cr-1Mo-0.3V BM at $23\text{ }^{\circ}\text{C}$ since the H loss after 1200 h is negligible. In the case of WM, this loss at $23\text{ }^{\circ}\text{C}$ is somewhat higher, but the trapped-retained H content remains high after 1200 h of outgassing. At $100\text{ }^{\circ}\text{C}$, the impact of trapping is reduced for both BM and WM; outgassing occurs to larger degree than at $23\text{ }^{\circ}\text{C}$. H retention is higher in the case of BM than for WM, reflecting stronger H trapping and a reduced effective H diffusivity for the former. The H outgassing behavior for the 2¼Cr-1Mo-0.3V steel under study is in accordance with what was observed during the European ELIXIR project. The data presented in Figures 12 and 13 are limited, but sufficient to estimate the trap-sensitive effective H diffusivity ($D_{\text{H-Eff}}$) for 2¼Cr-1Mo-0.3V BM and WM at $23\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$. The results are presented in Figure 14 and are in agreement with the European ELIXIR data. Specifically, for the API program steel, the $D_{\text{H-Eff}}$ is $5.9 \times 10^{-9}\text{ cm}^2/\text{s}$ for BM and $1.9 \times 10^{-8}\text{ cm}^2/\text{s}$ for WM at $23\text{ }^{\circ}\text{C}$, and is $5.3 \times 10^{-8}\text{ cm}^2/\text{s}$ for BM and $1.5 \times 10^{-7}\text{ cm}^2/\text{s}$ for WM at $100\text{ }^{\circ}\text{C}$. For comparison based on Figure 6^[24], the reported $D_{\text{H-Eff}}$ is $7 \times 10^{-8}\text{ cm}^2/\text{s}$ at $23\text{ }^{\circ}\text{C}$ and $3 \times 10^{-7}\text{ cm}^2/\text{s}$ at $100\text{ }^{\circ}\text{C}$, each for Cr-Mo-V base plate. Collectively, and compared to the typical H diffusivity for Cr-Mo at $25\text{ }^{\circ}\text{C}$ ($1.3 \times 10^{-6}\text{ cm}^2/\text{s}$), the data in Figure 14 show the strong impact of V_XC_Y -based H trapping on H diffusivity.

Several points are notable in the context of the current IHAC study. The data in Figures 12 and 13 are consistent with the lack of H loss during ambient temperature shipment between France and the United States. Moreover, these data show that H loss at $100\text{ }^{\circ}\text{C}$ is only significant for times in excess of 200 h for BM and in the range of 20 h to 100 h for WM. This behavior is consistent with the fact that H loss was not significant for the elevated-temperature IHAC experiments, as confirmed by the cored cylinders taken to document the H concentration remaining in the C(T) specimen at the end of rising K testing. Collectively, these data show the strong impact of V_XC_Y -based H trapping on H diffusivity.

Table 7—Measured H Concentrations After Isothermal Outgassing of 2¼Cr-1Mo-0.3V for the Indicated Time-Temperature Conditions

Isothermal Soaking Duration (h)	Specimen			
	Base Metal		Weld Metal	
	23 °C	100 °C	23 °C	100 °C
0.1 (Co)	8.5	8.5	7.1	7.1
8				6.5
24			7.2	6.0
100				5.7
240	8.4	6.8	6.9	5.2
720	8.4	5.6	6.1	3.8
1200	8.4	4.5	6.5	3.7
All H concentrations were measured by extraction at $650\text{ }^{\circ}\text{C}$ and are in wppm.				

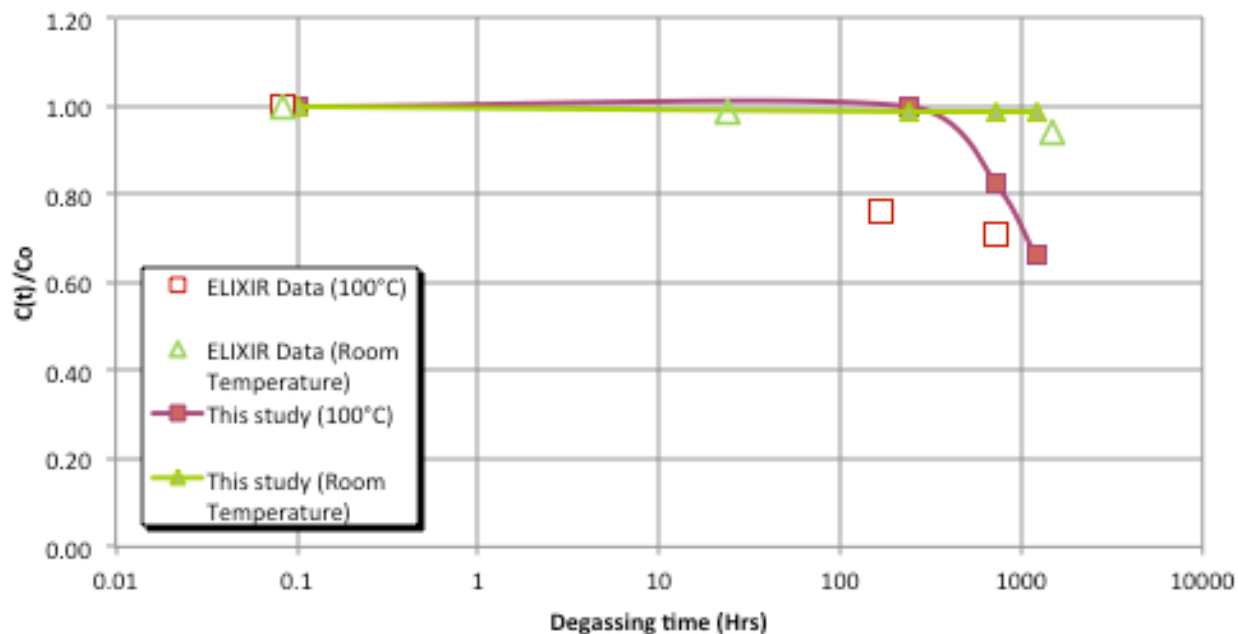


Figure 12—Time-dependent H loss during isothermal exposure of 2 1/4 Cr-1 Mo-0.30 V base metal in moist air at 23 °C and 100 °C.

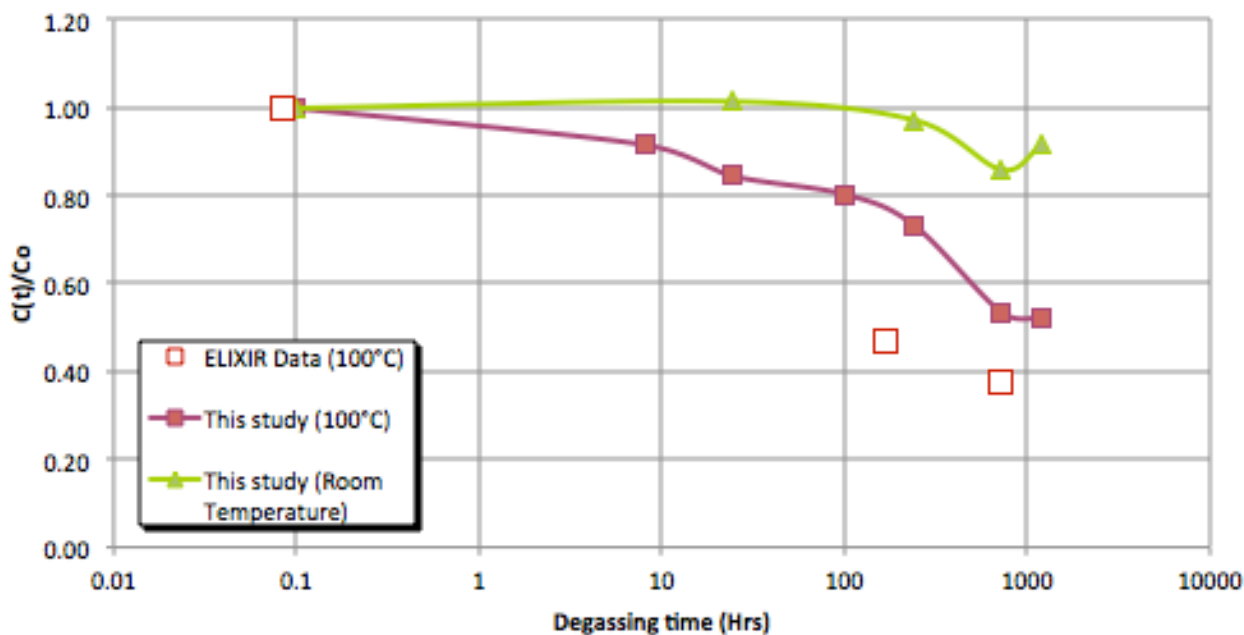


Figure 13—Time-dependent H loss during isothermal exposure of 2 1/4 Cr-1 Mo-0.27 V weld metal in moist air at 23 °C and 100 °C.

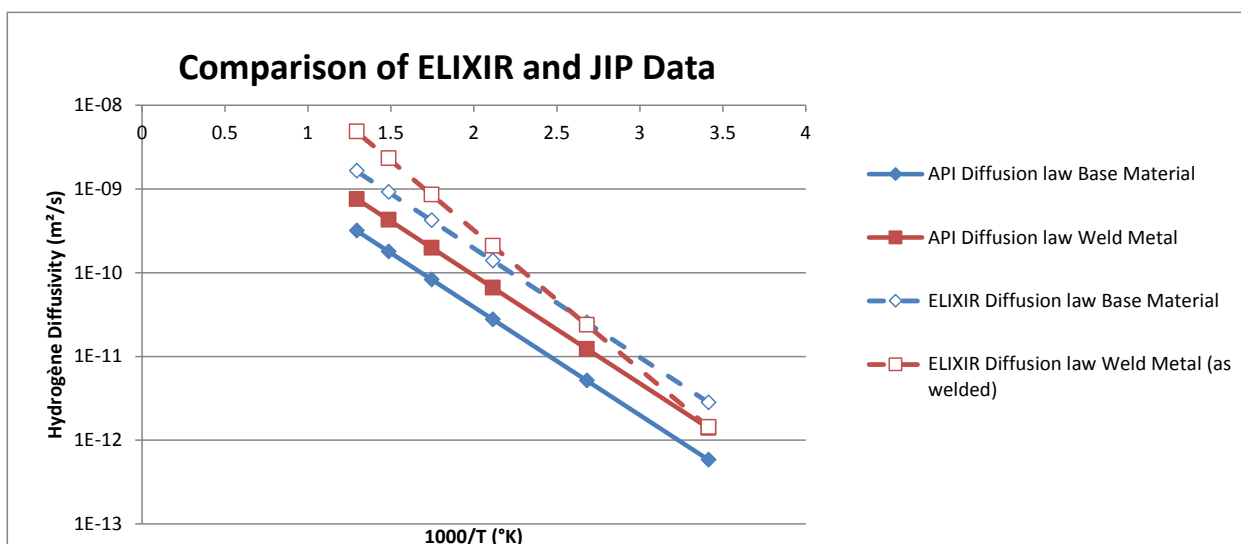


Figure 14—The temperature dependence of trap-sensitive effective H diffusivity ($D_{\text{H-Eff}}$) for weld metal and base plate of the 2¼Cr-1Mo-0.3V steel used in this API study of IHAC, compared to literature data from the results of the European ELIXIR study^[24].

Fracture Toughness Without H

Fracture toughness tests were performed on the base and weld metals of 2¼Cr-1Mo-0.3V, after the step-cool treatment but without hydrogen precharging to provide baseline fracture toughness values. Results are presented in Figure 15 for slow-rising K loading at 26 °C and 100 °C. The associated DCPD and load vs CMOD plot for one of these experiments (BM at $dK/dt = 2 \text{ MPa}\sqrt{\text{m/h}}$) is shown in Figure 16 (top), coupled with the amplification of the definition of crack initiation at K_{JICi} (Figure 16, bottom). Stress intensity factor was determined from the elastic plastic J-integral analysis, and the applied loading rate was atypically slow ($dK/dt = 2 \text{ MPa}\sqrt{\text{m/h}}$ at 23 °C and $20 \text{ MPa}\sqrt{\text{m/h}}$ at 100 °C) but identical to that employed for the IHAC experiments.

Each steel exhibited stable R-curve tearing, rather than unstable fracture, for each temperature and consistent with the high upper-shelf toughness of each steel. The tabulated fracture toughnesses, K_{JIC} , are based on the 0.2 mm (in Δa) offset blunting line intersection specified by ASTM 1820-13. Toughnesses ranged from $228 \text{ MPa}\sqrt{\text{m}}$ to $345 \text{ MPa}\sqrt{\text{m}}$ for the two stressing temperatures and WM or BM in Figure 15. The elastic-plastic K level at the load where DCPD first detected the onset of crack growth was essentially $200 \text{ MPa}\sqrt{\text{m}}$ for each condition in Figure 15; this toughness is an early-stage initiation value, K_{JICi} .

Each form of this modern high-purity steel is very tough at each temperature, consistent with the FATT value of -52°C and Charpy impact energy of 208 J at 23°C for the step-cooled WM. The Charpy impact energy of the BM was 289 J at -18°C , before step cool, but a FATT for the step-cooled microstructure was not determined. Given the low J-factor of this Cr-Mo-V BM, the FATT is very likely well below ambient temperature. Surprisingly, the weld metal exhibits somewhat higher toughness than the base metal (Figure 15). The toughness of each microstructure is mildly reduced at the higher temperature. In all cases crack extension was stable and fracture was via microvoid coalescence, as shown in Figure 17. These findings are consistent with the reported behavior of low alloy ferritic and bainitic steels at upper shelf temperatures.

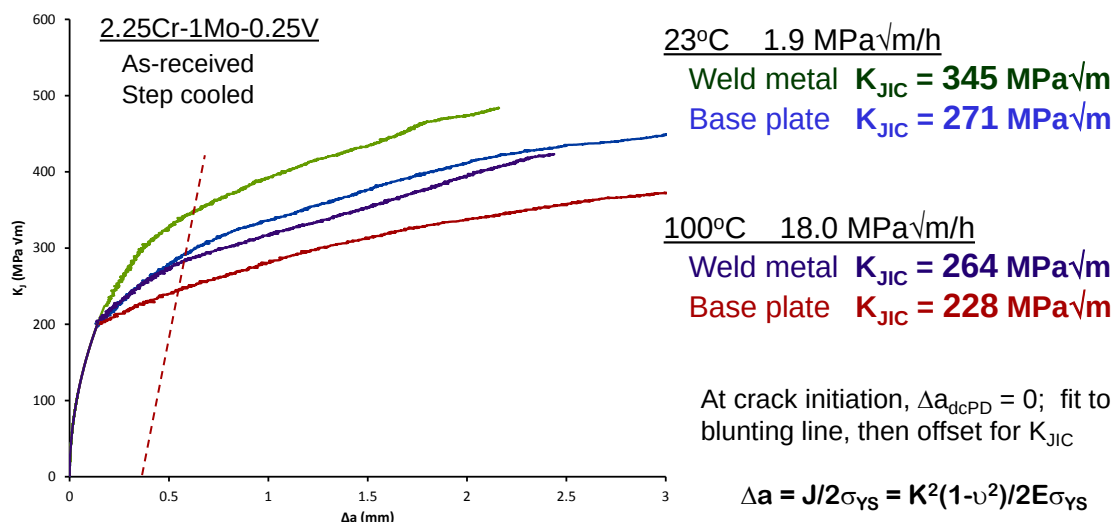


Figure 15—R-curve based fracture toughness for step-cooled 2¼Cr-1Mo-0.3V base plate and weld metal at two loading temperatures.

DCPD Measurement of Crack Length and H-cracking Properties

Crack length was measured using the DCPD technique. Established relationships provided in [ASTM E1737-98](#) were used to correlate the change in measured potential difference to a change in crack length. These relationships require the subjective selection of U_0 , the potential value measured at the onset of crack extension and corresponding to a reference crack length. Any increase in the measured potential prior to U_0 is assumed to result from experimental artifacts, such as crack tip plastic blunting, and is neglected in the analysis. Any increase in measured potential beyond U_0 is assumed to result from crack extension. Changes in the crack tip strain field occur when a stationary crack propagates, and the result is that a growing crack remains sharp without continued blunting ^[29,30].

DCPD provides a high-resolution measurement of crack length; however, several factors can diminish the accuracy of these measurements, including the extent of crack tip blunting. Ideally, the measured DCPD remains constant until the onset of crack extension. In reality there are a number mechanisms that may lead to increases in DCPD during rising displacement and stress intensity, prior to the onset of physical crack extension. First, voltage measurements used for DCPD analysis are typically small, with a necessary resolution of less than 0.2 μV . These small voltages are sensitive to change in temperature, either of the test specimen, wiring, or electronics, as well as bias voltages that may develop in response to electric or magnetic fields. Good measurement techniques should largely mitigate these sources of error. For example, temperature effects on alloy resistivity as well as thermally induced “thermocouple” voltages at probe contact points were minimized by the use of current reversal and a reference probe measurement ^[31]. However, remaining-small errors in DCPD can confound determination of the onset of H cracking.

A primary source of uncertainty associated with DCPD crack length measurements is the difficulty of separating potential increases resulting from specimen deformation, particularly crack tip plasticity plus blunting, from those due to crack extension. Both elastic and plastic strain may affect the DCPD measurements. Plastic strain at the crack tip develops prior to crack extension in tough materials, and results in increased alloy resistivity. Elastic strains may lead to geometric changes in the shape of the specimen, which in turn affects the resistance of the specimen. Strain around the loading pin holes, for example, have been shown to lead to slight nonlinearities in the DCPD vs CMOD plot. Each of these DCPD error sources rises with increasing applied K . Identification of the DCPD value associated with the onset of stable crack extension in a slow-rising K IHAC or HEAC experiment is often subjective. A second complication can arise if the crack surfaces are both at least partially electrically conducting, and in contact prior to the onset of loading. Subsequent loading causes crack opening, which reduces the level of current flow through the contacting—conducting crack faces, leading to a false rise in DCPD that is not due to crack extension. Effects of crack tip plasticity/blunting are particularly important for H-cracking-resistant alloys and crack growth rates that are slow relative to the accumulation of crack tip strain. Crack surface electrical contact effects on DCPD are often prominent in HEAC situations involving high-purity H_2 , which reduces surface-insulating oxide film ^[32].

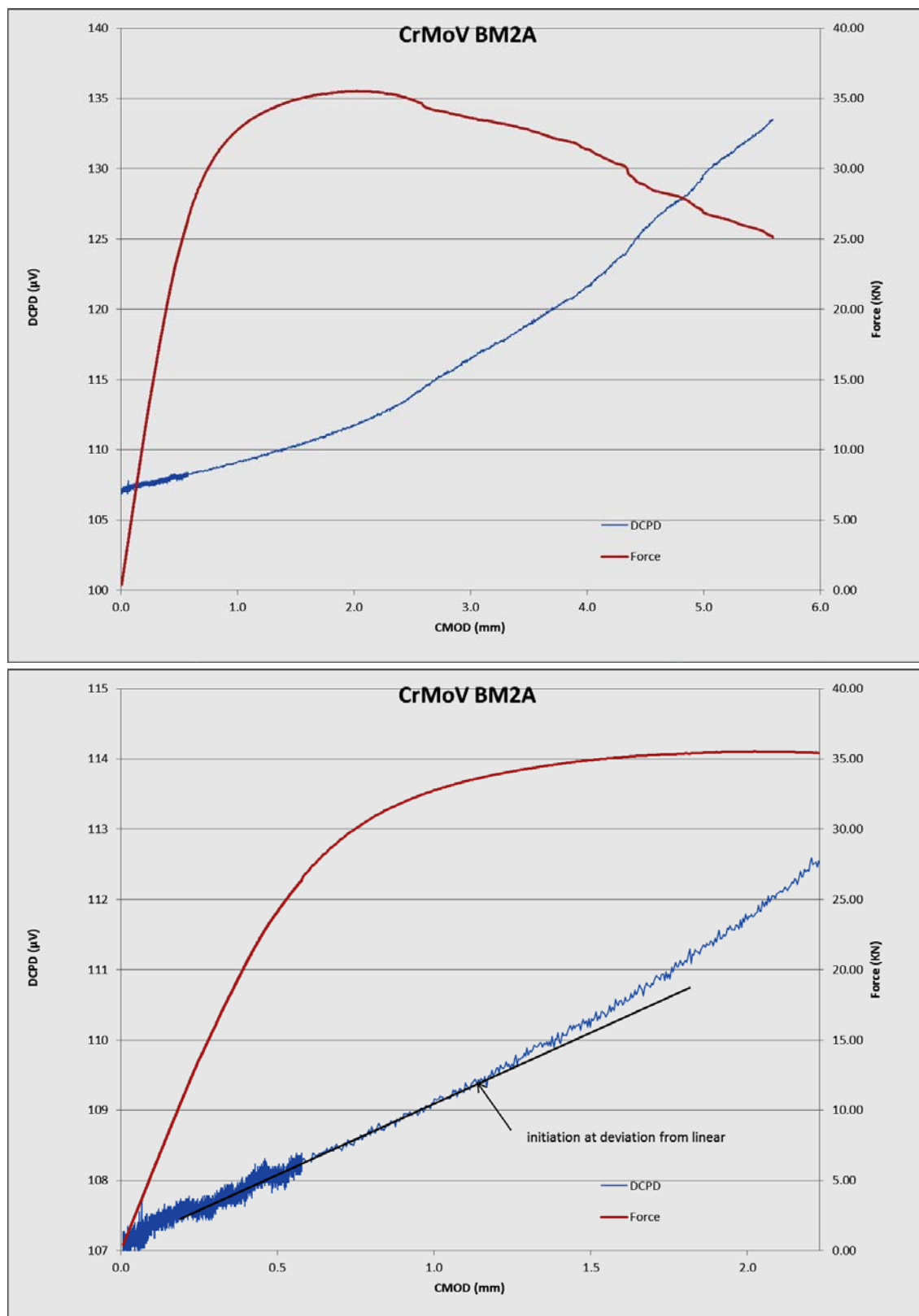


Figure 16—(top) Load and DCPD vs CMOD, and (bottom) definition of the onset of stable crack propagation based on amplified DCPD vs CMOD; each for $2\frac{1}{4}$ Cr-1Mo-0.3V base metal without precharged H and stressed under slow-rising K ($2 \text{ MPa}\sqrt{\text{m/h}}$) in moist air.

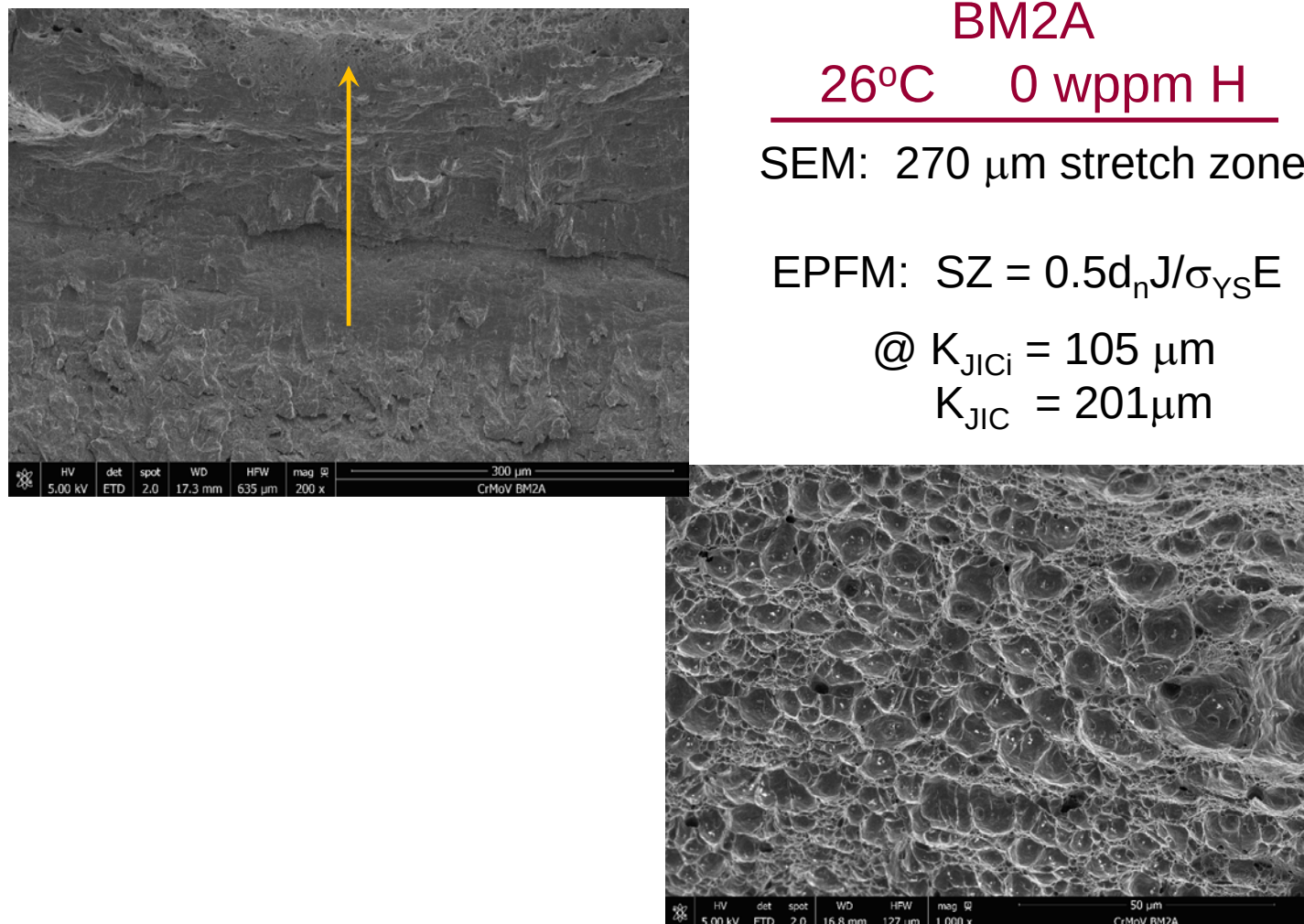


Figure 17—Scanning electron fractographs showing ductile fracture in 2¼Cr-1Mo-0.3V base metal at 23 °C. A stretch zone, measured to equal 270 μm , was present ahead of the fatigue precrack (arrow in the top-left image), and fracture was characterized by microvoid-based damage (bottom-right image). Elastic-plastic fracture mechanics based estimates of the stretch zone, based on the half-crack tip opening displacement, are given for K at the offset blunting line definition of toughness (K_{JIC}) and for K at the point of DCPD-indicated crack formation.

For the present API work with H-cracking-resistant Cr-Mo-V steel, an important objective is to accurately determine the value of K_J at the onset of stable crack extension due to H in either IHAC or HEAC situations. That is, the goal is to identify the lowest level of applied K that produces such organized cracking; this is a reasonable-conservative definition of K_{IH} . If this initiation point is not detected, then the reported value of K_{IH} will be too high and nonconservative in an engineering fitness-for-service or MPT analysis. On the other hand, if microstructurally distributed or isolated regions of H damage are detected by high-resolution DCPD, and a K_{IH} assigned to this situation, then the value may be overly conservative if such damage does not link-up to constitute an important degradation mechanism for a thick-wall reactor. This latter assignment of a lower bound K_{IH} may not be ideal, but is preferable to an overly high value of K_{IH} assigned due to poorly interpreted DCPD data. As such, significant effort was expended to ensure this selection was made accurately for the results presented here. Precise identification of the onset of stable crack extension is typically not critical for measurement of an offset blunting line definition of the onset of crack growth (e.g. J_{Ic} in Figure 15) since the R-curve is not significantly changed by variations in the identified initiation point.

Analysis of an IHAC experiment conducted at 25 °C demonstrated the importance of proper interpretation of the DCPD change during slow-rising K loading in H-cracking-resistant 2¼Cr-1Mo-0.3V base metal, and

justified K_{IH} definition based on analysis of DCPD vs CMOD during rising K [20]. Two approaches were assessed based on the first nonlinearity in measured DCPD vs either CMOD or J . The J -integral based approach was advocated as most accurate for characterizing IHAC in Cr-Mo and Cr-Mo-V steels by Shimazu and coworkers [17–19]. Compact tension specimens of 2¼Cr-1Mo-0.3V BM, without and with precharged H, were subjected to the slow-rising displacement experiment with DCPD monitoring. The resulting crack growth resistance curves are shown in Figure 18 for two specimens (BM2A and BM8A) corresponding to hydrogen-free and hydrogen-charged base plates, respectively. K_{IH} for H-precharged Cr-Mo-V, and K_{JICi} for noncharged material, measured using the first-resolved departure from linear DCPD vs CMOD curve, equal 136 MPa√m and 196 MPa√m for specimen BM8A and BM2A, respectively. In contrast, K_{IH} and K_{JICi} , measured using the first-resolved departure from linear DCPD vs J curve, equal 223 MPa√m and 251 MPa√m for specimen BM8A and BM2A, respectively. The supporting plots of DCPD vs CMOD and J for the specimen with precharged H (BM8A) are shown in Figure 19. Clearly, very small differences in the interpretation of the DCPD signal result in very large differences in K_{IH} .

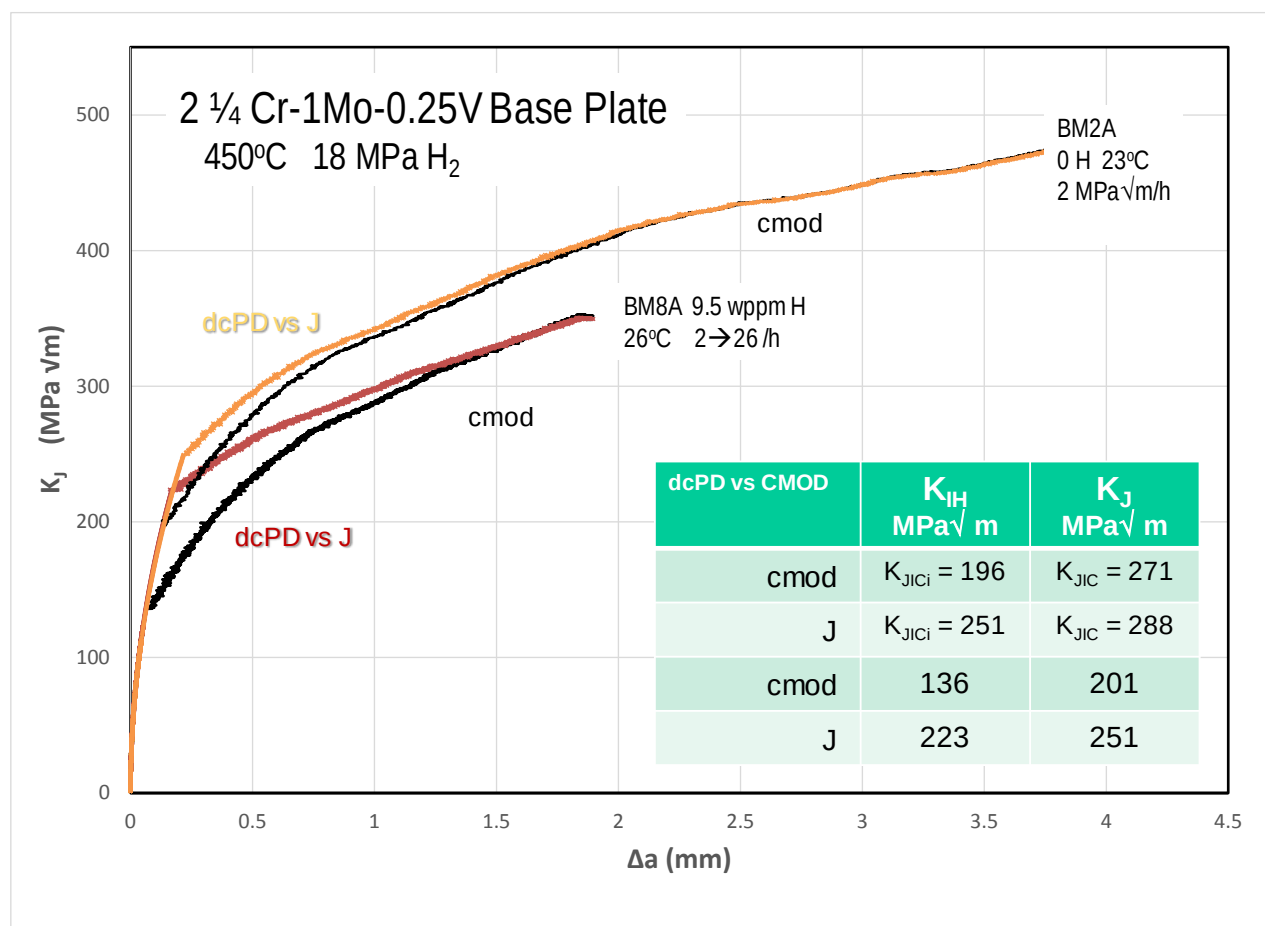


Figure 18—Crack extension vs applied K_J for C(T) specimens of 2¼Cr-1Mo-0.3V base metal, with and without precharged H (see Table 8 and ensuing discussion for experimental details). Data for each specimen were analyzed based on either: (a) DCPD vs CMOD or (b) DCPD vs the J -integral to define the onset of crack extension at the indicated value of K_{IH} (with H) and K_{JICi} without H.

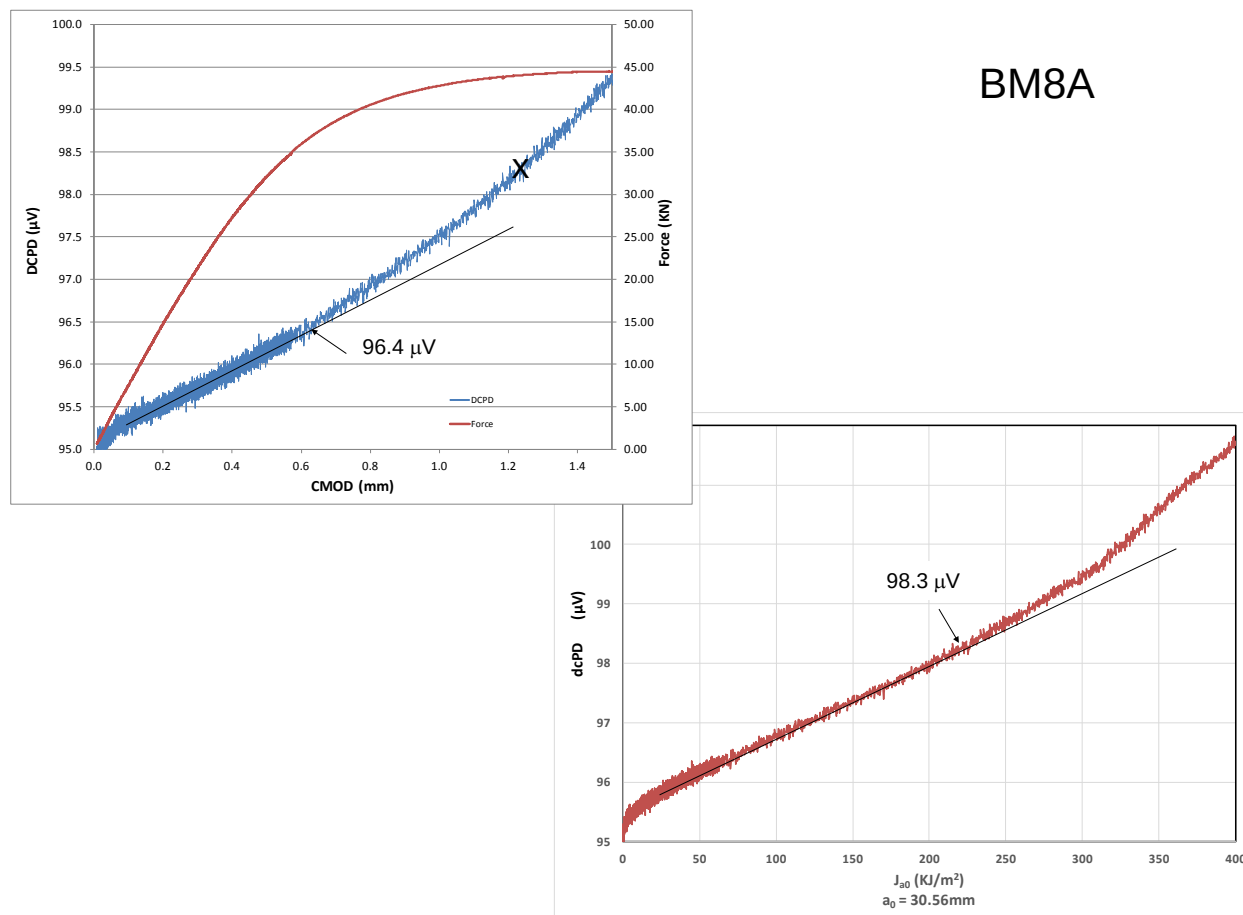


Figure 19—(top left) DCPD vs CMOD and (bottom right) DCPD vs the J-integral to define the onset of crack extension at the indicated value of K_{IH} for specimen BM8A of $2\frac{1}{4}\text{Cr-1Mo-0.3V}$ containing precharged H.

Following the comparison in Figures 18 and 19, DCPD vs CMOD analysis was used for all cracking experiments during the current API program. Specifically, K_{IH} was defined by identifying the nonlinearity in the rising DCPD vs CMOD signal that corresponds to the onset of organized H cracking. This point was equated to Δa_{IHAC} of 0 by adjusting U_0 in Johnson's equation to convert DCPD to crack length and then fitting this K_{IH} value to the assumed calculated blunting line. Subsequent K_I vs Δa points were calculated from DCPD values. The claim that DCPD vs J-integral analysis yields a relevant threshold for the onset of IHAC^[17–19] was not supported by the current experiments^[20]. K_{IH} values from DCPD vs J are not conservative, and this approach was not used.

Experimental results described in the following sections justify the conclusion that K_{IH} from analysis of DCPD vs CMOD yields the correctly conservative and rigorous indication of the onset of organized IHAC extension in $2\frac{1}{4}\text{Cr-1Mo-0.3V}$. These analyses centered on scanning electron microscopy (SEM) of the microscopic features of the crack surface immediately adjacent to the fatigue precrack, compared to the characteristics of H cracking presented in a latter section, as well as to the cleavage crack produced by post-test fracture in liquid nitrogen. Determination of the extent of actual crack extension is complicated by the presence of a stretch zone that occurs during crack tip blunting prior to H or cleavage crack extension. This stretch zone is particularly dominant for alloys that resist H cracking until relatively high levels in the range of 75 MPa $\sqrt{\text{m}}$ to 150 MPa $\sqrt{\text{m}}$ for steels. Figure 20 shows the region just beyond the precrack for $2\frac{1}{4}\text{Cr-1Mo-0.3V}$ specimen BM2A (noncharged base metal), BM8A (H_2 precharged base metal), and WMA4 (H_2 precharged weld metal). In the absence of predissolved hydrogen, the stretch zone is smooth and appears to result due to deformation at high K. If present, hydrogen promotes a zone that contains crack-like damage concomitant with blunting deformation, as demonstrated by the images in Figure 20 for specimens BM8A and WMA4. SEM