B.13 "Degradation of Fracture Resistance: Low Temperature Crack Propagation (LTCP) in Nickel-Base Alloys,"

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This topical paper provides a summary of the information currently available on a form of fracture resistance degradation called Low Temperature Crack Propagation (LTCP). LTCP is a form of hydrogen embrittlement which has not yet been identified in commercial nuclear reactors but which causes severe degradation of the fracture resistance of certain nickel-base alloys in laboratory tests performed under specific test conditions. In this paper, the term "LTCP fracture toughness" will be used instead of "fracture toughness (J_{IC})", and "LTCP tearing modulus" instead of "tearing modulus (T)", to describe this phenomenon when using J-R type of tests. The tearing modulus is a measure of the tearing resistance after J_{IC} is exceeded.

The laboratory test results indicate that the LTCP fracture toughness of alloys 600 and 690 in low-temperature water is lower than the fracture toughness (test in air), but that the difference is relatively small[1]. Therefore LTCP is not considered to be an important degradation mechanism for alloys 600 and 690. However, alloys X-750, 182/82, and 152/52 (in order of decreasing susceptibility) all suffer substantial degradation of LTCP fracture toughness in laboratory tests in hydrogenated water when the following conditions are met:

- The test temperature is less than 150°C;
- The dissolved hydrogen concentration in the environment is between 150 and 0 cm^3 H_2/Kg H_20;
- Properly-oriented sharp cracks (e.g., fatigue cracks) are present that are open to the hydrogenated environment;
- The sustained stress intensity factor is higher than the equivalent critical stress intensity factor for LTCP determined from fracture testing, and;
- The stress intensity ramp rate (loading rate) is slow.

Mills et al.[1,2,3,4,5,6,7,8], Lenartova[9], and Symons[10] have performed studies on Ni-base alloys in low-temperature environments. A recent (2004) report by Brown and Mills[5] provides a thorough summary of some of these studies for alloys 82H, 52, and 690. A comparison of load-displacement curves for as-welded alloy 82H specimens is shown in Figure B.13.1[5]. For non-precharged specimens (Figure B.13.1(a)), the material response changes from ductile in 338°C hydrogenated water (similar to air) to brittle (intergranular) in 54°C hydrogenated water. The degree of embrittlement and the intergranular nature of cracking observed in 54°C water can be reproduced in specimens pre-charged in high-pressure hydrogen and then tested in air (Figure B.13.1(b)). This implies that the degradation is due to hydrogen-induced intergranular cracking. The presence of hydrogen at the crack tip, regardless of its source, reduces fracture resistance mostly by reducing grain boundary cohesion and promoting planar slip[7]. The combination of hydrogen-precharging and testing in hydrogenated water (54°C water with 150 cm^3 H_2/Kg H_20) results in additional degradation of LTCP fracture toughness (Figure B.13.1(b)). Presumably, hydrogen from the water further increases the hydrogen concentration ahead of the crack and reduces the loss of pre-charged hydrogen from the crack tip region[7]. The type of intergranular cracking associated with LTCP in the case of 82H welds is believed to be caused by hydrogen trapping by fine niobium and titanium-rich carbonitrides at grain boundaries[6].

In 54°C water with 150 cm^3 H_2/Kg H_20 at an average pH of 10.2, the LTCP fracture toughness was an order of magnitude lower than the elastic-plastic fracture toughness, J_{IC}, (test in air) for alloys 82H, and 52, and 5 times lower for alloy 690[8]. The LTCP tearing modulus (test in environment) was two orders of magnitude lower than the tearing modulus (test in air) for alloys 82H, and 52[8]. However, the tensile properties of the alloys were unaffected by the environment, except for the total elongation of the weld materials[8]. For all alloys considered, LTCP fracture toughness and LTCP tearing modulus generally increase with increasing water temperature and decreasing hydrogen concentration – these effects are illustrated for alloy 52 in Figure B.13.2. The LTCP fracture toughness is also recovered at high rates of stress intensity factor increase (loading rates), presumably because there is insufficient time to embrittle grain boundaries ahead of the crack.

LTCP does not initiate at as-machined notches, but has been shown to initiate at sharp natural weld defects[5]. Testing showed that weld root defects and fatigue pre-cracks exhibit similar LTCP responses[5]. Mills et al. were not able to conclude (from the results of cooldown testing of alloy 82H under constant displacement[5]) whether or not residual stress contributes to LTCP. Given these results, residual stress cannot be eliminated as a contributor to LTCP, to date.

An EPRI study confirmed the Mills et al. test results for alloy 82H[11]. In rising-load tests at a temperature of 54°C in pH 10 water with 150 cm^3 H_2/Kg H_20, the LTCP fracture toughness of alloy 82H was an order of magnitude lower than the fracture toughness. Alloy 182 was also investigated in this study and its LTCP fracture toughness was also an order of magnitude lower than the fracture toughness under similar test conditions. Reducing the concentration of hydrogen to 100 cm^3 H_2/Kg H_20, and testing at pH 7 in simulated primary water, did not alter the magnitude of the difference between the LTCP fracture toughness and the fracture toughness in alloy 182. A current EPRI study is investigating the effects of chemical conditions closer to those typical during shutdown as well as the effects on LTCP in alloy 182 of using stress corrosion cracking (SCC) to produce the starter cracks instead of fatigue. The current test conditions are 30 or 10 cm^3 H_2/Kg H_20 water at 54°C, pH of 4.5, and an extension rate of 10^{-6} in. s^{-1}. The preliminary results for the tests with fatigue pre-cracks indicate that alloy 182 still exhibits a factor of 5 difference in 30 cm^3 H_2/Kg H_20 water between the LTCP fracture toughness and the fracture toughness and a factor of 4 difference in 10 cm^3 H_2/Kg H_20 water. Reducing the pH from 7 to 4.5 slightly increases the LTCP susceptibility (slight reduction in LTCP fracture toughness from pH 7 to 4.5). The data also indicate that LTCP fracture toughness is lower for a high temperature SCC starter crack than for a transgranular fatigue crack. Finally, the data indicate that as the dissolved hydrogen in the environment is decreased, part of the LTCP fracture toughness is recovered; but the LTCP fracture toughness in environment with no dissolved hydrogen is still lower than the fracture toughness.

Alloy X-750 is a precipitation-hardened high-strength nickel-base alloy used for bolts and springs in PWR service. Several studies related to LTCP have been performed on this alloy by Mills et al.[2] and by Symons[10]. X-750 is highly susceptible to LTCP below 150°C in pre-cracked specimens, especially in earlier heat treatments (AH and BH), with growth rates as high as 7 mm/min[2]. It appears that phosphorous and sulfur at grain boundaries act as hydrogen traps and increase the LTCP susceptibility[2]. The grain boundary carbides were shown to control the embrittlement of this alloy[10]. Some testing performed by Mills et al. in argon-sparged water[2], which corresponds to a non-hydrogenated water environment, shows that K_{Pmax} (stress intensity at maximum load) obtained during a rising load test is lower in non-hydrogenated water than in air for X-750[2]. These observations suggest that the corrosion-generated hydrogen at the crack tip is sufficient to cause embrittlement for alloy X-750 in non-hydrogenated water.

The critical source of hydrogen for LTCP appears to be the environmental hydrogen, as the hydrogen has to diffuse only for a very short distance to get to the highly strained region ahead of the crack tip (Figure B.13.3) and therefore the hydrogen concentrations required to embrittle the crack tip in a water environment are very low (probably on the order of a few ppm)[5,10]. By contrast, in precharged specimens tested in air, hydrogen levels at the crack tip approach zero. The critical cracking location moves inboard toward the peak hydrostatic stress location where strains are much lower (Figure B.13.3); hence, higher local hydrogen concentrations are needed to embrittle grain boundaries. The hydrogen previously diffused in the metal from operation can be an additional hydrogen source for LTCP; but it is not identified as sufficient on its own, as the hydrogen concentrations in the bulk of the metal resulting from operation are low compared to the concentration required to embrittle hydrogen-precharged specimens.

EPRI has begun an assessment of whether or not the conditions necessary for the occurrence of LTCP exist in PWRs[12]. The necessary conditions for LTCP are material susceptibility, low temperature, hydrogen concentration, sharp cracks, sustained stress/strain level, and low strain rate. The hydrogen and temperature conditions that cause LTCP can be present in some PWRs depending on plant and shutdown practices[13,14], but do not appear to be present in PWR startups[15]. The sharp cracks that cause LTCP to initiate can potentially be present in the form of SCC cracks[16,17] or lack-of-fusion defects in alloys 82/182[18] and particularly in alloys 52/152, which exhibit weldability problems[19]. Some stress analyses for components like reactors vessel nozzles have been performed for critical PWR shutdown conditions. Preliminary results suggest that actual stress intensity factors in PWR components are lower than the equivalent critical stress intensity factor for LTCP for detectable crack sizes, but high enough to raise some concern. The current stress analysis for an RPV outlet nozzle butt weld with an ID weld repair showed that stress intensity factors were lower than the equivalent critical stress intensity factor determined from fracture testing for a circumferential flow. For an axial flaw equal to or under 0.5 inch deep, the current stress analysis also showed that stress intensity factors were lower than the equivalent critical stress intensity factor. Additional analyses are necessary, including some repaired components cases and using stress redistribution with crack growth for the stress intensity factors calculation. Finally, the strain rates during shutdown appear to be low enough that there is sufficient time for hydrogen to embrittle the region ahead of the crack.

Additional work is required to determine unequivocally whether or not LTCP of nickel-alloy components can occur under PWR primary system service conditions. Nevertheless, several interim conclusions can be reached at this point:

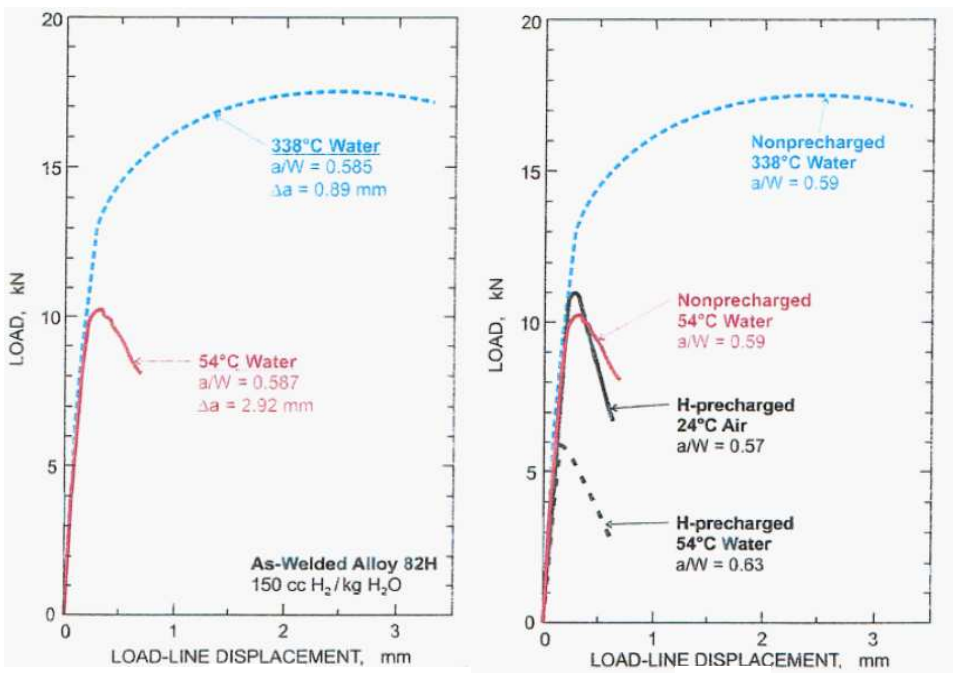
- First, because LTCP is only significant at temperatures below 150°C, it is not an issue either during normal power operation or during those stages of plant cool-down and start-up when the temperature of the primary coolant is above 150°C.

- Second, LTCP is unlikely to occur during either the stages of plant shut-down when the system is depressurized and hydrogen peroxide has been added or those stages of plant start-up when the temperature is below 150°C, because the primary coolant is not hydrogenated during these periods and the calculated hydrogen concentrations resulting from previously diffused hydrogen in the material are low compared to the concentration required to embrittle hydrogen-precharged specimens.

- Third, although most of the conditions required for LTCP are (or, potentially, could be) satisfied during the stages of cool-down when the coolant is hydrogenated and the temperature is below 150°C, additional stress analyses are required to determine whether or not the mechanical requirements (K levels) for LTCP identified in the

laboratory tests are likely to be met in any nickel-alloy components, as well as additional testing to investigate the effects of loading, as most of the tests performed on LTCP to date are rising load tests.

Finally, additional laboratory tests and plant impact assessments should be considered to determine whether stopping hydrogenation of the primary coolant at an earlier stage of plant cool-down would be an effective and acceptable countermeasure to LTCP.



(a) (b)

Figure B.13.1 Load-displacement curves for as-welded 82H[5]

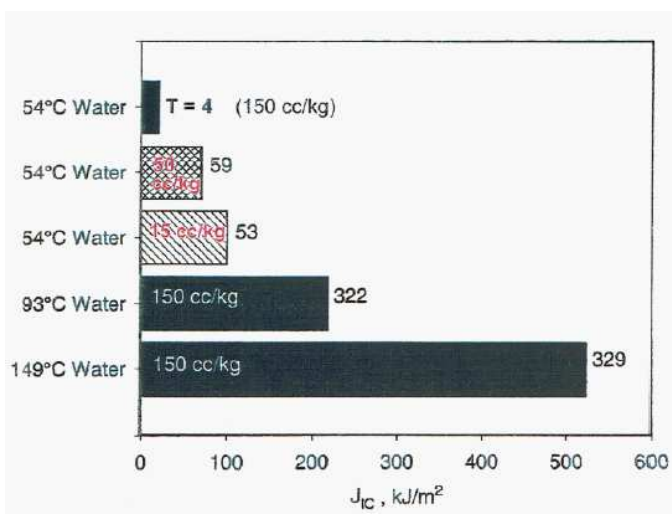


Figure B.13.2 LTCP fracture resistance (in water) of alloy 52 welds (values of LTCP tearing resistance are provided beyond each bar)[1,5]

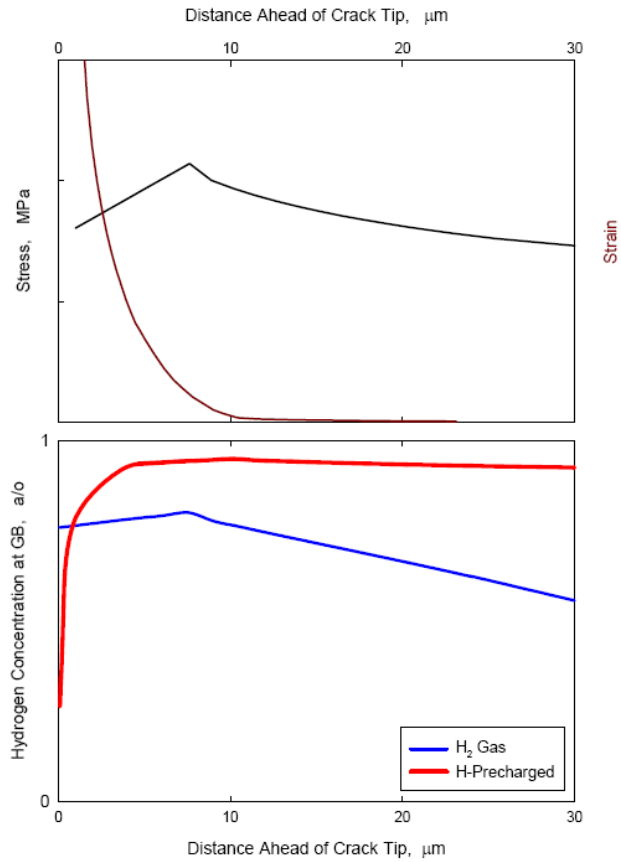


Figure B.13.3 Stress, strain and hydrogen concentration at grain boundaries for either specimens in environmental hydrogen (H_2 gas) or hydrogen precharged specimens (H-precharged), as a function of distance ahead of the crack tip[5]

References for B.13

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