Metallurgy for Industries

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High temperature hydrogen attack (HTHA)

Susceptibility and detection technique

High temperature hydrogen attack is often misinterpreted with hydrogen stress cracking, hydrogen embrittlement, hydrogen induced cracking, hydrogen blistering, Stress oriented hydrogen induced cracking etc. HTHA as the name suggests is the damage to steels exposed to hydrogen at high temperature, while others are the cases where steel is damaged at low temperatures from hydrogen entering the steel from aqueous corrosion mechanisms or from of metal working operations such as welding or electroplating.

High temperature hydrogen attack (HTHA) is observed in steels exposed to high temperature above 200 deg. C. At high temperature atomic hydrogen diffuses in steel. This hydrogen reacts with Carbon of steel and forms methane [CH4]. This collects and forms voids at grain boundaries

$$MC + 4H = M + CH_4$$

These bubbles exert pressure and also coalesce resulting into fissures. The growth of voids and fissures weakens the metal and the latter develop into cracks. Besides formation of micro cracks and fissures, the subject reaction not only decarburizes the steel, but also reduces its toughness. It may not be accompanied by loss of metal thickness.

The degree of hydrogen attack depends upon temperature, hydrogen partial pressure, stress level, exposure time, steel composition and structure.

In ferritic steel, the tendency of HTHA increases with rise in operating temperature, hydrogen partial pressure, exposure time and stress levels. Annealed or normalized and tempered steels

Microstructure of the Month

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Magnification: *1000x*

MOC: *T91*

Component: *Super-heater Tube*

Observation: *The photograph shows SEM image after metallographic specimen preparation. The arrows point locations of creep voids in microstructure of tempered martensite. The general condition of tube indicates onset of creep damage and is classified nearly to TW507-VGB-Class 3a or empirically between stage III and IV as per classical creep damage charts.*

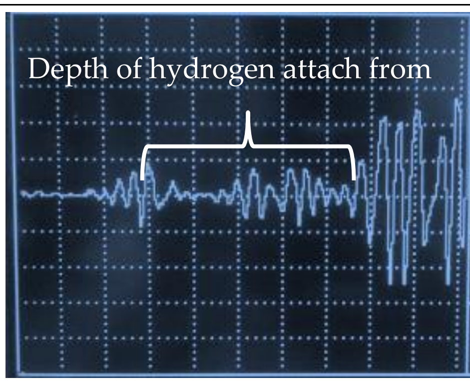
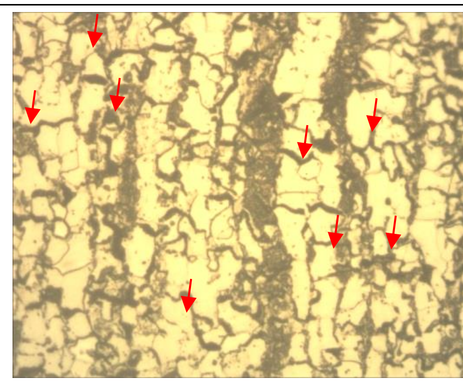
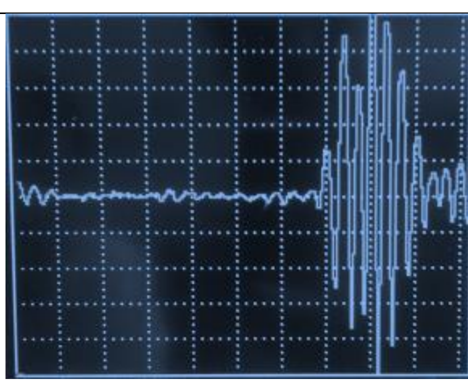
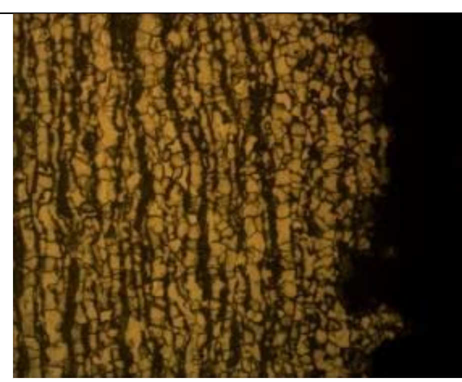
Useful hints: *SEM is a useful tool in identifying material degradation; especially at initial stage of creep damage. It is necessary to perform thickness & OD measurement along with in-situ metallography & hardness measurement of tubes* having low primary stress levels have been satisfactorily used for HTHA applications. Secondary stresses like thermal stresses or those induced by grinding can play a major role in HTHA in some cases. Post weld heat treatment (PWHT) of chromium-molybdenum steels in hydrogen service improves resistance to high temperature hydrogen attack. The PWHT stabilizes alloy carbides. This reduces the amount of carbon available to combine with hydrogen, thus improving high temperature hydrogen attack resistance. The solubility of hydrogen in austenitic stainless steel is of greater magnitude than for ferritic steels. The diffusion coefficient of hydrogen through austenitic stainless steel is roughly two orders of magnitude lower than for ferritic steels.

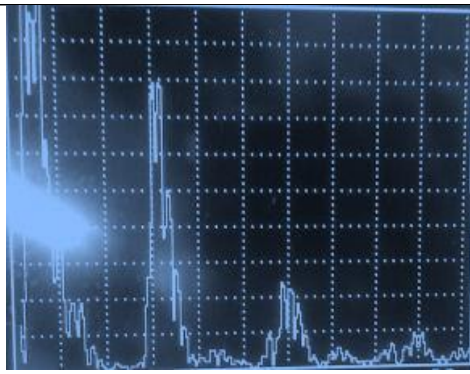
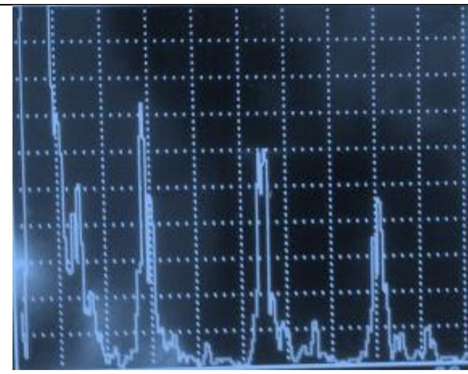
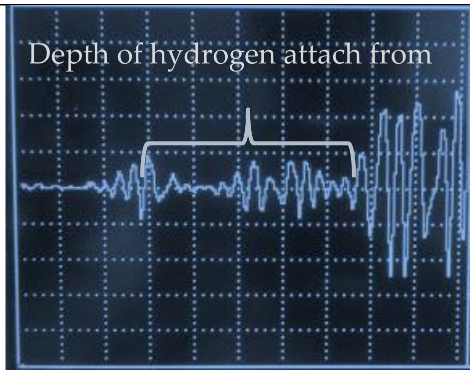
Nelson curves as per API 941 depict safe operational limits for Carbon and 1.25Cr0.50Mo steels. These diagrams have been updated number of times by API. However, Nelson curves cannot be used for newly developed materials.

Detection of HTHA becomes vital for inspection of plant equipment/pipings that are susceptible. TCR Advanced has designed a procedure based on API 941 for detection and estimation of HTHA by ABUT – Advanced Back scattered ultrasonic testing.

Due to formation of fissures inner side, attenuation due to scattering of ultrasound is observed. This results in appreciable change in velocity – especially shear wave velocity. Depth of attack can be determined by analyzing back scattered patterns. By carrying out attenuation measurements, ratio of shear wave to longitudinal wave velocity and recoding back scattered pattern, we can not only determine the possibility of HTHA but also calculate its depth.

A case study shown below gives a very good insight into detection and estimation of depth for HTHA.

	
Ultrasonic back scattering technique :- shows effect of hydrogen attack	Microstructure of tube showing high temperature hydrogen attack (HTHA tube) – fissures shown by arrow
	
Ultrasonic back scattering technique :- shows general	Microstructure of tube showing general corrosion on ID

corrosion on ID surface without hydrogen attack	surface (good tube – free from high temperature hydrogen attack)
	
Attenuation measurement: - Scan of HTHA tube. 2nd Back wall echo is at 20%FSH and 3rd Back wall echo at 10%FSH indicating appreciable attenuation of ultrasound energy	Attenuation measurement: - Scan of good tube. 2nd Back wall echo is at 60%FSH and 3rd Back wall echo at 40%FSH, indicating no significant attenuation in the ultrasound energy
	
Ultrasonic back scattering technique: Effect of hydrogen attack is seen up to depth of 4.5mm	Macro etched tube shows high temperature hydrogen attack (HTHA tube) – depth of attack @ 4mm

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