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A microstructure-based mechanism of cracking in high temperature hydrogen attack

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ABSTRACT

High Temperature Hydrogen Attack (HTHA) of steels plagues higher temperature industrial applications, especially in the petrochemical industry, due to the lack of a mechanistic understanding of the phenomenon and the use of empirically established design criteria, such as the Nelson curves. By using advanced microscopy techniques to explore the microstructure immediately ahead of crack tips and along cavitated grain boundaries, we gained a better understanding of the physical processes occurring early during the HTHA damage process, which can guide the development of models for the degradation process accounting for methane formation and creep cavitation. The results confirm the fundamentals of previously proposed models, but also provide finer details than have been previously known. Based on the underlying deformation and grain boundary fracture, we propose a model for material failure underlying HTHA.

1. Introduction

High temperature hydrogen attack (HTHA) is a problem which plagues petroleum refinery and petrochemical plant equipment fabricated from carbon and low alloy steels, resulting in early replacement of components and, occasionally, failures. On rare occasions, HTHA results in catastrophic failures of equipment and loss of life, of which the explosion at Tesoro Anacortes Refinery in 2010 is a recent tragic example [1]. At the Tesoro Refinery, a carbon steel heat exchanger shell failed, although the operating conditions are thought to have been below the previously established safe limits. Subsequently, the American Petroleum Institute (API) has issued an updated 8th edition of API Recommended Practice 941 [2]. This publication [2] presents a series of curves used extensively in the refining and petrochemical industries known as “Nelson curves”, which establish the safe operating limits of steels in high temperature, high pressure hydrogen. The 8th edition of API RP 941 added a new curve for non-post weld heat treated (non-PWHT) carbon steel that lowers safe operating conditions relative to the previous Nelson curve for carbon steel. This new curve was established based on empirical evidence, using reports of plant failures in recent years.

Use of C-½Mo steels raised similar concerns in industry, with the Nelson curve delimiting the safe conditions being constantly lowered in the hydrogen vs temperature diagram and warnings added due to reported failures occurring below the previously existing safe conditions between the early 1970s and early 1990s. The Nelson curve for C-½Mo steel was removed from API RP 941 in the early 1990s, with the recommendation that the carbon steel curve be referenced. The history of the Nelson curves is summarized in API Technical Report 941 - the technical basis document for API RP 941.

While the Nelson curves have generally been used successfully for many years, the issues with carbon steel and C-½Mo steel curves highlight the need for a better understanding of the phenomenon. Considerable work was done in the 1980s and early 1990s [3–10] to understand the kinetics and mechanism of HTHA. While much of that work was done on higher alloy steels such as 2¼Cr-1Mo, a workhorse alloy for heavy wall pressure equipment in the industry, some was done on carbon steel. However, since then, very little significant work on the mechanisms or modelling of HTHA has been reported in the literature. And, importantly, the fundamental studies have not been successful at supplanting the empirical models, such as the Nelson curve.

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HTHA is understood to be the interaction between hydrogen which dissolves into the steel and the carbon in the steel present as either interstitial carbon or, more likely, in carbides [7,11]. The hydrogen and the carbon react to form methane. The methane, as a large molecule, cannot diffuse out of the bulk of the metal and collects at microstructural features, such as grain boundaries, inclusions, and free surfaces, and precipitates there in the form of methane-filled bubbles [3,7,12–14]. These bubbles grow and coalesce until fissures form, leading to failure, usually intergranular in character [4,7,11,15–19].

These stages were first described decades ago, and while experimental support exists for these stages, an understanding of the processes occurring in the material does not exist. As most in-depth studies of HTHA are not recent, excepting the work of Lundin et al. [20] which is focused on mechanical performance instead of mechanistic understanding, they were unable to take advantage of new instrumentation that is now available which could provide insight into the material processes that occur. This new study applies some of these new techniques in order to gain a fundamental understanding of the mechanism of damage development of the early stages of HTHA cracking.

2. Materials and experimental procedures

The samples examined in this study were coupons cut from different locations on a C-½Mo steel depentanizer reboiler. The reboiler was in service for 53 years with a fluid containing a partial pressure of 1.5 MPa H_2 that entered at a temperature of 400 °C and left 15° cooler (385 °C). One coupon was taken from the hotter end, and two were taken from the cooler side. The focus of this study is understanding the mechanism of early stages of bubble formation and cracking due to HTHA and these locations were chosen as representative of the profuse incipient damage due to HTHA; other areas of the reboiler showed advanced damage, such as step-wise cracking, blistering, and large weld root cracks [21]. The composition of the steel is given in Table 1. The microstructure is a rolled ferritic/pearlitic steel, with the grain size varying with location, Fig. 1. Whether this variation in grain size is due to inhomogeneities during rolling and forming or due to the long lifetime at different elevated temperatures is unknown. The pearlite structure is a little unusual, tending to occur in packets of cementite plates separated by regions of clean ferrite, all within the same grain. This is likely due to the extended lifetime at elevated temperature, though it is unclear if dissolution and reaction with the hydrogen was also an important factor in the development of this microstructure.

Samples were polished and etched with a 2% nitric acid in methanol solution to reveal the interior cracks and HTHA damage and the surrounding microstructure. A JEOL 6060LV scanning electron microscope (SEM) fitted with an Oxford instruments EDX detector was used for microstructural characterization. Focused-ion beam (FIB) machining was used to extract samples from specific locations for transmission electron microscopy (TEM) analysis. A Helios 600i FIB was used both for imaging and for sample fabrication. Samples were examined in a JEOL 2010 LaB6 TEM.

3. Results

The HTHA damage manifested itself primarily in cracking. Cracks appeared throughout the cross section of the wall, Fig. 2. Cracks tended to be parallel to the rolling direction, not through-thickness of the vessel wall, Fig. 2a. Cracks were primarily intergranular in nature, which, due to the rolled microstructure, allowed the cracks to be straight in nature, Fig. 2b. Crack branching appeared to be nearly non-existent. In a few cases, short segments of the cracks were transgranular in nature, connecting two larger intergranular segments, though, as suggested by the discontinuous crack in Fig. 2c, this process may happen later in the process when the crack is sufficiently large. Cracks appeared to be associated with inclusions. Flat inclusions consisting of Mn or Al rich sulfides or oxides were frequently found within the cracks. While occasionally round inclusions were found located in the interior of the grain, a more common morphology appeared to be flat, aligned with the rolling direction, and grain boundary inhabiting.

By sectioning the cracks, it is evident that they are intergranular in nature, Fig. 3a. There is a clear separation between the ferrite grain and the pearlite grain in Fig. 3a, and the crack appears to be along the grain boundary, with no portion of either grain attached to an opposing side. The pearlite grain shows clear cementite

Table 1
Composition of C-½Mo steel.

	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Al	N	Fe
mass %	0.184	0.22	0.68	0.019	0.0180	0.14	0.07	0.20	0.49	0.001	0.0042	remainder

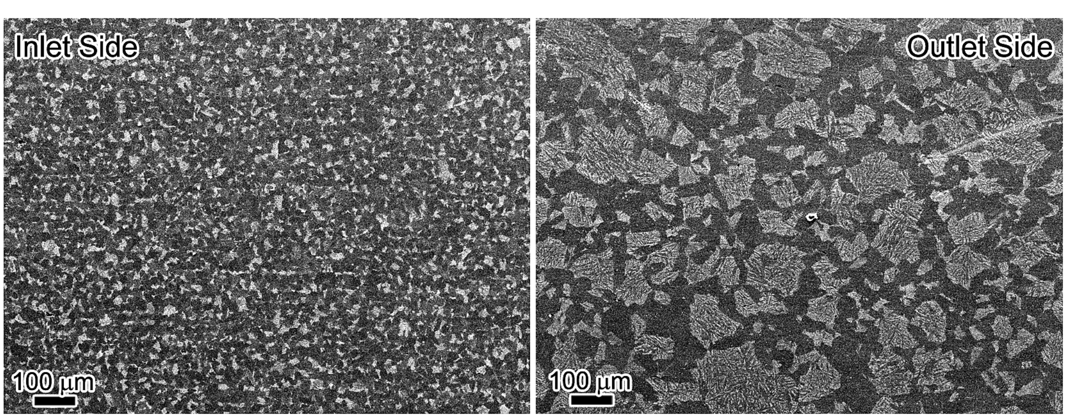

Fig. 1. C-½Mo steel microstructure at different locations on the reboiler after 53 years in service at 400 °C (inlet side) or 385 °C (outlet side) with partial pressure of H_2 of 1.5 MPa. SEM micrographs.