Influence of surface martensite layer on hydrogen embrittlement of Fe-Mn-C-Mo steels in wet H$_2$S environment

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ARTICLE INFO

ABSTRACT

This study investigated the effect of thermally induced surface martensite layer on hydrogen embrittlement of Fe-16Mn-0.4C-2Mo (wt.%) (16Mn) and Fe-25Mn-0.4C-2Mo (wt.%) (25Mn) steels through slow strain rate stress corrosion cracking testing and proof ring testing in wet H$_2$S environment. The 16Mn steel had a surface layer of less than 150 μm in depth containing ε-martensite, α′-martensite and austenitic twins. The martensite layer is found to reduce the hydrogen embrittlement resistance of the steel. In comparison, the 25Mn steel developed a full α′-martensite surface layer, which exhibited practically nil effect on the hydrogen embrittlement resistance of the steel. The ε-martensite provides much larger interface areas with the mechanical twins of the austenite in the 16Mn steel than the α′-martensite/austenite interfaces in the 25Mn steel. These interfaces are hydrogen trapping sites and are prone to initiate surface cracks, as observed in the scanning electron microscope. The formation of the cracks is attributed to hydrogen concentration at the ε-martensite and austenitic twin interfaces, which accelerates material fracture.

Introduction

A common hazard encountered in oil and gas exploration is the presence of H$_2$S in the product stream [1]. The presence of H$_2$S in oilfields imposes serious challenges to oilfield equipment and pipeline steels in causing mechanical failure and corrosion related problems. Hydrogen embrittlement is a major cause of steel failure in H$_2$S containing oilfields. Each year, tens of millions of dollars are needed to replace and repair pipes and vessels due to hydrogen embrittlement [2,3]. Degradation of mechanical properties as a result of hydrogen impregnation is of particular concern for high strength alloys [4]. Owing to this, much effort has been made to develop hydrogen embrittlement resistant high grade steels (e.g., API 5CT-P110, with yield strength of 758 MPa) for oil well casing pipes for application in H$_2$S containing environments. The demands for high strength for load bearing and durability and at the same time for high ductility for better resistance to

hydrogen embrittlement impose a dilemma for alloy selection in oilfield equipment and pipelines designs.

One promising candidate material is austenitic high-Mn twinning-induced plasticity (TWIP) steels [5–7]. These steels have excellent combination of both strength and ductility, with high hardenability for self-strengthening in service and high formability for fabrication [8,9]. These steels derive their ductility from mechanically induced austenitic twins. For example, a deformation-strengthened Fe-30Mn (wt.%) TWIP steel may typically have a yield strength of 920 MPa and an elongation of 25% [10]. In addition, the fcc structure of the austenite phase of these steels also has a high solubility and low diffusivity of hydrogen, rendering it high resistance to hydrogen embrittlement [11–13]. Because of these, austenitic TWIP steels are considered good candidates for oilfield equipment and pipelines [5], particularly for applications in H_2S containing oil and gas environments [6,7].

It is known that hydrogen embrittlement resistance of steels is sensitively related to its microstructure [14–19]. For TWIP steels, it has been reported that hydrogen-assisted cracking usually initiates at grain boundaries and deformation twins [20,21]. Using electron channeling contrast imaging technique, Koyama et al. demonstrated that deformation twins assist intergranular cracking and crack propagation [20]. Chun et al. studied the effect of Al addition in TWIP steels on their hydrogen embrittlement resistance [22], and found that the reduced dislocation density in TWIP steels due to the addition of Al enhanced their resistance to hydrogen embrittlement by eliminating hydrogen diffusion channels [23]. It has also been shown that Ti precipitates lower hydrogen embrittlement resistance by causing a ductile to brittle transition of the host matrix at near the hydrogen-trapping TiN particles [24]. Park et al. studied the effect of grain size on hydrogen embrittlement of Fe-18Mn-0.6C TWIP steel, and found that decreasing grain size from 79.8 μm to 6.4 μm enhances the resistance to hydrogen embrittlement of the TWIP steel [25]. The improved resistance to hydrogen embrittlement with reduced grain size is attributed to the reduction of deformation twin density, which can reduce intergranular cracking and crack propagation and the lowered hydrogen content per unit grain boundary as a result of strong grain size refinement [26].

Martensite is another common microstructural constituent in TWIP steels. In these steels there are two types of martensite, i.e. the hexagonal ε-martensite and the tetragonal α′-martensite [8]. Their influences on hydrogen embrittlement of TWIP steels are much less understood [27]. It is generally believed that ε-martensite promotes hydrogen embrittlement of austenitic steels [28,29], largely based on the observation that the fracture plane {111}$_\gamma$ in hydrogen-charged austenitic steels coincides with the ε habit plane, which indicates that the ε-martensite can be in some way activated in the crack opening. However, contradictive views have also been reported in the literature. Teus and Shivanyuk showed that ε-martensite reduces hydrogen embrittlement of austenitic steels by preventing localization of plastic deformation [30,31]. Perng and Altstetter observed that the threshold stress intensity increased and crack growth rate decreased in deformed 301 steel containing more α′-martensite [32], and attributed this to the effect of the martensite in distributing

hydrogen more uniformly within the matrix instead of concentrating at crack tips [32]. Chun et al., however, reported the increase of hydrogen-caused degradation on strength and elongation in steels containing more ε-martensite. They attributed this to the initiation and propagation of cracks in the regions of ε-martensite, which is harder than the austenite matrix [27]. Therefore, it is clear that the understanding of the effect of martensite on hydrogen embrittlement for austenitic steels is confused and uncertain. It is important to clarify the influences of ε-martensite and α′-martensite on hydrogen embrittlement of TWIP steels.

Martensite in steels can be formed by fast cooling from high temperatures [27] or induced by deformation. In addition, the ε-martensite has also been reported to form upon hydrogen charging [30,31,33]. This has been rationalized in that hydrogen decreases the electron energy of the hcp crystal lattice relative to the fcc lattice, thus decreasing the thermodynamic stability of the fcc austenite of the steels [30]. The hydrogen-induced $\gamma \rightarrow \varepsilon$ transformation has also been reported to be reversible [34]. As hydrogen is removed from the matrix, e.g., by forming hydrides [35], the ε martensite formed is found to revert back to austenite [34]. The hydrides formed can be brittle and deteriorate the hydrogen embrittlement resistance of the steels [35,36]. Mn content in steels is also known to have direct influence on the formation of martensite. Mn is an effective austenite stabilizer. It increases stacking fault energy and resists deformation-induced martensite and hydrogen-induced martensite processes [37–39]. The type of martensite formed is also found to be influenced by Mn content in steels. Schumann reported that Fe-(10–14)Mn steel contained both ε-martensite and α′-martensite at room temperature and Fe-(14–27)Mn steel exhibited only ε-martensite after the same heat treatment [8].

Martensites formed by different means are expected to be accompanied with different metallurgical conditions of the steel matrix. Martensite produced by cold working is always accompanied with higher densities of dislocations and deformation austenitic twins. In comparison, martensite formed by heat treatment or hydrogen impregnation is likely to co-exist with precipitates, hydrides and certain grain structures. In this regard, studies of the influences of martensite on hydrogen embrittlement are inevitably associated with the effects of other microstructural factors, imposing challenges to delineating the effect of martensite and establishing a clear understanding of its effects.

This study was conducted to investigate the effects of surface ε-martensite and α′-martensite on hydrogen-induced degradation of mechanical properties of high strength TWIP steels in wet H_2S environment.

Experimental procedure

Two high-Mn steel ingots with nominal compositions of Fe-16.0Mn-0.4C-2Mo (wt.%) (denoted 16Mn hereafter) and Fe-25.0Mn-0.4C-2Mo (wt.%) (denoted 25Mn) were prepared by induction melting. The ingots were hot forged and homogenized at 1150 °C for 2 h. The forged billets were then hot rolled at 950 °C into 20 mm thick strips and finally cold rolled into 10 mm thick strips, followed by a final anneal at 750 °C for 1 h