Studying Hydrogen Embrittlement in Nano-twinned Polycrystalline Fe-12.5Mn-1.2C Austenitic Steel

Mahmoud Khedr, Wei Li and Xuejun Jin

Abstract Embedding austenitic structures with nano-twinned grains is a promising technique to enhance its strength and ductility, nano twins can be introduced via thermo-mechanical processing or via electro-deposition. In the current study, ternary Fe-Mn-C austenitic steel was cold rolled then subjected to flash annealing to keep some nano twins within the matrix. It was found that, the nano twinned condition showed better resistance to Hydrogen embrittlement (HE) than the as received state. In addition, notched samples charged with hydrogen were tensile tested to investigate the contribution of the nano-twinned grains in impeding cracks initiation/propagation, it was concluded that the prior twins distributed homogeneously the internal stresses inside the austenitic grains during the plastic deformation, which prevented cracks propagation at earlier strain level, and this delayed time till fracture happened.

Keywords Hydrogen embrittlement · Austenitic steels · Pre-induced twins

Introduction

Austenitic steels are famous with its usages in the applications related to serving in hydrogen environment, however, improving its resistance to hydrogen embrittlement(HE) is very important issue [1]. According to the literatures [2, 3], the HE resistance of austenitic steels was improved by decreasing grains sizes or alloying with Al. The target of the current work is to provide a new method to enhance the

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HE resistance of coarse grained high C-Mn steel via embedding the structure with nano-scale twins.

Nanos-scale twins can be introduced to FCC structures via thermo-mechanical processing or by electro-deposition [4, 5]. The nano-twinned structures showed enhanced strength and ductility, in addition to retarding cracks propagation compared with the not twinned grains [6], since that, twin boundaries are considered as planar defects which can hinder dislocations mobility [7]. On the other hand, existing of internal defects such as twins, work as hydrogen trapping sites, and it may affect hydrogen diffusivity [2].

Experimental Work

Materials

In the current work, commercial Hadfield steel containing Fe, 1.15 wt% C and 12.45 wt% Mn was investigated, it contains single phase of austenite. The as received condition was prepared by hot rolling followed by water quenching.

Introducing Nano Twin Plates via Cold Rolling then Heat-Treating

To embed the austenite phase with deformation twins, cold rolling was performed. The cold rolled specimens showed ductility less than 4% [8], so that, it was annealed at 915 °C for 90 s, in order to reduce the micro-strains, while the short time of annealing was selected to keep some nano twins within the structure, and to avoid de-twinning associated with long holding time. The heat-treated samples are named CR90.

Hydrogen Charging and Tensile Testing

Hydrogen charging was carried out via electro-chemical charging in aqueous solution of 3% NaOH and 3 g/l NH_4SCN with 16.8 mA/cm^2 current density, for 24 h at 80 °C. A platinum wire was used as a counter electrode.

Samples for tension test were prepared according to the ASTM standard (E 8M-03) with gauge dimensions of $25 \times 6 \times 1$ mm^3, tested at slow strain rate (SSRT) of 4×10^{-5} s^{-1}. Using of the notched specimens during the tension test is an indicator of crack initiation and propagation sites [9]. Details about notch dimensions were presented elsewhere [10].

Characterization

The characterizations of the microstructure of Hadfield steel imply using of optical microscopy via (OM, Zeiss), and to get more details about twins structures, thin foils with diameter of 3 mm for transmission electron microscopy (TEM) were prepared by using ion beam polishing system (Gatan 691). Scanning electron microscopy (SEM) was performed by a JEOL JSM7600F. After tension test, samples within the gauge area were selected to measure it hardness according to Vickers scale (HV) under load of 100 g for 10 s as a penetration holding time.

Results and Discussion

Tension Test Results

Table 1 summarizes the results of the tension tests of the as received and cold rolled then heat-treated samples (CR90) with and without H charging. The mechanical behavior of the CR90 is better than the as received condition. After H-charging, yield strength of the as received was slightly decreased, while in the CR90 it was nearly not affected.

The Microstructure of the Gauge Area After Tension Test

Figure 1 shows the microstructure in the gauge area after fracture in both the as received and CR90 conditions, with and without hydrogen. Generally, the amounts of twin boundaries are higher in the CR samples. it seems that, the existence of hydrogen affected the process of initiating mechanical twins intensively in the as received condition, which may be related to dislocations cross slipping enhanced by hydrogen [1], and consequently the amount of induced twins were negatively affected.

Table 1 The mechanical properties of the as received and CR90 before and after H-charging

Condition	As received		CR90	
	Without H	With H	Without H	With H
YS (MPa)	361.2	353.6	374.3	373.9
UTS (MPa)	840.5	718.2	1028.4	973.1
Elongation (%)	29.2	23.1	41.1	39.3
Loss in UTS due to H-charging (%)	15.3		2.7	
Loss in Elongation due to H-charging (%)	22.5		6.1	

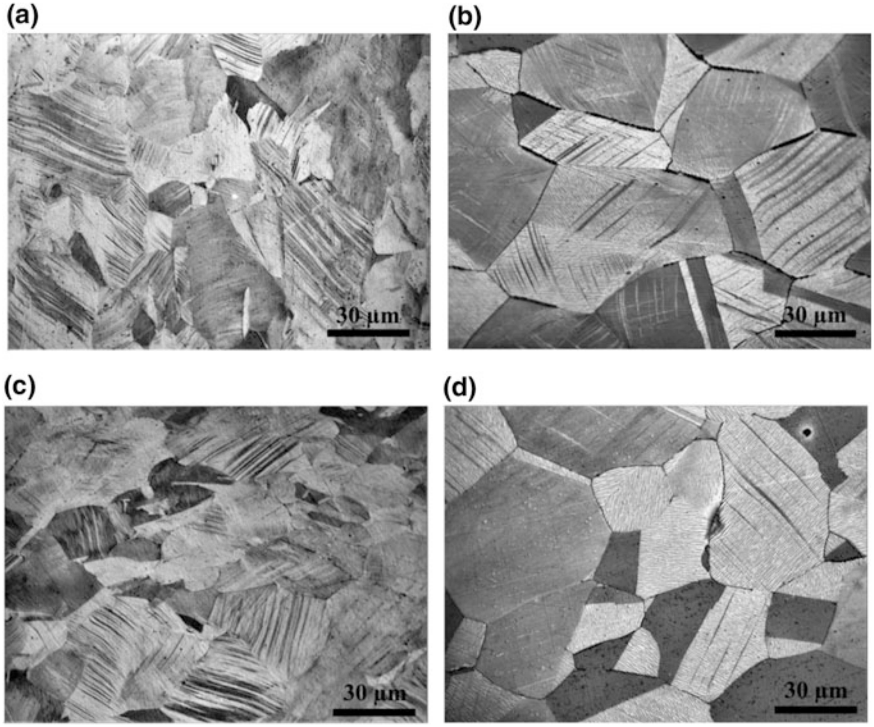

Fig. 1 The micrographs after tension test through the gauge area, at the CR90 (**a**, **c**), and as received condition (**b**, **d**), without H (**a**, **b**), and with H (**c**, **d**)

Notched Samples

Figure 2 shows a longitudinal section of the notched specimens at the two sides with hydrogen, in both as received and cold rolled conditions. Usually cracks are formed in the two sides of the notches during the tension test, while due to strain localization in Hadfield steel [11], fracture will start from one side then it will propagate to the other side [12]. Nevertheless, as shown in Fig. 2a, in the as received condition that was charged with hydrogen, only one crack was initiated and then propagated to the other side, which is an indicator of slip localization due to existence of hydrogen [13, 14]. On the other hand, in the CR90 condition that was charged with hydrogen, many cracks were initiated together due to the existence of the pre-induced twins in both 3% and 5% strain as shown in Fig. 2b and c. The pre-induced twins enhanced the homogeneous distribution of internal stresses during the plastic deformation, and this prevented crack propagation in an early stage of strain compared with the as received condition. Moreover, twins assisted crack propagation along grain boundaries at the interception with twin tips [1]. Cracks were propagated at around 3% strain in the as received condition,

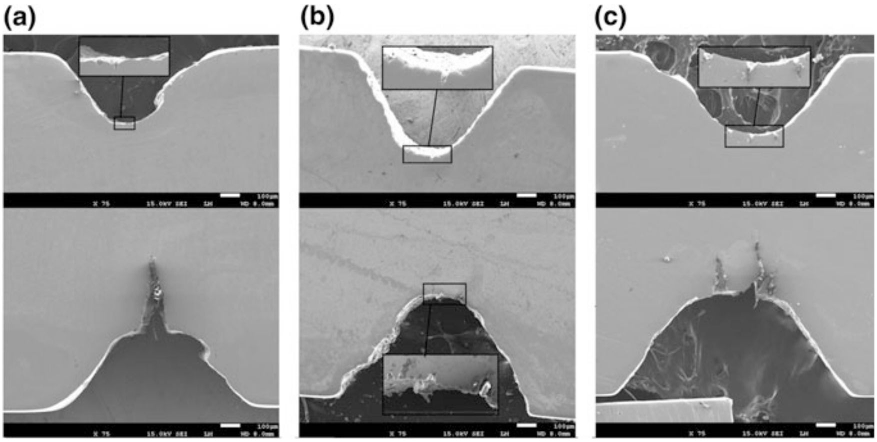

Fig. 2 Cracks initiation and propagation in the notched tension test specimens after H-charging, as received condition at 3% strain (**a**), and cold rolled at 3% and 5.5% strain respectively (**b**, **c**)

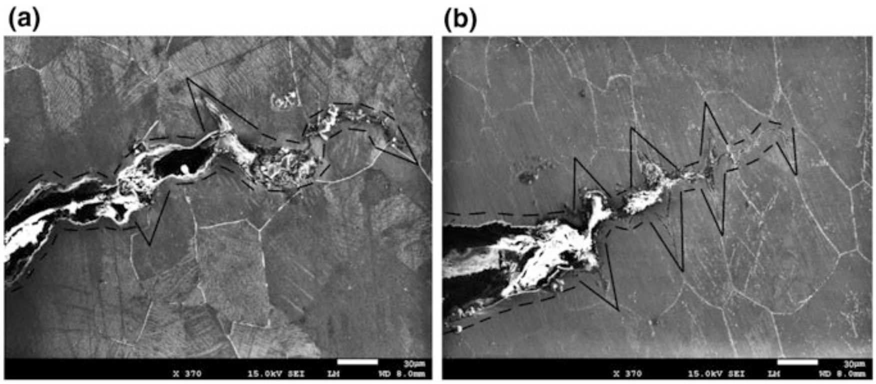

Fig. 3 The microstructure of the notched samples showing cracks paths, **a** the as received and **b** cold rolled conditions. The dotted lines show the crack propagation path, and the solid lines show the cracks initiation sites

while it propagated at 5.5% strain in the cold rolled samples. It worth mention that, the number of cracks in the notched area at the cold rolled condition are more than the as received.

Figure 3 shows the microstructure of the notched specimens under SEM after etching with Nital, in order to spot more light on the crack initiation and propagation in the as received and cold rolled samples. It is clear that the cracks are distributed homogeneously in the cold rolled samples, in addition, cracks were initiated from grain boundaries [12] during its propagation.

Table 2 Variation of hardness values in the as received and CR90 samples with and without hydrogen

Condition	As received		CR90	
	Without H	With H	Without H	With H
$HV_{0.1}$	445 ± 14	374.7 ± 30	502.1 ± 14	490.7 ± 13

Hardness Results

It was reported that, hardness values are dependent of the twins volume fraction in austenitic steels [15], so that hardness was measured in the gauge area after tension test. Table 2 shows the results of hardness on Vickers scale. The results show that, the cold rolled samples are having higher hardness values, and this may refer to more twin plates, but it will be better to enhance it with TEM.

TEM Results

Figure 4 shows the TEM results of the as received and CR90 conditions charged with hydrogen. As shown in Fig. 4a, it is clear that the initial nano twins introduced in the CR90 worked as barriers to dislocations movements and resulted in forming of very twin plates in spite of existing of hydrogen. On the other hand, as shown in Fig. 4b, twins were relatively thicker after H-charging, and it may be related to

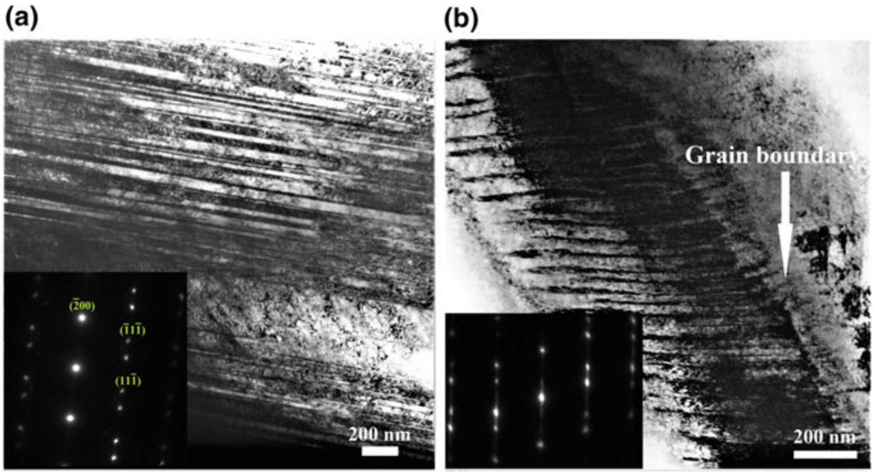

Fig. 4 TEM results using [110] zone axis after tension test of specimens charged with hydrogen. CR90 at (**a**), and as received at (**b**)

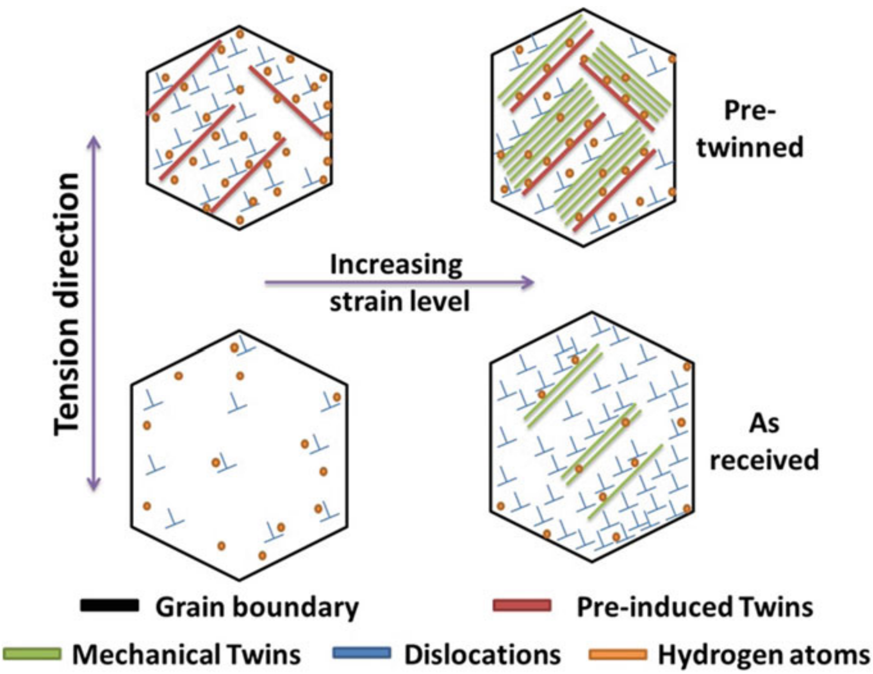

Fig. 5 Graphical illustration showing the effect of the pre-induced twins on preventing dislocations slip after H-charging in the cold rolled sample and consequently inducing more mechanical twins, while in the as received sample mechanical twinning was limited (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

pilling up of the enhanced dislocations mobility on grain boundaries due to hydrogen entry, and it can refer to promoting more trans-granular fracture in the fracture surface revealed by Michler et al. [13].

Figure 5 shows illustration graph of the effect of the pre-induced twins in inhibiting dislocations slip after H-charging, and consequently increasing dislocations dissociation rate to form mechanical twins and distributing the internal stress homogeneously. Nevertheless, at the not-twinned sample, the amount of mechanical twins at fracture are lower than the pre-twinned sample due to dislocations mobility enhanced by hydrogen atoms, while there was no more obstacles to these dislocations like the pre-twinned sample, in addition, dislocations were accumulated on grain boundaries causing local stress concentrations that resulted in inter-granular fracture [13]. Moreover, it is important to note that the twin boundaries in Hadfield steel are containing tremendous amounts of dislocations [16].

Conclusion

Embedding coarse grained austenitic steel with nano twin plates resulted in increasing hydrogen embrittlement resistance of Hadfield steel. Moreover, notched samples confirmed that, the internal stresses were homogeneously distributed through the austenite matrix.

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References

1. Koyama M, Akiyama E, Lee YK, Raabe D, Tsuzaki K (2017) Overview of hydrogen embrittlement in high-Mn steels. Int J Hydrog Energy 42:12706–12723
2. Park I, Jeong K, Jung J, Lee C, Lee Y (2012) The mechanism of enhanced resistance to the hydrogen delayed fracture in Al-added Fee18Mne0.6C twinning-induced plasticity steels. Int J Hydrog Energy 37:9925–9932
3. Ryu JH, Kim SK, Lee CS, Suh DW, Bhadeshia HKDH (2013) Effect of aluminium on hydrogen-induced fracture behaviour in austenitic Fe–Mn–C steel. Proc R Soc A 496:1–14
4. Yan FK, Liu GZ, Tao NR, Lu K (2012) Strength and ductility of 316L austenitic stainless steel strengthened by nano-scale twin bundles. Acta Mater 60:1059–1071
5. Lu K, Lu L, Suresh S (2009) Strengthening materials by engineering coherent internal boundaries at the nanoscale. Science 324:349–352
6. Chowdhury P, Sehitoglu H, Rateick R (2016) Recent advances in modeling fatigue cracks at microscale in the presence of high density coherent twin interfaces. Curr Opin Sol State Mater Sci 20:140–150
7. Greer JR (2013) It's all about imperfections. Nat Mater 12:689–690
8. Khedr M, Li W, Jin X (2016) The effect of deformation twins induced previously by cold rolling on the mechanical behavior of Hadfield steel. Paper presented at the 1st ICAS and 3rd HMnS, Cheng Du, China, 16–18 Nov 2016
9. Wang M, Akiyama E, Tsuzuki K (2007) Effect of hydrogen on the fracture behavior of high strength steel during slow strain rate. Corr Sci 49:4081–4097
10. Zhu X, Li W, Zhao H, Wang L, Jin X (2014) Hydrogen trapping sites and hydrogen-induced cracking in high strength quenching & partitioning (Q&P) treated steel. Int J Hydrog Energy 39:13031–13040
11. Canadinc D, Efstathiou C, Sehitoglu H (2008) On the negative strain rate sensitivity of Hadfield steel. Scr Mater 59:1103–1106
12. Koyama M, Akiyama E, Tsuzaki K, Raabe D (2013) Hydrogen-assisted failure in a twinning-induced plasticity steel studied under in situ hydrogen charging by electron channeling contrast imaging. Acta Mater 61:4607–4618
13. Michler T, Marchi CS, Naumann J, Weber S, Martin M (2012) Hydrogen environment embrittlement of stable austenitic steels. Int J Hydrog Energy 37:16231–16246
14. Nagumo M (2004) Hydrogen related failure of steels—a new aspect. Mater Sci Tech 20: 940–950

15. Tewary NK, Ghosh SK, Bera S, Chakrabarti D, Chatterjee S (2014) Influence of cold rolling on microstructure, texture and mechanical properties of low carbon high Mn TWIP steel. Mater Sci Eng A 615:405–415
16. Idrissi H, Renard K, Schryvers D, Jacques PJ (2010) On the relationship between the twin internal structure and the work-hardening rate of TWIP steels. Scr Mater 63:961–964