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# Improving hydrogen embrittlement resistance of Hadfield steel by thermo-mechanical flash-treatment

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ABSTRACT

Nano-twins microstructures were introduced in a high carbon manganese steel by a novel flash thermo-mechanical treatment in order to achieve high resistance to hydrogen embrittlement. Nano-twinned grains decreased hydrogen diffusivity through the bulk material, although it absorbed more hydrogen than the twins-free specimens. Moreover, it was shown that after electrochemical hydrogen charging, the nano-twins microstructures can reduce dislocations glide during plastic deformation, resulting in forming of fine twin plates.

## 1. Introduction

Industrial applications of many components require more reliability to be operated safely under the existence of gaseous hydrogen. Hydrogen Embrittlement (HE) refers to the degradation in the mechanical properties by hydrogen which leads to premature failure of the metallic materials. Nevertheless, different grades of steels are susceptible to HE, when it services in hydrogen environment *e.g.* pressure containers, or contains free hydrogen after processing e.g. melting and pickling [1–10].

Normally, austenitic steels have higher HE resistance than their martensitic or bainitic counterparts due to the higher solubility and much lower hydrogen diffusion coefficients in FCC substrates than BCC structures [11,12]. The value of stacking fault energy (SFE) affects the deformation mode of the austenitic steels intensively [13–15], and, after H-charging, SFE decreases [16], which in role may result in martensite transformation in the low SFE ($< 18\,mJ/m^2$) austenitic steels [10].

Yamada et al. [17] found that, materials with high SFE ($> 41\,mJ/m^2$) were positively affected after H-charging, because the deformation mode was changed from slip dislocation gliding into deformation twinning. However, austenitic steels with high contents of austenite stabilizers such as nickel are not economy in industry applications. While those steels alloyed with carbon and manganese e.g. TWIP suffers HE due to promoting twinning in early stages of deformation, at where cracks are initiated at the intersections with secondary twin and/or grain boundaries [18,19].

The existing of coherent twin boundaries (CTBs) can enhance the strength and ductility of the FCC structures [20–24], since that twin boundaries are planar defects which can hinder dislocations mobility [25]. Moreover, the activation energy for desorption of hydrogen stored in dislocations and grain boundaries is equal to half the value required to desorb hydrogen from twin plates [26,27], on the other hand, internal defects like carbides precipitates, dislocations, and twins can work as hydrogen trapping sites [26–32], which can decrease hydrogen diffusivity through the matrix [33].

Hadfield steel is a traditional high carbon austenitic steel, SFE ranges between 23 and 50 $mJ\,m^{-2}$ [34–37]. According to the literature, it is worth noting that the effect of hydrogen in Hadfield steel is an interesting issue. Astafurova et al. [34] showed that, a single crystal Hadfield steel was positively affected with H-charging due to forming more deformation twins during plastic deformation. But in polycrystalline Hadfield steel, Michler et al. [3] found that hydrogen can cause intensive dislocations piling up on twins and grain boundaries and finally resulted in inter-granular and trans-granular fracture. The controversial effect of twin and grain boundaries on the plastic deformation with the help of hydrogen is crucial but not clearly demonstrated up to date.

The objective of the current study is to analyze the interaction between hydrogen and twin plates by introducing mechanical twins in advance via a thermo-mechanical process, the grain size was maintained the same and both precipitations and martensitic transitions were avoided.

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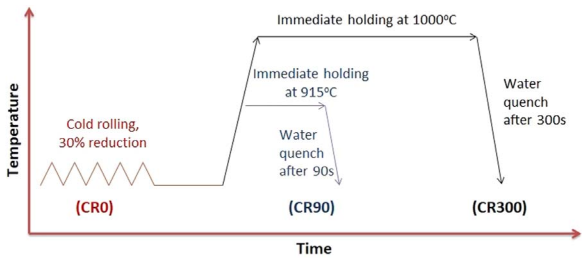


**Fig. 1.** Graphical indication showing samples codes after cold rolling and annealing followed by water quenching.

## 2. Experimental methods and characterizations

### 2.1. Materials and heat treatments

In the study, a commercial Hadfield steel containing Fe, 1.15 wt% C and 12.45 wt% Mn was investigated, it was subjected to hot-rolling at 1060 °C followed by water quenching (as received condition). According to the thermodynamics model presented by Saeed-Akbari et al. [38], SFE of Hadfield steel being approximately 35 $mJ/m^2$, which is high enough to prevent martensite transformation during cold rolling [15].

Deformation twins were introduced to Hadfield steel via cold rolling, with total thickness reduction of 30% (CR0). The residual strains accompanying the cold rolling processes were eliminated by holding the cold rolled plates at 915 °C for 90 s followed by water quenching (CR90). To achieve fully reversion, cold rolled samples were annealed at 1000 °C for 300 s (CR300). Fig. 1 shows a scheme of the thermo-mechanical heat-treatments.

### 2.2. Hydrogen charging

Hydrogen was introduced to the specimens via electro-chemical charging using 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 to increase the diffusion rate of H through the samples [26]. A platinum wire was used as a counter electrode. After H-charging, the amount of absorbed hydrogen was evaluated by LECO TCH600 thermal desorption device, with heating rate of 65 °C/s, the average reading of two samples was recorded.

### 2.3. Tension test

Dog-bone shaped samples for tension test were prepared according to the ASTM standard (E 8M-03) with gauge dimensions of 25 × 6 × 1 $mm^3$, tested in room temperature immediately after H-charging at strain rate of $4 \times 10^{-5}\,s^{-1}$ to allow hydrogen diffusion during the plastic deformation [6]. The term $El_{loss}$% refers to the total elongation loss, which is defined to quantify the susceptibility to HE, it can be calculated as follows:

$$El_{loss}\% = \frac{100 \times (El_{unch} - El_{charg})}{El_{unch}} \tag{1}$$

where $El_{unch}$ is the total elongation% without hydrogen, and $El_{charg}$ is the total elongation% after charging with hydrogen [11]. Another parameter, the reduction of the fracture stress (RFS) or loss in ultimate tensile strength (loss UTS), can also be used to describe the HE susceptibility, it can be calculated from Eq. (2) as follows:

$$RFS\% = 100 \times (1 - \frac{\sigma_f}{\sigma_{f0}}) \tag{2}$$

where $\sigma_f$ and $\sigma_{fo}$ are the fracture stresses (or UTS) of the charged and the uncharged specimens respectively [2].

### 2.4. Microstructure characterizations

Samples for optical microscopy (OM) were mechanical grinded by SiC sand papers, then polished by 1 μm diamond paste, followed by chemical etching with Nital (2% $HNO_3$) for 10–30 s. X-Ray Diffraction (XRD) was powered by RIGAKU ULTIMAIV running at 40 kV and 30 mA using copper tube conducted between 35° and 140° with speed of 2° per minute. Hardness tests were performed according to Vickers scale (HV) under load of 100 g for 10 s as a penetration holding time.

The fracture morphology was observed using scanning electron microscopy (SEM) with a JEOL JSM7600F, field emission electron microscope. Thin circular foils with diameter of 3 mm for transmission electron microscope (TEM) were mechanically cut, it was polished down to 60 μm using sand papers, then it was thinned at incidence angle (10°) using ion beam polishing system (Gatan 691) operated at 5 kV until a hole was created at the center of these foils.

### 2.5. Calculating dislocations densities

Dislocations densities were evaluated by analyzing the austenite peaks profiles obtained by XRD, crystallite size and microstrain values were estimated using the Rietveld analyses via the MAUD program [39–41]. Lattice constant ($a$), dislocations densities ($\rho_d$), crystallite sizes ($D$), and micro-strains ($\varepsilon$) were calculated by analyzing the XRD diffraction patterns via MAUD algorithm [40,42–46]. Dislocation densities ($\rho_d$) can be calculated according to Eq. (3) as following, [41,47]:

$$\rho_d = \frac{7.52 \times (\varepsilon^2)^{0.5}}{D \times b} \tag{3}$$

where $b$ is the Burgers vector.

### 2.6. Hydrogen permeation test

Hydrogen permeation test was performed in order to compare hydrogen diffusivity in CR90, and CR300 conditions, and consequently study the effect of the prior twins on hindering hydrogen mobility through the material. Hydrogen diffusion coefficient (D) was calculated using a modified Devanathan-Stachurski (D-S) cell according to the international standard ISO 17081 [48,49], however, details of the permeation test were discussed elsewhere [6,33,48–50].

D-S cell consists of two chambers, one for H-charging, and the other one is to detect hydrogen entry, and consequently depending on the breakthrough time ($t_b$) starts after H-charging in the first chamber until H-entry in the second chamber, and membrane thickness (L), D can be calculated according to Eq. (4), as following [10]:

$$t_b = \frac{L^2}{15.3 * D} \tag{4}$$

## 3. Results

### 3.1. Microstructural characterization

Fig. 2(a, b and c) show the optical microstructure of as received, CR300 and CR90 specimens, the cold rolled microstructure has average grain size of 33 ± 6 μm. In addition, annealing time less than 30 min at temperature 1000 °C doesn't affect the grain size [51,52]. The remaining twin plates after cold rolling then heat-treating are very clear in Fig. 2.c. Deformation twins in CR90 was illustrated with TEM in [53]. Fig. 2.d showing no existence of carbides precipitations.

Fig. 3 shows the XRD diffraction patterns of the CR300, CR90, and CR0 samples, peaks profiles confirm the existing of full austenite phases.