Effect of Hydrogen on Toughening of a Low Alloy Steel

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A low alloy steel containing 0.10C, 0.25Si, 0.87Mn, 0.56Cr, 0.47Ni, 0.21Mo, 0.023S and 0.01P (mass%) was cold rolled to 1.6 mm thick sheets and recrystallised at 700°C to get ferrite grains of 8, 21.5 and 32.5 μm with a random distribution of some spheroidal carbide particles and a few inclusions. Tensile specimens prepared from these sheets were cathodically charged in 1 N NaOH and 0.1 N H₂SO₄ solutions for periods varying from 2 to 24 h, with a current density of 50 mA/cm². Tensile tests were carried out with a cross-head velocity of 1.2 mm/min, fracture surfaces were examined by SEM and the deformed structure was examined by TEM. The increase in hydrogen content, up to a certain limit, has been effective to cause an increase in both ultimate tensile stress and % elongation resulting in a toughening of the steel, while the work hardening is not remarkable. Increase in the ferrite grain size has been observed to enhance this effect. The tensile behaviour has been correlated with observed fracture characteristics and dislocation substructure in the ferrite matrix. The toughening effect has been explained in the light of dislocation solute interactions and the damage caused by hydrogen.

KEY WORDS: cathodic charging; tensile behaviour; toughening; ferrite grain size; low alloy steel; hydrogen.

1. Introduction

It is well-known and universally accepted that hydrogen embrittles iron and steel when present in a sufficient quantity. However, its reported effects on mechanical properties of steels have been widely different, sometimes controversial, conflicting and not unambiguous. High purity iron with hydrogen is sensitive to the strain rate and testing temperature in respect of the appearance of sharp yield point1) and has been shown to be both softened and hardened.1,2) Steels under an applied stress, in the presence of hydrogen, may behave in strangely different manners which are not only dependant on the chemistry, microstructure, processing history, impurity content and strength level of a steel but also on the hydrogenation and stressing conditions.3–20)

The present paper represents a portion of the study on mechanical behaviours of a low alloy steel with different ferrite grain sizes, hydrogenated by electrolytic charging under widely different conditions.

2. Experimental

A low alloy steel containing 0.10C, 0.25Si, 0.87Mn, 0.56Cr, 0.47Ni, 0.21Mo, 0.023S and 0.01P in mass% was cold rolled to a thickness of 1.6 mm by 70% reduction. Pieces of cold rolled sheets were recrystallised at 700°C under a cover of used charcoal for 24, 72 and 120 h and the grain size of ferrite was measured by intercept method. Tensile specimens of 60 mm gauge length (Fig. 1) were prepared from the heat treated sheets after grinding on emery papers to a thickness of 1.5 mm.

Tensile specimens were cathodically charged in 1 N NaOH (low fugacity) and 0.1 N H₂SO₄ (medium fugacity) solutions for periods varying from 2 to 24 h with a current density of 50 mA/cm². The electrolytes were poisoned by adding 5 mg of As₂O₃ per litre for preventing recombination of evolving hydrogen atoms. Pieces of graphite and lead sheets were used as anodes for NaOH and H₂SO₄ respectively. The charged specimens were cleaned under running water and immediately preserved in liquid nitrogen until the start of tensile test.

Tensile test was done at room temperature in a screw type hard beam testing machine at a cross-head velocity of 1.2 mm/min and load–elongation curves were plotted on a strip chart recorder. Fracture surfaces were studied by scanning electron microscope (SEM) immediately after tensile tests. Transmission electron microscopic (TEM) studies thin foils were prepared from pieces of about 8 mm in length, cut from fracture end of the tensile specimens, by preparing from the heat treated sheets after grinding on emery papers to a thickness of 1.5 mm.

Fig. 1. Dimensions of tensile specimens.
grinding and twin-jet polishing in an electrolyte of 10% perchloric acid and acetic acid.

For analysis of hydrogen content of the charged specimens, a new set of recrystallised specimens of dimensions 60×12.5×1.5 mm were charged with identical charging conditions, and hydrogen content of the charged specimens was analysed by LECO R H-2 Hydrogen Determinator.

3. Results

3.1. Microstructures

Microstructure of the heat treated samples consisted of recrystallised ferrite grains with a random distribution of spheroidal carbides and a few inclusions (Fig. 2). The average grain sizes of ferrite were measured to be 8, 21.5 and 32.5 μm after recrystallisation for 24, 72 and 120 h respectively. TEM microstructures of the tested specimens have shown a decrease in dislocation cell size with a consequent increase in dislocation density with the increase in hydrogen content. Figure 3 shows clearly the dislocation cell structure to be smaller in a hydrogenated specimen compared to that in an uncharged specimen.

3.2. Hydrogen Content and Surface Appearance

Hydrogen contents of the charged specimens of ferrite grain size 21.5 μm are shown in Fig. 4. Average values of at least three analyses of identically treated specimens showed a linear increase in hydrogen content with the increase in period of charging in the electrolytes. There was no appreciable difference in hydrogen content of the specimens of different ferrite grain sizes for any of the periods of charging in 1 N NaOH. Charging in 0.1 N H₂SO₄ for shorter periods also caused little difference in hydrogen content with different ferrite grain sizes, although longer periods caused a slightly higher hydrogen content in the specimens of smaller grains. For 24 h of charging, the specimens of 8, 21.5 and 32.5 μm ferrite grain sizes showed a difference in hydrogen content by about 1.5 ppm.

After charging in the electrolytes the specimen surface appeared to be as clean as before. However, longer periods (16 and 24 h) of charging in 0.1 N H₂SO₄ produced a few small blisters on the specimen surface.

3.3. Tensile Behaviour

A few load–elongation curves are shown in Fig. 5. Uncharged specimens have always shown a sharp yield drop with prominent upper and lower yield loads. The charged specimens except a few charging conditions imparting smaller amounts of hydrogen have not shown such features. For the sake of easy comparison, in this study, the average load at yield point elongation zone has been considered to be the load at yield point, and yield stress (YS) of the specimens is reported on the basis of this value of load. YS has decreased monotonically with an increase in the charging time in both the electrolytes (Figs. 6(a)–6(c)) i.e., with the increase in hydrogen content. Figures 6(a–
also show that for every charging condition the larger the ferrite grain size (corresponding to longer recrystallisation period) the greater is the loss in YS.

Charging has dominantly increased both ultimate tensile stress (UTS) and % elongation of the steel (Figs. 6(d)–6(i)). With the increase in time of charging, UTS in the case of 1 N NaOH and both UTS and % elongation in the case of 0.1 N H$_2$SO$_4$ have declined after attaining peaks. The longer periods (16 and 24 h) of charging in 0.1 N H$_2$SO$_4$ have induced a loss in both UTS and % elongation. 1 N NaOH, however, has induced no loss in UTS except a marginal one in the specimens of largest ferrite grain size, charged for 24 h. Charging in higher fugacity 0.1 N H$_2$SO$_4$ has not only reduced the value of UTS peaks but has also shifted these peaks to shorter charging times. There is also an increase in the UTS peak values with the increase in ferrite grain size.

Increase in the period of charging in 1 N NaOH has monotonically increased the % elongation, and the larger the ferrite grain size the higher is the increase in % elongation for a particular charging period. On 0.1 N H$_2$SO$_4$ charging, % elongation peaks have attained higher values and have shifted to a shorter charging time with the increase in ferrite grain size. However, the loss in ductility on longer charging in this higher fugacity solution is more influenced by the ferrite grain size compared to a gain in ductility for shorter periods of charging.

The effect of ferrite grain size on tensile behaviour of the charged steel has been analysed and discussed in detail elsewhere. Necking of the specimens and the consequent % reduction in area, although not measured, have been noted to be reduced with the increase in hydrogen content, even though % elongation is quite high.

The log–log plots of true stress and true strain of the tested specimens up to maximum loads have shown a straight line relationship, and slopes of these straight lines have shown that the values (0.24–0.27) of strain hardening coefficient ‘$n$’ of the charged specimens are slightly higher than that (0.23) of uncharged specimens. The higher value is associated with the higher hydrogen content. The specimens of sufficiently high hydrogen content have also indicated a change in strain hardening coefficient with the increase in flow stress with a distinct change in slope of this straight line relationship as shown in Fig. 7. This clearly indicates that the strain hardening effect of hydrogen is mainly limited to certain initial stage of plastic deformation and beyond this stage hardening effect is very little. This effect is consistent with the observed nature of load elongation curves (Fig. 5).

3.4. Fracture Characteristics

Fracture mode of the specimens charged for shorter periods in 1 N NaOH is very similar to those of uncharged specimens, characterized by the formation of dimples and tearing of the regions in between dimples. Although the
overall fracture characteristics are highly ductile in nature, a gradual change has been noted with the appearance of decohesion microvoids (arrowed) formed in tear zones around dimples and a few small regions of quasi-cleavage mode of fracture (indicated by box) on charging for longer periods (Fig. 8). In the specimens charged for shorter periods in 0.1 N H$_2$SO$_4$ the fracture modes are similar to those observed in the specimens charged for longer periods in 1 N NaOH. On longer charging in 0.1 N H$_2$SO$_4$ the fracture is characterized by a gradual reduction in dimple size, and increased number and more uniform distribution of decohesion microvoids and quasi-cleavage regions (Fig. 9). The gradual changes in fracture modes has been noted to be enhanced in the specimens of larger ferrite grain size. Details of the change in fracture modes have been published earlier.\textsuperscript{21}

4. Discussion

The bulk concentration of hydrogen in a specimen, as shown in Fig. 4, is influenced by the charging time and the fugacity of electrolytes, the current density being same for all the specimens. Higher fugacity of an electrolyte leads to higher rate of hydrogen absorption by a specimen surface and consequently a higher amount of hydrogen diffusion into its interior. Hydrogen content of the ferrite matrix seems to cross the saturation limit on charging for longer periods in 0.1 N H$_2$SO$_4$ leading to the formation of blisters. Hydrogen introduced by charging remains as interstitial solutes in the ferrite matrix. The distribution of hydrogen atoms, however, may not be uniform from surface to interior of a specimen and can be preferentially trapped at grain boundaries, dislocations, interfaces of ferrite with carbides and inclusions.

The simultaneous increase in UTS and % elongation under certain conditions of charging evidently indicates that hydrogen can make the steel tougher, although not to a great extent. The decrease in YS, in consistence with earlier observations,\textsuperscript{8,22–24} clearly indicates hydrogen to soften the steel. Possible explanations for this softening may be a) a reduction in the magnitude of Peierls–Nabarro stress field by solute atoms,\textsuperscript{1} b) enhancement of the mobility of the dislocations as a result of elastic interaction with solute atoms,\textsuperscript{25} and c) a reduction in the effectiveness of solutes as dislocation pinning points resulting from the formation of small solute clusters.\textsuperscript{26} Because of non-spherical symmetry\textsuperscript{27} of the strain field of hydrogen in $\sigma_{te}$ a hydrogen atmosphere formed around a screw dislocation becomes asymmetrical under an externally applied stress, which results into an additional force acting on the dislocation.\textsuperscript{28,29} This additional force helps the external stress to make the dislocations move.\textsuperscript{28} Since room temperature dif-

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**Fig. 7.** Log–log plot of true stress vs. true strain of a specimen recrystallised for 72 h at 700°C and cathodically charged in 1 N NaOH for 8 h.

**Fig. 8.** SEM fractographs of specimens; (a) recrystallised for 24 h and charged for 16 h in 1 N NaOH, and (b) recrystallised for 120 h and charged for 24 h in 1 N NaOH.

**Fig. 9.** SEM fractograph of a specimen recrystallised for 24 h and charged for 16 h in 0.1 N H$_2$SO$_4$ solution.
fusivity of hydrogen in \( \epsilon_{\text{fus}} \) is about 10\(^4\) times greater than the next largest interstitial,\(^{26}\) a dislocation can move along with its hydrogen atmosphere because of a high binding energy between them,\(^{31}\) and if strain energy of a dislocation is reduced in the presence of a hydrogen atmosphere, external stress necessary to operate a Frank–Read source is reduced. External stress needed for operating a Frank–Read source has been calculated to be reduced by about 20\% when a screw dislocation is surrounded by the critical hydrogen concentration.\(^{28}\) In-situ environmental cell high voltage electron microscopy has also directly shown hydrogen to enhance dislocation motion and dislocation multiplication.\(^{32-34}\)

In steels the presence of C, N and other solutes generally exerts a pinning effect on dislocations. It may, however, be presumed that the additional force upon a screw dislocation developed in the presence of a hydrogen cloud around it may be sufficiently high to annul the restraining effect of other solutes, if the concentration of hydrogen in the solute cluster is sufficiently high. Moreover, for a very low strain rate, \(3 \times 10^{-5} \text{s}^{-1} \) employed in this study, the critical temperature at which the rate of hydrogen diffusion is equal to the speed of dislocation motion, is much below room temperature.\(^{29}\) Therefore, the asymmetrical hydrogen atmosphere formed around a screw dislocation, even in the presence of other solutes, can produce an additional force on the dislocation at the testing temperature enhancing the multiplicity of a dislocation and also operating a Frank–Reed source at lower applied stresses. The higher the bulk concentration of hydrogen the higher is the concentration around screw dislocations and therefore, the lower is the YS, and the higher is the UTS resulted from work hardening due to interaction of dislocations of a larger density. The enhanced mobility and higher multiplication of dislocations (under the influence of hydrogen clouds) also enhance plastic deformation leading to a higher % elongation. The increase in % elongation is simultaneous with an increase in UTS specially for shorter periods of charging (Figs. 6(d)–6(i)). The higher dislocation density and smaller dislocation cell size in hydrogenated specimens revealed by TEM studies (Fig. 3) corroborate and thereby confirm these effects. Moreover, King and Block\(^{35}\) have suggested that crack tip stress field exerts an attractive force on solute atoms. The hydrogen cloud around a moving dislocation may, therefore, communicate an attractive force between the dislocation and crack tip stress field leading to a higher ductility and a highly ductile fracture, as observed in this study, specially for the specimens charged for longer periods in 1 N NaOH and for intermediate periods in 0.1 N H\(_2\)SO\(_4\).

When plastic deformation occurs the yield shear stress \(\tau_y\) required to move dislocations across an active slip plane is related to the equivalent force \(f_y\) per unit length of a dislocation and the lattice Burger vector \(b\) by the equation \(\tau_y = f_y / b\) where \(f_y\) is the summation of the effects of Peierls–Nabarro lattice resistance, solid solution strengthening and work hardening.\(^{36}\) Since hydrogen lowers Peierls–Nabarro lattice resistance and causes solid solution softening, the effect of higher dislocation densities (resulted from enhanced dislocation generation) on strengthening of the steel is balanced by a higher plastic deformation causing a reduction in dislocation cell size because of an enhanced dislocation motion. This leads to a low value of \(n\). Hydrogen may also induce a change in active slip systems under an increased applied stress.\(^{29}\) The activation of different slip systems seems to influence the strain hardening tendency of the steel leading to a lower and different value of \(n\) at a later stage of deformation of specimens containing higher hydrogen.

It has been shown\(^{37}\) that hydrogen enhances plastic instability of the steel apparently by causing block slipping and initiation of void formation around carbide and impurity particles at lower applied stresses. The damage effect increases with the increase in hydrogen content and becomes more prominent with the formation of decohesion microvoids at the later stages of plastic deformation. The damage effects counter the work hardening effect. The increase in ductility is, therefore, a combined effect of solid solution softening and damage caused by hydrogen. A notable feature of the occurrence of a good amount of elongation with little increase in applied load till fracture, in the load–elongation curves of hydrogenated specimens (Fig. 5), is apparently due to the spread of damage effects over a large volume of a specimen. This effect causes the absence of dominant localized necking leading to an inappreciable reduction in area of these tensile specimens.

Although interaction energy of an edge dislocation with hydrogen is about twice that of a screw dislocation\(^{28}\) and this interaction hinders mobility of the dislocation,\(^{38}\) the enhancement of plastic deformation is little affected because of higher mobility and multiplication of screw dislocations. Restraining the mobility of edge dislocations may, however, contribute to the increase in strength. With the increase in hydrogen content of the steel when the hydrogen concentration around a screw dislocation approaches a saturation limit the effect of external force to produce asymmetric arrangement of hydrogen atoms around it decreases effecting a reduced mobility of the dislocation.\(^{29}\) This effect in combination with the restrained mobility of edge dislocations reduces plasticity and toughness of the steel and induces formation of decohesion microvoids and quasi-cleavage mode of fracture under tensile load\(^{39}\) under a situation of a reduced atomic bonding energy\(^{40}\) with a high hydrogen concentration in localized regions of the matrix.

The effects of increasing ferrite grain size, either beneficial or detrimental on the tensile properties, has been attributed\(^{21}\) to the effective increased concentration of hydrogen in the grain body as hydrogen trap density at ferrite grain boundaries may maintain a certain ratio to grain body hydrogen concentration.

5. Conclusions

(1) Presence of hydrogen, below the limit of its saturation in ferrite matrix, softens the steel by lowering its YS and increasing % elongation and also hardens the steel by raising its UTS. Thus the steel is effectively toughened. Further increase in hydrogen, however, induces a loss in both UTS and % elongation.

(2) The pinning effect of other solutes on screw dislocations is reduced by the formation of solute clusters with hydrogen atoms which reduces YS of the steel, and enhanced mobility and multiplication of screw dislocations,
as a result of their interaction with hydrogen atoms, increases plasticity of the steel.

(3) Enhanced mobility and multiplication of screw dislocations causes a simultaneous increase in plastic deformation and increase in strength due to work hardening under an applied load. Work hardening effect also changes with the increase in hydrogen content. Restricted mobility of edge dislocations in the presence of hydrogen results in an additional increase in strength of the steel.

(4) A sufficiently high concentration of hydrogen induces damage effects in the steel, which causes an additional contribution to the % elongation, a decrease in the chance of localized necking and reduction in area of a tensile specimen.

(5) As hydrogen concentration increases damage effects of hydrogen predominates over its beneficial effects on plastic deformation and work hardening leading to an adverse effect on strength and ductility of the steel.

REFERENCES