EFFECTS OF HYDROGEN AND IMPURITIES ON FRACTURE BEHAVIOUR OF A LOW STRENGTH Cr-Mo STEEL

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ABSTRACT

The interaction between hydrogen and impurities promoting brittle fracture in a low strength Cr-Mo steel has been studied. It has been observed that the steel investigated can be made susceptible to intergranular cracking resulting in minimum fracture toughness (G_c) when both impurities and hydrogen are present at the grain boundaries. The effect appears to be synergistic in nature and can be alleviated by de-embrittlement treatment.

KEYWORDS

Hydrogen embrittlement; impurity segregation; intergranular failure; temper embrittlement; cohesive strength; de-embrittlement; brittle fracture.

INTRODUCTION

Low alloy steel containing impurity elements (As, Sb, Sn, S, P) exhibit intergranular brittle fracture, when held or slowly cooled through the temperature range of 350-580 C. This phenomenon, known as temper-embrittlement occurs due to segregation of impurities to grain boundaries (Briant and Banerji, 1978; Olefjord, 1978) during heat-treatment or high temperature service. The most common indications of the phenomenon are : (a) an increase in ductile-brittle transition temperature, (b) a reduction of toughness and (c) a change in fracture mode from predominantly ductile to brittle intergranular failure. On the other hand, brittle fracture of steel can be induced by absorbed hydrogen which segregates to regions of high lattice expansion due to an applied tensile stress. It is generally felt that elements causing temper embrittlement, enhances the hydrogen-embrittlement susceptibility also (Yoshini and McMahon, 1974; Jokl and Co-workers, 1980). Yoshino and McMahon (1974) have demonstrated that the embrittlement induced by impurity segregation and that caused by hydrogen are at least additive in a 5 per cent nickel high strength steel. However for low strength steels (yield stress less than 800 MN/m^2) it is generally believed that the individual effects of temper-embrittlement (TE) and hydrogen embrittlement (HE) in causing intergranular cracking is fairly weak (Inoue, Yamamato and Nagumo, 1980) and for this class of steel, the interactions between the two (TE and HE) with regard to brittle fracture of steel have so far received very little experimental attention. In the present investigation, the temper embrittlement and hydrogen embrittlement of a quenched and tempered Cr-Mo steel (Yield strength, 650 MN/m^2) have been studied in order to further elucidate the interaction between hydrogen and impurities, promoting brittle fracture of the material.

EXPERIMENTAL PROCEDURE

The chemical composition of the steel is shown in Table 1. The material, received in the form of a 12.0 mm thick plate was austenitised at 910 C (1 h), water quenched, tempered at 620 C (1.5 h), followed by water quenching. This quench and temper heat-treatment (QT) resulted in a typical tempered martensitic structure. Standard Charpy V-notch specimens, three-point bend test pieces (5x6x55 mm) having a central 45 V-notch (2 mm deep and 0.25 mm root radius) and flat tensile specimens were machined from the transverse direction of the heat-treated plate. Two-third of the test pieces were given a temper-embrittling heat treatment (TE) as per the following schedule.

580 C (1 hr) $\xrightarrow{\text{Furnace Cooled}}$ (FC) 550 C (5 hrs) $\xrightarrow{\text{FC}}$ 508 C (20 hrs)

$\xrightarrow{\text{FC}}$ 460 (40 hrs) $\xrightarrow{\text{FC}}$ 400 (200 hrs) $\xrightarrow{\text{FC}}$ to room temperature.

Half of the TE samples were de-embrittled (DEMB) by reheating at 600 C (1 h) followed by water quenching. Hydrogen was introduced in QT, TE and DEMB specimens by cathodic charging at room temperature in an aqueous electrolyte (4 per cent H_2SO_4 with 12 mg/lit of arsenic) at a current density of 20 mA/cm^2 for 1 h, and this resulted a hydrogen concentration of about 2 - 3 ppm. Impact, slow bend and tension tests of uncharged samples were carried out in the temperature range, 77-373K. The later tests were carried out in an Instron machine, using a cross-head speed of 8.33×10^{-6} m/s. The hydrogenated samples were tested by tension and slow bend in the temperature range, 200 - 300K, employing the same cross head speed as used for uncharged samples. Fractured surfaces were examined by a scanning electron microscope.

TABLE 1 CHEMICAL COMPOSITION OF THE STEEL (in wt%)

C	Cr	Ni	Mo	Mn	P	S
0.25	3.25	0.2	0.5	0.5	0.03	0.026

RESULTS

Room temperature tensile properties of QT, TE and DEMB states in uncharged and hydrogen charged conditions show that hydrogen did not affect yield stress but reduced ultimate stress and ductility. The impact toughness values of the QT, TE and DEMB states plotted as a function of temperature (Fig. 1) indicate that TE treatment increased ductile to brittle transition temperature (DBTT, temperature corresponding to fracture energy equal to 50 per cent of upper shelf energy). Furthermore DEMB treatment partially restored the loss of toughness (due to TE), as indicated by a smaller rise in DBTT. Fractographic surfaces of samples broken below DBTT, showed transgranular cleavage (Fig. 2b) in QT condition and predominantly intergranular failure in TE state (Fig. 2a). From bend tests, the general yield stress (σ_{GY}) and bend angle (θ_f) at fracture were determined in the temperature range, 200-300K. The general yield stress was calculated using the relationship (Knott, 1974).

$$M_{GY} \quad (P_{GY} \times \tfrac{1}{2} \text{ bending arm}) = \sigma_{GY} \; B(W-a)^2/2\sqrt{3}$$

(using von Mises criterion) (1)

where P_{GY} is general yield load, W = specimen width, B = specimen thickness and M_{GY} is the bending moment necessary to spread yield in the net section. The values of σ_{GY} for QT, TE and DEMB states plotted as a function of temperature (Fig. 3) showed that temperature dependence of σ_{GY} was not affected by TE or DEMB treatment. Similar trends were observed for hydrogen charged samples also but were not included for the sake of clarity.

Bend angles (θ_f) for three states (QT, TE & DEMB) in both uncharged and hydrogen charged conditions are shown as a function of testing temperature in Fig. 4. All the curves (θ_f versus T) showed an upper shelf, a lower shelf and a transition region, very similar to typical impact energy-temperature curves, of Fig. 1. The embrittling effect of hydrogen is clearly demonstrated from the facts that it has caused a reduction in upper shelf values as well as a shift of (θ_f - T) curves to higher temperatures for all the three states (QT, TE & DEMB). Further more the reduction in upper shelf value due to hydrogen charging is maximum in case of TE samples, thereby suggesting that hydrogen embrittlement is more severe in presence of impurity segregation (caused by temper embrittling treatment).

Thus the results of bend tests clearly demonstrate the detrimental effects of hydrogen and impurity segregation on the fracture behaviour of the steel. However the interaction between the hydrogen embrittlement (HE) and temper embrittlement (TE) can be more explicitly described by considering the individual effects of the two (HE & TE) on crack resistance force, G_C. Therefore an attempt has been made to calculate G_c values from the experimentally determined general yield and bend angle values. Following Wells (1961-62) the notch tip displacement

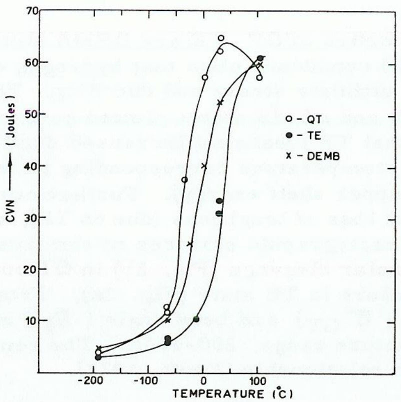


FIG. 1. IMPACT ENERGY (CVN) Vs TESTING TEMPERATURE FOR QT, TE AND DEMB STATES.

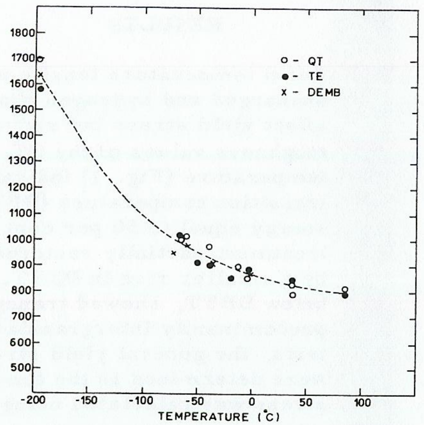


FIG. 3. PLOT OF σ_{GY} VERSUS TESTING TEMPERATURE OBTAINED IN SLOW BEND TEST.

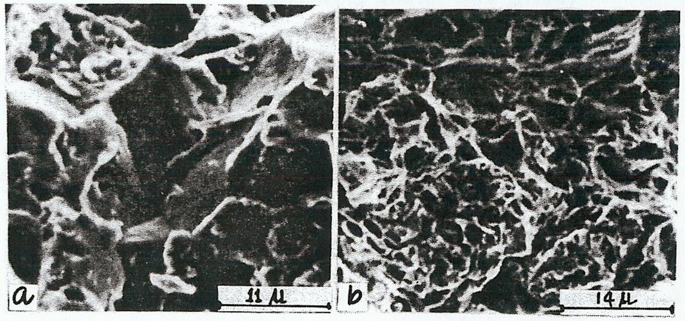


Fig. 2. SEM Fractograph Of Impact Samples

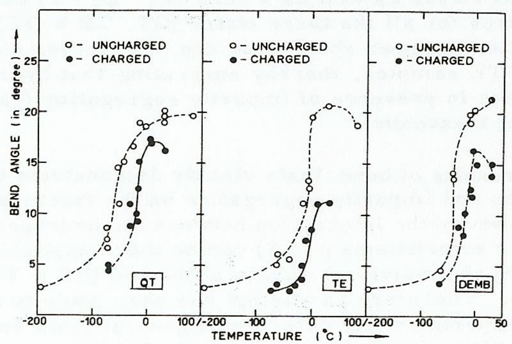


FIG. 4. PLOT OF BEND ANGLE (θ) AT FRACTURE AS A FUNCTION OF TESTING TEMPERATURE.

TABLE 2 SUMMARY OF FRACTOGRAPHY

STATE	CONDIT-ION	TESTING TEMPERATURE	FRACTURE MODE	FIGURE	REMARKS
QT	UN	77 K.	Cleavage	Not in cluded	
QT	UN	273 - 300 K	MVC (P)	6 (a)	
QT	H	200 K	TG BF	6 (b)	
QT	H	273 - 300 K	TG BF	6 (c)	
TE	UN	220 K	TG BF	6 (d)	GB Cracks are also seen
TE	H	220 K	IG (P)	6 (e)	Occasional TG BF features are also present.
TE	UN	273 - 300 K	MVC	6 (f)	Occasional GB cracking are also present
TE	H	273 - 300 K	IG	6 (g)	
DEMB	UN	200 K	TG BF	Not included	
DEMB	H	200 K	TG BF	Not included	
DEMB	UN	273 - 300 K	MVC (P)	Not included	
DEMB	H	273 - 300 K	TG BF	6 (h)	Occasional GB cracks are also seen.

UN = UNCHARGED, H = HYDROGEN CHARGED, MVC = MICRO VOID COALESCENCE,
(P) = PREDOMINANT, TG BF = TRANS GRANULAR BRITTLE FRACTURE,
Gb = GRAIN BOUNDARY IG = INTER GRANULAR.

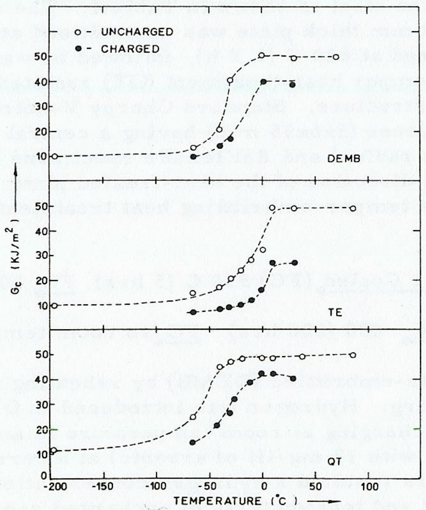
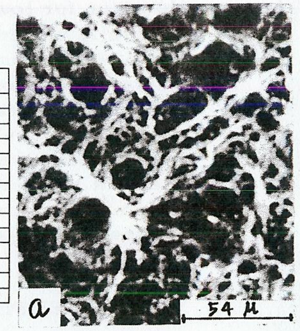
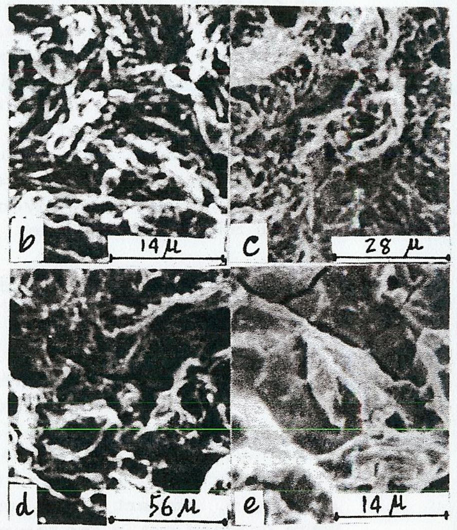


FIG. 5. PLOT OF G_c AS A FUNCTION OF TEMPERATURE WITH AND WITHOUT HYDROGEN FOR ALL THE THREE STATES





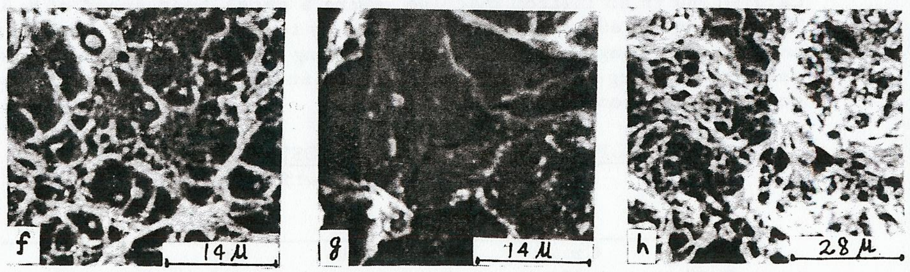


Fig. 6. SEM Fractograph Of Bend Samples

$$2V(C) = a\,\theta \quad (2)$$

where 'a' is a constant, approximately one half the ligament (W-a). For the bend specimens used in the present study, the equation (2) reduces to

$$V(C) = 3 \times 10^{-3} \times \theta \quad (3)$$

Kimura and Masumoto (1980) has shown that V(C) can be correlated to

$$G_C = \sigma_{GY} \times V(C) = 3 \times 10^{-3}\, \sigma_{GY}.\, \theta \quad (4).$$

Although the equation (4) is valid under plain strain condition and in presence of a sharp crack, it may be used to interpret the present experimental results at least in a qualitative way.

Figure 5, shows plots of G_C as a function of temperature for all the three states in uncharged and hydrogen-charged conditions and it varies with temperature in a similar way to the variation of bend angle with temperature (Fig. 4). It is to be noted that in both Fig. 4 and Fig. 5, the effect of TE is felt as an increase in transition temperatures (defined as temperature corresponding to mid-shelf values of θ_f and G_C). The magnitude of the rise in transition temperatures is identical, for about 50 C. For DEMB treatment the shift is about 20 C only, thereby supporting the impact test results (Fig. 1) that DEMB treatment partially restored the loss of toughness suffered from TE heat treatment. However hydrogen has caused an appreciable reduction in upper shelf toughness values (G_C values) as well as an increase in transition temperatures in all three states (QT, TE and DEMB). It is also observed that hydrogen-charging has caused maximum reduction in upper shelf G_C value in case of TE state. Further it should be noted that the upper shelf G_C value at 300K of QT state remains practically unaffected by TE treatment, while it is reduced by hydrogen-charging by about 10 KJ/m^2. On the other hand, when QT state of this steel is first given TE treatment and subsequently hydrogen-charged, the reduction in upper shelf G_C is about 24 KJ/m^2. Therefore it is reasonable to suggest that in low strength steel of the type used in the study, hydrogen-induced embrittlement becomes very pronounced because of prior weakening of grain boundaries by segregated impurities. Results of fractographic studies (Table 2) lends additional support to the mechanical test results as discussed above. The fractured surfaces of QT, TE and DEMB samples in uncharged condition show typical ductile failure (Fig. 6 (a), (f)) in the upper shelf region. Hydrogen charging promotes brittle fracture in all three cases (Fig. 6 (c), (g) & (h)). Further hydrogen causes intergranular fracture in TE state but hydrogen-charged QT and DEMB failed by transgranular cleavage. The fact that combined effects of hydrogen and impurities led to intergranular fracture, support the hypothesis that hydrogen embrittlement is enhanced by prior weakening of grain boundaries by segregated impurities. The present results also indicate that the interaction of impurities and hydrogen can be synergistic and the effect might be moderated by eliminating or reducing grain boundary segregation of impurities (such as DEMB treatment).

DISCUSSION

It is well known that hydrogen does not change the yield or flow stress but reduces the total strain to fracture and a corresponding reduction in ultimate stress. Thus the present results of the influence of hydrogen on tensile properties are consistent with known characteristics of internal hydrogen embrittlement. It is also known that effect of hydrogen is enhanced by slow strain rate and moderately high temperature. Results of slow bend tests of present work have demonstrated that bend tests can clearly bring out the detrimental effects of hydrogen at least in a qualitative way. The most interesting observation of this study demonstrates that like in high strength steels (Yoshino and McMahon, 1974; Mabuchi, 1982), the combined effects of impurity segregation and hydrogen caused maximum embrittlement in a low strength steel used in the present case. It has been pointed out by Mabuchi (1982) that a steel in quenched and tempered condition and in the presence of impurity elements at grain boundaries should be treated as a composite material because of the fact that the grain boundary and the matrix will have different chemical composition and hence different physical properties. It is also known that a crystalline solid fails by brittle fracture (by transgranular or intergranular fashion), when the local stress reaches the cohesive strength of a particular crystallographic plane or an intercrystalline boundary. The cohesive strength of a crystalline plane or an intercrystalline boundary can also be reduced by local hydrogen concentration. Because of its high mobility in the ferrite lattice at room temperature, hydrogen diffuses under the influence of an applied tensile stress and concentrates in regions of maximum hydrostatic tension. The equilibrium concentration of hydrogen (C_H) in the stressed lattice is given by the following equation (Li, Oriani and Darken, 1966)

$$C_H = C_0 \exp \frac{\Omega\, \theta}{RT}$$

where Ω : the atomic volume of hydrogen in the lattice

θ: the hydrostatic stress $= 1/3\,(\sigma_1 + \sigma_2 + \sigma_3)$

C_0: the equilibrium concentration of hydrogen in an unstressed lattice

The maximum hydrogen enrichment at full constraint can be estimated for steels with various levels for yield strength using $\Omega = 2.0\ cm^3/mol$, T = 300K and R = 8.32 x 10^7 erg/mol K. The enrichment of hydrogen C_H/C_o for the present steel having yield strength 650 MN/m^2 (6.5 x 10^9 $dyne/cm^2$) will be 4.6 in the presence of the maximum hydrostatic tension (i.e. in the plastic zone ahead of notch). In absence of impurity segregation (i.e. when grain boundary and matrix have comparable cohesive strength), the result of the stress induced hydrogen concentration is transgranular cleavage fracture at stress/temperature conditions, where plastic rupture would normally be observed. Fractographic results of this study showing transgranular cleavage failure in QT and DEMB samples confirm this concept. When intergranular impurity segregation is also present, the local value of hydrogen concentration (C_{OB}) at grain boundary could be larger than in the lattice due to an affinity of hydrogen for segregated impurities at the grain boundaries. This effect was estimated to be about $C_{OB}/C_o \simeq 7$ by Oriani and Josephic (1974). This large concentration of hydrogen at grain boundaries reduces the cohesive strength of grain boundary to a much greater extent than the matrix resulting in intergranular failure with a very low value of G_c. According to Briant, Banerji and McMahon (1977) when sulphur is present an additive or even synergistic hydrogen accumulation can be foreseen. Further, many studies correlating the grain boundary phosphorous concentration and hydrogen cracking sensitivity of high strength steels have shown that in the absence of this impurity, hydrogen cracking progresses in a transgranular manner. The steel used in the present work contains about 300 ppm each of S&P. Therefore combined effects of these impurities and hydrogen appear to be synergistic and can lead to intergranular brittle fracture even at low strength level, as noted in fractured samples of hydrogen-charged TE sample.

CONCLUSION

The following conclusions can be made from this study :

1. Low alloy steel of low yield strength can be made susceptible to intergranular cracking when both impurity segregation and hydrogen are present.
2. It is necessary to have impurities at the grain boundaries for hydrogen embrittlement with intergranular fracture mode.
3. Deembrittlement treatment can be successfully employed to reduce the susceptibility to intergranular cracking.

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