



DEVELOPMENT OF HSLA STEEL FOR HYDROGEN SERVICE IN OIL AND GAS INDUSTRIES

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ABSTRACT

A dual-phase X65 steel (DPS) was tempered at 300 °C and 500 °C respectively, for periods ranging from 24 hours to 72 hours. Tempering converts the martensite to (α +Fe₃C), relieves the residual stresses, and causes precipitation of microalloy carbides, and their eventual coarsening. The strength and ductility of the tempered steel are determined by the combined effect of these microstructural changes. Fine dispersions of microalloy precipitates can enhance the uncharged and charged strength by impeding dislocation glide, and by distributing trapped hydrogen homogeneously, such that the critical hydrogen concentration required for crack nucleation at traps is not attained. The charged ductility is improved simultaneously. It is concluded that tempering at 500 °C for 24 hours or at 300 °C for 72 hours approximately, results in an excellent resistance to hydrogen embrittlement which makes this material a potential candidate for oil and gas industries where hydrogen embrittlement is an oft-recurring phenomenon. Mechanical test results, scanning electron microscope (SEM) observations, and quantitative energy dispersive x-ray (EDX) analysis data are reported.

Keywords: *Hydrogen embrittlement, microalloy carbides, martensite, tempering, dual phase, high strength low alloy steel*

(α + Fe₃ C)

1. INTRODUCTION

The detrimental effect of hydrogen ingress on the strength and ductility of steel that results in hydrogen embrittlement (HE) and catastrophic failures is well documented. Thus, HE and the brittle mode of fracture, which it gives rise to is a serious concern in petroleum related industries. Environment sensitive fracture (ESF) in general, and that related to hydrogen, in particular, constitute over 25 percent of failures experienced in the oil and gas industry [Kermani, 1995]. These failures can often impose heavy economic penalties.

Recently, the premature hydrogen induced cracking (HIC) of drill string components has acquired increased significance in drilling engineering design and research. These failures take place more often in directional wells and are rarely noticed until a washout or a twist off occurs [Kermani, 1989, Hampton, 1987]. It is now recognized that, most of these failures are induced by a corrosion fatigue process that involves cyclic stresses in the presence of drilling fluids which assist in the nucleation and propagation of corrosion fatigue cracks. Studies of these problems have been meagre [Kermani, 1989, Dale, 1986, Gonzalez-Rodriguez, and Procter, 1993]. In production facilities, HE is emphasized by describing the significance of H₂S-containing media in the choice of production tubing and in corrosion fatigue of marine structural steels. The selection of materials is determined by mechanical properties, resistance to both corrosion damage and sulphide stress cracking (SSC), as well as availability and cost. SSC is caused by a combination of tensile stress and a H₂S-containing environment. H₂S, in such circumstances has a two-fold role: It lowers the solution pH and it facilitates the entry of atomic hydrogen into the material [Kermani, et al., 1991].

Considering the limitations of NACE MRO175 [NACE Standard, 1994] to address solution chemistry, the limits of sour service have been redefined for a range of carbon and low alloy steels as well as corrosion resistant alloys. Thus, plots correlating solution pH with H₂S partial pressure in a domain type relationship have been developed [Kermani, et al., 1991, Kermani, et al., 1993]. The domains characterize the suitability of different materials and tubular products with respect to their SCC behaviour [Kermani, et al., 1991].

The presence of H₂S, CO₂ and brine in crude oil not only accelerates corrosion rates, but also can cause environmental fracture enhanced by increased uptake of hydrogen atoms by the steel. In addition to SSC in oil and gas transportation pipelines, absorption of hydrogen generated by

corrosion of carbon steels in wet H₂S-containing media can induce blistering in pipeline steels. Blistering cracks along the rolling direction of the steel are associated with inclusions and segregations. The terms hydrogen induced cracking (HIC), hydrogen pressure cracking and hydrogen induced stepwise cracking are used to describe this phenomenon.

Many large marine fixed gas and oil production platforms are constructed from relatively low strength C-Mn marine structural steels. The fatigue performance of these steels when stressed in saline solutions has been widely researched. [Sentence, 1991, Turnbull and Saenz De Santa Maria, 1988, Dover and Dharmavasan, 1992, Kermani and Abbassian, 1993, ASME, Case, 1991, Liaw, 1992]. These studies have shown that saline environments increase the fatigue crack propagation rates, compared to the values measured in air, by a factor of 2-4, depending on the stress intensity range and the cathodic protection level.

In corrosion fatigue incidents, hydrogen entry occurs during exposure to the saline environment and this causes the observed hydrogen embrittlement (HE). The resulting acceleration in crack growth rate decreases the predicted life of tubular joints [Dover and Dharmavasan, 1992, Kermani and Abbassian, 1993]. Recent investigations [Alp, and Iskandrani, 1985, Alp, et al., 1987, Alp, et al., 1989, Alp, and Iskandrani, 1991, Alp, et al., 1991, Alp, et al., 1995, Alp, et al., 1997] strongly indicate microalloyed steels containing vanadium, niobium and titanium to be amenable to acquire resistance to hydrogen embrittlement (HE) when subjected to an appropriate thermomechanical treatment. Against this background, this paper describes the effect of tempering on the resistance to (HE) of a DPS microalloyed to contain V, Nb, and Ti.

2. EXPERIMENTAL METHODS

2.1 The Material

The chemical composition of the X65 steel is given in Table 1. Rectangular blocks of the steel, approximately 14 mm in thickness were procured from the British Steel Corporation in England. The steel was hot-rolled to a thickness of about 2 mm.

Table 1. The Chemical Composition (weight %) of X65 Steel.

C	Mn	V	Nb	Ti	Si	S	P	Cr
0.05	1.4	0.06	0.04	0.01	0.2	0.006	0.017	0.01
Co	Cu	Al	Sn	Ni	As	Ca	Mo	Fe
0.01	0.32	0.042	0.01	0.25	0.0001	0.01	-	balance

Dumb-bell shaped miniature tensile test specimens of 20mm gauge length, 5mm width and 1 mm thickness machined from the rolled sheets with their long axis parallel to the rolling direction were polished to ¼ micron finish prior to hydrogenation.

2.2 Dual-Phase Treatment and Tempering

The specimens are dual-phase treated by soaking at 850 °C in the inter-critical temperature region for 20 minutes for equilibrium partitioning of alloying elements between proeutectoid ferrite and austenite. This is followed by quenching into an ice-water bath at 0 °C. Separate groups of DPS specimens were tempered at, 300 °C and 500 °C respectively for periods ranging from 24 hours to 72 hours. Tempering is followed by rapid quenching into a well stirred bath of ice-water mixture at 0 °C.

2.3 Hydrogenation, Mechanical Testing, and Scanning Electron Microscopy (SEM)

The hydrogenation unit essentially comprises an electrolytic cell with a platinum anode and a steel specimen as the cathode immersed in a dilute solution of sulphuric acid as the source of hydrogen ions. A trace of arseneous oxide first dissolved in a small volume of sodium hydroxide solution, is added to the electrolyte to prevent the recombination of H⁺ ions. The specimens are charged with hydrogen, only along the gauge length (20mm). A constant current density of 10 mA/cm² is applied for a period of 30 minutes. Tensile specimens were stressed uniaxially, maintaining a constant cross-head speed of 2 mm/minute. Experiments were performed in triplicate to check reproducibility. Thus the data points in Figs 1-6 represent averages of the pertinent mechanical properties. Reproducibility was found to be excellent with a standard deviation of 0.75 for strength and 0.91 for elongation. Fractographic features of interest were studied using SEM. EDX was used to carry out elemental spot analysis.

3. DISCUSSION OF RESULTS

3.1 Dual- Phase Treated X65 Steel

The dual-phase microstructure consists of martensite islands engulfed by a highly ductile ferritic matrix. The steel exhibits a clear yielding behaviour at a stress level of about 549 MPa. The ultimate tensile strength (UTS) is 671 MPa. The tensile ductility is calculated to be around 24%. Despite the strengthening achieved by the austenite to martensite transformation the largely ferrite matrix confers a commendable level of ductility upon this steel. The dual- phase hardness is, around 96HR_B.

3.2 Tempering at 300 °C

The major structural changes occurring during tempering of steel are well established [Speich and Leslie, 1972]. In HSLA steels, the physical processes taking place during tempering and the concomitant property changes tend to be more involved than those observed in plain carbon steels. In general, the initial stages of tempering at a given temperature are characterized by a

decrease in mechanical strength which is attributed to martensite-to- ($\alpha + \text{Fe}_3\text{C}$) transformation. The conversion of martensite into a dispersion of cementite in the absence of microalloying elements results in softening. However, when potent carbide-forming elements exist in the steel, their respective carbides are also precipitated simultaneously with cementite and this compensates for part of the strength loss arising from transformation of martensite to ($\alpha + \text{Fe}_3\text{C}$).

The mechanical behaviour of DPS tempered at 300 °C and 500 °C for 24, 48 and 72 hours is illustrated in Figs 1-6. Tempering at 300 °C for 24 hours reduces the yield strength and the UTS to 441 MPa and 563 MPa respectively. The elongation falls to 21.75%.

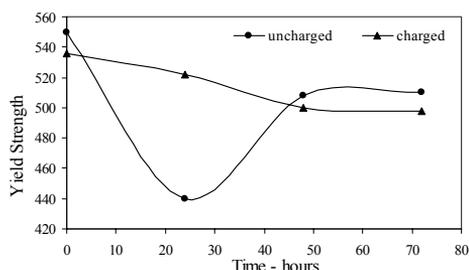


Figure 1. Variation of yield strength with tempering time at 300 °C before and after charging with hydrogen.

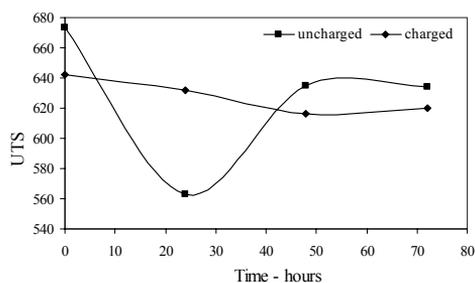


Figure 2. Variation of UTS with tempering time at 300 °C before and after charging with hydrogen.

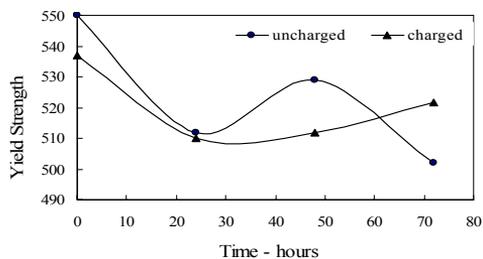


Figure 3. Variation of the yield strength with tempering time at 500 °C prior and subsequent to hydrogenation

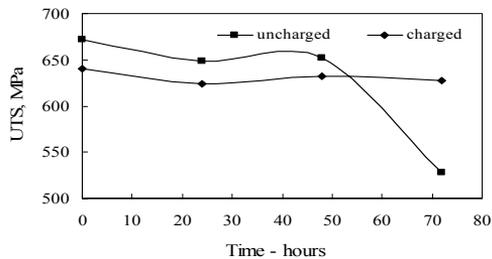


Figure 4. Variation of UTS with tempering time at 500 °C prior and subsequent to hydrogenation

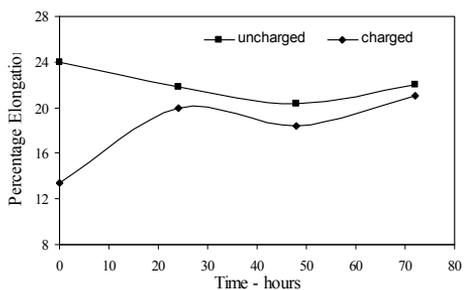


Figure 5. Elongation vs tempering time at 300 °C

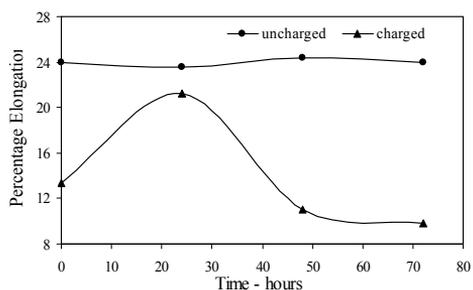


Figure 6. Elongation vs tempering time at 500 °C

The micro-alloying additions Nb, Ti, and V present in the steel used are known to be carbide-formers. Upon quenching from high annealing temperatures, these elements tend to precipitate their respective carbides or carbonitrides which result in a relative strengthening of the steel. The efficacy of the strengthening due to these carbides depends on their solubilities, size, shape, distribution, volume fraction, locations (grain boundaries, dislocations or slip planes), the degree of coherency with the matrix, and the annealing as well as the tempering temperature. Thus, at any tempering temperature cementite conversion from martensite on one hand and the nucleation and growth of carbides of microalloying elements on the other, present two conflicting trends. The net effect, is determined by the relative predominance of the two competing factors.

Accordingly, with increasing tempering time (48 hours) at 300 °C, the strength registers a significant increase indicating microalloy carbide precipitation to be preponderant. The yield strength, and the UTS reach 507, and 635 MPa respectively, while the tensile ductility attains 20.5%. It is evident that both the tempered yield and the tensile strengths experience a significant increase and reach their highest respective values after about 50 hours.

Upon ageing for 72 hours at 300 °C the yield strength increases slightly to about 510MPa indicating a greater density of obstacles tending to anchor around gliding dislocations. Precipitation, temperature, time (PTT) curves constructed for a HSLA steel containing niobium (0.04%) and aluminium (0.08%) have demonstrated precipitation to commence around 900 °C [Wang and Akben, 1986]. The solid solubilities of the microalloyed carbides and nitrides are approximately an order of magnitude less in ferrite than in austenite. Hence, given the prerequisite time for atomic diffusion, substantial precipitation of the relevant microstructural constituents occurs. Medium sized precipitates ($\sim 10^2$ nm) of NbC and TiC have been observed to precipitate on grain boundaries and substructures. At relatively lower temperatures, rows of fine NbC, TiC and V (CN) particles (10^{-1} nm in size) precipitate at interfaces. At low temperatures NbC, TiC and V(C, N) form fine and semi-coherent precipitate clusters (<10 nm) in ferrite [Meyer, et al., 1986].

Considering that the solubility of Nb in austenite is $\sim 0.0083\%$ [Irving, et al., 1967], in the upper ferrite temperature range, significant Nb supersaturation results in the formation of very fine, semi-coherent NbC particles causing considerable strengthening. Likewise, an extremely fine dispersion of TiC in ferrite contributes to strength. Unlike Nb and Ti, V exhibits marked solubility in steel. The relatively high solubility of the compounds in vanadium alloyed steels causes the precipitation in low carbon steels to go through undercooling down into the range of ferrite, where considerable precipitation strengthening occurs. In quenched and tempered steels the additional increase in strength witnessed upon tempering [Meyer, et al., 1986] at relatively lower temperatures is principally ascribed to VC precipitation.

It is well established that the austenite transformation is accompanied by a significant increase in volume. This induces residual tensile stresses in the matrix surrounding the martensite islands, and subjects the martensite to compressive residual stresses. The tensile component of the residual stresses in the ferrite matrix would be additive to the applied tensile stress such that specimens

stressed in tension tend to fail prematurely. Hence, relief of residual stresses contributes positively to the overall strength.

Figure 3 depicts the variation of ductility with tempering time at 300 °C and 500 °C. Tempering at 300 °C decreases the ductility of the uncharged steel. This fall in elongation is the sum total of such contributions that arise mainly from martensite to $(\text{Fe}_3\text{C} + \alpha)$ transformation and microalloy carbide precipitation (leading to hardening). Tempering beyond about 50 hours at 300 °C improves the tensile ductility probably due to partial softening of the matrix which becomes progressively denuded with respect to carbon as well as substitutional solute atoms.

3.3 Tempering at 500 °C

As the pertinent data indicates clearly, the yield strength, and the tensile strength pass through maxima following tempering at 500 °C for about 50 hours. The tensile ductility reaches its pre-tempering value of 24% and remains constant irrespective of the tempering time.

The development of strength in this steel during tempering at 500 °C is primarily attributed to the beneficial influence of microalloying elements in general and that of vanadium in particular. Vanadium first retards softening and then brings about secondary hardening. Despite the fact that hardness decreases at higher tempering temperatures due to over ageing, vanadium still exercises an increased resistance to tempering. This is in agreement with the observations of [Grange et al., 1977 and Krauss, 1980]. Alloying elements influence the extent of tempering by virtue of being dissolved in austenite at the annealing temperature. The solute retained in martensite can affect temperability primarily by influencing the subsequent carbide precipitation and growth by participating in the carbide reaction; modifying the distribution of dislocations during tempering by inhibiting recovery, and by dislocation annihilation and polygonization. This occurs above 400°C [Pickering, 1977] when carbide precipitation inhibits recrystallization and grain growth of the ferrite matrix and prevents cross slip of dislocations. Retardation of softening in the early stages of tempering due to the presence of vanadium is rated at 80 HV/1%V [Grange et al., 1977]. This is attributed to delayed Fe_3C formation whose growth rate is diminished by the lowering of carbon activity in ferrite by vanadium. Niobium exhibits a similar influence to that of vanadium in this respect.

In addition to the strengthening of the DPS tempered at 500 °C, an impressive tensile ductility level of 24% is maintained. Progressive precipitation of microalloy carbides and concurrent dissolution of cementite in the ferrite matrix enhances the work-hardening capability of the matrix, thus permitting the plastic deformation to be widely spread. This is particularly significant, since an acceptable level of ductility is prerequisite in selecting a material for use in hydrogenous media. In this respect titanium exerts a beneficial effect by the formation of the titanium carbosulphide ($\text{Ti}_4\text{C}_2\text{S}_2$) precipitate, instead of MnS which deforms into undesirably long

strings during rolling. $Ti_4C_2S_2$ remains underformed during rolling and is more stable than MnS. Hence, the cold formability of the steel is improved by restraining MnS formation [Liu, et al., 1989].

3.4 The Effect of Hydrogenation on the Mechanical Properties of Tempered DPS.

Hydrogenated DPS is characterized by a yield strength of 537MPa, tensile strength of 642MPa, and an elongation of 24 %. Hydrogen diffuses to the ferritic regions stressed in tension around martensite and accumulates there to play a negative role in crack initiation with or without the application of an external stress.

The beneficial effect of tempering at 300 °C in mitigating the detrimental role of hydrogen is strikingly clear. The yield and tensile strength of hydrogenated specimens decreased slowly with tempering time (Figs 1 and 2). For the specimens tempered at 300 °C for 24 hours and charged, the yield strength, tensile strength, and tensile ductility are maintained at 521 MPa, 632 MPa and 20% respectively.

Thus, tempering at 300 °C commences an onset of precipitation of finely dispersed coherent microalloy carbide particles, which act as benign traps for lattice hydrogen. The vast population of these traps serves to distribute hydrogen homogeneously such that, its concentration at any one trapping site does not exceed the critical level required for microcrack initiation. Accordingly, as depicted in Fig 5, tempering at 300 °C for progressively longer times increases the ductility by increasing the number density of benign microalloy trap sites for hydrogen. The binding of hydrogen at such trapping sites has been reported [Podgurski and Oriani, 1972, Pressouyre and Berstein, 1978, Stevens, 1984, Asaoka et al., 1977]. Another advantage of tempering is the relieving of residual stresses associated with martensite transformation. The achievement of high charged ductility (21%) and strength in DPS tempered for 72 hours at 300 °C is particularly significant.

Tempering at 500 °C for 24 hours results in a charged yield strength of 510 MPa. The ultimate tensile strength is maintained at 623 MPa (Fig 4). The strength maxima observed in Fig 3 and 4 are attributed mainly to secondary hardening due to VC and TiC precipitation. A substantial increase in the charged ductility of specimens tempered for 24 hours compared to the untempered is noted (Fig 6). Prolonged ageing (72hours), however, causes reduction in strength, which is ascribed partly to precipitate coarsening. VC precipitation on dislocations also influences the elongation negatively. Dislocations thus impeded, give rise to higher yield and tensile strengths, and reduced elongation associated with localized plastic deformation.

3.5 The Effect of Hydrogenation on the Mode of Fracture

The mode of fracture of the DPS is predominantly ductile and characterized by microvoid coalescence (Figs 4a, and 4b). This is in agreement with previous observations [Alp et al., 1988]. Upon hydrogenation, however embrittlement sets in. The numerous rosettes observed in the fracture surface even at low magnification (Fig.5) are indicative of susceptibility to HE, which

causes about 45% loss of ductility. Close observation of the rosettes shows these locally embrittled sites to be frequently associated with non-metallic inclusions (Fig. 6) of the oxide, sulphide or oxy-sulphide type. The matrix surrounding the rosette retains appreciable ductility (13%) as evidenced by fine dimples (Figs 5, 6).

Tempering at 300 °C for 24 hours leads to a predominantly dimpled microstructure (Fig 7). Hydrogenation causes localized embrittlement in the form of shallow rosettes (Fig 8) engulfed by a rim of microvoid coalescence and finely dimpled matrix, signifying substantial ductility (20%), and enhanced strength.

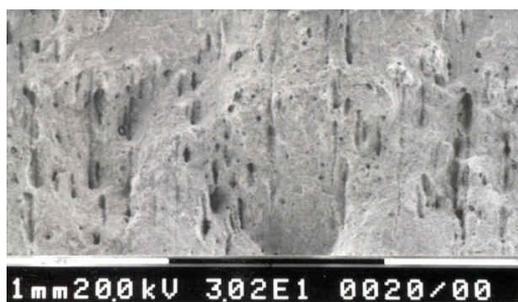


Fig 4a. Fracture surface of DPS ▲
b. Ductile fracture in DPS, as evidenced by microvoid coalescence. ►

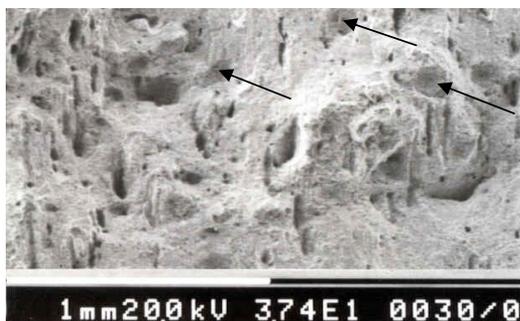
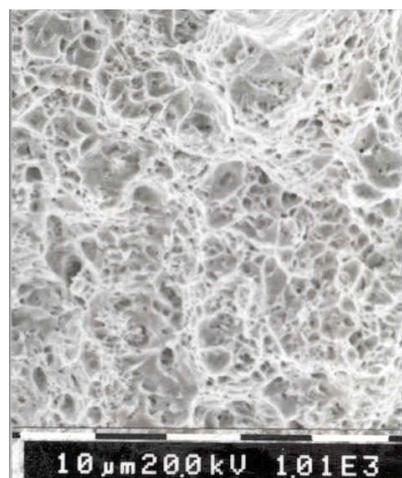
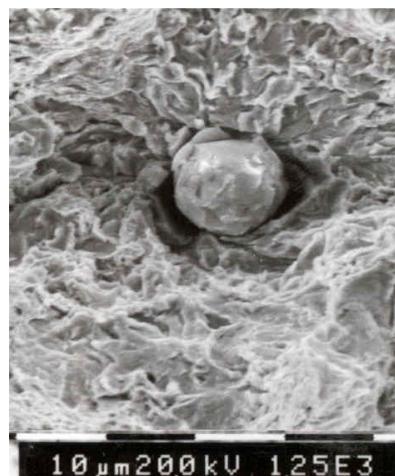


Fig. 5 Rosettes (arrowed) in charged DPS. ▲

Fig.6 A rosette with an inclusion in charged DPS. ►



With extended (72 hours) tempering at 300 °C the ductile mode of fracture persists. The tensile ductility makes a measurable gain (7.3%) and reach 22%. It is believed that the fine dispersion of microalloy carbide particles play a paramount role in partitioning hydrogen homogeneously so that the critical hydrogen concentration required to nucleate a hydrogen-induced crack (HIC) at these sites is generally not attained. Thus, the number density of embrittled rosettes is effectively diminished. Fig 9 depicts a precipitate acting as an innocuous site for hydrogen trapping. Matrix ductility evidenced by extensive dimpling in close proximity to the precipitate is suggestive of the resistance of the steel to HE.

Tempering at 500 °C for 24 hours further elevates the strength and the ductility. The resulting microstructure is depicted in Fig 10. As in previous instances, a good combination of strength and ductility is characterized by fine microvoids homogeneously distributed throughout the matrix. Typically, brittle cementite films at prior martensite/ferrite interfaces play the usual detrimental role on the strength and elongation. Hydrogenation does not alter the yield strength, while the tensile strength and the ductility are lowered slightly to 623 MPa and 21.15% respectively. These changes are reflected in the microstructural observations recorded in Fig 11. Although few hydrogen-induced rosettes associated with inclusions are detected, a ductile matrix around microalloy precipitate is prevalent (Fig. 12). Secondary hardening in specimens aged at 500 °C is thought to accrue from precipitation of VC on dislocations.

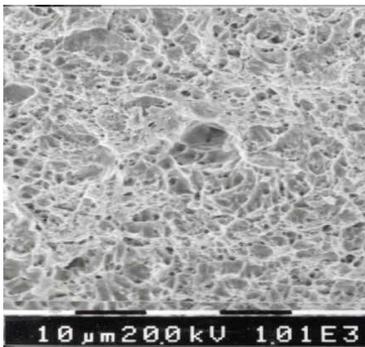


Fig. 7 Ductile dimpling in steel tempered at 300 °C for 24 h.

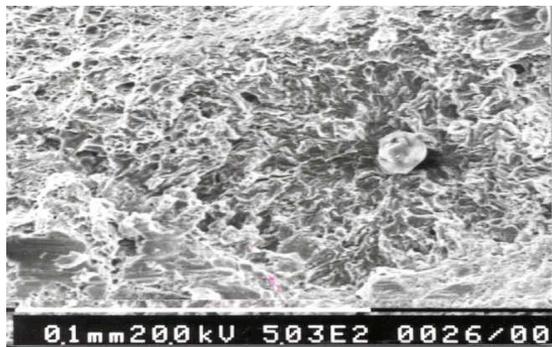


Fig. 8 A rosette embedded in ductile matrix in steel tempered at 300 °C for 24 h.

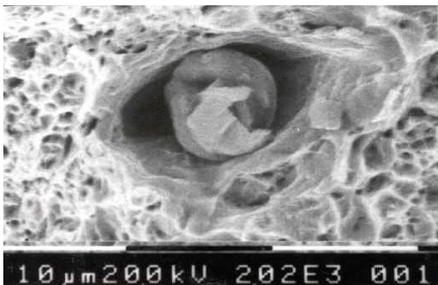


Fig. 9 A microalloy precipitate as benign site.

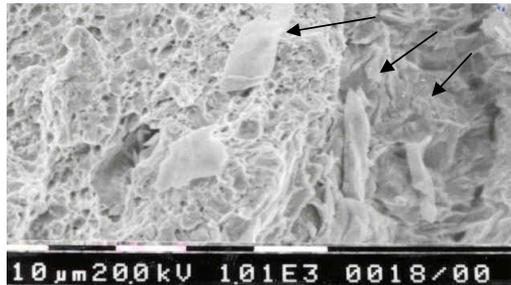


Fig. 10 Ductile dimples in steel tempered at 500°C for 24 h, with Fe₃C film (arrowed).

The microstructure arising from tempering at 500 °C for 48 hours consists of the usual features already discussed. Hydrogenation results in embrittlement as evidenced by the rosetted fracture surface characteristics. Non-metallic inclusions act as trap for hydrogen, leading to internal hydrogen pressure build-up and eventual HIC. The major event which occurs during tempering at 500 °C for 72 hours is microalloy precipitate coarsening. Hydrogenation alters the fracture surface appearance, such that brittle facets and large embrittled rosettes associated with coarse particles and complex aggregates (Fig 13) acting as HIC nucleation centres are the dominant characteristics. Accordingly, the ductility is reduced to a minimum value of 10%. An EDX analysis of the inclusions showed them to be composed of mainly iron, with some Si, Cl, K and Mn, probably in the form of SiO₂, K₂O and MnS respectively (Fig. 14). A detailed investigation on a similar steel has shown most of the non-metallic inclusions associated with fracture surfaces to consist of complex mixtures of oxides, sulphides or silicates [Bin Zakaria, 1989] with traces of microalloy elements in the form of their respective carbides.

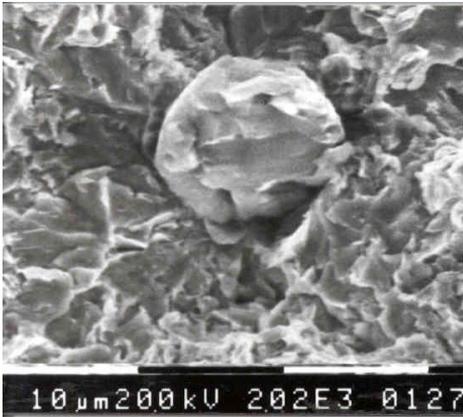


Fig. 11 An oxide inclusion as HIC initiation site.



Fig. 12 A microalloy precipitate in ductile matrix.



Fig. 13 An Aggregate of inclusions as HIC site.

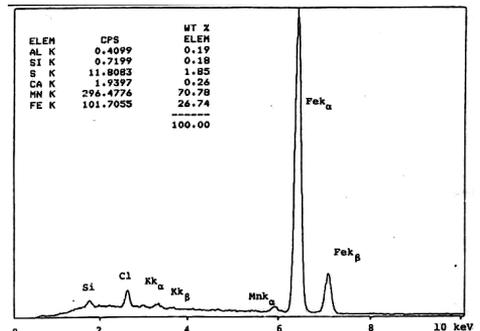


Fig. 14 EDX plot for the inclusion in Fig. 13.

4. CONCLUSIONS

1. The X65 microalloyed steel in the dual-phase state possesses a good combination of strength and ductility. Upon hydrogenation of the untempered DPS, the ductility is decreased markedly. The degradation of ductility is attributed to an interaction between hydrogen and residual tensile stresses resulting from martensite formation.
2. Tempering mitigates HE by precipitating a fine dispersion of microalloy carbides which serve as benign traps for hydrogen and by relieving the residual stresses associated with martensite transformation.
3. Tempering at 300 oC for 24 hours yields a high tensile ductility of about 20% at the expense of slightly lowering the yield strength and the UTS to 522 MPa and 633 MPa respectively. The tempered DPS having these properties can be considered to be a candidate material for tubular products for hydrogen service in the oil and gas industries.

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