# THE EFFECTS OF HYDROGEN ON THE MECHANICAL PROPERTIES OF A 2¼ Cr Mo ALLOY STEEL

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## ABSTRACT

The effect of hydrogen on the mechanical properties of a low alloy steel (2¼ Cr 1 Mo) with low and high phosphorus contents was studied by slow tensile testing and metallographic examination of fractures. The high phosphorus steel was examined with and without rare earth additions of cerium and lanthanum. Specimens were heat treated to produce temper embrittled and retoughened structures and their fracture surfaces examined in situ in the Auger microscope. Samples were electrolytically charged in hydrogen and slow tensile tested over a range of temperatures. Although the hydrogen caused a large reduction in ductility, especially at low temperatures, there was not always a change in fracture mode. At a hydrogen concentration of 4.5 ppm the fracture mode changed from quasi-cleavage and microvoid coalescence at ambient temperatures, to quasi-cleavage or pure cleavage at $-80°C$, for all specimens except the temper embrittled. The temper embrittled material fractured intergranularly at $-80°C$ indicating a cooperative effect between phosphorus and hydrogen at that temperature. Evidence for grain boundary segregation of phosphorus was obtained from Auger spectroscopy. In all cases hydrogen increased the flow stress of the alloys, the effect becoming more pronounced at room temperature.

## KEYWORDS

Fracture toughness, hydrogen embrittlement, low alloy steels.

## INTRODUCTION

One of the most widely used steels for thick-walled structural applications has the base composition 2¼ Cr 1 Mo. Previous work has indicated that this steel is susceptible to temper embrittlement caused by the segregation of Mn and Si, together with impurities such as P and Sn, to prior austenite grain boundaries (Yu and McMahon, 1980). Evidence for the impurity segregation has been provided by Auger electron spectroscopy (AES) (see also Hippsley, Knott and Edwards, 1980, and Wada and Hagel, 1976).

Hydrogen is also known to be a potent embrittling agent for steels, reducing the ductility and significantly accelerating crack growth rates in a critical range of temperatures and strain rates. This degradation of properties is found to a greater or lesser extent whether cracking proceeds by a dimple-rupture-hole growth mechanism, cleavage, or by intergranular fracture (Beachem, 1972). For low strength steels hydrogen tends to degrade the properties without changing the fracture mode (Thompson, 1974); for higher strength steels hydrogen induces failure at lower stress intensity levels and this can also lead to a change in fracture path, with a quasi or brittle cleavage failure becoming intergranular in steels with grain boundary segregation (Beachem, 1972).

Many similarities have been noted in the literature between the phenomena of hydrogen embrittlement and temper embrittlement of alloy steels. Attempts have been made to examine the possibility of a synergistic effect between the two forms of embrittlement. These studies have shown that such interactions do indeed exist, and that the presence of impurities in a steel can often increase the propensity to grain boundary failure in the presence of hydrogen (Yoshino and McMahon, 1974; and Yakedai and McMahon, 1982). Although the temper embrittlement of $2\frac{1}{4}$ Cr 1 Mo steels has been widely studied, we are not aware of any work that has attempted to see if co-operative effects of temper embrittlement and hydrogen embrittlement might also be important in this alloy. One of the aims of the present investigation was to characterize the nature of the embrittlement of a $2\frac{1}{4}$ Cr 1 Mo steel after a variety of heat treatments and to investigate the role of hydrogen and its influence on the mechanical properties of the alloy.

### EXPERIMENTAL MATERIALS, PROCEDURES AND TECHNIQUES

#### Steels Received, Composition and Heat Treatment

The chemical compositions of alloys supplied by Dr. W. Tyson of CANMET are presented in Table 1. Two alloys designated A, one a pure and the other a

TABLE 1   Chemical Compositions of $2\frac{1}{4}$ Cr 1 Mo Steels WT%

|     | Alloy A (pure) | Alloy B | Alloy D* |
| --- | --- | --- | --- |
| C   | 0.12   | 0.11   | 0.12   |
| Cr  | 2.33   | 2.25   | 2.29   |
| Mo  | 1.01   | 1.01   | 0.98   |
| Mn  | 0.47   | 0.46   | 0.53   |
| Si  | 0.37   | 0.37   | 0.48   |
| P   | 0.005  | 0.038  | 0.039  |
| Sn  | 0.001  | 0.001  | 0.001  |
| S   | 0.005  | 0.005  | 0.002  |
| Al  | 0.033  | 0.035  | 0.038  |
| Ni  | <0.01  | <0.01  | <0.005 |
| V   | <0.005 | 0.003  | <0.005 |
| Fe  | bal    | bal    | bal    |

commercial steel, were received in the normalized and tempered condition. (925°C 1 hr air cooled, 725°C 3/4 hr air cooled). Alloys B and D (containing cerium and lanthanum) were austenitized for 1 hr at 675°C, air cooled and then step cooled from 595°C to 470°C over a period of a week to produce

temper embrittlement (identified as B1 or D1). Some of alloys B and D were further heat treated at 650°C for $\frac{1}{2}$ hr (B2) and 3 hrs (B3 or D3) in an attempt to retoughen the steel.

Optical metallography performed on these steels identified alloy A (commercial) as consisting mainly of bainite with a hardness of 14 RC. Samples B1, B2, and B3 did not differ in structure optically and had the same hardness of 21.5 RC. In each case the microstructure was that of tempered martensite. Samples D1 and D3 were very similar to B1, B2, B3 except for a higher inclusion content.

#### Specimen Preparation

Smooth round button end tensile samples of all the above heat treated steels of gauge diameters 4 mm (0.160") were machined from 13 mm (0.5" plate) with tensile axes normal to the rolling direction. Charpy test specimens were also prepared from B1, B2, B3, D1 and D3 plate, again normal to the rolling direction. Also the B1, B2 and D1 materials were machined to make round specimens with a diameter of 3.6 mm (0.144") length of 28 mm (1 1/8"), and a sharp notch was inserted 10 mm (0.40") from one end, for subsequent fracture and examination in the Auger microscope.

#### Hydrogen Charging and Analysis

Preliminary charging experiments were carried out on Auger fracture samples and tensile samples. All material was electropolished in a solution of 5% perchloric acid in glacial acetic acid and charged in a solution of 0.1N $H_2SO_4$, with 1 mg/l of $As_2O_3$ added as a hydrogen recombination poison. The samples were charged at a range of current densities for times up to 18 hrs and then washed in distilled water and transferred to a solution of 0.1N NaOH. The decay current associated with hydrogen diffusing out of the sample was recorded and the hydrogen content determined from the area under the current vs time curve. These values were compared to those measured by analysis in a Leco hydrogen analyser. Good agreement was observed between the two methods of measuring hydrogen contents for a given condition of cathodic charging.

Selected samples were sectioned and examined in the scanning electron microscope to determine whether cathodic charging had produced any damage.

Tensile samples were coated with acid resistant lacquer on all but the gauge length and charged at a current density below that which produced voids and cracks (70 Am$^{-2}$ for 3 hrs) and then transferred to liquid nitrogen to prevent loss of hydrogen.

#### Mechanical Testing

Tensile tests of both charged and uncharged A, B1, B3, D1 and D3 were performed at a strain rate of $3.5 \times 10^{-4}$ s$^{-1}$ on an MTS testing machine at temperatures between -80°C and 25°C. The test temperatures below ambient temperature were obtained by immersing specimens in baths of dry ice and methanol. After testing the reduction in area at the fracture surface was calculated from measurements made using, firstly, an optical microscope, and secondly, vernier calipers. For each condition of charging and microstructure several broken halves were stored in liquid nitrogen, immediately after testing, for hydrogen determination. The fracture surface for each test sample was examined in the scanning electron microscope to determine

the fracture mode. To ensure that no permanent damage was produced during charging, several samples were charged, then outgassed at 300°C for 2 hrs and tested.

## EXPERIMENTAL RESULTS

### Hydrogen Charging

It was observed that hydrogen charging at > 70 $Am^{-2}$ resulted in the formation of internal cracks and voids. The higher the current density for a given charging time the greater the extent of damage i.e. larger voids and cracks. For this reason the mechanical property tests described below were carried out following charging at 70 $Am^{-2}$ for 3 hrs which gave a hydrogen content of 4.5 ppm.
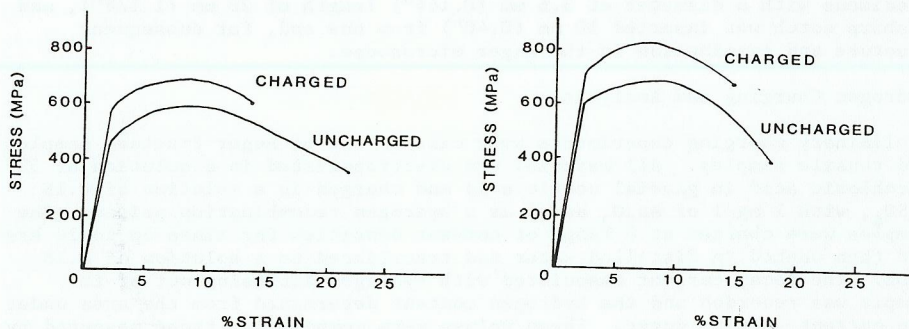


Fig. 1  Stress-strain curves of charged and uncharged specimens tested at room temperature.

### Mechanical Properties

The effect of hydrogen on the stress-strain curves of low phosphorus and high phosphorus steels is shown in Fig. 1. In both cases hydrogen, present at about 4.5 ppm, increased the yield stress and decreased the ductility, fig. 2.

The associated reductions in area are plotted as a function of temperature in Fig. 3. The hydrogen-free samples were ductile at all temperatures from -80°C to 25°C, while when hydrogen was present, the specimens become more brittle as the temperature decreased. The high phosphorus steels, both with and without rare earth additions, behave the same way as the low phosphorus steels.
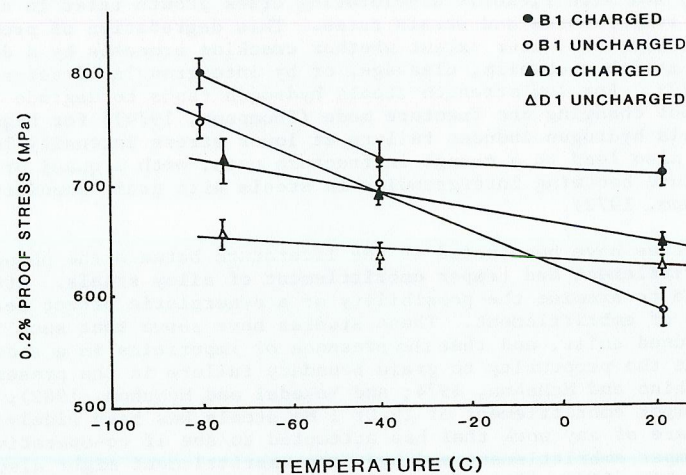


Fig. 2  0.2% Proof stress vs temperature for B1 and D.

Some hydrogen escaped from the specimens during the test; Table 2 indicates that the loss varied from about 47% to about 4% of the initial amount (about 4.5 ppm).

TABLE 2  $H_2$ Contents (ppm) After Testing Specimens with 4.5 ppm Hydrogen Initially

| Test Temperature | RT | -40°C | -80°C |
|---|---|---|---|
| A | 3.14 ± 0.56 | 2.39 | 3.88 ± 0.52 |
| B1 | 3.83 ± 0.50 | 3.71 ± 0.71 | 4.03 ± 0.28 |
| B2 | 4.00 ± 0.91 | 4.28 ± 0.44 | 3.51 |
| B3 | 3.51 | 3.29 | 2.89 |
| D1 | 5.62 ± 0.61 | 3.77 ± 0.07 | 4.00 |
| B3 | 3.04 ± 0.62 | 3.74 ± 0.88 | 3.76 ± 0.23 |

The uncharged samples failed by microvoid-coalescence at all temperatures. The hydrogen charged samples had different failure modes at different temperatures. Specimens fractured at 25°C had some ductile dimple rupture and some quasi-cleavage fracture. (Fig. 4a). Failure was almsot entirely quasi-cleavage at -40°C (Fig. 4b) with some intergranular facets present in the high phosphorus steel (B2). At -80°C the pure sample of the low phosphorus steel failed by cleavage, while the commercial form exhibited quasi-cleavage failure i.e. cleavage with ductile tearing. The high phosphorus steels failed either intergranularly (B1, B2, D1) or by quasi-cleavage (B3, D3); Fig. 5.
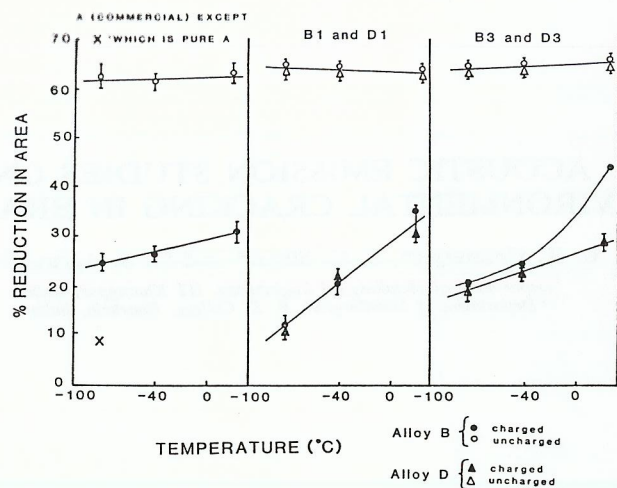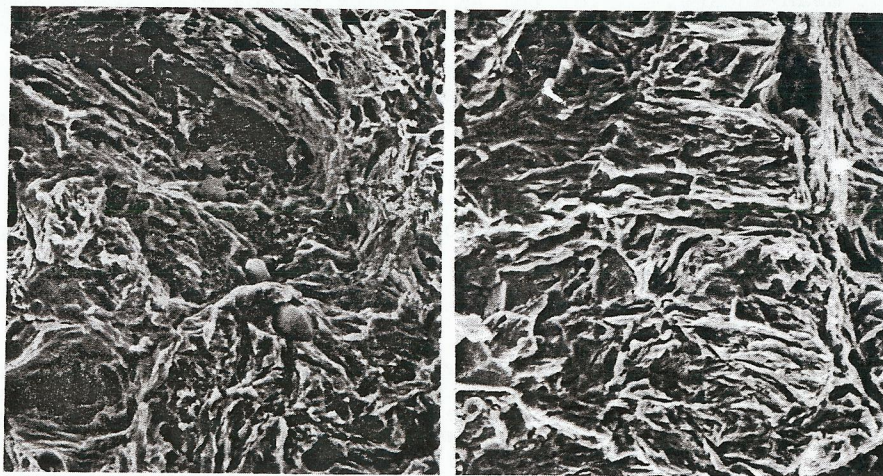
Fig. 3. % Reduction in area at fracture for A, B1, B3, D1 and D3. The curves without error bars are the results of one test per temperature.
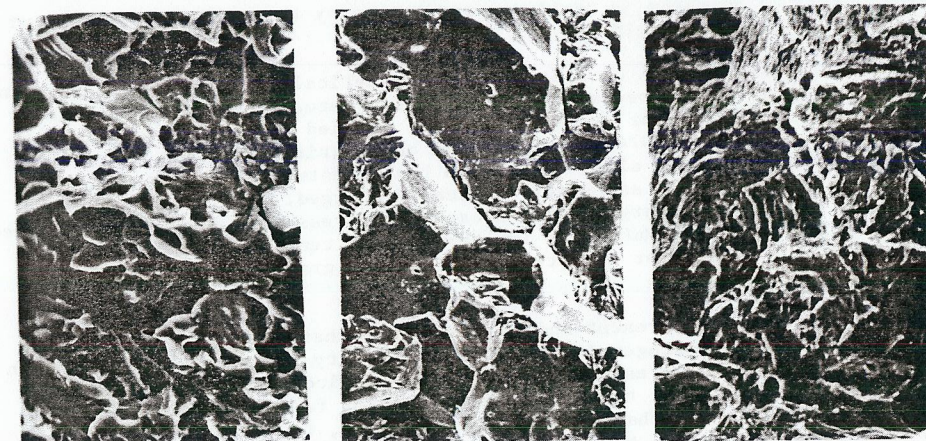


(a) 25°C, 1200X       (b) -40°C, 1040X

Fig. 4. Scanning electron migrographs of alloy B1 charged to 4.5 ppm hydrogen content and tensile tested.

Impact tests on the high phosphorus steels at -40°C showed little difference between B1 (32 ± 6J) and B2 (35 ± 4J) but B3 was much tougher (140 ± 11J). Tests on D1 at the same temperature gave 11 ± 2J with D3 tougher at 54 ± 12J.



(a) Alloy A pure, 1200X    (b) Typical of B1 and    (c) Typical of A
                          D1, 530X            (commercial) B2,
                                                Be and D3, 750X

Fig. 5. Scanning electron migrographs of alloys charged to 4.5 ppm hydrogen content and tensile tested at -80°C.

Auger Spectroscopy

The results of the Auger specroscopy tests will be presented elsewhere. Briefly they showed enhanced levels of P segregation up to 4.6% of a mono-layer in sample B1 at the grain boundaries compared to 1% in the transgranu-lar fracture areas on the same sample.

## EFFECT OF HYDROGEN AND EMBRITTLING AGENTS ON MECHANICAL PROPERTIES

The effect of hydrogen on these three forms of alloys B, D and also alloy A closely parallel the results obtained by Thompson, (1976a) for fracture strain of a high strength low alloy steel in the simulated heat affected zone of a weld. He showed a progressive change in fracture mode, from cleavage or quasi-cleavage to microvoid coalescence, still with a ductility loss, with increasing tests temperature. In this study, ambient temperature, slow strain rate tensile tests showed that hydrogen reduced the ductility and changed the fracture mode from microvoid coalescence (uncharged) to quasi-cleavage (cleavage with some ductile tearing) and microvoid coalescence. The fact that hydrogen can create a loss of ductility and still produce a fracture which is either completely or partially one of microvoid coales-cence has been shown by Thompson,(1974, 1976a).

At -40°C all alloys A, B and D exhibited a quasi-cleavage failure with no microvoid coalescence. This can be explained in terms of an increased ten-dency for hydrogen interaction at trap-sites, some of which are crack nuclei or growing cracks. Reducing the test temperature to -80°C produced different fracture modes for the various materials. Alloy A failed by a pure cleavage fracture (Fig. 5 (a)) whereas B1, B2 and D1 (high P) failed intergranularly (Fig. 5(b)). The retoughened steels (B3 and D3) however, fractured trans-granularly with some ductile tearing (quasi-cleavage). The intergranular failure, coupled with the presence of P at the grain boundaries in B1, B2 and D1 indicates that a synergistic effect exists between hydrogen and

phosphorus. A decrease in ductility may accompany this effect (Fig. 3) but the evidence is not conclusive.

Work by Thompson (1976b) on specimens electrolytically charged with hydrogen with no applied stress revealed an interaction between hydrogen and other embrittling species. For example, Thompson studied the Fe-C-Sb system used by Rellick and McMahon, (1974) in their work on impurity rejection embrittlement. Specimens of the alloy were given heat treatments similar to those by Rellick and McMahon, and electrolytically charged. The crack paths obtained in cathodic charging with no applied stress were identical to those found by Rellick and McMahon for low temperature tension. Their work provided strong evidence for an interaction between grain boundary embrittling Sb and H.

It seems evident from present and previous work that intergranular cracking in the presence of hydrogen is a result of impurity segregation at the grain boundaries. From the present results we can conclude that phosphorus in itself is not sufficient to produce intergranular failure in slow-strain rate tensile tests but that when hydrogen charged, the presence of hydrogen as well as phosphorus at the grain boundaries can lower the strength of the boundaries, so that crack growth can occur along these grain boundaries at lower values of stress intensity than for fracture in the (also hydrogen weakened) grains themselves.

SUMMARY

The embrittlement of 2¼ Cr 1 Mo steel, with and without rare earth additions, by hydrogen, was found to increase with decreasing temperature. The fracture mode of hydrogen charged samples was quasi-cleavage and microvoid coalescence, quasi-cleavage, pure cleavage or intergranular, depending on the alloy, its heat treatment and the tensile test temperature. As the test temperature was decreased the fracture became more brittle. At -80°C the fracture mode was dependent on the presence of phosphorus at the grain boundaries. For phosphorus enriched grain boundaries, intergranular failure occurred, whereas phosphorus free grain boundaries provided a quasi-cleavage fracture. This is strong evidence for a synergistic effect between P and H.

ACKNOWLEDGEMENT

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