Variation in diffusible Hydrogen Content and Hydrogen Assisted Cracking Susceptibility Of Cr-Mo Steels

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ABSTRACT

In this paper results obtained from diffusible hydrogen (H_D) measurement and hydrogen assisted cracking susceptibility (HAC) of three different Cr-Mo steel welds are discussed. H_D measurements were carried out using a gas chromatograph and HAC susceptibility studies using the UT-modified hydrogen sensitivity test (UT-Modified HST). Specimens for both these studies were prepared by employing identical welding parameters. Results showed that with increase in alloy content the cracking susceptibility of the steel increased while H_D content in the weld decreased. The decrease in the H_D content is explained based on decrease in the apparent diffusivity and increase in the apparent solubility of hydrogen with alloy content. These are in turn attributed to increase in the density of hydrogen traps with alloy content. Regression analysis of the results showed that it is possible to predict the safe preheat temperature for the steel from the composition if H_D content in the weld is known.

INTRODUCTION

Cr-Mo steels, extensively used for high temperature applications in power plants and petrochemical industries, are susceptible to hydrogen assisted cracking (HAC) in the weld due to their relatively high alloy content and hardenability. One of the methods to prevent HAC is to reduce the diffusible hydrogen content (H_D) in the weld which is achieved by using low hydrogen welding consumables and proper preheating of the job. H_D content in the weld produced by using a particular type of consumable and process is measured using standard methods available for H_D measurement (1-3). The purpose of these methods is to find out the H_D content in the weld due to external sources of hydrogen like moisture in the flux coating of the electrode. During these measurements it is assumed that H_D content does not depend on the composition of the weld metal. However, it is known that at low temperatures, the apparent diffusivity of hydrogen decreases and the apparent solubility increases significantly with alloy content and microstructure of steels (4-6) which have been attributed to trapping of hydrogen atoms at various defects that are present in the steel (7). Effect of trapping on H_D content measured is neglected in the standard measurement methods and it is assumed that higher the H_D content in the weld, higher would be its susceptibility to cracking. In this context it may be noted that due to relatively hard microstructure of the weld and HAZ in the as-welded condition, density of hydrogen traps in Cr-Mo steel welds is high and it increases with alloy content. High trap density should have an effect on the H_D values obtained from the standard methods of measurement of these steel welds. However, for a given external source of hydrogen, variation in H_D content for different

Table 1 : Chemical Composition of the Steels (Wt. %)

Element	c	Ni	Cr	Mn	si	S	p	MO
2.25 Cr-1 Mo Steel	0.12	0.16	2.18	0.46	0.25	0.001	0.01	1.0
9 Cr-1 Mo Steel	0.072	*	8.24	0.36	0.206	0.001	0.02	1.0
0.5 Cr - 0.5 Mo Steel	0.22	*	0.50	0.30	*	0.009	*	0.43

not determined

Cr-Mo steels as a function of alloy content has not been studied.

In the present study, diffusible hydrogen measurement and HAC susceptibility studies on three different Cr-Mo steels have been carried out. Specimens for both cracking test and hydrogen measurement were prepared exactly in indentical manner and critical preheat temperatures to avoid cracking were determined and H_D content in the welds were measured for different hydrogen concentrations in the arc atmospheres. It was found that while the cracking susceptibility increased, the H_D content decreased with alloy content in the steels. Thus the present study shows that H_D content in the weld is a function of composition of the weld as well as the external sources of hydrogen.

EXPERIMENTAL WORK

The Cr-Mo steels employed in this study are 0.5 Cr – 0.5 Mo, 2.25 Cr – 1 Mo and 9 Cr – 1 Mo steels. Prior to testing these were in the form of plates (normalised and tempered condition). The chemical composition of the steels is given in Table. 1. Specimen blanks of dimensions 40x15x3 mm, machined out from the plates were used for preparation of specimens for both H_D measurement and cracking susceptibility studies.

Preparation of Specimens

Bead-on-plate welds were made on the specimen blanks using autogenous gas tungsten arc welding (GTAW) process. Before welding specimen blanks were held on a copper fixture so that fast, uniform cooling rate is obtained for each specimen. Copper fixture was also provided with provisions for preheating so that specimen blanks along with the copper fixture can be preheated to required temperature before welding. Hydrogen in the weld was introduced by mixing it with argon shielding gas. It was possible to achieve different levels of hydrogen contents in the weld by varying the concentration of hydrogen in the shielding gas. Table 2 gives the details of the welding parameters employed.

Measurement of Diffusible Hydrogen Content

Immediately after welding, specimens were removed from the copper fixture and transferred into a specimen chamber. This chamber is tested for helium leak tightness before use and is provided with an inlet and an outlet which are connected to leak tight needle valves. Specimen chamber is closed immediately after transferring the specimen, then flushed and filled with argon to a known pressure. Then the chamber containing specimen was kept in an oven for 72h at 45±2°C. Hydrogen diffused out from the sample is collected inside the chamber. The chamber

Table 2 : Welding Parameters For Preparation of Specimen

Current	90A
Voltage	10–12 V
Speed	125 mm/min
Arc Gap	1.6 mm
Gas Flow Rate	10 lit./min. of argon

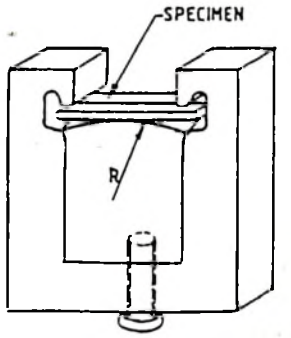

Fig. 1 :
Schematic of UT-Modified HST Jig.

is then connected to a calibrated gas chromatograph and hydrogen concentration in the gas mixture contained in the chamber is measured. This measurement set-up is a slightly modified version of that reported by Quintanna and Dannecker (8). By knowing the volume of the chamber and the pressure of the gas, it was possible to find out amount of hydrogen that evolved from each of the specimens. Volume of the weld metal was estimated from the cross sectional area of the fused metal and the length of the weld bead. From this H_D content in the weld in ml/100g of fused metal was estimated by assuming the density of the steel as 7.9 gm/cc. Specimens were prepared with concentration of hydrogen in the shielding gas varying from 1 to 5 vol.% and H_D content in the specimens were measured.

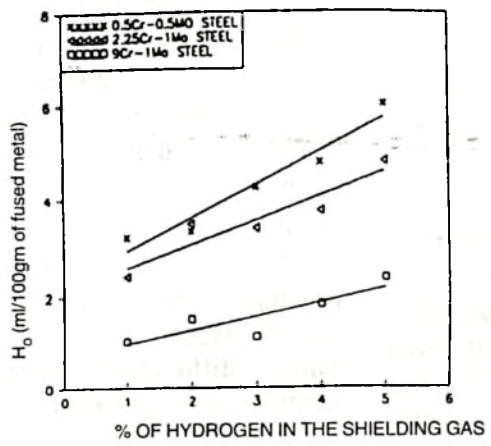

Fig. 2 : Variation of H_D with Vol.% of Hydrogen in the Shielding gas

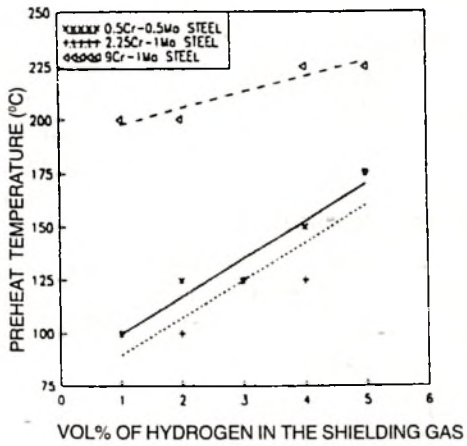

Fig. 3 : Variation of Preheat Temperature with Vol.% of Hydrogen in the Shielding Gas

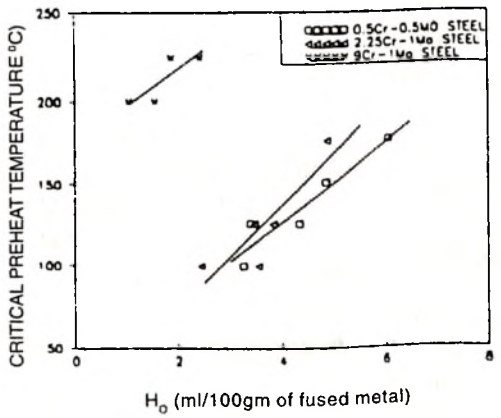

Fig. 4 : Variation of Preheat Temperature with H_D Content in the Shielding Gas

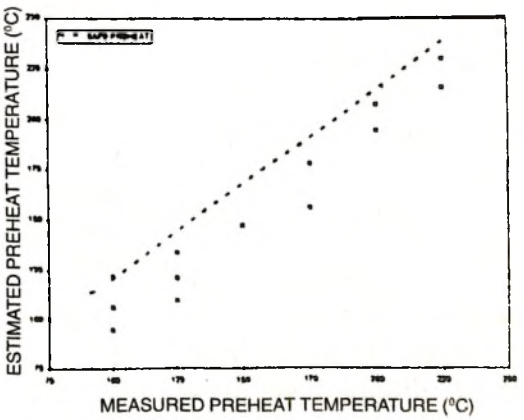

Fig. 5 : Comparison between Measured and Estimated Preheat Temperatures

HAC Susceptibility

HAC susceptibility was studied using the University of Tennessee modified hydrogen sensitivity test (UT-Modified HST) (8). Specimen dimensions are same as those used for H_D measurement. After welding, specimens were allowed to cool up to 50°C in the copper fixture, then removed, strained to a strain of -4% in a straining jig shown in Fig. 2, for 24h. and checked for cracks. Strain 'ε' is estimated from the diameter 'R' of the die block and the thickness 't' of the specimen using the following equation.

$$\varepsilon \sim t/2R$$

In order to determine the critical preheat temperature (minimum temperature that would prevent cracking) for a given concentration of hydrogen in the shielding gas, copper fixture along with the specimen was preheated to different preheat temperatures before the welding was carried out. In the case of specimens prepared with preheating, they were allowed to cool to preheat temperature in the fixture, removed and cooled in air to 500°C and then strained for 24h. The minimum temperature at which two or more specimens did not crack in repeated tests was chosen as the critical preheat temperature. Critical preheat temperatures for all the three steels for different vol % of hydrogen in the shielding gas were determined using this test.

RESULTS

Variation of H_D With Hydrogen Content in the Shielding Gas

Figure 2 shows the variation of H_D with vol% of H_2 in the shielding gas for the three steels. Each data point shown in the figure is the average of three or more experimentally determind H_D values. It may be seen that for a given vol % of hydrogen in the shielding gas it is maximum for 0.5Cr – 0.5Mo steel and minimum for 9Cr – 1Mo steel. As the concentration of hydrogen in the shielding gas increased from 1 to 5 vol%, H_D content for 0.5Cr – 0.5Mo steel varied from 2.5 to 6ml/100 g of the fused metal and for 9Cr. – 1Mo steel it varied from 1.3 to 2.5 ml/100 g of fused metal. For 2.25Cr – 1Mo steel corresponding variation was from 2.3 to 4.5 ml/100 gm of fused metal. Thus the results show that the H_D content in the weld varies not only with concentration of hydrogen in the shielding gas but also with the alloy content. Higher the alloy content, lower is the H_D content in the weld for a given concentration of hydrogen in the shielding gas.

Variation of Critical Preheat Temperature with Hydrogen Content in the Shielding Gas

Variation of critical preheat temperature with concentration of hydrogen in the shielding gas is shown in Fig. 3. For a given concentration, critical preheat temperature was maximum for 9Cr – 1Mo steel. As the hydrogen content in the shielding gas increased from 1 to 5 vol%, the critical preheat temperature varied in a narrow range of 200 to 225°C. For both 0.5Cr – 0.5Mo and 2.25Cr – 1Mo steels the corresponding variation was from 100 to 175°C. Thus the results of cracking tests clearly show that susceptibility to HAC is the highest for 9Cr – 1Mo steel, among the three steels studied.

In actual welding conditions, unlike in the present study, the main source of hydrogen is the moisture content in the electrode coating. It is difficult to quantify the hydrogen that enters the weld metal from the moisture that may be present in the electrode coatings. Further, not all hydrogen that is present in the weld, but only diffusible hydrogen contributes to cracking. Due to these reasons it is more appropriate to represent critical preheat temperature as a function of H_D content rather than concentration of hydrogen in the shielding gas. Such a diagram is shown in Fig 5. It may be seen that for all the three steels critical preheat temperature increases with H_D content. Further it also shows that low H_D content in high alloy steel does not mean less susceptibility to HAC.

DISCUSSION

The results clearly show that even though HAC susceptibility increases with alloy content in the

steel, H_D content for the welds made under identical conditions decreases with alloy content. This decrease in H_D of the steels with alloy content can be attributed to decrease in apparent diffusivity and increase in apparent solubility with alloy content. It has been shown by various investigators, (4-6, 9-11) that the apparent diffusivity of hydrogen in quenched steel (for which structure is expected to be fully martensitic as in the case of welds prepared for H_D measurement) decreased from $3x10^{-6}$ to $1x10^{-8}$ cm^2/s as Cr content increased from < 1wt.% (mild steel) to 12 wt.%(12 Cr steel). Similarly, apparent solubility of hydrogen varied from $4^{-5}x10^{-5}$ to $3x10^{-3}$ mol/cm^3 Fe as the Cr content increased from 1 to 12 wt.%. Decrease in apparent diffusivity of hydrogen with alloy content has also been reported by Kushido and Kudo (12). Their studies also revealed that susceptibility to hydrogen embrittlement increases with decrease in apparent diffusivity.

The observed decrease in apparent diffusivity and the increase in solubility with alloy content has been attributed to hydrogen trapping which is defined as the ability of hydrogen in solid solution to interact with various microstructural defects. Trapping of hydrogen by defects has been studied using autoradiography (13,14). In one of the studies carried out on Fe-9Cr steel, it has been shown that martensite interface and martensite-ferrite interface act as very effective traps for hydrogen (13). In another study carried out on quenched Cr-Mo and plain carbon steels, it is shown that the martensite laths and prior austenite boundaries act as traps for hydrogen in these steels (14). It also revealed that more hydrogen is trapped in Cr – Mo steel than in plain carbon steel under identical conditions. From all these works reported by various investigators, it can be concluded that less hydrogen would be diffused out from a steel of higher alloy content than from a steel of lower alloy content if hydrogen evolution is carried out at temperatures close to ambient (the temperature range in which apparent diffusivity varies with composition). Further it also suggests, susceptibility to hydrogen embrittlement would be higher if the diffusivity is lower. These conclusions are in agreement with the results obtained from the present study.

Prediction of Preheat Temperature from H_D Content and Composition

Figure 4 shows that critical preheat temperature increases with both H_D content and alloy content of the steel. Hence regression analysis of the data was carried out to predict the critical preheat temperature from the composition of the steel and H_D content in the weld. The following equation provided the best correlation with a R^2 value of 0.94 and standard error of determination of 12.2.

$$T^0\ (C) = 25.7H_D + 330C + 25.3Cr - 63$$

Where Cr and C are in wt.% and H_D is in ml/100gm of fused metal.

A comparison of measured and estimated preheat temperature is shown in Fig. 5. The dotted line shown in figure estimates the upper boundary which gives the safe preheat temperature above which no cracking may take place for a given steel weld of known composition and H_D content. This line is represented by equation (2) with a slight modification; the constant '63' changed to '45'.

Thus analysis of the results shows that it is possible to predict the safe preheat temperature from the composition of the steels if H_D content in the weld is known.

Practical Implications

The results discussed here indicate that it is not appropriate to use the H_D values obtained for alloy steel consumables after depositing them on base plate made of steels conforming to specifications ASTM A36 or SAE1020 or BIS226 or 2002 or 2062 as recommended in different standard methods of measurement of diffusible hydrogen (1-3). This is because, diffusivity of hydrogen at ambient temperature can be vastly different for the consumables and the base plate materials, if there

is a significant variation in their composition; which in turn means hydrogen diffused out from the base and the weld metals can be different. Dilution of the weld metal by the base metal would also influence the hydrogen diffused out. Hence, for H_D measurement of alloy steel consumables it is better to use steels of matching composition for depositing the consumables rather than those recommended in different standards.

As hydrogen assisted cracking occurs due to interaction of hydrogen atoms with defects in the weld, especially in those regions where stresses are high, it is reasonable to assume that all hydrogen atoms, except those trapped at strong traps (like TiC, from which hydrogen atoms are not released even if the steel is heated to 200°C) and those that would have combined to form hydrogen molecules at pores or inclusion-matrix interface contribute to cracking. However, as the decrease in apparent diffusivity and increase in apparent solubility at low temperatures with increase in alloy content indicate, not all hydrogen atoms trapped at various defects are released when hydrogen collection is carried out at temperatures close to ambient. Hence, low H_D levels obtained from such measurements, especially in the case of alloy steels may be misleading and does not assure low hydrogen levels in the welding consumables. Hence, it is recommended to carry out collection of hydrogen for H_D measurement at higher temperatures (~150°C) so that most of the trapped hydrogen atoms would be released. H_D content thus measured may be a better parameter to represent the susceptibility of the weld to HAC than that obtained from measurement carried out after collection at temperatures close to ambient.

CONCLUSIONS

The major conclusions from the present study are the following

1. Both H_D content and HAC susceptibility vary with alloy content in the steels. H_D decreases with alloy content while HAC susceptibility increases with alloy content.
2. This can be attributed to increase in the density of defects which trap hydrogen atoms in the steels with alloy content.
3. It is possible to predict the minimum preheat temperature from the chemical composition if the H_D content in the weld is known.
4. Modification in the standard methods of H_D measurements may be required to classify the welding electrodes based on their hydrogen levels, especially in the case of high alloy steels as most of the hydrogen atoms remain trapped in the steel at various defects and do not diffuse out at temperatures close to ambient.

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