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A New Method to Measure the Diffusible Hydrogen Content in Steel Weldments Using a Polymer Electrolyte-Based Hydrogen Sensor

A new sensor for detecting hydrogen shows similar results as the gas chromatography detection method

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ABSTRACT. A new technique to measure the diffusible hydrogen content in steel weldments is described. The sensor, developed at the Indira Gandhi Center for Atomic Research, is a conducting polymer film coated with Pd on either side. One side of the sensor was exposed to an argon-hydrogen gas mixture and the other side to air. The current flowing through the sensor was directly proportional to the hydrogen content in the gas mixture. Hydrogen measurements were also carried out by gas chromatography and one to one correspondence between the results from the gas chromatography and the new sensor was obtained. In addition to these results, advantages of the new sensor over presently available methods for measurement of diffusible hydrogen and its limitations are also discussed in this paper.

Introduction

The amount of diffusible hydrogen in a steel weldment is an important criterion for classification of welding consumables. It is used extensively for predicting the susceptibility of the weldment to hydrogen-assisted cracking and estimation of the minimum preheat temperature during welding to prevent cracking (Ref. 1). The most widely used method for measuring diffusible hydrogen content in the weldment is the mercury method (Refs. 2–5). In this method, hydrogen evolved from the weldment is collected over a mercury column and its volume is measured. Other liquids such as glycerin, alcohol, etc., have also been used for measuring diffusible hydrogen (Ref. 6). Among these, glycerin is more widely used than the others (Refs. 7, 8). However, it is reported that many gases, including hydrogen, are not completely insoluble in glycerin, and therefore, the results obtained are inconsistent and hence less reliable, particularly when diffusible hydrogen is present in small quantities (Refs. 9, 10).

Health hazards associated with mercury and the long period of time required for collection of hydrogen are the main drawbacks associated with the mercury method. Moreover, evolution of any other gas from the weld will result in overestimation of the hydrogen content. These limitations of the mercury method led to the development of alternative methods for measurement of diffusible hydrogen. Among them, the most popular method is the gas chromatography (GC) method. In this method, the specimen is transferred to a leaktight chamber after welding, and hydrogen is allowed to evolve for a fixed time at a fixed temperature. When hydrogen evolution is complete, the chamber is connected to a GC and the total amount of hydrogen present in the chamber is measured. The main advantage of this technique is that it can separate other gases present and measure only hydrogen. Further, as the evolution is taking place inside the chamber, it is feasible to heat the chamber to accelerate the hydrogen evolution so that measurement can be carried out within a few hours of welding. Comparable results have been obtained from both the GC method and mercury method (Ref. 10), and hence, the GC method has been introduced into standards (Refs. 2, 11) as an optional method for the measurement of diffusible hydrogen, in addition to the mercury method. Determination of diffusible hydrogen content by a mass spectrometer has been also reported (Refs. 12, 13). However, commercial applications of this technique are limited because of

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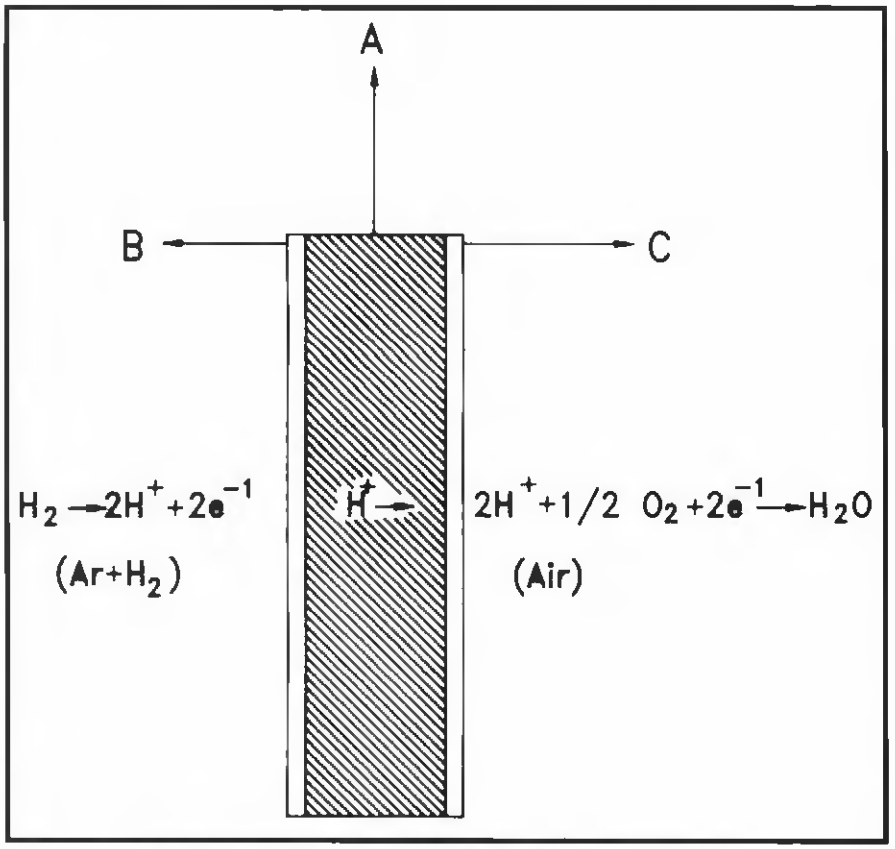

Fig. 1 — Schematic representation of reactions taking place at the sensor.

the high cost of the equipment. This paper discusses the suitability of a new hydrogen sensor developed at the Indira Gandhi Center for Atomic Research, Kalpakkam, India, for estimation of the diffusible hydrogen content in weldments. Measurements were carried out using both the GC and the new sensor and fairly good correlation has been obtained between these two methods. As the sensitivity of the sensor is found to be superior to that of a thermal conductivity detector used in GC, evolution of hydrogen from the sample as a function of time can be also studied.

Experimental

Sensor

The sensor consisted of a conducting polymer made from polyvinyl alcohol and phosphoric acid. The polymer was cast as a film, coated with palladium on either side and electrical leads were taken. One side of the coated polymer was exposed to the argon-hydrogen gas mixture and the other side to air. Thus, the sensor consisted of hydrogen-exposed inner palladium film and air-exposed outer palladium film with conducting polymer sandwiched in between, which acted as a fuel cell. The short-circuit current was measured and was found to be linearly dependent on hydrogen concentration in the argon-hydrogen gas mixture. A schematic of the reactions occurring at the sensing and counter electrodes is indicated in Fig. 1.

Preparation of Specimen

Diffusible-hydrogen measurements were carried out using a 0.5Cr-0.5Mo steel. The nominal composition of the steel was C, 0.22 wt-%; Cr, 0.50 wt-%; and Mo, 0.43 wt-%. Specimens identical to those used for the University of Tennessee Modified Hydrogen Sensitivity Test (UT-Mod. HST) were prepared for this purpose (Ref. 14). The specimens dimensioned measuring 40 x 15 x 3 mm were clamped in a copper fixture shown in Fig. 2. Autogenous bead-on-plate welds were made on the specimen using the GTAW process. The welding parameters employed are shown in Table 1. Hydrogen was introduced into the weld metal by mixing it with argon shielding gas. Hydrogen content was varied from 1 to 5 vol-% in order to obtain different levels of diffusible hydrogen content in the weld metal. Welding parameters were chosen such that the penetration of the weld bead was nearly half the specimen thickness.

Table 1 — Welding Parameters

Arc voltage	10–12 V
Current	90 A
Welding speed	125 mm/min
Gas flow rate (Ar)	10 L/min
Arc Length	1.5 mm

Measurement of Diffusible Hydrogen

Immediately after welding, the specimen was removed from the copper fixture and transferred to a specimen chamber shown in Fig. 3. This specimen chamber is a slightly modified version of that described by Quintana and Dennecker (Ref. 14). It was subjected to helium leak testing in vacuum, and the leak rate was found to be less than 10^{-8} std. cc/min. Volume of the chamber in the closed condition was measured within an accuracy of 1 cc. After the specimen was placed in the chamber, the chamber was flushed and then filled with argon gas up to a pressure of 4 kg/cm^2 (3.87 bar or 56.9 lb/in.^{2}). Hydrogen was then allowed to evolve from the sample into the chamber for 72 h at 45° ±3°C. The chamber was then ready for hydrogen measurement.

A schematic of the experimental setup used is shown in Fig. 4. The concentration of hydrogen in the chamber was measured using both GC and the polymer sensor. The specimen chamber was connected to the gas sampling valve, which extracted a known volume of gas from the chamber and injected it into the carrier gas. The detector (GC/sensor) gave a signal corresponding to concentration of hydrogen in the chamber. As only a small volume of gas is sampled during each measurement, it is possible to repeat the measurements often using one specimen. Both GC and the sensor were calibrated prior to actual measurement for every set of measurements. One set of measurements consisted of the determination of hydrogen concentration in four different chambers containing four different specimens prepared under identical conditions. From the concentration of hydrogen in the gas mixture, the total volume of hydrogen gas present in the chamber can also be calculated from the initial pressure of the gas and the volume of the chamber (volume of each specimen was separately measured and subtracted from the chamber volume). As the concentration of hydrogen in the chamber is only in ppm level, the increase in the pressure of the gas due to evolution of hydrogen in the chamber was assumed to be negligible.

Since the bead-on-plate welds were prepared without any filler-metal addi-

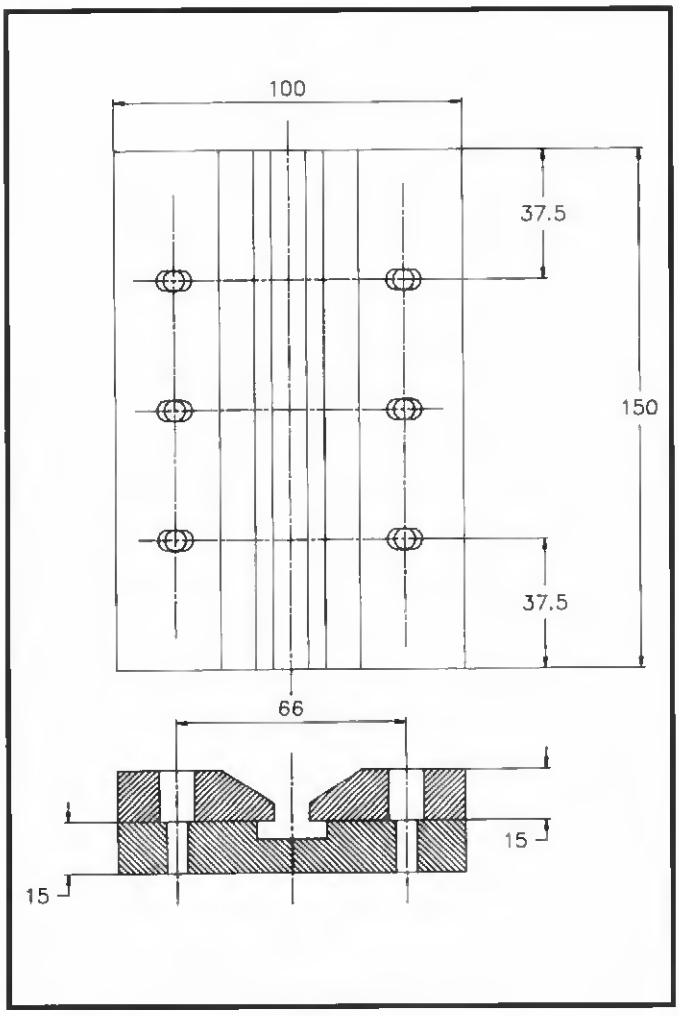

Fig. 2 — Plan and sectional view of copper fixture.

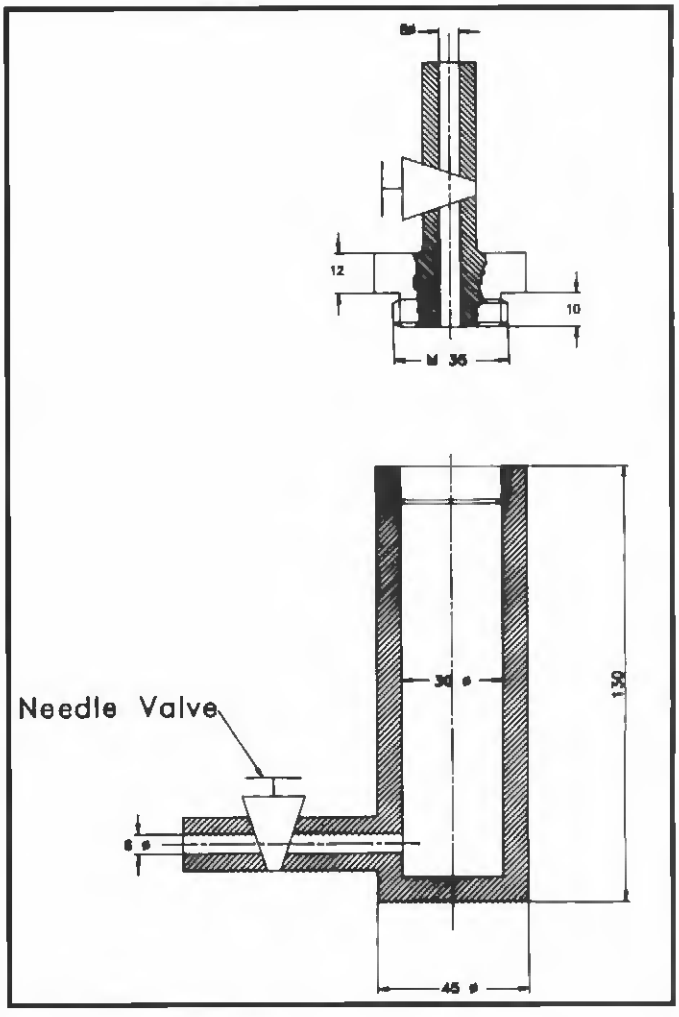

Fig. 3 — Cross section of the specimen chamber with plug.

tion, the volume of the weld metal was determined and the diffusible hydrogen content was represented as mL per 100 cc of weld metal. The volume of weld metal was calculated from the length of the weld bead and its cross-sectional area. The cross-sectional area was measured at two different locations, and the average value was taken. For each measurement, the weld bead region was divided into several small rectangles of 0.5 mm width and a length equal to the depth of penetration as shown in Fig. 5. Depth of penetration was determined employing an optical microscope provided with a moving stage. Total area of all such rectangles is approximately equal to the area of cross section of the weld.

Results

Figure 6 shows typical calibration curves for GC and the sensor. The figure illustrates the variation of signal intensity with the concentration of hydrogen in the argon-hydrogen gas mixtures. The response for both equipment is linear and any unknown concentration of hydrogen in a given argon-hydrogen gas mixture can be estimated from these graphs.

A total of 19 samples was used for the measurement of diffusible hydrogen content. The concentration of hydrogen as measured by GC is plotted against that determined by the sensor and is shown in Fig. 7. Results obtained clearly establish that there is a very good correlation between the two techniques for hydrogen measurement and that the newly developed sensor can be reliably employed as an additional method for measuring hydrogen concentration in Ar-H_2 gas mixtures.

After obtaining a concentration of hydrogen in the chamber, diffusible hydrogen content for 100 cc of the weld metal was estimated for each specimen from the volume of specimen, volume of chamber, pressure of gas inside the chamber and volume of weld metal. Variation of weld metal hydrogen content with vol-% of hydrogen in the shielding gas for GC and the sensor is shown in Fig. 8. Each value shown in the figure is an average of four measurements (except for 5 vol-% of hydrogen for which it is an average of three measurements). It can be seen that almost identical values of hydrogen content were obtained for both methods. It may also be noted that the hydrogen content varies linearly with vol-% of hydrogen in the shielding gas.

Discussion

From the above results, it is indicated that the newly developed sensor can be used to measure diffusible hydrogen in the weldments, even though dimensions of the specimen used are different from that recommended by different standards (Refs. 2, 4). Laboratory tests have shown that this sensor is highly sensitive and responds even if hydrogen is present below ppm levels. Hence, it may be possible to study evolution of hydrogen from the weldment as a function of time using this sensor. Furthermore, at pre-

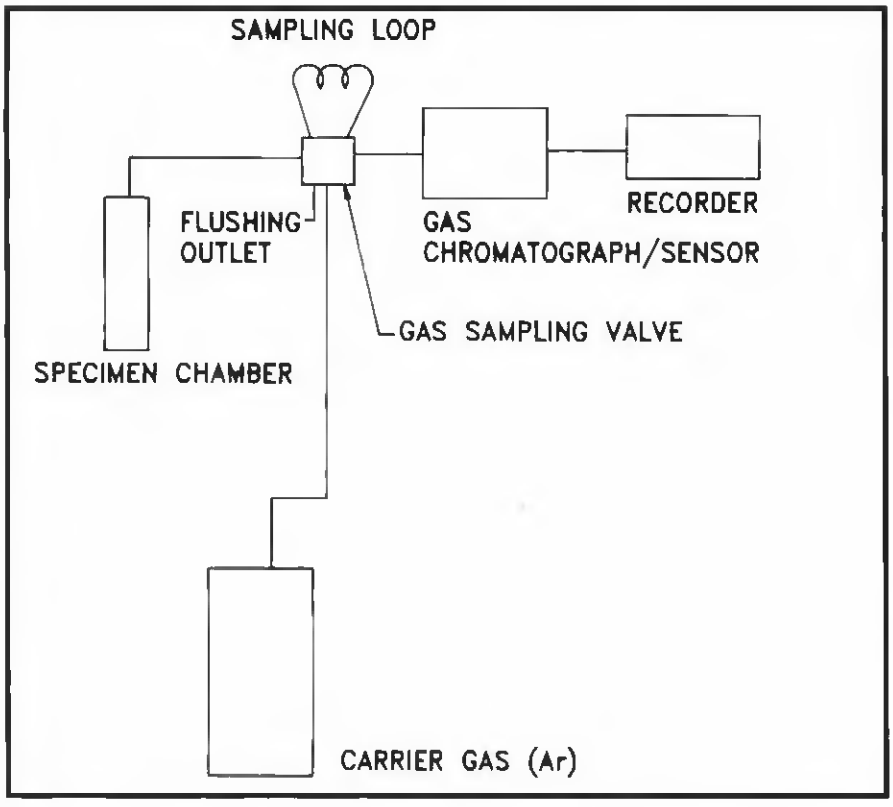

Fig. 4 — Line diagram of the experimental setup to measure diffusible hydrogen in the weld.

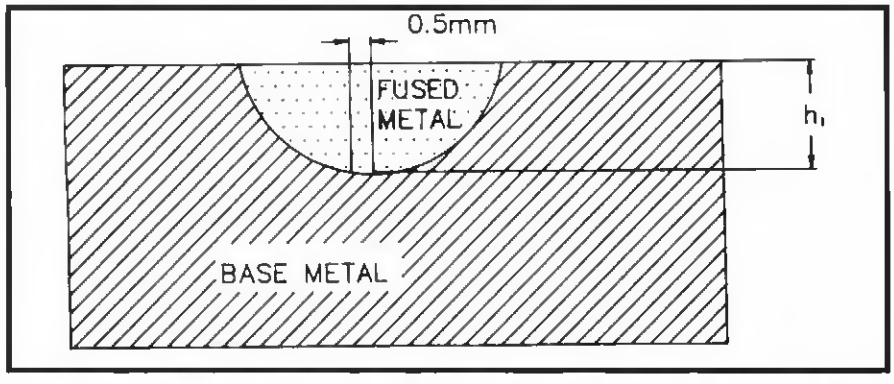

Fig. 5 — Schematic representation showing measurement of area of cross section of the weld.

sent, diffusible hydrogen measurements and tests for hydrogen-assisted cracking susceptibility are carried out using different specimens. Cracking tests that require only a small specimen and a straining jig, such as the UT-Modified Hydrogen Sensitivity Test (Ref. 14), are now available to assess cracking susceptibility. Due to the very high sensitivity of the sensor, it can be used to study the evolution of hydrogen from the specimen as the cracking test is in progress, if the specimen, along with the jig, can be contained in the chamber and the hydrogen inside the chamber is continuously monitored. This can certainly lead to a better understanding of the phenomenon of hydrogen-assisted cracking.

As it was required to make measurements using both GC and the sensor, only the concentration of hydrogen inside the specimen chamber was measured by sampling a known volume of gas from the sampler. The measurement setup can be suitably modified to measure total hydrogen present inside the chamber instead of a concentration. Similarly, calibration has to be carried out using different known volumes of hydrogen instead of known concentrations of Ar-H_2 mixtures. This would make the measurement easier, as it is not necessary to know the volume of the specimen chamber and the pressure of the gas to obtain the total hydrogen evolved. The only disadvantage in this mode is that only one measurement can be carried out for one specimen. It may be noted that the commercially available dedicated GC-based diffusible hydrogen measuring equipment measures the total hydrogen evolved instead of concentration of hydrogen in the chamber.

Though the results indicate that the sensor can be a good technique for measurement of diffusible hydrogen in the welds, it is not without limitations. Its long-term stability needs to be improved; and hence, it is desirable to calibrate the sensor just before actual measurements are carried out. Minor variations in the measurement parameters affect the signal significantly, and hence, measurement and calibration has to be carried out exactly under identical conditions. Another limitation is the life of the sensor. It has been found that life of the sensor is only about six months, and hence, periodic replacement or regeneration of the sensor is required. However, it may be noted that preparation of the sensor is neither difficult nor costly, and hence, replacement of the sensor once in six months may be viable and affordable. Furthermore, the sensor is presently in the developmental stage, and it may be possible to solve most of these problems as the understanding of the sensor improves.

Conclusions

A new hydrogen sensor based on conducting polymer has been successfully developed to measure the diffusible hydrogen in weldments. It has been found that the results are as reliable and consistent as obtained from a gas chromatograph, and hence, this new sensor can be used for measuring diffusible hydrogen in weldments.

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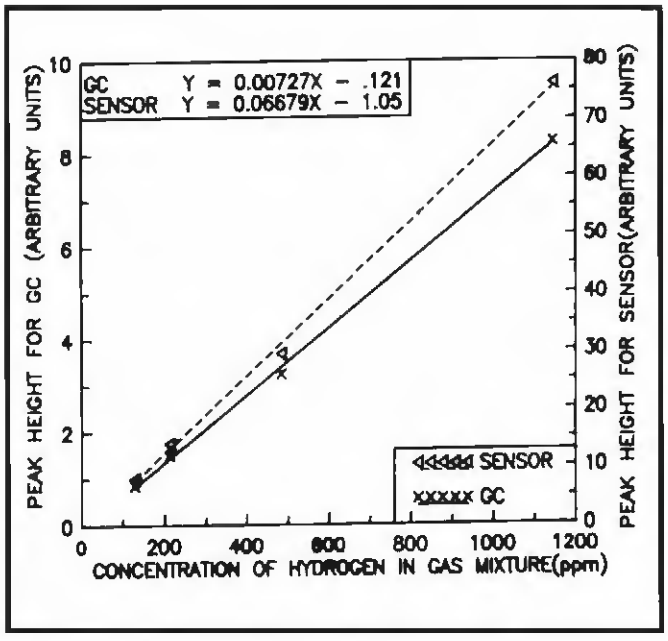

Fig. 6 — Calibration curves for sensor and GC using same set of calibration gases.

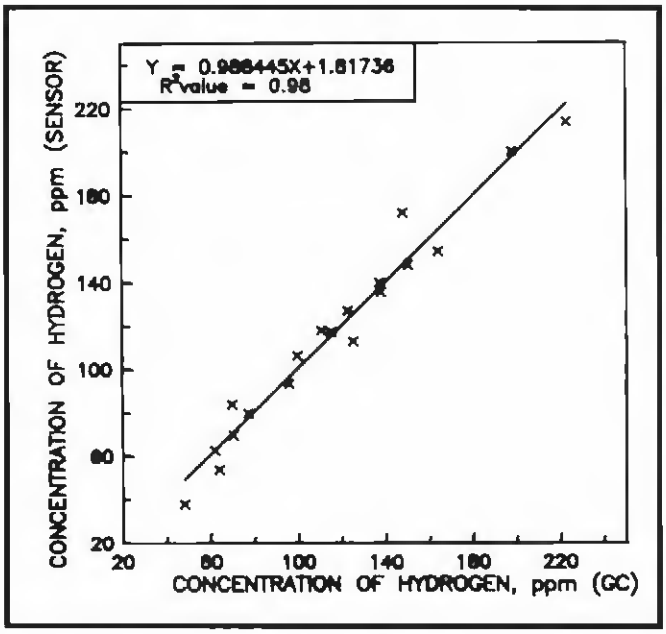

Fig. 7 — Correlation of hydrogen concentration measured using GC and sensor.

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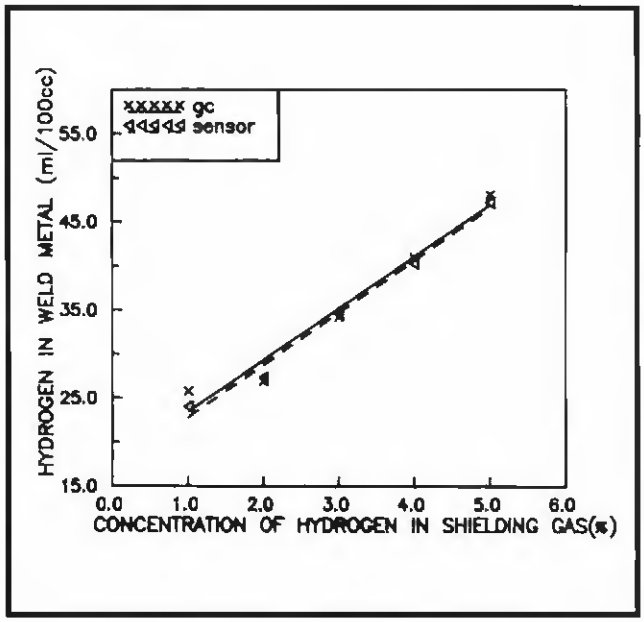

Fig. 8 — Variation of diffusible hydrogen content with vol-% of hydrogen in the shielding gas obtained using both GC and sensor.