The Determination of Hydrogen Distribution in High-Strength Steel Weldments Part 2: Opto-Electronic Diffusible Hydrogen Sensor

A hydrogen sensor was developed that generates results in less than an hour and allows analysis to be done on the actual welded structure

BY R. D. SMITH II, D. K. BENSON, I. MAROEF, D. L. OLSON AND T. R. WILDEMAN

ABSTRACT. In Part 1, methods for measurement of hydrogen distributions in high-strength welded steel using laser ablation were described. Part 2 will elaborate on an advanced design for a diffusible hydrogen sensor that utilizes the optoelectronic properties of a hydrogen-sensitive material such as tungsten (VI) oxide, WO_3. The sensor generates the necessary analytical signal in less than one hour and has been calibrated to yield results in mL/100 g weld metal. The sensor is extremely sensitive to hydrogen and relatively inexpensive. An array of sensors could conceivably be used to measure diffusible hydrogen distributions across the weld face with a resolution of approximately one millimeter. The sensor shows excellent promise as an advanced hydrogen measurement technique, and research is continuing to establish procedures for transfer to industry.

Introduction

A sensor for measuring diffusible hydrogen content in welded steel, which is based on the chemochromic reaction of certain transition metal oxides (Ref. 1) with hydrogen in air, was investigated. The reaction is catalyzed by palladium or platinum (Ref. 2), which adsorbs hydrogen on the surface and converts it to its atomic form. The hydrogen diffuses into the oxide and reacts to form an ion-insertion compound. The optical properties of the compound are altered and can be detected visually or spectroscopically.

R. D. SMITH II is with DCH Technology, Valencia, Calif. D. K. BENSON is with National Renewable Energy Laboratory, Golden, Colo. I. MAROEF, D. L. OLSON and T. R. WILDEMAN are with Colorado School of Mines, Center for Welding, Joining and Coatings Research, Golden, Colo.

The chemochromic (color change due to a chemical reaction) material used was a thin film of tungsten (VI) oxide, WO_3. For the purposes of hydrogen detection, the gas must be able to freely penetrate the film. A porous, low-density film is therefore desirable; evaporative deposition provides films with these properties.

The reaction of hydrogen and WO_3 in air is represented by the equations

$$Pd + xH_2 + x/4O_2 + WO_3 \leftrightarrow H_xWO_3 + x/2H_2O + Pd$$

$$h\nu + W^{5+}(A) + W^{6+}(B) \rightarrow W^{6+}(A) + W^{5+}(B)$$

The hydrogen reacts reversibly to form a "hydrogen tungsten bronze." Electrons are localized on W^{5+} sites and optical absorption occurs by electrons undergoing W(V)- W(VI) intervalence transfer. The transferred electrons can be considered as small polarons, or electrons trapped in distorted lattice sites (Ref. 3). These electrons are thought to be responsible for the chemochromic effect. The partially reduced tungsten absorbs light in the red region of the visible spectrum, causing the complex to appear dark blue.

The reaction of WO_3 with hydrogen in the presence of a catalyst is well documented and sensors have been previously devised for detecting hydrogen (Ref. 4). In particular, fiber-optic sensors for hydrogen leak detection in air (Refs. 5–7) and plate-like sensors for hydrogen-producing bioorganisms (Ref. 8) have been developed. The same concept was applied to detection of hydrogen evolving from the weld metal of high-strength steel samples.

KEY WORDS

Diffusible Hydrogen
Optical Fibers
Sensors
Hydrogen Distribution
Chemochromic Effect

Experimental

The sensors consisted of polymer optical fibers coated with thin films of WO_3 and palladium. The films were deposited by vacuum evaporation. The average thickness of the WO_3 films was 500 nm, and the thickness of the palladium films varied from 3 to 30 nm. The change in optical properties was measured using an infrared (IR) reflectometer equipped with a laser photodiode emitting at 850 nm. The reflectance decreased as the hydrogen concentration increased due to the color change in the WO_3 film, and was measured in units of reflected power (μW). The typical response of an unreacted sensor was approximately 1.5 μW. The sensors were extremely sensitive to hydrogen and would fully react to a mixture of one percent hydrogen in argon in only a few minutes, resulting in a power decrease of approximately 1.3 μW.

The response of the sensor to hydrogen diffusing from a weld was investigated by using a sensor housing designed for attachment to the base plate of a welded specimen. The design is shown in Fig. 1. The housing was fabricated from aluminum and contained a 27.9-mm section of optical fiber coated on one end with WO_3/palladium. The fiber was sealed inside the housing using paraffin wax. The housing was threaded to accept a stan-

Table 1 — Composition of Steels (%) and Welding Parameters Used

Element	HSLA 100	ASTM A36
C	0.055	0.051
S	0.012	0.015
P	0.008	0.008
Si	0.31	0.25
Cr	0.06	0.04
Ni	1.59	0.04
Mn	1.96	0.66
Cu	0.62	0.05
Mo	0.45	<0.01
Nb	0.026	<0.01
Ti	0.005	<0.01
Al	0.024	0.01
V	0.007	<0.01
B	0.0008	<0.0005
W	0.014	<0.01
Fe	8ase	Base
Pb	0.01	<0.01

Equipment used: Hobart Arcmaster 500/HMC 410 Controller
GMA heat input: 1.5 kJ/mm, 29 V, 440 A
Travel speed: 8.5 mm/s
Single bead on plate
Welding consumable: 1/16 in. (1.6 mm) low-carbon-steel, metal-cored welding wire (baked in vacuum furnace at 650°C for 1 h and stored at 150°C until use)

dard ST-type connector. The fiber-optic section was then matched to another cable using index-matching optical gel. The gel allowed the light from the photodiode to pass into the section with only a small decrease in power. The bottom of the housing was fitted with a small O-ring to form a seal with the metal surface. Pressure was applied to the sensor using a Plexiglas® plate to hold it in place.

Results and Discussion

Initial experiments were conducted on 51 x 51 x 12.7-mm gas metal arc welded (GMAW) specimens of ASTM A36 steel. The compositions of the steels along with the welding parameters used in this study are presented in Table 1. The sensor was placed directly adjacent to the weld deposit. Using this practice, it was found the amounts of hydrogen diffusing from the base plate were too small for a detectable response. The sensor was therefore modified to sample from the curved surface of the weld deposit using a rubber gasket adapter as shown in Fig. 2.

The experiments were repeated using ASTM A36 steel specimens. The specimens were baked in a vacuum furnace at 650°C for one hour before welding. The specimens were gas metal arc welded with 0.1% H_2/argon, then quenched in ice water and stored in liquid nitrogen (LN_2) until analysis. Data was collected using a general-purpose instrumentation bus (GPIB) interface connected to a laptop computer; measurements were made every minute. The results indicated the amount of hydrogen diffusing from the weld deposit was more than adequate for detection. A suite of experiments was performed on a specimen that was allowed to remain at room temperature for extended periods of time; measurements were made at one-hour intervals. The specimen was then quenched in LN_2 and the sensor was allowed to recover for three hours in a mixture of 20% oxygen/80% nitrogen. The experiments were repeated up to an interval of five hours after welding. The results are presented in Fig. 3. As shown by the response curves, the hydrogen from the weld deposit was still detectable by the sensor after a period of five hours.

The next set of experiments was designed to gain quantitative measurements from the steel specimens. For these experiments, HSLA 100 steel was gas metal arc welded using levels of 0.1, 0.5, 1.0 and 3.0% hydrogen in argon shielding gas. The specimens were baked in a vacuum furnace at 650°C for one hour before welding. The specimens were welded in duplicate; one set of specimens was analyzed by the standard gas chromatography (GC) method (AWS A4.3-93) to generate and report the results in mL/100 g weld metal. The other set was analyzed using the sensor.

From the sigmoidal shape of the response curves as shown in Fig. 3 it was decided to attempt and correlate the slope of the curve to the initial concentration in the specimen. The steady-state portion of the curve could be assumed to be proportional to the flux of hydrogen from the weld metal. To investigate this possibility, theoretical curves were generated using an

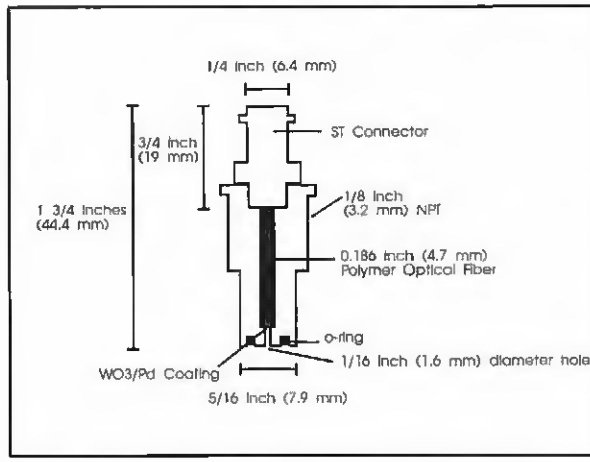

Fig. 1 — Design for prototype diffusible-hydrogen weld sensor.

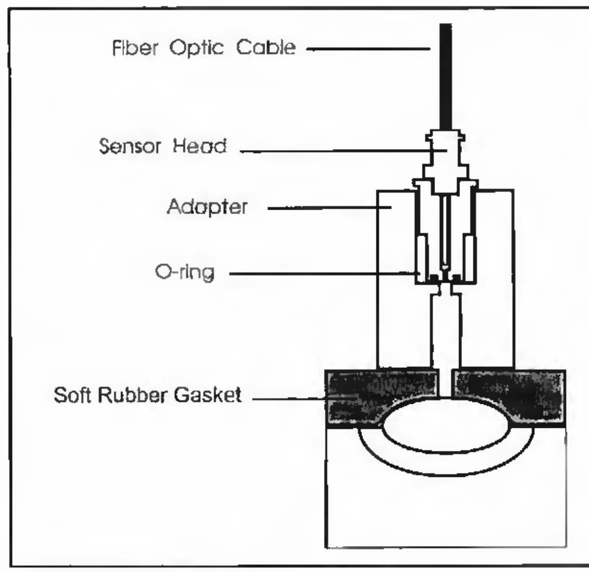

Fig. 2 — Design for prototype diffusible-hydrogen weld sensor with soft rubber gasket.

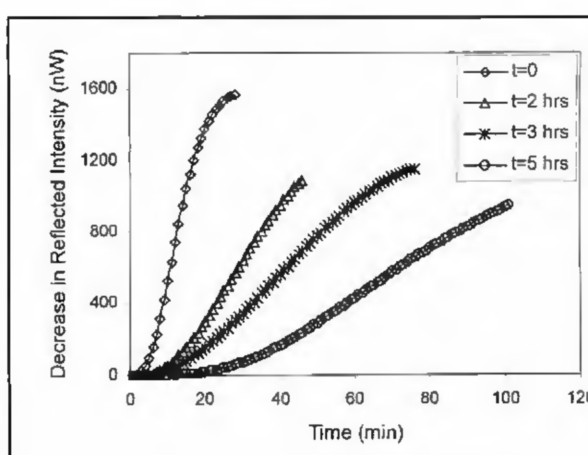

Fig. 3 — Hydrogen response data as a function of time after quenching for gas metal arc welded ASTM A36 steel (0.1% H_2/Ar shielding gas) using prototype diffusible-hydrogen sensor with soft rubber gasket.

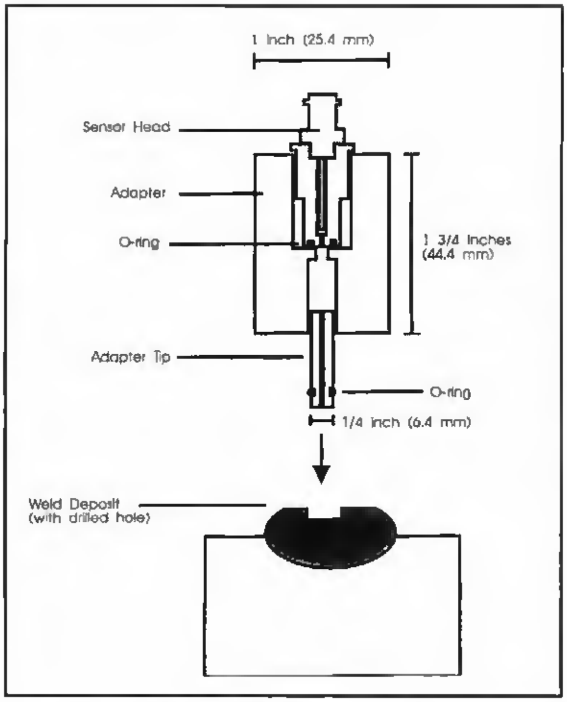

Fig. 4 — Proboscis adapter design for prototype diffusible-hydrogen sensor.

equation derived from the error function erf(x). The diffusion was assumed to occur from a semi-infinite plane sheet with a uniform initial concentration C_o throughout and a constant surface concentration of zero. For this case, the solution for the error function equation takes the form

$$M_t = 2C_o\left(\frac{Dt}{\pi}\right)^{1/2}$$

(Ref. 9) where M_t is the amount of hydrogen, D is the diffusion coefficient for hydrogen in a particular medium, C_o is the initial concentration and t is time. Solutions were generated for different initial concentrations as a function of time. The results were adjusted for the average amount of weld metal per specimen and multiplied by the ratio of surface area sampled to total area. The geometry of the weld metal was assumed to be cylindrical and the total diffusing area was taken to be one half the outside area of the cylinder plus the full area of both ends. The slope of the theoretical curves was calculated in units of µL/min. The slope of the response curve for each specimen was then calculated and converted to the same units using a calibration curve.

The initial data gathered with the gasket adapter yielded a correlation between the actual specimens and the theoretical values that was unsatisfactory. It was assumed the surface area actually sampled was greater than estimated due to a poor gasket seal. A new sensor adapter was, therefore, designed as shown in Fig. 4. The original sensor head was again used. The new adapter was threaded at both ends. One end accepted the sensor head and the other a proboscis-like tip that could be inserted into a hole drilled in the weld metal.

Three sets of specimens were welded and analyzed with three different sensors. Each sensor was calibrated prior to the analyses. The slopes for each response curve were calculated and compared to the theoretical data. Three values for the apparent diffusion coefficient of hydrogen in steel were used to calculate theoretical curves. A best fit was obtained with $D_{eff} = 7.5 \times 10^{-5}$ cm^2/s (Ref. 10). Figure 5 shows representative experimental data for the GMA-welded HSLA 100 steel specimens. Figure 6 shows the results of the diffusion calculations for five initial hydrogen concentrations.

Nineteen specimens were analyzed. Figure 7 shows the correlation between the standard GC test results and the slopes of the sensor response curves, as well as the theoretical curve derived from the diffusion equation. The correlation coefficient for the nineteen samples was 0.970. A statistical analysis was performed on the data set, and the residual standard deviation for the curve was found to be ± 0.00865 µL/min. Based on this result, the outlying data points were omitted and the data replotted. The results are presented in Fig. 8, with a correlation coefficient of 0.989.

The fit to the theoretical data is quite good, especially when the nonuniformity of the weld deposits is taken into account. These results indicate the sensor could be used as an analytical tool for diffusible hydrogen measurement in welded steel. Further research is needed to provide complete nondestructive testing of the weld by ensuring an adequate seal without drilling. A further modification could incorporate an array of fiber-optic sensors for determination of diffusible hydrogen distributions across the weld from traditional-type diffusible-hydrogen specimens, as shown in Fig. 9.

The advantages of using the sensor are numerous. The sensor response is ex-

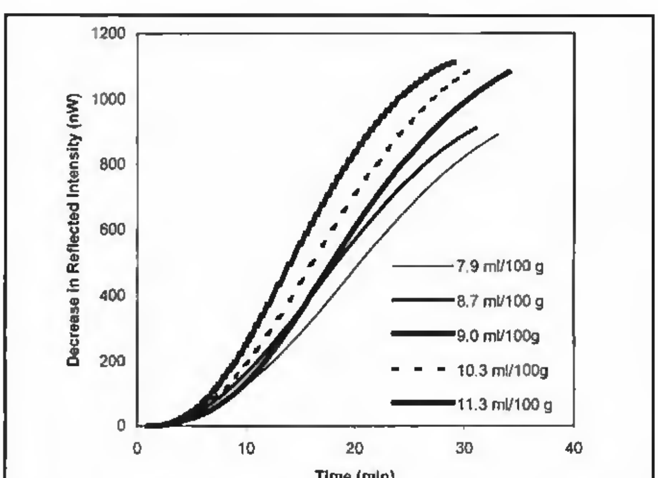

Fig. 5 — Experimental hydrogen-response curves for prototype diffusible-hydrogen sensor (gas metal arc welded HSLA 100 steel).

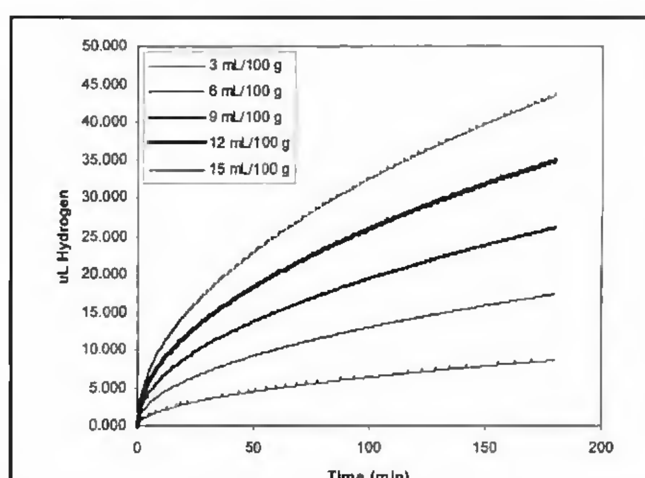

Fig. 6 — Theoretical hydrogen evolution curves using diffusion equation for semi-infinite plane sheet (based on erf(x); five different initial diffusible hydrogen concentrations; $D_{eff} = 7.5 \times 10^{-5}$ cm^2/s).

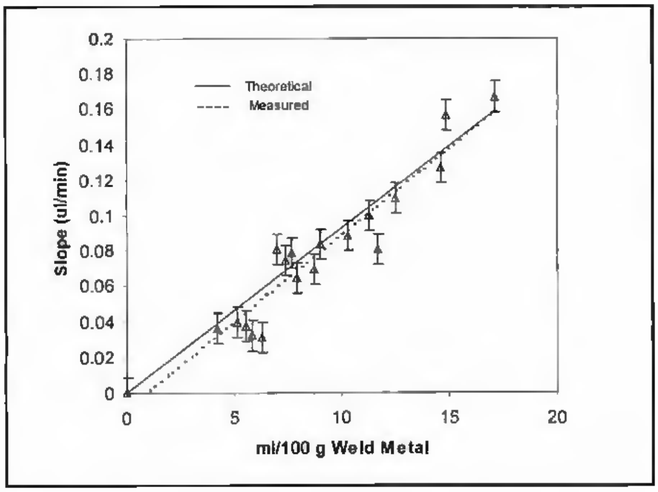

Fig. 7 — Comparison of experimental and theoretical data for fiber-optic, diffusible hydrogen sensor (gas metal arc welded HSLA 100 steel; $D_{eff} = 7.5 \times 10^{-5}$ cm^2/s; r = 0.970).

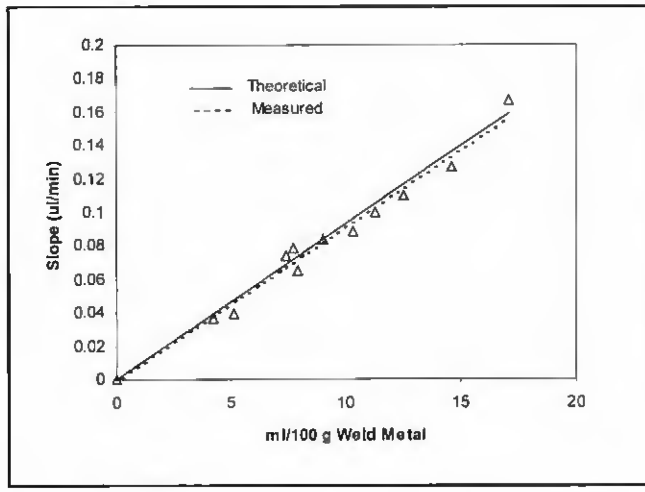

Fig. 8 — Comparison of experimental and theoretical data for fiber-optic diffusible-hydrogen sensor (gas metal arc welded HSLA 100 steel; $D_{eff} = 7.5 \times 10^{-5}$ cm^2/s; r = 0.989).

tremely rapid, with results obtained within ½ hour. The test may be performed on the actual welds on the structure, as opposed to a laboratory sample. The sensor is extremely sensitive and can analyze samples hours after welding. The equipment used is relatively inexpensive, and can be designed for use by trained welding personnel. It is anticipated that further refinement of the sensor design will provide the welding industry with a powerful tool for control of hydrogen damage in welded structures, especially those structures manufactured from high- strength alloys, where such control is most critical.

Conclusions

1) An optoelectronic diffusible-hydrogen sensor has been developed. The sensor generates results quickly, and allows analysis of an actual welded structure as opposed to a laboratory specimen.

2) The sensor has been calibrated to yield quantitative results for HSLA 100 steel in mL/100 g weld metal as a function of hydrogen diffusion rates from the sample surface. A resulting effective diffusion coefficient of 7.5×10^{-5} cm^2/s provides a good fit to measured data.

Acknowledgments

The authors wish to thank the National Renewable Energy Laboratory, Golden, Colo., for the use of its facilities. The authors also acknowledge and appreciate the support of the United States Army Research Office.

References

1. Granqvist, C. G. 1995. *Handbook of Inorganic Electrochromic Materials*. Elsevier Publishing Co., New York, N.Y., p. 81.

2. Khoobiar, S. 1964. Particle to particle migration of hydrogen atoms on platinum-alumina catalysts from particle to neighboring particles. *J. Phys. Chem.* 68: 411–412.

3. Lampert, C. M. 1984. Electrochromic materials and devices for energy efficient windows. *Solar Energy Mat.* II 11: 1–27.

4. Ito, K., and Ohgami, T. 1992. Hydrogen detection based on coloration of anodic tungsten oxide film. *Appl. Phys. Lett.* 60(8): 938–940.

5. Benson, D. K., Tracy, C. E., and Bechinger, C. 1996. Design and development of a low cost fiber optic hydrogen detector. *Proceedings of the DOE Hydrogen Program Meeting*, Vol. II, Miami, Fla., pp. 605–624.

6. Benson, D. K., Tracy, C. E., Hishmeh, G. A., Ciszek, P. A., Lee, S., and Haberman, D. P. 1998. Low-cost fiber-optic hydrogen gas detector using guided-wave surface plasmon resonance in chemochromic thin films. *Proceedings of the SPIE International Symposium on Industrial and Environmental Monitors and Biosensors*, Boston, Mass., pp. 185–202.

7. Benson, D. K., Tracy, C. E., and Bechinger, C. 1998. Fiber Optic Device for Sensing the Presence of a Gas. U.S. Patent 5,708,735.

8. Seibert, M., Flynn, T., Benson, D., Tracy, E., and Ghirardi, M. 1997. Development of selection and screening procedures for rapid identification of H_2 producing algal mutants with increased O_2 tolerance. *Proceedings of the 1997 Biohydrogen Meeting*, Waikoloa, Hawaii, pp. 227–234.

9. Crank, J. 1992. *The Mathematics of Diffusion*. Oxford Science Publishing Co., London, U.K., p. 32.

10. Völkl, J., and Alefeld, G. 1978. Diffusion of hydrogen in metals. *Hydrogen in Metals I*, ed. J. Völkl, and G. Alefeld, Springer-Verlag, New York, pp. 321–348.

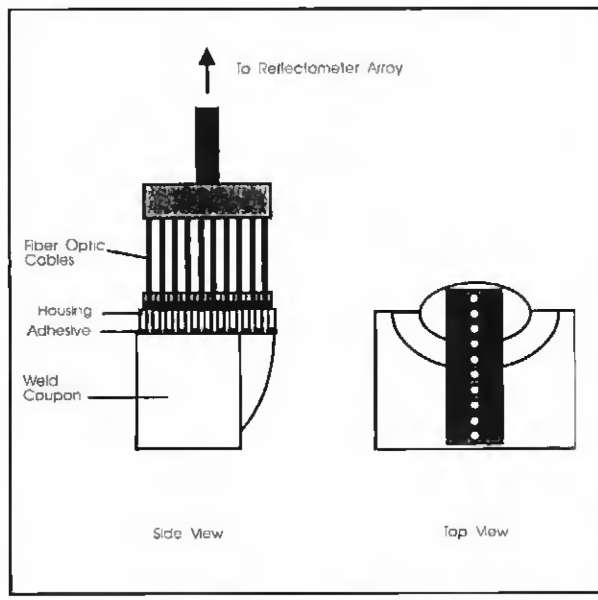

Fig. 9 — Design for fiber-optic, diffusible-hydrogen sensor array.