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HIGHLY SENSITIVE TAPERED FIBER-OPTIC SENSOR TO DETECT GASEOUS HYDROGEN IN LOW CONCENTRATIONS AND THE PROPOSAL TO USE IT AS A HYDROGEN EMBRITTLEMENT DETECTOR

A. S. Paterno[1] and H. J. Kalinowski[2], C. Legnani[3], M. Cremona[4]

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Resumo

Este trabalho descreve resultados preliminares da implementação de um sensor a fibra ótica para detecção de Hidrogênio molecular e gasoso. O sensor é fabricado em uma fibra ótica monomodo padrão com seu diâmetro estreitado pela técnica da varredura por chama, recoberto com um filme fino de Paládio. A presença de Hidrogênio sobre o filme altera o índice de refração do filme de Paládio provocando uma variação da atenuação da luz que atravessa o sensor. Resultados preliminares mostram que o sensor tem uma alta sensibilidade ao Hidrogênio gasoso. Testes preliminares estão sendo feitos em uma câmara evacuada onde foram instalados controladores de fluxo para controlar a vazão de Hidrogênio e Nitrogênio. Já que o sensor tem alta sensibilidade, sugere-se o uso do sensor para detecção de empolamento por Hidrogênio em oleodutos. Testes para verificação da sensibilidade do sensor ao Hidrogênio atômico utilizando uma célula onde o fluxo pode ser controlado são também sugeridos.

Abstract

This paper describes preliminary results on the implementation of a fiber optic sensor to detect molecular and atomic Hydrogen. The sensor is fabricated in a tapered fiber optic that is coated with a Palladium thin film. The presence of Hydrogen will change the refractive index of the film and this will cause the attenuation of the light that passes through the sensor to decrease. Preliminary results show that the sensor is highly sensitive to gaseous Hydrogen. The tests were made in a vacuum chamber, where the sensor is exposed to a controlled atmosphere of Nitrogen and Hydrogen with concentrations varying from 0% to 4% Hydrogen. Since the sensor is highly sensitive, it is also suggested the use of this sensor to detect Hydrogen embrittlement in pipelines and also a test to emulate the pipeline environment in an electrochemical cell, where the sensor can be exposed to atomic Hydrogen in a controlled manner.

1. Introdução

Fiber optic sensors for Hydrogen detection have been attracting attention in the last decade due to its potential high sensitivity and its principle of operation. They are excited by energies (light) well below the ignition limit of the detected gas and can be easily implemented to operate in a distributed configuration, therefore they become very attractive for applications in the oil and gas field. As a consequence, several fiber optic sensors have been proposed to detect gaseous Hydrogen using as an active material a metal that reversibly changes its optical properties when in

[1] Doutorando - Bolsista PRH10-ANP - CPGEI/UTFPR
[2] Professor Doutor - CPGEI/UTFPR
[3] Doutor - Física/PUC-RJ
[4] Professor Doutor - Física/PUC-RJ

contact with the gas. Usually, a thin film of Palladium is deposited over the region of the fiber that is going to sense the Hydrogen. This idea has been initially proposed by Butler (1984), where the variation of the thin film volume after the contact between the film and the Hydrogen caused the fiber to be stretched and this deformation was monitored using interferometric techniques. Butler (1994) also proposes a different approach using the detection of the variation of the reflectivity in a Palladium thin film coating a fiber optic tip. Every fiber optic sensor that has been proposed since then is based more or less on one of these principles.

The mechanical deformation caused by the volume change in the Palladium film can be detected by a Fiber Bragg grating (FBG) if the film is sufficiently thick and the fiber is tapered to facilitate the deformation of the FBG, as proposed by SUTAPUN(1999), where the author tapers the fiber by etching the cladding with acid. This sensor shows a very small sensitivity being also temperature dependent due to the FBG use. On the other sensitivity extreme, the most sensitive of the fiber optic sensors to detect gaseous Hydrogen are based on the interaction of the evanescent field of a fiber optic along a region of the fiber where the thin film of an active material is deposited, as proposed by Villatoro (2003). The variation of the refractive index of the film changes the attenuation of the light that traverses the sensor making an intensity-based device with a high sensitivity.

These sensors have only been tested using a Nitrogen-Hydrogen atmosphere and its dynamic range of operation is usually limited to an interval of 0% to 10% concentration of Hydrogen as reported by Sutapun(1999) and other authors, because the thin film may suffer the effects of Hydrogen embrittlement, however this topic of Hydrogen embrittlement has not yet been analyzed when considering the relation between the Palladium thin film performance on a silica fiber optic and its response to Hydrogen. As a consequence, the reasons why the sensor is only capable of operating subject to concentrations of less than 10% Hydrogen are still to be completely explained and solved and are the theme of a future work of the authors.

In this text the development of a methodology of fabrication of an evanescent field tapered fiber optic sensor to detect Hydrogen is described as well as some preliminary results showing its operation in a Hydrogen atmosphere. Some remarks on the methodology to test the sensor in order to indicate its potential use as a Hydrogen embrittlement sensor are also reported.

2. Theory

The sensor is made by depositing a Palladium thin film over a specially prepared region of the fiber optic. This section of the fiber with the thin film is tapered and the electromagnetic field is evanescent allowing its interaction with the Palladium coating. A diagram with the structure of the fiber optic and the metallic thin film along the region of the tapered sensor is schematically depicted in Figure 1. The film is deposited along a region with length L_W, the radius of the tapered fiber optic is r_W and the thickness of the Palladium thin film is t. The dotted line in the tapered region is assigned to the cross-section of the fiber also depicted in Figure 1.

2.1. Hydrogen sensing principle

Butler (1994) was the first to demonstrate that the reversible reaction of Hydrogen (H) with a thin film of Palladium (Pd) deposited on a fiber optic could be sensed, since the refractive index of Palladium changes when there is a Hydride (Pd_xH) formation, where x is the atomic ratio Pd/H. In the described sensor, the evanescent field interacts with the metallic film that has its optical properties, i. e., refractive index changed when there is Hydride formation.

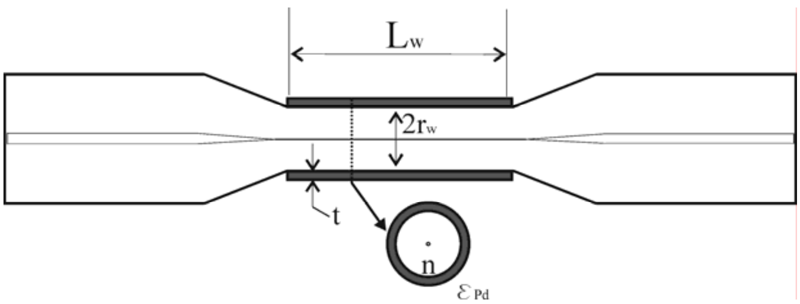

Figure 1. Profile of the fiber optic with a tapered region coated with a Palladium thin film with thickness t, along a length L_W, with radius r_W. The tapered region cross-section at a point associated to a dotted line is also illustrated.

The tapered fiber optic works as a multimode fiber supporting other LP_{0m} modes and the sensor works as a metallic cylindrical waveguide made of Palladium with a dielectric core, whose refractive index is the same of the fiber optic. The fabricated taper is adiabatic and as a consequence the fundamental mode of the fiber excites with high efficiency (higher than 99%) the fundamental mode of the taper. This fundamental mode in the sensor has its propagation constant altered by the interaction of the Palladium layer with its environment that causes the attenuation of the light that passes through the device to be differently attenuated depending on the concentration of Hydrogen. Because the Palladium layer that forms the coating of the sensor has a complex refractive index, the intensity of the light that is transmitted by the sensor is attenuated according to the variation of the effective refractive index of the Palladium layer as determined by the equation 1:

$$I=I_{out}\exp(2\Delta\alpha L_w) \qquad (1)$$

Where $k=2\pi/\lambda$ is the wave-number in free-space, λ is the wavelength of light in vacuum, I_{out} is the intensity at the output of the sensor with no Hydrogen, $\Delta\alpha=\alpha_{Pd}-\alpha_{PdH}$ is the difference between the attenuation constants of the fundamental mode when no Hydrogen is present and after the formation of PdH and L_w is the length of the region where the interaction takes place in the sensor. As a consequence, the sensor is then an intensity-based device. The intensity at the output of the sensor increases with an increase in the concentration of Hydrogen.

3. Fabrication of the sensors

3.1. Methodology and fabrication of the tapers

The fiber optic tapers are fabricated using a fiber optic coupler manufacturing machine modified to produce tapers with a length of 40mm. The tapers are fabricated using the traveling-burner technique with a Hydrogen torch that heats the fiber so that it can be stretched by translation stages, obtaining with that tapers as described by Birks (1992). The diameter of the taper is simultaneously monitored by a microscope. The tapers are produced in a standard single-mode telecommunications fiber optic (G652) and have a length of 40mm, a diameter of $2r_W$ =15μm and an exponential profile.

3.2. Fabrication of the sensors

After the fabrication of the tapers, they are cleaned in an ultrasound bath in isopropylic alcohol for 20 minutes. Prior to taper fabrication, the acrylate coating of the fiber is removed mechanically and the fiber is perfectly cleaned with acetone such as not to cause deformations in the taper during heating.

The thin film is deposited using an electron beam evaporation apparatus and the thin film thickness is monitored during the evaporation process. A Palladium slug (99.95%, Sigma-Aldrich) is used and a deposition rate of 1Å/s is set when the pressure in the evaporation chamber reaches less than 10^{-6}Pa. The sensor is fixed in a fiber optic holder that allows the fiber to be rotated after the evaporation. This device is depicted in Figure 2. It is capable of holding the fiber straight without using any kind of bonding. Besides, it is hexagonal such as to facilitate a number of rotations, when installed in an evaporation holder as shown in figure 3. Here we report results for a sensor with a thin film having a thickness of t=10nm.

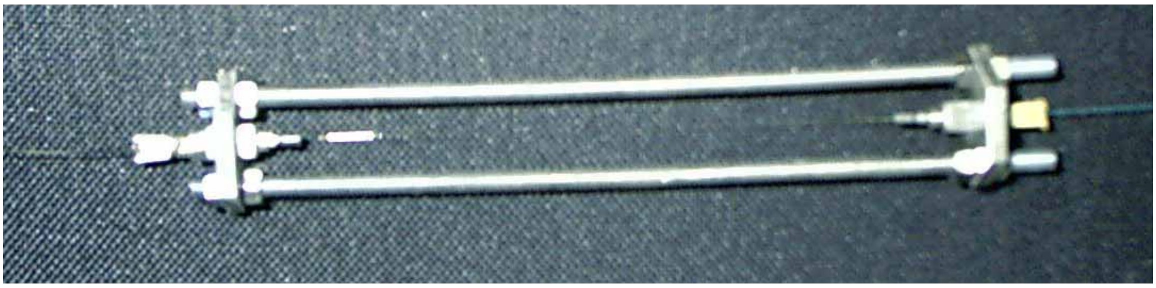

Figure 2. Fiber optic holder used to rotate the fiber optic sensor after each deposition.

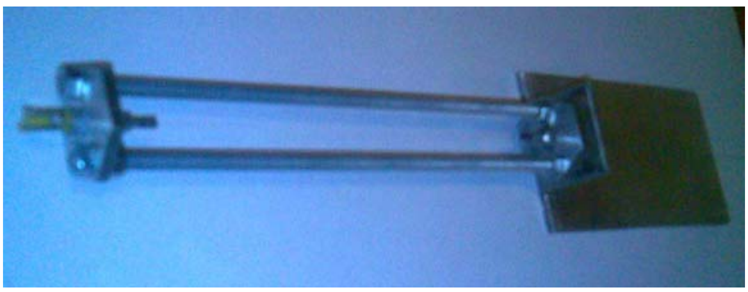

Figure 3. Fiber optic holder mounted in the evaporation holder that enables the rotation of the fiber after evaporation.

Several depositions are necessary in order to fabricate a more uniform film around the fiber. Sensors are evaporated rotating the fiber two, three and six times, but the response of the sensor suffers a greater influence if the film is deposited only once on a sensor. In this case, the sensor has its response depending on the polarization of the light that passes through the device.

Another method of producing the thin film has been tested using a thermal evaporation process. However, thermal evaporation of Palladium is not indicated and an e-beam method is preferable. More than 20 sensors have been fabricated with the thermal evaporation process and the efficiency of this method shows that only 25% of them worked properly. In the case of the e-beam method, this efficiency increases sensibly to more than 75%. Electro-deposition is another method that could be tested, but in this case, since no conductive layer is present on the fiber optic previous to the deposition, it would be necessary to use an electroless plating method or the deposition of a metallic interface layer (Ni or Cr, for example) to produce a conductive fiber optic surface in order to electro-deposit the Palladium film, as described by Schlesinger (2000).

3.3. Proposal to test the sensor

Only one method have been reported in the literature to test the Hydrogen detection with fiber optic sensors, namely, exposing the sensor to a controlled Hydrogen atmosphere in Nitrogen, in a sealed cell or even in an open environment, with the precaution that the concentration of Hydrogen be below the explosive limit of 4%. This flow control can be performed using rotameters or any mass flow controllers. Preliminary results are obtained here using this method by exposing the sensor to a controlled atmosphere of Hydrogen in Nitrogen inside a vacuum chamber, as shown in figure 4. However, in our case, the interruption of the flow is not possible to be obtained instantly and there is only the possibility of the control of very low concentrations of Hydrogen, only the response to a sudden exposure of a low Hydrogen flux is reported. We are working on a new system to test the sensor with higher concentrations.

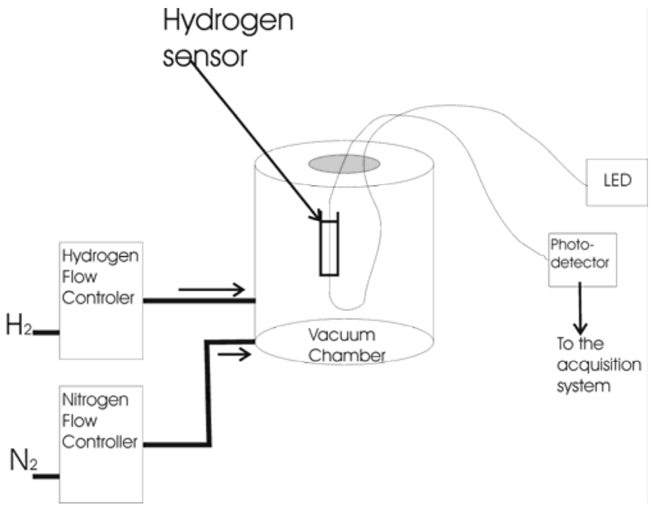

Figure 4. Diagram showing the setup to test the sensor in a controlled atmosphere. Dynamic tests are not possible in this system.

Another test that shows qualitatively the operation of the sensor can be easily obtained by exposing the sensor to an escape valve of a Hydrogen chamber, which is commonly used in laboratories that work with fiber optics to produce fiber Bragg gratings. This test is initially performed to evaluate if the sensor is properly working.

Considering the various sources of Hydrogen, as described in electro-deposition books like in Dini (1993), these processes could be used to test the sensors. For example, in electrochemistry, acid type corrosion, electrochemical cleaning, the reactions on the cathode during electroplating and pickling are potential tests for a sensor if these processes are properly controlled and one would be able to use it in order to characterize the device. Considering that these processes are the same that generate the Hydrogen that causes the embrittlement in the material, the idea of using this sensor to measure it is straightforward.

4. Preliminary results and discussion

Sensors with the characteristics mentioned in the previous section are tested in the chamber with a controlled atmosphere of Hydrogen. In this case, the sensor has a film with thickness of 10nm. In the testing system the flow of Hydrogen cannot be suddenly interrupted, therefore only the rise time response curve to a sudden flow of 4% Hydrogen concentration is shown in figure 5. The time response of the sensor is high, reaching a rise time value of 150s for such an exposure. This is a preliminary result, since a system to demonstrate complete results with a response of the sensor to different concentrations under different dynamic conditions are being developed at the present time. The response of the sensor after its exposure to a Hydrogen flow to the environment at the output of an escape valve is shown in figure 6. This result shows the ability of the sensor to detect Hydrogen in the atmosphere, working as an alarm to the presence of H_2.

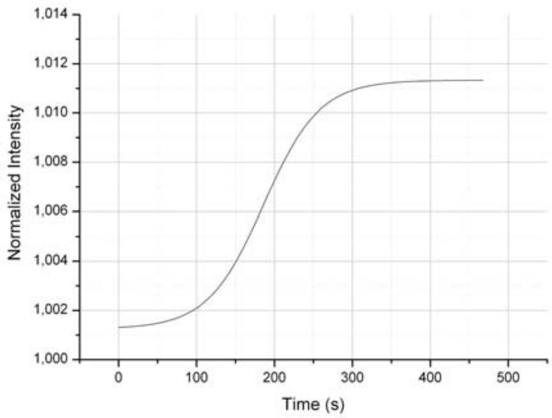

Figure 5. Response of the sensor to a sudden exposure to a 4% flow of Hydrogen in Nitrogen.

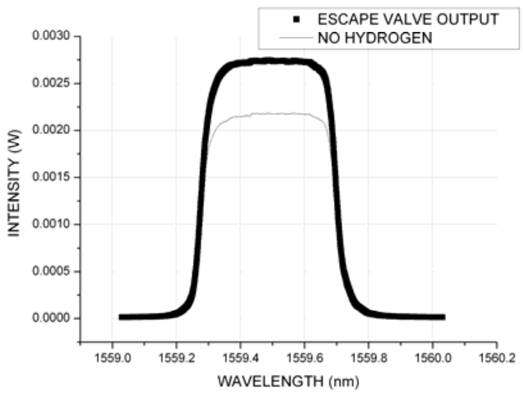

Figure 6. Response of the sensor to a sudden exposure at the output of an escape valve in a Hydrogen Chamber used to photosensitize fiber optic.

In figure 6, the light source used is a laser centered in 1560nm, and it is possible to observe an increase in the transmission intensity of the sensor when in contact with Hydrogen. This response would easily allow the implementation of an alarm with a very simple optoelectronic configuration.

5. Conclusions

The development of a methodology to fabricate fiber optic Hydrogen sensors in tapered fibers coated with a Palladium thin film is reported. Considering the high sensitivity of the sensor, different methodologies to test it are proposed such as to investigate if the sensor, given its high sensitivity, is a potential candidate to measure Hydrogen embrittlement conditions. Different methods of fabricating the thin-films on the fiber optic have been tested in order to evaluate which would produce the higher efficiency in the fabrication method. Thermal evaporation, since it is not indicated in the case of Palladium, shows a lower efficiency. As already expected, an e-beam technique to deposit the film shows a much better method. Electrochemical methods are suggested for this purpose. Preliminary results show qualitatively how sensitive and fast the sensor is to detect Hydrogen. The study will continue to evaluate how the thin film topography is altered after Hydrogen loading, and how it is related to the correct operation of the sensor. This will be possible after the implementation of the complete system to test the sensor under controlled conditions.

6. Aknowledgements

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