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Short Communication

New characterization methods for monitoring small resonant frequency variation: Experimental tests in the case of hydrogen detection with uncoated silicon microcantilever-based sensors

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ABSTRACT

The uncoated silicon microcantilever (USMC) operated in the dynamic mode is a new concept in the field of microcantilever-based chemical sensors. Due to the absence of a sensitive layer, this kind of microsensor can only be used for specific applications where it is known that only one chemical species may be varying in concentration, such as monitoring hydrogen release in radioactive waste disposal facilities. Usually, the relative variation of the USMC resonant frequency expected for low concentrations (≤2%) of hydrogen in nitrogen is below 50 ppm. As a result, the measurement of both the resonant frequencies, f_r, and the quality factor, Q, by classical methods, based on the gain spectrum (resonant peak and −3 dB bandwidth), is not sufficiently accurate. In this paper, new measurement methods for monitoring f_r and Q variations are proposed: (1) variation of gain and phase at fixed frequencies and (2) polynomial approximations of gain and phase spectra. The performance study of these characterization methods shows that monitoring f_r by using phase linearization yields the best signal-to-noise ratio (e.g., 100 at 0.6% of H_2 in N_2), with 0.02% as a limit of detection for hydrogen.

1. Introduction

1.1. Hydrogen release in radioactive waste disposal facility

After having concluded a feasibility study on deep geological disposal for high-level and intermediate level long-lived radioactive waste in 2005, the French national radioactive waste management agency (Andra) was charged by the Planning Act n° 2006-739 to study the design and the creation of an industrial center for geological disposal called Cigéo which must be reversible for at least a century-long period. Within the framework of this geological repository project, the observation and surveillance must contribute to acquire the knowledge required to run the disposal and its reversible management. Hydrogen release is expected in the radioactive waste disposal facility. It originates from (i) radioactive waste release (ii) and anoxic corrosion of metallic materials. In fact, some radioactive wastes (containing α, β, γ radioactivity) resulting from the reprocessing of irradiated fuels are embedded in bitumen matrix. The self-irradiation of the bituminized waste leads mainly to the production of radiolytic hydrogen (75–95 vol.% of produced radiolytic gas). In the deep geological disposal environments steel components would corrode to more oxidized corrosion products and hydrogen gas. The kinetic of Anoxic corrosion of Fe components is not well known, it is actually considered an average rate about 10 μm/year. This assumption still awaits experimental verification in the Underground Research Laboratory sited at Bure in the Meuse district and aims at studying the feasibility of the reversible geological disposal of high-level and long-lived intermediate-level radioactive waste in the Callovo-Oxfordian clay formation (east of France). Despite the fact that hydrogen releases are expected to be small (in the order of 430 mmol/h for each intermediate level nuclear waste), when ventilation stops with cell closure, concentrations would slowly and regularly increase. The first calculation gives 4% hydrogen content in the atmosphere of the radioactive waste cell in less than one year by the end of the oxic corrosion period.

Monitoring of repository structures contributes to security, safety and reversible management of the repository [1]. It is important as it relates to the guidance of the disposal process and to the corresponding decision-making process. In the upstream repository-design phases, the hydrogen monitoring system was planned to work under normal operating conditions and to

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withstand radiation exposure in case of an accidental event. There exist different kinds of hydrogen sensors, including those that are commercially available and others still under development [2]. In the present paper, the preliminary results concerning the development of microcantilever-based sensors without sensitive coating (Uncoated Silicon MicroCantilever, USMC) for hydrogen detection are presented.

1.2. Resonant frequency shifts of USMC-based sensors

In recent years, interest in microcantilever-based chemical sensing systems has risen due in part to their projected high sensitivity [3,4]. Because of the large ratio of surface area to volume, the microcantilevers are extremely sensitive to surface processes and can be used as micromechanical sensors [5] for high-resolution sensing and probing [6]. For chemical detection, the USMC-based sensors operated in the dynamic mode are used to measure mass density changes of one scalable analyte in gas mixture [7]. The operating principle of this unconventional use of a microcantilever is based on the fact that the resonant frequency of the microresonator depends on both the density and the viscosity of the surrounding medium. In the case of the out-of-plane mode of a wide microcantilever, it has been shown that the predominant effect causing the change in the microcantilever resonant frequency is due to the gas mass density variation [7]. In fact, when the surrounding fluid mass density increases (decreases), the equivalent effective mass of the microcantilever increases (decreases), thereby causing the resonant frequency to decrease (increase). The absence of a sensitive coating leads to a more reliable and reversible behavior because there is no significant absorption and desorption phenomena. However, the major drawbacks of such sensors is that there is no intrinsic selectivity; thus, these sensors can only be used for specific applications, such as when monitoring environments where it is known that only one gas concentration can vary [8].

The conventional method for monitoring the resonant frequency shift consists of searching for the resonant peak on the amplitude spectrum and tracking the change in the corresponding frequency. The relative variation of the resonant frequency in the case of low concentration of hydrogen (H_2) in nitrogen (N_2) is very small. For instance, using an USMC (length = 5 mm, width = 1 mm and thickness = 170 μm, resonant frequency approximately 10 kHz), a concentration of 0.2% of H_2 in N_2 corresponds to a resonant frequency change of approximately 0.02 mHz. Therefore, the conventional method does not prove to be sufficiently accurate to measure such a small shift in resonant frequency. This is mainly due to the difficulty of identifying precisely the resonant peak location due to the measurement noise.

The quality factor is a key parameter in resonating sensors because it determines the stability of the resonator in terms of resonant frequency. It is defined as the ratio of the vibrational energy stored in the system to the total energy lost per cycle. This parameter is also commonly used to characterize resonating sensors [9,10] that are typically used for viscosity measurements [11,12]. In high quality factor systems, and when the resonant peak is sufficiently high to contain the −3 dB bandwidth, the −3 dB measurement method is often used to calculate the quality factor. However, when the magnitude of the resonant peak is less than 3 dB, this method cannot be applied.

Other methods for monitoring the shift in resonant frequency consist of making measurements at a fixed frequency instead of using a frequency sweep. By fixing the measurement frequency at the value corresponding to the maximum slope of the gain [13], impedance [14] or phase spectra, changes in the resonant frequency can be detected simply by monitoring variations of response magnitude.

In order to reduce the impact of the noise, polynomial approximations for the gain or phase spectrum can be used. These polynomial approximations can also be used to analytically extract various response characteristics such as natural frequency, resonant frequency and quality factor.

In this paper, the different characterization methods using gain and phase spectra have been tested on measurement data obtained with a USMC device with integrated actuation and read-out systems. To generate measurement data, the sensor has been subjected to various concentrations of hydrogen in nitrogen. The study is focused on the performance of the different characterization methods in terms of signal-to-noise ratio (SNR) and the limit of detection (LOD) corresponding to a signal-to-noise ratio of 3. Following a description of the different methods to measure small shifts in resonant characteristics in section 2, the experiments using an uncoated silicon microcantilever-based sensor (USMC) for hydrogen detection are presented in Section 3. Finally, a comparison of the results of the different methods applied to these measurements are presented and discussed in Section 4.

2. Characterization methods

In this section, two conventional methods (Sections 2.1 and 2.2) and four novel characterization methods (Sections 2.3–2.6) are presented.

2.1. Variation of resonant frequency: Δf_r

The measurement of the resonant frequency shift, Δf_r, can be simply performed by looking for the resonant peak in the gain spectrum, then associating it with the corresponding frequency as shown in Fig. 1a. However, for small changes of the resonant frequency (USMC case) this technique is not very efficient because of the noise on the gain spectrum inducing significant measurement uncertainty. Nevertheless, eliminating the noise on the gain using appropriate fitting methods (Section 2.5) can considerably improve the efficiency of this characterization method.

2.2. Variation of quality factor: ΔQ

The conventional measurement method for extracting the quality factor from experimental measurements is the −3 dB bandwidth method, as shown in Fig. 1b. This technique can only be applied to high quality factor systems and it consists of calculating the ratio between the resonant frequency and the −3 dB bandwidth ($\Delta f_{-3\,\mathrm{dB}}$), measured on the gain spectrum:

$$Q = \frac{f_r}{\Delta f_{-3\,\mathrm{dB}}} \tag{1}$$

Just as was the case for the Δf_r method of the previous section, measuring changes in the quality factor by the −3 dB bandwidth method is not effective in the case of small resonant frequency changes and small quality factor changes, because this method requires not only the measurement of Δf_r, but requires also the measurement of $\Delta(\Delta f_{-3\,\mathrm{dB}})$, i.e., the change in the bandwidth.

2.3. Variation of gain at fixed frequency: ΔG_{FF}

After setting the measurement (actuation) frequency, f_{mes}, on the point approximately representing the highest slope in the gain spectrum, the characterization of the resonant frequency variation is possible, thanks to the gain variation obtained at f_{mes} as shown in Fig. 1c.

Moreover, to increase the measurement sensitivity and eliminate the noise on the gain, a linear fit can be applied to the portion