Mg-Ni-Zr glassy hydrides as a new class of optical hydrogen sensing materials for gas and liquid applications

M. Victoria[a], R.J. Westerwaal[a], B. Dam[a], and J.L.M. van Mechelen[b*]

[a] Department of Chemical Engineering, Materials for Energy Conversion and Storage, Delft University of Technology, Julianaweg 136, 2628 BL Delft, The Netherlands

[b] ABB Corporate Research, Segelhofstrasse 1K, 5405 Baden-Dättwil, Switzerland

* Corresponding author.
  E-mail address: dook.vanmechelen@ch.abb.com

Hydrogen sensors have the purpose of guaranteeing safety and controlling processes in a wide range of industrial and (future) consumer applications. Optical hydrogen sensing technologies, with the advantage of involving low energy densities, have been proposed in various forms such as (coated) nanostructures (dots, rods, etc.)[1], coated tapered fibers[2] and fiber-based micro-mirrors[3]. The sensing material influences directly or indirectly the optical response, which ranges from inducing (surface) plasmons, modifying waveguiding conditions to probing the transfer function within a spectroscopic measurement. Although the degree of engineering of these structures is highly advanced, the choice of the sensing material is almost always restricted to Pd, Y or Mg.[4] A major disadvantage of these materials is their low sensitivity in the relevant sensing range. In addition, thin film Pd and Mg require hydrogen partial pressures of the order of 10^1-10^2 mbar in order to optically change, which is outside the window of most applications. Recent work has shown that alloying Mg with Ti[5] and Pd with Au[4] both broadens the sensing range, thereby increasing the materials' sensitivity. However, in both cases the optical contrast is strongly reduced by adding metallicity to the original semi-transparent hydrides MgH_2 and $PdH_{0.7}$.

Since the sensing material is by far the most important part of the sensing design, it should be protected such that it can function in the targeted environment. This can be gas or liquid which contain constituents that may cause an erroneous reading due to their interaction with hydrogen, pollution of the sensing material, cross-sensitivity and so forth.

In brief, a hydrogen sensing design should fulfil a series of basic requirements which allow usage in industrial and future consumer applications, that can be summarized as:

- Optical response uniquely related to hydrogen partial pressure
- Large optical sensitivity in the hydrogen pressure and temperature range of interest
- Monotonous temperature dependence
- Reversible and repeatable optical response
- Environmental protection

Here we describe the route to a sensor design that takes all these points into account. We develop a new class of materials that has a substantially higher sensitivity while preserving a good optical contrast. Hereto, we add metallic glassiness of the Ni-Zr system to the well-known transparent Mg-Ni hydrides. The amorphization of the latter makes the thin film structure flexible and therefore its optical response repeatable and reversible within 0.1% for hundreds of cycles. We test practical usage of the sensing design in gas and liquid environments in the presence of contaminants.

The optical response of a sensing material depends largely on its thermodynamic properties. With increasing hydrogen partial pressure p_{H2}, the hydrogen concentration c_{H2} increases in a non-linear way for most materials. For single element hydrides at intermediate partial pressures, coexistence of several phases generally causes a sharp increase of c_{H2}. Represented as p_{H2} vs. c_{H2}, as commonly done for pressure-composition isotherms, this corresponds to a plateau region.

For hydride forming alloys, it has been shown that at intermediate hydrogen concentrations, c_{H2} is directly proportional to the relative transmissivity $\mathcal{T} = \ln(T/T_0)$, where T is the transmission of the hydrogenated film and T_0 of the as-deposited film.[6] A practical optical equivalent of the pressure-composition isotherm is therefore the so-called pressure-transmission isotherm (PTI) of p_{H2} vs. $\mathcal{T}$.

An optical sensing device has to determine p_{H2} from a change in $\mathcal{T}$. It thus has a sensitivity that is maximum in the plateau region and quickly decreases for pressures beyond this range. A sensing material of broader utility, with a wide sensing range and a sensitivity independent on the value of the hydrogen pressure, would need to show a monotonously increasing PTI. That is, the existing plateau needs to be strongly inclined. Recently, it has been shown that Mg-Ti alloys at

Mg/Ti $\approx$ 1 manifest a slightly inclined plateau as compared to pure MgH_x.[5] However, the plateau pressure of MgH_2 is about 10^1 mbar and alloying with Ti brings it down only by a small factor. Despite the slightly greater optical sensitivity than MgH_x, the sensing range is centred on pressures that are typically too large for applications. In addition, the optical contrast of Mg-Ti-H is small due to the formation of metallic TiH_2
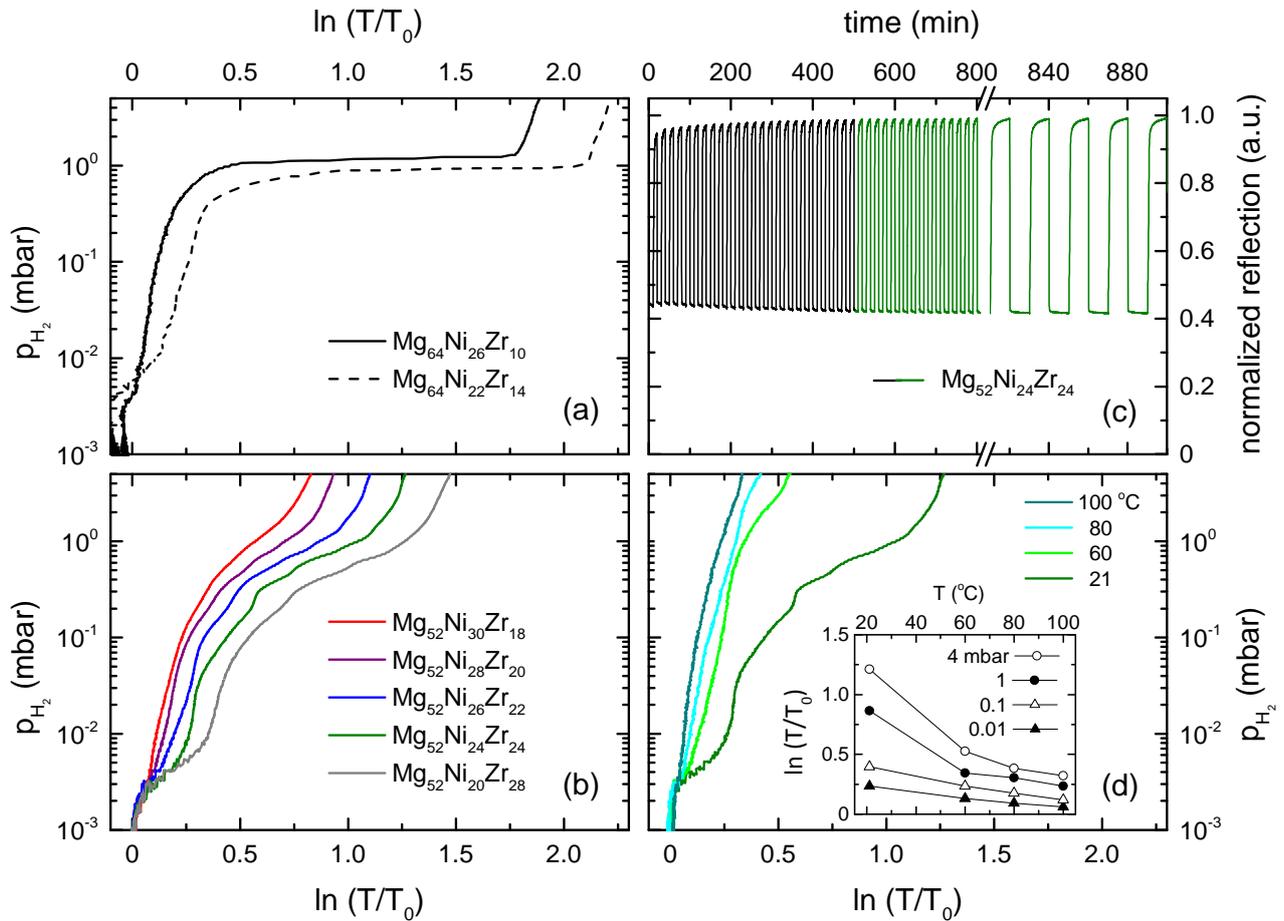
Figure 1 Pressure-transmission isotherms of selected Mg-Ni-Zr compositions (a) Zr poor and (b) Zr rich at 21 ºC gaseous environment. (c) Normalized reflection of $Mg_{52}Ni_{24}Zr_{24}$ during repeated hydrogenation at 40 mbar H_2. Green lines indicate a stable response. (d) Temperature dependence of PTI's of $Mg_{52}Ni_{24}Zr_{24}$. The inset shows the temperature dependence on the optical response $\mathcal{T}$ at selected levels of p_{H2}.

Amorphous alloys with an attractive hydrogen-hydrogen interaction, such as Ni-Zr, are shown to have steep hydrogen pressure-composition isotherms which lack signatures of a plateau.[7] In the presence of H_2, however, the Ni-Zr alloy remains metallic[8] and thus manifests a small optical change that is not ideal for optical sensing purposes. More suited would be to start with the Mg-Ni-H system and to add amorphousness by alloying with Zr. The advantage of the Mg-Ni-H system for an optical sensor material is its large optical change upon hydrogenation,[9] due to formation of both transparent Mg_2NiH_4 and

MgH_2.[10] At room temperature, the amorphous phase of Ni-Zr is energetically lower than its crystalline form only for ξ = Ni/Zr ratios between 0.6 and 3.5.[11] Therefore, in order to influence the degree of crystallinity of Mg-Ni by adding Zr, this ratio needs to be kept, contrary to ref. [12] where Zr only adds some metallicity to the system.

We have sputtered Mg-Ni-Zr gradient thin films with ξ in the previously mentioned range. X-ray diffraction in the as-deposited, hydrogenated and unloaded state was performed to investigate the crystalline structure of the $Mg_{52}Ni_xZr_y$ films with

ξ = 0.7-2.9. Besides the [111] and [220] reflections of Pd, none of the examined states showed any other reflections. This indicates amorphousness of all studied films and points to the remarkable observation that adding Mg to the Ni-Zr glass morphologically does not change its nature.

Figure 1a shows the PTI's for Mg-Ni-Zr compositions with small amounts of Zr and has ξ in the range where Ni-Zr forms a glass. Two trends are obvious: the smaller ξ, the lower the plateau pressure and the broader the plateau, which also shifts to larger values of $\mathcal{T}$. Following a scenario where Zr just substitutes Ni, then diffusion towards a hydrogen site on the larger Zr atom needs less energy and thus a lower pressure than for Ni. The increase to larger transmissions is due to the relative increase of Mg as compared to Ni, and thus the formation of MgH_2.

As we have recently demonstrated,[13] the influence of Zr and the Ni-Zr system becomes significant when Mg and Ni form the stoichiometric compound Mg_2Ni and Ni and Zr a metallic glass. Figure 1b shows that now the plateaus of the PTI's have changed to monotonous and steep slopes at the expense of slightly decreased maximum values of $\mathcal{T}$. Hereby, the hydrogen pressure range for which there is a measurable optical change has enormously increased as compared to traditional sensing materials such as Pd and its alloys.

An ideal PTI for sensing purposes would be a linear increase on a log-log scale. The latter since optical detectors possess logarithmic sensitivity, and hydrogen partial pressure levels required for applications are typically also logarithmically spaced. We therefore define an optical sensitivity S of the sensing material that can be calculated from the PTI's in the following way:

$$ S = \int_{\mathcal{T}_{min}}^{\mathcal{T}_{max}} \frac{d\log p_{H_2}}{d\mathcal{T}} \, d\mathcal{T}' $$

where $\mathcal{T}$ is normalized to its largest value $max(\mathcal{T})$. S is thus in fact a measure of the absence of plateau regions. Figure 2a shows S for Mg-Ni-Zr thin film compositions of Figure 1b. For compositions with Mg/Ni ~ 2, S strongly increases with ξ. It is interesting to note that S is minimum for ξ = 0.8-1.0, coinciding with the observation of the series of plateaus[13]. For Mg-Ni-Zr compositions of Figure 1a, which possess a plateau region, S is much smaller. In order to put these values in the context of typically used sensing materials, we have determined S based on reported PTI's for hydrogenated Pd[14], Pd-Cu[15] and Mg-Ti[14, 16] (see Figure 2a). Although Mg-Ti and Pd-Cu have slightly inclined plateaus, their sensitivity is far below our newly found class of amorphous Mg-Ni-Zr with Mg/Ni ~ 2.

Besides the sensitivity S equivalently important is the optical change $\Delta\mathcal{T} = |max(\mathcal{T}) - min(\mathcal{T})|$, mainly determined by the sensing layer and the catalyst. Since S is a property of the sensing material alone, we also consider here $\Delta\mathcal{T}$ of only the sensing layer. Through the Lambert-Beer law, $\mathcal{T}_{sensing} \propto (k_0 - k_H)$, where k_0 and k_H are the extinction coefficients in the as-deposited and hydrogenated state, respectively. $min(\mathcal{T})$ is determined by $k_0 \approx 4.0 \pm 0.5$ for all Pd- and Mg-based alloys[14, 17]. $max(\mathcal{T})$ depends strongly on the sensing material properties and thus on k_H. Figure 2b shows that k_H for Mg-Ni-Zr compositions of Figure 1(a-b) are in the vicinity of transparent Mg_2Ni, that is, midway between isolating MgH_2 [18] and very metallic Pd-Cu-H. Comparison of both S and k_H of other shown materials indicates that also from an optical contrast point of view Mg-Ni-Zr compositions with Mg/Ni ~ 2 are by far the best for sensing applications. Palladium, being the most widely used sensing materials has low sensitivity and very low transmission. Alloying increases the sensitivity, as reported,[4] but decreases even more the optical contrast.

For a specific application, the sensor performance can thus be tuned primary by the ratio Ni/Zr which is of leading influence for the sensitivity at Mg/Ni ~ 2. The absolute amount of Zr can further be used to tune the optical contrast.

A reproducible behaviour is a key asset for a sensor material. Figure 1c shows the behaviour of repeated hydrogenation of a Pd-capped $Mg_{52}Ni_{24}Zr_{24}$ thin film manifested by the change of the reflectivity during 50 periods. During the first ~ 25 cycles the optical response slightly increases, most probably due to relaxation effects thin film microstructure. Beyond this initial behaviour, the response becomes highly reproducible within 0.1%. This extreme level of reproducibility is due to the mechanical stability of the alloys, as confirmed by AFM measurements. Glassy alloys are more flexible than their crystalline counterparts. This is an onset for repetitive hydrogenation, which itself is always accompanied with expansion of the unit cell.
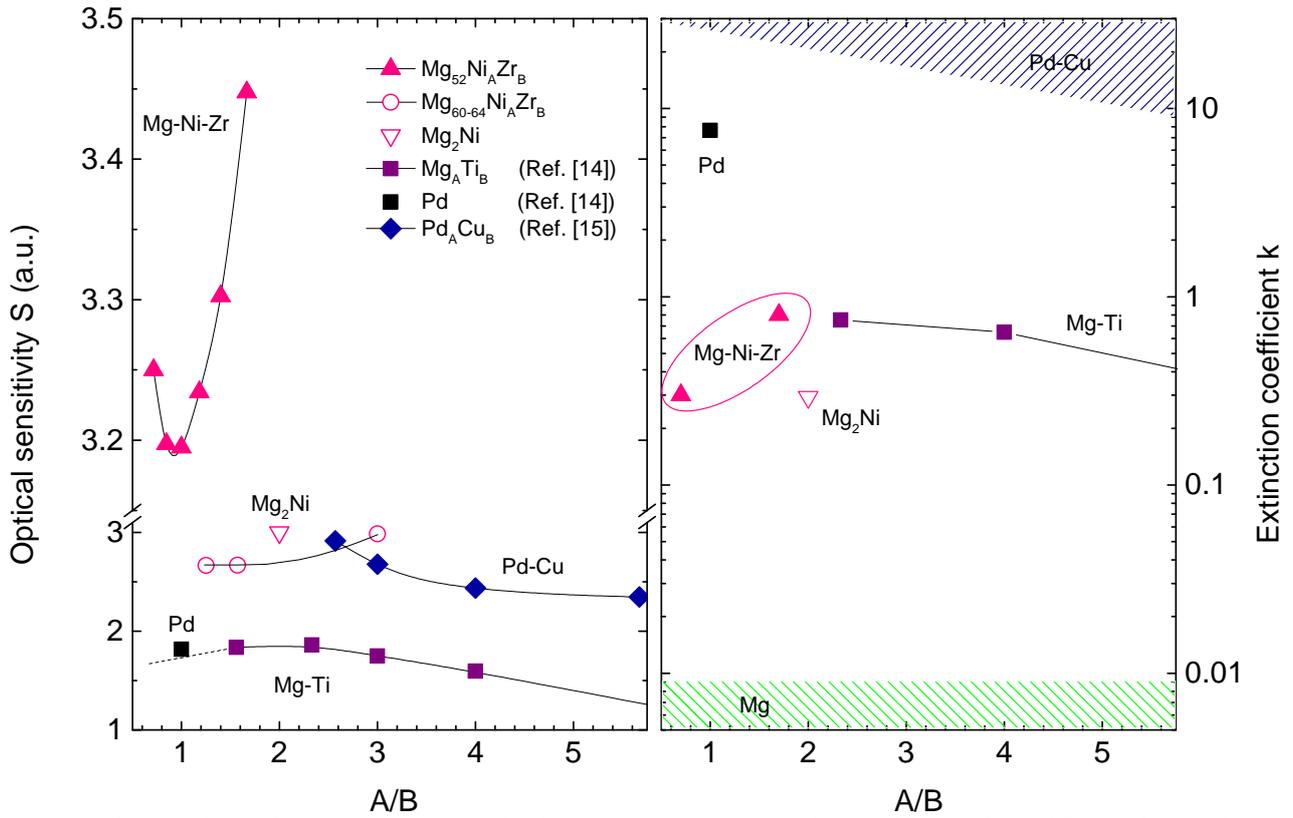
Figure 2 Comparison of (a) the optical sensitivity S and (b) the extinction coefficient k at 635 nm of Mg-Ni-Zr-H to often used hydrogen sensing materials.

Another requirement for a sensing material is a monotonous temperature dependence. Figure 1d shows the PTI's of $Mg_{52}Ni_{24}Zr_{24}$ between 21 and 100 ºC. With temperature $\Delta\mathcal{T}$ decreases, but removal of the sub-plateaus increases S. As can be seen in the inset, the temperature dependence of Mg-Ni-Zr is large though monotonous, and thus well suited for sensing applications.

Until here we have shown the functionality of the new class of Mg-Ni-Zr sensing materials in gaseous environments. Industrial applications often deal with dissolved hydrogen in liquids which range from water, oil, bitumen to more exotic ones such as liquid aluminium. Electrical transformers contain oil for cooling purposes. With time, degradation processes cause hydrogen to be released into the insulation oil. Monitoring the hydrogen content indicates the health status of the transformer and is important for safety and guaranteeing continuity of power delivery.

Requirements from the industry are detectability of critical hydrogen levels of 150 and 250 ppm H_2 in oil (i.e., 3-5 mbar H_2 in gas at 20ºC). Also good sensitivity is required during normal operation, between 5-150 ppm H_2 (0.1-3 mbar). The typical temperature range of the oil of most transformers is between 20-90 ºC.

In the following we will demonstrate the Mg-Ni-Zr sensing material in realistic transformer oil, in the temperature range of the application and in the presence of potential contaminants for the sensing layer and its catalyst. Recently, Mg-Ti micro-mirrors have been shown to sense the hydrogen concentration in oil, but key limitations were the applicability to temperatures above 80ºC and the contamination of the sensor at carbon monoxide concentrations typically encountered in the oil.[16]

We choose a fiber-based micro-mirror design due to the potential flexibility it provides inside the transformer. A $Mg_{52}Ni_{24}Zr_{24}$ thin film with Pd catalyst has been protected against the fluid and its constituents by a thin PTFE layer, known for its liquiphobic properties[19].

Figure 3a,b shows the optical response of the sensor at 21 °C and 60 °C as a function of time under for hydrogen partial pressures 25-1300 ppm in oil. The effect of the inclined PTI's caused by the glassiness of Ni-Zr is that distinct hydrogen levels correspond to distinct optical reflection levels. At 21 °C the sensor shows good sensitivity

below 300 ppm. At 60 °C this level increases to 400-1300 and is limited by the optical contrast of the sensing layer. These results contrast with Mg-Ti for which at both temperatures the first threshold value of 150 ppm did not have a unique optical response.[16]

As mentioned earlier, at a given hydrogen pressure, contaminants may influence the optical readout. In gasses these substances are mainly oxygen, CO and CO_2. It has been reported that alloying the Pd catalyst with Au reduces the hydration effect that oxygen has during dissociation of hydrogen on the catalyst surface.[16] Moreover, PTFE blocks the diffusion of carbon dioxide. Carbon monoxide is more tenuous and has the ability to block hydrogen dissociation sites on the catalyst, thereby preventing the uptake of hydrogen. This is illustrated in Figure 3c for a Pd-Au fiber-based sensing layer covered with PTFE. Under the influence of only 18 ppm CO partial pressure the optical response of the sensing material in gas quickly vanishes and the sensor becomes inert to hydrogen. Inspired by the blocking power of PMMA for CO,[20] though highly permeable for H_2,[21] we have added a thin layer of PMMA on top of Pd-Au. Figure 3d shows a very repeatable hydrogenation behaviour in the presence of 18 ppm CO. For most gas and liquid applications, however, the upper CO concentration limit is 1%. For the electrical transformer application this correspond to 1000 ppm dissolved CO in oil, and is also here considered the upper boundary. Figure 3e shows the response of a PMMA/PTFE covered Mg-Ni-Zr sensing layer after an incremental increase of CO in oil. The invariant behaviour proves the capability of PMMA to block CO. Adding the polymer PMMA-PTFE protection structure on top of the sensing layer makes the sensing design robust for detection in gases and liquids.

We have shown the optical properties of a new class of Mg-Ni-Zr hydrogen sensing materials and evinced their potential for sensing hydrogen in gasses and liquids. Most commonly used hydrogen sensing materials suffer from low optical sensitivity and little optical contrast between the as-deposited and hydrogenated state. Here we have shown that adding glassiness to a transparent hydride system tremendously increases the sensitivity while preserving the optical contrast of the original hydride. The Mg-Ni-Zr sensing material has been tested in gaseous and liquid environments in the presence of potentially harmful constituents. To ensure proper functioning of the sensing design, polymer protection layers have been applied and proven to function at elevated contaminants levels. The new sensing material can be applied to all optical designs, including nanostructures, where it will substantially improve the sensing performance as compared to traditionally used materials.
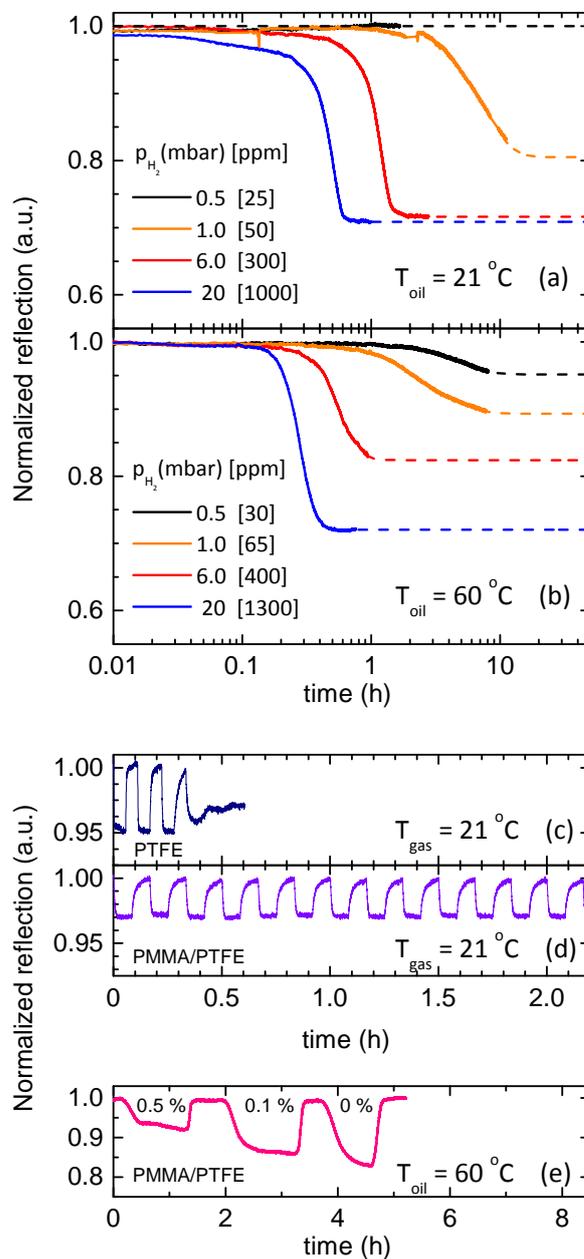
Figure 3. Optical reflection (normalized) of a Ti/Mg$_{52}$Ni$_{20}$Zr$_{28}$/Pd/PTFE fiber optic sensor in transformer oil at selected hydrogen partial pressures (a) at 21ºC (b) at 60 ºC, at 635 nm. The legend values in brackets are the hydrogen concentrations in oil calculated from the concentration of the gas mixture. Dashed lines are fits to the data using a sigmoid function. Exposure to CO in oil has been shown in gas for 30 nm Pd$_{81}$Au$_{19}$ covered with (c) 200 nm PTFE and (d) 50 nm PMMA/50 nm PTFE and in oil (e) for PMMA/PTFE protected Mg$_{52}$Ni$_{20}$Zr$_{28}$/Pd$_{90}$Au$_{10}$.

Mg-Ni-Zr gradient thin films are grown similarly as described by Gremaud et al.[5] for Mg-Ni-Ti. On top of the 5x70 mm glass substrate, a 3 nm Ti layer ensured sticking of the Mg-Ni-Zr sensing layer that was capped with 30 nm Pd. The PMMA and PTFE coatings were grown by magnetron co-sputtering in a separate chamber. The thickness gradient of Mg-Ni-Zr samples varied from 60 nm for Ni/Zr = 7 to 70 nm for Ni/Zr = 0.7. For experiments in oil, Mg-Ni-Zr thin films (~60 nm in thickness) are deposited on the cleaved and coating-free end of glass fibers. The fibers are polyimide coated multimode fibers with 15 µm coating on a 200 µm diameter core.

X-ray characterisation has been performed by x-ray diffraction (XRD) analysis using a Bruker D8 Advance equipped with Co source (α= 0.178897 nm). A polymer loading cell enabled in-situ examination at ~ 0.5 bar partial hydrogen pressure.

Optical characterisation in gas environments has been performed in a combinatorial way, using so-called hydrogenography[5]. The hydrogen loading cell was put in an oven to map out the temperature dependence of the sensing layer. The PTI's have been determined from averaging the three CCD channels. Measurements to test repeatability have been performed by repeatedly exposing the sensing layer to a mixture of H_2 in Ar and O_2 in Ar.

Optical characterisation in liquid has been performed by using a 250 ml oil bath, in direct contact with the ambient, in which continuously a gas mixture with a flow of 250 ml/min is dispersed. After 15 hydrogenation cycles in gas, the fiber tip has been immersed into the liquid in an area distant from the gas insertion to avoid gas bubbles reaching the sensor. The fiber is connected both to a tungsten halogen light source and an Ocean Optics USB2000 CCD-based spectrometer using an optical circulator. Before introducing hydrogen in the bath, the system was pre-flushed with 20% oxygen in argon to unload the sensor and to assure identical starting conditions. The temperature of the bath has been varied by using water tubes that are in direct and indirect contact with the bath.

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