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DOI
10.1117/12.3010123

Publication date
2024

Document Version
Final published version

Published in
Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2024

Citation (APA)
Dewi, H. S., Dissanayake, K. P., Schreuders, H., Bannenberg, L. J., & Groves, R. M. (2024). Towards hydrogen fueled aircraft: Metal hydrides for optical hydrogen sensors operating above room temperature. In B. Glisic, M. P. Limongelli, & C. T. Ng (Eds.), *Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2024* Article 129490E (Proceedings of SPIE - The International Society for Optical Engineering; Vol. 12949). SPIE. https://doi.org/10.1117/12.3010123

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Towards hydrogen fueled aircraft: metal hydrides for optical hydrogen sensors operating above room temperature

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ABSTRACT

Palladium thin films have been studied as hydrogen sensing materials and applied to variety of optical hydrogen sensors. Recently, tantalum has emerged as an attractive option for hydrogen sensing materials due to its broad sensing range and flexibility in tuning the sensing range by modifying the alloying composition or elements. Following the demand for optical hydrogen sensors for aerospace applications, testing the performance of hydrogen sensing materials is of interest. This work examines the optical response in respect to changing hydrogen concentrations and thermal expansion of palladium-gold ($Pd_{0.65}Au_{0.35}$) and tantalum-ruthenium ($Ta_{0.97}Ru_{0.03}$ and $Ta_{0.91}Ru_{0.09}$) thin films at temperatures similar to a hydrogen combustion engine. Our results suggest that tantalum-ruthenium alloys are suitable for sensing hydrogen from ambient temperatures up to 270°C because its low detection limit (0.01% of hydrogen in the atmosphere) is well below the explosive limit of hydrogen (4% of hydrogen in the atmosphere).

Keywords: palladium alloy, tantalum alloy, thin films, optical transmission, thermal expansion

1. INTRODUCTION

Transitioning to a clean energy source is essential to mitigate severe environmental damages caused by excessive use of fossil fuels. Hydrogen is of high demand as a clean energy carrier due to its high energy density per mass and water vapour as its main combustion product. Given its explosive characteristics, monitoring hydrogen leakages is crucial to ensure safe operation particularly in hydrogen fuelled aircraft. Accordingly, there is a need for hydrogen sensors which can detect low concentration hydrogen over a wide temperature range.

Fibre optic sensors are small in size, lightweight, and immune to electromagnetic interference and sparks.[1] They have a remote sensing capability that can be advantageous for aerospace applications. These sensors can be further developed to become hydrogen sensors by coating them with materials that can change optical properties in response to changing hydrogen concentration.[2–5] Palladium thin films have been studied as a sensing material on various configurations of fibre optic hydrogen sensors.[3,6–8] The material undergoes a first order phase transformation upon exposure to 1-10% of hydrogen concentration in the atmosphere. This leads to a significant optical contrast in a narrow sensing range below the explosive limit of hydrogen. However, such phase transition leads to hysteretic behaviour which can cause ambiguous optical response and limits the sensing accuracy. To address this issue, alloying elements, such as gold, have been introduced to suppress the hysteresis response at the expense of reduced optical contrast.[9]

Another emerging hydrogen sensing material is tantalum. Tantalum demonstrates a broad sensing range from 0.001% to 100% of hydrogen concentration in the atmosphere.[10] The addition of alloying elements can alter the sensing range, showcasing customisability and versatility for various applications.[11] Unlike palladium, tantalum does not demonstrate phase transformation related to hydrogen absorption,[12] meaning that a reversible and hysteresis-free optical response with respect to changing hydrogen concentrations can be easily achieved by tantalum.

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Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2024, edited by Branko Glisic, Maria Pina Limongelli, Ching Tai Ng, Proc. of SPIE Vol. 12949, 129490E · © 2024 SPIE · 0277-786X · doi: 10.1117/12.3010123

Hydrogen sensors operating in a hydrogen fuelled aircraft may be exposed to harsh environments. For instance, the area surrounding the aircraft combustion engine can easily reach temperatures above 100°C. These high temperatures pose challenges for the performance of the hydrogen sensing materials. Possible risks include (1) detection limit falling above the explosive limit of hydrogen due to shifting of the sensing range following a shift of hydrogen concentration window in which the material absorbs hydrogen according to Van't Hoff's law[13] and (2) interdiffusion of the thin film layers due to prolonged exposure to high temperatures.[14]

To develop a reliable hydrogen sensor and ensure safety of the hydrogen-fueled aircrafts, it is necessary to analyse the functionality of hydrogen sensing materials at temperatures similar to the environment in the aircraft. In this work, we examine the performance of palladium alloy and tantalum alloy in response to changing hydrogen concentrations at temperatures ranging from 28°C – 270°C. This work provides an overview on the functionality of $Pd_{0.65}Au_{0.35}$, $Ta_{0.97}Ru_{0.03}$, and $Ta_{0.91}Ru_{0.09}$ for hydrogen sensing at temperatures above ambient temperature.

2. METHODOLOGY

Our examinations consist of optical and structural characterisations on palladium-gold ($Pd_{0.65}Au_{0.35}$) and tantalum-ruthenium ($Ta_{0.97}Ru_{0.03}$ and $Ta_{0.91}Ru_{0.09}$) thin films. We have selected these materials because they are ones of the most promising hydrogen sensing materials identified in the literature. The following subsections describe the experimental details.

2.1 Fabrication of specimens

The specimens were fabricated using magnetron sputtering on quartz substrate in the size of $10 \times 10 \times 0.5$ mm^3, consisting of a 4-nm-thick adhesive layers (titanium), a 40-nm-thick sensing layer (palladium-gold or tantalum-ruthenium), and a 10-nm-thick catalytic layer for tantalum-ruthenium specimens ($Pd_{0.6}Au_{0.4}$). We kindly refer to our previous work for the exact deposition conditions.[11,15]

2.2 Measurement of the optical transmission

Optical transmission of the specimens was measured using hydrogenography.[16] The hydrogenography set-up consists of a pressurised chamber where the specimens were mounted, an oven to control the temperature of the pressurised chamber, an illumination source, a camera, and a PC connected to a pressure controller. Both the pressurised chamber and the oven have opening windows at the bottom and at the top that allow transmission from the illumination source to the camera.

We varied the partial pressure of hydrogen by using pre-mixed and calibrated mixture of hydrogen gas in argon. A Labview program running on a PC controls and records the gas pressure and flow during the measurements. We programmed increment and decrement steps of pressure (between 0.5 to 10^6 Pa) every 15-30 minutes in the pressurised chamber with a typical flow 10 – 20 ml/min. The hydrogen concentration in this study was calculated by comparing the measured hydrogen partial pressure to the atmospheric pressure (101 325 Pa).

The camera captured intensity of the transmitted light (450 – 700 nm) through the specimens. The relative optical transmission ($\ln(\mathcal{T}_{H_2}/\mathcal{T}_0)$) was approached using:

$$\ln(\mathcal{T}_{H_2}/\mathcal{T}_0) = \ln\left\{\frac{(t_H - t_{dark})}{(t_0 - t_{dark})}\right\} - \ln\left\{\frac{(t_c - t_{dark})}{(t_{c0} - t_{dark})}\right\} \quad (1)$$

where t_{H_2}, t_0, t_{dark}, t_c, and t_{c0} denotes the captured intensity during hydrogen exposure, without hydrogen exposure, dark noise, intensity from a reference sample, and its initial transmission respectively. The reference sample is a material that does not change optical properties upon contact with hydrogen. As such, the calculation can compensate intensity fluctuations from the light source. This experimental procedure was carried out at 28°C, 90°C, 150°C, 210°C, and 270°C.

2.3 Structural analysis

X-ray reflectometry (XRR) were performed in this study to observe the coherence of the thin-film layers and measure their thicknesses. The measurements were performed using a Bruker D8 Discovery (Cu Kα, $\lambda = 0.1542$ nm) with a LYNEXE XE detector and a Göbel mirror. The specimens were stepwise heated to 28°C, 60°C, 90°C, 120°C, 150°C, 180°C, 210°C, 270°C inside an Anton Paar XRK900 Reactor chamber (see reference[11] for details). The measurement started 15 minutes after the set temperatures were reached to ensure equilibrium and the specimens were exposed to surrounding air. The height and angle of the specimens were carefully re-aligned for every temperature to minimise the errors from mispositioning due to thermal expansion. The XRR measurements were carried out at the angle of 0 – 5° using 0.1 mm slits; one mounted directly, one mounted after the Göbel mirror and one before the detector.

3. RESULTS AND DISCUSSION

Figure 1 depicts the changes of relative optical transmission of palladium-gold and tantalum-ruthenium thin films with respect to changing hydrogen concentrations in the atmosphere. At 28°C (see Figure 1(a)), both palladium-gold and tantalum-ruthenium indicate gradual changes of the optical transmission values, although the two materials demonstrate distinct transmission behaviour. The gradual change begins at 0.01% for palladium-gold and 0.001% for tantalum-ruthenium samples. As the temperature increases to 270°C (see Figure 1(b)), no changes in transmission are observed for palladium-gold and this holds true also for tantalum-ruthenium at low hydrogen concentration (0.001 – 0.01%). The optical transmission of tantalum-ruthenium samples begin to change after exposure to 0.01% of hydrogen. These results suggest that reduced sensing sensitivity at low hydrogen concentrations should be expected at elevated temperatures.

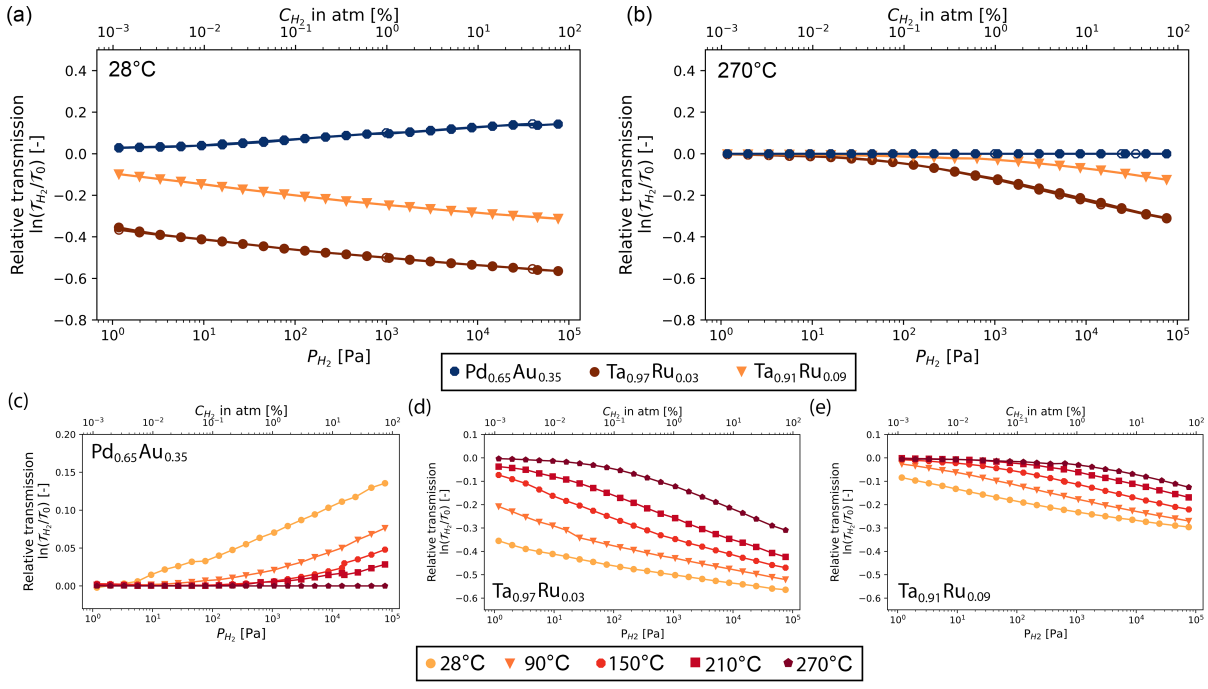

Figure 1. Changes of optical transmission of $Pd_{0.65}Au_{0.35}$, $Ta_{0.97}Ru_{0.03}$ and $Ta_{0.91}Ru_{0.09}$ in response to varying hydrogen concentrations relative to te transmission of the film in the absence of hydrogen ($\mathcal{T}_0$). (a) – (b) depict a comparison of all observed materials at 28°C and 270°C, while (c) – (e) demonstrate the influence of temperatures on the optical response for $Pd_{0.65}Au_{0.35}$, $Ta_{0.97}Ru_{0.03}$ and $Ta_{0.91}Ru_{0.09}$ respectively. The relative transmission values were calculated according to equation 1.

According to Figure 1 (c), reduced sensing sensitivity of palladium-gold already occurs at 150°C where changes in relative transmission only occur after 1% of hydrogen. This is crucial for safety purposes as the

explosive limit of hydrogen in around 4%.[17] Consequently, palladium-gold is unsuitable for hydrogen sensing at temperatures above 90°C. However, tantalum-ruthenium provides hydrogen sensing capability at concentrations as low as 0.01% even when the temperature reaches 270°C (see Figure 1(d)−(e)).

Repeatability of the optical response are crucial aspects for sensing accuracy and reliability. As $Ta_{0.97}Ru_{0.03}$ has shown a remarkable optical response up to 270°C, we tested the stability of its optical response by exposing the materials to 350 cycles of changing hydrogen concentrations (0.01% - 4% - 0.4%) at 270°C. Figure 2(a) depicts the relative transmission values acquired from cycle 300 up to cycle 350, with further emphasise on comparison of every 100 cycles shown in Figure 2(b). The transmission is consistent for the observed cycles, indicating high repeatability and endurance to high temperatures up to 270°C.

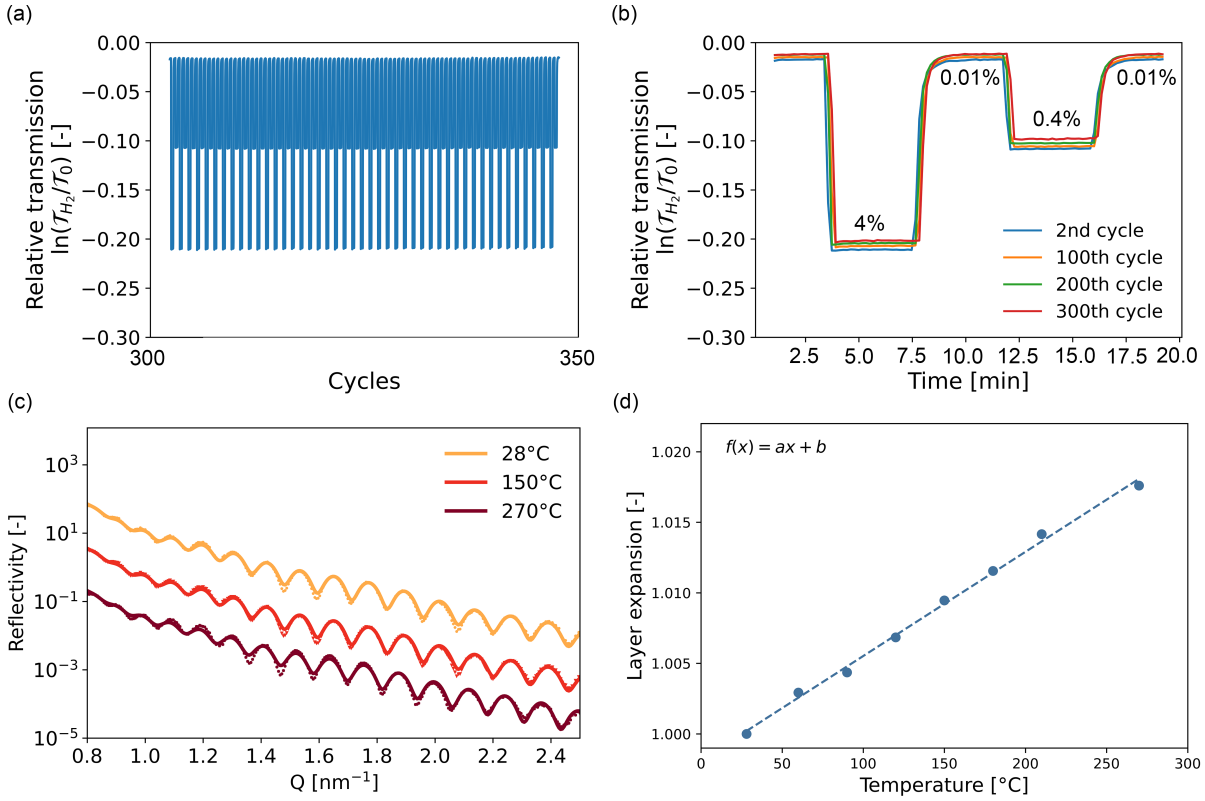

Figure 2. (a) Stability of $Ta_{0.97}Ru_{0.03}$ optical response at 270°C accompanied by (b) detail comparison of optical response every 100 cycles. (c) XRR measurement result of $Ta_{0.97}Ru_{0.03}$ at various temperatures (the data is shifted for better visibility) and (d) its linear thermal expansion derived from the measurement analysis.

As interdiffusion between thin film layers has been previously reported for some metal thin films,[14] we performed XRR measurement at elevated temperatures from 28°C to 270°C. Following the procedure mentioned in section 2.3, our measurement results demonstrate well-defined fringes, indicating the existence of the layered structure in the specimens which is confirmed by further fitting the data. Accordingly, we do not see any signs of interdiffusion which shows that the materials are stable up to 270°C. This is consistent with the stability test results which demostrate reversible optical response over 350 cycles at 270°C. The layer expansion of tantalum-ruthenium (see Figure 2(d)) was thus calculated by comparing the thickness measured at elevated temperatures to the thickness measured at 28°C. The volumetric thermal expansion coefficient derived from this measurement is $73.86 \pm 0.94 \times 10^{-6}$ K^{-1}, which is almost 4 times higher than the volumetric expansion coefficient of bulk tantalum (19.5×10^{-6} K^{-1}).[18] Thin films are known to have distinct thermal expansion coefficient compared to bulk materials due to substrate clamping and surface effects.[19]

4. CONCLUSION

Reduced sensitivity of $Pd_{0.65}Au_{0.35}$, $Ta_{0.97}Ru_{0.03}$, and $Ta_{0.91}Ru_{0.09}$ at low hydrogen concentrations is expected when the operating temperature increases above 90°C. Our measurement results suggest that at temperatures above 90°C, the low detection limit of $Pd_{0.65}Au_{0.35}$ is above 1%, while $Ta_{0.97}Ru_{0.03}$ and $Ta_{0.91}Ru_{0.09}$ yields a detection limit of around 0.01% and 0.1%, respectively at 270°C. The optical and structural analysis of $Ta_{0.97}Ru_{0.03}$ indicate that this material is stable upon repeated and prolonged exposure to hydrogen at 270°C. Hence, we propose $Ta_{0.97}Ru_{0.03}$ as the best performing hydrogen sensing materials at elevated temperatures up to 270°C.

ACKNOWLEDGMENTS

Authors acknowledge funding from the European Union Clean Aviation programme for the project HYDEA with the project number 101102019.

REFERENCES

[1] Jackson, D. A. and Jones, J. D. C., "Fibre optic sensors," *Optica Acta: International Journal of Optics* **33**, 1469–1503 (12 1986). doi: 10.1080/713821914.

[2] Butler, M. A. and Ginley, D. S., "Hydrogen sensing with palladium-coated optical fibers," *Journal of Applied Physics* **64**, 3706–3712 (10 1988).

[3] Westerwaal, R. J., Rooijmans, J. S., Leclercq, L., Gheorghe, D. G., Radeva, T., Mooij, L., Mak, T., Polak, L., Slaman, M., Dam, B., and Rasing, T., "Nanostructured Pd-Au based fiber optic sensors for probing hydrogen concentrations in gas mixtures," *International Journal of Hydrogen Energy* **38**, 4201–4212 (4 2013).

[4] Dai, J., Yang, M., Yang, Z., Li, Z., Wang, Y., Wang, G., Zhang, Y., and Zhuang, Z., "Enhanced sensitivity of fiber bragg grating hydrogen sensor using flexible substrate," *Sensors and Actuators, B: Chemical* **196**, 604–609 (2014).

[5] Fisser, M., Badcock, R. A., Teal, P. D., Janssens, S., and Hunze, A., "Palladium-based hydrogen sensors using fiber bragg gratings," *Journal of Lightwave Technology* **36**, 850–856 (2 2018).

[6] Chadwick, B., Tam-F, J., Brungsb, M., and Gal, M., "A hydrogen sensor based on the optical generation of surface plasmons in a palladium alloy," *Sensors and Acruators B* **17**, 215–220 (1994).

[7] Zhao, Z., Carpenter, M. A., Xia, H., and Welch, D., "All-optical hydrogen sensor based on a high alloy content palladium thin film," *Sensors and Actuators, B: Chemical* **113**, 532–538 (1 2006).

[8] Chen, K., Yuan, D., and Zhao, Y., "Review of optical hydrogen sensors based on metal hydrides: Recent developments and challenges," *Optics and Laser Technology* **137** (5 2021).

[9] Wadell, C., Nugroho, F. A. A., Lidström, E., Iandolo, B., Wagner, J. B., and Langhammer, C., "Hysteresis-free nanoplasmonic Pd-Au alloy hydrogen sensors," *Nano Letters* **15**, 3563–3570 (5 2015).

[10] Bannenberg, L., Schreuders, H., and Dam, B., "Tantalum-palladium: Hysteresis-free optical hydrogen sensor over 7 orders of magnitude in pressure with sub-second response," *Advanced Functional Materials* **31** (4 2021).

[11] Bannenberg, L. J., Schreuders, H., van Beugen, N., Kinane, C., Hall, S., and Dam, B., "Tuning the properties of thin-film TaRu for hydrogen-sensing applications," *ACS Applied Materials and Interfaces* **15**, 8033–8045 (2 2023).

[12] Bannenberg, L. J., Blom, L., Sakaki, K., Asano, K., and Schreuders, H., "Completely elastic deformation of hydrogenated Ta thin films," *ACS Materials Letters* **5**, 962–969 (4 2023).

[13] Bhuiya, M. M. H., Kumar, A., and Kim, K. J., "Metal hydrides in engineering systems, processes, and devices: A review of non-storage applications," *International Journal of Hydrogen Energy* **40**, 2231–2247 (2 2015).

[14] Poate, J. M., Turner, P. A., Debonte, W. J., and Yahalom, J., "Thin-film interdiffusion. i. Au-Pd, Pd-Au, Ti-Pd, Ti-Au, Ti-Pd-Au, and Ti-Au-Pd," *Journal of Applied Physics* **46**, 4275–4283 (1975).

[15] Bannenberg, L. J., Nugroho, F. A. A., Schreuders, H., Norder, B., Trinh, T. T., Steinke, N.-J., van Well, A. A., Langhammer, C., and Dam, B., "Direct comparison of pdau alloy thin films and nanoparticles upon hydrogen exposure," *ACS Applied Materials & Interfaces* **11**, 15489–15497 (May 2019).

[16] Gremaud, R., Broedersz, C. P., Borsa, D. M., Borgschulte, A., Mauron, P., Schreuders, H., Rector, J. H., Dam, B., and Griessen, R., "Hydrogenography: An optical combinatorial method to find new light-weight hydrogen-storage materials," *Advanced Materials* **19**, 2813–2817 (10 2007).

[17] on Air Quality in Passenger Cabins of Commercial Aircraft, C., [*National Research Council (US) Committee on Air Quality in Passenger Cabins of Commercial Aircraft. The Airliner Cabin Environment and the Health of Passengers and Crew. Washington (DC)*], National Academies Press (US), 2 ed. (2002).

[18] Eltherington, J., "Standard test method for linear thermal expansion of solid materials with a vitreous silica dilatometer," (1998).

[19] Fang, W. and Lo, C.-Y., "On the thermal expansion coefficients of thin films," *Sensors and Actuators A: Physical* **84**(3), 310–314 (2000).