	Experiment title: **In situ structural studies on PdCuAu membrane alloys under hydrogen**	**Experiment number**: 25-01-978
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Introduction

Pd membranes are an interesting option for H_2 purification in decentralized hydrogen production schemes where economics preclude application of industrial technologies such as pressure swing adsorption [1]. However, Pd membranes can embrittle and fail rapidly at low temperatures because of a wide miscibility gap in the Pd-H phase diagram below 300 °C and H_2 pressures up to 20 bar [2]. The reason is the large lattice parameter discrepancy of the associated α and β boundary hydride phases (3.895 Å and 4.025 Å, respectively, at room temperature) [3]. This gap can be reduced or closed by alloying with other metals which may also improve permeability, low-temperature stability, mechanical stability, or sulphur tolerance [2].

PdCuAu alloys are promising new materials for sulphur tolerant H_2 separation membranes but knowledge about hydride phases of these ternary alloys is sparse, i.e. the two-phase regime persists in hydrogenated PdCuAu alloys with equal Cu and Au amounts up to 10% each at room temperature [3]. Low-temperature stability and operation of such membranes depend critically on the size of the α/β hydride phase miscibility gap. Therefore we investigated for the first time this hydride miscibility gap for some model PdCuAu alloys via *in situ* X-ray diffraction (XRD) under H_2 above room temperature.

Experimental

Three PdCuAu alloy films were prepared via electroless plating on tubular ceramic substrates. The metals were deposited separately and subsequently alloyed through annealing under N_2 at 873 K following established procedures [4,5]. The obtained PdCuAu alloy films with thickness around 3 μm were detached from the ceramic substrates, and ca. 10×1 mm^2 strips were inserted into 3 mm wide quartz capillaries for *in situ* XRD measurements under H_2.

The XRD eperiments have been carried out using a high-resolution powder diffraction (HRPD) setup with spinning glass capillary that was developed at BM25A for *in situ* studies on solid-gas reactions under flowing atmospheres in isobaric and isothermal environments [6]. Sample pressure and temperature can be controlled between 10^{-3} and ca. 1300 mbar and -193–727 ºC [6]. Measurements on the PdCuAu alloys were carried out in transmission employing a $\Theta/2\Theta$ scattering geometry between room temperature and 200 ºC at photon wavelength $\lambda = 0.618886$ Å (20033.45 eV).

Results and Discussion

The three investigated PdCuAu alloys contained approximately 70% Pd (samples PCA9 and PCA10) and 84% Pd (sample PCA5) according to EDS analyses. All three ternary alloys exibited face-centered cubic (fcc) structures just as pure Pd and binary PdCu and PdAu alloys do in this Pd concentration range [4,5]. Upon H_2 exposure the fcc structures were retained but the XRD reflections shifted to lower angles because the alloy lattices expanded due to hydrogen incorporation. In general we started with exposure to ca. 1.3 bar H_2 at a given temperature which was close to the maximum pressure of the experimental setup. The alloys were completely transformed into the hydrogen-rich β hydride phase at lower temperatures. Then we monitored the response of the fcc 111 reflection as H_2 pressure was gradually reduced. Accordingly, the β hydride 111 reflection shifted back towards higher angles until the α hydride phase reappeared. Eventually the alloys transformed completely back into the latter hydrogen-poor phase at lower H_2 pressures.

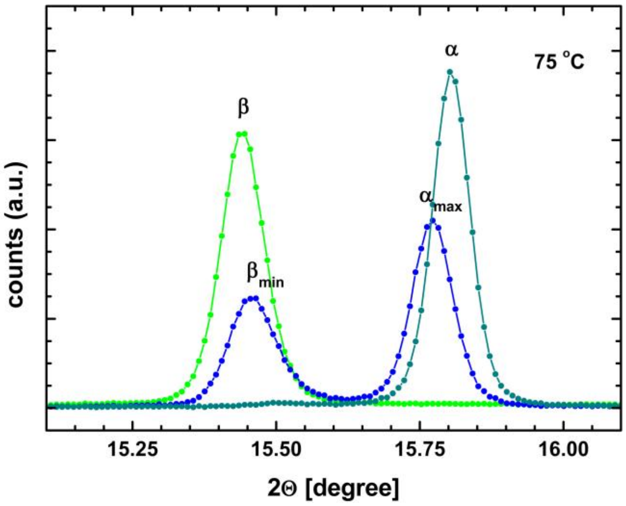

Figure 1. Fcc 111 reflections of alloy PCA5 with ca. 84% Pd at different hydrogen uptake and 75 ºC.

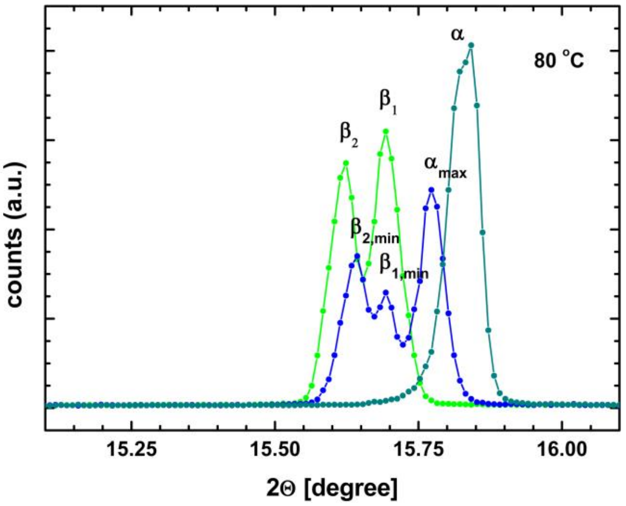

Figure 2. Fcc 111 reflections of alloy PCA10 with ca. 70% Pd at different hydrogen uptake and 80 ºC.

Figure 1 displays the corresponding XRD patterns of sample PCA5 at 75 ºC for example, i.e. the β hydride phase at 1.30 bar H_2, the mixed α/β hydride phase at 0.76 bar H_2 and the α hydride phase at 0.53 bar H_2. The mixed phase patterns indicate the boundary hydride phases from which the respective maximum α hydride and minimum β hydride lattice constants can be derived for each temperature. In this way we mapped the miscibility gap for alloy PCA5 up to 125 ºC. At room temperature the discrepancy of 0.087 Å between the lattice constants of the α and β boundary hydride phases is much smaller in alloy PCA5 than in pure Pd indicating that the hydride miscibility gap is noticeably reduced. At 125 ºC this discrepancy has shrunk further to 0.063 Å but it did not vanish yet showing that the hydride miscibility gap extends to higher temperatures in this alloy. However, PCA5 could not be transformed into the β hydride phase anymore above 125 ºC at our experimental H_2 pressure limit of 1.3 bar so that the miscibility gap could not be further explored.

Figure 2 shows analogous 111 XRD patterns of sample PCA10 recorded at 80 ºC. Unexpectedly two β hydride reflections appeared upon exposure to 1.3 bar H_2 despite that the XRD reflections of this alloy were rather narrow and symmetic in the absence of H_2. On the other hand, only a single 111 reflection for the α hydride boundary is observed although that feature appears to be less symmetric. The XRD patterns of sample PCA9 with similar Pd content as PCA10 exhibited very similar behaviour. This suggests that these samples consisted of two stoichimetrically different alloys with very similar lattice constants but quite distinct hydrogen solubility.

Indeed, palladium, copper and gold can form ternary alloys with differing stoichiometry but identical lattice constants because Cu addition leads to a contraction of the Pd lattice while Au addition results in lattice expansion. Thus, a series of ternary alloys with decreasing Pd content can be formed through careful balance of Cu and Au content that have identical lattice parameters [7] as we discussed previously for PdCuAg alloys [8]. However, hydrogen solubility decreases substantially in these alloys with decreasing Pd content [7] so that the apparent lattice equality is lifted upon exposure of the alloys to H_2. The origin and practical implications of this intriguing phenomenon in ternary Pd alloys is subject to further analyses in our laboratory.

Nevertheless, the hydride miscibility gap in PdCuAu alloys with lower Pd content is significantly reduced in comparison with PCA5 as indicated by the smaller discrepancey between the boundary hydride phase XRD reflections of PCA10 and PCA9. This suggests that the miscibility gap can be completely supressed by adding Cu and Au in sufficient and properly balanced amounts to Pd. Note also that the β hydride phase could not be formed anymore above 80 ºC for either of those two alloys at our experimentally accessible H_2 pressures.

Conclusion

The width of the hydride miscibility gap is significantly reduced as Cu and Au content are raised in PdCuAu alloys but still persists in ternary alloys with at least 70% Pd at temperatures up to 125 ºC. The miscibility gap could not be mapped at higher temperatures because the β hydride phase could not be formed anymore above that temperature at our experimental H_2 pressure limit of 1.3 bar. Surprisingly, two β hydride phases were found in some of the ternary alloys despite that these alloys appeared to be homogeneous in the absence of H_2 according to their XRD patterns. This indicates stoichiometric heterogeneity of those alloys which is attributed to the formation of alloys with similar lattice parameter but differing hydrogen solubility.

References

[1] Ritter, J. A.; Ebner, A. D. *Sep. Sci. Technol*. **2007**, *42*, 1123-1193.
[2] Yun, S.; Oyama, S. T. *J. Membr. Sci.* **2011**, *375*, 28-45.
[3] Sakamoto, Y.; Ishimaru, N. Mukai, Y. *Ber. Bunsenges. Phys. Chem.* **1991**, *95*, 680-688.
[4] Yuan, L.; Goldbach, A.; Xu, H. *J. Membr. Sci*. **2008**, *322*, 39-45.
[5] Shi, L.; Goldbach, A.; Zeng, G.; Xu, H. *Int. J. Hydrogen Energy* **2010**, *35*, 4201-4208.
[6] Salas-Colera, E.; Munoz-Noval, A.; Heyman, C.; Ania, C. O.; Parra, J. B.; Garcia-Granda, S.; Calero, S.; Rubio-Zuazo, J.; Castro, G. R. *J. Synchrotron Rad.* **2015**, *22*, 42-48.
[7] Galipaud, J.; Martin, M. H.; Roue, L.; Guay, D. *J. Phys. Chem. C* **2015**, *119*, 26451-26458.
[8] Zhao, L.; Goldbach, A.; Bao, C.; Xu, H. *ACS Appl. Mater. Interfaces* **2014**, *6*, 22408-22416.