



Regular Article

Effects of multiple hydrogen absorption/desorption cycles on the mechanical properties of the alloy system palladium/silver (wt% = 10–25)



K. Wald^a, J. Kubik^a, D. Paciulli^a, M. Talukder^a, J. Nott^a, F. Massicotte^b, K. Rebeiz^c, S. Nesbit^d, A. Craft^{a,*}

^a Department of Chemistry, University of Hartford, West Hartford, CT 06117, USA

^b Institute of Materials Science, University of Connecticut, Storrs, CT 06269, USA

^c College of Engineering, Phoenicia University, Zahrani, South Lebanon, Lebanon

^d Department of Mechanical Engineering, Lafayette College, Easton, PA 18042, USA

ARTICLE INFO

Article history:

Received 12 January 2016

Received in revised form 11 February 2016

Accepted 12 February 2016

Available online 27 February 2016

Keywords:

Palladium

Silver

Hydrogen

Embrittlement

ABSTRACT

Changes to the strength, hardness and ductility of a series of well-annealed palladium–silver alloys have been investigated as a function of the number of isothermal hydrogen absorption/desorption cycles the annealed alloy specimens were subjected to. The results indicate that the overwhelming majority of the changes to the mechanical properties occur as a result of the first hydrogen exposure treatment. The degree of change to the mechanical properties of the alloys has been found to be dependent on the silver content of each alloy, decreasing as the silver content increases.

© 2016 Elsevier Ltd. All rights reserved.

Technology that utilizes hydrogen is advancing at a rapid pace. But there are still obstacles that stand in the way of hydrogen's effective and efficient use in many areas of technology. One nagging issue that remains to be fully addressed is the issue of hydrogen embrittlement in many metallic materials. Be it in hydrogen fuel storage applications, nuclear reactor technology, the steel industry, or hydrogen purification applications, hydrogen embrittlement has been a problem [1,2].

Even with a well-studied metal–hydrogen system such as the palladium–hydrogen system, investigations continue into the effects of hydrogen absorption and desorption on its mechanical properties [3–9]. Several authors of the current study investigated the roles of several important hydrogen exposure parameters (e.g. hydrogen exposure temperature, amount of hydrogen absorbed, and number of absorption/desorption cycles) on the mechanical properties of palladium [7]. In virtually all situations investigated hydrogen absorption/desorption resulted in significant strengthening and hardening of the palladium matrix along with significant embrittlement. This latter fact creates a significant shortcoming to the use of palladium in many potential hydrogen-based applications.

Palladium–silver (Pd/Ag) alloys have garnered much attention for an important role they play in the broad area of hydrogen-based technology, namely hydrogen purification. Among the common methods of hydrogen separation/purification is the passage of a hydrogen-containing gas mixture through membranes composed of Pd/Ag [10–13]. One

attractive feature of Pd/Ag alloys in hydrogen applications is that they are much less susceptible to hydrogen embrittlement than pure palladium [10,14]. This fact is often mentioned in studies on the use of Pd/Ag alloys but very rarely is it quantitatively characterized. A recent study by several authors of the current investigation has quantitatively characterized the effects of the hydrogen exposure temperature on the mechanical properties of a series of Pd/Ag alloys [15]. That study revealed that Pd/Ag alloys are less susceptible to hydrogen embrittlement than pure palladium (under the conditions studied) but that the degree of mitigation of hydrogen embrittlement is dependent on silver content of the alloy. The present study shifts the focus from hydrogen exposure temperature to the equally important factor of the number of hydrogen absorption/desorption cycles the Pd/Ag alloys undergo. In particular, we report the results of a study into the changes in the strength, hardness and ductility/brittleness properties of a series of Pd/Ag alloys that vary in silver content from 10 weight % to 25 weight % silver caused by multiple isothermal low-temperature hydrogen absorption/desorption cycles.

Palladium:silver foils, 90:10, 80:20 and 75:25 wt.% (99.9% pure basis metal) of 0.25 mm thickness were used in this study (ACI Alloys, San Jose, CA, USA). Foil preparation and hydrogen exposure protocols were carried out as detailed in previous studies [2,15]. Isothermal hydrogen absorption was carried out at 323 K. Upon reaching an H/Alloy content of ~0.30 during hydrogen absorption, specimens were evacuated at 323 K for 24 h to remove all absorbed hydrogen. Respective sets of annealed specimens were subjected to 1, 2, 3, 4, 5, and 10 complete absorption/desorption cycles at 323 K.

* Corresponding author.

E-mail address: craft@hartford.edu (A. Craft).

Table 1

Mechanical properties of well-annealed palladium and palladium–silver alloys.

Mechanical property	Well-annealed Pd [17]	Well-annealed Pd/Ag (10%)	Well-annealed Pd/Ag (20%)	Well-annealed Pd/Ag (25%)
Yield strength (MPa)	60	92	119	124
Ultimate strength (MPa)	150	204	261	274
Total elongation (%)	21	20	20	20
Vickers microhardness (VHN)	65	81	101	113

Following each hydrogen exposure treatment on the specimens, tensile tests were carried out using an Instron Series IX Automated Materials Testing System using a constant elongation rate of 1.17 mm min^{-1} . Through an analysis of the stress–strain curves obtained from the tensile tests, values of the yield strength, ultimate strength and total elongation (elongation at the point of failure) of each respective specimen were determined. Specimens used for microhardness testing were subjected to a series of polishings culminating in a $0.05 \text{ }\mu\text{m}$ alumina polishing. Vickers microhardness tests were performed on a LECO Microhardness Tester using a load of 100 g.

To establish a baseline for the effects of hydrogen exposure on the mechanical properties of the alloy systems studied, specimens that were well-annealed in vacuo and not subjected to any hydrogen absorption/desorption cycles were first investigated. The yield strength, ultimate strength and total elongation for the well-annealed alloys were determined. These results, along with the Vickers microhardness values, are given in Table 1. For comparison, the values for vacuum-annealed pure palladium are included [16]. Inspection of the results for the vacuum-annealed samples shows that solid solution strengthening manifests itself in the palladium–silver alloy system. The values of

yield strength, ultimate strength and microhardness are found to increase in direct proportion to the weight % silver in the alloy. It is interesting to note from the total elongation values of the vacuum-annealed samples that the alloying of silver with palladium was found to have no significant discernible effect on brittleness/ductility, as the values for total elongation are essentially static. A similar consistency of brittleness/ductility as a function of silver content in well-annealed Pd/Ag alloys was found in an earlier study by several of the current authors [15].

Figs. 1–3 show plots of yield and ultimate strength, total elongation, and Vickers microhardness, respectively, as a function of the number of isothermal hydrogen absorption/desorption cycles experienced by well-annealed Pd/Ag alloys. To facilitate an appreciation of the role of silver content on each respective mechanical property, each set of plots is arranged such that the mass percent silver increases from plot b (10 wt% Ag) to plot d (25 wt% Ag); for comparison, similar plots for pure palladium are included as plot a in each figure [16]. In each plot, the value corresponding to zero cycles represents well-annealed specimens that had not been subjected to any hydrogen absorption/desorption cycles.

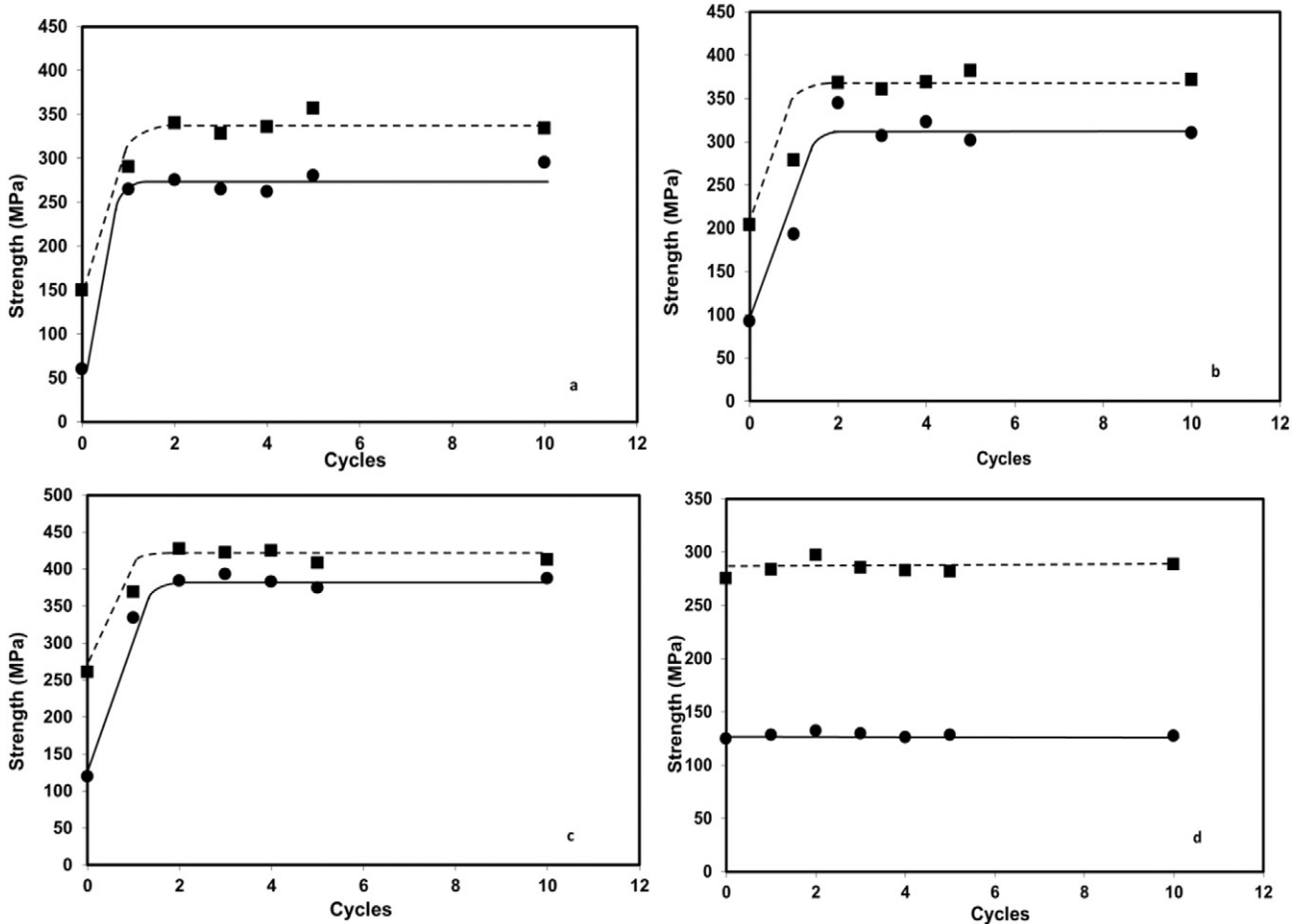


Fig. 1. Yield strength (●) and ultimate tensile strength (■) as a function of number of hydrogen absorption/desorption cycles: (a) pure palladium; (b) palladium–silver (10 weight %); (c) palladium–silver (20 weight %); (d) palladium–silver (25 weight %). Values corresponding to zero cycles correspond to well-annealed specimens that were not exposed to hydrogen.

The plots in Figs. 1–3 make certain things quite obvious. First, with the exception of the 25 wt% Ag alloy, hydrogen absorption/desorption cycling does have a significant effect on the strength, hardness and ductility/brittleness of the metal. The present results show that cycling causes an increase in strength (both yield and ultimate) and hardness while causing a decrease in elongation (i.e. ductility) in all but the 25 wt% Ag system. The observed loss of elongation (ductility) is synonymous with the occurrence of hydrogen embrittlement. Second, the present results indicate that the overwhelming majority of changes in strength, hardness and ductility occur as a result of the first absorption/desorption cycle. A modest additional increase in strength and hardness along with a modest additional decrease in ductility are found after a second absorption/desorption cycle. Beyond the second absorption/desorption cycle, further cycling results in little, if any, additional changes in the strength, hardness and ductility characteristics of the metals. Such findings for cycled pure palladium have been explained based on effects associated with the traversal of the ($\alpha + \beta$) miscibility gap in the palladium–hydrogen system during hydrogen absorption and desorption [7].

The present values for strength, hardness and ductility show that the changes in these properties caused by cycling well-annealed materials decrease as the percent silver in the alloy increases. If the role of solid solution strengthening is teased out from the observed changes in mechanical properties by expressing the fractional change (F.C.) in mechanical property as

$$\text{F.C.} = \frac{\text{final value} - \text{initial value}}{\text{initial value}}$$

then the decrease in the change in property as a function of increasing

silver content is apparent. In this calculation, the final value is taken as the average value of the property in the plateau region of each plot while the initial value is that of the well-annealed material (i.e. the zero cycle value). The absolute value is used to ensure a positive sign for values calculated using elongation values. The values for the fractional changes in the strength, hardness and ductility are given in Table 2. The results in Table 2 clearly reinforce the finding that as the silver content of a Pd/Ag alloy increases, the susceptibility of the alloy to changes in mechanical properties decreases, culminating in the ability of the Pd/Ag (25 wt%) alloy to retain the properties it possesses in the well-annealed state.

The present results beg the answers to two questions – why do the observed changes in mechanical properties diminish as the percent silver in an alloy increases and why do the overwhelming majority of the observed changes to the mechanical properties get generated during the first absorption/desorption cycle?

With regard to the influence of silver content on the degree of change to the alloys' mechanical properties, one likely and very prominent factor is the nature of the volume change that the alloy matrix experiences during hydrogen absorption and desorption. It has been found that the Pd/Ag–H system possesses an ($\alpha + \beta$) miscibility gap that is dependent on the composition of the palladium–silver alloy [17]. Similar to pure palladium, the α phase is a dilute solid solution of hydrogen in the metallic matrix while the β phase is a dense hydride phase, with the two phases having differing volumes. In the Pd/Ag–H system, as the silver content of the alloy increases, both the critical temperature and the width of the ($\alpha + \beta$) miscibility gap decreases. The decrease in the width of the miscibility gap indicates that magnitude of the discontinuous volume changes that accompany the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions diminish as silver content increases. Table 3

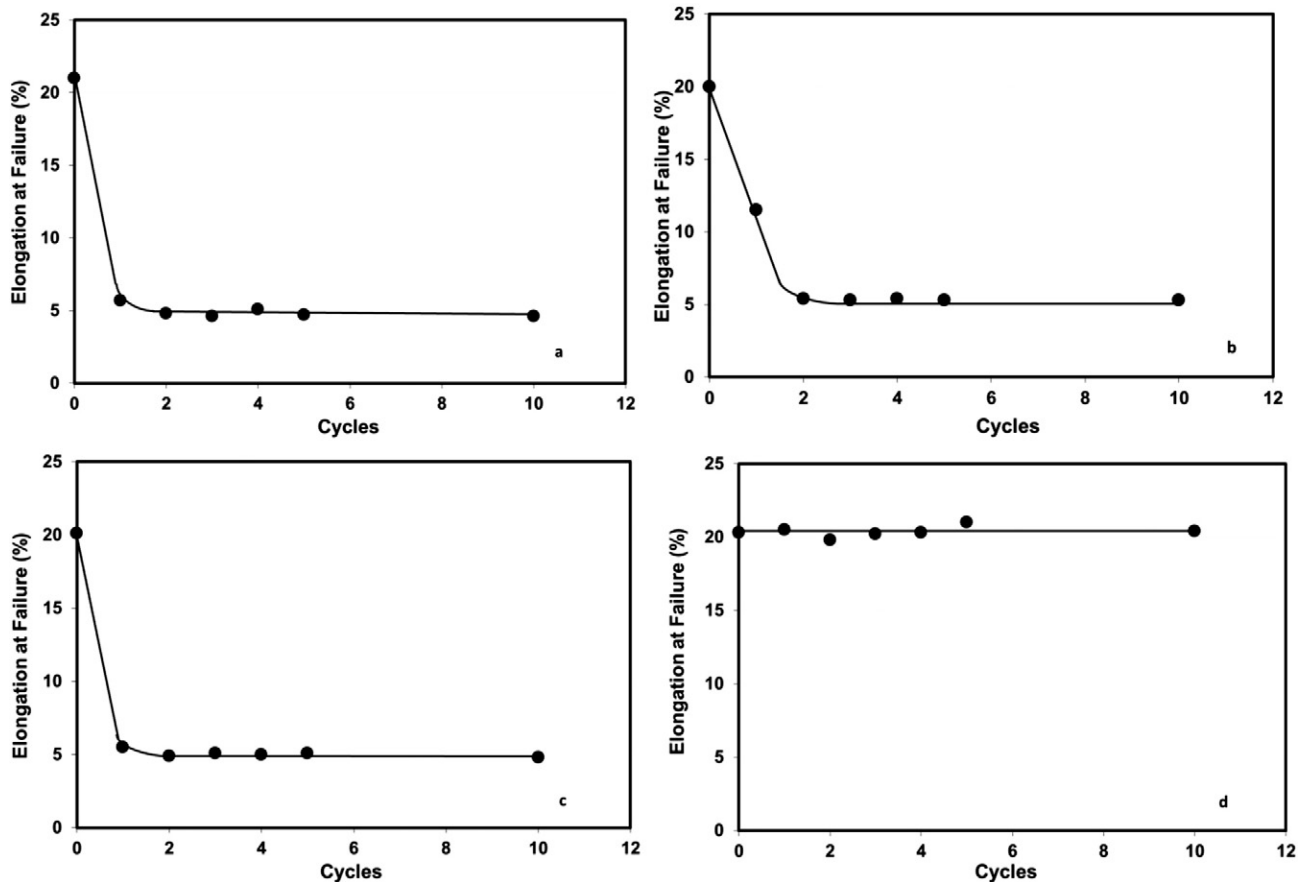


Fig. 2. Elongation at failure as a function of number of hydrogen absorption/desorption cycles: (a) pure palladium; (b) palladium–silver (10 weight %); (c) palladium–silver (20 weight %); (d) palladium–silver (25 weight %). Values corresponding to zero cycles correspond to well-annealed specimens that were not exposed to hydrogen.

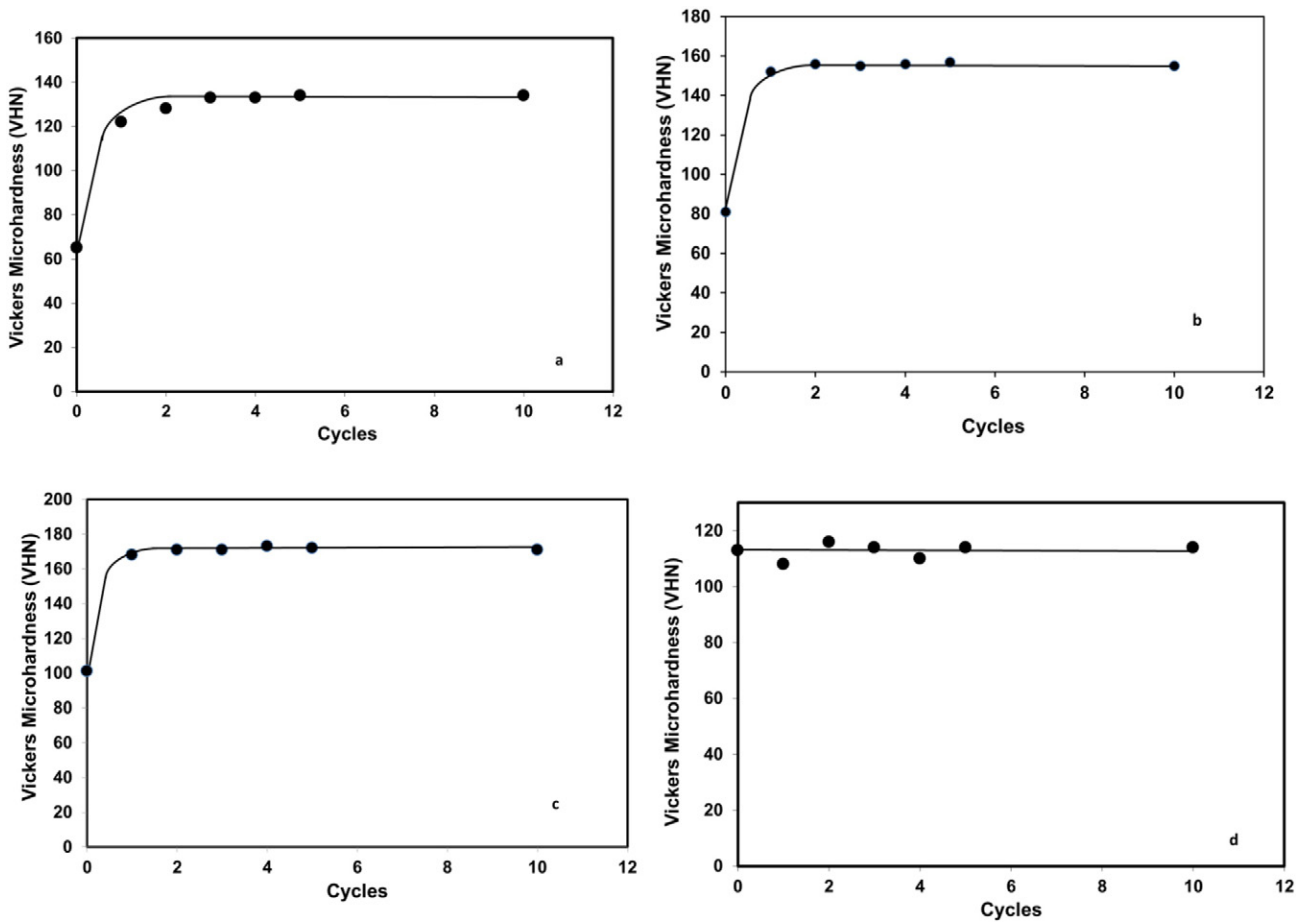


Fig. 3. Vickers microhardness as a function of number of hydrogen absorption/desorption cycles: (a) pure palladium; (b) palladium–silver (10 weight %); (c) palladium–silver (20 weight %); (d) palladium–silver (25 weight %). Values corresponding to zero cycles correspond to well-annealed specimens that were not exposed to hydrogen.

shows the critical temperatures, lattice constants for the limiting compositions of the α and β phases at 298 K, and the percent volume change due to the $\alpha \rightarrow \beta$ (or $\beta \rightarrow \alpha$) transition at 298 K for the three alloys involved in the present study [17]. The values in Table 3 quantitatively indicate that an increase in the silver content of the Pd/Ag alloys causes a progressive decrease in the width of the ($\alpha + \beta$) miscibility gap along with a progressive depression of its critical temperature. As the width of the miscibility gap decreases, the mismatch in volume between the α solid solution phase and the β hydride phase decreases, leading to fewer dislocations being generated during hydrogen absorption and desorption. The fewer dislocations generated result in less prominent changes in the mechanical properties of the alloy matrix due to hydrogen cycling. In the case of the Pd/Ag (25 wt%) alloy, the temperature at which hydrogen absorption/desorption occurred was above the critical temperature of the miscibility gap and thus no abrupt change in volume occurred during hydrogen cycling.

With regard to the preponderance of the changes in mechanical properties occurring during the first absorption/desorption cycle, the

influence of dislocations generated during cycling is likely to be a key factor again. Wang et al. have shown via hydrogen solubility measurements and transmission electron microscopy that one cycle of traversal through the ($\alpha + \beta$) miscibility gap in pure palladium gives rise to a significant build-up of dislocations [18]. That same study also found that additional cycles through the miscibility gap did not lead to significant additional increases in the dislocation density in the Pd matrix; the results indicated the achievement of a steady-state dislocation density after only 2–3 cycles through the miscibility gap due to the offset of the generation of additional dislocations by the annihilation of existing dislocations. Our results for the Pd/Ag alloys (with the notable exception of the 25 wt% alloy) are consistent with the establishment of a similar steady-state dislocation density after only 2–3 cycles through the respective miscibility gap in the alloy–H system. The establishment of a constant dislocation density translates into the lack of further changes to an alloy's mechanical properties as the number of hydrogen absorption/desorption cycles climb beyond 2 or 3.

Table 2

Fractional change (FC) in mechanical properties of hydrogen-cycled palladium and palladium–silver alloys.

F.C.	Pd	Pd/Ag (10%)	Pd/Ag (20%)	Pd/Ag (25%)
Yield strength (MPa)	3.34	2.56	2.08	0
Ultimate strength (MPa)	1.23	0.85	0.58	0
Total elongation (%)	0.78	0.75	0.73	0
Vickers microhardness (VHN)	1.08	0.91	0.69	0

Table 3

Miscibility gap parameters for Pd/Ag–hydrogen systems (based on data in Perrot et al. 2006).

Alloy	T_c (K)	α lattice constant @ 298 K (nm)	β lattice constant @ 298 K (nm)	$\Delta\text{volume}_{\alpha-\beta}$ (%)
Pure Pd	570	0.389	0.403	10.9
Pd/Ag (10 wt%)	451	0.392	0.401	7.1
Pd/Ag (20 wt%)	348	0.395	0.398	2.3
Pd/Ag (25 wt%)	290	–	–	–

References

- [1] S. Lynch, *Corros. Rev.* 30 (2012) 105.
- [2] J. Dahlmeyer, Tr. Garrison, Ty. Garrison, S. Darkey, F. Massicote, K. Rebeiz, S. Nesbit, A. Craft, *Scr. Mater.* 64 (2011) 789.
- [3] S. Goods, S. Guthrie, *Scr. Metall. Mater.* 26 (1992) 561.
- [4] J. Shenk, A. Moss, D. Jonsen, S. Nesbit, K. Rebeiz, A. Craft, *J. Mater. Sci. Lett.* 13 (1994) 496.
- [5] V.A. Golsov, *Platin. Met. Rev.* 43 (1999) 116.
- [6] G.I. Zhirov, M.A. Goltsova, G.E. Shatalova, *Int. J. Hydrog. Energy* 31 (2006) 231.
- [7] E. Dillon, G. Jimenez, A. Davie, J. Bulak, S. Nesbit, A. Craft, *Mater. Sci. Eng. A* 524 (2009) 89.
- [8] A. Kawasaki, S. Itoh, K. Shima, T. Yamazaki, *Mater. Sci. Eng. A* 551 (2012) 231.
- [9] J. Nunez, D. Yang, J. Kim, C. Park, L. Fonseca, *Nanotechnology* 24 (2013) 035701.
- [10] S. Tosti, L. Bettinali, V. Violante, *Int. J. Hydrog. Energy* 25 (2000) 319.
- [11] P. Millet, R. Ngameni, C. Decaux, S. Grioriev, *Int. J. Hydrog. Energy* 36 (2011) 4262.
- [12] A. Pozio, R. Jovanovic, R. Presti, M. De Francesco, S. Tosti, *Int. J. Hydrog. Energy* 37 (2012) 7925.
- [13] Y. Kato, K. Inoue, M. Urasaki, S. Tanaka, H. Ninomiya, T. Minagawa, J. Ryu, *Heat Transfer Eng.* 34 (2013) 917.
- [14] N. Timofeev, F. Berseneva, V. Makarov, *Int. J. Hydrog. Energy* 19 (1994) 895.
- [15] K. Rebeiz, J. Dahlmeyer, Tr. Garrison, Ty. Garrison, S. Darkey, D. Paciulli, M. Talukder, J. Kubic, K. Wald, F. Massicotte, S. Nesbit, A. Craft, *J. Energy Eng.* 141 (2015) 04014029.
- [16] G. Jimenez, E. Dillon, R. Miller, F. Massicotte, S. Nesbit, A. Craft, *Scr. Mater.* 59 (2008) 870.
- [17] P. Perrot, N. Moelans, N. Lebrun, in: G. Effenberg, S. Ilyenko (Eds.), *Noble metal ternary systems: phase diagrams, crystallographic and thermodynamic data*, Springer, Berlin, 2006.
- [18] D. Wang, T.B. Flangan, R. Balasubramaniam, *Scr. Mater.* 41 (1999) 517.