1. Introduction

If you Google the phrase “uses of hydrogen”, you quickly appreciate how versatile and important a substance hydrogen is. In addition to its many industrial uses, hydrogen’s use in energy related areas of science and technology is of critical importance. For example, hydrogen plays prominent roles in rocketry and petroleum refining. As a primary energy carrier, hydrogen has risen in prominence in the areas of fuel cell development and vehicle design. For all the attractive features possessed by hydrogen as an alternative energy carrier to fossil fuels, there are lingering issues that need to be addressed. Due to its flammability, one impediment to the use of hydrogen as an energy carrier is its safe storage. Another issue with the use of hydrogen as an energy carrier is the need to purify the hydrogen from impure sources (such as during steam methane reforming).

The ability of certain transition metals and alloys to absorb significant amounts of hydrogen has attracted attention regarding hydrogen storage and hydrogen purification. Once absorbed in the transition metal, hydrogen is no longer flammable and thus the metal provides a safe storage medium for the hydrogen. Additionally, some transition metals possess gas permeation characteristics that are almost 100% selective to hydrogen when exposed to hydrogen-containing gas mixtures and thus have been used as hydrogen-specific permeable membranes in hydrogen purification applications [1-5].

However, a nagging issue that arises with transition metal-hydrogen materials is that the metal tends to become quite brittle due to hydrogen absorption and desorption [6-8]. In many metal-hydrogen materials, hydrogen embrittlement compromises the mechanical properties (strength, hardness, elongation) of the metal, often to the point where mechanical failure becomes a concern. Is it possible to utilize transition metals and alloys in hydrogen technology and avoid the deleterious effects of hydrogen embrittlement? The ability of
the host metal to avoid hydrogen embrittlement would certainly make the use of metal-hydrogen materials more viable.

Perhaps no other transition metal has been studied more regarding hydrogen absorption than palladium. Palladium possesses many properties that make it very attractive for hydrogen storage and purification. Palladium has a high storage capacity for hydrogen. Palladium has fast uptake and desorption of hydrogen. Palladium absorbs hydrogen under non-extreme conditions of temperature and hydrogen pressure. Palladium is highly selective to hydrogen gas during permeation by gas mixtures. Therefore, it would appear that palladium should be a prime candidate as a safe storage material for hydrogen and as a viable hydrogen purification membrane. Unfortunately, palladium is highly susceptible to hydrogen embrittlement and susceptible to contamination from certain gaseous impurities, such as carbon monoxide and hydrogen sulfide, that diminish the ability of hydrogen to be absorbed. These drawbacks, along with cost considerations, diminish the attractiveness of palladium as a storage medium and as a hydrogen purification membrane [1, 9].

The alloying of palladium with other transition metals represents a means by which to alter the properties of palladium, and potentially mitigate some of the negative effects that are encountered during the use of palladium. For example, alloying palladium with silver results in alloys that, in several ways, are superior to pure palladium, particularly as hydrogen purification materials. Like pure palladium, palladium-silver alloys are virtually 100% selective to the absorption of hydrogen from a gas mixture [10–14]. Palladium-silver alloys have been found to have superior hydrogen transport properties and some resistance to hydrogen embrittlement, as compared to pure palladium [10–14]. With respect to the resistance of palladium-silver alloys to hydrogen embrittlement, most studies done in this area have been qualitative or, at best, limited in their quantitative characterization. However, several authors of the present investigation have carried out rigorous quantitative studies on hydrogen embrittlement in palladium-silver alloys [15–18]. These studies have indeed found that alloying palladium with silver can result in significant reduction in the susceptibility of the metal matrix to the damaging effects of hydrogen embrittlement.

In the realm of hydrogen purification materials, the alloying of palladium with copper has also drawn the attention of researchers. Like palladium-silver alloys, palladium-copper alloys have superior hydrogen transport properties compared to pure palladium. These alloys are virtually 100% selective to hydrogen permeation from a gas mixture. An attractive feature of palladium-copper alloys compared to palladium-silver is that the much lower cost of copper compared to silver makes palladium-copper alloys more economically viable. Beyond economic considerations, palladium-copper alloys show superior resistance to gaseous contaminants. Palladium-silver alloys do, like pure palladium, experience sulfur poisoning while palladium-copper alloys are much more resistant to sulfur poisoning [3–5].

Like palladium-silver alloys, there is evidence that palladium-copper alloys are less susceptible to hydrogen embrittlement than pure palladium [3–5, 19]. Additionally, like palladium-silver alloys, the evidence for the palladium-copper alloys’ resistance to hydrogen embrittlement lacks quantitative rigor. The current study begins introducing a more quantitative perspective to the resistance of palladium-copper alloys to hydrogen embrittlement. Though the most attractive palladium-copper alloy for hydrogen purification applications contains ~40 weight% copper, the current study focuses on alloys with copper weight percentages between 5 and 25. The present study quantitatively characterizes the strength, hardness, and ductility characteristics of a series of palladium-copper alloys with copper contents from 5 weight% to 25 weight%. The results should start to generate a fuller appreciation of the mechanical properties of palladium-copper alloys and the effects of hydrogen exposure on these mechanical properties.

2. Materials and Methods

Palladium-copper (99.9% pure basis metal) foils (ACI Alloys, San Jose, CA, USA) of 0.25 mm thickness were used in this study. These foils were unidirectionally cut into 38.1-mm-long by 6.4-mm-wide specimens. A reduced section of 3.2 mm width was ma-
chined into each specimen that was used for tensile testing. Specimens were lightly abraded with fine emery paper, then chemically polished in a 2:2:1 volume mixture of H$_2$SO$_4$:HNO$_3$:H$_2$O, followed by liberal rinsing, in an ultrasonic cleaner, with distilled water and then acetone. All specimens were then stress relieved in vacuo at 723 K for 48 h, followed by a 24 h annealing in vacuo at 823 K. These annealing temperatures were high enough to allow recovery of each specimen to a nearly defect-free state. Some of the vacuum-annealed specimens were retained for strength and hardness testing.

Hydrogen absorption/desorption by annealed specimens was carried out in an all-stainless-steel system of calibrated volumes. The temperature of the specimen chamber of the system was maintained at 323 K by a regulated water bath. Hydrogen gas pressures were measured with MKS diaphragm gauges. Specimens were exposed to a hydrogen pressure of 1.00 atm (1.01 $\times$ 10$^5$ Pa) and allowed to absorb hydrogen until no further hydrogen pressure decrease was observed, indicating that hydrogen absorption had ceased. Upon completion of hydrogen absorption, specimens were evacuated for 24 h at 323 K to remove all absorbed hydrogen. The evacuation was carried out via a vacuum system composed of a HyVac two-stage pump (HyVac Products, Pottstown, PA, USA).

Tensile tests were carried out, on both vacuum-annealed and hydrogen-cycled specimens, using an Instron Series IX Automated Materials Testing System (Instron Corporation, Norwood, MA, USA). Tensile stress–strain tests were performed at a constant elongation rate of 1.27 mm/min. Specimens used for microhardness testing were subjected to a series of polishings, culminating in a 0.05 micron alumina polishing. Vickers microhardness tests were performed, on both vacuum-annealed and hydrogen-cycled specimens, using a LECO Microhardness Tester (LECO Corporation, St. Joseph, MI, USA) using a load of 100 g.

3. Results and Discussion

Analysis of the tensile stress–strain curves from the present study allow the determination of the yield strength, ultimate strength, and elongation at failure for each alloy investigated.

3.1. Vacuum-Annealed Alloys

If one is to appreciate the effects of hydrogen exposure on the mechanical properties of palladium-copper alloys, then it seems obvious that baseline values of the mechanical properties are needed. A search of the literature failed to find any detailed quantitative information on the strength and hardness characteristics of the alloys studied in the present investigation. Thus, to establish the needed baseline values, tensile stress–strain tests and Vickers microhardness tests were performed on alloy specimens that underwent the vacuum annealing described in the Materials and Methods section.

Figures 1–3 show the strength, hardness, and ductility characteristics, respectively, of the vacuum-annealed alloys. For comparison, the corresponding values for vacuum-annealed pure palladium are included in each figure [20]. These figures clearly show that alloying palladium with copper generates significant solid solution strengthening. This finding is unsurprising. An inspection of the palladium-copper phase diagram shows that the binary palladium-copper system manifests interesting phase relationships at moderate and high copper contents [21]. However, in the palladium-rich region of the phase diagram, up to a copper weight percent of ~30%, palladium-copper alloys form a continuous series of solid solutions. Thus, all the alloys involved in the present study reside in the palladium-rich region of the palladium-copper system where solid solutions solely exist and the presence of solid-solution strengthening is, as has been found, expected in the alloys studied.
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Diagram, up to a copper weight percent of ~30%, palladium-copper alloys form a continuous series of solid solutions. Thus, all the alloys involved in the present study reside in the palladium-rich region of the palladium-copper system where solid solutions solely exist and the presence of solid-solution strengthening is, as has been found, expected in the alloys studied.

Figure 1. Ultimate strength (●) and yield strength (■) as a function of copper content.

Figure 2. Vickers Microhardness as a function of copper content.

Figure 3. Elongation at failure as a function of copper content.
Figure 1 clearly illustrates that the strength characteristics of the vacuum-annealed alloys depend significantly on the weight percent copper. Figure 2 shows a similar sensitivity of the alloys’ hardness to its weight percent copper. Interestingly, as shown in Figure 3, the ductility (as expressed by the elongation at failure) is relatively insensitive to compositional differences in the alloys investigated. As expected of solid solution strengthening, both the yield strength and ultimate strength of the alloys increased with an increase in copper content, as did the microhardness. The lack of significant dependence of elongation on copper content is not unheard of. Though solid solution strengthening has been observed to decrease the ductility in some systems [22], it has also been observed to increase the ductility [23]. Additionally, like the present study, an evaluation of the ductility of palladium-silver alloys found that the elongation at failure remained fairly constant (21% ± 1%) over a range of silver 5–25 weight% [16]. These variations in the behavior of ductility due to the formation of solid solutions is unexplained, but clearly points to a dependence on the particular substances that mix to form a solid solution. Though a search of the literature did not produce comparative values for the measured mechanical properties of the alloys studied, values for the ultimate strength and elongation at failure for a palladium-copper 40 weight% Cu alloy are available [4]. For the vacuum-annealed palladium-copper 40 weight% Cu alloy, the ultimate strength has been found to be 490 MPa while the elongation at failure has been found to be 22%. These values indicate, given the trends in the present results, that the values found for the alloys involved in the current study are reasonable.

The results for vacuum-annealed palladium-copper alloys are similar, in a general sense, to those found for vacuum-annealed palladium-silver alloys [16]. Over the same compositional range (5–25 weight% metal solute), strength and hardness increase with increasing solute content while the ductility is little affected by the weight percent copper or silver. In light of the broad similarities between the behavior of the palladium-silver and palladium-copper systems, a quantitative comparison of the manifestations of solid solution strengthening may offer guidance when deciding which alloy system is more appropriate in a given situation. Table 1 shows the percent change in yield strength, ultimate strength, microhardness, and total elongation for several palladium-silver and palladium-copper alloys of identical solute (silver or copper) weight percent. The percent change was calculated as:

\[
\% \text{ change} = \frac{(\text{value of alloy}) - (\text{value of pure palladium})}{(\text{value of pure palladium})} \times 100 \tag{1}
\]

Table 1. Percent change in mechanical property, relative to palladium, as a function of silver/copper content.

| Property               | % Solute | 5% Ag | 5% Cu | 15% Ag | 15% Cu | 25% Ag | 25% Cu |
|------------------------|----------|-------|-------|--------|--------|--------|--------|
| Yield Strength (MPa)   | 18       | 85    |       | 90     | 226    | 107    | 305    |
| Ultimate Strength (MPa)| 16       | 46    |       | 56     | 120    | 83     | 176    |
| Vickers Microhardness (VHN)| 9  | 36    |       | 43     | 72     | 74     | 111    |
| Total Elongation (%)   | 5        | 5     |       | 5      | 5      | 5      | 5      |

As can be seen from the values in Table 1, the degree of solid solution strengthening is greater in the palladium-copper system. The strengthening and hardening caused by the alloying of palladium with copper up to a weight percent of 25% significantly dwarfs the similar phenomena found in the palladium-silver system, in most instances by more than double. Thus, if strength and hardness enhancement are a requirement when choosing between the use of palladium-copper and palladium-silver alloys in an application, the present results clearly show that copper enjoys an advantage over silver as an alloying agent with palladium, at least up to a weight percent of 25%. If the choice between palladium-copper and palladium-silver alloys involves utilizations that expose the alloys to hydrogen, then the characteristics of vacuum-annealed alloys, though very important, are not the only properties that will be of interest in making an informed decision.
Now that the baseline tensile strength, hardness, and ductility properties of palladium-copper alloys, up to a copper weight percent of 25%, have been quantitatively characterized, how are these properties influenced by exposure to hydrogen, if at all?

3.2. Hydrogen-Cycled Alloys

When pure palladium undergoes a hydrogen absorption/desorption cycle under the conditions of the present study (323 K, hydrogen dosing pressure = 1 atm), the yield strength, ultimate strength, and hardness increase significantly while the ductility decreases significantly [20]. Do the palladium-copper alloys evaluated in the present study exhibit these tell-tale signs of hydrogen embrittlement?

As described in the Experimental section, the hydrogen-cycled alloy specimens were exposed to 1 atm of H$_2$ gas at 323 K and allowed to absorb the H$_2$ gas until equilibrium was reached (i.e., until hydrogen absorption ceased). Following the absorption of hydrogen, the specimens underwent complete desorption of the absorbed hydrogen gas. Following this absorption/desorption cycling treatment, the mechanical properties were measured using identical protocols to those used on vacuum-annealed specimens. Figures 4–7 show side-by-side comparisons of the yield strength, ultimate strength, microhardness, and total elongation, respectively, for vacuum-annealed versus hydrogen-cycled palladium-copper alloys.

![Figure 4. Yield strength of vacuum-annealed (black bar) and hydrogen-cycled (gray bar) alloys.](image1)

![Figure 5. Ultimate strength of vacuum-annealed (black bar) and hydrogen-cycled (gray bar) alloys.](image2)
Alloys. By way of comparison, under identical conditions of vacuum annealing and hydrogen absorption/desorption cycling, the palladium-silver alloy system shows evidence of hydrogen embrittlement up to a silver weight of ~20% [17]. Therefore, in terms of resistance to hydrogen embrittlement at 323 K, the current results indicate that the palladium-copper system is superior to the palladium–silver system, with the resistance to embrittlement setting in at a lower solute (copper versus silver) content.

The results are pretty clear. Both the 5 weight% Cu and 10 weight% Cu alloys clearly show significant strengthening and hardening along with significant loss of ductility due to undergoing a single hydrogen absorption/desorption cycle at 323 K. Beginning with the 15 weight% Cu alloy, the effects of hydrogen cycling have little, if any, influence on the alloys’ strength, hardness, and ductility. Figure 4 shows that the yield strength of the 5 weight% Cu alloy increased by ~107% as a result of hydrogen cycling and that of the 10 weight% Cu alloy increased by ~93%. With respect to the ultimate strength (Figure 5), the 5 weight% Cu alloy exhibited a ~56% increase due to hydrogen cycling while the 10 weight% Cu alloy exhibited a ~32% increase. Vickers microhardness (Figure 6) mimicked the strength characteristics. The 5 weight% Cu alloy experienced a ~53% increase in hardness while the 10 weight% alloy’s hardness increased by ~40% due to hydrogen cycling. The ductility (Figure 7) decreased by ~73% due to hydrogen cycling for the 5 weight% Cu alloy and by ~58% for the 10 weight% Cu alloy. Though the strength and hardness characteristics of the alloys with 15 weight% Cu and higher show no significant difference between vacuum-annealed and hydrogen-cycled specimens, the elongation at failure for the 15 weight% specimens show a decrease of ~13%. This seems to indicate that the ductility of the alloys may be a slightly more sensitive mechanical parameter in terms of resistance to hydrogen embrittlement.
of being influenced by hydrogen absorption/desorption cycling. The 20 and 25 weight% Cu alloys show no discernible change in ductility due to hydrogen cycling at 323 K.

Therefore, the present results show clear manifestations of hydrogen embrittlement in the palladium-copper 5 weight% copper and palladium-copper 10 weight% copper alloys. Additionally, there is tenuous evidence that a slight degree of hydrogen embrittlement may occur in the palladium-copper 15 weight% copper. There are no indications that hydrogen embrittlement occurs in the palladium-copper 20 and 25 weight% copper alloys. By way of comparison, under identical conditions of vacuum annealing and hydrogen absorption/desorption cycling, the palladium-silver alloy system shows evidence of hydrogen embrittlement up to a silver weight of ~20% [17]. Therefore, in terms of resistance to hydrogen embrittlement at 323 K, the current results indicate that the palladium-copper system is superior to the palladium–silver system, with the resistance to embrittlement setting in at a lower solute (copper versus silver) content.

It has been suggested that an important factor in the resistance to hydrogen embrittlement in certain palladium-based alloy systems is a suppression of a discontinuous phase transition from a dilute solution of hydrogen in the alloy matrix (referred to as the α phase) to a dense solution of hydrogen in the alloy matrix, referred to as a β hydride phase. Several authors of the current study have offered a detailed explanation of the suppression of the α to β phase transition in the palladium-silver-hydrogen system [15–18,20]. Since the details of the explanation of the suppression of the α to β phase transition are available elsewhere, we will offer a more cursory explanation here for the palladium-copper alloy system.

Figure 8 shows a schematic of a portion of the palladium-hydrogen temperature-composition phase diagram, where composition is represented as the H/Pd atomic ratio. As can be seen, two solid phases are present in this region of the phase diagram. The α phase is the aforementioned dilute solution of hydrogen in palladium and the β phase is the aforementioned hydride phase. The most prominent feature in this region of the palladium-hydrogen system is the coexistence region of the α and β phase, represented by the solid phase boundary. This coexistence region is referred to as a miscibility gap and it terminates at the critical point (labelled $T_c$, for critical temperature). The critical temperature of the palladium-hydrogen miscibility gap is ~570 K [24]. Upon hydrogen absorption and desorption at temperatures below the critical temperature, the palladium-hydrogen system will traverse the miscibility gap, causing a discontinuous nucleation and growth phase change between the α and β phases. The more hydrogen-rich β phase has a volume, at 298 K, that is ~10% larger than the α phase. Thus, at the interface between domains of the α phase and those of the β phase, the mismatch in volume creates dislocations and these dislocations progressively build up as the miscibility gap is traversed [25]. It is this buildup of dislocations that is thought to be the prime contributor to the increase in strength and hardness, along with the loss of ductility, that characterize the significant hydrogen embrittlement that is unfortunately characteristic of pure palladium’s interaction with hydrogen [20]. One way to mitigate hydrogen embrittlement in pure palladium is to utilize palladium at temperatures above the critical temperature. At these temperatures, the α to β (on hydrogen absorption) and the β to α (on hydrogen desorption) transitions occur in a homogeneous, continuous manner, without significant buildup of dislocations [18].

The alloying of palladium with certain metals has been found to affect the miscibility gap in the palladium-hydrogen system [26–28]. In the case of alloying palladium with copper, studies have shown that copper will suppress the miscibility gap. The net result being that the critical temperature is lowered, and the width of the miscibility gap decreases relative to the palladium-hydrogen system. This suppression is represented generically by the dashed boundaries in Figure 7, with the suppression increasing with an increasing amount of copper in the palladium-copper alloy. The suppression and decreasing width of the miscibility gap will impact the mechanical properties that are altered by traversal of the miscibility gap. The suppression of the miscibility gap reflects the fact that, at temperatures below $T_c$, the volume difference between the α and β phases has decreased, leading to fewer dislocations being generated during traversal of the narrowing two-
phase region. At temperatures above the critical point, the volume difference between the α and β phases completely disappears. With fewer dislocations being generated, the strength, hardness, and ductility parameters of the hydrogen-cycled alloy matrix will be less impacted by hydrogen exposure. The suppression of the miscibility gap in the palladium-silver-hydrogen system and its impact on the mechanical properties of the palladium-silver alloy matrix has been thoroughly characterized for alloys up to a silver content of 25 weight percent silver [15–18].

Pressure-composition isotherms, x-ray diffraction, and electrical resistance studies have been used to investigate the suppression of the miscibility gap in the palladium-copper-hydrogen system [29–32]. Though precise values of the critical temperature of the miscibility gap at specific copper contents were not determined, the studies indicate that the critical temperature drops below 298 K at a copper content of ~20 weight percent copper. This renders the current strength, hardness, and ductility results reasonable. Remembering that the hydrogen exposure temperature in the current study was 323 K, that certainly indicates that hydrogen exposure at 323 K will not involve traversing the miscibility gap in the 20 and 25 weight percent copper alloys, as 323 K is above T_c at these copper contents. This was borne out by the findings that the measured mechanical properties of the 20 and 25 weight% copper alloys were not meaningfully altered by hydrogen exposure relative to the properties of the vacuum-annealed alloys. The present results indicate that, for the 5 and 10 weight percent copper alloys, the critical temperature of the respective miscibility gap is above 323 K and the hydrogen exposure treatments at 323 K did involve traversal of the miscibility gap. In these alloys, the hydrogen exposure treatment generated dislocations due to the discontinuous α to β (on absorption) and β to α phase transition (on desorption) during hydrogen exposure. These dislocations spurred the observed increases in strength and hardness, along with the decreases in ductility (elongation at failure). The very subtle differences in the mechanical properties of vacuum-annealed and hydrogen-cycled palladium-copper 15 weight percent copper alloy indicate that the critical temperature of its miscibility gap is very close to 323 K. Thus, for this alloy, the hydrogen exposure treatment may have involved traversing the miscibility gap very close to the critical point. Traversal close to the critical point of the miscibility gap would involve the conversion between α and β phases that vary in volume to a very minor degree, resulting in minimal introduction of dislocations into the palladium-copper matrix. It is hoped that this explanation will be placed on firmer footing with future investigations on the present alloys that involve varying the temperature at which hydrogen absorption/desorption occurs.

![Figure 8. Schematic temperature-composition phase diagrams for the palladium-hydrogen system (solid line) and palladium-based alloy-hydrogen systems (dashed lines).](image-url)
4. Conclusions

The present results indicate that significant solid solution strengthening occurs in palladium-copper alloys with copper contents up to 25 weight percent. The degree of solid solution strengthening was found to be significantly greater than that found in comparable palladium-silver alloys. Of the palladium-copper alloys studied, it was found that significant hydrogen embrittlement occurred in those up to a copper content of 10 weight percent. Subtle indications point to possible modest hydrogen embrittlement in the 15 weight percent copper alloy. It is important to realize that the results for hydrogen embrittlement are limited specifically to hydrogen exposure conditions of 323 K and 1 atm H₂ pressure. The hydrogen embrittlement findings have been attributed to the impact that copper has on the discontinuous miscibility gap phase change in the palladium-hydrogen system.

Author Contributions: A.C. was the principal investigator on the project. S.N. carried out the stress-strain tests. All other co-authors were undergraduate students who performed specimen preparation work, vacuum annealing treatments, hydrogen-cycling treatments, polishing, and microhardness measurements. All authors contributed to the writing and editing of this manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are available upon request from the corresponding author.

Acknowledgments: The authors wish to thank Fred Massicotte of the Institute of Materials Science at the University of Connecticut for valuable assistance in measuring microhardness.

Conflicts of Interest: The authors declare no conflict of interest.

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