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EFFECT OF HYDROGEN ON TENSILE PROPERTIES OF PALLADIUM-HYDROGEN SYSTEM

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16. Abstract

Tensile properties of both annealed and as-received palladium wire were measured as a function of hydrogen content. Electrolysis at room temperature was the method used for hydrogen absorption. The yield stress, ultimate tensile stress, and elongation at maximum stress were determined and showed abrupt changes with respect to hydrogen content near the boundaries of the phase diagram. The dependence of the tensile properties on hydrogen content within a single phase region was interpreted in terms of electronic structure and work-hardening. Auxillary experiments were performed to substantiate that the formation of the β-phase by the electrolytic absorption of hydrogen produced work-hardening.

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EFFECT OF HYDROGEN ON TENSILE PROPERTIES OF PALLADIUM-HYDROGEN SYSTEM

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SUMMARY

Tensile properties of both annealed and as-received palladium wire were measured as a function of hydrogen content. Electrolysis at room temperature was the method used for hydrogen absorption. The yield stress, ultimate tensile stress, and elongation at maximum stress were determined and showed abrupt changes with respect to hydrogen content in the neighborhood of the boundaries of the phase diagram. The dependence of the tensile properties on hydrogen content within a single phase region was interpreted in terms of electronic structure and work-hardening. Auxiliary experiments were performed to substantiate that the formation of the β-phase by the electrolytic absorption of hydrogen produced work-hardening.

INTRODUCTION

Physical properties of some transition metals are profoundly influenced by hydrogen in the metal lattice. Because the hydrogen concentration in palladium (Pd) can be readily varied continuously up to a one-to-one atom ratio and because the atom ratio can be accurately determined, extensive studies have been made of this metal. Some of the properties studied in relation to hydrogen concentration in palladium are electrical resistivity (refs. 1 and 2), magnetic susceptibility (ref. 3), crystal structure (ref. 1), electrode potential (ref. 1), hardness (ref. 1), Young's modulus (ref. 1), and breaking strain (ref. 1). Most of these properties show notable changes at hydrogen to palladium atom ratios (H/Pd) near 0.02 and between 0.55 and 0.6. These two regions correspond to phase boundaries: the α-phase with a lattice parameter of 3.890 to 3.895 Å (389.0 to 389.5 pm) exists for ratios from zero to 0.02; the β-phase with a lattice parameter of 4.025 Å (402.5 pm) exists for ratios from 0.6 to 1.0. At atom ratios between 0.02 and 0.6, the α- and β-phase coexist (refs. 4 and 5).

While published data (refs. 1, 6, and 7) on the tensile properties of palladium are incomplete, they do suggest that changes could occur near H/Pd values of 0.02 and 0.6. For example, Krüger and Jungnitz (ref. 6) have shown that Young's modulus and breaking strain have a broad maximum near H/Pd of 0.08. Also, Takagi and Sugeno (ref. 7) state that the ultimate tensile stress and elongation increase as H/Pd increases from zero to 0.02: above a H/Pd of about 0.02 these properties decrease. (The value reported in ref. 7 is 0.2. However, an author informed us that this value is a misprint and should be 0.02.) In both references 6 and 7 the data points are not sufficiently close to define well the inflection points on the various tensile property curves. Furthermore, some of the data of these investigators appear to be conflicting. The data of Krüger and Jungnitz (ref. 6) indicate that hydrogen reduces elongation of annealed palladium while Takagi and Sugeno (ref. 7) report that hydrogen charging increased the ductility of as-received palladium.

Obviously, more definitive work is needed and that is the purpose of the work reported here. Also, the understanding and techniques developed with palladium might be used advantageously to guide studies of more complicated metal-hydrogen systems. The tests were performed on both annealed and as-received specimens for H/Pd up to 0.9. We determined values for the yield stress (YS), ultimate tensile stress (UTS), and elongation at maximum stress. The results are interpreted in terms of electronic structure and work-hardening.

EXPERIMENTAL

The experimental work involved specimen preparation, tensile tests, and the determination of the hydrogen concentration.

Specimen Preparation

The Pd wire was obtained from commercial suppliers and was 0.25 millimeter in diameter. These wires had the manufacturers' stated impurity level, including interstitials, of less than 0.01 percent. Our residual resistivity measurements confirmed this level of purity. Greatly enlarged shadows of the wires indicated that the wire diameter varied by 5 percent (10 percent in cross-sectional area). Some specimens were annealed before charging with hydrogen. The rest were charged in the as-received condition. The annealing was accomplished by joule heating to 1120 K in a vacuum of 5×10^{-8} torr (7×10^{-6} N/cm^2). All specimens were then cut into about 8-centimeter lengths and rinsed in acetone and then in chloroform. Immediately before the hydrogen absorption, the specimens were soaked for several minutes in concentrated hydrochloric acid and were carefully rinsed with distilled water.

Hydrogen absorption at room temperature by electrolysis has been discussed elsewhere (ref. 2) and is briefly described here. The specimen was the cathode of an electrolytic cell. The anode was a spectrographic grade graphite rod. The electrolyte was 0.1 normal sulfuric acid containing formalin and sodium sulfide. These additives allowed rapid charging of the specimens to high hydrogen concentrations. The various concentrations were achieved by varying the charging time.

Some specimens were given further treatment to determine if any permanent changes occurred in the palladium lattice which were not dependent on the actual presence of hydrogen. These specimens were first charged either to $H/Pd \simeq 0.02$ or to $H/Pd > 0.55$. The hydrogen was then completely removed (as shown by analysis) by aging overnight at room temperature in a mixture of 2 or 3 cubic centimeters of 30 percent hydrogen peroxide and 100 cubic centimeters of 0.1 normal sulfuric acid (ref. 2).

The effect of handling the annealed specimens prior to tensile testing was evaluated through the use of three sets of specimens. The first set was cold-worked more than under normal handling by deliberately bending the specimens. The second set had normal handling. The third set of specimens was annealed (some at 1200 K), and extreme care was used to prevent cold-working of the portion of the specimen that was critical for the tensile testing.

Tensile Testing

An Instron tensile testing apparatus was used; the specimen was held by two steel grips. One grip was attached to the load cell and the other to the movable crosshead of the tensile machine. The wire was wrapped once around a 6.25-millimeter-diameter post on each grip and was secured to the grip by tightening the end under a bolt. The length of the test section (i.e., the length of wire between the post centers) was 25.4 millimeters. The crosshead speed was 2.54 millimeters per minute. All tensile tests were done at room temperature and were allowed to proceed until the specimen broke.

The data were obtained in the form of load-elongation curves on strip chart recordings. The UTS, YS, and elongation at maximum stress were obtained from these strip charts. The YS is the stress corresponding to 0.2 percent permanent extension. The errors associated with the noise in the amplifier and with shifts in the calibration of the Instron are no more than 2 percent. The maximum error in elongation measurement due to tightening of the wire around the posts is estimated to be a maximum of 20 percent of the reported values.

Determination of Hydrogen Concentration

The atom ratio, H/Pd, was determined in the two portions of each specimen immediately adjacent to the point of rupture. The portions used were from 3 to 5 millimeters long. The method of analysis has been discussed previously (ref. 2). In brief, the method consisted in desorption of the hydrogen from the specimen at 573 K for 1/4 hour in an evacuated quartz container. The gases were expanded into a mass spectrometer which was used to determine the amount of hydrogen. The amount of palladium was determined by weighing the discharged specimen.

The error in the H/Pd values is primarily due to uneven charging along the specimen. This error was estimated by comparing the H/Pd obtained for the two segments of the specimen adjacent to the point of fracture. The average difference in these values was about 5 percent of the reported H/Pd for all the specimens where the $H/Pd > 0.1$ and about 15 percent for the specimens where the $H/Pd < 0.1$. In other words, the error is about 0.003 for the H/Pd near 0.02 and 0.03 for the H/Pd near 0.55. These uncertainties were deemed acceptable for this work.

RESULTS

Most of the data are presented as graphs in which the UTS, YS, or the elongation at maximum stress is plotted against H/Pd (figs. 1 to 3). The elongation is expressed as percent elongation. The YS curves for annealed and as-received palladium are shown in figure 1. The curve for annealed palladium shows a sharp rise as hydrogen increases up to H/Pd near 0.02. Between H/Pd values of 0.02 and about 0.55, the slope is not as steep. Above H/Pd of about 0.55, the change in hydrogen concentration does not appear to influence the YS. The data for as-received palladium show that the YS is much greater at all values of H/Pd than for annealed palladium. The two curves show opposite effects in the region of H/Pd above 0.02. The YS of annealed palladium shows an increase before becoming constant. The YS of as-received palladium shows a gradual decrease as H/Pd goes from about 0.02 to 0.9.

Figure 2 illustrates the effect of hydrogen on the UTS. The UTS for as-received palladium was much greater than that for annealed palladium over the entire hydrogen concentration range. However, both curves were very similar in appearance. That is, there is a sharp increase in UTS as H/Pd increases from 0 to about 0.02. The UTS then decreases as H/Pd increases to about 0.55. Above this value, the UTS appears to be constant with increasing hydrogen concentration.

Figure 3 illustrates the effect of hydrogen on the elongation at fracture. The curves for as-received and for annealed palladium appear to coincide with each other and have the same general shape as the UTS curves.

Table I presents tensile data for hydrogen-free palladium ($H/Pd \lesssim 0.0004$) that had been subjected to various treatments. The treatments for annealed palladium include normal handling, special handling to minimize cold work, special handling to increase cold work, and complete hydrogen removal at room temperature from specimens after charging to either the α-phase ($H/Pd \approx 0.02$) or the β-phase ($H/Pd \gtrsim 0.55$). The general agreement in the data for uncharged palladium with varying amounts of cold work indicated that normal handling procedures did not adversely affect the specimens. The desorption experiments for α-Pd yielded data which were identical with those for the uncharged specimens. The UTS and YS for palladium desorbed from the β-phase were significantly higher than for annealed palladium, and the elongation was less.

Table I also lists data for as-received specimens. The treatments for these as-received specimens were normal handling and complete hydrogen removal at room temperature after charging to the β-phase ($H/Pd \gtrsim 0.55$). Higher YS and UTS were also noted in the desorption experiments for as-received specimens.

DISCUSSION

From the data, it is obvious that the tensile properties are highly dependent on the phase involved. In the α-phase region, an increase in hydrogen concentration is accompanied by an increase in the value of the tensile properties studied. In general, the curves indicate that the tensile properties are not affected by changes in the hydrogen concentration within the β-phase region. (The YS of as-received palladium appears to continue to decrease with increasing H/Pd in the β-phase (fig. 1(b)). However, the scatter in the data probably obscured the small change in slope to horizontal that is needed to support the other observations concerning the β-phase.) Because the effect of hydrogen on the tensile properties depends on the phase involved, we shall discuss the properties of the α-phase and the β-phase independently. We assume the mixture rule can be applied when both phases are present, that is, for $0.02 \lesssim H/Pd \lesssim 0.55$.

The α-phase

The increases for YS and UTS observed in the α-phase are typical of what is termed solution strengthening. Two important considerations for solution strengthening are changes in lattice parameter and electron-atom ratio (ref. 8, p. 169). Recent works show a linear increase in YS with increasing electron-atom ratio (ref. 8, p. 171). These works are for the most part concerned with substitutional alloying in copper. In our work, the hydrogen atom enters interstitially rather than substitutionally. We assume the hydrogen, by entering interstitially, does not add to the atom count but that its electron does add to the electron count. Thus, the electron to atom ratio increases. In keeping with this, we observe a linear increase in YS with this increase in electron-atom ratio. Also, in α-Pd, there is a small and linear increase in lattice parameter with increasing H/Pd, in agreement with the recent ideas (ref. 8, p. 169).

The increasing elongation with increasing H/Pd for α-Pd agrees with the work of Takagi and Sugeno (ref. 7) for as-received palladium. We show somewhat similar data for annealed palladium. However, Krüger and Jungnitz, who did work with annealed palladium, report no data in this region (between H/Pd = 0 and 0.08). We are not able to determine the cause for the increased elongation. However, we believe that the increased electron concentration on the palladium atom is at least partially responsible.

The fact that both YS and elongation increase with increasing H/Pd leads to a similar dependence of UTS upon H/Pd.

The β-phase

There are two aspects of the β-phase to be considered. The first is the effect on tensile properties due to the addition of hydrogen within the β-phase. The second is the relative values of tensile properties of the β-phase with respect to the α-phase.

In general, the figures show that a change of hydrogen concentration within the β-phase region has little or no effect on the tensile properties. In the β-phase region, we have sodium chloride type structure. An increase in the hydrogen content decreases the vacancy concentration of the hydrogen lattice. Thus, we cannot consider the hydrogen ion to be merely an impurity as we did in the α-phase. The addition of hydrogen ions is no longer equivalent to a simple increase in the electron-atom ratio. And we are not surprised to find the absence of solid solution strengthening. Furthermore, the relative constancy of the lattice parameter in β-Pd (4.025 Å; 402.5 pm) is another reason for the independence of tensile properties on hydrogen concentration.

Before comparing the results for α-Pd with those for β-Pd, it is interesting to look at the basic difference between α-Pd and β-Pd. In α-Pd there are essentially 10 outer electrons, while in β-Pd there are at least 10.6 outer electrons. In α-Pd there are empty 4d states throughout its composition range, which is characteristic of transition metals. In contrast, β-Pd has its d-states filled and thus is similar to the noble metals. In table II, we show a comparison of the cohesive energies of the transition metals, nickel, palladium, and platinum, with their respective neighboring noble metals, copper, silver, and gold (ref. 9, p. 427). In each case, the noble metal has exactly one more electron than its corresponding transition metal. The table shows that each transition metal has a higher cohesive energy than its respective noble metal.

In the past, cohesive energy has been related to the manner in which the outer electron states are filled (ref. 9). Thus, we speculate that the filled d-bands of β-Pd tend to decrease its cohesive energy with respect to α-Pd. With this decrease in cohesive energy, decreases in YS and UTS are in general expected, as shown in figures 1(b), 2(a), and 2(b).

In figure 1(a), however, we find that for annealed palladium, the YS of the β-phase is greater than the YS of the α-phase. We attribute this to work-hardening caused by the deformation of the lattice when hydrogen enters and converts the α-phase to the β-phase. This is somewhat supported by the data in table I. As shown in this table, palladium, obtained by desorbing hydrogen from the β-phase, exhibits increases in YS and UTS. The values of YS and UTS obtained by desorption approach the values of the as-received or work-hardened palladium. We attribute these higher values of YS and UTS to work-hardening. We prefer to think the work-hardening is caused during the absorption rather than the desorption process. As-received palladium also shows this work-hardening effect after hydrogen is desorbed from the β-phase but to a lesser degree than the annealed material. We should note further that, when annealed palladium is desorbed from the α-phase, the work-hardening effect is absent. Thus, as we reexamine figures 1 and 2, the relative values of the tensile properties for the α- and β-phases must be considered to be the combined effect of work-hardening and the aforementioned electronic structure.

The brittleness found in the elongation curves for β-Pd is associated with the severe strain-hardening caused by formation of the β-phase. One effect of this brittleness is that the YS and UTS coincide for $H/Pd \gtrsim 0.55$.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 20, 1970,
129-03.

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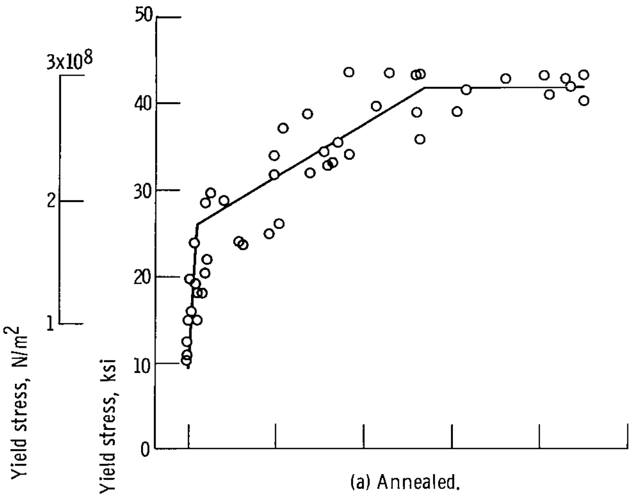
TABLE I. - TENSILE PROPERTIES OF PALLADIUM

[Specimens containing no hydrogen ($H/Pd \overline{<} 0.0004$).]

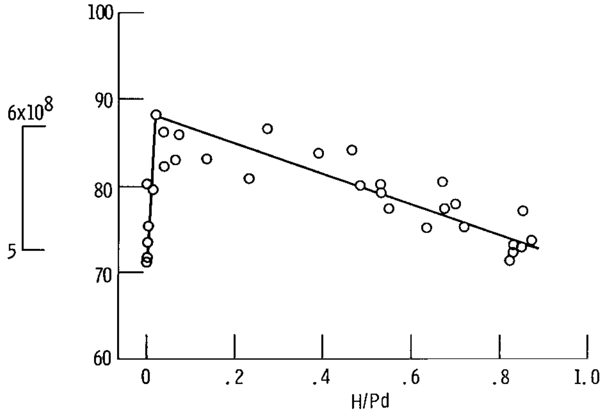
Specimen	Yield stress		Ultimate tensile stress		Elongation, percent
	psi	N/m^2	psi	N/m^2	
Annealed					
Uncharged, regular handling	10 to 15	6.895 to 10.343×10^7	24 to 26	16.548 to 17.927×10^7	6 to 18
Uncharged, minimum cold work	6 to 13	4.137 to 8.964×10^7	18 to 23	12.411 to 15.859×10^7	7 to 14
Uncharged, enhanced cold work	14 to 15	9.653 to 10.343×10^7	24 to 27	16.548 to 18.617×10^7	6 to 12
Discharged from α-phase	15 to 16	10.343 to 11.032×10^7	22 to 23	15.169 to 15.859×10^7	6 to 10
Discharged from β-phase	33 to 54	22.754 to 37.233×10^7	34 to 54	23.443 to 37.233×10^7	2 to 4
As-received					
Uncharged regular handling	71 to 80	48.955 to 55.16×10^7	75 to 80	51.713 to 55.16×10^7	3
Discharged from β-phase	91 to 92	62.745 to 63.434×10^7	92 to 97	63.434 to 66.882×10^7	4 to 5

TABLE II. - COHESIVE ENERGY OF NOBLE METALS AND NEIGHBORING TRANSITION METALS

Metal	Cohesive energy	
	kcal/mole	kJ/mole
Nickel	85	355
Copper	81	338
Palladium	110	460
Silver	68	284
Platinum	127	531
Gold	92	384

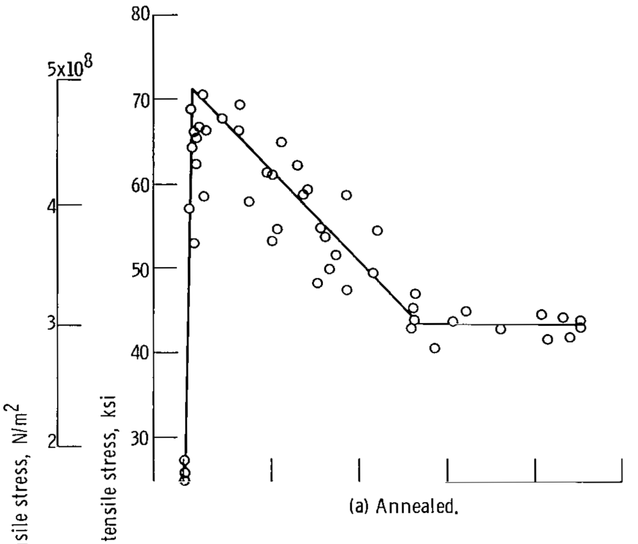


(a) Annealed.

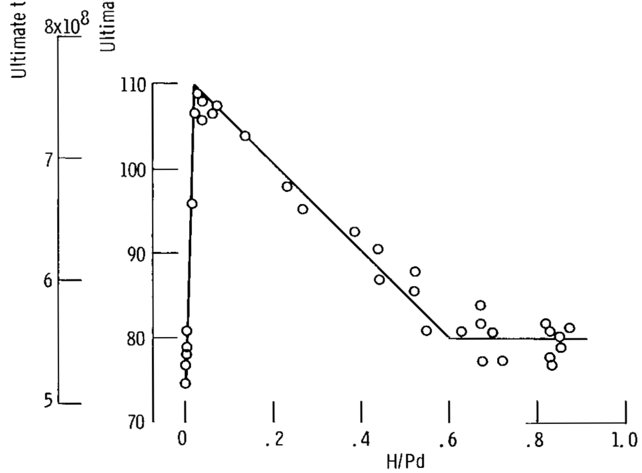


(b) Unannealed.

Figure 1. - Effect of hydrogen-pladium atom ratio (H/Pd) on yield stress for palladium.

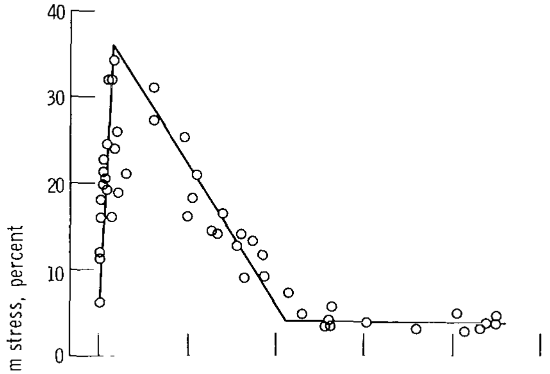


(a) Annealed.

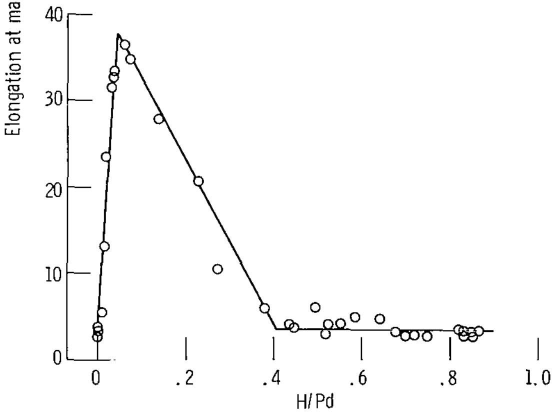


(b) Unannealed.

Figure 2. - Effect of hydrogen-palladium atom ratio (H/Pd) on ultimate tensile stress for palladium.



(a) Annealed.



(b) Unannealed.

Figure 3. - Effect of hydrogen-palladium atom ratio (H/Pd) on elongation at maximum stress for palladium.

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