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Research Article

Fabrication and Characterization of Palladium–Boron Alloys Used in LENR Experiments

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Abstract

Most Low Energy Nuclear Reaction (LENR) electrochemical experiments have been performed with commercially pure palladium cathodes. There has also been interest in the use of alloys of palladium, which retain the ability of that element to absorb high fractions of deuterium, but also offer better mechanical properties. Alloying palladium with low levels of boron is a prime example. The fabrication and characterization of Pd–B alloys is described in this paper. Three alloys with nominal composition in weight percent of boron, 0.25, 0.5 and 0.75, were produced by arc melting, followed by annealing. Transmission electron microscopy and X-ray diffraction showed them to consist of two face-centered cubic phases with different lattice parameters, one dispersed as fine particles within the other. It was found that these alloys produce highly reliable LENR results.

Keywords: Annealing, Excess heat, Face-centered cubic, LENR, Palladium–Boron alloys, X-ray diffraction

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1. Introduction

Low Energy Nuclear Reactions (LENR) have four remarkable empirical characteristics, which make them very attractive as future energy sources. They (a) do not involve dangerous radiation during operation, (b) do not leave radioactive waste, (c) emit no greenhouse gases and (d), very significantly, provide energy gains. The gain is defined as the ratio of the output thermal energy to the input electrical energy, which initiates and controls the LENR.

The attractive features of LENR are currently counterweighted by two major scientific problems. The first is the lack of understanding of the mechanisms that cause LENR. There have been dozens of theories, but none of them has been adequately developed for quantitative comparison with measurements. The second challenge involves the materials used in LENR experiments. Many experiments have shown that the production of LENR depends on some presently unknown characteristics of materials. It is not known if either the composition or structure, or possibly both

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of those characteristics, determine the efficacy of LENR materials. This causes the irreproducibility issue for energy generation from heavy water electrolysis (the Fleischmann–Pons effect) when palladium metal is used as the cathode.

Palladium has a Face Centered Cubic (FCC) structure with properties akin to gold, i.e., soft, ductile, and resistance to corrosion. It is worth noting that palladium is not tarnished by dry or moist air at room temperature, but at about 600°C a thin oxide film forms in air. Above 800°C, the superficial oxide decomposes, leaving a clean metal surface. Some oxide formation occurs again above 1000°C [1]. The intrinsic hardness and tensile strength of palladium are too low for many applications. The addition of boron to palladium within the solubility limit creates two FCC phases with different lattice parameters, one phase being distributed as fine particles within the other phase.

The Pd–B system has been studied for almost 70 years. A 1996 review of the system contains 19 references [2]. A paper on the Pd-rich part of the Pd–B phase diagram published in 2006 cites 24 papers [3]. The preparation of single-phase alloys made of palladium and other minor elements has been known. For example, various palladium alloys which include boron were reported, such as Weber et al. US Patent No.5,518,556 (a boron-containing surface layer), Hough et al. US Patent No. 4,341,846 (an electroless Pd–B plating material), Smith Jr. et al. US Patent No. 4,396.577 (a brazing alloy containing boron, palladium and other metals) and Prosen US Patent No. 4,046,561 (an alloy for porcelain applications containing palladium, boron and other metals). However, what is lacking in these patents is a palladium and boron composition of sufficient strength to be used as a reactive structure rather than a coating material. Such a bulk material also may be used in thin hydrogen purification membranes or as an electrode in a heat-generating process.

Based on almost 30 years of research, two sources of palladium materials yielding good reproducibility for generation of excess enthalpy effects have been identified: (1) palladium materials prepared by co-deposition method and (2) Pd–B alloys. A common feature for both these methods is that they yield palladium that is relatively free of oxygen as an impurity. A beneficial effect of the added boron is that it minimizes the activity of dissolved oxygen in the palladium by converting it to B_2O_3 during processing. The low density B_2O_3 floats to the surface and is removed during the molten phase of the Pd–B alloy preparation. Further, the creation of two FCC phases makes the material harder and less susceptible to cracking. That is attractive for some applications. In particular, it is the likely explanation for reproducible LENR energy generation.

This paper deals with the fabrication, characterization, and evaluation of Pd–B alloys, which have produced excess enthalpy in nearly every experiment [4,5]. Two US Patents have been granted for these materials [6,7]. Success in producing LENR energy with these materials is described in a companion paper [8]. Plans for the employment of Pd–B alloys in a new program are described in another planned paper [9]. The focus of this paper is on the production and processing of Pd–B alloys, including the effects of annealing for different times at different temperatures and cold deformation. Those activities are described in Section 2. Since the mechanical and many other properties of palladium depend on purity, elemental analyses and X-ray diffraction studies will be presented and discussed in Section 3. The Section 4 summarizes the reported activities and characteristics of the Pd–B alloys, and LENR results obtained with them.

2. Production and Processing of Pd–B Alloys

A copper hearth with the cavity containing the Pd and B, suitable for arc melting and cooling, was employed. Although there are several other forms of heating that would be suitable, an electric arc is preferable. Copper is preferably used as the material for the hearth because of its excellent thermal conductivity to remove useless heat during the arc melting process. The copper hearth has a lower melting point than either boron or palladium. Hence, it was cooled by water flowing within it to prevent the copper from melting into the alloy. The hearth, and the mixture resting upon it, were cooled by the transfer of heat from the arc to the alloy composition, and then through the hearth to the coolant water. Exposure to air cannot be allowed because oxygen or air would oxidize the palladium and the boron, ruining the process. The process was performed in a container that was evacuated and then backfilled with a noble gas, typically high purity argon.

The processes used to produce the Pd–B alloys started with boron in powder form, commonly referred to as five-nines boron (99.999% pure). It was first placed within a cavity in the hearth structure. After the weighed boron powder was dispensed into the structure, the weighed amount of Pd sponge was placed on top of it. The palladium was a pure palladium sponge form, commonly referred to as five-nines palladium (99.999% pure). It was positioned in the compartment in that manner, so that it was overlying the boron powder in the cavity. The denser palladium over-layer prevented splatter or other loss of the boron. Additionally, the lower melting point of palladium allowed it to form a protective shell over the boron before the boron begins mixing with the palladium. This arrangement enabled the metal to melt first and envelop the boron powder, which insured little or no loss of the boron powder during the melting and alloying.

A typical arc melting apparatus having 12 V and 300 A (3.6 kW) was used for the melting. The two electrodes used for the arc melting are a tungsten tip immediately above the sample and the copper hearth. The melting was performed at about 2100°C. The melting point of boron, the higher of the pair, is 2079°C so the melting must be done at least at this temperature. However, the temperature should not exceed about 2200°C or the boron will begin to vaporize. The melting time was about five minutes. A melting time greater than 10 min at the high temperatures would result in vaporization of a portion of the boron.

After the initial melting to mix the loose boron powder into the palladium, the mixture was cooled for approximately 30 min, and then turned over in the circular cavity in the copper hearth with the tungsten tip. Then, the melting, cooling, and turning over steps were repeated as often as necessary to eliminate any boron or palladium pockets, and for thoroughly mixing the material into a solution of a desired homogeneity. The steps were repeated anywhere from about 3 to 10 times. The molten solution was homogenized by a combination of gravity and uncontrolled movements within the melts. Finally, the alloy button was transferred to a slot-shaped cavity in the copper hearth for a final melting to produce an ingot of the alloy about 15 cm long and 1 cm in lateral oval cross section.

After the homogeneous alloys were prepared, the material underwent additional steps of swaging or rolling, if so desired, for reducing the alloy to a fixed diameter or plate. After the material was swaged or rolled, the alloy is annealed to reduce the residual stress. The alloy begins at room temperature and is heated to approximately 650°C. for about two hours. The time and temperature in this step are important because too high a time or temperature would result in a larger grain size of the composition which would detract from hardness, and may render the composition ineffective. After annealing, the alloys were cooled to room temperature. The composition resulting from the above process has boron in an interstitial solid solution within in the palladium, with the alloy having a two-phase structure.

The Pd–B alloy produced contains about 0.1–0.8% by weight boron, and hence, from about 99.2 to 99.9% by weight percent palladium. Three compositions were prepared with nominal 0.25, 0.5 and 0.75 wt.% B compositions. The amount of boron in the mixture appears to be critical. It has been found that the amount of boron must be maintained below 2 wt.% of the mixture for full dissolution of the boron. Anything more will react with the palladium, preventing formation of the two solid solution phases. Hence, the amount of boron placed in the cavity for each case was chosen to be small enough not to form a compound of boron in the palladium. However, it was sufficient to react with impurity oxygen in the palladium, while the boron and palladium were molten. Typically, about 100 g of palladium was used, with amounts of boron consistent with the ranges noted above.

The phases of the two-phase structure have the same crystal structure, but different sets of lattice parameters. It was found, and is shown below, that the crystals of the second phase were larger than the crystals of the first phase. The diameter of the crystallites in the first phase was in the range of 1–10 nm, whereas the diameter of the crystallites in the second phase is much larger. The differing sizes of the crystals of the phases creates a “miscibility gap”, as shown in the phase diagram of Fig. 1. This means that the miscibility of the two phases with each other is high because the crystals of the smaller first phase can easily rest in gaps between the larger crystals of the second phase. This filling of the gaps of the larger crystals binds the crystals of both phases together and results in a hardened composition. A more recent phase diagram is shown in Fig. 2. It is little different from the diagram in Fig. 1.

3. Results and Discussion

Three Pd–B alloys were prepared with the aim to achieve 0.25% B, 0.50% B and 0.75% B in accordance with the details given above. The final composition of the three alloys was 0.18% B, 0.38% B and 0.62% B based on Glow-Discharge Mass Spectroscopy (GDMS). Analysis is shown in Table 1. The overall decrease in the boron content after processing, compared to targeted content, was due to the formation of B_2O_3 by reacting with the dissolved oxygen in palladium. Boron acts as scavenger for oxygen during processing. The low density B_2O_3 floats to the surface, and is removed during the molten phase of the Pd–B alloy preparation. Table 1 shows relatively high concentrations of Si, Fe, Rh and Pt in most of the diverse materials, including wire from the Naval Air Warfare Center (NAWC).

To make electrodes from the compositions, the alloys were swaged to 0.4 cm diameter. The swaged rods were cut to length, and machined into usable electrode forms, commonly a few cm in length. The samples were annealed at 650°C for 2 h and furnace cooled to room temperature. A similar procedure was followed for plates or thin foils after rolling instead of swaging. If the annealing is done at different temperatures and different times, the grain size will be affected. An example is shown in Fig. 3. It gives the actual composition of boron as compared to attempted

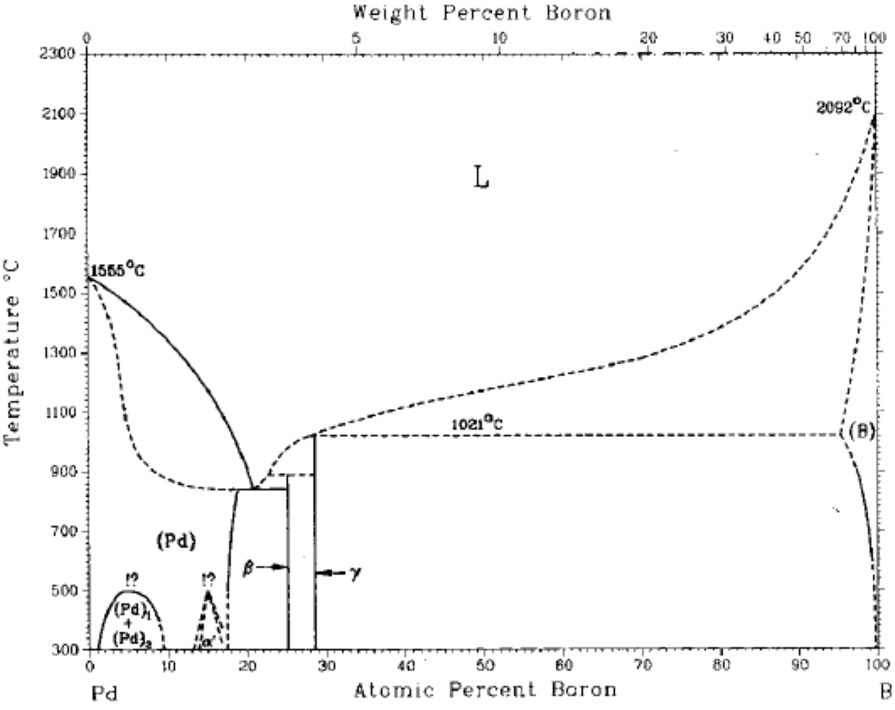


Figure 1. Binary phase diagram of Pd–B system from Binary Alloy Phase Diagrams, Editor-in-Chief: Thaddeus B. Massalski, Volume 1, p. 372, American Society for Metals (August 1987).

composition of 0.25 wt.% B, 0.50 wt.%B and 0.75 wt.% B. Grain size has two major effects: (1) the smaller the grain size, the larger strength and (2) diffusion rates are times higher in grain boundaries, compared to bulk, so that loading with deuterons will be faster in small grain size materials. Detailed analyses of the effects different annealing temperatures and times on grain size are described in [2].

X-ray diffraction studies were carried out to characterize the three compositions of the two-phase Pd–B alloy. The diffraction patterns were obtained with a Phillips diffractometer with generator settings of 50 kV, 30 mA and a copper target. Two distinct phases of the same cubic structure were found in all three compositions of the alloy, as shown in Fig. 4. Lattice parameters for the samples were measured. As can be seen in Fig. 5, the two distinct phases have the same crystal structure but different lattice parameters. The lattice parameter in a first phase remains constant with changes in the boron content of the alloy, whereas the lattice parameter of a second phase increases with an increase in the boron content. As the boron content increases, the fraction of crystals in the second phase increases at the expense of the first phase, as expected.

The 0.62% B sample was studied with a transmission electron microscope. A typical micrograph is shown in Fig. 6. The micrograph shows two phases, one minor (black) in the matrix of major phase (white). Figure 7 shows the Selected Area Diffraction (SAD) pattern of the same as Fig. 6. It shows rings along with the main diffraction spots, indicating no intermetallic compound. Lattice parameters of the two phases measured from X-ray diffraction and SAD are consistent, so they both confirm the production of the Pd–B alloys.

Table 1. Glow-discharge mass spectroscopy (GDMS) analyses of various cathode materials (concentrations in ppm by weight).

Element	NAWC wire	NRL Pd	Pd–0.62B	Pd–0.38B	Pd–0.18B
B	0.007	<0.001	6200	3800	1760
c	<1	0.02	<1	<5	<1
N	<3	0.03	<0.1	<0.1	<5
O	<10	0.45	<10	<10	<20
Mg	0.009	1.2	3.5	2.7	2.9
Al	0.63	0.53	4.1	3.3	1.5
Si	3.5	0.31	15	11	6.8
Ca	0.29	0.58	7.9	2.9	2.4
Cr	0.21	1.2	0.98	1.1	1.1
Mn	0.004	0.75	8.2	5.9	2.6
Fe	2.9	33	56	47	36
Ni	0.03	0.85	1.4	1.7	1.6
Cu	0.76	27	26	26	16
Zn	0.02	1.2	2.3	1.7	1.6
Zr	0.04	0.3	3.9	0.79	0.84
Rh	4.2	11	11	9.6	8.5
Ag	0.45	0.71	0.75	1.4	1.5
W	0.10	3.8	2.2	1.0	0.67
Pt	2.2	30	47	38	18
In	<0.05	<0.05	<0.05	1.9	1.2
Au	1.0	0.17	0.2	0.65	0.22
Ir	1.1	0.4	0.33	0.23	0.18

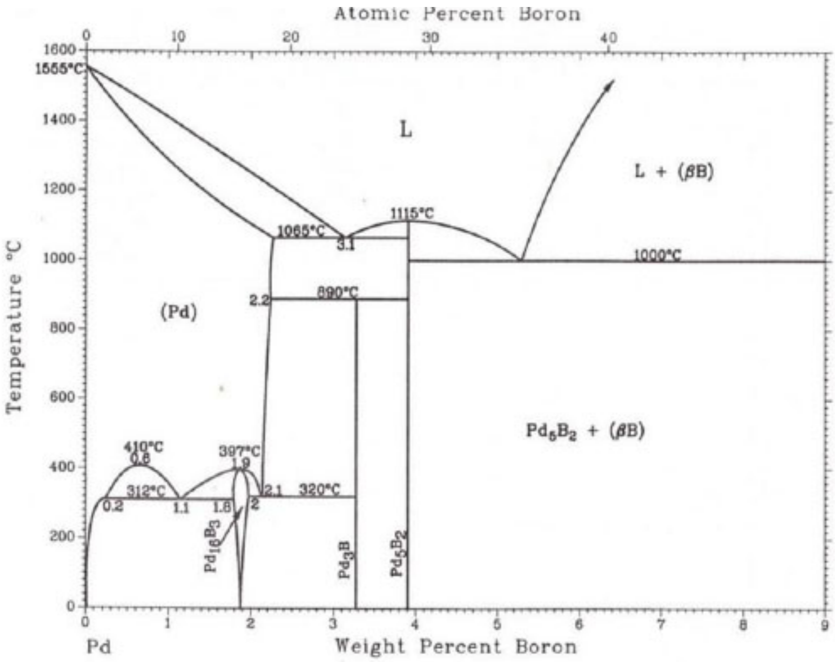


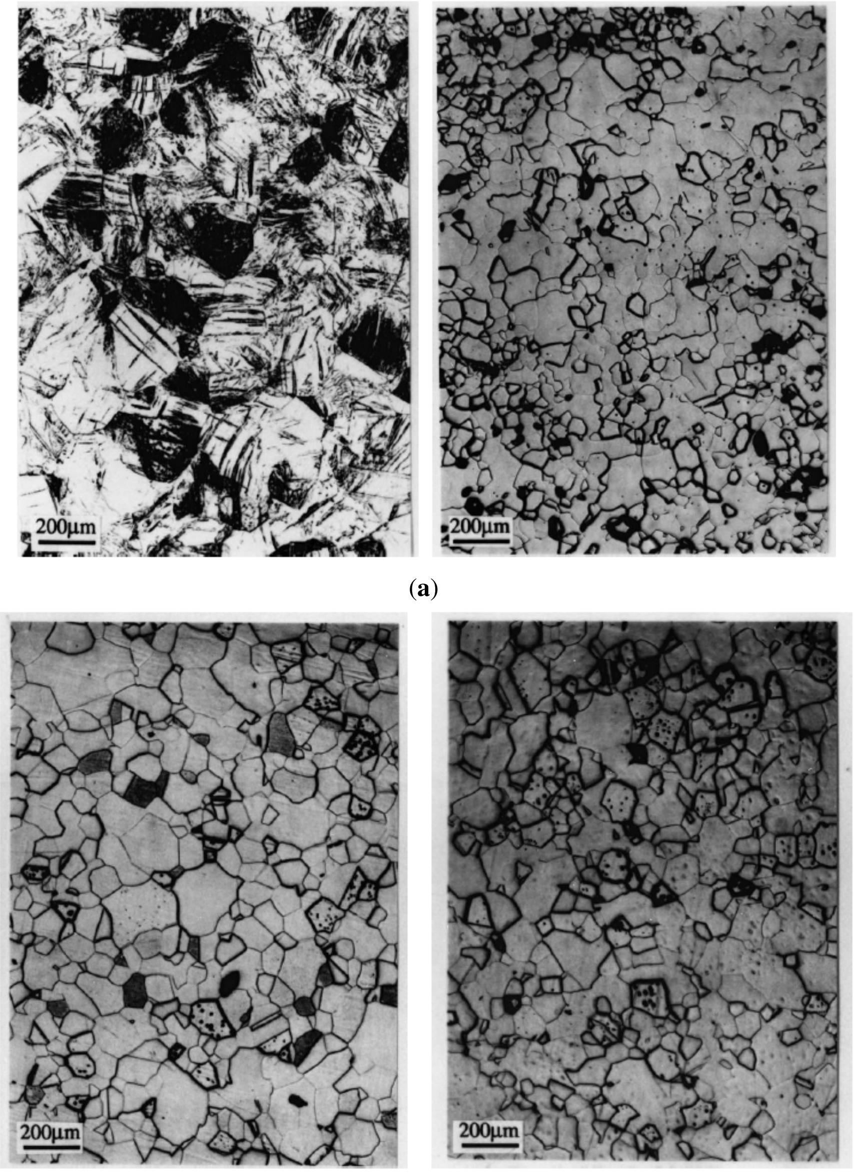
Figure 2. A revised binary phase diagrams of Pd–B system from ASM International Handbook, Volume 3, Alloy Phase Diagram, pp. 2–83 (1999).

4. Summary and Discussion

Three compositions of Pd–B alloys were prepared and characterized. Preparation of the palladium alloys with low boron contents were done in order to keep within the miscibility regime. The compositions had nominal boron concentrations of 0.25, 0.50, 0.75 wt.% B. GDMS analyses of the three as-prepared materials showed 0.62, 0.38 and 0.18 wt.% B. Annealing of the swaged sample at 650°C for 2 h resulted in grain sizes of about 100 μm. The alloying with boron expands the palladium lattice by forming an interstitial alloy with palladium [10]. X-ray diffraction studies showed two distinct phases of the same face centered cubic structure with different lattice parameters. The lattice parameter of one phase remains constant with changes in boron content, whereas the lattice parameter of the other phase increases with the increase in boron content. As the boron content increases, the fraction of one phase decreases at the expense of the other phase.

The alloys described in this paper have proven to be effective in production of energy by LENR. They gave excess powers in seven out of eight experiments in China Lake, California. The materials also produced energy in one study in the New Hydrogen Energy laboratory in Japan, and in another in a private laboratory in California. Three different calorimeters were employed in that set of 10 studies. It was found that excess power appears early in experiments with these Pd–B alloys, in contrast to most other LENR experiments. Details of the past measurements are available [8]. Plans to use these Pd–B materials in future experiments are also documented [9].

Despite all the early work on the Pd–B system, and the LENR-motivated work in the past quarter of a century, there remain several issues regarding the system and its success in LENR experiments. We conclude by noting and commenting briefly on them:



(**a**)

(**b**)

Figure 3. (a)*Left*: Pd-0.62 wt.% B as swaged. *Right*: Pd-0.62 wt.% B annealed at 650°C for 2 h (grain size about 95 μm). (b) *Left*: Pd-0.38 wt.% B annealed at 800°C for 1 h (grain size about 100 μm). *Right*: Pd-0.18 wt.% B annealed at 800°C for 1 h (grain size about 125 μm), percentages of boron are actual compositions.

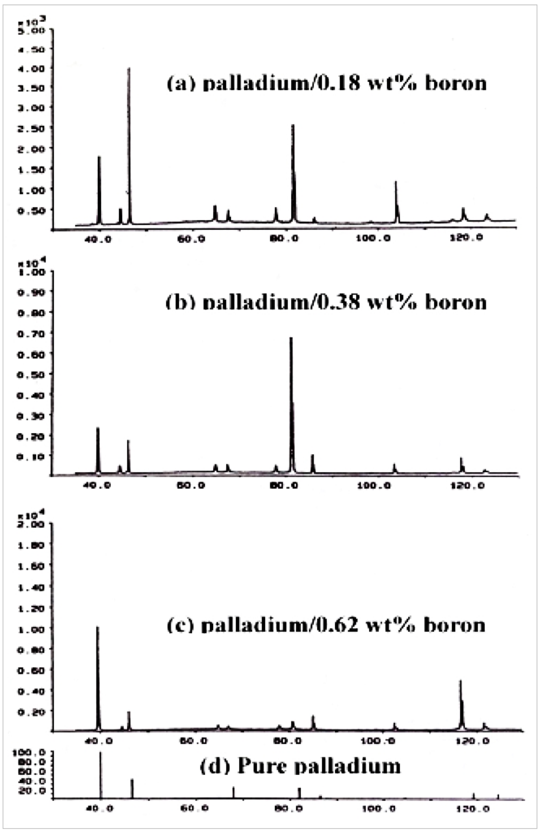


Figure 4. X-ray diffraction patterns of (a) Pd-0.18 wt.% , (b) (b) Pd-0.38 wt.% boron, (c) Pd-0.62 wt.% boron, and (d) pure palladium.

(A) Presence of B as a nuclear reactant. There is ample evidence from the production of helium during LENR experiments, and its correlation with heat production in over a dozen experiments. However, there has been discussion about the possibilities that lithium or boron are also reactants in LENR experiments. This remains an open question.

(B) Oxygen gettering. The possibly deleterious role of oxygen in LENR experiments has made it desirable to eliminate oxygen from materials in such experiments. Sometimes that was done by use of an oxygen-free atmosphere while alloying. The possibility that boron getters residual oxygen in the arc melter used for preparation of our alloys was discussed in this paper. That process is consistent with observations, but not proven.

(C) Increased mechanical strength. The mechanical properties of our Pd–B alloys were not measured. However, it is clear that their strength is much greater compared to pure palladium due to the boron-produced dispersoids and the observed grain structure. The influence of mechanical properties on the generation of LENR is another open question. If there is such an influence, it might be either direct or indirect, the result of a change in materials characteristics causing changes in diffusion or other processes.

(D) Less volumetric expansion? The amount of expansion of cathode materials has been found to be important in

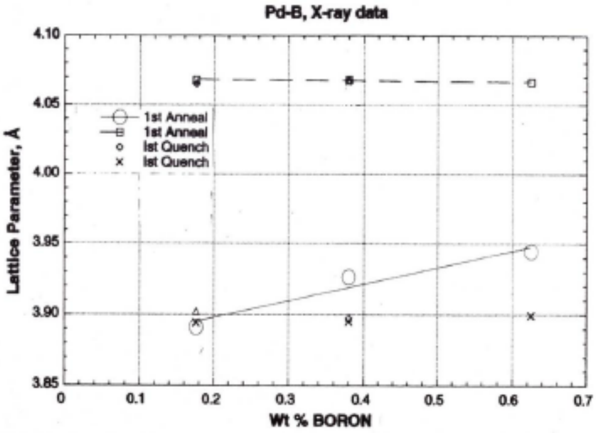


Figure 5. Two distinct phases having same crystal structure, but different lattice parameters, are shown. The lattice parameter in a first phase remains constant with changes in the boron content of the alloy, whereas the lattice parameter of a second phase increases with an increase in the boron content.

some LENR experiments. Maintenance of volume might be related to lesser production of voids and cracks, and the greater retention of deuterium in the metallic lattice.

(E) Asymmetric loading and deloading. It appeared that the rates of loading deuterons into the Pd–B alloys were greater than the rates of deloading after voltages to cells were turned off. This might be due to the mechanical and expansion characteristics just noted. However, it is realized that any alloy changes during loading. That is, the material during loading is different from the material during deloading.

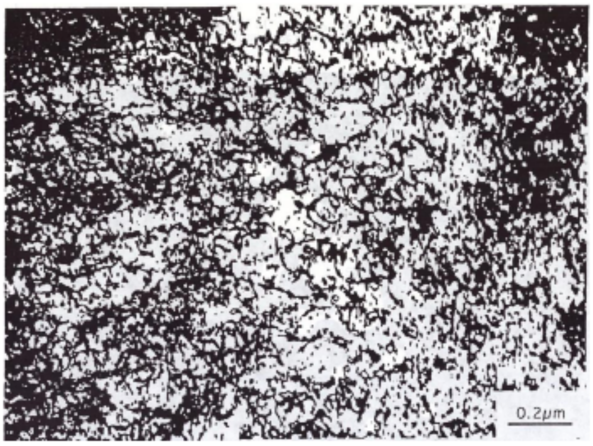


Figure 6. Transmission electron micrograph of Pd–0.62 wt.% B showing two phases. The minor phase is roughly 1–10 nm in diameter.

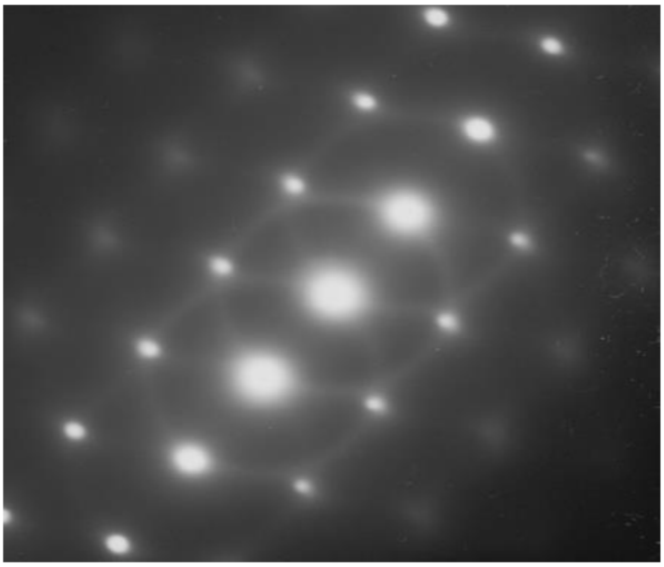


Figure 7. Selected area diffraction pattern of the same material and area as in Fig. 6 showing rings along with the main diffraction spots.

Appendix: Other Applications of Pd–B Alloys

The alloys produced in this work show the same or better strength than pure palladium with much less thickness. This is advantageous for the creation of hydrogen purification membranes because less palladium would be needed to create a membrane and achieve the same results. This is, sturdy membranes of much less thickness are enabled compared to using palladium alone. Put another way, the increased hardness means that a much smaller amount of expensive palladium may be used to provide a membrane of the same capacity compared to costly palladium alone. This would allow much greater membrane capacity through reduced material costs. How much the thickness of the membrane would be able to be decreased with the present composition would depend upon such factors as the geometrical design, gases to be purified, and the extent of purification desired.

The hardened Pd material would also be advantageous for use as electrodes in etching, polishing, electrochemical machining, semiconductor wafer manufacture and other electrochemical processes. Palladium cathodes hardened by alloying, as described in this paper, retain their superior electrical characteristics and resist erosion better than pure palladium.

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