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Hydrogen solubility of bcc PdCu and PdCuAg alloys prepared by mechanical alloying

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ABSTRACT

Face-centered cubic (fcc) $Pd_{100-x-y}Cu_xAg_y$ alloys (with *x* ranging between 0 and 65 at.% and *y* ranging between 0 and 20 at.%) were prepared by mechanical alloying of elemental metal powders in the presence of 2 wt% NaCl acting as a process control agent. Transition to the body-centered cubic (bcc) phase was achieved for some compositions by a subsequent annealing treatment at 400 °C. The resulting solids were consolidated into pellets by cold-pressing and their hydrogen solubility was assessed by chronoamperometry in alkaline aqueous solution. Hydrogen solubility increased with palladium content for both fcc and bcc phases. Replacing copper with silver resulted in an increase in hydrogen solubility of the bcc PdCuAg alloys.

1. Introduction

Hydrogen gas is an important commodity in the industrialized world, with applications in petroleum refineries, the chemical industry (e.g., the production of ammonia), and even food processing [1]. As its combustion only yields water, hydrogen may be also considered the transportation fuel of choice for fuel cell or internal combustion engine vehicles resulting in a decrease in anthropogenic CO_2 production [2]. However, for hydrogen vehicles to be competitive with common diesel and gasoline-powered automobiles, the cost of hydrogen must be below $4 per kilogram, production and delivery costs included [3]. In the industrial production of hydrogen, hydrogen purification processes account for 50–80% of total capital investment [4]. The most common purification methods implemented in the industry are pressure swing adsorption and cryogenic distillation, two processes that require rather high energy [5,6]. Alternatively, hydrogen separation may be achieved through the use of membranes that are permeable only to hydrogen, such as palladium and palladium alloy membranes. With palladium membranes, highly pure hydrogen (>99.9999%) may be continuously produced with 99% recovery [5].

The alloying of palladium with other metals is one method used to overcome the drawbacks of pure palladium [7–9]. In fact, pure palladium membranes suffer severe poisoning by H_2S. This gas is concomitantly present in steam reforming of natural gas or in coal gasification processes, two important industrial methods used in the large-scale production of hydrogen. Furthermore, the high cost of palladium and its sensitivity for hydrogen embrittlement when operating at temperatures below 300 °C are other drawbacks which have relegated pure palladium membranes to small-scale hydrogen production only. Currently, binary or ternary alloys with Cu, Ag, Au, Y, Fe and other metals are being studied in order to improve the performance of pure Pd membranes. PdCu alloys are particularly interesting as they present permeability as high as that of pure palladium (1.1×10^{-8} and 1.4×10^{-8} mol m^{-1} $s^{-1} \cdot Pa^{-0.5}$ at 623 K, for Pd and $Pd_{47}Cu_{53}$ alloy, respectively) [10] due to a crystallographic phase transition from face-centered cubic (fcc) to body-centered cubic (bcc).

Similarly to PdCu, PdCuAg ternary alloys also present a bcc structure when Pd is between 36 and 46 at% and if Ag does not exceed 3 at% [11]. Previous studies were published on the hydrogen solubility of PdCuAg alloys with both fcc and bcc phases. Tosques et al. [12] analyzed fcc-PdCuAg alloys prepared by electrodeposition. In this case, hydrogen solubility was measured in alkaline solution at room temperature, using an electrochemical method. When replacing Cu with Ag while maintaining a constant palladium content, two antagonist effects influence hydrogen solubility, namely lattice expansion and changes in the coordination sphere of hydrogen in the alloy's octahedral sites. In fact, hydrogen solubility is favored as the lattice expands by replacing Cu with Ag. However,

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introducing additional Ag atoms to the alloy will unfavorably increase the number of octahedral sites with one or more Ag atoms in the nearest neighbor shell of Pd atoms, which have a detrimental effect on the hydrogen solubility. In another study, Nayebossabri et al. [13] presented their results with bcc-PdCuAg alloys. The samples were prepared by cold-rolling cast ingots and hydrogen solubility was measured in the gas phase at high temperature ranging between 350 and 400 °C. Two different compositions were studied ($Pd_{45.8}Cu_{51.9}Ag_{2.3}$ and $Pd_{45.1}Cu_{51.0}Ag_{3.9}$) which showed that as temperature increases, solubility either decreases (for the alloy with 2.3 at.% Ag, solubility varies from 9.7×10^{-6} to 7.5×10^{-6} $Pa^{-0.5}$ at 350 and 400 °C, respectively) or increases (for the alloy with Ag 3.9 at.%, solubility varies from 7.7×10^{-6} to 5.15×10^{-5} $Pa^{-0.5}$ at 350 and 400 °C, respectively).

The present study investigates the hydrogen solubility of PdCuAg ternary alloys with a bcc phase. First, the alloys with fcc phase were prepared by mechanical alloying. Transition to the bcc phase was then achieved with heat treatment. Pellets of the alloyed powders were prepared and hydrogen solubility was measured through a chronoamperometric method in alkaline solution. In the bcc phase, higher contents of palladium or silver led to an increase in hydrogen solubility.

2. Experimental

2.1. Mechanical alloying

$Pd_{100-x-y}Cu_xAg_y$ alloys (with x varying between 0 and 65 at.% and y varying between 0 and 20 at.%) were prepared via mechanical alloying using a Spex 8000 laboratory mill. Elemental Pd (99.99% purity, −200 mesh), Cu (99.9% purity, −170 + 270 mesh) and Ag (99,999% purity, −200 mesh) powders were introduced into a hardened steel grinding vial (capacity of 55 mL), using NaCl (2 wt%) as a process control agent (PCA). A total of 2 g of solid material was used in each preparation. Three hardened steel balls (two with a diameter of 6.3 mm and one with a diameter of 7.8 mm, for a total mass of 4 g) were used as the grinding medium in a 2:1 ball-to-powder ratio (BPR). The alloy composition was controlled by varying the ratio between the metallic powders. The grinding vials were loaded and sealed under an argon atmosphere inside a glove box. Total milling time was 18 h.

Some of the powders were heat-treated at 400 °C for 5 h under an inert Ar atmosphere (flow rate = 231 mL min^{-1}) to obtain the thermodynamically stable phase.

2.2. Physicochemical characterization

The morphology of as-milled powders was examined through scanning electron microscopy (SEM) on a JEOL JSM-6300 microscope with an accelerating voltage of 5 kV and a working distance of 8 mm. Pd, Cu and Ag contents were then estimated through energy dispersive spectroscopy (EDX, from Oxford Link ISIS) with an accelerating voltage of 20 kV and a working distance of 15 mm. The standard deviation of each measurement was below 3 at%. The composition was taken to be the average of three measurements. Iron was present in all mechanically-alloyed powders at less than 1 at%.

The crystallographic structure of the powders was determined via X-ray diffraction (XRD) measurements on a Bruker AXS D8 Siemens X-ray diffractometer with Cu Kα radiation (weighted average wavelength of 1.54184 Å) operating at 40 kV and 40 mA. The angular step size was 0.07° and the data acquisition time was 8 s per step. As-prepared samples were analyzed from $2\theta = 35–95°$, and from $2\theta = 25–95°$ after annealing. The lattice parameters were calculated using Bragg's law,

$$a = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2sin\theta} \quad (1)$$

where a is the lattice parameter, λ is the wavelength of the Cu Kα radiations (1.5418 Å), and h, k, l are the Miller indices.

2.3. Hydrogen solubility measurements

The hydrogen solubility in the alloys was determined through an electrochemical method. In order to use PdCuAg alloys as working electrodes, the powders were pressed on titanium powder (99.5% purity, 325 mesh) at 20 tonnes·cm^{-2} for 10 min. The obtained pellets (diameter of 1.1 cm and thickness of *ca.* 2 mm) were then connected to a copper wire using silver conductive epoxy adhesive on the titanium side (back of the pellet) to ensure electrical connectivity. Only the side with PdCuAg alloys was in contact with the aqueous solution. The back of the pellet and the copper wire were affixed to a glass tube with epoxy glue.

The PdCuAg working electrode was placed inside a 250 mL beaker containing 50 mL of 0.1 M NaOH solution prepared from NaOH salt (Alfa Aesar 99.99% Metal Basis) dissolved in ultra-pure de-ionized water (resistivity > 18.2 MΩ cm^{-1}). A platinum foil connected to a platinum wire was used as the counter electrode and a mercury/mercuric oxide (Hg/HgO) electrode was used as the reference electrode (+950 mV vs RHE; all potentials will be expressed with respect to the Reversible Hydrogen Electrode (RHE) scale in the following discussion). The solution was continuously purged with argon placed directly under the PdCuAg working electrode. In addition to reducing the amount of hydrogen in solution, the Ar flow cleans the electrode surface by removing hydrogen bubbles which could otherwise hinder hydrogen absorption.

The hydrogen solubility of the PdCuAg alloys was determined by potential step chronoamperometry. This method consists in applying a sufficiently negative potential (E_{neg}) where hydrogen is absorbed for a certain time (t_{neg}), and then a more positive potential (E_{pos}), where hydrogen is oxidized and desorbed for a certain time (t_{pos}). The current measured during E_{pos} results from the oxidation of hydrogen atoms that were previously absorbed in the alloys during E_{neg} [14]. Thus, the columbic charge corresponding to the integration of this oxidative current is a measure of the number of hydrogen atoms previously absorbed in the alloy (H). The determination of the H value, with the M value already known (M is the amount of alloy used in the pellet preparation) leads to determination of the H/M ratio, which corresponds to hydrogen solubility and is commonly expressed as an atomic percentage.

For each case, a first step with an absorption potential (E_{neg}) of −500 mV was applied during a time t_{neg} of 1, 2, 3 and 4 h. This was achieved using a Biologic SP300 instrument with EC-Lab V10.02 software. This first step enabled us to determine the absorption time required to attain maximum hydrogen solubility, i.e. when a constant charge was attained. Having determined optimal absorption time, hydrogen absorption was further measured at −400, −500 and −600 mV to complete the activation of the electrode. Following each E_{neg}, hydrogen oxidation was promoted at $E_{pos} = +450$ mV until a stable current value (typically −50 μA) was reached. In general, t_{pos} was two to three times the value of t_{neg}.

The effect of the PCA on pure Pd was checked to determine if NaCl had a negative impact on the hydrogen solubility. This was done by comparing the hydrogen solubility of as-received Pd and Pd ball milled with NaCl. The hydrogen solubility was 69 ± 1 wt%, indicating that NaCl does not act as contaminant.