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Hydrogen-induced phase transformation in internally oxidized $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$

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Abstract

Samples of a $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ alloy which had been cold worked and internally oxidized for 72 h at 1073 K were submitted to high hydrogen pressure, at 3.5 GPa for 5 h at 1073 K. The phase transformations were analysed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The X-ray results for the internally oxidized sample revealed the formation of PdO and $PdRhO_2$. In the samples submitted to high hydrogen pressure, it was observed that in both cases, a phase separation had been induced by hydrogen at high temperature, which suggests the formation of Pd-rich hydride phase and a Rh-rich phase. The TEM analysis of these samples revealed the formation of a Rh-Pd phase, which presented some faceted semi-coherent interfaces with Pd matrix. The formation of this ordered compound, which possesses Rh_3Pd stoichiometry, is attributed to hydrogen induced vacancies in the alloy.

Keywords: Vacancy; Hydride; Phase separation; Internal oxidation; Pd alloys

1. Introduction

Hydrogen-induced phase transformation in crystalline metals and alloys has been exhaustively reported in recent years [1–6]. Such examples are the amorphization observed in pure Zr and its alloys [1], the martensite transformation in Ni–Ti and also in the stainless steels [3], as well as classical hydride formation in crystalline or amorphous alloys [4,5]. Additionally, H-induced lattice migration, HILM, has also been reported [7], which can be explained by the production of vacancies in heavily hydrogenated metals and alloys [8–10].

Recently Wang et al. [6] observed the interaction of hydrogen with internally oxidized Pd–Rh alloys. They showed, as the product of internal oxidation in the Pd–Rh system, the $PdRhO_2$ oxide, which was determined by Shannon et al. [11].

For heat treatments involving high pressure of hydrogen, Flanagan et al. [7] observed phase separation in palladium-rich alloys like Pd–Rh, Pd–Ni, Pd–Co. In these alloys, it is common to observe hydride formation in Pd and phase migration of the other element in the Pd structure.

A promising application for Pd alloys is in composite palladium-oxide systems, which have been studied in two different configurations. One refers to Pd deposited on the surface of ceramics [12] and in the other, Pd and other oxidizable elements are alloyed and then submitted to internal oxidation [13]. The aim of this work is to characterize the effects of high hydrogen pressure on a $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ alloy with and without internal oxidation.

2. Experimental techniques

A button of the $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ alloy was prepared by arc-melting from the pure elements. The products of the melt were cold worked into foil with thickness of 120 μm. Subsequently, part of the alloy has been cold worked and heat treated in air for 72 h at 1073 K for its internal oxidation. Oxidized and non-oxidized samples were submitted to high hydrogen pressure of 3.5 GPa at 1073 K for 5 h.

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In the high hydrogen pressure test, disks of 7 mm diameter of each sample were encapsulated together with an internal hydrogen source in an NaCl container (7 mm in diameter and 8 mm high) impermeable to hydrogen. The high hydrogen pressure was applied using a belt-type press. The hydrogen provider was a pellet of $C_{14}H_{10}$ which, when heated, decomposes irreversibly above 400 °C and supplies free H_2 that can react with the sample. The sample and the $C_{14}H_{10}$ pellet were separated by a BN disk 0.1 mm thick in order to avoid possible carbon diffusion. The resulting samples were characterized by a X-ray diffraction procedure using a Siemens D-5000 diffractometer which operated with Cu Kα radiation.

After high hydrogen pressure treatment, samples were then prepared for TEM analysis as disks of 3-mm diameter by ion milling. The TEM analysis was carried out using a Philips 300 kV microscope.

3. Results and discussion

Fig. 1 shows X-ray diffraction results for the $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ alloy in the following conditions: cold worked (Fig. 1a) and oxidized at 1073 K for 72 h (Fig. 1b). It is observed in Fig. 1a that the cold worked alloy presents only diffraction peaks due to an f.c.c. structure. The Pd–Rh system forms a metastable solid solution for any concentration range and have a miscibility gap [14]. In the case of Ce, a low concentration is insufficient to create compounds with Pd or Rh. Fig. 1b exhibits diffraction peaks due to two oxides, PdO and another oxide which can be indexed as $PdRhO_2$ structure [14].

Fig. 2 shows X-ray diffraction results for samples of $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ submitted to high hydrogen pressure. In Fig. 2a, it can be seen for the cold worked samples and in Fig. 2b for the oxidized samples, that in both cases the hydrogen created new peaks in the X-ray diffraction patterns. These peaks are due to phase separation in the alloy which is consistent with results reported by Fukai et al. [9]. This phase separation can be attributed to formation of a Pd-rich hydride (A peaks) and Rh-rich metallic phase (B peaks). It can also be observed in Fig. 2 that for the cold worked sample, the peaks associated with the Rh-rich phase are weaker than in the oxidized sample shown in Fig. 2b.

The main difference between the degree of phase separation for the cases above can be justified in terms of the elements that auto-diffuse in the alloy during high hydrogen pressure experiments. For the cold worked sample, the Rh and Ce are free, in solid solution in the Pd matrix and therefore both can auto-diffuse in the Pd. In this case, vacancies produced by high hydrogen pressure can be effectively consumed in the diffusion process of these two elements in the Pd. For the alloy submitted to internal oxidation of Ce, fine and long CeO_2 precipitates result. Thus during high hydrogen pressure treatment, the Ce in the precipitates cannot move though the structure.

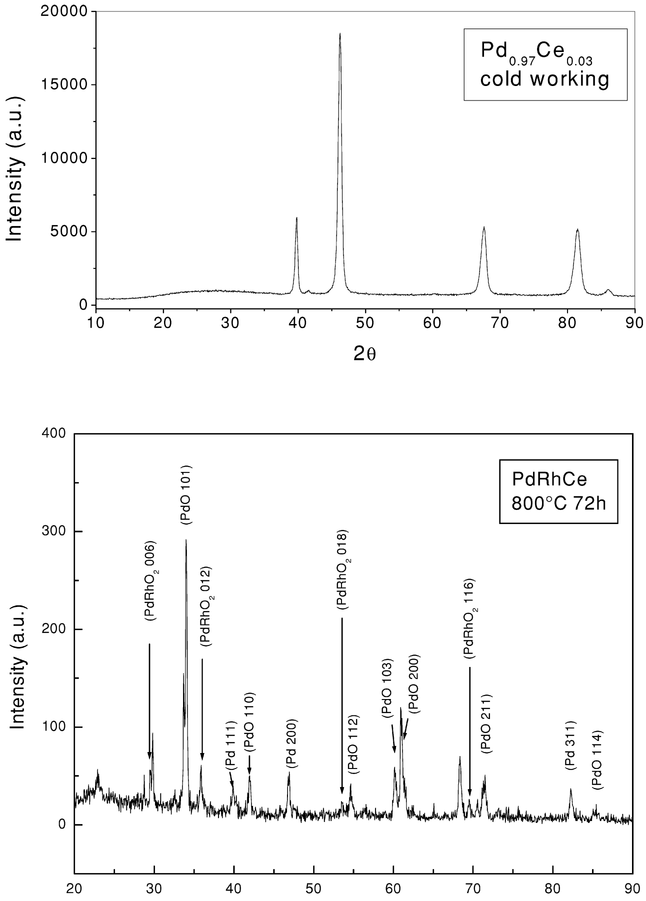

Fig. 1. X-Ray diffractogram for the $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ alloy under the conditions: (a) cold worked and (b) internally oxidized for 72 h at 1073 K.

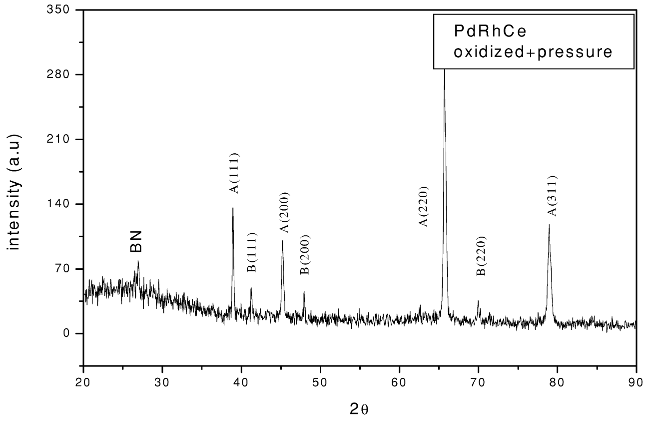

Fig. 2. X-Ray diffractogram for the $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ alloy submitted to high hydrogen pressure of 3.5 GPa for 5 h at 1073 K in the samples: (a) cold worked and (b) internally oxidized for 72 h at 1073 K.

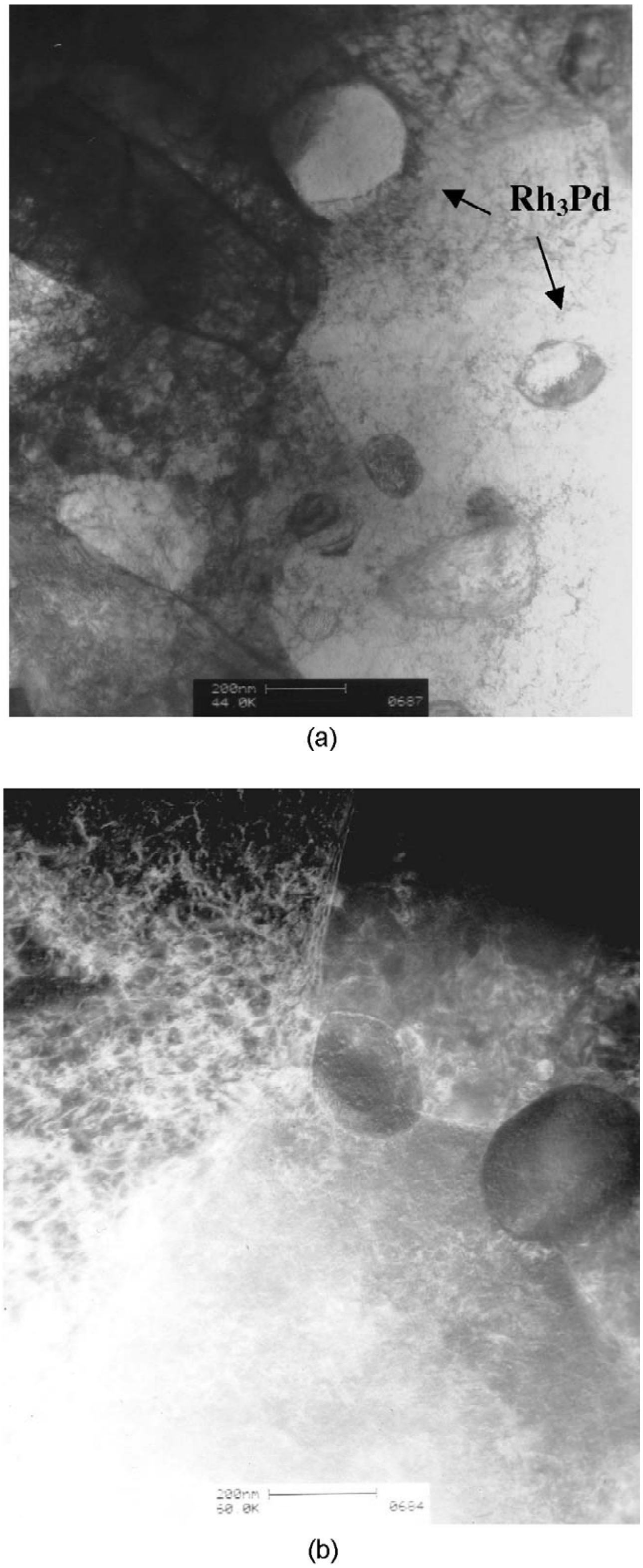

Fig. 3. TEM micrograph for the $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ alloy, showing precipitates of Rh_3Pd in the sample subjected to cold working and then treated with high hydrogen pressure of 3.5 GPa, for 5 h at 1073 K.

Figs. 3 and 4 show the TEM micrographs of the $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ in the cold worked and internally oxidized conditions, respectively. It can be seen in both cases that Rh-rich precipitates form. Most of the precipitates observed are spherical in shape or partially faceted as shown in Fig. 3a,b, which suggests semi-coherence with the Pd matrix. The EDS analysis in the TEM, for many precipitates, permits the determination of the average composition of the precipitate, which was found to be 75 ± 3 wt% Rh and 25 ± 3 wt% Pd. For both conditions, the precipitates can be defined as Rh_3Pd.

Fukai [9] attributed the existence of internal vacancy sources distributed more or less uniformly in the Pd–Rh alloy to phase separation. These sources are able to supply vacancies even for short treatment times. This argument can be used to explain the rapid diffusion observed in the Pd–Rh alloy when submitted to 5 GPa between 500 and 600 °C, where a phase transformation take place in 200 s.

There are many classical mechanisms for the production of vacancies in the metals and alloys such as: vacancy diffusion from the surface to the bulk of metal [15], climbing of dislocations; stacking faults, the reduction of grain boundaries and grain boundary sliding [16]. However, it would not be expected that a single mechanism could be solely responsible for the creation of superabundant vacancies, especially in this case where the sample is compressed hydrostatically in the presence of hydrogen, thereby generating a hydride phase.

It is very important to note that the precipitate composition in relation to the Pd/Rh ratio is the reverse of that for the overall, Pd-rich, composition of the alloy. Finally, hydride formation in Pd takes place more easily than in Rh and the atomic radius of Rh is smaller than Pd, making it possible for Rh to transform into the phase with Pd by means of a rapid diffusion mechanism in the ordered phase with Pd.

4. Conclusions

Internal oxidation of $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ alloy for 72 h at 1073 K promotes the formation of PdO and $PdRhO_2$ which were characterized by X-ray diffraction. Cold worked and internally oxidized samples were submitted to a high hydrogen pressure of 3.5 GPa for 5 h at 1073 K. The results reveal hydrogen-induced phase separation at this high temperature. This phase separation involves the formation of a Pd-rich hydride and a Rh-rich phase. TEM analysis of these samples revealed the formation of a Rh–Pd phase, which exhibited semi-coherent interfaces with the alloy matrix. The formation of this ordered compound, which possesses Rh_3Pd stoichiometry, is attributed to hydrogen-induced vacancies in the alloy.

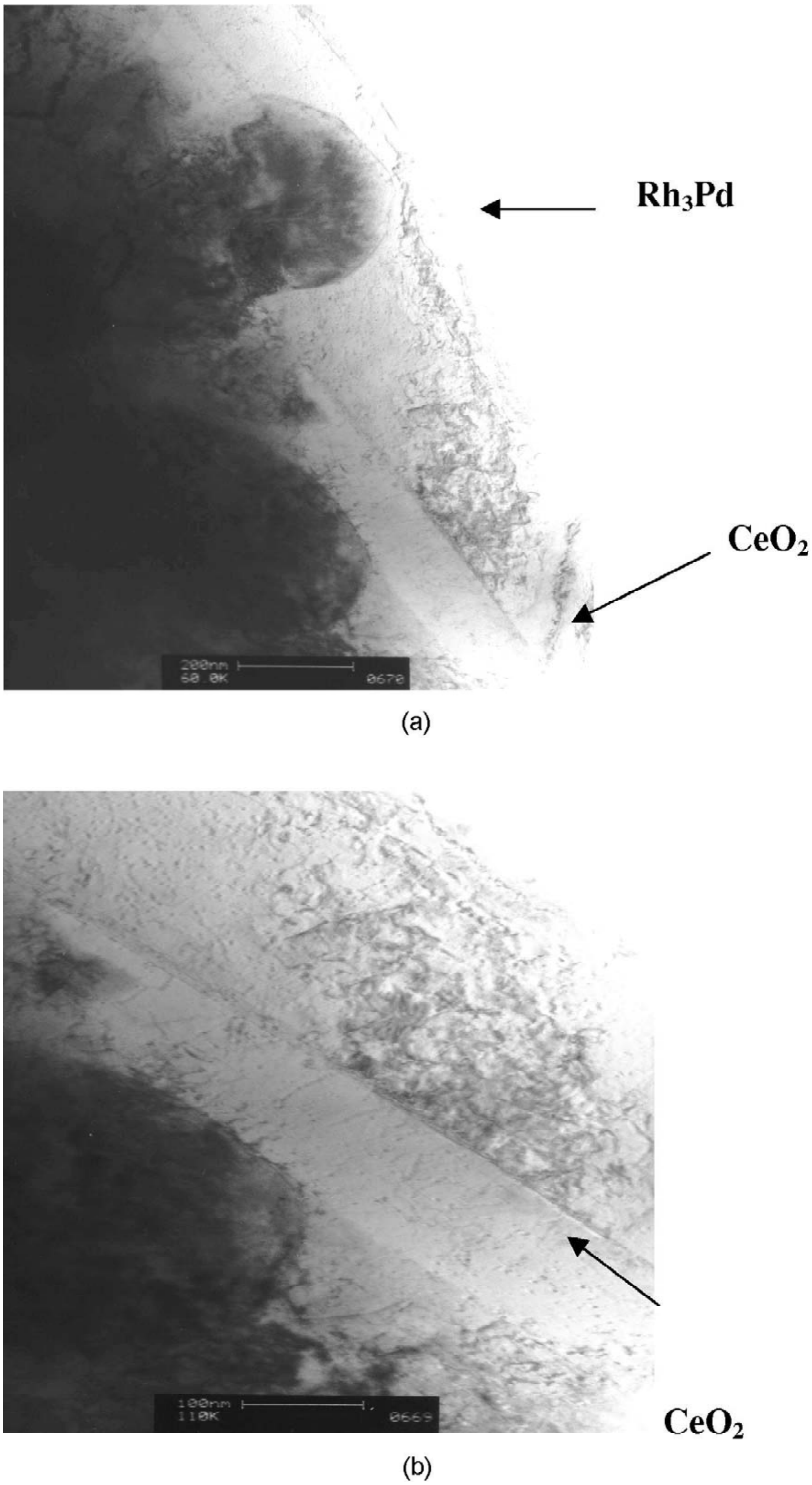

Fig. 4. TEM micrograph for the $(Pd_{0.8}Rh_{0.2})_{0.97}Ce_{0.03}$ alloy showing precipitates of Rh_3Pd and CeO_2 in the sample which had been internally oxidized and then subjected to high hydrogen pressure of 3.5 GPa for 5 h at 1073 K.

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