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Analysis of the nanopores produced in nickel and palladium by high hydrogen pressure

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Abstract

Samples of pure nickel and palladium were submitted to a high hydrogen pressure (HHP) of 3.5 GPa at 800 °C for 5 h. Analysis of the resulting structural modification was performed using X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM) and small-angle X-ray scattering (SAXS), the latter specifically for Ni. The formation of superabundant vacancies (SAVs) was observed in the structure in both cases. For Pd, the pores, which formed by the coalescence of vacancies, had dimensions of 20–30 nm when present in the interior of the metal and 1–3 μm when condensed at the surface. The pores were seen to be dispersed homogeneously across the surface of Pd. For Ni, however, pores were created preferentially at the grain boundaries, which promoted significant decohesion in the metal. The distribution of pores induced by heat treatment of Ni subjected to HHP was determined by SAXS analysis and two populations of pores, with population mean diameters of 50 and 250 Å, were observed.

Keywords: High hydrogen pressure; Vacancy; Hydrogen–metal reactions

1. Introduction

High hydrogen pressure experiments have been shown to be a powerful tool in materials science [1–6]. Interest is not only limited to a comparison with data referring to measurements obtained at atmospheric pressure but, in many cases, includes the use of high hydrogen pressure as the only way to synthesize new phases and thus to develop new phase diagrams. From the thermodynamic point of view, hydrogen insertion into a metallic lattice (gas–solid reaction), when undertaken at high pressure, leads to a strong modification of the corresponding metal–hydrogen phase diagram. Thus, at rather low temperatures, rapid diffusional processes involving metallic species, which usually only take place at higher temperatures, may be activated, giving rise to so-called hydrogen-induced lattice migration [5].

In 1994, Fukai and Okuma [1] discovered, by in situ X-ray diffraction experiments on Ni and Pd at high hydrogen pressures and temperatures, that a gradual lattice contraction took place over several hours, and they suggested that it was due to the formation of a large number of metal atom vacancies, amounting to ca. 10 at.% [1]. In pure Pd, a significant contraction was observed, which they attributed to 20 at.% of generated vacancies [2]. For pure Ni, Osono et al. [3] observed the formation of cracks in the surface after hydrogenation. Later, utilizing in situ experiments, Fukai et al. [4] observed the formation of 30 at.% of vacancy–hydrogen clusters.

In general, during the relaxation of pressure, a proportion of hydrogen is released from the metal and vacancies can segregate to defects to form small nanopores. This study aimed at evaluating the formation of superabundant vacancies in pure Pd and Ni and to characterize the distribution of nanopores produced by HHP using different experimental techniques.

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2. Experimental techniques

Disk-shaped samples of pure Pd and Ni, with thicknesses of 120 and 20 μm, respectively, and 7 mm in diameter, were submitted to high hydrogen pressure. Each metal sample was encapsulated together with an internal hydrogen source in a NaCl container impervious to hydrogen. The HHP was applied using a belt-type press to generate a pressure of 3.5 GPa at 800 °C. The hydrogen source 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 100 μm thick.

Samples were characterized by XRD immediately after the hydrogenation procedure using a Siemens D5000 powder diffractometer operated with Cu Kα radiation. After XRD, samples of Pd were prepared for TEM investigation by cutting 3 mm discs and then subjecting them to dimpling and ion milling using a Gatan 600 dual ion mill. For the TEM analysis a Philips 300 kV microscope was used.

Samples of Ni were characterized by SEM and analyzed using SAXS at room temperature, utilizing the SAXS camera of the beam line of the National Synchrotron laboratory at LNLS, Brazil. These measurements were undertaken in transmission geometry with $\lambda = 1.608$ Å to optimize transmission through the sample and to eliminate fluorescence of the Ni. The SAXS curves were determined by collecting the small-angle X-ray scattering via a linear, position-sensitive, gas-type detector set in the wavelength range $0.01 \leq q \leq 0.20$ Å^{-1}. It was not possible to perform the SAXS analysis of Pd by using the LNLS facilities because of the strong absorption by Pd and the maximum energy limitation of the beam.

3. Results and discussion

Fig. 1 shows SEM micrographs of a Ni sample submitted to HHP at 3.5 GPa for 5 h at 800 °C and subsequently heat treated in air at 800 °C for 1 h. This heat treatment was intended to evaluate the presence of vacancies via the formation of pores created by the coalescence of such vacancies, which migrate to the surface of the metal in order to minimize the free energy of the Me–Vac–H system. The presence of cracks can be observed, especially at the grain boundary. These cracks are formed by the preferential coalescence of pores along the grain boundaries in Ni, which promotes a separation at grain boundaries of about 1–3 μm. The pores nucleated in the grain boundaries in Ni are of the same order of magnitude as the pores in Pd [6]. This behavior is very different from Pd hydrogenated under the same conditions, where nanopores are evenly dispersed over the whole surface. In this case, no preference is exhibited with respect to the specific regions the migration of pores occurs. X-ray diffraction analysis of pure Ni submitted to high hydrogen pressure reveals extra lines, as shown in Fig. 2, which suggest the creation of a vacancy-ordered phase.

The preferential migration of pores to the grain boundaries in Ni can be attributed to the greater mobility that hydrogen possesses at grain boundaries. Arantes et al.

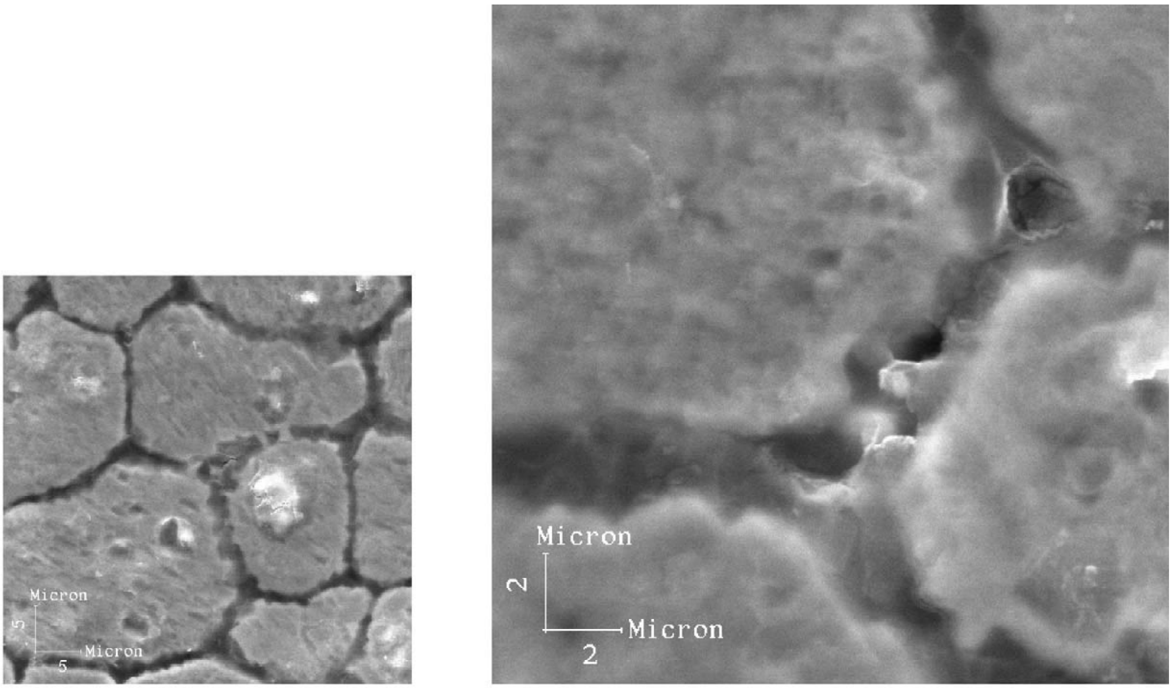

Fig. 1. SEM of Ni maintained under a HHP of 3.5 GPa for 5 h at 800 °C and then heat treated at 800 °C for 1 h.

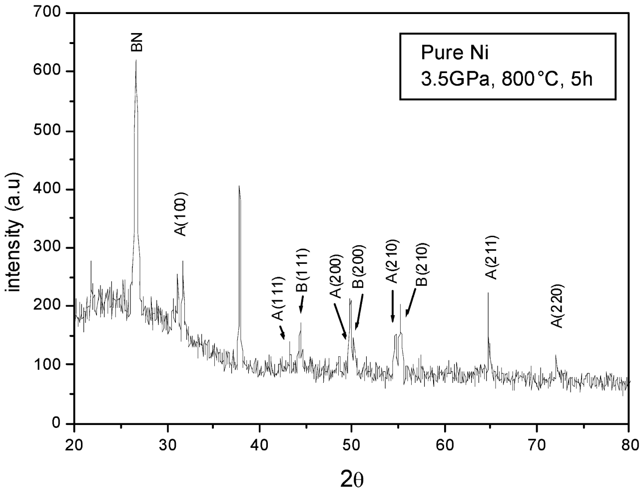

Fig. 2. XRD of Ni maintained under a HHP of 3.5 GPa for 5 h at 800 °C, showing two sets of diffraction lines, a vacancy-ordered phase (A) and Ni (B).

[7] observed that hydrogen permeation is faster in nanocrystalline Ni than in microcrystalline Ni. They attributed this increase to the greater solubility and diffusivity of hydrogen in the nanocrystalline material and especially to the contribution of grain boundaries in this respect. However, this behavior can be better confirmed by the results obtained by Schober and Dieker [8] who observed, by autoradiography, preferential hydrogen segregation to the grain boundaries in Ni.

During the application of high hydrogen pressure to Pd at different temperatures, many defects can be generated, especially hydride phase transformation. For temperatures close to or below 600 °C, the main mechanism is the generation of dislocations. However, for temperatures above this, where interatomic diffusion is more important, vacancies are produced. At 800 °C, superabundant vacancy phases appear, the diffraction patterns of which exhibit extra lines in addition to those of the basic f.c.c. structure [6]. These extra lines can be accounted for in terms of a super cell structure that results from vacancy ordering, thus showing for the first time that the vacancy-ordered state can be retained at room temperature. This experimental observation indicates the presence of vacancies in the hydrogenated phase as well as in the corresponding outgassed phase. This phase has already been reported by Fukai [2] and corresponds to a vacancy concentration of 0.20. This concentration is in agreement with that determined from the lattice parameter of the corresponding outgassed sample concentration. Fig. 3 shows the SEM of Pd heat-treated after high hydrogen pressure exposure, resulting in the coalescence of pores at the surface. It can be seen that, in this case, pores are precipitated across the whole surface without any preferential localization, unlike Ni.

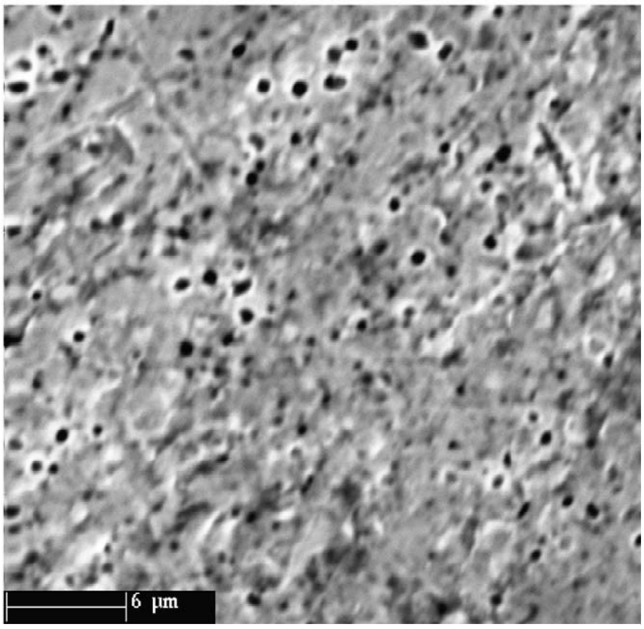

Fig. 3. SEM of Pd maintained under a HHP of 3.5 GPa for 5 h at 800 °C and then heat treated at 800 °C for 1 h.

If defects had existed at the surface of the metal before the heat treatment, the vacancies generated should have migrated to the defect-rich zone forming pores in this region. Indeed, Fig. 4 shows the preferential migration of pores in the deformed region of Pd foil which had previously been locally deformed by folding and unfolding.

The nanopores formed by migration of vacancies during relaxation of HHP can be observed by TEM analysis. Fig. 5 shows Pd after HHP exposure, without heat treatment.

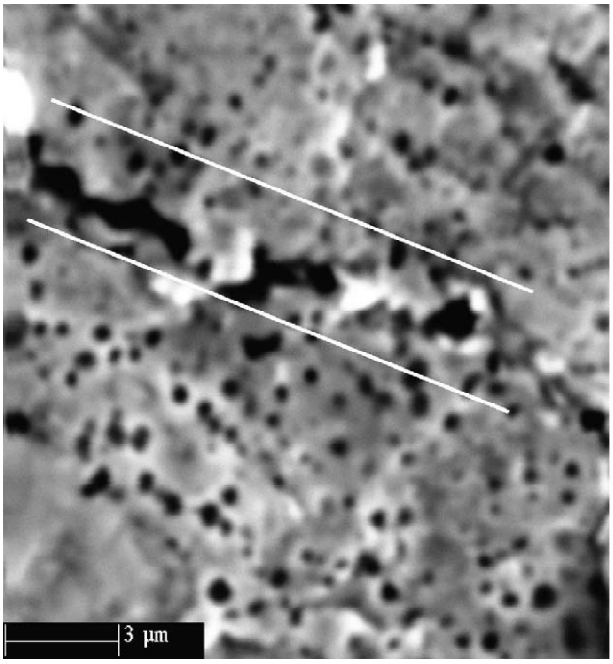

Fig. 4. SEM of Pd maintained under a HHP of 3.5 GPa for 5 h at 800 °C, folded and then heat treated at 800 °C for 1 h.

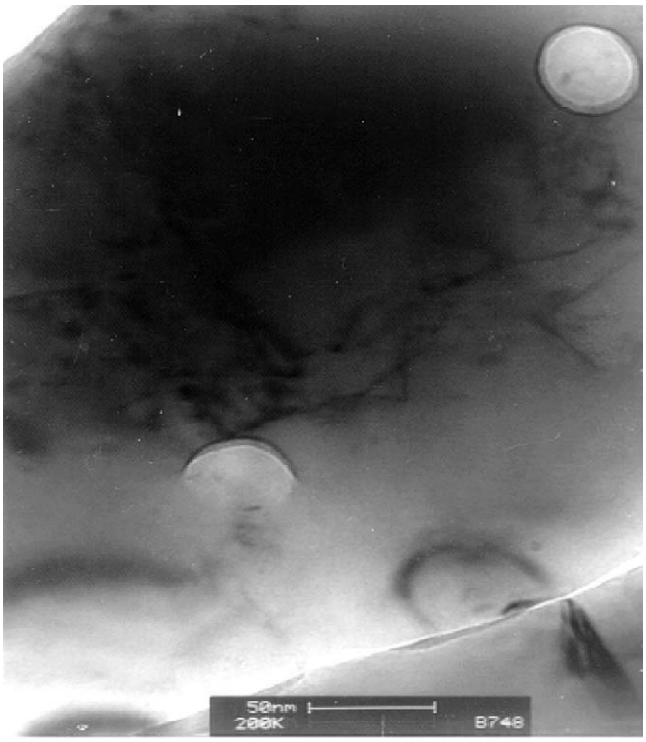

Fig. 5. TEM of Pd maintained under a HHP of 3.5 GPa for 5 h at 800 °C.

The presence of nanopores about 10–20 nm in diameter can be observed. After subsequent heat treatment these pores migrated to the surface and formed large pores (Figs. 3 and 5). As Ni exhibited strong decohesion along the grain boundaries, it was very difficult to prepare sample foils for TEM. Therefore, we decided to use SAXS analysis to determine the pore distribution in the sample. We used a Ni foil submitted to ultra-high-pressure hydrogenation to evaluate the pore density and then we compared it with non-hydrogenated material. In addition, a hydrogenated sample was heat treated in a resistance furnace at 600 °C and new scattering curves were obtained for this sample after 20 and 40 min of heat treatment. The SAXS curves in Fig. 6 show a clear evolution with hydrogenation and heat treatment. A high scattering power was observed, which indicates that migration and coalescence of the pores produced by the hydrogenation and heat treatments occurred.

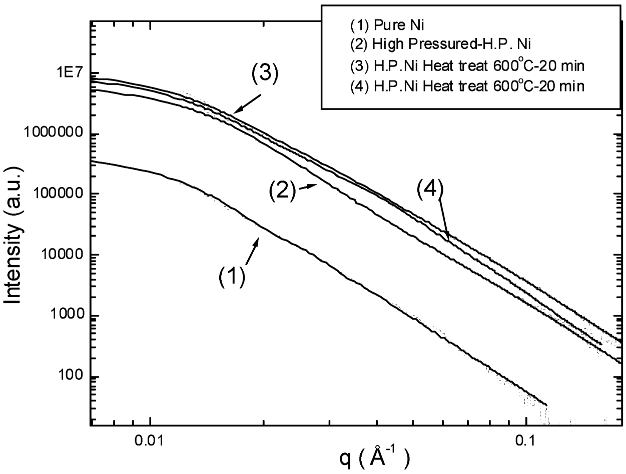

Fig. 6. SAXS curves obtained for Ni submitted to a HHP of 3.5 GPa at 800 °C for 5 h, and subsequently heat treated at 600 °C for 20 and 40 min.

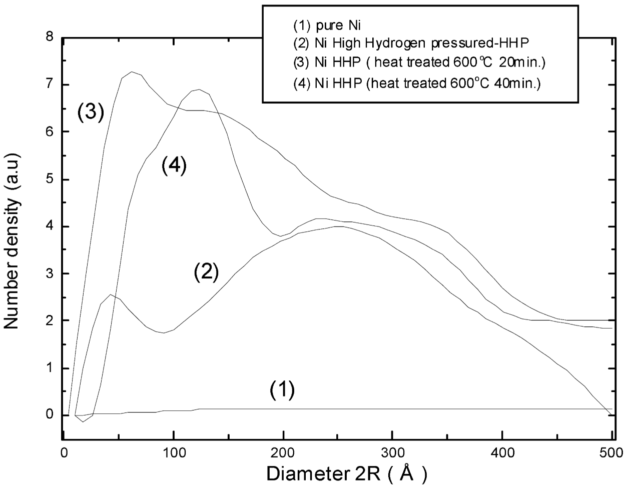

Fig. 7. Size distribution of nanopores in Ni submitted to a HHP of 3.5 GPa at 800 °C for 5 h, and subsequently heat treated at 600 °C for 20 and 40 min.

In order to characterize the system better, and to determine the distribution of pore sizes, the scattering curves were analysed using the GNOM software [9], considering a volume distribution of spheres of radius *R*:

$$D_p = 4/3\pi R^3 N(R) \tag{1}$$

The results obtained are shown in Fig. 7, where it can be seen that, after HHP, the Ni sample contained a high density of pores, with two peaks in size distribution of average diameters 50 and 250 Å. After heat treatment at 600 °C for 20 min, to promote the coalescence of vacancies, we observed new pores of diameters of 50 to 65 Å. We also observed pores of about 150 Å in diameter. After heat treatment at 600 °C for 40 min, growth occurred of the existing pores of 150 Å diameter. The peak of the larger pores, of about 250 Å, was observed to remain virtually unaltered.

4. Conclusions

Pure nickel and palladium submitted to high hydrogen pressure exhibited a significant generation of pores, which indicates the formation of superabundant vacancies. In nickel, defects are considered to be generated by the migration of pores preferentially to grain boundaries, while for palladium the pores are dispersed evenly across the whole sample surface. For Pd, the pores, formed by the coalescence of vacancies, have dimensions of 20–30 nm inside the metal and 1–3 μm when condensed at the surface. The distribution of pores induced by heat treatment of Ni exposed to high hydrogen pressure was determined by SAXS analysis and two pore distributions with average diameters of 50 and 250 Å were observed.

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