



Hydrogen solubility and vacancy concentration in nickel single crystals at thermal equilibrium: New insights from statistical mechanics and *ab initio* calculations



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ABSTRACT

The hydrogen solubility and the vacancy concentration in Ni single crystals at thermal equilibrium have been determined from a combination of mechanical statistics and *ab initio* calculations of the Gibbs free energy up to $P_{H_2} = 0.1$ GPa and 1700 K. We consider that the H atoms can be located in the interstitial sites but also in the displacement field generated by a vacancy to create H-vacancy clusters. The solution and the H-vacancy clusters defect formation free energies are expressed as a sum of a vibration and an electronic contributions. We find that the H-vacancy interactions are significant inside the vacancy core and we show that the H-rich vacancy clusters have a negative free energy at high P_{H_2} , similarly to the case of fcc Fe. Then, we compute the H solubility and the vacancy concentration for a wide range of μ_{H_2} . The calculated solubility at $P_{H_2} = 1$ bar is in agreement with previous experimental data. Although the vibration contribution dominates the temperature dependence of the solution and formation free energies, the electronic excitations only can lead to a marked deviation of the solubility at high temperature. The vacancy formation is promoted at high P_{H_2} with a significant contribution to the trapping of the H atoms inside the vacancy core at low temperature. However, the total number of vacancies remains too small and has a minor effect on the apparent solubility in single crystals up to $P_{H_2} = 0.1$ GPa.

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1. Introduction

The interactions between hydrogen and materials can strongly affect the physical and the chemical properties of the host matrix [1]. In the case of metals, the insertion of H in the interstitial sites and/or around crystalline defects can lead to reversible or irreversible effects on the mechanical properties and favored embrittlement at different scales (see Refs. [2–8] for a partial review on the topic). Therefore, the apparent or effective solubility of hydrogen in metals at a representative scale of the microstructure has to be known to design tough materials under aggressive environmental conditions. In the present study, we focus on the solubility of hydrogen in nickel since this material and nickel-based alloys are commonly used in metallurgical industry and have many technological applications.

The apparent solubility of hydrogen in polycrystalline nickel has been investigated extensively for a long time ago since the

pioneering work of Sieverts [9]. It can be accessed from electrochemical permeation tests [10–17] or from gas equilibrated-quench-analyze experiments [18–21]. By using the latter technique, it has been shown that polycrystalline samples in equilibrium with a H_2 gas atmosphere at $P_{H_2} = 1$ atm can incorporate between 3.2×10^{-5} H/Ni and 4.5×10^{-5} H/Ni at ambient temperature and up to 3.4×10^{-4} H/Ni at 1000 K [9,18,21–23]. The temperature dependence of the solubility shows a large deviation from the Arrhenius law for $T > 1000$ K [18]. Unlike the case of polycrystalline Ni, few data on the solubility of H in single crystals are available in the literature. The solubility measurements of Eichenauer et al. [24] and Stafford and McLellan [18] from gas equilibrated experiments at $P_{H_2} = 1$ atm point up that the solubility is about two times lower in single crystals compared to polycrystalline samples in the 650 K – 1000 K temperature range. The difference of solubility between single crystals and polycrystals becomes smaller at higher temperature and the deviation from the Arrhenius law is unclear in single crystals.

The deviation of the solubility from the Arrhenius law in polycrystalline Ni has been attributed to the presence of interstitial sites with differing energies where the H atoms can be located [11] or to

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the H-vacancy interactions [25,26]. Actually, crystalline defects, such as dislocations, grain boundaries or point defects, can influence the apparent solubility of H in metals through a trapping phenomenon or a short-circuit diffusion path [1,5,27]. Reversible and irreversible traps for hydrogen can be distinguished from their depth energy levels according to the classification given by Pressouyre [27]. The displacement fields induced by dislocations, coherent precipitates and vacancies are considered as reversible traps with an energy level between 0.1 eV and 0.4 eV [5,28–31] while dislocation and vacancy cores are acting as irreversible traps with an energy level above 0.5 eV [1,5,32–35]. For nickel, the H trap binding energy in the vacancy core has been evaluated between -0.28 eV and -0.22 eV from recent *ab initio* calculations at 0 K [36–39]. In addition, it has been suggested that the vacancies in this metal can incorporate up to 6 H atoms to form H-vacancy clusters at static conditions [37,39–43] and may lead to a significant evolution of the apparent solubility. However, such H-rich vacancy clusters become unstable under high H_2 chemical potential in the case of fcc Fe [39] and the stability of the H-rich defects in Ni proposed by Connétable et al. [37] is questionable.

The hydrogen-vacancy interactions may have major implications in the degradation mechanisms of metals [44–48]. In particular, the lattice parameters of the metal-hydrogen alloys decrease with the incorporation of H and indicate the formation of new vacancies, called superabundant vacancies (SAV), at high P_{H_2} [4,46,49–51]. A linear relation between the vacancy concentration and the hydrogen content in nickel has been found for high hydrogen pressures ($P_{H_2} = 2.4$ – 5.5 GPa) and high temperatures (940–1200 K) [52] where nearly stoichiometric Ni–H hydrides are stable [4,53–55]. The formation of SAV has been also observed in electrodeposited nanocrystalline materials at room temperature after an electrochemical charging step [49,56]. These superabundant vacancy concentrations may arise from a large decrease of the vacancy formation energy in metal-hydrogen solid solutions compared to H-free samples [41]. Several thermodynamic models have been used to explain the superabundant vacancy formation mechanism and the stability of such H-decorated vacancies [25,39,40,57,58]. These models have been formulated on the base of the thermodynamic equilibrium involving the solution energy of H incorporation in the interstitial sites of a perfect crystal and the formation energy of H-vacancy clusters. The distribution of the H atoms and the vacancies has been taken into account from the Maxwell–Boltzmann statistics [59], the Fermi–Dirac distribution function [25,42,60–62] or from a linear mixing of the Ni–H solid solution [40]. However, no non-configurational entropic contributions have been taken into account in these models and no clear correlations have been made between the presence of vacancies and the macroscopic solubility of hydrogen in nickel so far.

In this paper, we determine the solubility of hydrogen and the vacancy concentration in nickel single crystals at thermodynamic equilibrium for a wide range of H_2 chemical potentials from *ab initio* calculations. We calculate the solution Gibbs free energy of incorporation of H in the interstitial sites of a perfect crystal. We extend the calculations to the formation Gibbs free energy of H-vacancy clusters where H can be located inside the vacancy core or in the elastic displacement field generated by the defect. The Gibbs free energy is taken as a sum of lattice vibrations and electronic excitations contributions. Then, the macroscopic apparent solubility and the vacancy concentration are determined from statistical mechanics involving the configuration entropy and the Gibbs free energies by minimizing the total free energy expressed in the grand canonical potential. This procedure has been proposed for Al [61] and austenitic steel (Fe- γ) [60]. Finally, we compare our results with previous gas equilibrated-quench-analyze experiments at $P_{H_2} = 1$ bar where the chemical potential of gaseous hydrogen is

calculated at finite temperature including the rotation, the translation and the vibration modes of the H_2 molecule. Based on these results, the thermodynamic conditions of the previous experimental results found in the literature are discussed.

2. Methods

2.1. Energy and entropy of bulk Ni and Ni–H alloys at finite temperature

The determination of the solubility of hydrogen in nickel single crystals from *ab initio* calculations at finite temperature needs the computation of the energy and the entropy of perfect Ni, Ni crystal containing a vacancy and Ni–H alloys. For the latter, we consider H in the interstitial sites of a perfect crystal and in the displacement field generated by a vacancy. We use the results obtained in our previous study dedicated to the calculation of the vacancy concentration in Ni at thermal equilibrium for the energy and the entropy of the crystal containing a H-free vacancy [63]. In the case of Ni–H alloys in a vacancy-free crystal, hydrogen is incorporated in the octahedral site and in the tetrahedral site, even several experimental and *ab initio* studies suggest that H atoms occupy octahedral sites only [22,36,37,64,65]. The procedure is extended to the incorporation of H in the interstitial sites of the displacement field generated by a vacancy in the crystal. The location of H in the H-vacancy clusters investigated in this study is shown in Fig. 1. These clusters involve the O1 and T1 sites inside the vacancy core, the O2 site tangent to it and other sites (T2, O3, T3) in the short-range elastic displacement field of the defect.

Ab initio calculations are based on the density functional theory [66,67] (DFT) within the PBE functional [68] implemented in the PWSCF code of the Quantum Espresso package [69]. We use pseudopotentials built with the projected augmented wave method [70,71] to describe the ion–electrons interactions of Ni and H. The plane wave cutoff of the pseudopotentials is set to 60 Ry and a Fermi–Dirac smearing of 0.002 Ry is used to broaden the electronic density of states.

The energy and the entropy of pure Ni and Ni–H alloys are calculated with a supercell built on a $4 \times 4 \times 4$ repetition of the primitive Ni lattice (64 Ni atoms). Increasing the supercell size to a $5 \times 5 \times 5$ repetition of the primitive lattice (125 Ni atoms) decreases the H solution energy of 4 meV and the vacancy formation

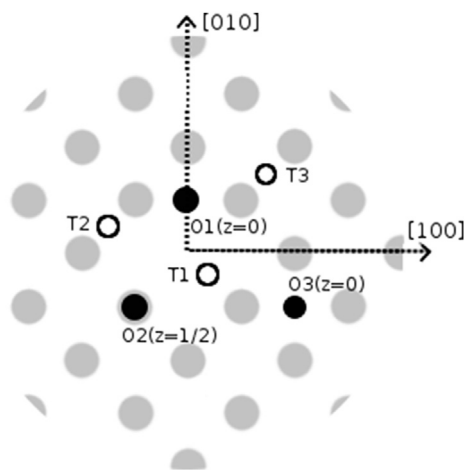


Fig. 1. Location of the H atom in the H-vacancy clusters investigated in this study. The vacancy is at the origin of the coordinate framework and the H atom is located in the interstitial sites inside the vacancy core (O1 and T1), tangent to it (O2) or in the elastic displacement field (T2, O3, T3).

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