

Solubility of Hydrogen and Vacancy Concentration in Nickel from First Principles Calculations

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ABSTRACT

The hydrogen solubility and the vacancy concentration in Ni single crystals at thermal equilibrium with a H₂ gas have been determined from a combination of first principles calculations and statistical mechanics up to the melting point. We show that the H solubility increases and the vacancy formation is promoted at high P_{H₂}. The apparent solution enthalpy and entropy are extracted from the fit of the solubility with the Sieverts's law. We show that our results are in good agreement with previous experimental data at P_{H₂}=1 bar. The vacancy concentration increases with P_{H₂} whatever the temperature but the effect of H is more significant at low temperature. However, the vacancy concentration and the H solubility in single crystals remain small and a comparison with the experimental data on polycrystals indicates that the grain boundaries may play the most important source of superabundant vacancies and preferential sites for H incorporation.

INTRODUCTION

The incorporation of hydrogen in metals can strongly affect the physical properties of the host matrix and can lead to irreversible damages. Therefore, the solubility of hydrogen in metals is a fundamental data to design new protections preventing hydrogen embrittlement and safety materials. However, the apparent H solubility can be influenced by the presence of crystalline defects such as point defects, dislocations or grain boundaries. In particular, it has been suggested that hydrogen promotes the formation of vacancies, called "superabundant vacancies" which participate extensively to the mechanisms of degradation of metals [1-3]. In this study, we determine the vacancy concentration and the hydrogen solubility in nickel single crystals at thermodynamic equilibrium with a H₂ gas up to the melting temperature from a combination of first principles calculations and statistical mechanics. Hydrogen is incorporated in the interstitial sites of a perfect crystal but also in the sites inside and around the vacancy core delimited by the first shell of atoms around the center of the defect. Finally, we discuss the contribution of hydrogen to the formation of vacancies.

THEORY

The H solubility and the total vacancy concentration have been calculated from the minimization of the free energy J of the crystal in the grand canonical ensemble containing hydrogen atoms, vacancies and hydrogen-vacancy clusters:

$$\begin{aligned}
J = & N_{octa} \times G_{octa}^{sol} + N_{tetra} \times G_{tetra}^{sol} \\
& + \sum_{\{H-vac\}} N_{site-iH} \times G_{site-iH}^f + N_{vac} \times G_{vac}^f \\
& - TS^{conf}
\end{aligned} \tag{1}$$

where $N_{octa,tetra}$ denotes the number of interstitial sites occupied by H, $N_{site-iH}$ the number of H-vacancy clusters involving i H atoms in the interstitial sites located in the core or tangent to the vacancy core and N_{vac} the number of thermal vacancies of pure Ni. $\{H-vac\}$ is the ensemble of the H-vacancy clusters investigated in this study. Here, we consider that H atoms cannot associate since it has been shown that the H_2 molecule is unstable in the crystal and inside the vacancy [4]. The total H solubility C_H is taken as the sum of the solubility of H in the interstitial sites of a perfect crystal and the concentrations of the H-vacancy clusters. The total vacancy concentration C_{vac} is the sum of the vacancy concentration at thermal equilibrium and the concentrations of the H-vacancy clusters. The vacancy concentration at thermal equilibrium for pure Ni has been determined in a previous study [5]. The configuration part of the entropy S^{conf} takes into account the distribution of H in the interstitial sites out of the displacement field generated by the vacancy, the distribution of the vacancies and the way to distribute the H atoms in a single H-vacancy cluster. The solution and the H-vacancy cluster formation Gibbs free energies G^{sol} and G^f are computed following their thermodynamic definitions involving the number n of H atoms in a H_2 gas at the chemical potential $\mu_{H_2}^g(P, T)$:

$$G^{sol,f}(P, T) = H^{sol,f}(P, T) - TS^{sol,f}(P, T) - n \frac{1}{2} \mu_{H_2}^g(P, T) \tag{2}$$

The solution and H-vacancy clusters formation enthalpies and entropies are calculated at constant pressure by taking into account the contribution due to the vibration of the lattice in the quasi-harmonic approximation and the contribution of the electronic excitations at finite T. The chemical potential of the H_2 gas is expressed for an ideal gas, which is valid for $P_{H_2} \leq 0.1$ GPa and is calculated from the vibration, the translation and the rotation partition functions. All of the thermodynamic quantities in equation (2) are determined from first principles calculations with the density functional theory implemented in the PWSCF code of the Quantum Espresso package [6]. We use pseudopotentials for Ni and H built with the PAW method [7] and the PBE functional to describe the exchange-correlation potential [8]. Details of the calculations and the positions of H in the displacement field induced by a vacancy can be found in our recent studies [9,10].

RESULTS AND DISCUSSION

H solubility in Ni single crystals

The solubility of hydrogen for several H_2 pressures is displayed in figure 1. The H concentration in Ni is enhanced at high H_2 pressure. At 1000 K, the H concentration increases from 3.08×10^{-4} H/Ni at $P_{H_2} = 1$ bar to 9.68×10^{-3} H/Ni at $P_{H_2} = 0.1$ GPa. The comparison of our results with the previous experimental data of Stafford and McLellan at $P_{H_2} = 1$ bar are in good

agreement for $T > 900$ K [11]. The population analysis shows that more than 99% of the H atoms occupy the interstitial sites of a perfect crystal whatever the H_2 pressure up to 0.1 GPa. Among the sites in the displacement field induced by a vacancy, about 68 % and 23 % of the atoms occupy the octahedral site and the tetrahedral site inside the vacancy core at 1000 K.

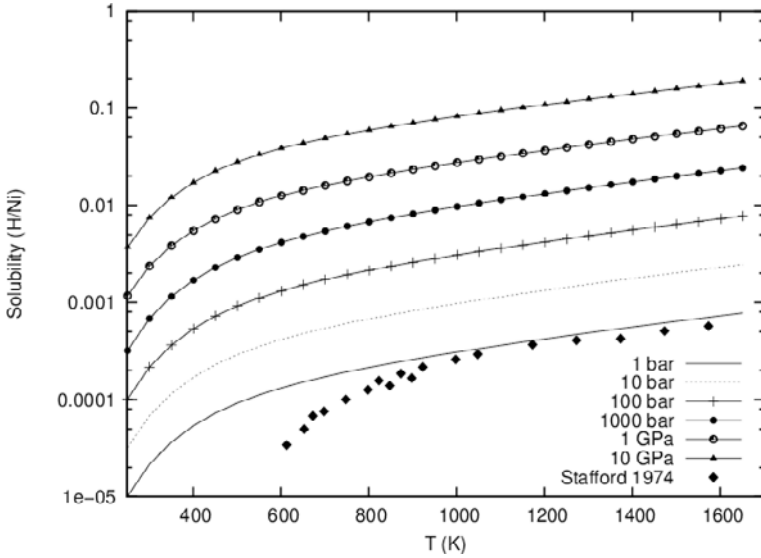


Figure 1. Solubility of hydrogen in Ni single crystals in equilibrium with a H_2 gas at several pressures in the 250 K-1700 K temperature range. A comparison with the experimental data of Stafford and McLellan at $P_{H_2}=1$ bar is provided [11]. The data given for $P_{H_2}=1$ GPa and $P_{H_2}=10$ GPa may be affected by the non-ideality of the gas.

In order to give a more quantitative comparison of our model with experiments, we fit the solubility data obtained from first principles calculations with the Sieverts’s law which link the solubility C_H to the solution enthalpy and entropy ΔH_s and ΔS_s , respectively:

$$C_H = \sqrt{\frac{P}{P_0}} \exp\left(\frac{\Delta S_s}{k_B}\right) \exp\left(\frac{-\Delta H_s}{k_B T}\right) \quad (3)$$

The results displayed in figure 2 indicates that the solution entropy increases with the H_2 pressure for a given solution enthalpy. This tendency reflects the increasing of the solubility with the gas pressure. A comparison of the solution enthalpy and entropy with available experimental data [11-13] indicates that our model reproduces the apparent solubility with a good approximation at this scale at least at $P_{H_2}=1$ bar.

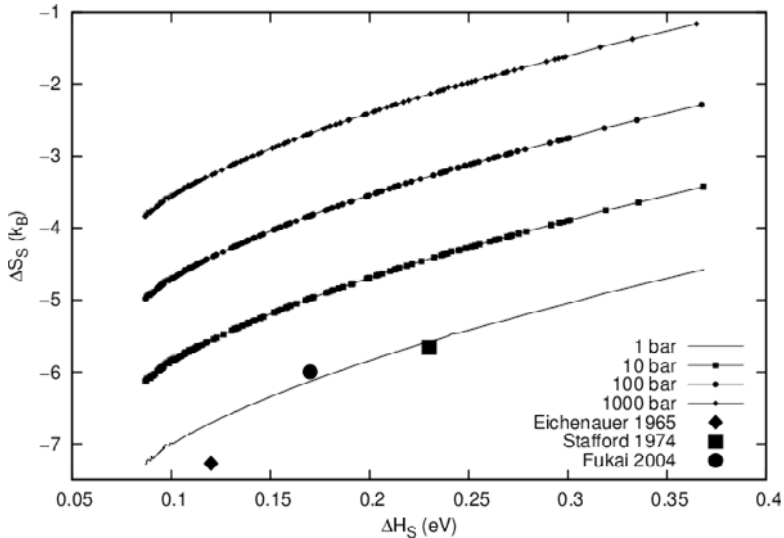


Figure 2. Solution entropy as a function of the solution enthalpy for several H₂ pressures. We provide a comparison with the experimental data of Eichenauer *et al* [12] and Stafford and McLellan [11] for single crystals and the data of Fukai [13] for polycrystals at P_{H₂}=1 bar.

Total vacancy concentration

The results exposed in figure 3 shows that the total vacancy concentration increases with the H₂ pressure and the temperature. However, the vacancy concentration remains small and does not exceed 7.4×10^{-4} vacancy/atom at T=1700 K and P_{H₂}=0.1 GPa. In particular, it is interesting to note that the vacancy concentration is more dependent to the H₂ pressure for T < 400 K. This indicates that the effect of H on the formation of the vacancies is more pronounced at low temperature. Previous measurements of the vacancy concentration in Ni polycrystals in the 2.4 GPa -7.4 GPa P_{H₂} pressure range and T > 930 K gives values about 0.3 vacancy/atom for the nearly stoichiometric Ni-H hydride [14]. According to the results given in figure 1, the H solubility in Ni is believed to be lower than 0.25 H/Ni at high P_{H₂}, far from the stability of the stoichiometric Ni-H hydride. Therefore, the large differences between the vacancy concentration and the H solubility between single crystals and polycrystals indicate that the grain boundaries may be the most active sources of superabundant vacancies and the preferential sites for H sinks.

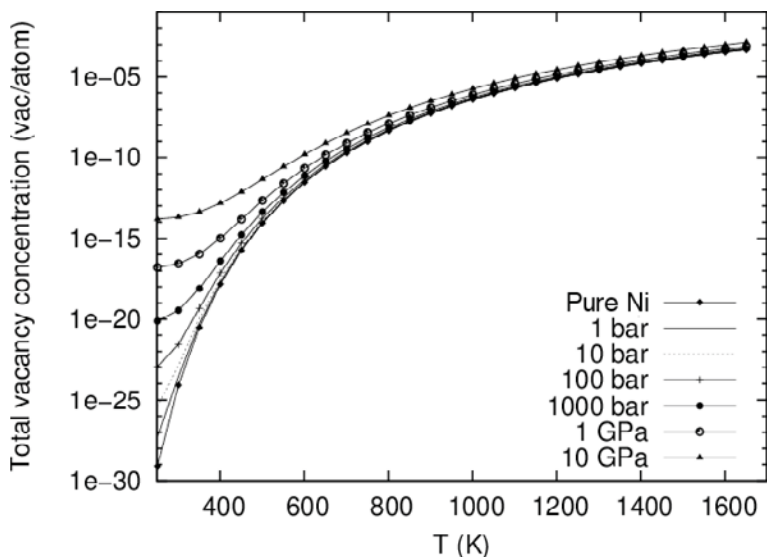


Figure 3. Total vacancy concentration in Ni single crystals in the 250 K-1700 K temperature range for several H₂ pressures. The vacancy concentration for pure Ni is taken from reference [5]. The data given for P_{H₂}=1 GPa and P_{H₂}=10 GPa may be affected by the non-ideality of the gas.

CONCLUSIONS

We have determined the H solubility and the total vacancy concentration in Ni single crystals at thermal equilibrium with a H₂ gas up to T=1700 K. We use a combination of first principles calculations and statistical mechanics to address this issue. We show that our model reproduces experimental solubility data at P_{H₂}=1 bar. The presence of hydrogen promotes the vacancy formation with a more significant effect at low temperature. This study is a first step in the determination of the global apparent solubility in a real crystal.

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