Statistical Monolayer Modeling of Hydrogen Absorption in Mg-33Ni

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ABSTRACT – In this work, we investigate hydrogen absorption in Mg-33Ni using a statistical monolayer model. Stereographic parameters, occupancy rate *n*, site density *Nm*, and binding probability *P*, are determined as functions of the initial temperature. The model enables quantitative evaluation of the hydrogen saturation ratio (H/M_{sat}), absorption energy (ε), and Gibbs free energy (ΔG) as functions of temperature and pressure. The resulting parameters provide insight into the energetic landscape and site-occupancy behavior governing hydrogen uptake in Mg-33Ni. This approach offers a robust framework for understanding and optimizing hydrogen storage in magnesium-based alloys.

Keywords: **Hydrogen absorption; Mg-33Ni alloy; Statistical monolayer model; Stereographic parameters; Thermodynamic functions**

1. INTRODUCTION

Hydrogen storage remains a technological barrier to the development of hydrogen-based energy systems [1]. Mg-based alloys are promising candidates owing to their high gravimetric storage capacity, low cost, and abundance [2]. However, limitations related to slow absorption kinetics and high operating temperatures restrict their practical implementation [3]. Combining magnesium with transition metals such as nickel has proven effective in improving both the hydrogen storage capacity and the sorption kinetics, while also creating more favorable thermodynamic conditions for hydrogen uptake and release [4]. Understanding hydrogen absorption in Mg-Ni alloys at the microscopic level is essential for optimizing their performance. Classical thermodynamic analyses often rely on Van't Hoff relationships and empirical modeling, but these approaches do not fully capture site-occupancy behavior or the distribution of binding energies [5]. The statistical monolayer model provides a more rigorous framework by describing hydrogen uptake in terms of stereographic parameters such as the occupancy rate n, maximum site density Nm, and binding probability P. These parameters quantify the energetic heterogeneity of absorption sites, the cooperativity of the process, and the favored occupancy conditions.

In this work, we apply the statistical monolayer model to analyze hydrogen absorption isotherms of the Mg-33Ni alloy at 533 K, 573 K, and 588 K. The objective is to extract stereographic parameters and derive thermodynamic quantities including the hydrogen saturation ratio H/M_{sat}, absorption energy ε, and the Gibbs free energy ΔG. The results offer valuable insight into the temperature and pressure dependence of the hydrogen–metal interaction and clarify the mechanisms governing hydrogen storage in this system.

2. METHODOLOGY

Hydrogen absorption isotherms of Mg-33Ni were measured by [6]at temperatures of 533 K, 573 K, and 588 K. For the present study, a monolayer model with a single discrete site type was applied. The model is based on the following key assumptions:

- Hydrogen behavior: hydrogen is considered as an ideal gas, an approximation valid at low to moderate pressures.
- Degree of freedom: the model considers the two principal degrees of liberty for H_2:
  - Translation temperature $\theta_{Tr} \approx 10^{-15}$ K.
  - Rotation temperature $\theta_{rot} \approx 85.3$ K.
- Site occupancy: the adjustable number of H (N_a) is accommodated within a fixed number of interstitial receptor sites (N_m) distributed per unit mass of the absorbed material.

The reversible hydrogen storage reaction is represented as:

$$M + \frac{n}{2} H_2 \leftrightarrow MH_n \quad (1)$$

Where M is the metal, n is the stoichiometric factor, and MH_n is the metal hydride. Here, H_n represents an aggregate of n hydrogen atoms occupying a single interstitial site.

As the sorption process involves particle exchange with a hydrogen gas reservoir, the grand canonical ensemble is the appropriate framework for its analysis. The associated partition function is defined as:

$$Z_{gc} = \sum_{N_i} e^{-\beta(-\varepsilon-\mu)N_i} = 1 + e^{\beta(\varepsilon+\mu)} \quad (2)$$

Where:

- N_i is the occupation state of a site (0 or 1).
- ε_i is the absorption energy per site.
- μ represent the chemical potential of the H absorbed-desorbed.
- $\beta = 1/k_{BT}$, with T as the absolute temperature and k_B as Boltzmann's constant.

The average number of occupied sites, N_0, is derived from the grand canonical potential and, for a single site type, is expressed as:

$$N_0 = n_1 N_{01} = n_1 \frac{N_{1m}}{1+\left(\frac{P_1}{P}\right)^{n_1}} \quad (3)$$

Where P_1 is the half-saturation pressure of the site, defined as:

$$P_1 = K_B T Z_{ge}{}^{-\beta\varepsilon_1} \quad (4)$$

ε_1 represents the absorption energy per molecule. The half-saturation pressure indicates the affinity of a site for hydrogen: lower P_1 corresponds to stronger binding.

Experimentally, hydrogen storage capacity is conventionally expressed as the H/M ratio, representing the number of hydrogen atoms absorbed per metal atom in the host alloy. This quantity is directly related to the number of occupied sites. It is calculated as:

$$\left[\frac{H}{M}\right]_1 = \frac{n_1 N_{1m}}{N_{1m}\left(1+\left(\frac{P_1}{P}\right)^{\left(\frac{n_1}{2}\right)}\right)} = \frac{\left[\frac{H}{M}\right]_{1sat}}{1+\left(\frac{P_1}{P}\right)^{\left(\frac{n_1}{2}\right)}} \quad (5)$$

3. RESULTS AND DISCUSSION

a. Fitting of the absorption isotherms

The proposed model was applied to fit the hydrogen absorption isotherms. The comparison between the model predictions and experimental measurements (**Figure 1**) demonstrates very good agreement, with a coefficient of determination of R^2=0.99.

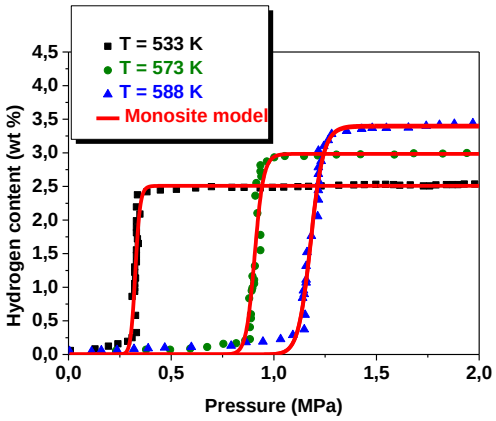

Figure 1: Hydrogen absorption isotherms fitted using the proposed model

b. Stereographic parameters

Table 1: Fitted parameters

T	533K	573K	588K
n_1	28.06	42.72	38.11
N_{m1}	0.09	0.07	0.08
P_1	0.32	0.9	1.17

The occupancy parameter n increases with temperature, indicating enhanced cooperative behavior. Nm remains nearly constant, while P increases significantly, showing a higher probability of hydrogen occupying sites at elevated temperatures.

4. CONCLUSIONS

The statistical monolayer model successfully describes hydrogen absorption in Mg-33Ni. Temperature strongly influences stereographic parameters and thermodynamic quantities, clarifying the mechanisms

governing hydrogen uptake. The model provides a robust framework for optimizing magnesium-based hydrogen storage materials.

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