

Statistical model of defects in Al-H system

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Vacancy and hydrogen concentrations in Al were determined by first-principles calculations and statistical-mechanics modeling, as functions of temperature and hydrogen chemical potential μ_H . Formation energies of Al vacancies, H interstitials, and H-Al vacancy complexes were obtained from first-principles calculations. The statistical-mechanics model incorporated these energies and included configurational entropy contributions through the grand canonical ensemble. We found that the hydrogen chemical potential under different chemical environments plays an important role in determining the relative equilibrium defect concentrations in the Al-H system. Estimates of the hydrogen chemical potential during hydrogen charging were obtained experimentally. At comparable the calculated concentrations are consistent with these values, along with previously reported measurements of hydrogen concentration.

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I. INTRODUCTION

Hydrogen, the lightest element in nature, has attracted a lot of interest because of its chemical activity. In particular, hydrogen in metals has been widely studied due to the potential importance of metal hydride in hydrogen storage and purification applications.¹ It is well known that H can greatly modify the properties of metal or alloy (e.g., H induced embrittlement)² but the mechanism and detailed interactions between H and metals are still not well understood. Due to its small size, light weight, and complex bonding properties, it is experimentally difficult to determine the exact structure of H-metal compounds and it is generally believed that H behaves much like a liquid in solid metals, due to its high mobility.³ Recently several theoretical works have been published aiming to reveal the structural properties of Al-H system.⁴⁻⁷

Previous experiments suggest that the structure and properties of Al-H systems are different under various H charging conditions.⁸ Recently, it was shown that under strong H charging conditions in chemical or electrochemical experiments, large voids in Al can be formed.^{9,10} Hydrogen-induced lattice contraction in Al has also been observed. In contrast, lattice expansion normally occurs in other face-centered-cubic (fcc) metals.¹¹⁻¹³ Thus it will be interesting to investigate defect properties in aluminum exposed to H under weak to aggressive hydrogen charging conditions.

In the low-concentration limit, H exists as an impurity defect in Al and interacts with native Al vacancy defects. A number of theoretical studies have shed light on the position of interstitial hydrogen atoms in Al as well as their energetics.^{4,5} It is widely believed that H prefers tetrahedral (T_d) interstitial sites rather than octahedral (O_h) sites. In monovacancies in Al, H also prefers T_d sites as opposed to the vacancy center.⁵ As stated above, hydrogen is very active and behaves like a liquid in the Al lattice, and thus static energy calculations alone cannot reveal the distribution of H in Al. Previous thermodynamic studies of hydrogen-vacancy interactions in aluminum relied on experimental values of

defect energies.^{6,7} Here we will combine first-principles total-energy calculations with statistical-mechanics analysis to investigate defect distributions in Al-H under thermal equilibrium conditions. Furthermore, we have also measured the hydrogen chemical potential in different alkaline solutions for comparison with our numerical results.

II. STATISTICAL MECHANICS MODEL

We describe the equilibrium defect distribution in the multicomponent system by a grand canonical ensemble, where the chemical potentials of each component and numbers of various point defects are treated as variables. This statistical-mechanics modeling approach had been successfully applied to determine the concentration of point defects in binary NiAl and FeAl alloy systems.¹⁴

In this paper, we model the point defect concentrations in the Al-H system by considering the grand canonical potential J in a grand canonical ensemble,

$$J = U - TS + PV - \sum_i N_i \mu_i. \quad (1)$$

Here N_i and μ_i are the particle number and chemical potential of component or defect i , U is the internal energy, T is the temperature, S is the system entropy, P is the external pressure, and V is the system volume. Here we keep the system volume fixed, which is a reasonable approximation for the low hydrogen concentration limit and the atmospheric pressure condition. In the equilibrium state at given temperature, pressure and chemical potentials, the free energy J is minimized with respect to the particle number,

$$\frac{\partial J}{\partial N_i} = 0. \quad (2)$$

By solving this equation, we obtain the particle number under thermal equilibrium at the given conditions.

Several kinds of point defects in the Al-H system are considered in this paper. First, vacancies generally exist in solids

above zero temperature. Vacancies in pure aluminum have been studied by a number of experiments and calculations. It was suggested that at low concentrations, monovacancies are preferred over divacancies.¹⁵ In this paper, we consider only monovacancies as the prototype vacancy defects in the Al-H system. At low concentrations, hydrogen can occupy several possible positions, including two kinds of interstitial sites in the fcc lattice—octahedral and tetrahedral sites. According to previous theoretical studies, hydrogen prefers tetrahedral site in Al (Refs. 4 and 5); our calculations also confirmed this. Thus we consider only tetrahedral sites in our statistical model. Hydrogen can also enter monovacancy sites of Al to form H-vacancy complexes. Previous theoretical calculations suggested that in the H-vacancy complex, the H atom is located off center close to one side of the vacancy cavity (in a geometry that is very close to the tetrahedral interstitial site in the fcc Al).^{4,5} Therefore, we will also consider the tetrahedral interstitial site as the occupation site for H in a H-vacancy complex.

Neglecting defect-defect interactions at low concentrations, the total free energy of the system can be written as

$$J = U - TS - \mu_{\text{Al}}N_{\text{Al}} - \mu_{\text{H}}N_{\text{H}}, \quad (3)$$

$$S = k_B \ln \frac{M!}{N_v^{\text{Al}}! N_v^{\text{H}}! N_v^{\text{H}_2}! (M - N_v^{\text{Al}} - N_v^{\text{H}} - N_v^{\text{H}_2})!} \frac{(2M - 8N_v^{\text{Al}} - 8N_v^{\text{H}} - 8N_v^{\text{H}_2})!}{N_i^{\text{H}}! (2M - 8N_v^{\text{Al}} - 8N_v^{\text{H}} - N_i^{\text{H}} - 8N_v^{\text{H}_2})!} 8^{N_v^{\text{H}}} 28^{N_v^{\text{H}_2}}. \quad (7)$$

In such a grand canonical ensemble, the defect energies are defined as

$$\varepsilon_\alpha = E_\alpha - E_0, \quad (8)$$

where E_α is the total energy of the supercell with specific defect type α and E_0 is the total energy of the corresponding perfect Al supercell without defects. The defect type α can be a monovacancy, interstitial hydrogen or H-vacancy complex. The defect formation energies can be calculated by

$$\Delta E_\alpha = \varepsilon_\alpha + n_{\text{Al}}\mu_{\text{Al}} + n_{\text{H}}\mu_{\text{H}}. \quad (9)$$

Here n_{Al} and n_{H} are the corresponding atom number differences with respect to the perfect supercell.

III. RESULTS AND DISCUSSION

We performed first-principles total-energy calculations to determine the formation energies of the various defects mentioned above. The calculations are based on the density-functional theory (DFT) with the generalized gradient approximation of Perdew-Burke-Ernzerhof, implemented in the VASP code.^{16,17} Only the valence electrons are treated explicitly and their interactions with ionic cores are described by projector augmented wave pseudopotentials.¹⁸ The wave functions are expanded in-plane waves with an energy cutoff 350 eV, which is chosen to be sufficiently high to obtain

$$U = M\varepsilon_{\text{Al}} + N_v^{\text{Al}}\varepsilon_v^{\text{Al}} + N_i^{\text{H}}\varepsilon_i^{\text{H}} + N_v^{\text{H}}\varepsilon_v^{\text{H}} + N_v^{\text{H}_2}\varepsilon_v^{\text{H}_2}, \quad (4)$$

$$N_{\text{Al}} = M - N_v^{\text{Al}} - N_v^{\text{H}} - N_v^{\text{H}_2}, \quad (5)$$

$$N_{\text{H}} = N_i^{\text{H}} + N_v^{\text{H}} + 2N_v^{\text{H}_2}. \quad (6)$$

In our model, the number of fcc lattice sites (M) is fixed while the numbers of Al and H atoms are allowed to vary according to the defect populations in the system. We have two types of atoms—Al and H—and four types of defects—monovacancies (N_v^{Al}), interstitial hydrogen (N_i^{H}), one H-vacancy complex (N_v^{H}), and two H-vacancy complexes ($N_v^{\text{H}_2}$). At low concentrations, the internal energy of the system can be determined from first-principles total-energy calculations of the energies of the various isolated defects. The calculation of configurational entropy assumes that atoms in Al can occupy two types of sites, the fcc lattice site and the tetrahedral interstitial site. In particular, Al atoms always occupy fcc sites and H tetrahedral sites. According to the lattice geometry, there are M fcc sites, $2M$ tetrahedral interstitial sites, and eight possible sites for hydrogen in a monovacancy. Then the configuration entropy for a given set of defect concentrations is

converged cohesive energy for both Al and H. For bulk Al, we use $24 \times 24 \times 24$ Monkhorst-Pack grids k -point sampling in the Brillouin zone.¹⁹ The calculated lattice constant and cohesive energy are 4.04 Å and 3.74 eV, as compared to experimental values 4.05 Å and 3.39 eV. For defect energy calculations, we choose a cubic supercell containing 108 fcc Al atoms and $8 \times 8 \times 8$ k -point grids, which have been used successfully in previous first-principles studies.^{4,5} In hydrogen molecule calculations, a $20 \times 20 \times 20$ Å cubic supercell was used to cancel image interactions. All the calculated values are listed in Table I.

Once the energetics of various defects have been determined, their equilibrium concentrations can be calculated from the chemical potentials of Al and H. These chemical potentials depend on variables such as temperature, pressure, and/or chemical charging in an electrochemical cell. First, we consider the equilibrium between Al and H₂ gas. Assuming that H₂ gas can be regarded as ideal, its chemical-potential evolution with temperature at one atmosphere pressure can be written as

$$\mu_{\text{H}} = -\frac{7}{4}k_bT \ln \frac{T}{7.55} - E_d, \quad (10)$$

where E_d is the dissociation energy of an H₂ molecule, 3.35 eV according to our DFT calculation. For Al, the chemical potential is approximately independent of temperature. Thus,

TABLE I. Formation energies of defects, binding energy of defect complexes, and chemical potentials of Al and H. The binding energy is defined as energy difference between the complex and the sum of the corresponding single defects. Values from prior calculations and experimental measurements are listed for comparison.

	Present work (eV)	Prior work (eV)	Experiment (eV)
Vacancy	0.60	0.54 ^a	0.67 ^b
T_d interstitial H	0.74	0.69 ^c	0.60–0.71 ^d
One H vacancy (formation)	1.00	0.90 ^c	
One H vacancy (binding)	–0.34	–0.33 ^c	–0.52 ^e
Two H vacancy (formation)	1.38		
Two H vacancy (binding)	–0.70	–0.70 ^f	
μ_{Al}	–3.74		–3.39 ^g
μ_{H}	–3.35	–3.36 ^f	–2.26 ^h

^aReferences 4, 5, and 20.

^bReference 21.

^cReference 5.

^dReferences 22–25.

^eReference 2.

^fReference 4.

^gReference 26.

^hReference 27.

we use its calculated bulk chemical potential (3.74 eV), which is considered to be constant.

Figure 1 shows defect concentrations as a function of temperature in the range of 200–950 K. All defect concentrations increase with temperature as expected. The most abundant defects are monovacancies. With regard to hydrogen-related defects, monovacancy complexes with two hydrogen atoms ($C_v^{\text{H}_2}$) are at very low concentration over the whole temperature range. Thus, single-hydrogen defects predominate in this environment. Interstitial H atoms are approximately one order of magnitude more abundant than one H-vacancy complexes, even though the H-vacancy complex has a negative binding energy (Table I). This is due to the energy cost of vacancy formation in Al. The typical hydrogen concentration in experiments is around 10^{-6} – 10^{-8} at room temperature at 1 atm and was suggested to be 10^{-6} at 930 K, the melting point of Al.²³ In our calculations at around 900 K, the total H concentration is 5×10^{-8} . Thus the

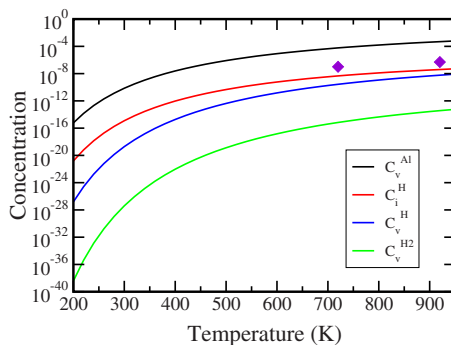


FIG. 1. (Color online) Concentrations of defects vs H_2 gas temperature at 1 atm. The purple diamond points are experimental data.

orders of magnitude of the calculated monovacancy and H-interstitial concentrations, and their temperature dependences agree with these experimental values.

We are more interested in the properties of the Al-H system under aggressive hydrogen charging condition. Recently, we devised a technique to measure the hydrogen chemical potential during chemical charging of Al in alkaline solutions.^{28,29} With this measurement, our statistical model can be used to determine the state of hydrogen in the metal. A two-compartment electrochemical cell was assembled with an annealed 25- μm -thick Al foil acting as a membrane separating the two solutions. One side of the foil had been coated with a 0.05- μm -thick Pd layer. The cell compartment on the Pd side contained a reference buffer solution at pH 7.0 while that on the Al side was filled with an aqueous NaOH solution of specified pH 11, 12, 12.5, 13, or 13.5. Pd metal was chosen because it is known to readily absorb hydrogen and the hydrogen chemical potential μ_{H} in Pd is sensed electrochemically by the Pd open circuit potential,³⁰

$$\mu_{\text{H}} = -(E - E_{\text{H}_2}^0) - 2.303 \frac{RT}{F} \text{pH} + \frac{1}{2} \mu_{\text{H}_2}^0, \quad (11)$$

where $\mu_{\text{H}_2}^0$ is the chemical potential of ideal H_2 gas at 1 atm, pH refers to the solution in contact with the Pd, E is its open circuit potential, $E_{\text{H}_2}^0$ is the standard electrode potential for the hydrogen electrode, R is the universal gas constant, and F is the Faraday constant. In the experiments, E was continuously monitored after exposure of the Al side to the charging solution. The two-compartment cell design has been used for many years to study the permeation dynamics of hydrogen through metals;³¹ our implementation among the first to focus on equilibrium measurements.³²

When the pH on the Al side was 12.0 or greater, E decreased to a stable plateau at which μ_{H} was determined by the equilibrium of Pd with its hydride. At pH 12.5 or greater, E decreased further below the hydride plateau to another stable value corresponding to $\mu_{\text{H}} - \frac{1}{2} \mu_{\text{H}_2}^0 = 0.5$ – 0.6 eV. It is possible that this μ_{H} value corresponds to a state of Pd at high H chemical potential, such as a vacancy-ordered Pd hydride found previously.¹¹ In any case, we conclude that the H chemical potential on the Al side during the charging experiment is at least 0.5–0.6 eV.

For comparison, the calculated defect concentrations in the system at 300 K are shown in Fig. 2. The predicted concentrations of all defects increase exponentially with chemical potential. At low charging conditions, H interstitials predominate. However, the concentration of the two H-vacancy complexes increases more rapidly with μ_{H} than those of other defects. The two H complexes become more abundant than the one H complex at around -2.985 eV and its concentration exceeds that of interstitial H beyond -2.765 eV. When the H chemical potential is increased 0.56 eV above the ideal-gas reference, from -3.35 to -2.79 eV, the total H concentration is found to be around 1000 appm. Under such charging conditions, the calculated numbers of H interstitials and two H-vacancy complexes are comparable. Previous experiments have found that the hydrogen concentration reaches 1000 appm under cathodic charging, chemical

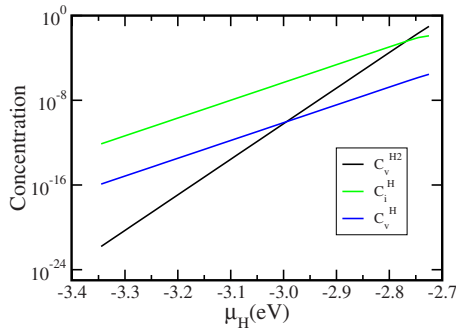


FIG. 2. (Color online) Defect concentrations under different charging conditions vs hydrogen chemical potential. $C_v^{H_2}$ becomes larger than C_v^H and C_i^H at sufficiently large hydrogen chemical potential.

charging, or plasma charging.^{8,33} Thus, measurements of both μ_H and the hydrogen concentration under aggressive H charging conditions appear to be consistent with the present simulation results.

IV. SUMMARY

We combined first-principles calculations with a statistical model to study the properties of defects in the Al-H system

under different thermal and chemical conditions. In thermal equilibrium with H_2 gas, defect concentrations increase with temperature. Among hydrogen-related defects, interstitial H dominates over H-vacancy complexes. The concentrations given by first-principles calculation are consistent with previous experiments. Under stronger chemical charging conditions, concentrations of H defect complexes increase very rapidly as the hydrogen chemical potential increases. At high chemical potential, two H-vacancy complexes become more abundant than one H complex. Experiments have suggested that under certain chemical charging conditions, the AlH_3 hydride phase is eventually formed.³⁴ In our model, we have only studied defect types in the low-concentration limit. However, the model can be further extended to include more complicated defect complexes so that the conditions for hydride and void formation can be simulated.

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