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Migration mechanism in defect metal hydrides containing superabundant vacancies

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1. Introduction

In the presence of interstitial H atoms, the concentration of M-atom vacancies is enhanced dramatically, forming a defect structure containing superabundant vacancies (SAVs). The diffusivity of M atoms is enhanced accordingly. Physically, these phenomena are the result of the lowering of the formation energy of a vacancy by trapping H atoms [1, 2].

A Monte Carlo calculation on the SAV formation process revealed that, in hydrides of fcc metals, two distinct defect phases are formed; a vacancy-ordered phase of high concentrations of vacancies on the $L1_2$ structure, and a vacancy-disordered phase of relatively low concentrations where vacancies are randomly distributed over the M lattice. Transitions between these two phases take place, as shown in Fig.1 [2].

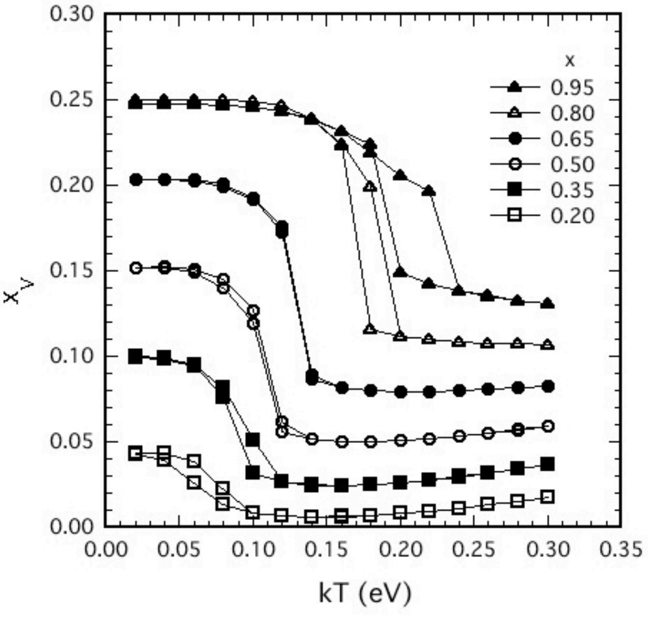

Figure 1. Temperature dependence of the vacancy concentration for several different H concentrations, x=[H]/[M], calculated for e_b=0.4 eV.

Note that, in both phases, the vacancy concentration is many orders of magnitude higher than in pure metals. The present paper addresses, specifically, the migration of H atoms and M-atom vacancies in the vacancy-disordered phase.

Experimental data available for Pd, Ni and Nb indicate that the migration energy of a vacancy is increased by amounts comparable to the migration energy of an H atom, and the pre-exponential factor is reduced by 1 ~ 2 orders of magnitude [3 ~ 5].

2. Calculation

The atomic jump rate varies from site to site according to variable local environments. In the present calculation, this effect is included approximately as a change in energy caused by Vac-H interaction. The energy of a vacancy with r neighboring H atoms is lowered by re_b (r=0, 1, 2, … 6), and that of an H atom with r' neighboring vacancies by $r'e_\mathrm{b}$ (r'=0, 1, 2). Assuming a saddle-point energy to be everywhere the same, the jump rate of a vacancy can be written

$$W_v=W_0\exp[-(e_m{}^v+re_b)/kT],$$

where W_v, $e_m{}^v$ are the jump rate and the migration energy of a vacancy, respectively. For an H atom, W_v, $e_m{}^v$ and r are to be replaced by W_H, $e_m{}^H$ and r', respectively. The pre-exponential factor is assumed to be the same for both vacancies and H atoms.

The diffusion coefficient can be obtained by following the motion of tagged H atoms and vacancies as a function of time, *i.e.* $D=\langle \boldsymbol{R}^2\rangle/6t$, where $\boldsymbol{R}$ is the atomic displacement in time t.

Actual calculations have been performed for a system consisting of 100 × 100 × 100 sites, containing H atoms of x=[H]/[M]=0.1. Energy parameters approximately corresponding to the Ni-H system have been adopted: $e_m{}^v$=1.0 eV, $e_m{}^H$=0.4 eV and e_b=0.4 eV.

3. Conclusion

Results obtained for kT=0.15 eV (close to the melting point) show that the diffusivity of vacancies is nearly 2 orders of magnitude smaller than that of H atoms, and reduced by another 2 orders of magnitude by trapping H atoms.

More detailed examination of the problem, including its temperature dependence, is in progress.

References

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