# EXPLORING THE ROLE OF SUPERABUNDANT VACANCIES ON H RELATED FRACTURE: BULK SIMULATIONS.

D. Tanguy [1,2], D. Delafosse [2] and M. Mareschal [1].
1 Centre Européen de Calcul Atomique et Moléculaire, ENS-Lyon (France)
2 Ecole des Mines de Saint-Etienne, UMR CNRS 5146, Saint-Etienne (France)

ABSTRACT:

We present an atomic scale Monte Carlo simulation of superabundant vacancies in the Al-H system, with particular attention paid to their ordering. This equilibrium simulation is performed in an (M, $N_H$, p, T) statistical ensemble where the number of lattice sites M and the number of hydrogen particles $N_H$ are constants. The number of metal particles can fluctuate to accommodate the creation of vacancy hydrogen complexes $VH_n$ according to the fixed chemical potential of the metal. This ensemble is chosen to mimic the damaged zone ahead of a stress corrosion crack, where the hydrogen concentration is high and the vacancies are produced internally either by dislocation annihilation or at grain boundaries. The main focus of this calculation is the degree of order in the system, as a function of the temperature and the hydrogen concentration. At $C_H$=1% and room temperature, we show that the $VH_n$ complexes cluster in the form of chains, lying in the <110> directions. The probability of finding large clusters is high enough to further consider their implication in hydrogen damaging.

## INTRODUCTION:

The formation of superabundant vacancies in metal-hydrogen systems was discovered by Fukai during high temperature, high $H_2$ pressure experiments [1, 2]. Originally observed in Ni and Pd, this phenomenon is present in a wide range of systems (see [3] for a review). At high temperature, the vacancies are formed on the surfaces and diffuse inside the sample. The hydrogen atoms, which originally occupy the interstitial positions, are trapped in vacancies. A lattice contraction is observed. Vacancy concentrations as high as 25% can be found. The mobility of the clusters under these conditions is high enough for the clusters to order in the $L1_2$ structure when approaching 25% atomic concentration.

High temperature and high gas pressure are not necessary for the stability of the clusters, although they do enhance the kinetics of their formation and ordering. Indeed, thermal desorption spectra (TDS) of electrodeposited metals (Cu and Ni [4]) show peaks similar to those obtained after exposure to high temperatures and high pressures. Electrolytic charging of high purity Al single crystals with hydrogen [5] showed a similar contraction of the lattice parameter. Some ordering of the clusters, at room temperature, have been reported [5], as well as $H_2$ bubbles formation after moderate heat treatments [6].

The trapping of H in vacancies has been extensively studied by ion implantation and positron annihilation [7] and by electronic structure calculations using the Effective Medium Theory (EMT) (for a review see [8]). The global picture is that H “occupies” an off-center position, in classical mechanics terms, with a high binding energy. Multioccupation is possible but the H-H interaction is repulsive, which leads to lower binding energies when the H atoms interact. For example, a vacancy in nickel can be occupied by 6 H in octahedral off-center positions. The binding energy is 0.44 eV for the two first H and 0.28 eV for the others [9]. In aluminum, the interstitial position in the bulk is not fully determined between the octahedral and the tetrahedral site. Fast Ion Channeling experiments have shown that the tetrahedral position should be preferred, at least in the vacancies [10]. This has been confirmed by recent Ab Initio calculations [11], even if the binding energy (0.33 eV) [11] is not in full agreement with experimental data and EMT (0.52 eV) [12]. Finally, the stability and the ordering of vacancy-hydrogen clusters have been investigated by Ab Initio calculations in $\alpha$-Fe [13]. The authors show that $VH_2$ lines or tablets are energetically favored at low temperature and suggest that these anisotropic defects can play a role in crystallographic transgranular fracture in steels.

In this work, we present a new Monte Carlo simulation whose final goal is to study the equilibrium of vacancy-hydrogen clusters at pre-existing crystalline defects, such as grain boundaries (GB) or dislocations. Since realistic defects require at least several thousands of particles in the simulation box, the energetic model is the semi-empirical Embedded Atom Method (EAM) [14]. The equilibrium is treated in the framework of classical statistical mechanics. In the first part, the interatomic potential and the simulation are presented. In the second part, results on $VH_n$ stability and ordering at $C_H$=1% at. and $T\in[300K,700K]$ in the bulk are reported. The interest in $VH_n$ precipitation in larger structures such as chains or platelets originates in a previous simulation work [15] on the H segregation to the $\Sigma=5$ (310) [001] symmetrical tilt boundary. It appeared that H induced a change of the GB core structure which could be interpreted as the formation of deep traps, similar to those in a vacancy. At that time, the creation of vacancies was not considered explicitly in the simulation, so the GB structure was constrained to stay close to its original structure, which is not realistic considering that H embrittlement of grain boundaries are often associated with noticeable amounts of plastic deformation between the two grains.

## METHOD:

The interatomic potential used for this study is an EAM potential. The Al interactions are taken from [16] and the Al-H and H-H interactions have been fitted to reproduce the trapping of H to a vacancy in Al. The details are given in [15]. With this potential, the binding energy to the vacancy of a single H atom is 0.53 eV which reproduces the experimental value of 0.52 eV given by ion-beam experiments [12]. The position is tetrahedral and displaced by 0.32 Å from the bulk tetrahedral position towards the center of the vacancy, along the <111> direction. The H-H interactions are repulsive pair interactions [15]. The formation energies of the $VH_n$ clusters at T=0 and p=0, per hydrogen atom, as well as the mean segregation energy are given in Table 1. The energy reference is the hydrogen in interstitial position in a bulk tetrahedral site.

| $n_H$ | $\overline{\Delta}E_{seg}(eV)$ | $E_f^c(eV)$ |
|---|---|---|
| 0 | 0 | 0.69 |
| 1 | -0.53 | 0.16 |
| 2 | -0.52 | -0.18 |
| 3 | -0.49 | -0.26 |
| 4 | -0.44 | -0.26 |
| 5 | -0.4 | -0.27 |
| 6 | -0.36 | -0.25 |
| 7 | -0.32 | -0.22 |
| 8 | -0.29 | -0.2 |

Table 1 : Mean segregation energy $\overline{\Delta}E_{seg}(eV)$ and formation energy $E_f^c(eV)$ per hydrogen atom computed at T=0 and p=0 (only the configurations of lowest potential energy are represented).

Table 1 shows that at fixed hydrogen quantity and imposed chemical potential for the metal (grand canonical ensemble), the $VH_5$ cluster should be favored at low temperature since it has the lowest formation energy per hydrogen particle. The Monte Carlo simulation will show that at room temperature it is not the case, especially because of the appearance of short range order (SRO).

The Monte Carlo simulation is used to compute statistical averages on microscopic configurations which represent the equilibrium of the system in an ensemble that we chose to mimic a specific experimental situation. This situation is close to what we think approximates the damaging conditions ahead of a stress corrosion crack. That is, the hydrogen is forced into the sample by diffusion from the surface of the crack were repassivation occurs. We skip over the kinetic of hydrogen diffusion and consider a large sample with a fixed hydrogen quantity. We simulate the vacancy creation without any specified microscopic mechanism (which might be, for instance, dislocation annihilation or dislocation recombination at the grain boundaries…) by considering the system in equilibrium with a particle reservoir. This is obtained by imposing the chemical potential of the metal. It is taken as the mean free energy of the perfect crystal at zero pressure. Therefore, in this ensemble, the number of hydrogen particles is fixed and the number of metal atoms can fluctuate. The crystal is represented by a lattice whose nodes are either occupied or empty, like in an Ising model. Furthermore, as relaxations are important for crystalline defects, each occupied node has an extra continuous variable which is the displacement of the particle from its lattice site. The details on the ensemble definition and the simulation will be detailed elsewhere [17]. For a good sampling of the microstates many different Monte Carlo moves are used:

- displacement of the metal and H particles,
- volume fluctuations,
- insertion/removal of metal particles (spin flip on the metal lattice),
- H exchanges between interstitial sites,
- cluster moves, where a vacancy and the H inside it are exchanged with a metal particle, as a single unit.

The computation box is cubic and contains 16*16*16 fcc unit cells which corresponds to 16384 fcc lattice nodes. The quantity of H particles is fixed to 1% of the metal nodes. Periodic boundary conditions are imposed in every direction.

## BULK PHASE DIAGRAM IN Al-H :

We compute the equilibrium superabundant vacancy concentration in the bulk at $C_H$=1% and T between 300K and 700K. Fig.1 shows the convergence of the concentration of the different clusters at T=400K. The dominant species are $VH_2$, $VH_3$ and $VH_4$ (Fig. 2). The total number of vacancies is high (3000ppm). Its main dependance is with H concentration and only to a lesser extent with the temperature and the degree of order.

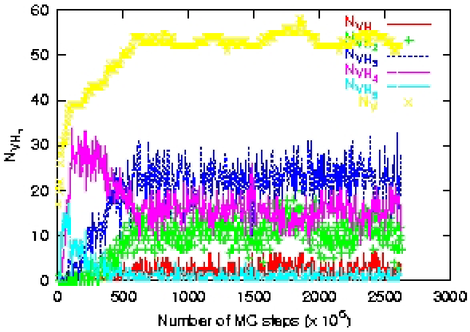


Fig. 1 : Convergence of the vacancy-hydrogen concentrations at T=400K and $C_H$=1%.

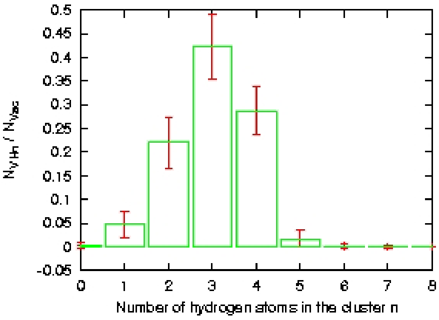


Fig. 2 : Distribution of the $VH_n$ at T=400K and $C_H$=1%. The bars represent the mean square deviation that gives an idea of the concentration fluctuations.

Our main concern is to know if these vacancies have a tendency to segregate. We imagine that nanometer scale tablets or chains of $VH_n$ might have an impact on the mechanical properties either by pinning the dislocations or simply by creating weak points which could be the early stages leading to an embrittled structure. The degree of order is quantified by measuring short range order parameters (SRO) (Warren-Cowley SRO) $\alpha_{nm}$. We compute the pair correlation function:

$$\left\langle p_n p_m \right\rangle = \left\langle p_n \right\rangle \left\langle p_m \right\rangle \left(1+\alpha_{nm}\right) \qquad (1)$$

where $p_n$ is the occupation number on site n and whose value is 0 if the site is occupied by a metal atom and 1 if it is occupied by a vacancy. The brackets represent the statistical average, that is the average over all the microstates generated by the simulation. If no long range order is present, the value of the pair correlation function does not depend on the position n where it is measured, but only on the vector **m**-**n**. Therefore the short range order parameter ($\alpha_{klm}$) is given below (Fig.3) as a function of the lattice vectors (klm) from the origin. If the system is a random solid solution of vacancies, the site occupancies are not correlated ($\left\langle p_n p_m \right\rangle = c^2$). Furthermore, the average occupation on every site is equal to the overall vacancy concentration c. Equation (1) gives $\alpha_{klm}=0$ for a random solid solution. Positive values of $\alpha_{klm}$ indicate that the vacancies tend to cluster (segregation). Negative values correspond to the formation of ordered domains, like the $L1_2$ phase observed in the Ni-25%$VH_6$ system. In this ordered phase, each site has all its first neighbors of the opposite chemical nature. The evolution of the order parameter with temperature at CH=1% is given in figure 3. At high temperature (600K), the order parameter is close to 0 for every pair, except for the first neighbor pair. It means that, even at high temperature, the formation of a cluster of two $VH_n$ is more probable in this system than in a random solid solution. If the temperature decreases, the order parameters rise, especially for the pairs aligned with the <110> directions. This is the signature of the clustering of the $VH_n$ along (110) directions, as it can be checked directly from the microstates (Fig. 4 and 5).

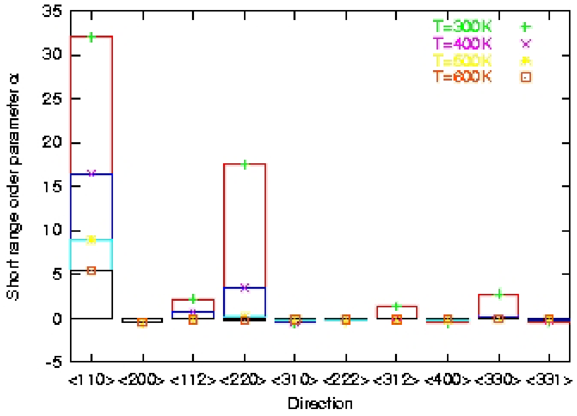
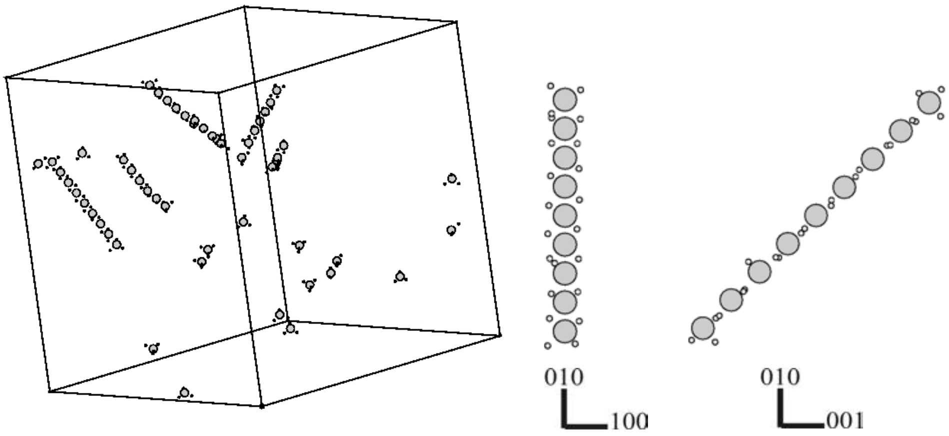


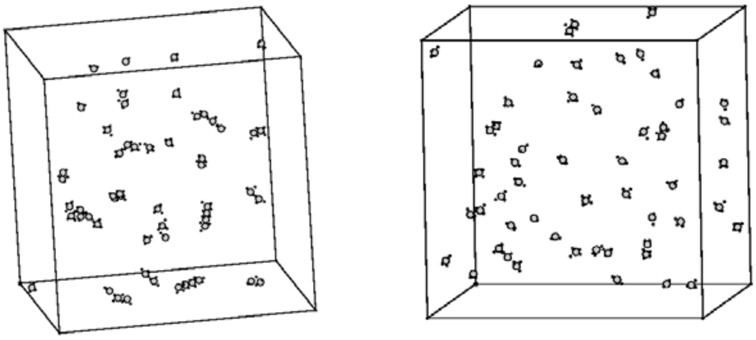
Fig. 3 : Evolution of the SRO parameter (Eq. 1) as a function of the temperature for $C_H$=1%. Note the peaks for the [110], [220] and [330] pairs at low temperature. They correspond to the clustering of mainly $VH_2$ in the form of chains along <110> directions (Fig. 4). (The lattice parameter is normalized to 2.)

It can be mentioned that the clusters only correspond to short range order, that is: they are not localized at a definite position in the system but are only related to vacancy concentration fluctuations and therefore constantly appear and disappear. The distribution of cluster sizes is given in Fig. 6 for T=300K and 400K. Even if the statistics is limited in Fig. 6a, due to the decrease of the acceptance ratio in the vicinity of the phase transition, the histogram clearly shows that large clusters with more than 20 vacancies are not improbable so that the influence of such clusters on the mechanical properties deserves further attention.



(a) (b) (c)

Fig. 4 : (a) A typical microstate of the system representing the equilibrium at T=300K and $C_H$=1%. The large circles are vacancies and the small ones are hydrogen particles (the radius of the vacancy is drawn smaller so that the hydrogen atoms inside the vacancies can be visible). (b) and (c) Details of the $VH_2$ chains lying along (110).

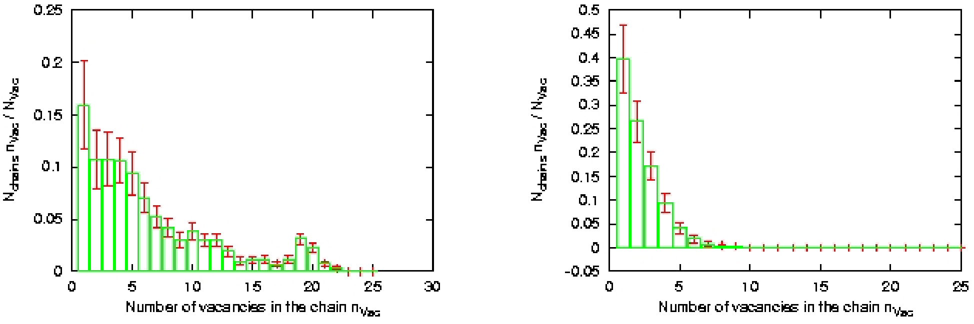


(a) (b)

Fig. 5 : Microstates at T=400K (a) and at T=600K (b) for $C_H$=1%.

## CONCLUSION:

In summary, we have developed a Monte Carlo simulation which describes the equilibrium of a model mixing discrete degrees of freedom (site occupancies) and continuous degrees of freedom (particles positions and volume). The result is the generation of microscopic configurations corresponding to a statistical ensemble where (M, $N_H$, p, T) are fixed. That is, the chemical potential of the metal is preliminary computed for a perfect crystal as a function of T and p, and then, imposed. The number of metal particles can fluctuate, but the system is constrained by the lattice and the maximum number of particles is constant. The system equilibrates by creating vacancies whose concentration depends on the initial concentration of hydrogen in the system, the metal chemical potential (or pressure) and the temperature. The volume fluctuates in a constrained subspace because of the imposed crystalline structure. Specific Monte Carlo moves have been implemented for sampling the configurations of a single vacancy occupied by several hydrogen atoms (H exchanges and displacements), as well as sampling the arrangement of the clusters in the



(a) (b)

Fig. 6 : Histograms of cluster sizes at T=300K (a) and T=400K (b).

system. These are cluster moves where a vacancy and the H contained in it are exchanged as a single unit with a metal particle. This is crucial for the ordering of the clusters.

The simulations show a clear tendency towards demixion. However, at room temperature, the ordering is only short range. With the potential used for the Al-H system, at $C_H$=1% at. the vacancy-hydrogen clusters order in the form of chains lying along <110> directions. At all other temperatures, the SRO is still present, but the chains are smaller.

Future work may be oriented in two directions: first, by generating microscopic configurations with several vacancy-hydrogen cluster concentrations and degree of order, and running a dislocation through it, the pinning effect of such structures could be evaluated; second, the cluster concentration could be calculated at grain boundaries as a function of the orientation. The structure and mechanical properties of the grain boundaries with segregated hydrogen and with segregated hydrogen-vacancy clusters could be compared.

Bibliography:

[1] Y. Fukai, N. Ōkuma, Jpn. J. Appl. Phys. 32 (1993) L1256-1259.
[2] Y. Fukai, N. Ōkuma, Phys. Rev. Lett. 73 (1994) 1640-1643.
[3] Y. Fukai, J. Alloys Comp. 356-357 (2003) 263-269.
[4] Y. Fukai et al., J. Alloys Comp. 356-357 (2003) 270-273.
[5] H. K. Birnbaum et al., J. Alloys Comp. 253-254 (1997) 260-264.
[6] P. Rozenak, E. Sirois, B. Ladna, H. K. Birnbaum and S. Spooner, J. of Alloys and Compounds (2004) under press.
[7] S. M. Myers et al., Rev. Mod. Phys. 64 (1992) 559-617.
[8] J. K. Nørskov and F. Besenbacher, J. Less-Common Metals 130 (1987) 475-490.
[9] S. M. Myers, P. Nordlander, F. Besenbacher and J. K. Nørskov, Phys. Rev. B 33 (1986) 851.
[10] J. P. Bugeat, A. C. Chami and E. Ligeon, Phys. Lett. A 58 (1976) 127.
[11] C. Wolverton, V. Ozoliņš, M. Asta, Phys. Rev. B 69 (2004) 144109.
[12] S. M. Myers, F. Besenbacher and J. K. Nørskov, J. Appl. Phys. 58 (1985) 1841.
[13] Y. Tateyama and T. Ohno, Phys. Rev. B 67 (2003) 174105.
[14] M. S. Daw and M. I. Baskes, Phys. Rev. B 29 (1984) 6443.
[15] D. Tanguy and T. Magnin, Phil. Mag. 83 (2003) 3995.
[16] F. Ercolessi and J. B. Adams, Europhys. Lett. 26 (1994) 583.
[17] D. Tanguy and M. Mareschal (in preparation).