Molecular dynamics based study on the effect of hydrogen on the mechanical properties of Fe-C system

Carlos Martínez¹, Rajwinder Singh¹, Roger Eybel², Mamoun Medraj¹*  
¹Department of Mechanical, Industrial and Aerospace Engineering, Concordia University, Montreal, Canada  
²Safran Landing Systems, Ajax, Ontario, Canada  
*mamoun.medraj@concordia.ca

Abstract — Hydrogen Embrittlement (HE) refers to the degradation of mechanical properties in metals due to the presence of absorbed hydrogen (H) atoms, as these are small and can easily diffuse into the solid metals. As a result, the metallic components can fail catastrophically during service due to HE. Steels susceptibility to HE is one of the main topics in current HE research as H has a high mobility in iron (Fe). In this paper, single crystal from the Fe-C and Fe-C-H systems are modelled using molecular dynamics (MD), in order to study the effects of H on the mechanical properties of the Fe-based materials. The single crystal is subjected to a tensile load in the longitudinal axis for the time necessary to detect differences in the deformation behavior of the material. Four main results are discussed: stress-strain response, change in phase distribution, change in vacancy count and dislocation density. Overall, results show a degradation in the mechanical properties with the random addition of H atoms into the Fe-C system, this degradation being more pronounced as H concentration increases: the peak stress and corresponding strain are reduced, vacancy formation is increased, and dislocation density is reduced. Additionally, a change in phase distribution with applied strain is observed.

Keywords - steel; hydrogen embrittlement; tensile loading; molecular dynamics

I. INTRODUCTION

HE effects on the mechanical properties of structural metals, which often lead to premature or catastrophic failure, have been well recognized for more than a century and attracted a very large research attention for decades [1]. Inherently, HE has been an important issue in industrial applications and is especially concerning in steels because of the high mobility of H in Fe [1]. Extensive experimental work has been done, which has led to the suggestion of various HE mechanisms such as Hydrogen Enhanced Localized Plasticity (HELP), where H accumulated at dislocations, precipitates, and grain boundaries, among other locations, decreases the interaction energy of dislocation-obstacle interactions [2-5]; Hydrogen Enhanced Decohesion (HEDE), which proposes that interstitial H lowers the cohesive strength by dilatation of the atomic lattice [5,6]; Hydrogen Enhanced Strain Induced Vacancies (HESIV), where H enhances the generation of strain-induced vacancies, neatly expressed in its name [5,7–9].

Over the years there has been increased use of atomistic simulations to test nanoscale systems in order to better understand the mechanisms for HE in metals [1,4,10–14]. While MD can help to a great degree in understanding HE in metals (hoping to study mechanisms such as HELP, HEDE and HESIV), it is limited by a few factors, such as the need for a validated interatomic potential, simulations being normally performed at very high loading rates (which minimizes or eliminates important kinetics that happen at lower rates, like H diffusion, plastic flow, and slow crack growth) and limitation of computational power [1,10,11]. These factors are being addressed overtime as more interatomic potentials are developed, validated, and computational power is steadily increased, leading to more complex simulations and reduced computational time. On the other hand, by performing targeted simulations, it is possible to qualitatively (and sometimes quantitatively) evaluate in detail the proposed mechanisms of H effects in metals [11]. Nonetheless, due to the factors already mentioned, MD results must be objectively evaluated based on their dependency on the details of the interatomic potential [10]. While the literature regarding the MD approach to HE in metals is very extensive, there still seems to be an area of opportunity regarding the study of the overall response in the mechanical behavior of Fe-C systems with the addition of H, especially with recently developed interatomic potentials.

In the present work, MD based simulations are carried out to simulate the tensile deformation behavior of Fe-based single crystal due to the presence of H at different concentration levels.

II. MODEL SETUP

All atomic models were created using Atomsk [15,16], which is a command-line program to create, manipulate and convert data files for atomic-scale simulations. The MD simulations are carried out using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD software [17] developed by Sandia National Laboratories. Results from the simulation are mainly post-processed in OVITO (mostly for results visualization and data extraction) [18] and MATLAB (for plot generation and calculations) [19].

This work is sponsored by Safran Landing Systems and the Natural Sciences and Engineering Research Council of Canada (NSERC).
The schematic of the atomic model used to perform the simulations is shown in Fig. 1. The basic model is composed of around 93000 Fe atoms in a Body-Centered Cubic (BCC) phase and 1951 C atoms (which equals to 0.45 weight %), placed at octahedral interstitial sites. The orientation selected is $X[\bar{1}10]$; $Y[111]$ $Z[112]$ and the simulation box dimensions are approximately 69 Å × 48 Å × 321 Å. In this basic Fe-C system, H atoms are added randomly at tetrahedral interstitial sites [20] (which provide potential minima, thus becoming favorites sites) to get concentrations in atomic percent (at. %) of 1, 3, 5 and 8.

The boundary conditions are kept periodic in each axis, meaning that particles can interact across the boundary, and any atom that crosses the boundary re-enters on the other end [21].

III. RESULTS AND DISCUSSION

Even though all the systems are strained up to 1.005, results are taken and analyzed up to a strain of ~ 0.2 as it is more than enough to capture the difference in the deformation behavior among them. Four main results are reported for each system: the strain-stress response, change in phase (BCC, FCC, HCP, and others) distribution with applied strain and change in vacancy count as well as dislocation density with applied strain.

A. Stress-strain response

Fig. 2 shows the stress-strain response for all systems. The stress is extracted directly from the component of the pressure tensor in the Y direction. A general trend is observed where the addition of H lowers the peak stress obtained, and also the strain corresponding to each respective peak stress. Table 1 shows a comparison between the peak stress and the corresponding strain for all the Fe-C-H systems relative to the Fe-C system. This behavior could be due to the HESIV mechanism increasing the formation of strain-induced vacancies and the H facilitating phase transformation more and more as concentration increases. More information is given in the following sections.

![Figure 2. Comparison of stress-strain curves for Fe-C and Fe-C-H systems](image)

<table>
<thead>
<tr>
<th>System</th>
<th>Peak stress (GPa)</th>
<th>Change (%)</th>
<th>Strain at peak stress</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-C</td>
<td>19.70</td>
<td>-</td>
<td>0.0926</td>
<td>-</td>
</tr>
<tr>
<td>Fe-C-H, 1 at.% H</td>
<td>18.96</td>
<td>-4%</td>
<td>0.0886</td>
<td>-4%</td>
</tr>
<tr>
<td>Fe-C-H, 3 at.% H</td>
<td>18.34</td>
<td>-7%</td>
<td>0.0872</td>
<td>-6%</td>
</tr>
<tr>
<td>Fe-C-H, 5 at.% H</td>
<td>17.24</td>
<td>-12%</td>
<td>0.0833</td>
<td>-10%</td>
</tr>
<tr>
<td>Fe-C-H, 8 at.% H</td>
<td>15.30</td>
<td>-22%</td>
<td>0.0773</td>
<td>-17%</td>
</tr>
</tbody>
</table>

B. Change in Vacancy count with strain

The formation of vacancies in the system during deformation is measured with the Wigner-Seitz defect analysis tool [25] inside OVITO. In a general sense, it works by comparing each of the deformed states of the system with sites established in the reference state (just before loading). If any site has a change in the number of atoms (i.e. either more or fewer atoms) a defect is detected. When a site is not occupied by at least one atom anymore, it is counted as a vacancy.
As shown in Fig. 3 and Table II, the number of vacancies formed increases with H concentration. Table II compares the number of vacancies formed at a strain of 0.2. It can be noted that the drastic increase in the number of vacancies happens at the strain where the peak stress is obtained in each system, and then increases steadily again. This could be attributed to the drastic change in the phase relative distribution right after the peak stress is reached (in which coincidentally vacancy formation increases drastically at this point), but after this drastic transformation takes place, it slows down significantly. More details about phase transformation are shown in the next sections.

![Vacancy Count With Applied Strain](image)

**Figure 3.** Comparison of increase in vacancy count with applied strain among Fe-C and Fe-C-H systems

<table>
<thead>
<tr>
<th>System</th>
<th>Number of vacancies</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-C</td>
<td>9929</td>
<td>-</td>
</tr>
<tr>
<td>Fe-C-H, 1 at.% H</td>
<td>11866</td>
<td>20%</td>
</tr>
<tr>
<td>Fe-C-H, 3 at.% H</td>
<td>13024</td>
<td>31%</td>
</tr>
<tr>
<td>Fe-C-H, 5 at.% H</td>
<td>14374</td>
<td>45%</td>
</tr>
<tr>
<td>Fe-C-H, 8 at.% H</td>
<td>16075</td>
<td>62%</td>
</tr>
</tbody>
</table>

Li et al. [14] reported the interaction of dislocations and hydrogen-vacancy complexes in α-Fe using MD simulations and revealed that, unlike a lattice vacancy, a hydrogen-vacancy complex is not absorbed by dislocations moving through the lattice. This thereby increased vacancy concentration upon plastic deformation in α-Fe system with H. Based on these results, H could very well be playing a role in forming more vacancies and resisting their absorption by dislocations during plastic deformation.

Matsumoto et al. [4] studied the effects of H in BCC Fe by performing three kinds of MD simulations (crack growth, nanoindentation, and tensile loading), using an interatomic potential for BCC Fe modified to include pseudo-hydrogen thermodynamic effects on the lattice defect energies. They confirmed that both yielding and rupture occur earlier in the model and presented a small amount of dislocation motion before rupturing in a brittle manner along the grain boundaries. Also, an increase in the generation of vacancies during loading is observed, agreeing with the HESIV mechanism. On the other hand, in the Fe simulated without pseudo-hydrogen effects, intergranular fracture did not occur, and a large amount of dislocation motion was observed. In addition, the nanoindentation simulation shows the generation of many vacancies throughout the sample simulated with pseudo-hydrogen effects, confirming again the HESIV mechanism at play. Between these outcomes, the HESIV mechanism can be directly related to the results presented in this paper, as increasing H concentration increases the vacancies formed with applied strain.

Sugiyama and Takai [26] experimentally studied the role of H in the formation behavior of various lattice defects in pure Fe specimens, induced by plastic strain, using low-temperature thermal desorption spectroscopy (L-TDS). It was concluded that H effectively enhances vacancy formation and localization of dislocation configuration near the grain boundaries, but without affecting the number of dislocations formed. This can serve to support current simulation results, as experimentally it is shown that vacancy formation during applied strain increases as H concentration increases.

### C. Change in phase distribution with strain

Phase type identification is performed using the Common Neighbor Analysis (CNA) tool in OVITO [27]. Before loading, the basic phase arrangement is mostly BCC and the rest is “Other”. This is due to the presence of interstitial atoms (both C and H) that distort the basic BCC arrangement. As such, OVITO identifies those as a non-standard phase under the label “Other”. As the C content is kept constant, increasing H concentration increases the number of non-standard phases and decreases the amount of BCC phases before loading. Another phenomenon is that, in all systems, the amount of HCP and FCC phases that form during loading, become more significant as H concentration is increased. As they even appear in the Fe-C system, it is believed that the presence of interstitial C plays a role in the conversion from BCC to FCC and HCP, and increasing H concentration accentuates this conversion. This is confirmed by running a pure Fe system, resulting in no phase transformation from BCC to FCC and HCP. Fig. 4 shows the phase distribution in the Fe-C system, Fig. 5 in the Fe-C-H system with H concentration at 3 at. %. By comparing both figures visually, it can be seen that a higher amount of BCC phase transforms to FCC and HCP. Fig. 6 shows the phase distribution for the pure Fe system, with no transformation as mentioned before.

Jiang et al. [28] studied the effects of vacancies on plasticity and the phase transformation of single crystal iron under shock loading, performing MD simulations. It was observed that vacancies and vacancies-induced dislocations loops provided preferential nucleation sites for transformation, facilitating phase transition from BCC to HCP. This could explain, in a sense, why the phase transformation occurs earlier in the presence of H, as vacancies increase with H concentration.
Nguyen et al. [29] studied the BCC to FCC phase transition induced by interstitial C in Fe, performing first-principles simulations, and concluded that C at the octahedral interstitial sites promotes the transformation from BCC to FCC while it prevents the transition in the opposite direction. Moreover, Castedo et al. [30], performing first-principles simulations, studied the role of interstitial H on the phase transformation of iron from BCC to HCP along Bain’s pathway. They concluded that the presence of H at the octahedral interstitial sites creates an internal stress field that can be released via the distortion of the lattice, promoting BCC to FCC to HCP transformations. The findings from these two different texts support the results shown in this writing. Rohr et al. [31] studied the behavior of high-strength steel (NiCrMoV) over a wide range of strain rates (reaching as high as 1.78 x 10⁶ s⁻¹), performing various tests (tensile tests, modified Taylor impact and planar plate impact) and observe that a BCC to HCP transformation takes place at high pressures (in excess of 13 GPa), which is comparable to the stress range obtained in our simulations. Luu and Gunkelmann [32] studied the pressure-induced phase transformation in Fe and Fe-C using molecular dynamics, albeit performing hydrostatic and uniaxial compression (instead of tensile loading) in single crystal and polycrystalline systems. They employed several EAM potentials, coupling a recently developed Fe potential that closely describes BCC to HCP transition in Fe with several well-known Fe-C potentials. They observed this phase transformation at high pressure (around 39.3 GPa). Interestingly, they reported that C increases the transformation energy barrier, raising the Fe-C phase transformation pressure by a factor of 1.5. With these results in mind, it would be interesting to additionally vary the C concentration and monitor how it affects the phase transformation, as the C weight % was not altered in the present work. This can be considered in the future.

Koyama et al. [33] studied the effects of H on γ (FCC)-ε (HCP) martensitic transformation in an Fe-15Mn-10Cr-8Ni steel, performing tensile tests with and without H. It was concluded, among other things, that H increases the elastic strain energy required for ε-martensite nucleation, but also increases the number density and fraction of ε-martensite at an identical strain, promoting a nucleation process associated to dislocation motion. This can be generally compared to the results shown in this paper, as they indicate more HCP phase formation as H concentration increases.

D. Change in Dislocation density with strain

Using OVITO dislocation analysis (DXA) tool [34,35], dislocation data can be extracted from each system. It identifies all the defects in the crystal, determines the Burgers vectors and outputs a line representation of the dislocations. Each one of these representations has a starting point and an endpoint, the two defining the orientation of the dislocation line, which can be connected to other dislocation lines (forming a junction). The dislocation line color refers to the type of dislocation: green represents 1/2 <111> (which is the vast majority dislocation type shown) and pink <100> . By using this tool in all systems, the number and length of dislocations were extracted, and dislocation density (nm/μm³) was calculated. As a general pattern, it can be seen that increasing H concentration results in a decrease in dislocation density. Nonetheless, in the system with 1 at. % H, the dislocation density starts to increase from a strain of ∼0.15 and is actually the highest at a strain of 0.2 as shown in Fig.7. In addition, Fig. 8 shows a visual comparison between the Fe-C and Fe-C-H systems with 3 at. % H, for both the phase and dislocation distribution. The state shown is at a strain level with one of the highest dislocation densities in the Fe-C system (strain of ∼0.125). Likewise, the Fe-C-H system is shown at the same strain level. By comparing visually, the dislocation density is lower in the Fe-C-H system, as illustrated by the shorter lines of dislocations compared to the Fe-C system. This could be due to the HELP mechanism, enhancing the
mobility of dislocations. However, this needs further investigation.

![Dislocation Density With Applied Strain](image)

**Figure 7.** Variation in dislocation density with applied strain for Fe-C and Fe-C-H systems

**Figure 8.** Comparison of phases and dislocation distributions between Fe-C and Fe-C-H (3 at. % H) systems at similar strain level of $\sim 0.125$

### IV. CONCLUSION

This paper compares the Fe-C and Fe-C-H systems and finds that hydrogen significantly affects the system's mechanical properties during tensile loading, as evidenced by changes in stress-strain curves, increased vacancy formation, and reduced dislocation density. It suggests that hydrogen facilitates the transformation of the BCC phase into the FCC and HCP phases, but the role of carbon in initiating this conversion is not fully established in the literature.

This study lays the foundation for further research on the impact of hydrogen on the mechanical behavior of Fe-C systems. Future studies could include varying carbon concentration, testing under compressive loads, using larger models, utilizing polycrystalline models, and incorporating cracks in the system.

### ACKNOWLEDGMENT

Many thanks to the Digital Research Alliance of Canada for providing great HPC service and very attentive support to run all simulations.

### REFERENCES


