

## MOLECULAR DYNAMICS SIMULATIONS OF HYDROGEN-DISLOCATION INTERACTION IN IRON NANOCRYSTALS

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**Abstract.** Hydrogen embrittlement of steels, and in metals in general, has been a subject of interest for the last sixty years. Nevertheless, the very specific mechanisms of embrittlement are still argued, where mixed effects of material characteristics are expected to play a role on the embrittlement/failure of the material. In the current study, atomistic simulations for iron nano-pillars (BCC) are conducted, with the existence and absence of hydrogen atoms, to study the hydrogen embrittlement phenomena. A focus is put on studying hydrogen's effect on plasticity evolution, e.g. the evolution of dislocation-densities under the existence of hydrogen atoms; The atomistic simulations help to give a new insight into the phenomena, by rather focusing on collective hydrogen interaction with existing dislocation networks in the material, along with the effect of hydrogen on densities evolution over time. Furthermore, a study of several models with different sizes, initial dislocation-densities and hydrogen concentration is conducted to study these effects on hydrogen embrittlement phenomena.

### 1 INTRODUCTION

Hydrogen embrittlement of steel, has been a subject of interest for the last sixty years. The phenomena is well documented to cause early failure of steel at lower stresses and strain loads, thus been considered as a critical risk due to its potential for causing catastrophic failure, endangering lives and properties. Reduction in ultimate strengths and ductility, initiation and acceleration of cracking, blister forming, cold cracking, flaking, and contribution to stress corrosion cracking, are some of the main effects of hydrogen on steel. Some of these diverse effects can be mainly attributed to the switch to a non-ductile fracture mode.

The complexity of hydrogen interaction with steel and its failure, made it very complicated to develop a unified understanding of the hydrogen embrittlement mechanism. Experimental studies up to date offered conflicting results; for example, while some researchers reported a decrease in flow stress in Fe [1,2,3] in the presence of hydrogen, others reported an increase in the flow stress[4,5]. Therefore, even with the huge literature and research efforts done so far, a single dominant mechanism cannot be defined.

The two major accepted mechanisms for explaining hydrogen embrittlement are Hydrogen Enhanced Decohesion (HEDE)[6,7], and Hydrogen Enhanced Localized Plasticity (HELP)[8]. The HEDE mechanism simply proposes that dissolved hydrogen weakens the atomic binding forces in the metal lattice, resulting in the possibility of premature brittle fracture; this is mainly attributed to the easier propagation of cracks in the metal due to the weaker bonds. The HELP mechanism proposes that hydrogen influences the plasticity of the metal, as a result of the interaction with existing dislocations. Hydrogen is proposed to enhance dislocation mobility. This is supported by evidence of increased dislocation mobility observed in *in situ* TEM experiments[9,10,11]. However, the HELP mechanism by itself can't explain the premature fracture phenomenon caused by hydrogen.

Better understanding of the role of the hydrogen will result in reliable computational models that incorporate hydrogen effects and diffusion through dislocation-densities evolution laws. These models will be able to capture materials behavior over several length scales. Previous development has resulted in identifying the specific mechanisms for strengthening and toughening high-strength steel alloys, as well as specific techniques to control localization in these microstructures [12,13]. Optimization of the microstructure shall provide an alternative approach to control hydrogen diffusion and therefore its impact on the mechanical properties of different materials including high-strength steel alloys.

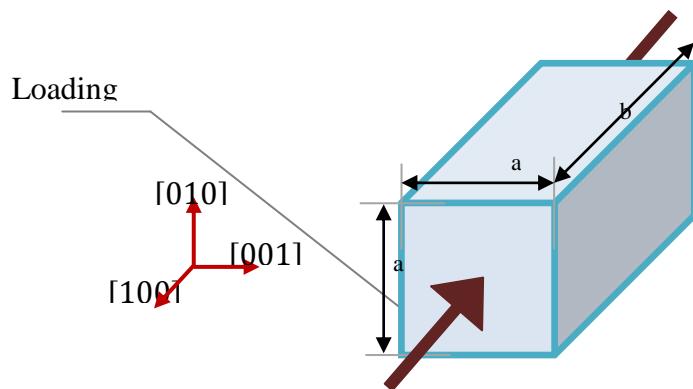
In this paper, atomistic simulations been performed to study the collective effect of hydrogen on plasticity evolution in BCC Iron nano-pillars; the simulations provides an insight of how does dissolved hydrogen affect existing dislocation networks. The current work focuses on studying plasticity evolution in single crystal  $\alpha$ -Fe, through studying dislocation-densities evolution under uniaxial load, with and without the existence of hydrogen. Different pillar sizes, hydrogen concentration, and initial dislocation-densities were studied to help understand some of the hydrogen effects on plasticity of Iron.

## 2 METHODOLOGY

The atomistic simulations in the current study been conducted using LAMMPS[14]. The details of the interatomic potential for hydrogen-iron interaction in BCC iron[ $\alpha$ Fe-H] are reported by Ramasubramaniam et al.[15]. Square prism  $\alpha$ -Fe single crystals were studied; two different cross sections of 20x20 and 40x40 nm are reported. The pillars have [100] crystals orientation relative to the loading direction. Periodic boundary conditions were employed along the loading direction of [100], while the other surfaces were kept as free surfaces. The length of the crystal along the periodic direction is 40 and 60 nm for the small and the large models respectively; this resulted in a size of about 1,391,00 and 8,291,00 atoms for both models. Two different concentrations of hydrogen are assumed; 20 and 40 mass ppm for the charged models; along with the uncharged (0 ppm) models. For charged models, hydrogen atoms were randomly introduced into tetrahedral sites in the iron lattice, as an energy

favorable site of hydrogen in BCC iron cells[16].

In order to study the plasticity evolution effect, different Initial dislocation-densities been introduced for each size of the model; an initial number of 64, 128, and 256 random edge/screw dislocations simulating the different  $\{110\} <111>$  slip systems are reported for each model size and hydrogen concentration. Dislocations were introduced using the anisotropic displacement field reported in the following study[17]. Each number of initial dislocations corresponds to a different initial dislocation density, dependent on the model size; for statistical analysis, the evolution of dislocation densities was studied as a percentage of the initial dislocation densities.



**Figure 1:** Sketch Of Model Cell And Loading Directions

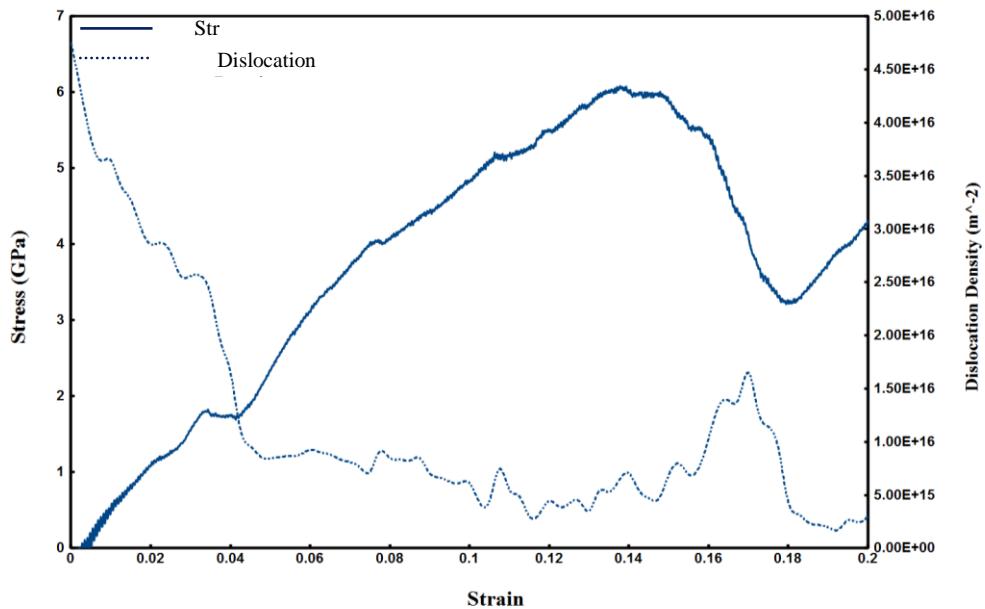
The atomistic simulation starts with energy minimization, where atoms are relaxed using a conjugate gradient algorithm in order to minimize the total potential energy at 0 K. Energy minimization is allowed to run for 1 ps. Next, the system temperature increases to 300° K and relax for a period of 20 ps. This step will allow the system to reach an equilibration state before applying the load. Equilibration occurs under a canonical NVT (constant number of atoms, volume and temperature) ensemble with a Nosé-Hoover thermostat. The model is deformed by compressing the pillar with a constant engineering strain rate of  $10^8 \text{s}^{-1}$  along the [100] direction and up to a 20%engineering strain. A time step of 1 fs is applied. The temperature is kept constant at 300 K along deformation using a Nosé-Hoover thermostat under canonical NVT. Visualization of dislocation networks is achieved using the Common Neighbor Analysis (CNA) method[18,19]; AtomEye[20] and the DXA tool[21] combined with ParaView were both used alternatively to analyze the system.

### 3 RESULTS

In this paper, 18 different models has been studied, comprising two different model sizes, three hydrogen concentrations, and three initial dislocation densities. A focused study will be presented on one of the small models without/with hydrogen, to illustrate the deformation behavior for the Fe nano-pillar in general and show the hydrogen effect on it. At the end, a statistical analysis is performed using all the 12 models to draw conclusions on the effect of hydrogen on deformation in  $\alpha$ -Fe.

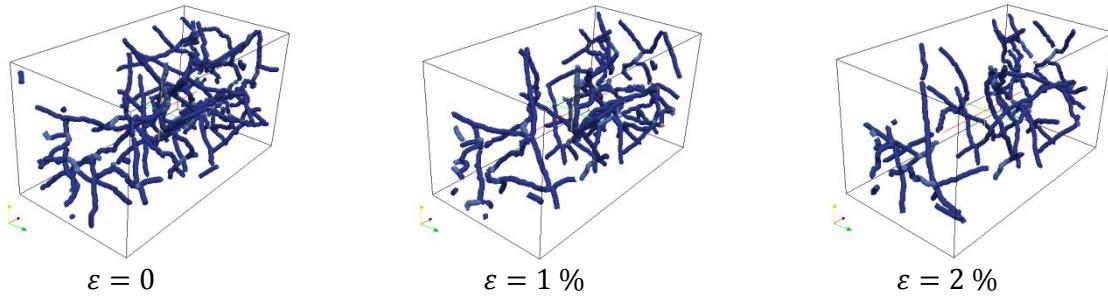
### 3.1 Results Of Small Size Model (20x20x40 nm) - Without Hydrogen

The current result is of a model with dimension of (20x20x40 nm) and initial dislocation-densities of  $4.75 \times 10^{16} \text{ m}^{-2}$  and no hydrogen been introduced. The model initially contains 64 dislocations, which corresponds to a dislocation density of  $4.75 \times 10^{16} \text{ m}^{-2}$  that can be considered as a high dislocation-densities. The stress-strain behavior along with the corresponding evolution of dislocation densities for the model is shown in Figure 2.



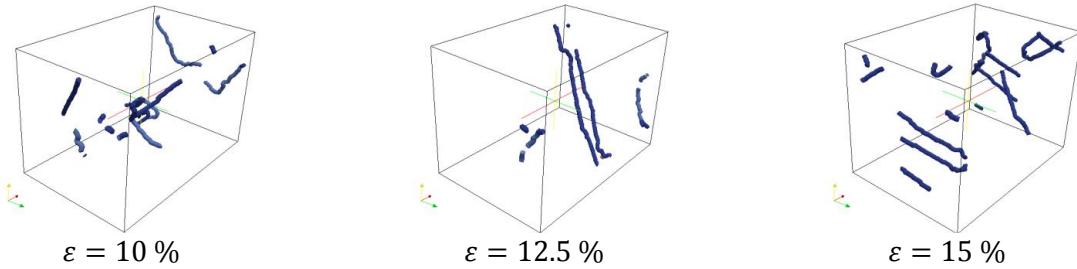
**Figure 2:** Stress-Strain Vs. Dislocation Density Evolution - Iron Only Model

A careful study of the stress-strain and dislocation densities curves shows the model deformation behavior can be explained by two main stages. The first stage, which extends up to 8%, strain is marked by continuous reduction in the dislocation-density; the dislocation-density decreases from  $4.75 \times 10^{16} \text{ m}^{-2}$  to  $8.44 \times 10^{15} \text{ m}^{-2}$ . This reduction is a result of dislocations escaping to the free surface of the nano-pillar. Where, the rate of dislocations escape is higher than the rate of dislocations nucleation that causes the continuous drop in the dislocation-density in this stage of deformation. Dislocation near the free surfaces are the first to escape as expected, Figure 3, while most of the dislocations located at the center of the model are kept intact. This can be explained by the dislocation stress field of other surrounding dislocations that act as obstacles to their movement. Nevertheless, once the applied stress is high enough to overcome other dislocations stress field the dislocations at the center start to move to the free surface where they are annihilated. The rapid escape of dislocations to the surface can be shown in the fluctuations of the stress-strain curve, especially for the first 4% strain. The fluctuation is a result of continuous stress relief due to the successive dislocation gliding and annihilation.



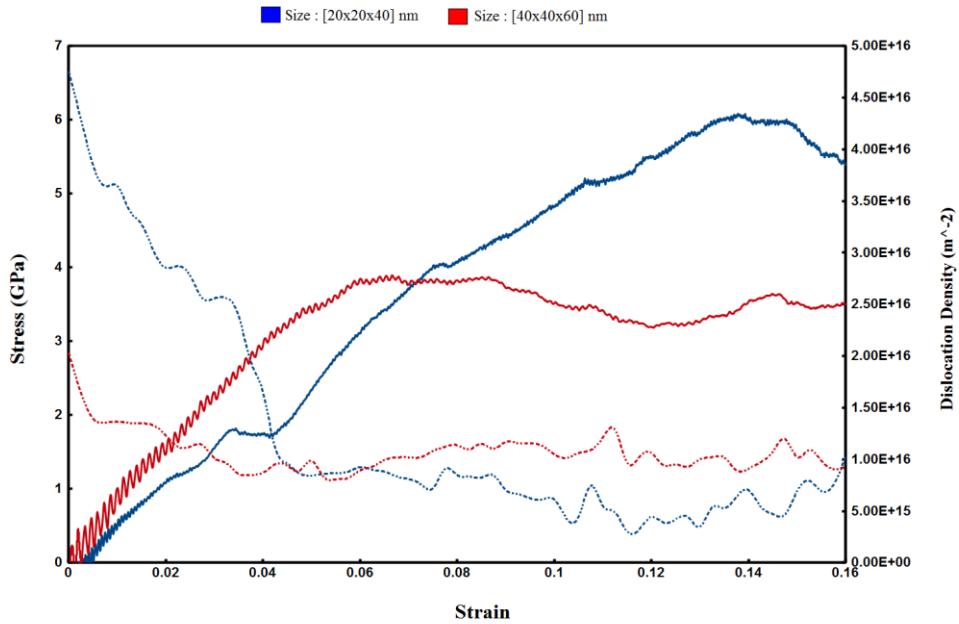
**Figure 3:** Initial Retention Of Dislocations Near The Core; Dislocations Near The Surface Escape First

In the second stage, dislocation-density reaches an equilibrium state where the dislocation escape-rate becomes almost equivalent to dislocations nucleation-rate as shown in. Figure 4. Dislocation nucleation can be the result of dislocation emission from immobile defects and/or surface-assisted dislocation nucleation; where the latter mechanism of dislocation nucleation has been reported as the predominant mechanism in nano-pillars of the current size scale[22,23,24].

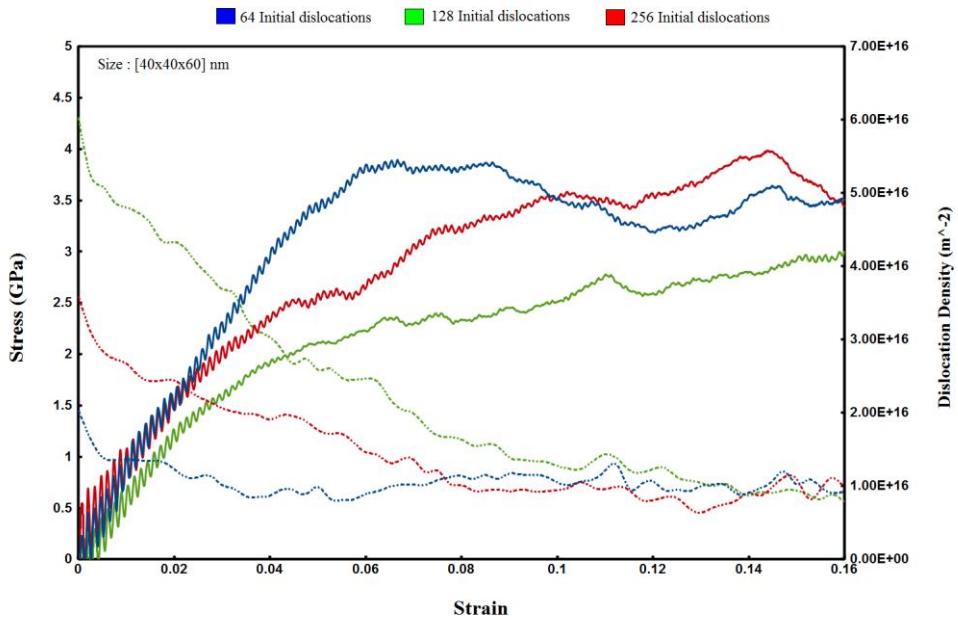


**Figure 4:** An Almost Constant Dislocation Density; Rate Of Exhaustion = Rate Of Nucleation.

The deformation behavior compassing the above two-stages was found for all the models in the current study. The larger-size models shows a distinction between both stages as well; with only variance being the lower stresses and higher dislocation-densities at the second stage as shown in Figure 5. This imply that the larger size model has higher dislocation-density at the second stage of dislocation where rate of exhaustion = rate of nucleation. This can be attributed to the ability of the larger size to nucleate more dislocation as it has a higher surface area, thus increasing the possibility of surface-assisted nucleation. The saturating dislocation-density in the second stage found to be related to the model size. Figure 6. Compare models of the same size and different initial dislocation-densities that illustrate the same saturation dislocation-density; where the high density model exhibits a high dislocation exhaustion rate up to the saturation level. Therefore, initial dislocation-density effect is only limited to the first stage of deformation where an increase of dislocations exhaustion rate is illustrated up to the start of the second deformation stage where the rate of exhaustion = rate of nucleation.



**Figure 5:** Comparison Between Models Of Different Sizes With The Same Initial Number Of Dislocations

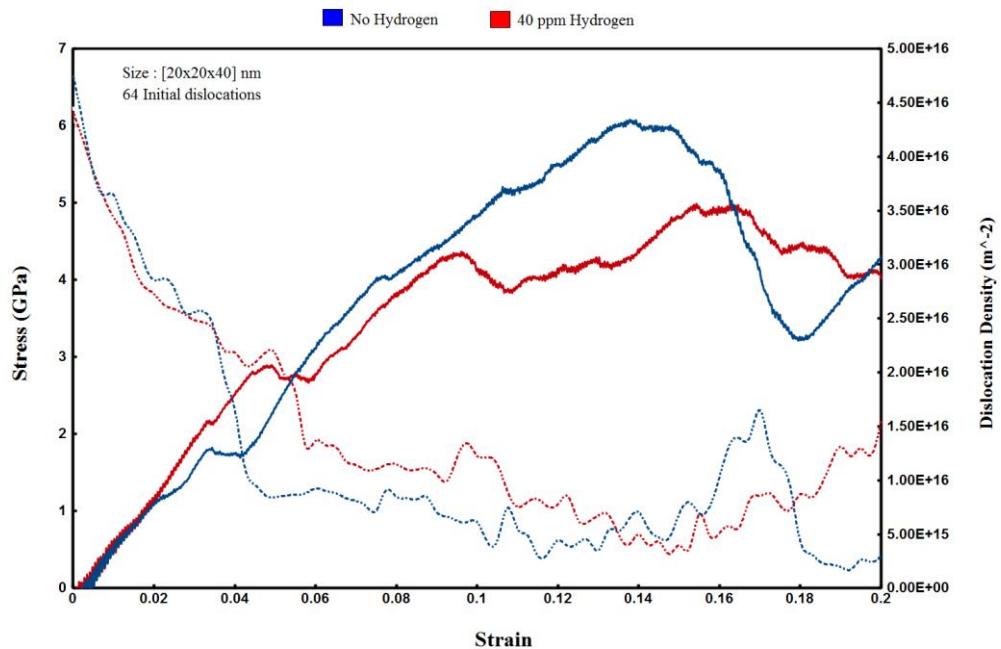


**Figure 6:** Comparison Between Models Of The Same Size, With Different Initial Dislocation Density

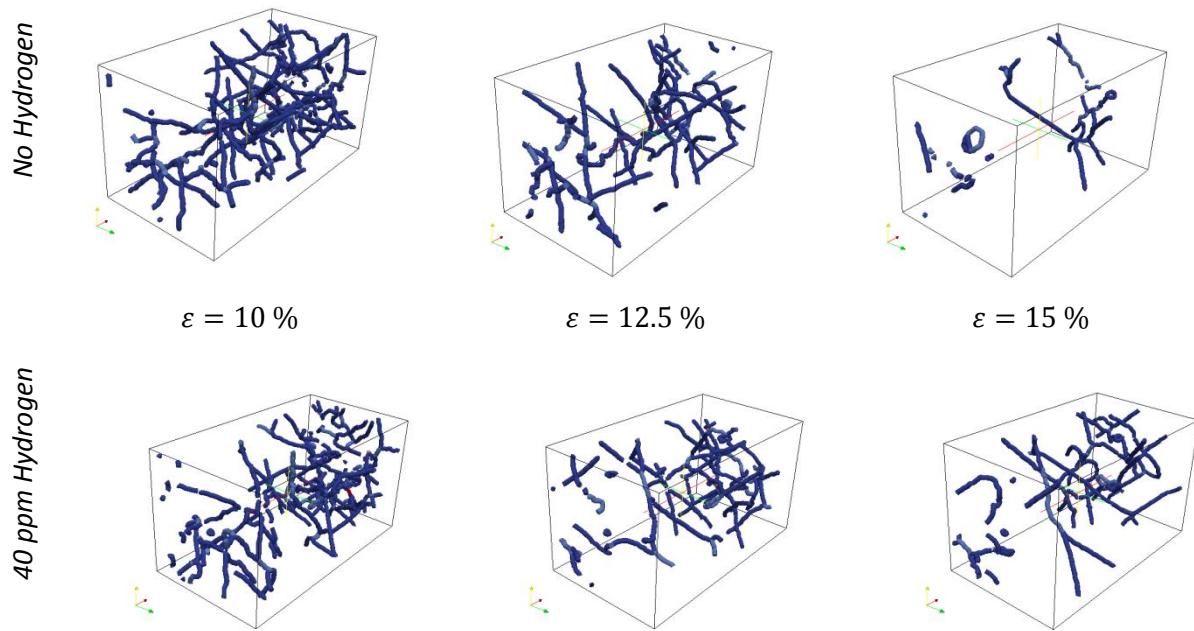
### 3.2 Results Of Small Size Model (20x20x40 nm) - Charged [40ppm Hydrogen]

The uncharged models studied above are now to be compared with a charged models of the same size and initial dislocation density; the only difference is the hydrogen content. The stress-strain curve along with dislocation density evolution is shown in Figure 7.

An examination of the figure shows that Hydrogen has a clear effect on the first stage of deformation, as it is clear that the charged model maintains a higher dislocation-density throughout the first stage up to the saturation of dislocation-density level. The described effect suggests that hydrogen reduces the rate of dislocation escape to the free surfaces.



**Figure 7:** Comparison Between Charged And Uncharged Models



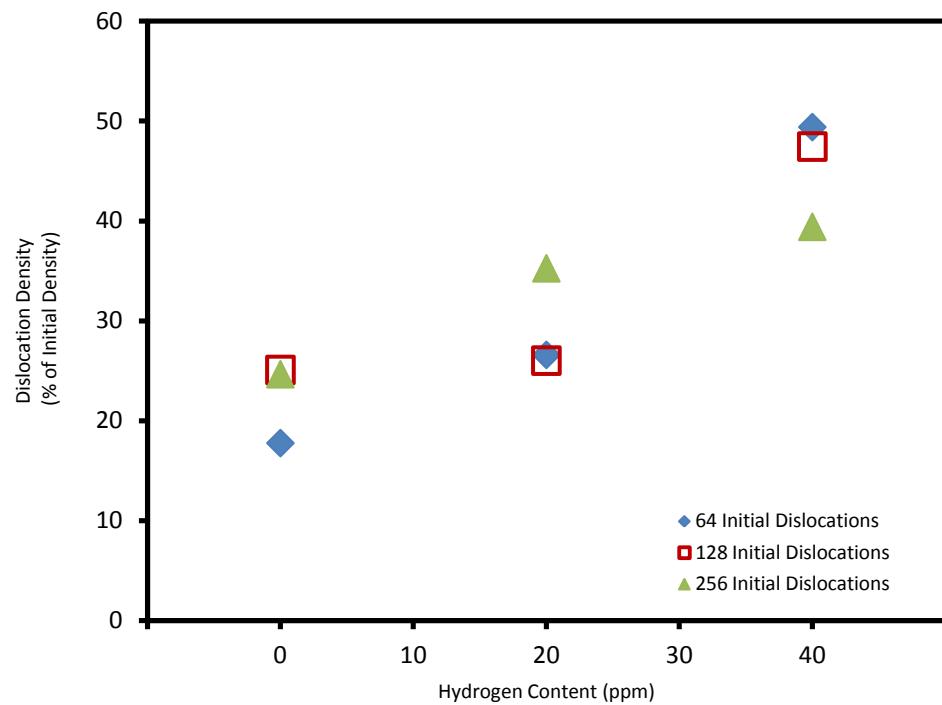
**Figure 8:** Initial Dislocation Density Retention For Uncharged And Charged Models

Figure 8 further signifies the effect of hydrogen on the existing dislocations-network; the figure clearly shows how the charged model is able to retain a higher dislocation-density. This behavior suggests that hydrogen makes it more difficult for existing dislocations to escape to the surface by acting as an obstacle to their movement to the surface. This contradicts the suggested effect of hydrogen to increase dislocation mobility, and rather has a halting effect on dislocation especially with the presence of high dislocation-densities.

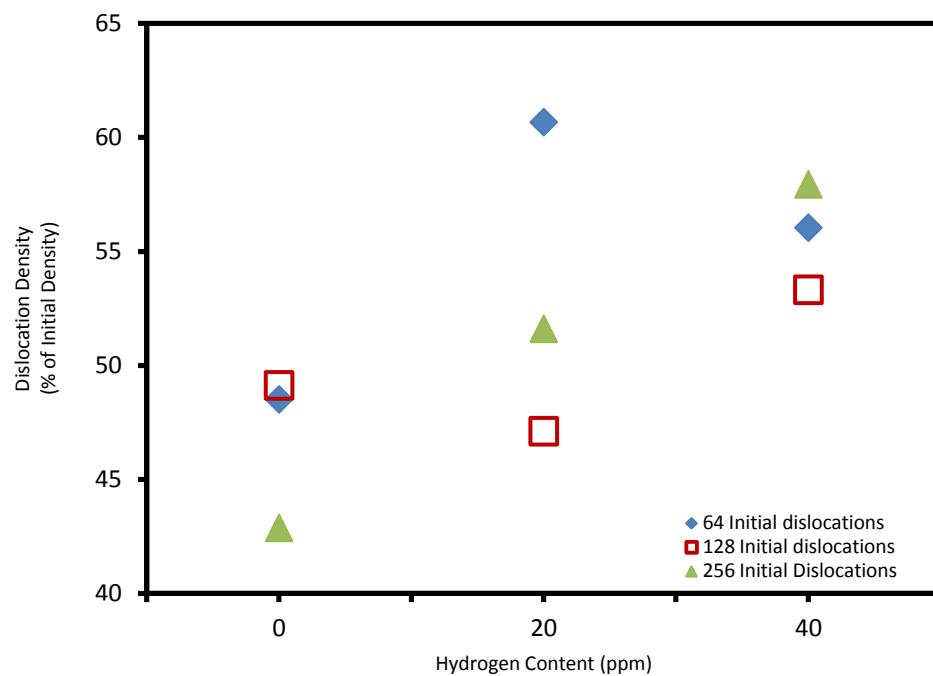
### **3.3 Statistical Analysis of Hydrogen Effect On The Retention Of Initial Dislocations Densities**

The effect of hydrogen on the retention of initial dislocation densities was observed in all the 12 charged models; a plot of the dislocations densities as a percentage of the initial dislocation-density for charged and uncharged models are shown in Figure 9 and Figure 10. Figure 10. clearly shows the effect of hydrogen in the first stage of deformation. Performing statistical analysis using the analysis of variance (ANOVA) technique, on the percentage of retained dislocation densities for both the charged and the uncharged models, using a 95% confidence interval, shows that the difference between the models is statistically significant; analysis is carried out for each model size separately, and each analysis proves that hydrogen has a statistically significant effect on dislocation retention or the dislocation escape rate at this deformation stage.

However, stresses variance for both uncharged and charged models is not significantly different, under the same analysis conditions. The effect of increasing the hydrogen concentration from 20 to 40 ppm was not proven statistically significant as well; however, comparing any of the two concentrations with uncharged models show that hydrogen, has an effect on the dislocation escape rate; it is however unclear what effect does have increasing or decreasing the hydrogen content on the pronunciation of that effect on dislocations. Further studies with different Hydrogen concentration is proposed in the future to identify the effect of increasing and decreasing the concentration of hydrogen, and whether it directly affects the ability of the material to retain initial dislocations i.e. the higher hydrogen concentration, the higher the retention of initial dislocations; or to determine if it is just a matter of a certain threshold of concentration needed to obtain and maintain this effect.



**Figure 9:** Retention Of Initial Dislocation Densities Versus Hydrogen Content [Small Models]



**Figure 10:** Retention Of Initial Dislocation Densities Versus Hydrogen Content [Large Models]

#### 4 CONCLUSIONS

Atomistic simulations for BCC iron-hydrogen system have been conducted to study the Hydrogen embrittlement phenomena; 18 different models has been studied and compared, comprising two different model sizes, three hydrogen concentrations, and three initial dislocation densities. Iron is proven to be sensitive to hydrogen content; its deformation behavior varies under the influence of hydrogen. Hydrogen atoms act as an obstacle to initial dislocations movement; impeding their movement and reduces their rate of escape to the surface. Therefore, hydrogen enables the material with high initial dislocation densities to retain their initial densities and reduce their exhaustion rate.

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