

A Theoretical Investigation on the Role of Microstructural Particularities on the Hydrogen Embrittlement of Nickel Alloys

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ABSTRACT

Precipitation hardened (PH) nickel alloys have been extensively used in diverse applications in the oil and gas industry due to its high strengths and outstanding corrosion resistance in several aggressive environments. Despite of their known high corrosion properties, hydrogen embrittlement is one common failure reported by the industry for this class of alloys.

PH nickel alloys exhibit complex microstructures, composed by diverse secondary phases. Numerous research activities to study the mechanisms behind hydrogen embrittlement have been carried out in the last years and are still a point of debate in the oil and gas community, mainly when it comes to the interaction of these microstructural features with the hydrogen uptake provided by the service environment. Several mechanisms have been proposed to explain the role of hydrogen in the microstructure of metallic materials. Hydrogen enhanced decohesion (HEDE) has been proposed as the mechanism behind the intergranular character of some of the fracture surfaces, being explained by the presence of grain boundary decoration. However, materials having a very limited amount of precipitates in the grain boundaries still can be susceptible to hydrogen embrittlement. When presenting a transgranular failure mode, the mechanism proposes that the cohesive strength between the metal atoms is reduced by the presence of hydrogen in the bulk. In spite of these observations, limited work is available in the literature in regards to microstructure features and a complete understanding of their roles on the hydrogen embrittlement.

This work is based on a cooperation with the Max Planck Institute for Iron Research in Düsseldorf, Germany. The interaction of hydrogen with microstructure elements primarily present in nickel-based alloys was fundamentally studied using ab-initio and atomistic models, showing that the strength and

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hardness levels are not primarily decisive for the susceptibility to hydrogen embrittlement, but rather the microstructure.

Key words: Precipitation Hardened Nickel Alloys, Hydrogen Embrittlement, ab-initio calculations, simulation and modeling, corrosion resistant alloys

INTRODUCTION

Precipitation hardened (PH) nickel alloys have been broadly used in various applications in the oil and gas industry thanks to its high strengths and outstanding corrosion resistance in several aggressive environments. Alloy 718 (UNS¹ N07718), Alloy 925 (UNS N09925), Alloy K-500 (UNS N05500), Alloy 725 (UNS N07725), and others are among the most used PH nickel alloys in the oil and gas industry. Despite of their known high corrosion properties, hydrogen embrittlement is one common failure reported by the industry for this class of alloys.¹⁻⁴

Most of the PH hardened nickel alloys, due to the fact of being alloyed with niobium, titanium and/or aluminum, are hardened through the precipitation of the intermetallic phases Gamma-Prime, a cubic face-centered L₁₂ ordered Ni₃(Al,Ti) phase, and Gamma-Double-prime, a cubic face-centered DO₂₂ ordered Ni₃Nb phase. Additionally, these alloys may precipitate the non-avoidable carbonitrides, and the Delta and Eta phases, which can be detrimental to the alloy's mechanical and corrosion properties.

The precipitation of diverse secondary phases concedes to PH nickel alloys complex microstructures, which have been incentive for numerous research activities to study the mechanisms behind hydrogen embrittlement. The outcomes of these researches are commonly in debate within the oil and gas community, mostly in the matter of the interaction of microstructural features with the hydrogen uptake provided by the service environment.

Diverse mechanisms have been proposed to explain the numerous aspects observed. When the fracture surfaces present an intergranular character, the fracture is elucidated by the presence of grain boundary decoration. Hydrogen Enhanced Decohesion (HEDE) is the name given for this suggested mechanism. However, the current state of the art of manufacturing processes enables the production of materials having a very limited amount of precipitates in the grain boundaries. Even with grain boundaries with less precipitation or free of precipitation, PH alloys can still be susceptible to hydrogen embrittlement.⁵ In these cases, a transgranular mode of failure is usually detected. For these fractures, the mechanism proposes that the cohesive strength between the metal atoms is lowered by the presence of hydrogen in the bulk material. In spite of these observations, limited work is available in the literature in regards to microstructure features and a complete understanding of their roles on the hydrogen embrittlement.

The HEDE mechanism seems to be the most relevant for the present alloys, however it neglects the effects of hydrogen on the ductile processes.

AB-INITIO CALCULATIONS

Initial Considerations for system simplification

All of the phases present in the precipitation hardened nickel alloys obviously present a very complex chemistry. For example, in the Gamma-Prime phase, it is known that titanium may be present as a substitute element for aluminum in Alloy 718.⁶ Nevertheless, the inclusion of the full chemical complexity

¹ Unified Numbering System (UNS)

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of phases and matrix is not feasible on the simulations and therefore all of the participating phases were simplified to make the calculations possible. In Alloy 718, for example, the relevant precipitates are Gamma-Prime, Gamma-Double-Prime, Delta-Phase and the Niobium-Carbides. The Gamma-Prime was considered in the simulations to be composed only by nickel and aluminum (Ni_3Al). The Gamma-Double-Prime was considered to be composed by nickel and niobium only (Ni_3Nb), as well as the Delta-Phase. The carbide phase was considered to be formed by carbon and niobium, only. Taking that in consideration, example atomic cell arrangements of these phases are shown on **Figure 1**.

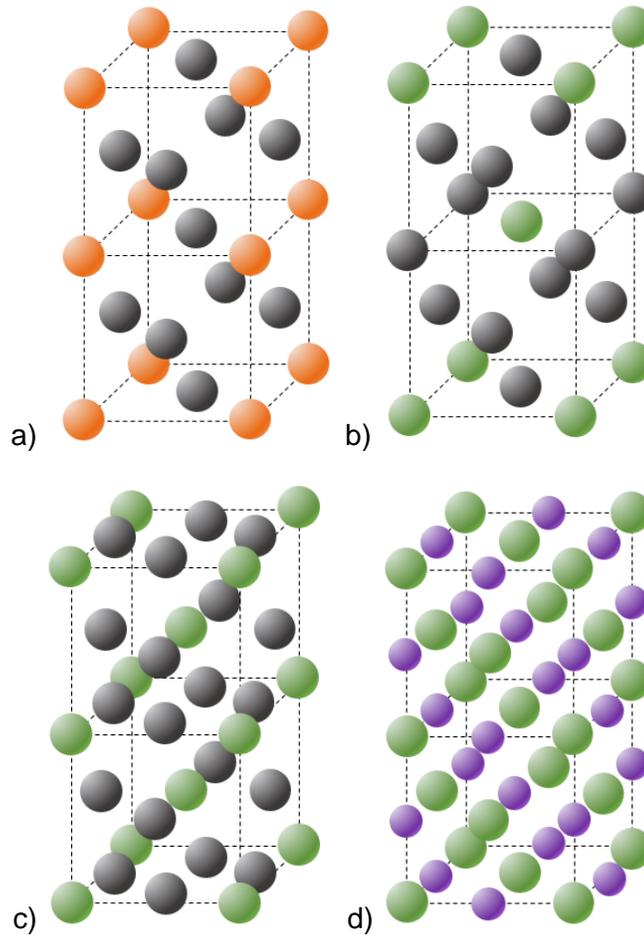


Figure 1: Atom cell arrangements of relevant phases precipitated on Alloy 718 a) Gamma-Prime, b) Gamma-Double-Prime, c) Delta-Phase and d) Niobium-Carbides. The grey spheres represent nickel atoms, the orange spheres represent aluminum atoms and the purple spheres represent carbon atoms.

It is believed that the present set of simulations, despite the simplifications assumed, provides genuine insight into features of the particular alloys.

Hydrogen Solution enthalpy on phase boundaries

The interaction of hydrogen with the microstructural features of PH nickel alloys has been investigated through the application of ab-initio calculation methods. First, the probability of incorporation of hydrogen into different positions at the relevant phase boundaries was established by taking in consideration the calculated solution enthalpies, which were calculated using ab-initio density functional theory (DFT).

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A negative solution enthalpy indicates high solubility of hydrogen, while a positive solution enthalpy indicates low solubility. In terms of exemplification, the solution enthalpies of hydrogen occupying different positions in the interface of the Gamma-matrix with the Gamma-Prime precipitate are shown on the diagram of **Figure 2**. The Gamma-matrix is considered, for the calculations, to be composed by nickel atoms, only.

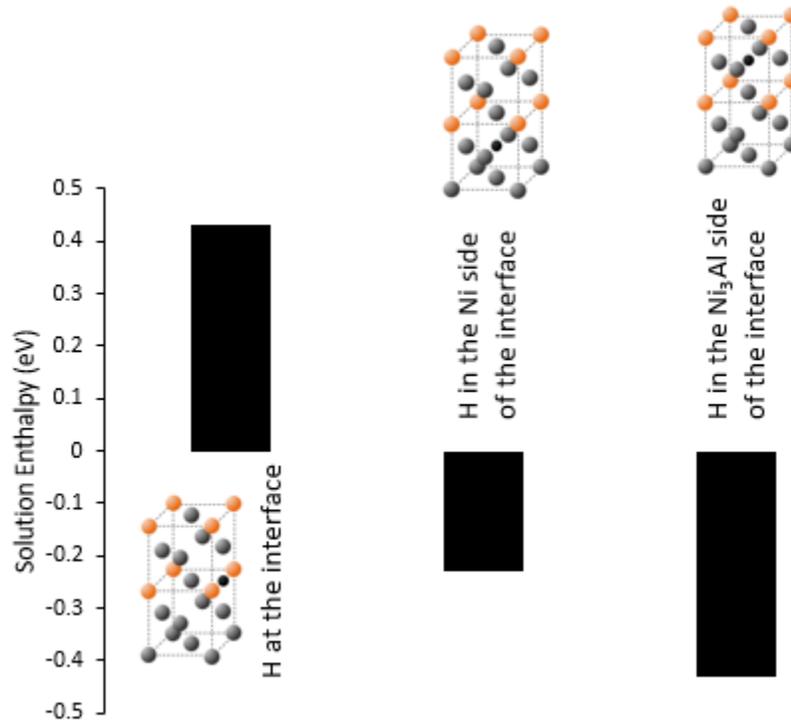


Figure 2: Calculated solution enthalpies of hydrogen in different positions at the Gamma/Gamma-Prime phase boundary

The same calculation was done for all combinations of phases (Gamma/Gamma-Prime, Gamma/Gamma-Double-Prime, Gamma/Delta, Gamma/Carbide and Gamma-Prime/Gamma-Double-Prime) in order to define the preferred position occupied by an atom of hydrogen in the phase interfaces. With that done, traction tests with and without hydrogen atoms could be simulated.

Simulated traction tests

Quantum-mechanical approach was used to simulate traction tests. A simulation cell containing 96 atoms, 48 belonging to pure nickel (matrix) and 48 belonging to the precipitated phase was used in order to reduce numerical effort. A static tensile strain was applied to the simulation cell incrementally, and the resulting structure is relaxed. The same simulation was performed on a cell without hydrogen and in the same cell with hydrogen atoms. When a cell with hydrogen atoms was considered, the hydrogen atom occupied the most energetically favorable position in the boundary between the two considered phases, which was determined during the first stage of the studies, by the lower solution enthalpy.

For the combination Gamma/Gamma-Prime, the presence of hydrogen does not affect the atomic structure and the energy-strain curves produced by the simulation are almost coincident, as shown on **Figure 3**. The elongation to failure is about 32 % for the cells with and without hydrogen.

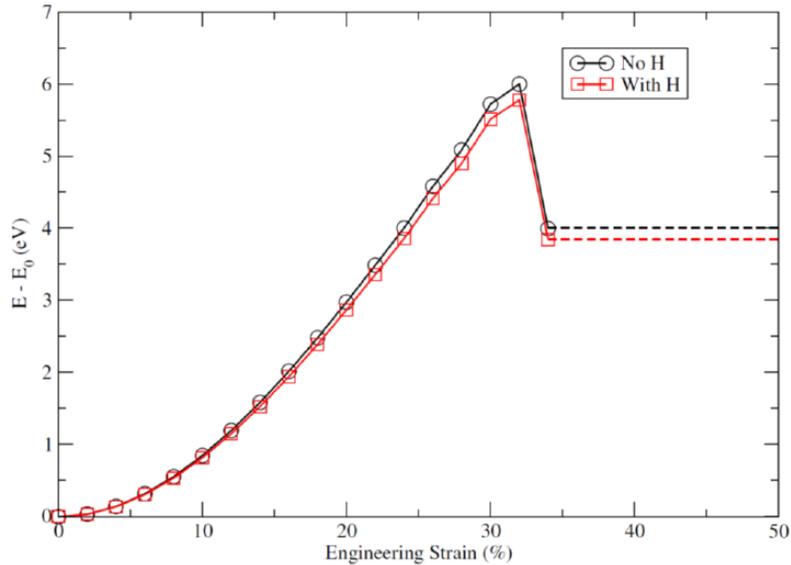


Figure 3: Energy of the simulation cell (eV) containing Gamma/Gamma-Prime as a function of the applied strain. The black line represents the energy of the structure without hydrogen and the red atom represents the energy of the structure with one hydrogen atom occupying its energetically preferential site on the interface

On the other hand, the combination Gamma/Gamma-Double-Prime seems to be highly affected by the presence of hydrogen atoms in the most energetically preferential site of the interface. The presence of hydrogen at the interface has a very strong influence on the atomistic structure, causing a large rearrangement of the atoms close to the interface of the phases under tensile strain. **Figure 4** shows the energy-strain curves produced by the simulations, where the red energy curve (representing the cell with hydrogen) lies below the black curve (representing the system without hydrogen). The elongation to fracture decreases in the presence of hydrogen and the energy barrier to fracture sharply declines. With these results, we conclude that the hydrogen affects largely on the stability of the Gamma/Gamma-Double-Prime phase boundary under traction.

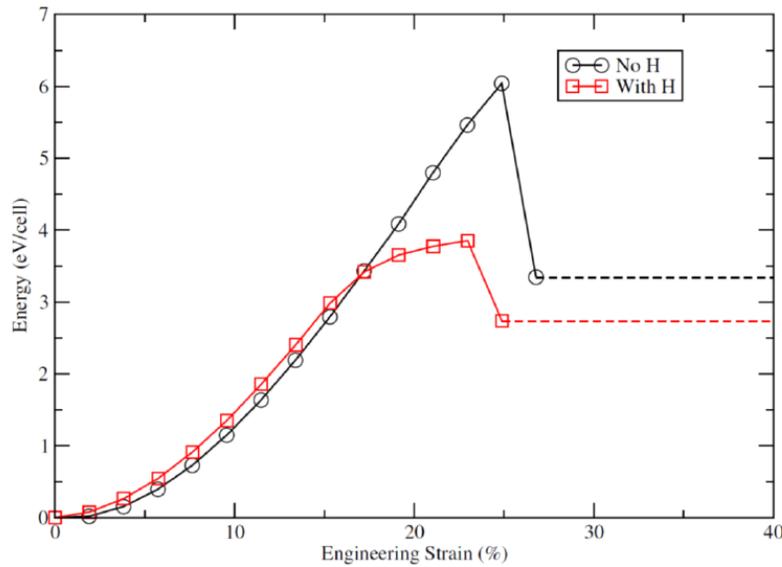


Figure 4: Energy of the simulation cell (eV) containing Gamma/Gamma-Double-Prime as a function of the applied strain. The black line represents the energy of the structure without hydrogen and the red atom represents the energy of the structure with one hydrogen atom occupying its energetically preferential site on the interface

The coherent Gamma/Delta phase boundary was also studied, although a coherent Delta-Phase is unlikely to precipitate, due to the lattice mismatch between both Gamma and Delta. Nevertheless, we would like to carry out the simulations with similar approach that was used for the Gamma-Double-Prime boundary. The energy-strain curves of the cells with and without hydrogen atoms are shown on the diagram of Figure 5. The elongation to fracture of the Gamma/Delta Phase boundary is low from its nature, indicating that this phase boundary is weaker. Both energy-strain curves with and without hydrogen are almost overlapping, showing that hydrogen has a very little impact on the energetic stability of this – coherent – phase boundary.

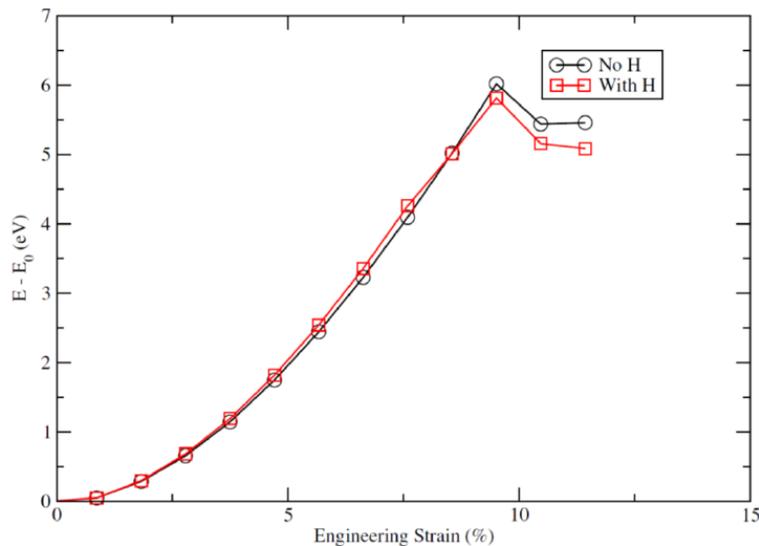


Figure 5: Energy of the simulation cell (eV) containing Gamma/Delta as a function of the applied strain. The black line represents the energy of the structure without hydrogen and the red atom represents the energy of the structure with one hydrogen atom occupying its energetically preferential site on the interface

Assuming that co-precipitation may occur in Alloy 718 during the age hardening,⁷ the system Gamma-Prime/Gamma-Double-Prime was also investigated. The solution energies of hydrogen within the cell that were calculated in the first phase of these studies show that there is no tendency for hydrogen segregation in the region of the phase boundary and hydrogen will preferentially occupy the positions in the interior of Gamma-Prime precipitation, where its solution enthalpy is more favorable. It means that the impact of hydrogen in the interface between the Gamma matrix and Gamma-Double-Prime may be considered to be the most relevant to the mechanical properties, due to the more favorable energy nature of the system, when hydrogen is occupying this position.

EXPERIMENTAL INVESTIGATIONS

Experimental investigations were carried out and published elsewhere^{8,9} in order to check the validity of the results obtained by the theoretical calculations. In the experimental studies, four laboratory model heats with chemical composition changes were melted. The aim was to produce materials containing only, or at least for the most part, one or the other hardening precipitate – the Gamma-Prime and the Gamma-Double-Prime.

Heat A was melted with chemical composition similar to Alloy 718 according to the API 6ACRA chemical composition to be used as a reference. Heat B was melted with similar composition as Heat A, but without the addition of niobium, in order to produce a material with only Gamma-Prime precipitation. Heat C also had similar composition, but without the addition of Aluminum, in order to produce a material with mainly Gamma-Double-Prime and Heat D, instead of no niobium addition, was melted with a reduced content of niobium in order to have comparable but opposite amounts of Gamma-Prime and Gamma-Double-Prime in comparison to Heat C. A summary of the chemical composition changes and expected amount of hardening phases is presented on **Table 1**.

Table 1
Chemical composition modifications made on model alloys in order to allow the validation of theoretical studies and fraction of the precipitated phases Gamma-Prime and Gamma-Double-Prime

Model Heat	Comment	Nb (wt.%)	Ti (wt.%)	Al (wt.%)	Fraction of Gamma-Prime (%)	Fraction of Gamma-Double-Prime (%)
A	Reference	4.89	0.95	0.51	9.26	8.5
B	Without Nb	0.02	0.90	0.51	4	0
C	Without Al	5.20	0.94	0.01	3.87	11.47
D	Reduced Nb	3.55	0.93	0.54	9.02	4.34

Due to the absence of niobium and the originally low amounts of aluminum in the standard chemical composition of Alloy 718, Heat B had a very low amount of precipitation and could not extensively contribute to the validation of the theoretical results. However, heats C and D could be directly compared to the reference heat, with fractions of Gamma-Prime and Gamma-Double-Prime comparable to the standard composition of Alloy 718, while having the less representative phase in lower fractions of about 4%.

Neutron Diffraction methodologies were used to try to access the sizes of the Gamma-Prime and Gamma-Double-Prime precipitates. The particles have sizes between 10 and 17 nm. Nevertheless, there can be a high error on these measures due to the very small and overlapping peaks of Gamma-Prime

and Gamma-Double-Prime in the diffraction spectrums and therefore these data is not going to be disclosed in this paper. Other phases are not present or only in negligible amount and the grain size is about the same in all of the alloys, varying from ASTM-Nr. 2.5 to 3.5.

Slow Strain Rate Tensile (SSRT) tests were carried out in order to rank the model alloys according to their resistance to hydrogen embrittlement. In this kind of tests, smooth round tensile specimens are submitted to a slow strain rate of $1 \times 10^{-6} \text{ s}^{-1}$ while in contact with an inert or a hydrogen-containing environment. The plastic elongation to failure ratios between samples tested in inert and aggressive environments are calculated and they give indication regarding the hydrogen embrittlement resistance of each material.

In the formerly investigations, deionized water at 40 °C was used as inert environment and a 0.5 M H_2SO_4 solution with an applied cathodic current of 5 mA.cm² at 40 °C was used as aggressive environment.

The average plastic elongation to failure ratios determined for samples of Heats A, B, C and D are given on **Table 2**, where a direct relationship between the Gamma-Double-Prime fraction can be done with the hydrogen embrittlement resistance of model alloys based on Alloy 718. As the Gamma-Double-Prime fraction increases, the average plastic elongation ratio decreases, meaning a higher loss of ductility caused by the hydrogen environment in material containing more Gamma-Double-Prime.

Table 2
Average plastic elongation to failure ratio of model alloys after SSRT tests for the access of the hydrogen embrittlement resistance

Heat	Average plastic elongation to failure ratio (%)
A	59.5
B	101.8
C	39.5
D	92.1

These results validate, then, the drop of energy shown by the simulation cell Gamma/Gamma-Double-Prime when a hydrogen atom is occupying the preferential site on this phase boundary.

CONCLUSIONS

The theoretical and experimental studies on the effect of hydrogen in the microstructure of precipitation hardened nickel alloys allowed the understanding of the effect of each separated phase on the hydrogen embrittlement susceptibility of these materials, as never done before.

Both the theoretical and experimental investigations show that the Gamma-Double-Prime has a negative impact on the hydrogen embrittlement resistance of the materials containing this kind of precipitate. The theoretical results show that the presence of a hydrogen atom in the interface between the Gamma matrix and the Gamma-Double-Prime precipitate largely affects the stability of the phase boundary under traction forces, reducing the elongation to fracture, as confirmed by the experimental results.

The studies conclude that Gamma-Prime and the coherent Delta-phase boundary may not play a role (or may not play an important role) on the hydrogen embrittlement susceptibility of the alloys.

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