Microstructure of CRA bolts used subsea in relation to resistance to hydrogen embrittlement

A dissertation submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

by

Baber Saleem
Department of Engineering
University of Leicester

June 2017

Doctoral Committee:
Prof Hongbiao Dong Supervisor
Prof Jingzhe Pan
Prof Steven David Kenny Loughborough University
Abstract

The physical characteristics of hydrogen embrittlement failure of subsea bolts operating under CP are surface cracks at thread and shank area and for some cases they are completely ruptured from the shank area. The metallurgical reason for failure already reported by researchers (including for Inconel718) was the interaction of hydrogen atoms with grain boundary precipitates (Ni$_3$Nb $\delta$) resulting in hydrogen assisted intergranular cracking.

Inconel 718 was received as rectangular block (RB) and bolts ($\Phi$28mm). They were heat treated as per API 6A718 specifications. The yield strength and vickers hardness found for API aged RB specimen S2$_{API}$ was 840MPa and 340HV respectively. On the other hand API bolt was found with bulk yield strength of 880MPa and vickers hardness in the range 370–400 HV (bulk to edge of the bolt). The structure of bolt (bulk, shank and thread) and rectangular block was investigated, using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), to understand the reason for this difference. The experimental results were compared with theoretical predictions.

The microstructure of the API bolt shows no evidence of intergranular (Ni$_3$Nb $\delta$) precipitates and the nano-structure revealed $\gamma'$ and Ni$_3$Nb $\gamma''$ precipitates. This suggest that for Inconel718 in the form of bolts the theory of intergranular cracking hydrogen enhanced decohesion at the grain boundary matrix precipitate interfaces is not specifically relevant instead the transgranular oversized $\gamma'$ precipitates (50nm $\gamma'$ at thread edge of the bolt) and the elongated metastable $\gamma''$ discs (50–100nm at shank and thread edge of the bolt) could act as initiation point for HEDE. Moreover, it was also found that threading of the bolt (after heat treatment) results in shearing of $\gamma'$ precipitates at threads edge. These sheared $\gamma'$ precipitates could aid in trapping hydrogen atoms under CP in service leading to HEDE.

The newly developed bolting materials Incoloy 945 and its higher strength version 945x (as rectangular and cylindrical blocks) were added for structural investigation because of lower content of Nb present in their matrix than 718.

Finally, as future work, the structure of 718, 945 and 945x alloys were selected for assessing susceptibility to hydrogen embrittlement using slow strain rate testing under CP.
To my Parents and Wife
Acknowledgements

I would like to sincerely appreciate and thank Professor Hongbiao Dong for his support and supervision throughout my life at University. He was always a beacon of inspiration during my undergraduate degree (as 3rd year project supervisor) and for PhD research work. I would always admire him for his encouragement, trust and patience. I will never forget his efforts and emotional support which helped me to reach this far in engineering studies. Your contributions mean a lot to me, In sha ALLAH I would continue to work hard, learn and improve, thank you!

The experimental work presented in thesis was carried out at University of Leicester engineering department in mechanics of material (MoM) lab. I would greatly appreciate Graham Clark (lab technician) and Vinay Patel (experimental officer) for their technical support and patience in training me the fundamentals of the laboratory equipment especially focused ion beam (FIB), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). All experiments were carried out under their supervision.

Special thanks goes to the fellow research students at University: Ramy, Kevser, Ali, Nawshin, Xing, Reza, Dhuha, Ahmed and Mazin. The presence of all of you around me in the office always makes me feel happy. Many thanks for making me laugh so much after a long tiring TEM day. You all will be missed for making my last year so much joyful and memorable. I will surely look back and always remember four years of research work at University with fond memories.

The studentship assistance provided by engineering and physical science (EPSRC) was accepted with sincere thanks.

Last but not least, my deepest thank to my family far from Pakistan and France. Especially, grateful to my Mother for her love and continuous support throughout my life and to my lovely fiancée Maryam who always being a spark of encouragement in harsh time of my life, her phone calls and smile always cheered me up whenever needed.
## Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
<td>Face Centered Cubic</td>
</tr>
<tr>
<td>BCC</td>
<td>Body Centered Cubic</td>
</tr>
<tr>
<td>BCT</td>
<td>Body Centered tetragonal</td>
</tr>
<tr>
<td>CTOD</td>
<td>Crack tip Opening Displacement</td>
</tr>
<tr>
<td>HE</td>
<td>Hydrogen Embrittlement</td>
</tr>
<tr>
<td>HAC</td>
<td>Hydrogen Assisted Cracking</td>
</tr>
<tr>
<td>HEE</td>
<td>Hydrogen Environment Embrittlement</td>
</tr>
<tr>
<td>HEDE</td>
<td>Hydrogen Enhanced Decohesion</td>
</tr>
<tr>
<td>HELP</td>
<td>Hydrogen Enhanced Localised Plasticity</td>
</tr>
<tr>
<td>AIDE</td>
<td>Adsorption Induced Dislocation Emission</td>
</tr>
<tr>
<td>HIE</td>
<td>Hydride Induced Embrittlement</td>
</tr>
<tr>
<td>HEEI</td>
<td>Hydrogen Environment Embrittlement Index</td>
</tr>
<tr>
<td>FPZ</td>
<td>Fracture Process Zone</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
</tr>
<tr>
<td>SAVs</td>
<td>Superabundant Vacancies</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>LM</td>
<td>Light Microscopy</td>
</tr>
<tr>
<td>$K_{th}$</td>
<td>Threshold Stress Intensity</td>
</tr>
<tr>
<td>YS</td>
<td>Yield Strength</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate tensile strength</td>
</tr>
<tr>
<td>NTS</td>
<td>Notch Tensile Strength</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>BCT</td>
<td>Body Centered Tetragonal</td>
</tr>
<tr>
<td>CRAs</td>
<td>Corrosion Resistant Alloys</td>
</tr>
<tr>
<td>M C,Ns</td>
<td>Metal Carbides and Nitrides</td>
</tr>
<tr>
<td>AR</td>
<td>As Received</td>
</tr>
<tr>
<td>ST</td>
<td>Solution treated</td>
</tr>
<tr>
<td>STA</td>
<td>Solution treated plus aged</td>
</tr>
<tr>
<td>NS</td>
<td>Non-Standard</td>
</tr>
<tr>
<td>HTHP</td>
<td>High Temperature High Pressure</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>wt %</td>
<td>Weight Percentage</td>
</tr>
</tbody>
</table>
Contents

Abstract ............................................................................................................................................. 2

Acknowledgements .......................................................................................................................... 4

Nomenclature .................................................................................................................................. 5

CHAPTER 1. Introduction .................................................................................................................. 10
  1.1. Degradation ............................................................................................................................ 10
  1.2. CRA Bolts ................................................................................................................................ 11
  1.3. CRA Bolting Materials ........................................................................................................... 13
    1.3.1. Inconel718 ..................................................................................................................... 13
    1.3.2. Incoloy 945 and 945x ................................................................................................. 14
  1.4. Research Aim ......................................................................................................................... 15
    1.4.1. Flow chart ..................................................................................................................... 15

CHAPTER 2. Literature review on Physical Metallurgy of Ni-base Alloys .................................... 17
  2.1. Metallurgy - Nickel Alloys ..................................................................................................... 17
  2.2. Role of each alloying element ............................................................................................... 17
  2.3. Phases of Nickel Based Alloys ............................................................................................... 19
    2.3.1. Gamma Phase (γ) ........................................................................................................... 19
    2.3.2. Gamma Prime Phase (γ') ............................................................................................. 20
    2.3.3. Gamma Double Prime (γ'') ......................................................................................... 21
    2.3.4. Carbides ......................................................................................................................... 21
    2.3.5. Borides ............................................................................................................................ 22
    2.3.6. Topological Closed Packed (TCP) Phases ................................................................ 23
    2.3.7. Grain size and Dislocations ......................................................................................... 24

CHAPTER 3. Literature on Hydrogen Embrittlement (HE) ............................................................. 30
  3.1. Hydrogen Embrittlement ........................................................................................................ 30
  3.2. Challenge for CRA Bolts used subsea .................................................................................. 31
  3.3. Hydrogen Evolution into CRA Bolts ..................................................................................... 34
  3.4. Hydrogen Entry into Metal .................................................................................................... 35
  3.5. Defects in Lattice .................................................................................................................... 39
    3.5.1. Hydrogen Diffusion Concept ....................................................................................... 40
  3.6. Hydrogen Interaction with defects ....................................................................................... 44
    3.6.1. 1D Dislocations - Line Defects .................................................................................. 44
    3.6.2. Internal Boundaries ...................................................................................................... 46
  3.7. Parameters Effecting Hydrogen Assisted Cracking (HAC) .................................................. 47
5.5. Discussion

5.4.2.

5.3.2

5.2.1. Metallurgy of Inconel718

4.2.4.

4.1.4. γ’ Coarsening Simulations

3.9.3.2 Hydrogen-enhanced localised plasticity (HELP)

3.9.3.1 Hydrogen-enhanced Decohesion (HEDE)

3.9.2. Fractography

3.9.1. Mechanical Behaviour of INCONEL718

3.8. Hydrogen transport and effect in Ni-Fe-Cr Alloys

3.7.3. Material

3.7.2. Sample Preparation

3.7.1. Hydrogen Environment Embrittlement Testing

3.6.3. Time Temperature Transformation (TTT) Diagram of Alloy 945 and 945x

3.6.2. Thermotech - Equilibrium Phase Simulations

3.6.1. Time Temperature Transformation (TTT) Diagram of Alloy 718

3.5.4. η’ Coarsening Simulations

3.5.3. Equilibrium Phase Simulations

3.5.2. Equilibrium Phase Simulation of Alloy 945 and 945x

3.5.1. η’ Coarsening Simulations

3.4. Chapter Summary

3.3. Experimental Procedure and Method

3.2. Material

3.1. INCONEL718

2.2. Thermotech - Equilibrium Phase Simulations

2.1. Time Temperature Transformation (TTT) Diagram of Alloy 718

1.1. Metallurgy of Inconel718

1. Introduction

0.1. Material
5.5.2. Effect of heating parameters on morphology of second phase of Bolt and RB............. 133
5.5.3. Hardness and Tensile data of Bolt and RB ............................................................... 137
5.5.4. Hydrogen embrittlement susceptibility - $\gamma'$ size, metastable $\gamma''$ and Dislocations..... 141
5.6. Chapter Summary ........................................................................................................ 149

CHAPTER 6. Micro and Nano structure of New CRAs - INCOLOY 945 and 945x................. 151
6.1. Metallurgy - Incoloy 945 and 945x ........................................................................... 151
6.2. Experimental Procedure ........................................................................................... 152
  6.2.1. Materials ............................................................................................................... 152
  6.2.2. Sample Preparation ............................................................................................... 153
  6.2.3. 945 and 945x in the form of bolts ......................................................................... 154
6.3. Microstructural analysis ............................................................................................. 155
  6.3.1. Grain size after heat treatments ........................................................................... 155
  6.3.2. Morphology and distribution of M(C, N)s .......................................................... 156
6.4. $\gamma'$ precipitates in 945 and 945x ........................................................................... 161
  6.4.1. Morphology and Distribution of $\gamma'$ ............................................................... 161
  6.4.2. Identification and Evolution of $\gamma'$ ................................................................. 166
6.5. Chapter Summary ..................................................................................................... 171

CHAPTER 7. Conclusions and Future Work ...................................................................... 173
7.1. Conclusions ............................................................................................................... 173
7.2. Future Work .............................................................................................................. 174
  7.2.1. Slow Strain Rate Testing ..................................................................................... 174
  7.2.2. Heating Parameters for Slow Strain Rate specimens ......................................... 176
References ......................................................................................................................... 178
Appendix A ....................................................................................................................... 190
CHAPTER 1. Introduction

1.1. Degradation

Hydrogen Embrittlement (HE) has been a persistent problem for the design and integrity of structural materials in oil, gas and petroleum industries. Despite decades of research, professionals and experts have yet to fully understand the mechanism. The underlying properties of engineering materials depend strongly upon microstructure. It is therefore important to possess comprehensive understanding of (micro and nano)-structure with different phases and their vulnerability to hydrogen embrittlement (HE). The consequence of hydrogen metal interaction has always been considered as detrimental in terms of mechanical degradation and decreasing fracture toughness. If observe materials structure at micro and nano level, the word ‘embrittlement’ may be related to transition from ductile to brittle state because of the interaction of hydrogen atoms with metal atoms. The catastrophic failures of high strength steels, stress corrosion cracking (SCC) of ferritic stainless steel, chloride stress corrosion cracking (CLSCC) of austenitic steel and environment step wise cracking of nickel alloys under hydrogen influence is regarded as embrittlement with loss of fracture toughness and mechanical strength. However, in order to counter embrittlement problem the aim is always to develop a rigorous model for predicting when, where and how hydrogen embrittlement will occur.

The effect of hydrogen embrittlement was first reported in 1875 by W.H. Johnson with title ‘some remarkable changes produced in iron by the action of hydrogen and acids’ [1]. The basic general mechanism behind this type of deterioration involves the ingress of hydrogen into structural materials, an event that can seriously reduce the ductility and load bearing capacity. This cause cracking and catastrophic brittle failures at stresses below the yield stress of susceptible materials. It involves cracking of precipitation hardening materials, martensitic steels or weldments when exposed to conditions which inject hydrogen into component. The most vulnerable structural materials are high strength steels, nickel based alloys, titanium alloys and aluminium alloys. It can be linked to corrosion reaction as hydrogen may be produced by methods such as rusting, cathodic protection (CP) and electroplating. Some other manufacturing operations such as welding (dissociation of cellulosic electrodes), phosphating and pickling result in ingress of hydrogen. Materials subject to these processes are susceptible to hydrogen embrittlement but final baking heat treatment is applied as precaution to expel any trap hydrogen. Moreover, B.Civata [5] in his research eradicate the risk affiliated with pickling process by removing the acid usage from the cleaning stage and adopted a mechanical cleaning process prior to galvanising, thereby minimize the risk of hydrogen cracking failure. Thus, it is now possible to galvanised bolts, which it once considered cannot be galvanised due to hydrogen
cracking issue and users are now sure that they are using safe and risk-free components but still HE problem exist in service.

Mainly during cathodic protection (CP) in service the hydrogen ingress the components. The hydrogen produce during cathode reaction enter the metal in atomic form rather be all evolved as a gas into the surrounding environment: two hydrogen atoms combine to form a molecule H₂ which is stable state. For hydrogen to be detrimental it must be in atomic form to enter the lattice structure. Under normal conditions, metals undergo substantial plastic deformation when subjected to axial load or force. This plasticity originates from nano and micro sized voids/inclusions to generate dislocations (movement of atoms that serve to relieve stress in the lattice) within the metal. The desirable properties of metal alloys such as ductility and toughness rely on the nano and micro sized voids in structure, unfortunately these voids attract hydrogen atoms. For example in steels [2], hydrogen atoms diffuses along the grain boundaries and combine with carbon, which is alloyed with iron in steel lattice to form methane gas (CH₄), which is not mobile and collects in small voids preventing any dislocations to move along the grain boundaries thus builds up enormous pressure and stress which initiate crack. At normal room temperature, the hydrogen atoms are absorbed into the metal surface and diffused into metal lattice. Then tend to gather at voids or other lattice defects. Then at critical stress concentration crack propagate and the direction is transgranular. However, at high temperatures the absorbed hydrogen tends to gather at grain boundaries and stress-induced cracking is then intergranular.

1.2. CRA Bolts

Corrosion resistant alloys (CRAs) in the product form of bolts or fasteners are used under subsea for many years for integration of critical well components. The important prerequisite for selection of corrosion resistant alloys (CRAs) include life time integrity and optimum heat treatment. This is presented as a challenge that needs to be met to ensure best performance. The bolts used subsea withstand harsh environment, such which contain corrosive inhibitors, pressure, temperature and critical stress. The combination of all these factors contribute towards hydrogen assisted cracking (HAC). However, in order to avoid environment induced cracking these bolts are protected using cathodic protection (CP). As an example, Figure 1.1.0 (a) shows AISI 8740 steel fasteners that were used under CP but unfortunately failure occurred resulting in complete separation between head and shank area. Multiple initiation points and secondary cracking were observed with surface cracks at thread and shank area. White calcareous deposits under fastener head and over shank area was evidence of cathodic protection. Generally, for any hydrogen embrittled fastener, multiple initiation points and secondary cracks with surface cracks at thread and shank area of fastener were observed. Another case in which grade 8 high strength
Steel fasteners that were used under subsea for integration of well components resulted in hydrogen failure. Fractography of hydrogen cracked grade 8 fastener reveals intergranular cracking when examined under SEM, as shown in Figure 1.1.0 (b). Again, white calcareous deposits under fastener head and at threaded area was evidence of cathodic protection (CP). The physical characteristics also reveal surface cracks at thread and shank area. The metallurgical reason found for intergranular cracking was the interaction of H atoms with matrix precipitate interfaces. Similar mode of failure has been reported for Inconel625 bolts (aged for 48hr at 650°C subsequent of thread rolling) used in a Taperlockflange of a subsea completion system under CP. After that failure, great emphasis was placed at manufacturing sequence. The cold rolling of threads was directly followed by heat treatment leading to hardness variation across the bolt: cold rolled thread region having local hardness of 530 HV30 as opposed to bulk region with hardness of 350 HV30 [64]. This made the basis for manufacturing of a bolt out of the as received (AR) bolt in the current work: AR bolt was rolled to make it a rolled bar and subsequently threads were machined after the final heat treatment applied. This manufacturing route has its draw back and will be discussed.

![Figure 1.1.0](image)

**Figure 1.1.0.** (a) AISI 8740 steel fasteners exposed to subsea environment under cathodic protection (CP) induce H atoms in to structure which result in hydrogen embrittlement (HE) and complete separation between head and shank area [3]. (b) SEM reveals intergranular cracking at grain boundaries for grade 8 high strength steel fastener[4]. Multiple initiation points and secondary cracking with apparent surface cracks (circled in red) [5] along with white calcareous deposits at thread and shank area can be seen in (a) and (c).

Over the past few decades significant improvements have been made for the processing of the corrosion resistant alloys (CRAs) which are used as bolts. In the modern offshore oil and gas industry developing high temperature, high strength and corrosion resistant bolts, specifically resistant to HE, from such CRAs is the benchmark to be achieved and would be
considered as improvement and efficiency. This was the reason why Incoloy 945 and 945x alloys were developed to replace the existing CRA alloys in the oil and gas market, specifically 718. Still the threat of HE to these new CRAs is present because these Incoloy’s are hybrid of Inconel 718 and 925. Constant development in future generation of CRAs containing significant amount of at least ten other elements led to dramatic change, not only at manufacturing and processing level but also at structural level. This is because when designing CRA bolts great emphasis is placed to meet manufacturing and operating standards for improved integrity and longevity.

Offshore oil and gas environment is highly corrosive in nature because of the presence of seawater, hydrogen sulphide (H₂S) and extreme temperature and pressure. CRA bolts used in this environment are under cathodic protection, which cause the formation of atomic hydrogen (H₂ → 2H) on surface that may diffuse into bulk lattice causing hydrogen embrittlement (HE). The factors which effect HE susceptibility are divided into three categories: metallurgical; which mainly include grain size, crystal structure, vacancies(defects), amount of cold work, dislocations, and precipitates [6,7]; thermo-mechanical processing: that increase strength and hardness level making them more prone to HE [8,9] and environmental: that include temperature, pressure, cathodic potential, stress, strain and strain rate [9]. Correlation between these factors is needed which aid to better understand hydrogen induced failure of susceptible bolts. The bolt’s material response is difficult to interpret because of the complex composition, vulnerable phases and different hydrogen cracking mechanisms occurring simultaneously.

1.3. CRA Bolting Materials

1.3.1. Inconel 718

Over the past decades continuous development has been made to introduce high strength alloys in terms of increase toughness and resistance to corrosion. Primary choice adopted by many industries found to be nickel base alloys with complex atomic concentration of elements [10]. They have excellent physical properties such as strength and creep resistance close to their melting point [14]. This alloy class possess significant attributes of high temperature stability, weldability and formability but solution to corrosion problem (specifically hydrogen embrittlement) persist for scientific researchers and needs to be resolved.

A range of nickel base alloys have been developed to counter the problem of corrosion (i.e. hydrogen assisted cracking under cathodic protection (CP) in oil and gas sector. Inconel 718 being one of them has been developed in 1950’s by international nickel company. It’s use extend from aerospace industry (double aged) as turbine application withstanding high temperature, pressure and creep resistance to oil and gas industry having API specification
because of moderate strength, fracture toughness and corrosion resistance. Nowadays, oil and gas wells are drilled deeper into coastal areas with high pressure, temperature and more corrosive environment. Thus the need for a versatile alloy is more than ever before. Alloy 718 having unique combination of room temperature strength and aqueous corrosion resistance made its used as bolts, shafts and safety valves with exposure to corrosive conditions. Its high strength and corrosion resistance are attributes but service failures present a challenge in material selection, heat treatment, life cycle, performance, integrity and cost. The main failure mechanism reported was hydrogen induced stress cracking (HISC) or hydrogen embrittlement (HE) resulting from hydrogen charging under cathodic protection (CP). A number of investigation reports [42-44] already have been published, including for alloy718, about the failure of critical well components i.e. fasteners, sub surface safety valves (SSSV) and connections, which was mainly due to presence of second phase at intergranular positions.

### 1.3.2. Incoloy 945 and 945x

INCOLOY 945 with incredible strength was introduced in 2008 by modern operators to compete with the oil and gas work horse Inconel 718 in withstanding the higher requirements of deeper drilling. The alloy is a precipitation hardened and corrosive resistant Ni-Fe-Cr alloy. Its nickel content (47wt%) though less than 718 (53wt %) provides excellent stress corrosion cracking resistance, ductility, and impact strength. Later in 2011, 945x (54wt% nickel content) a higher strength version was introduced. These alloys can be used in high pressure high temperature (HPHT) applications and are qualified to NACE MR0175/ISO 15156-3 level V and VI [13]. The alloys are designed for oil and gas applications specifically down-hole oil well hardware and surface well components e.g. tubular products, subsurface safety valves, hangers, packers, tool joints, pump shafts and bolts [13]. These new alloys ensure safe, reliable and economical extraction of crude oil and gases from subsea reservoirs with extended exposure to extreme environments. INCOLOY’S accompanied with slightly reduced toughness at low temperatures with high mechanical strength. They have greater copper content than INCONEL718 which help to improve corrosion resistance and machinability.
1.4. Research Aim
The nickel alloys INCONEL718, INCOLOY 945 and 945x have been allocated as the project core materials. They have been in service as CRA bolts because of unique combination of physical and mechanical properties i.e good corrosion resistance, ability to be heat treated to various strength levels and high tensile strength. Oil grade alloy INCONEL718, defined by API specification 6A718, and the more recently developed alloys INCOLOY 945 and 945x has been chosen to investigate their (micro and nano)-structure for hydrogen assisted cracking (HAC) susceptibility. The reason already established in HAC literature for CRAs by many researchers was the presence of intergranular precipitates but still the role of precipitates at transgranular regions during HAC is unclear and needs investigation. Thus, these transgranular precipitates in the as-received (AR) and heat treated (HT) API 718 bolts were investigated from edge and bulk area and compared with 718 in the form of rectangular block. In order to compare the structure and to observe the effect of machining on bolts. One of the as received 718 bolt was rolled down to remove the threads. Then after that it was rolled down as bar of Φ22mm and subsequently solution annealed and aged as per API 6A718 specification. The final stage was machining of threads. Whereas, newly developed 945 and 945x were received in the form of bulk (rectangular and cylindrical blocks) for investigation. The alloys were heat treated as per heat treatment designated in standards: 718 heat treated as per API 6A718 specification and 945/945x as conventional double aged.

The research project was sponsored by engineering and physical science research council (EPSRC), which was aimed to develop hydrogen assisted cracking (HAC) theory for these precipitation hardening alloys. The research presented in chapters 4, 5 and 6 is thermodynamic modelling, comprehensive structural and mechanical characterisation using ThermoCalc, JMatPro, light microscopy (LM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), vickers hardness (HV) and tensile testing. The objective was to identify nano phases that could be responsible for HE susceptibility (specifically in 718 bolts) apart from intergranular precipitates. These findings would help to evaluate the slow strain rate testing (SSRT) results of smooth and notch specimens under CP and in-air for CRA alloys having targeted micro and nano structure, (future work).
1.4.1. Flow chart

**Figure 1.1.0.** The flow chart illustrate the work flow of the research project.

The chapter 2 describes the general physical metallurgy of nickel alloys which is related to Inconel718, Incoloy 945 and 945x. Case studies reported in literature were added and discussed to get an insight of HE susceptibility of the alloy 718. Whereas chapter 3 describes: the challenge CRA subsea bolts are exposed to: hydrogen entry into the alloy, interaction of hydrogen with defects in lattice, parameters effecting HE, understanding characteristic features of hydrogen assisted fracture and HE mechanisms.
CHAPTER 2. Literature review on Physical Metallurgy of Ni-base Alloys

2.1 Metallurgy - Nickel Alloys

In modern industrial world components are now made up of Nickel (Ni) based alloys which have much durability, corrosion resistance, creep resistance and high strength over a larger range of temperature. The element nickel Ni have a face centred cubic (FCC) structure from ambient temperature to the melting point 1455°C, which represent an absolute limit for the temperature capability of the nickel based superalloys. Its high tolerance for alloying elements without phase in-stability makes it a unique element. Numbers of alloying elements are often greater than ten making a complex alloy ever engineered by man. These elements are taken from the d block of transition metals from periodic table. The behaviour of each alloying element and its influence on the phase stability depends strongly upon their position in periodic table. A class of elements include nickel, cobalt, chromium, ruthenium, molybdenum, rhenium and tungsten. These elements have atomic radii not very different from that of nickel. They all prefer to partition to austenitic γ (gamma) and hence have stabilising effect. Other class of elements include aluminium, titanium, niobium and tantalum. These elements have greater atomic radii and promote the formation of ordered phases such as Ni₃ (Al, Ta, Ti) known as γ' precipitate often coherent with the γ phase matrix [10]. Most nickel alloys contain 10-20% Chromium, 5-10% cobalt, up to 8% aluminium or titanium and small amounts of boron, carbon and zirconium.

2.2 Role of each alloying element

Alloying elements have their influence on the structure, process ability and performance of the alloys. The role of each element is mentioned below:

Al It helps in the creation of γ' phase and promote the formation of stable Al₂O₃ alumina surface scale which protects the alloy against further oxidation.

Cr plays a role as solid solution strengthening element and act as essential element in hot corrosion and oxidation resistance. It also forms topologically closed packed (TCP) brittle phase which is detrimental to high temperature properties.

Mo It strengthens the γ/γ' phases but has a negative influence on corrosion resistance of Ni based alloys.

Ta It strengthens the γ' by substituting for Al in γ', particularly increases high temperature strength. It also segregates to the inter-dendritic region and decrease the density inversions which will cause the nucleation of spurious grains.

W It improves high temperature capability, segregates strongly to the γ dendrites and increases the potential for nucleation and growth of grain defects at high levels.
Re It improves high temperature capability, hot corrosion and oxidation resistance at the expense of density.

Nb and Ti It strengthen the γ’ by substituting for Al in γ’, particularly increasing high temperature strength but their excessive amount make alloy prone to TCP phase precipitation.

Co It contributes to the strength by ordering γ’ phase which is homogeneously distributed in the γ matrix.

B and Zr It strengthen the grain boundaries but lower the incipient melting point.

C It helps in forming MC carbides which are grain boundary strengtheners. It contributes positively to castability since it helps in reducing the oxides.

Y It improves the adherence of Al₂O₃ protective layer formed at high temperature.

Ru It boosts the stability of alloy structure and increases the strength.

Hf It improves alloys castability. [11]

---

**Figure 2.1.0.** Periodic table showing partition of elements in Nickel based alloys; those which constitute in γ matrix, γ’ and grain boundary [11].
Table 2.0. The effect of each alloying element on the micro-structural behaviour of Ni base alloys.

Adapted from [12]

2.3 Phases of Nickel Based Alloys

2.3.1 Gamma Phase (γ)

It is face centred cubic (FCC) structure nickel base austenitic phase called gamma (γ). It has large number of solid solution strengthening elements such as Tungsten (W), Molybdenum (Mo), Chromium (Cr), Iron (Fe), Aluminium (Al), Titanium (Ti) and Cobalt (Co) [10]. Adding Chromium to the gamma phase results in to form protective scale Cr$_2$O$_3$ (having low cation vacancy content) which helps to restrict diffusion rate of metallic elements outward and oxygen, nitrogen, sulphur and other corrosive elements inward [35]. To demonstrate the strengthening potency of solid solution elements, we consider alloy having γ phase of atomic percent composition as follows:

<table>
<thead>
<tr>
<th>Element</th>
<th>Matrix Strengthening</th>
<th>Increase in γ volume fraction</th>
<th>Grain Boundaries</th>
<th>Other Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>Moderate</td>
<td>Moderate</td>
<td>M$_2$C$_6$ and M$_7$C$_3$</td>
<td>Improves corrosion resistance; promotes TCP Phases</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Decreases oxidation resistance; promotes TCP phases σ, Laves</td>
</tr>
<tr>
<td>W</td>
<td>High</td>
<td>-</td>
<td>-</td>
<td>Promotes TCP phases σ and μ(Mo, W)</td>
</tr>
<tr>
<td>Ta</td>
<td>High</td>
<td>Large</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>High</td>
<td>Moderate</td>
<td>M$_6$C and MC</td>
<td>Increases density</td>
</tr>
<tr>
<td>Nb</td>
<td>High</td>
<td>Large</td>
<td>NbC</td>
<td>Promotes γ and δ phases</td>
</tr>
<tr>
<td>Ti</td>
<td>Moderate</td>
<td>Very Large</td>
<td>TiC / TiN</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>Moderate</td>
<td>Very Large</td>
<td>-</td>
<td>Al improves oxidation resistance</td>
</tr>
<tr>
<td>Co</td>
<td>Slight</td>
<td>Moderate in some alloys</td>
<td>-</td>
<td>Raises solidus; may raise or lower solvus</td>
</tr>
<tr>
<td>Re</td>
<td>Moderate</td>
<td>-</td>
<td>-</td>
<td>Retards coarsening; increases misfit</td>
</tr>
<tr>
<td>C</td>
<td>Moderate</td>
<td>-</td>
<td>Carbides</td>
<td>-</td>
</tr>
<tr>
<td>B, Zr</td>
<td>Moderate</td>
<td>-</td>
<td>Inhibit carbide coarsening; improve grain boundary strength; improve creep strength and ductility</td>
<td></td>
</tr>
</tbody>
</table>

Lattice ‘parameter or constant’ is the physical dimension (3D - with three lattice constants $a$, $b$ and $c$) of unit cells in crystal lattice. The measuring units of the lattice constant are Angstrom Å.
The change in lattice constants for binary addition to the nickel content of \(\gamma\) matrix and flow stress at room temperature is estimated to be:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ti</th>
<th>Mo</th>
<th>W</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Al</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant</td>
<td>0.006</td>
<td>0.035</td>
<td>0.038</td>
<td>0.033</td>
<td>0.020</td>
<td>0.011</td>
<td>0.025</td>
<td>0.006</td>
</tr>
<tr>
<td>Flow Stress (\text{kgf/mm}^2)</td>
<td>4</td>
<td>17</td>
<td>18</td>
<td>16</td>
<td>5.6</td>
<td>1.8</td>
<td>20</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Adapted from [58]

Lattice constant of 0.025 and flow stress of 20 \(\text{kgf/mm}^2\) makes aluminium a potent solid solution element. Tungsten (W), Chromium (Cr and Molybdenum (Mo) serve strongly as solid solution strengtheners whereas Cobalt, Titanium, Iron and Vanadium act as weak solid solution strengthening elements [58].

### 2.3.2 Gamma Prime Phase (\(\gamma'\))

It is FCC phase of \(A_3B\) compound \(\left(L_{12}\right)\) with 0.1% lattice (\(\gamma\)) mismatch; has homogeneous nucleation of which precipitates around 620°C with low surface energy and long-time stability. Hagel and Beattie [15] observes that at early stage \(\gamma'\) are like spheres with 0-0.2% lattice mismatch, then cubes at mismatch around 0.5-1.0% and then plates at mismatch above about 1.25%. They are coherent precipitates with \(\gamma\) matrix. The elements which normally opt for A are Ni and Co and for B are Al, Ti, Nb and Ta. It is unique intermetallic phase with strength increasing with temperature and contributes remarkable strength to the Ni alloy by interacting with dislocations. It has solvus temperature around 900-920°C [16].

The ductility associated with \(\gamma'\) come up in contrast to the TCP brittle phases. With thermal exposures of 0.6\(T_m\) and above, \(\gamma'\) precipitates began to increase in size helping dislocations to pass. According to Hume-Rothery’s, \(\text{Ni}_3\text{Al}\) is the most stable \(A_3B\) phase, with \(\text{Ni}_3\text{Ti}, \text{Ni}_3\text{Nb}\) and \(\text{Ni}_3\text{Ta}\) with decreasing stability respectively [17].
Figure 2.1.1. Showing in (a) Typical Ni base alloy showing γ /γ' phase (cubes). (b) Crystal Structures of γ matrix (Ni-FCC) (left) and γ' Ni$_3$Al phase of Ni base alloy - Ni at the face of each unit cell and Al (or Ti, Nb) at each corner (right) [18].

2.3.3 Gamma Double Prime (γ'')

It is body centre tetragonal (bct) DO$_{22}$ crystal structure with composition Ni$_3$Nb, which is believed to be one of the key phase influencing the properties of nickel alloy. They precipitate at higher temperatures above ~720°C and have solvus temperature around 900-920°C [16, 19]. γ'' with elongated platelets exhibits high hardening. However, this metastable phase tend to be replaced by stable delta (δ) phase after long term exposure to temperature above 650°C [27].

Figure 2.1.2. Crystal structure (body centred tetragonal BCT) of γ'' phase [20].

2.3.4 Carbides

Carbon is normally added between 0.05-0.2 percent in nickel alloys. Carbon tend to react with reactive and refractory elements to form MC carbides that reside at the grain boundaries, $M$ being mostly Nb and Ti. However, investigators and researchers found MC carbides detrimental to alloy properties by reducing ductility so they have reduce carbon to very low levels. MC
carbides on the other hand are beneficial for grain boundary strengthening and reduce grain sliding. They are also helpful in increasing alloy rupture strength at high temperature. The common nickel alloy carbides are primary MC and secondary M₆C₃, M₆C and M₂₃C₆. MC type carbides having cubic or script morphology are normally distributed randomly. M₆C precipitate as blocky or widmanstatten morphology and M₂₃C₆ tend to reside at grain boundary with irregular discontinuous blocky particles. Carbides are heterogeneously nucleated throughout the alloy both at transgranular and intergranular positions. The list of reactive and refractory elements forming carbides are Nb, Hf, Ti, and Ta. The less reactive elements like Mo and W also substitute for M atoms in carbides. During heat treatment MC decomposes yielding carbon which ingress the alloy and start number of important reactions. The formation of M₂₃C₆ by the following reaction is an important reaction:

\[
MC + γ \rightarrow M_{23}C_6 + γ'
\]

Or

\[
(Nb,Ti, Mo)C + (Ni,Cr, Al, Ti) \rightarrow Cr_{21}Mo_2C_6 + Ni_3(Al, Ti) - 1.0
\]

Reaction was assumed by metallographic observations of phase transformations at grain boundaries by Sims and Phillips [21]. The above reactions have been observed at temperature about 980°C and also at low temperature around 760°C. M₆C also found by the same reaction as:

\[
MC + γ \rightarrow M_6C + γ'
\]

Or

\[
(Nb, Ti, Mo)C + (Ni,Co, Al, Ti) \rightarrow Mo_3(Ni, Co)_3C + Ni_3(Al, Ti) - 1.1
\]

Also M₂₃C₆ and M₆C interact and form one from the other depending on the alloy.

\[
M_6C + M' \rightarrow M_{23}C_6 + M'' - 1.2
\]

\[
Mo_3(Ni,Co)_3C + Cr \leftrightarrow Cr_{21}Mo_2C_6 + (Ni,Co,Mo) [21]
\]

2.3.5 Borides

They are infrequently present at the grain boundary with Boron 50-500 ppm in superalloys. They tend to block the onset of grain boundary tearing under creep rupture loading. Borides are hard refractory particles with blocky to half-moon morphology [21].
2.3.5 **Topological Closed Packed (TCP) Phases**

They are undesirable inter-metallic compound phases and their crystallographic structures have common features. For any superalloy their composition is to be chosen to avoid rather than promoting the formation of these compounds. The TCP phases with brief description are listed below:

*Sigma (σ)* phase has hexagonal geometry with composition formula \((\text{Cr}, \text{Mo})_x(\text{Ni}, \text{Co})_y\); (where \(x\) and \(y\) vary from 1 to 7) and generally grows through \(\gamma'\) particles. It has detrimental effect with plate like morphology and hardness on alloy properties. They are source for crack initiation and propagation leading to low temperature brittle fracture. It contains high amount of refractory elements sapped from \(\gamma\) matrix resulting in loss of solution strengthening \([21]\).

*Laves phase* has general formula \(A_2B\), where \(A\) mostly \(\text{Nb}\) and \(B\) as heavy element. It requires 10-12% of \(\text{Nb}\) content.

\(\mu\) - has plate like morphology and detrimental for properties with composition i.e. \(\text{Co}_7\text{Mo}_6\).

*Delta Phase (δ)* incoherent stable orthorhombic crystal structure of \(A_3B\) type compound, as shown in Figure 2.1.3(a) with composition \(\text{Ni}_3\text{Nb}\). It precipitates normally around 700°C on the grain boundaries with thin plates extending to grains and its solvus temperature is around \(\sim 995°C\). They are also present in coarse or globular particles in thermo-mechanically processed materials. Their rate of precipitation increases around 900°C. As both \(\gamma''\) and \(\delta\) phase are \(\text{Nb}\) based which implies that \(\delta\) phase precipitation occurs with the loss of \(\gamma''\) phase. Its morphology contributes to the loss of hardness because of depletion of \(\gamma''\) in \(\gamma\) matrix and its presence in the structure lead to increased susceptibility to hydrogen cracking. However, \(\delta\) phase has some beneficial effects which are limiting grain growth during solution heat treatment \([22]\) and resistance to grain boundary creep fracture \([23, 24]\).

![Figure 2.1.3(a). The schematic showing crystal structure of δ (Ni3Nb) phase. [20]](image)
2.3.6 Grain size and Dislocations

Grain Size [25] is critical to the strength of Ni base alloys, excessively fine grains decrease creep and rupture strength whereas excessively large grains have lower tensile strength. A balance must be made to achieve intermediate grain size to optimize the alloy strength [21]. The rupture life and creep resistance increased as component thickness to grain size ratio increased. The grain size can be controlled by various modern techniques. MC carbides can be used to control the size of the grains since they pin the grain boundaries and inhibit grain growth. Grain size measurement can be made using the standard test method ASTM E112 or can be measured with the light microscopy (LM) by counting the number of grains in a selected area and computing the number of intercepts (N) which grain boundary makes with the random line drawn of certain length L. Then the average diameter of the grains along the random line can be calculated as

\[ D = \frac{L}{N} \]

For strengthening the matrix of alloy impurities or precipitates are introduced of the right size with heat treatments or ageing process; thus, to increase the yield strength of alloys dislocations are resisted by these precipitates either by cutting or bowing around them, as presented in Figure 2.1.3(b):

\[ \Delta \tau = \frac{Gb}{L - 2r} \]

\[ \Delta \tau = \frac{\gamma \pi r}{bL} \]

**Figure 2.1.3(b).** The schematic of cutting and bowing (looping) of precipitates by dislocations. Where \( G = \) Shear Modulus; \( b = \) burger Vector; \( L = \) Inter-atomic spacing; \( r = \) second phase particle radius; \( \tau = \) shear stress needed for passing the dislocation and \( \gamma = \) Anti-phase boundary energy.
The best resistance to dislocations movement occur at some intermediate precipitate radius denoted by \( r_{\text{critical}} \) where maximum strengthening for any specific alloy structure occur, shown in Figure 2.1.3(c). It is widely accepted that precipitate hardening is one of the most efficient method to improve the strength of alloys by introducing impure particles in the matrix. If we see Figure 2.1.3(c) it is evident that there is a critical radius at which maximum strengthening occurs. This \( r_{\text{critical}} \) is typically 5-30nm [205], after that cutting phenomenon of the particles is dominant. Thus, it is very important to know the maximum size of the particles present in the matrix of the alloy which might exceed the \( r_{\text{critical}} \) resulting in shearing or cutting.

![Figure 2.1.3(c)](image)

**Figure 2.1.3(c).** Schematic showing the critical radius of second phase particle where maximum strengthening can occur. Adapted from [205]

*Dislocations* always travel in pair in nickel base alloys which was supported by the findings in [26][159] using in-situ transmission electron microscopy as shown in Figure 2.1.4. The leading dislocation passing through \( \gamma \) phase cannot enter \( \gamma' \) phase without the formation of an anti-phase boundary (APB). Then the secondary dislocation is needed to remove the anti-phase boundary created by the first dislocation. The anti-phase boundary energy \( \gamma_{\text{APB}} \) is the activation energy required by dislocation to pass through the particles (\( \gamma'/\gamma'' \)) either by cutting or bowing. TEM dark field image in Figure 2.1.4(a) showing sheared \( \gamma' \) particles of size 140 nm in Nimonic 105 and dislocations travelling in pair in Nimonic PE16 having \( \gamma' \) size of 16nm. The schematic of dislocations travelling in pair is shown in Figure 2.1.5. Where pair of dislocations (1) and (2) passing through the \( \gamma \) matrix and interacting with \( \gamma' \) particles. \( \lambda \) is distance between particles, \( r \) is
the radius of the particles and \( \tau \) is the applied stress in the direction of moving dislocations. The interaction of dislocations with hydrogen atoms will be discussed later in section 3.8.

**Figure 2.14.** In-situ transmission electron microscopy reveals that dislocations travel in pair through \( \gamma / \gamma' \) Ni alloy microstructure. (a) Dark field micrograph showing sheared \( \gamma' \) particles of size 140 nm in Nimonic 105 and (b) showing dislocations travelling in pair in Nimonic PE16 where \( r = 8 \text{nm} \), imaged after unloading [26] [159].
Figure 2.1.5. Illustration of dislocations travelling in pair and shearing of ordered γ’ spherical particles (a) weak dislocation pair (b) strong dislocation pair. [160]

2.3.7 Nickel Based Superalloys

The nickel based alloys can be age hardened with 70% volume fraction of coherently precipitating spherical or cuboid phase Ni₃(Al, Ti, Nb) (γ’) in a polycrystalline Ni solid solution (γ phase). After long term exposures at temperatures above 650°C results in γ’ phase to be replaced by stable γ’, hexagonal Ni₃Ti, ETA₀ phase in form of coarse platelets. This transformation is associated with considerable loss in strength. Other phase that is metastable, forms preferentially at low to medium temperatures, of Ni₃Nb (γ’’’) with a body centered tetragonal (BCT) structure of fine platelets. This unstable phase tends to be replaced by stable Ni₃Nb orthorhombic δ phase of coarse platelets after extended exposure to temperature above 650°C[27]. The coherency of γ’ with γ phase gives remarkable properties for nickel base superalloys. γ’ has an ordered cubic crystal structure and hence precipitates evenly throughout the γ matrix and increase stability [28]. The volume fraction, size and spacing of γ’ is crucial for mechanical properties of the alloys depending on operating conditions. The morphology of γ’ could often lead to lattice strain because of γ –γ’ misfit and resistance to dislocation motion through the γ phase particularly when the γ’ particles are finer in size.
Figure 2.1.6. SEM image on the left and high magnification TEM image on right of γ matrix, showing spherical γ’ particles and dislocations network travelling through γ phase [29].

![SEM and TEM images](image)

Table 2.1. Nominal composition of Inconel 718, Inconel 925 and Incoloy 945 and 945x. Adapted from [32]

<table>
<thead>
<tr>
<th>Alloy (wt.%)</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Nb</th>
<th>Ti</th>
<th>Al</th>
<th>Cu</th>
<th>Fe</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNS N07718</td>
<td>53.7</td>
<td>18.25</td>
<td>2.9</td>
<td>5.07</td>
<td>0.99</td>
<td>0.55</td>
<td>0.01</td>
<td>Bal</td>
<td>0.04</td>
<td>0.025</td>
<td>0.08</td>
</tr>
<tr>
<td>UNS N09925</td>
<td>43.5</td>
<td>20.7</td>
<td>3.0</td>
<td>0</td>
<td>2.2</td>
<td>0.2</td>
<td>1.75</td>
<td>Bal</td>
<td>-</td>
<td>0.03</td>
<td>1</td>
</tr>
<tr>
<td>UNS N09945</td>
<td>47.0</td>
<td>20.5</td>
<td>3.2</td>
<td>3.1</td>
<td>1.5</td>
<td>0.15</td>
<td>2.0</td>
<td>Bal</td>
<td>-</td>
<td>0.005-0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>UNS N09945x</td>
<td>53.5</td>
<td>20.5</td>
<td>3.2</td>
<td>4.0</td>
<td>1.5</td>
<td>0.10</td>
<td>2.0</td>
<td>Bal</td>
<td>-</td>
<td>0.005-0.04</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The nominal composition of 718, 945, 945x and 925 in weight percentage (wt %) is shown in Table 2.1. The general physical metallurgy of all these nickel alloys share some common metallurgy. As already described earlier, the γ matrix is composed of disordered face centered cubic (FCC) structure nickel base austenitic phase called gamma γ. It has large number of solid solution elements such as Tungsten (W), Molybdenum (Mo), Chromium (Cr), Iron (Fe), Aluminium (Al), Titanium (Ti) and Cobalt (Co). Al and Cr form Al₂O₃ and Cr₂O₃ protective oxide films respectively that increase corrosion resistance [35]. The nickel content, above 42wt%, is generally needed for resistance to aqueous stress corrosion cracking [35], whilst molybdenum and chromium give the alloy general pitting corrosion resistance in reducing acid and alkali solutions [56][57]. Al and Ti are the primary precipitation strengthening components that form
part of γ' and most importantly Nb form γ'' and δ [58]. Whilst Ti increases the strength and
hardness of the alloy, an excessive amount is known to degrade micro-structural stability [59]. Al
increases the volume fraction of γ' [60] which may be expected to increase hardness further.
However, high aluminium contents reduce the lattice mismatch or coherency strain resulting in
a net decrease in hardness [60]. Similarly, the amount of Nb content is critical for any alloy as it
might aid in precipitating deleterious intergranular phases i.e δ and laves, or transgranular
metastable γ'' phase which significantly increase hardness and strength. This could be the reason
that 945 and 945x (hybrid of alloys 718 and 925) composition have been varied in terms of
change in Nb and Ni content.

These complex alloyed materials ensure safe, reliable and economical extraction of crude
oil and gases from subsea reservoirs with high temperature, pressure and H₂S contents. Whilst in
subsea, parts exposed to seawater are subjected to cathodic protection in the form of sacrificial
anodes: a means of protecting ferritic components from corrosion. CP has proven a cost-effective
and reliable way of preventing corrosion. As already described, the method has been linked to the
evolution of atomic hydrogen, whereupon embrittlement of neighbouring components may
occur. Hydrogen embrittlement (HE) has been a persistent problem for the design and integrity
of structural materials in various industries and despite decades of research [45-51] the
mechanisms for HE (will be discussed in detail under section 3.9.2) are not yet fully understood
with constant development of different methods to decrease HE sensitivity [52-54].
CHAPTER 3. Literature on Hydrogen Embrittlement (HE)

Extensive research [45-51] has been conducted over the past century to address HE phenomenon. A number of different mechanisms and remedies have been proposed to control hydrogen induced damage. Unfortunately, a rigorous model of predicting and quantifying HE in complex engineering materials, when exposed to hydrogen environments, has not been validated so far. This report is an effort to summaries the micro-structural features of CRA bolts and highlight the potential secondary phase responsible for HE susceptibility. This would help to analyze slow strain rate (SSR) testing of CRA alloys under CP. This is an effort that would help to assess HAC susceptibility for future CRA 718 bolts and hope to minimize the number of costly in-service failures. The failure reported for 718 revealed the deleterious role of intergranular precipitates but no evidence exists for any nano phase.

3.1. Hydrogen Embrittlement

Almost [69] every next generation alloy used in oil and gas industry for transportation, storage and integration are challenged by the reality of hydrogen which initiates a variety of degradation modes. This degradation in the form of hydrogen cracking depends strongly upon time and operating conditions i.e. stress, temperature and hydrogen source. The degradation of alloys under hydrogen influence (internal and external) is categorized as external hydrogen assisted cracking (EHAC) or hydrogen environment assisted cracking (HEAC) which relates to interaction of mechanical stresses (load), temperature and atomic hydrogen (H+ present in the lattice (or crystallographic planes), under direct exposure to hydrogen or hydrogen bearing gases or electrolyte during cathodic protection (CP). Whereas, internal hydrogen assisted cracking (IHAC) relates to the atomic hydrogen that ingress through the material at manufacturing level or when exposed to hydrogen containing medium, which lead to significant reduction of strength, ductility and cracking resistance. This study of hydrogen induced damage encircles around crack initiation, crack tip propagation, crack tip stress concentration, fracture mechanics and localised elastic plastic fracture zone. Hydrogen damage mechanism for stress corrosion cracking (SCC) and corrosion fatigue also lie under the banner of HEAC.

Hydrogen environment cracking is influence with the type of environment, as environment lead to different fracture path with unique appearance and localised plastic deformation (slip distribution) around cracks is experienced when compared to inert medium. The cracks (transgranular or intergranular) are dominant in susceptible structures such as HAZ region in steel weld microstructure, which is exposed to high temperature resulting in transformation of microstructure from ferrite to austenite and some into harder phase such as
martensite [63]. Similarly, nickel alloys containing delta phase on grain boundaries and some extending to grains are more vulnerable to HE cracking and dramatically reduce ductility [62]. High degree of cracking is observed under ambient temperatures (25°C) and generally associated in the temperature range between -100 and 200°C [63].

3.2. Challenge for CRA Bolts used subsea

Oil and gas wells which are now drilled deeper into coastal areas constitute of critical components integrated together under high pressure, temperature and extremely corrosive environment. Thus, there is always a need for versatile alloy that can be used specifically for integration purpose under range of environmental conditions. Over the past decades continuous development has been made to introduce high strength fastener materials in terms of increase toughness and resistance to corrosion. The primary choice adopted by many industries found to be low alloy steel grades and nickel base alloys. They have complex atomic concentration of elements having good physical properties such as high strength and corrosion resistance [10][30] but due to costly in-service HE failures of critical components i.e. fasteners and valves, solution to HE problem persist for scientific researchers.

Bolts and nuts which are made up of steel (e.g. ASTM 320 Grade L7, L7M, L43 bolts with ASTM 194 Grade 4, 7M, 7 nuts) and nickel base CRA's (Grade 725, 660, 686, 625,718, 945,945x) are usually selected for joining of components [64]. These bolts in service despite having high strength and corrosion resistance become prone to hydrogen assisted intergranular matrix/particle interface cracking when exposed to hydrogen source [42-44]. This HE failure is related to fastener hardness, strength level, pre-tensioning or release torque, microstructure phases and prior to service heat treatment. In one of hydrogen induced cracking of fasteners incident [64] where torque released was measured to be around 100-110 Nm but the required pre-tensioning torque during installation specified in the standards was 70Nm. This increase of pre-tensioning (or work hardening) significantly alters the hardness and strength levels of bolts. It is worth noting from hardness verification testing statistics that 17% of the fasteners installed had hardness above 380 HV10. Thus, pre tensioning factor could play a crucial role in bolt service life but the reported failure cases solely from this practice are few [64]. However, strength, hardness and hydrogen cracking of such bolts depend strongly upon structural features such as grain size, morphology of secondary phase, composition and segregation of secondary phase at intergranular positions. The main fasteners for example L7 of low alloy steel, if found to be out of specifications then attributes of that could be increased hardness (430-450 HV10), yield strength (1250-1300 MPa) and low tensile elongation ~10%. HE failure mode characteristics would be intergranular cracking prior to austenite grain boundaries, secondary cracking, multiple initiation points with apparent surface cracks and white calcareous deposits (evidence of
hydrogen charging under cathodic protection) at thread and from shank to bolt head. Another example of HE failure case experienced during on shore refurbishment of some subsea 'Xmastree' reported in [64], which occurred 10 years back at North sea on pressure and temperature transmitter KX flange, where ASTM 320 L7 specified low alloyed steel fasteners or screws found to be broken, shown in Figure 3.2.1(a)-(b). SEM micro fractography of these low alloyed steel fasteners reveal intergranular cracking, shown in Figure 3.2.1(c).

Figure 3.2.1. (a) The failure of transmitter flange showing brown rust deposits on surface. Whereas, (b) showing ASTM 320 L7 specified low alloyed steel fasteners (type M10x70/80) broken from thread (1) and (2), and complete separation from head area (3), with white calcareous deposits as evidence of cathodic protection under service. SEM fractography revealed intergranular cracking. Taken from [64]

Nowadays, INCONEL, INCOLOY and MONEL alloys are commonly used CRAs for manufacturing range of critical well components including fasteners and other downhole accessories and surface equipment. These complex alloyed fasteners ensure safety, integrity, reliability and economical extraction of crude oil and gases from reservoirs. Inconel718 (Ni-Fe-Cr) alloy being one of them has been developed in 1950's by international nickel company. Its use extend from aerospace industry (double aged – YS1034MPa (min)) as turbine application withstanding high temperature, pressure and creep resistance to oil and gas industry (single aged – YS827MPa (min)) because of high strength, toughness and corrosion resistance. Alloy718 having unique combination of room temperature strength, aqueous corrosion resistance and having ability to be heat treated to various strength levels made its use as fastener with exposure to corrosive conditions under cathodic protection(CP).

The studies have shown that first aged hardened alloy which was designed in 1984 specifically for oilfield applications was Incoloy 925. NACE MR0175 allows alloy 925 to be used
under roughly the same conditions of temperature and pressure as alloy 718 [65]. However, the yield strength range (758 – 862 MPa) of alloy 925 is lower than alloy 718 [66] but this is a low cost alternative for some well equipment and have superior corrosion resistance in certain oil patch environments than alloy 718 because it is niobium (Nb) free and cannot form delta phase [67][68]. The high credentials of 718 and 925 alloys are still not enough to pave their way in most of the corrosive environment where higher strength and superior corrosion resistance is required. Hence the aim was to develop a cost effective hybrid of alloys 925 and 718, containing best of both the alloys, higher strength capability and corrosion resistance. Finally, after continuous search for more economical, corrosion resistant and higher strength has led to introduce a new class of alloy, naming INCOLOY, with even lower base metal cost than INCONEL 718. As already mentioned, newly developed INCOLOY 945 is high strength, precipitation hardened and corrosion resistant Ni-Fe-Cr alloy. Its nickel content (47wt %) though less than INCONEL 718 (53wt %) but provide excellent stress corrosion cracking, ductility and impact strength. Later, 945x was introduced with YS up to 1138MPa. These alloys can be used in high pressure high temperature (HPHT) applications and are qualified to NACE MR0175/ISO 15156-3 level V and VI. Their excellent corrosion resistance, low cost and high strength may eventually dominate the market share for alloy 718 [65].
3.3. Hydrogen Evolution into CRA Bolts

A number of methods are being used to protect CRA bolts from corrosion environment in which they are operating. As already mentioned hydrogen ingress to fastener lattice is the first step towards hydrogen assisted cracking. The embrittlement process is complex and depends on many parameters which will be discussed in detail later. The most common method of protecting material structures from environment corrosion is cathodic protection (CP).

\textit{Cathodic Protection} (CP): It is one of the effective methods known as corrosion inhibitor to protect alloys being used in many applications from corrosion. Structures that are protected through this method include water storage tanks, ships, pipelines, ports, piers etc. The first use of CP was on British Navy Ship (1822), HMS Samarang \cite{71} by Sir Humphery Davy. The body of ‘samarang’ was made of copper and was protected using zinc anodes. Later with some success, large number of steel components (ships) was dipped into molten zinc for corrosion prevention. It was not until 1920s the technology reached oil transportation sector but this time to protect subterranean pipelines \cite{72}.

The cathodic hydrogen evolution occurs in several steps from aqueous electrolytes. However, the individual equations may vary depending upon electrolyte but the overall hydrogen evolution reaction (HER) or for simplification common dissociation reactions are:

\begin{align*}
\text{H}_2\text{O} & \quad \longrightarrow \quad \text{H}_3\text{O}^+ + \text{OH}^- \quad \text{(water)} - 1.3 \\
\text{HCL} + \text{H}_2\text{O} & \quad \longrightarrow \quad \text{Cl}^- + \text{H}_3\text{O}^+ \quad \text{(Acid)} - 1.4
\end{align*}

Where \( \text{H}_3\text{O}^+ \) is positively charged species that forms when water (\( \text{H}_2\text{O} \)) picks up a hydrogen cation (\( \text{H}^+ \)).

Hence hydrogen evolution through different solutions will be as following:

\[ 2\text{H}_3\text{O}^+ + 2e^- \rightarrow \text{H}_2 + 2\text{H}_2\text{O} - 1.5 \]
In alkaline solutions $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ – 1.6

The common reaction at cathode with metal (M) which is being protected undergoes following reaction:

In acid solution \[ \text{H}_3\text{O}^+ + \text{M}^+ \text{e}^- \rightarrow \text{MH}_{\text{ads}} + \text{H}_2\text{O} - 1.7 \]

In alkaline solution (electrolysis of water) \[ \text{H}_2\text{O} + \text{M}^+ \text{e}^- \rightarrow \text{MH}_{\text{ads}} + \text{OH}^- - 1.8 \]

Where MH$_{\text{ads}}$ represent hydrogen atom adsorb at metal surface. After this reaction, the next step of HER depends upon the nature of electrode metal, cathodic current density and operating environment.

3.4. Hydrogen Entry into Metal

The small amount of hydrogen that is evolved from cathode enters into metal lattice. However, the rate of hydrogen entry into metals depends upon several factors such nature of metal (or alloy), electrolyte composition, alloy composition, condition of surface, current density at cathode, temperature, pressure, electrode potential etc.

Two different models have been proposed for hydrogen entry in to metal lattice. The first by Bockris and co-workers [73-76] proposed that hydrogen entry into metal lattice through adsorbed state (MH$_{\text{ads}}$) and is identical to state in which hydrogen is absorb into metal lattice which then could lead to hydrogen evolution. The following sequence of cathode reactions depicts in the model:

\[ \text{H}_3\text{O}^+ + \text{M}^+ \text{e}^- (\text{slow}) \rightarrow \text{MH}_{\text{ads}} + \text{H}_2\text{O} - 1.9 \]

\[ \text{MH}_{\text{ads}} \leftrightarrow \text{MH}_{\text{ads}} - 2\text{H}_2\text{O} - 2.0 \]

\[ \text{MH}_{\text{ads}} + \text{MH}_{\text{ads}} \rightarrow \text{H}_2 + 2\text{M} - 2.1 \]
Here, $\text{MH}_{\text{abs}}$ is hydrogen absorbed in metal lattice and $k_1$, $k_2$, $k_3$ and $k_4$ are rate constants of various steps. This model predicts that entry rate of hydrogen to metal lattice is directly proportional to amount of adsorbed hydrogen atoms onto metal surface [77].

The secondary model by Bagotskaya and Frumkin [78] state that hydrogen enters in to metal lattice in atomic form in which it is discharged and the intermediate state in which metal enters the lattice is not similar with adsorbed intermediate state, which result in hydrogen evolution. The cathodic reactions occur in the following sequence:

i) $\text{H}_3\text{O}^+ + \text{M} + e^{-} \xrightleftharpoons[k_{-4}]{k_{4}} \text{MH}_{\text{abs}} + \text{H}_2\text{O} - 2.2$

ii) $\text{H}_3\text{O}^+ + \text{M} + e^{-} \rightarrow \text{MH}_{\text{ads}} + \text{H}_2\text{O} - 2.3$

iii) $\text{MH}_{\text{ads}} + \text{MH}_{\text{ads}}k_3 \rightarrow \text{H}_2 + 2\text{M} - 2.4$

In the equations used above $k_4$ and $k_4$ are rate constants.

The evolution of hydrogen results in the degradation of protective coatings, allowing hydrogen to come into contact with the surface of the metal. A comprehensive summary of adsorption processes is given by Barnoush in [77].

There are certain species that are found to be responsible for hydrogen promotion or entry in to metal or alloys operating in liquid or gaseous environments. The list include certain compounds of the phosphorus; arsenic; antimony (V-A Periodic Group), Sulphur; Selenium; tellurium (VI-A Perodic Group), the anions CN-(cyanide); CNS-(rhodanide); I-(Iodide), the compounds of iron CS$_2$ (carbon sulphide); CO (carbon monoxide), CON$_2$H$_4$(Urea) and CSN$_2$H$_4$(thiourea). Most effective promoters are those compounds made from elements of group V-A and VI-A. However, there are little indications or actions of promotion for mercury (Hg), Tin (Sn) and Lead (Pb) salts along with fluoride and bromide ions but are considered as weak and inconsistent [77].

In subsea, corrosion resistant alloys have their cracking because of two different mechanisms, Hydrogen Embrittlement (HE) and Stress Corrosion. Hydrogen cracking occurs due to cathodic reaction in which hydrogen ions ($\text{H}^+$) from corrosive environment diffuse, according fick's law of diffusion (described in detail later), through the CRA lattice and lower the ductility which results in embrittlement or hydrogen induced cracking (HIC). If the material under CP is also bearing sufficient stress then it leads to hydrogen induced stress cracking (HISC) or cracking in $\text{H}_2\text{S}$ environment would result in sulphide stress cracking (SSC). The severity of HISC and SSC increases from low temperature to room temperature. Stress corrosion cracking (SCC) on the
other hand relate to anodic reaction in which crack is initiated and propagated under stress by dissociation of electrolyte, well fluid (chloride or $H_2S$) into ions. Loss of metal at the edge of crack continues until brittle fracture occurs. SSC by $H_2S$ is similar to chloride SCC and potential for SCC increases with higher temperatures and concentrations of $H_2S$, chloride and elemental sulphur. Nickel (austenite-FCC) has been used as a key element to avoid or delay such cracking. Figure 3.2.3 shows change of hydrogen environment embrittlement index (HEEI) *(for more detail about HEEI, see page 45, 55, 63)* which is a parameter for measuring severity of HE, as the nickel content increases. It is shown that for Ni-Fe-Cr alloys HEEI begin to decrease after Ni content of $\sim 33\text{wt}\%$. The smaller value of HEE index suggested that this material strength grade is more susceptible to hydrogen embrittlement. The detail about hydrogen environment embrittlement index (HEEI) will be discussed in detail later this report. Similarly the Figure 3.2.4 shows time to cracking (hours) changes as Ni content varies in different alloys (nickel content of alloy 718, 945 and 945x is highlighted).

![Figure 3.2.3](image)

**Figure 3.2.3.** The graph shows hydrogen environment embrittlement index (HEEI) for Ni-Fe-Cr superalloys and austenitic stainless steel as function of Ni content (wt\%) [69]. *Red dotted arrows indicate Ni content in alloys 718, 945 and 945x.*
The graph shows susceptibility of cracking depending upon nickel content in a range of materials from duplex stainless steel to nickel alloys [70].

The increase of Ni content in alloys though decreases the HEE index but increase the time to cracking which is attributed as enhanced ductility. It should be noted that presence of interstitial hydrogen in lattice always found to be prejudicial for global performance and more specifically for mechanical properties such as ductility, strength and fracture toughness. Hydrogen as being interstitial solute considered to be universally adverse. It basically lowers the fracture energy (reduce fracture toughness) of the defect and encourage cleavage brittle fracture. The interaction of hydrogen with secondary phase in bulk lattice is key phenomena that needs to be understood and is aim of the study. The data already published by some researchers [42, 43] for the effect of hydrogen on properties of corrosion resistant alloys including Inconel718 [44] suggest a detrimental role of secondary phase particles on grain boundaries. However, still a rigorous method that predicts HE susceptibility and its affiliation with secondary phase particles with aid of fractography needs to be developed. A number of hydrogen embrittlement mechanisms have been proposed already e.g. Hydrogen enhanced localised plasticity (HELP); Hydrogen enhanced decohesion (HEDE); Hydride Induced embrittlement (HIE) and Adsorption Induced Dislocation Emission (AIDE), but these involve assumptions that limit their use and
3.5. Defects in Lattice

There are several defects that are critical to the mechanical properties of metal or alloys. These defects with their brief description are listed below:

**Dislocations** are line defects around which some of the atoms of the crystal lattice are mis-aligned. Dislocation presence results in lattice distortion. The direction and magnitude of such distortion is expressed in terms of *Burger Vector (b)*. There are two main types of dislocations, *edge* and *screw* dislocation, Figure 3.2.5.
Generation and movement of screw dislocation

Figure 3.2.5. Schematic shown for Edge (top) and Screw (bottom) dislocations. [79]

For an edge dislocation burger vector $b$ is perpendicular to the dislocation line, whereas in screw dislocation it is parallel. In metallic materials, $b$ is aligned with close packed crystallographic directions and its magnitude is equivalent to inter-atomic spacing.

**Grain boundaries** occur where the crystallographic direction of the lattice abruptly changes. This usually occurs when two crystals begin growing separately and then meet. They impede dislocation movement and act as a strengthening mechanism but the presence of grain boundaries can be initiation point for corrosion and creep.

**Stacking faults** occurs in a number of crystal structures but the common example is in close packed structure. FCC structures differ from HCP structure only in stacking order both structures have close packed atomic planes with six fold symmetry, the atoms form equilateral triangles. For the FCC structure stacking sequence is $ABCABCABC$ and for HCP it is $ABABAB$ [80].

**Twinning** occurs when two separate crystals share some of the same crystal lattice points in a symmetrical point. It results when portion of the crystal takes an orientation of the rest of un-twinned lattice in a definite symmetrical way. The twinned portion of crystal is mirror image of parent crystal [81].

**Void**s are small regions where there are no atoms and can be considered as cluster of vacancies which are generally thought as deleterious.

**Impurities** can cluster together to form small regions of a different phase. They are often called precipitates which enhance material properties.

**Precipitates** can be coherent and in-coherent which have different implications on the microstructure and properties of alloys (see section 'Phases of Nickel Based Alloys' for more detail).

**3.5.1. Hydrogen Diffusion Concept**

**Diffusion** [82] is the fundamental material science concept in which mass or heat flow from one place to another at atomic or ionic molecular scale. When dealing with solids, diffusion can be thought of as movement of atoms from one atomic site (vacancy-defect in lattice) to another. However, there is energy barrier, $Q$, also known as activation energy that needs to overcome when atom changes site. Diffusion in solid also depends on temperature, as on high temperature atoms gain enough thermal energy to move to another site. The probability of atom
overcoming the energy barrier \((Q)\) is determined by Boltzman statistics, which is function of height of energy barrier \((Q)\) and temperature \((T)\) of the system.

\[
P = A \exp\left(-\frac{Q}{K_b T}\right) - 2.5
\]

Where \(K_b\) is the boltzmann constant

There are two types of diffusion mechanisms: substitution diffusion and interstitial diffusion. Atoms sometime substitute other atoms in the bulk lattice or reside in the interstice if it is small atom. However, substitution or swapping of atoms require a lot of energy which is practically not feasible so there are vacancies present in the lattice as defects which helps substitutional diffusion to occur. Diffusion of atoms is therefore dependent upon the presence of vacancies in the lattice and rate of diffusion is dependent on two factors: ease of atoms to move in to vacancy and ease of formation of vacancies in the lattice. This dependence upon presence of vacancies makes substitutional diffusion slower than interstitial diffusion. Whereas in interstitial diffusion atoms are free to move to adjacent interstice. There is still an energy barrier to overcome but it is lower due to smaller atom size and there are lots of vacant site where atoms can diffuse into.

**1D-Random walk** Consider an atomic lattice with lattice parameter \(\lambda\). The atoms at atomic site oscillate \(n\) times with vibration frequency \(v\). The atoms will make random jumps left or right moving a distance \(d\) when left for time \(t\).

For random walk, mean diffusion distance moved \(\bar{x}\) is equal to the following:

\[
\bar{x} = \lambda \sqrt{n} - 2.6
\]

\[
\bar{x} = \lambda \sqrt{vt} - 2.7
\]

In a crystal lattice, concentration of impurity atoms, \(C\) (atoms \(m^{-3}\)) is not constant and there is concentration gradient across the lattice which acts as driving force for diffusion of impurity atoms.

**Fick's 1st Law** states that concentration gradient \(\frac{\delta C}{\delta x}\) to the flux \(J\) (number of atoms passing through unit area in unit time) of atoms within the crystal.

\[
J = -D\left(\frac{\delta C}{\delta x}\right) - 2.8
\]
Where, $D$ is the diffusivity of the diffusing material. We can modify the equation of mean diffusion distance and can derive the equations from it as below.

$$\bar{x} = \lambda \sqrt{vt} - 2.9$$

$$D = \frac{1}{6} v \lambda^2 - 3.0$$

$$\bar{x} = \sqrt{6Dt} - 3.1$$

$$\bar{x} \approx \sqrt{Dt} - 3.2$$

However, Fick's 1st law is valid only to situations in which concentrations at two points are constant [82].

**Fick's 2nd law** states that how concentration gradient changes with time. The following equation below represent the variables involve.

$$\frac{\delta C}{\delta t} = D\left(\frac{\delta^2 C}{\delta x^2}\right) - 3.3$$

As an example, we analyse and assume a constant concentration hydrogen source diffusing into steel bar from one side and steel bar has semi-infinite length. Assuming, hydrogen will diffuse into steel and steel will not diffuse at all.

First the boundary conditions for solving the above case are defined:
Concentration of Hydrogen at the start is zero; \( C(x > 0, t=0) = 0 \)

Concentration at \( x=0 \) is constant; \( C(x=0, t) = A \)

\( C(x,t) \) is the concentration of the impurity, hence the solution for \( C \) will be:

\[
C(x, t) = A - \operatorname{erf} \left( \frac{x}{2 \sqrt{D t}} \right) - 3.4
\]

**NOTE:** where \( \operatorname{erf} \) is the error function

The general equation of hydrogen diffusivity into alloys on which many authors [92][94][95], have shown understanding and agreed is given below:

\[
D_H = A \exp \left( -\frac{Q}{RT} \right) - 3.5
\]

Where, \( Q= \) Activation energy for hydrogen diffusion; \( R= \) Gas constant; \( T= \) Absolute Temperature

Diffusion of hydrogen through corrosion resistant alloys CRAs is of interest to the material engineers in the modern world. Hydrogen permeation and diffusion have been investigated by several authors [92][94][95], including for Inconel 718 [121][126] over the range of temperature 80-500°C. All studies were in good agreement and the resulting relationship of \( D_H \), hydrogen diffusivity, against the absolute temperature \( T \) for Inconel 718 is expressed by the following relationship (in \( m^2 s^{-1} \)) [110]:

\[
D_H = 4.06 \times 10^{-7} \exp \left( -\frac{Q}{RT} \right)
\]

However, the change in temperature \( T \) results in significant change in activation energy \( Q \) for hydrogen to diffuse through the lattice of Inconel718 because of quantum effect. It is important to consider the effect at room temperature, where \( Q \) is approximately 50 KJ\( mol^{-1} \) for Inconel 718 (taken from [110]). Further, extrapolating the Arrehenius relation the diffusion coefficient \( D_H \) for Inconel 718 at room temperature can be expected to be about \( 10^{-15} m^2 s^{-1} \).

Also, permeation depth of hydrogen due to lattice diffusion can be approximately given as:

\[
x = \sqrt{2D_H t} - 3.6
\]

Hence, close approximation of hydrogen penetration depth during cumulated time for cathodic charging and SSRT test can be calculated using the equation depending on hydrogen diffusion constant (\( D_H \)) of material under investigation and charging time (\( t \)).
3.6. Hydrogen Interaction with defects

The defects in the metal lattice are always considered as impurities or imperfections which hinders or interact with the path of diffusing hydrogen, thus effect the mechanism of hydrogen embrittlement (HE). Though we have scant knowledge about these interactions at atomic scale in alloys but we do have assumptions based theories for hydrogen induced damage in ideal or perfect metal lattice (see section ‘3.9.2). Figure 3.2.6 shows schematic of metal lattice which illustrate different types of defects that could be present for interaction with hydrogen atoms.

![Figure 3.2.6](image_url)

**Figure 3.2.6.** A schematic illustration of hydrogen atoms (in red) accumulation or trapping at grain boundaries, dislocations, surface and sub-surface sites, along with conventional hydrogen solubility as interstitial dissolution. Note: grain boundaries and vacancies trap hydrogen differently than lattice, whereas, at edge dislocations hydrogen segregation region would be expected of cylindrical shaped. Adapted from [77]

The defects which are often seen in metal lattice are commonly dislocations, grain boundaries, voids or vacancies, traps sites at surface, interstitial, subsurface sites etc. They are briefly described next along with their interaction with hydrogen atoms:

3.6.1. 1D Dislocations- Line Defects

It is the presence of dislocations and their ability to readily move under influence of stresses induced by external loads that leads to the characteristic malleability of metallic materials. Dislocation moving under stress is called slip and is responsible for plastic deformation in metallic alloys. Strain in the lattice and dislocations entangling with each other are critical to material behaviour [79].

*Hydrogen interaction* with dislocations in metal or alloys is of great importance because of localised plasticity flow and hydrogen mobility. The relationship between dislocations and
hydrogen atoms is critical because of the ability of hydrogen atoms to reduce fracture toughness. Solute hydrogen tends to segregate around dislocations and dislocation cores forming an atmosphere. The interaction between stress field of dislocation and strain field around hydrogen interstitial atom results in formation of elastic energy. Around edge, screw and all mixed dislocations have continuously increasing stresses towards the core causing range of binding energies [83].

There have always been conflicting results regarding the theory postulated by authors that presence of hydrogen can increase or decrease the flow stress within same material. Taking example of nickel [84] where increase in flow stress has been found but opposite has found by Kimura and Birnbaun [85].

Hydrogen atom in fcc metal have associated strain of cubic symmetry which is because hydrogen interstitial occupy octahedral sites. However, for bcc metals these interstitials tend to reside at tetrahedral sites resulting in tetragonal distortion but experimental evidence suggest little or no distortion. The interaction energy (ε) is simplified in general as the product of stress and strain tensor, as shown:

\[ \varepsilon = (\sigma_1 + \sigma_2 + \sigma_3)\frac{V_H}{3} - 3.7 \]

Where \( \sigma \) are principle stresses and \( V_H \) is partial molar volume.

Specifically for an Edge dislocation the equation can be rewritten as:

\[ \varepsilon = \left( \frac{A}{r} \right) \sin \Theta - 3.8 \]

Where \( r \) is distance from dislocation core; \( \Theta \) is angle between glide plane and position vector \( r \) and \( A \) is material elastic constant together with burger's vector of dislocation and partial molar volume of hydrogen.

Site energy \( \varepsilon \) for hydrogen atom depends upon coordinates \( r \) and \( \Theta \) [77]. It is believed that segregation of hydrogen atoms to dislocations result in formation of localised regions of higher hydrogen concentrations. These regions have their own energy barriers because of elastic strain of hydrogen atoms; making a boundary between 'cloud' of local hydrogen concentration and surrounding matrix. It is also worth noting that experimental characterisation of interaction of dislocations with hydrogen atoms in presence of small volume fraction of lattice defects would be difficult. There are other methods which can be used for interaction study in hydrogen charged and hydrogen free specimens i.e. stress strain relationship from tension, compression and nano-indentation [86-88]. The last method nano-indentation is believed to be best technique for studying interaction between hydrogen atoms and dislocations by confining a probed volume of
material to a scale comparable to defect size [77]. Further, for probing at small volumes; numerical simulation method is proposed to understand the influence of solute hydrogen on dislocation interaction and in situ thin stressed TEM foils (equipped in TEM with straining stage and environment cell to add dissociated hydrogen into specimen) are also used to characterise dislocation arrangements under TEM [8][89][90].

3.6.2. Internal Boundaries

**2D Planar Defects** Grain boundaries (Gbs) are considered as defects in the lattice structure and their interaction with hydrogen interstitials result in intergranular hydrogen embrittlement. This type of induced damage is facilitated by Gbs by providing low energy pathway for hydrogen diffusion and is not particularly confined to bcc or fcc materials. This low energy pathway enhances diffusion process and backed up by many experimental studies including [91][92]. Some other investigations [93][94] regarding grain boundary diffusion in nickel also support the results that Gbs diffusion rates were of several orders of magnitude greater that experienced in crystalline matrix. However, these investigation or studies face challenges because of the fact that hydrogen may be trapped at vacancies or dislocations present within Gbs [95]. Further in addition, there are other non-metallic compounds such as carbides, nitrides, and oxides which provide hindrance to hydrogen atoms. Hence, it is not simple to define the relationship between hydrogen diffusion through Gbs and trapping at these defects. The reason could be structural complexities for internal boundaries i.e. including grain boundaries and phase boundaries having range of hydrogen binding energies depending upon coincidence and orientation relation respectively. The theoretical modelling has not yet reached a state of defining the range of binding energies for each different trap [77].

**3D - Point defects** Vacancies are the simple form of defects with an empty lattice site. They are believed to be entropically stabilised and are always present in the lattice of any material [96]. Hydrogen atoms always trap at such defects and several studies investigated their interaction with these defects [97][98][99] Whenever, the state of chemisorption (which involves chemical reaction between adsorbate and surface and new bonds are created at adsorbant surface) of hydrogen is energetically favoured over interstitial solution hydrogen, as in normally occurring event, hydrogen is driven to the vacancy. Vacancy appear to be free surface for hydrogen atom to be trapped in, thus the volume associated with the vacancy is relatively large which results in the large binding energy comparable to hydrogen in chemisorbed state [77]. The equilibrium concentration of vacancies in a metal lattice changes with ingress of hydrogen and estimated vacancy concentration can obtain a value as high around 23% [99]. Also some experiments [97] revealed that hydrogen atoms could induce ‘superabundant vacancies’ (SAV) in metals. Further, Fukai and Okuma [100] experienced decrease in lattice parameter during annealing Pd-H and Ni-
H in hydrogen at 5GPa-1000K. These experiments suggested that though hydrogen atoms originally are present at interstitial positions in bulk matrix but they are trapped (3-6 hydrogen atoms because of large free space in a single vacancy) with high binding energies to these vacancies. Under ambient temperature and pressure conditions, approximately 6 hydrogen atoms tend to be trapped corresponding to number of octahedral sites in a single vacancy.

### 3.7. Parameters Effecting Hydrogen Assisted Cracking (HAC)

Most common way to understand the effect of hydrogen on mechanical properties is to perform mechanical tests with samples charged with hydrogen and then compare with those tested without hydrogen (in-air). The degree of embrittlement can be measured using hydrogen environment embrittlement Index (HEEI), which will be discussed in more detail. The mechanical testing normally conducted at cyclic or static loading with hydrogen charging by In situ, electrochemically, external gas phase or by plasma at range of temperatures and pressure. These differences in parameters result in discrepancies in the output data for same metal or alloys. The effect of each factor on embrittlement susceptibility is critical to understand and an effort has been made to collect not all but at least some experimental data for some materials (i.e. including Inconel718) under hydrogen induce damage with varying conditions of parameters.

#### 3.7.1. Pressure

The increase in hydrogen pressure means increase in hydrogen embrittlement susceptibility and/or with exponential decrease of embrittlement index from unity. The number of atomic hydrogen per unit volume increases with increasing hydrogen pressure if consider temperature as constant. This would increase dislocation emission from the crack tip and localised embrittlement in front of crack area. A number of alloys including Inconel718 has been tested for HEE index based on _notch tensile strength (NTS) ratio_ under high pressure hydrogen and the results have been shown in Figure 3.2.7[101][102]. Further, the Figure 3.2.8 shows the effect of hydrogen pressure on threshold stress intensity value (K\(_{\text{th}}\)) for Inconel 718 and Incoloy 903 at room temperature. This can be thought of as when hydrogen pressure increases hydrogen atoms are attracted to the defect or crack site, thus the threshold stress intensity for fracture reduced below the value at which dislocation emission occur, which is alternative or counter mode that leads to crack blunting and reject cleavage like brittle fracture[142]. On top of increase hydrogen pressure, Robertson [126] had concluded in his study about hydrogen transport and embrittlement results for Inconel718 and Incoloy903. He postulated about the metallurgical factors responsible for embrittlement and stated that little difference exist between hydrogen transport parameters for the two alloys but Incoloy903 was found to be resistant to formation of deleterious phases hence less vulnerable to hydrogen embrittlement. Inconel718 on the other
hand with the ability to form delta δ phase (Ni₃Nb) is more damaged or hydrogen embrittled [110][117].

![Figure 3.2.7](image1.png)

**Figure 3.2.7.** Effect of hydrogen pressure on HEE index of various superalloys including Inconel718. Taken from [69]

![Figure 3.2.8](image2.png)

**Figure 3.2.8.** Effect of hydrogen pressure on threshold stress intensity value for Inconel 718 and Incoloy 903 [69].

Recent studies [103],[104] reveal the relationship between hydrogen environment embrittlement index and hydrogen pressure, which state that a power law exist with exponential function of hydrogen pressure.

\[
\text{HEEI} = \alpha (P)^{-3.9}
\]

Where \(\alpha\) is proportional constant, \(P\) is hydrogen pressure in MPa and \(n\) represent material embrittlement severity and decaying exponential value.
In the past, the relationship was based upon Sievert’s pressure gas law in which the degree of embrittlement was believed to be approximately equal to square root of hydrogen pressure \[ \sqrt{P_{H_2}} \] [105][106].

### 3.7.2. Temperature

Temperature has always been an important factor to consider for hydrogen embrittlement (HE). HE effects occur over a wide range of temperatures from cryogenic temperatures (~200°C) to room temperature and then to high homologous temperature. For example, Figure 3.2.9(a) shows HEE index of three Nickel based superalloys i.e. Inconel718 [107], EP741 and EP99 [108] based on area reduction ratio. Specifically, for Inconel718 the HEEI is most severe around room temperature and still evident with HEEI greater than 0.60 with high temperature close to ~500°C. For EP741 and EP99 the HEEI is least around room temperature but become more prominent at high temperature ~490°C. Whereas, HEEI based on notch tensile strength ratio for Astroloy, Inco100, Merl 76 and Waspaloy is very severe around ~500°C and approximately negligible around room temperature, as shown in Figure 3.2.9(b)[109]. This may be because of the process in which high thermal activation energy that is available at high temperatures allow hydrogen atoms to react chemically with precipitates or impurities at grain boundaries, known as hydrogen reaction embrittlement (HER). This HER process add further fracture features at high temperature when compare to fracture appearance around room temperature.
Figure 3.2.9. Effect of temperature on HEE index based on (a) area reduction ratio (RA) and (b) notch tensile strength (NTS) for (a) Ni-based superalloys (b) Nickel based powder metallurgy (PM) superalloys [69].

3.7.3. Heat treatment

The degree of hydrogen embrittlement for certain type of alloys is significantly affected by heat treatment and product morphology. Therefore, the shape of the fastener with thread, shank and head area could have different implication on severity of HE based on Area reduction (AR) or notch tensile strength (NTS) ratio. Heat treatment effect on Inconel718 has been very profound in wrought product form. The heat range for annealing process is from 955 – 1050 °C (for project alloys it was between 1030-1300°C) which shows significant variations in HEEI; severe embrittlement (HEEI~0.54) when solution annealing temperature is ~955°C and slight embrittlement (HEEI~0.83) when solution annealing is high around 1037°C. Solution annealing at 1250°C for Inconel718 in project 22577 is to dissolve back as many MC carbides into matrix as possible as they are potential hydrogen traps. The data for Inconel718 (in combination of five different heat treatments and product forms) has been collected. This effect of heat treatment and product morphology (i.e. include weld and heat affected zone (HAZ)) on HE based on notch tensile strength (NTS) ratio is shown in Table 3.0. With further heat treatment for ageing on both set of solution annealing temperatures results in decrease of HEEI from unity or enhance hydrogen embrittlement effects. (Table 3.0 will be discussed in more detail). This might be because of the metallurgical precipitates (see section 'Hydrogen transport and effect in Ni-Fe-Cr Alloys' for more detail) that nucleates within grains and at grain boundaries during the entire heat treatment process.
<table>
<thead>
<tr>
<th>Heat treatment and ageing schedule for Inconel718</th>
<th>Product form</th>
<th>HEE Index (NTS)</th>
<th>H Pressure (MPA)</th>
<th>Temp (°C)</th>
<th>Strength in Helium (MPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat treatment A:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>940°C/1h (Solutionised)</td>
<td>Rolled.bar</td>
<td>0.54</td>
<td>34.5</td>
<td>22</td>
<td>1952 1124 1393</td>
</tr>
<tr>
<td>720°C/8h (1st Ageing)</td>
<td>Forging</td>
<td>0.59</td>
<td></td>
<td></td>
<td>2000 1097 1366</td>
</tr>
<tr>
<td></td>
<td>Plate</td>
<td>0.86</td>
<td></td>
<td></td>
<td>1979 1097 1414</td>
</tr>
<tr>
<td></td>
<td>Plate (weld metal)</td>
<td>0.79</td>
<td></td>
<td></td>
<td>1421 1034 1193</td>
</tr>
<tr>
<td></td>
<td>Plate (weld HAZ)</td>
<td>0.63</td>
<td></td>
<td></td>
<td>1828</td>
</tr>
<tr>
<td>Heat treatment B:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>940°C/1h (Solutionised)</td>
<td>Rolled.bar</td>
<td>0.70</td>
<td>34.5</td>
<td>72</td>
<td>1655 876 1255</td>
</tr>
<tr>
<td>815°C/8h (1st Ageing)</td>
<td>Forging</td>
<td>0.76</td>
<td></td>
<td></td>
<td>1745 855 1228</td>
</tr>
<tr>
<td></td>
<td>Plate</td>
<td>0.86</td>
<td></td>
<td></td>
<td>1731 917 1303</td>
</tr>
<tr>
<td></td>
<td>Plate (weld metal)</td>
<td>0.78</td>
<td></td>
<td></td>
<td>1241 869 1145</td>
</tr>
<tr>
<td></td>
<td>Plate (weld HAZ)</td>
<td>0.75</td>
<td></td>
<td></td>
<td>1393</td>
</tr>
<tr>
<td>Heat treatment C:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1050°C/0.3h (Solutionised)</td>
<td>Rolled.bar</td>
<td>0.71</td>
<td>34.5</td>
<td>22</td>
<td>2221 1110 1345</td>
</tr>
<tr>
<td>760°C/10h (1st Ageing)</td>
<td>Forging</td>
<td>0.76</td>
<td></td>
<td></td>
<td>2338 1166 1366</td>
</tr>
<tr>
<td></td>
<td>Plate</td>
<td>0.70</td>
<td></td>
<td></td>
<td>2207 1152 1407</td>
</tr>
<tr>
<td></td>
<td>Plate (weld metal)</td>
<td>0.77</td>
<td></td>
<td></td>
<td>1848 1138 1372</td>
</tr>
<tr>
<td></td>
<td>Plate (weld HAZ)</td>
<td>0.72</td>
<td></td>
<td></td>
<td>2076</td>
</tr>
<tr>
<td>Heat treatment D:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1025°C/10min (Solutionised) no ageing</td>
<td>Rolled.bar</td>
<td>0.83</td>
<td>34.5</td>
<td>22</td>
<td>1124</td>
</tr>
<tr>
<td>Heat treatment E:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1025°C/10min (Solutionised)</td>
<td>Rolled.bar</td>
<td>0.71</td>
<td>34.5</td>
<td>22</td>
<td>2200 1152 1379</td>
</tr>
<tr>
<td>760°C/9.5h (1st Ageing)</td>
<td>Forging</td>
<td>0.70</td>
<td></td>
<td></td>
<td>2221 1166 1393</td>
</tr>
<tr>
<td></td>
<td>Plate</td>
<td>0.75</td>
<td></td>
<td></td>
<td>2200 1172 1428</td>
</tr>
</tbody>
</table>

Table 3.0. Effect of heat treatment on various product form of Inconel718 and their corresponding HEE index based on NTS ratio at room temperature. Adapted from [69]

Generally, the effect of secondary phase with hydrogen has always been an important thing to consider and several studies [62] [110] with practical experiments have been carried out to investigate the mechanism of embrittlement and even in current study the aim was to identify the potential susceptible secondary phase under the applied heat treatment, which could assist to analyse slow strain rate mechanical tests under CP.


3.8. Hydrogen transport and effect in Ni-Fe-Cr Alloys

The study of hydrogen transport in superalloys is the fundamental necessity to understand hydrogen embrittlement mechanism. The corrosion resistant alloys which are exposed to highly corrosive offshore oil and gas environment under cathodic protection have to endure hydrogen evolution from surface to inner lattice structure. This transport depends significantly upon temperature, as high temperature applications have higher rates of diffusion and solubility, when compared to applications running close to room temperature. Ability of the alloys to be supersaturated with large amount of hydrogen and then upon operating conditions (temperature, pressure, stress, strain and strain rate) result in failure of material \([111]\). As mentioned earlier, a number of metallurgical factors also contribute to embrittlement process which includes dislocations, crystal structure, voids, precipitates, degree of cold work and grain boundaries \([112][113]\). The optimum combination of heat treatment give rise to strength and hardness for any alloy, contrarily increase susceptibility to hydrogen embrittlement \([111][114]\). An exact mechanism for embrittlement is difficult to predict because of the complex microstructure \(\text{because of interaction of hydrogen with metallurgical factors at atomistic scale}\).

Hence, it could be postulated that understanding atomic hydrogen diffusion \(\text{according to fick's laws}\) through CRA\'s crystal structure would be an asset to access actual embrittlement. The diffusivity \(D\) and permeability \(\phi\) appear to be following Arrhenius relationship over temperature range of \(\sim 210-430 \, ^\circ C\). Whereas solubility \(S\) is the ratio of permeability and diffusivity \(\phi/D\) and rely upon microstructure and composition.

The three basic hydrogen transport equations \(\text{temperature dependent}\) are the following:

\[
\phi = \phi^* \times \exp\left(-\frac{E_\phi}{RT}\right) \quad - 4.0
\]

\[
D = D^* \times \exp\left(-\frac{E_D}{RT}\right) \quad - 4.1
\]

\[
S = S^* \times \exp\left(-\frac{E_S}{RT}\right) \quad - 4.2
\]

Where, \(\phi^*, D^*, S^*\) are constants and \(E_\phi, E_D, E_S\) are the activation energies; \(T\) absolute temperature \(\text{(Kelvin)}\) and \(R\) universal gas constant.

Luckemeyer-Hasse and Schenck \([115]\) first observed the effect of crystal structure on hydrogen solubility by measuring the amount of hydrogen absorbed while heating iron through \(\alpha - \gamma\) transition and then through the \(\gamma - \delta\) transition. They have also investigated the effects on important alloying elements such as Ni and Cr of hydrogen solubility. Hydrogen transport and hydrogen embrittlement properties for Ni-Fe-Cr is important since major nickel based superalloys are entirely based upon the ternary system of Ni-Fe-Cr, including the project alloys
718, 945 and 945x. Ternary Ni-Fe-Cr alloys demonstrate higher hydrogen solubility with temperature than Fe but less than Ni, as shown in Figure 3.3.0.

![Figure 3.3.0. Solubility of hydrogen at standard pressure in Chromium (Cr), Iron(Fe), Nickel(Ni) and in two ternary Fe-Cr-Ni alloys. [115]](image)

Corrosion resistant alloys (CRA) with localised crystal defects in lattice are the key positions for the trapping of hydrogen and hence effect hydrogen solubility. The micro-structural trapping sites which are under extremely high local concentrations of hydrogen (they are capable of storing) could be grain boundary carbides [116], delta δ [117], grain boundary region [118], dislocations [119] and voids [120].

**Hydrogen Permeation through Inconel 718:** Josiah et al [121] performed hydrogen permeation studies on Inconel 718 foils (50µm thick and 4cm in diameter) in three metallurgical conditions i) Cold worked ii) Solutionised at 976°C for 0.5h then oil quenched to room temperature iii) precipitation hardened (PH) at 739 °C for 8 h, then at 635°C for 10 h and thin oxide layer that formed on the surface at elevated temperatures was removed using mechanical abrasion. The aim was to calculate hydrogen diffusion (\( D_H \)) and solubility coefficient (\( C_{aap} \)) in each condition. The experimental cell for hydrogen permeation measurements, TEM microstructures along with permeability transients (detailed in next paragraph for their extraction) are presented in Figure 3.3.1 and 3.3.2 respectively and diffusion and solubility coefficients from each condition are presented in Table 3.1.

Experimental ‘Devanathan-Stachurski’ cell was used to perform hydrogen permeation experiments. *All experiments were operated at 50°C using circulating water bath.* The specimens were coated with ~20nm Pd on both sides using vacuum evaporation. The specimens were then
clamped between the charging and measurement cells (both made of pyrex). The exposed area of membrane in each cell was about 5.7 cm$^2$. Hydrogen was generated at constant current density of 1.6 mA/cm$^2$ in 0.1 M NaOH in charging cell. Whereas, in the measurement cell hydrogen diffusion was quantified by measuring the anodic current between the specimen and the Pt counter electrode at +300 mV vs. a saturated calomel electrode (SCE) in 0.1 M NaOH. The Inconel 718 membrane was shared between both electrochemical cells, acting as working electrode in the measurement cell (right) and the cathode in hydrogen generation cell (left). The constant current density in charging cell between the specimen (as cathode) and Pt anode was supplied by Mastech HY 3005D DC power supply. Further, the anodic current in the measurement cell was recorded using Gamry model G-750 potentiostat (operated with floating ground) and in absence of charging, the decay transients were obtained. Prior to running the apparatus, measurement cell was operated (before charging cell) for 5-6 days until the anodic current dropped to ~30 nA/cm$^2$ and remained constant. This ensures that all oxidizable impurities are removed from the measurement cell (oxidation cell) prior to obtaining the hydrogen permeation transients.

![Diagram of experimental cell for hydrogen permeation experiments.](image)

Figure 3.3.1. Schematic of experimental cell for hydrogen permeation experiments. [121]
NOTE: Heat treatment applied = Solutionised at 976°C for 0.5 h; Precipitation Hardened at 739°C for 8 h, then at 635°C for 10 h.

Figure 3.3.1. TEM images are shown on left and repeated hydrogen permeation transients (1\textsuperscript{st}, 2\textsuperscript{nd} ; 3\textsuperscript{rd}) on right through Inconel718 membranes in the following conditions: a) Cold rolled b) Solutionised and c) Precipitation hardened (PH). [121]
The TEM microstructures of alloy 718 membranes for different conditions are presented in Figure 3.3.1 (left). Transient graphs for each condition is an evidence of both reversible and irreversible hydrogen trap sites. Dense dislocation tangles were observed in (a) cold rolled and few in (b) solutionised condition. Whereas in (c) precipitation hardened membrane display characteristics of γ matrix and ordered γ’ precipitation. If we consider these as metallurgical defects or trapping sites, then in solutionised membrane ‘defect density’ is quite low when compare to cold rolled and precipitation hardened samples. The effective hydrogen diffusion coefficients (Table 3.1) extracted from rise and decay transients are nearly indistinguishable. Similarly, the first rise transient for cold rolled and precipitation hardened membranes is lower than the subsequent transients which suggest lattice solubility may dominate during the first transient and have little effect on transients to follow because most of the hydrogen trapping sites (irreversible or reversible) are filled. This is probably due to the high number of dislocations in cold rolled conditions whereas precipitation hardened may have local high concentration of delta δ, γ’, MCN’s etc. As already mentioned earlier, M (C, N) carbides and nitrides are used to control the size of grains since they pin the grain boundaries and inhibit grain growth. Commonly found carbides or nitrides in alloy 718 are NbC or TiN, they normally were observed on grain boundaries and within grains. In Inconel 718, 77-87 kJ/mol has been suggested as activation energy (Q) for hydrogen atoms to be trapped in carbide particles [122]. Activation energy of 58 kJ/mol has been proposed as the criterion to determine whether the hydrogen already trapped in a site can be released reversibly or not [123]. Whereas, the binding energy to delta (δ) particles is 30 kJ/mol, which make it less than 58 kJ/mol [122]. Presence of both δ and M (CN) carbides at grain boundaries or within grains might be critical to hydrogen embrittlement (HE). Solutionised
sample only contain M (C,N) distributed randomly throughout the bulk matrix along with few dislocations. Dislocations and coherent precipitates are considered as reversible traps with binding energies typically between 4.8 and 14.5 kJ/mol respectively [119][124][125]. It is also possible that each trap whether reversible or irreversible could have multiple hydrogen binding energies to determine analytically. The repeated permeation transients, as shown in Figure 3.3.2 provide evidence for irreversible hydrogen trapping in the colled rolled and precipitation hardened specimens but the intensity of transients (1st, 2nd and 3rd) were fairly constant in the solutionised condition as evidence by the permeation transients with minimum difference between them, Figure 3.3.2.

\[\gamma'\] for PH membrane might or might not be coherent with the \(\gamma\) matrix because of their size range (20-50nm); however, misfit/incoherency could still be an important entity to consider. It was not surprising that average diffusion coefficients (see Table 3.1) is significantly higher (5.3-6.8 x 10\(^{-11}\) cm\(^2\)/s) for solutionised than for cold rolled (3.3-4.2 x 10\(^{-11}\) cm\(^2\)/s) and precipitation hardened (2.1-2.9 x 10\(^{-11}\) cm\(^2\)/s) membranes. Which was only possible when associated with metallurgical defects present in each condition as already discussed earlier.

### 3.9. Hydrogen Environment Embrittlement Testing

Slow strain rate testing (SSRT) helps to evaluate the properties of material in terms of reduction ratio of reduced area (RA) from smooth specimen and reduction ratio of notch tensile strength (NTS) from notched specimen. We will be testing both smooth and notch specimens as comparison and observe the change in behaviour. Hydrogen environment embrittlement index (HEEI), the term consecutively used in previous sections of report, is the ratio which denotes severity of degradation of superalloys under mechanical loading with exposure to hydrogen environment and to air or inert environment. Hence, these mechanical property ratios i.e. notch tensile strength (NTS), reduction in area (RA) and percentage elongation (PE) are HEE index. These indexes are critical for selecting or screening superalloys for specific environment condition. HEEI close to unity is preferred for any alloy in order to maximise hydrogen embrittlement resistance. A number of researchers in history, including Walter et Chandler [129] and Haris et Van [130] perform laboratory tests on notched specimens to gain HEEI. Table 3.2 shows extracted information from these tests; a general category for hydrogen embrittlement and their respective HEEI with screening notes for each material that fall into that category.
<table>
<thead>
<tr>
<th>Hydrogen embrittlement category</th>
<th>HEE index (NTS ratio)</th>
<th>Material screening notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Negligible</strong></td>
<td>1.0 – 0.97</td>
<td>Materials can be used in the specified hydrogen pressure and temperature range with fracture mechanics and crack growth analysis in hydrogen</td>
</tr>
<tr>
<td><strong>Small</strong></td>
<td>0.96 – 0.90</td>
<td>-</td>
</tr>
<tr>
<td><strong>High</strong></td>
<td>0.89 – 0.70</td>
<td>Cautiously use only for limited applications with detailed fracture mechanics and crack growth analysis in hydrogen.</td>
</tr>
<tr>
<td><strong>Severe</strong></td>
<td>0.69 – 0.50</td>
<td>Not recommended for usage at specific pressure and temperature where the HEE index is measured</td>
</tr>
</tbody>
</table>

Table 3.2: Material screening remarks against hydrogen embrittlement based on HEEI from NTS ratio. Adapted from [69]

3.9.1. Mechanical Behaviour of INCONEL718

Fournier et al reported in [110] the effect of internal hydrogen (pre charged specimens) and external hydrogen (hydrogen charged during deformation) and observed whether they were related to the same HE mechanism. The room temperature cathodic hydrogen embrittlement susceptibility of alloy 718 (smooth specimens: 15mm gage length; 4mm diameter; solution treated at 955°C - 1hr furnace cooled then 720°C – 8hr cooled at 50°C/hr plus 620°C- 8hr then air cooled to room temperature (RT)) was investigated by slow strain rate (SSR) test. The grain size was about 20µm and TEM studies reveal that γ'/γ'' (15% volume fraction) were about 30-50nm disc shaped. Further, grain boundaries were decorated with continuous film of δ delta phase. The tests performed on charged and uncharged specimens suggest that hydrogen embrittlement and reduction of ductility is correlated with hydrogen segregation to moving dislocations and transport by these dislocations for the cracking to occur.
Result of slow strain rate test conducted with alloy 718 (hydrogen charged during deformation) at strain rate of $5 \times 10^{-7}/s$ is presented in Figure 3.3.2 as stress strain curve.

**Figure 3.3.2.** Stress strain behaviour of smooth Inconel 718 specimens which are strained under different test conditions i.e. Air, free potential and under current density [110].

Specimens strained in air, in 1 N $H_2SO_4$ at free potential and in 1 N $H_2SO_4$ with applied current density of 100 mA/cm$^2$. With free potential, similar behaviour is observed as compare to air with minor reduction in strain (%). However, applying current density leads to significant reduction of fracture strain.

Pre-charged specimens, which go through SSRT tests, fracture strain increases with increasing strain rate ($5 \times 10^{-7}/s$ to $5 \times 10^{-3}/s$) and no significant effect at last strain rate $5 \times 10^{-3}/s$. The results are shown in Figure 3.3.3.
The ductility of hydrogen free specimens decreases with decreasing strain rate. Pre-charged hydrogen embrittlement is more pronounced at $5 \times 10^{-7}$/s, less marked at $5 \times 10^{-5}$/s and disappears at $5 \times 10^{-3}$/s [110].
3.9.2. Fractography

The SEM images in Figure 3.3.4 are fractography images taken after slow strain rate testing of Inconel 718 under CP. Whereas, in Figure 3.3.5 hydrogen pre charged specimens shows apparent surface cracks because of increasing strain rate from $5 \times 10^{-7}/s$ to $5 \times 10^{-3}/s$.

(Left) (a) Transgranular fracture surface and some intergranular decohesions at $5 \times 10^{-7}/s$ with $1 \text{NH}_2\text{SO}_4 - 100\text{mA/cm}^2$ (b) detail of (a) showing 1μm planar cleavage micro facets. (Right) (a) Fracture surface at $5 \times 10^{-5}/s$ with 1 N $\text{H}_2\text{SO}_4 - 100\text{mA/cm}^2$ (b) detail of (a) showing 1μm planar cleavage micro-facets.

**Figure 3.3.4.** SEM images of Inconel 718 fracture specimens after SSR testing under CP. [110]
Figure 3.3.5. Surface Cracks on hydrogen pre-charged specimens deformed at strain rates (a) $5 \times 10^{-3}$ /s, (b) $5 \times 10^{-5}$ /s, (c) $5 \times 10^{-7}$ /s, (d) Detail of (b) showing transgranular mode of initiation.\[110\]

**NOTE:** Number of surface cracks increases with increasing strain rate.

Thus in terms of crack initiation behaviour observation, Fournier et al [110] in their conclusion points out an important difference between internal and external hydrogen embrittlement. They stated that in contrast to ingress of hydrogen during SSR testing, hydrogen pre-charged specimens undergo multiple transgranular surface cracking, as evident in Figure 3.3.5. These surface cracks tend to increase further with increasing strain rate.
**Notch rupture sensitivity of Inconel718:** The SEM images in Figure 3.3.7(a)(b) are taken from the study of Liu et al. [117], they presented the fracture morphology of notch tensile specimens of Inconel718 tested in 1mol (NaHSO₄ and KHSO₄) solution. The Inconel718 specimens were received as forged plates of 3mm thickness that were annealed at 980°C for 1hr followed by water quenching (WQ). The heat treatment applied to notch tensile specimens is given in Table 3.3.

<table>
<thead>
<tr>
<th>Heat treatment Type</th>
<th>Heat treatment</th>
<th>Expected secondary phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventionally annealed</td>
<td>~955°C WQ</td>
<td>δ</td>
</tr>
<tr>
<td>Conventionally annealed and</td>
<td>~955°C WQ 720°C-8h plus</td>
<td>δ, γ” and γ’</td>
</tr>
<tr>
<td>Conventionally aged</td>
<td>621°C-8h AC</td>
<td></td>
</tr>
<tr>
<td>Higher solution annealed</td>
<td>1040°C 1h WQ</td>
<td>(δ, γ” and γ') - free</td>
</tr>
<tr>
<td>Higher solution annealed plus</td>
<td>720°C-8h plus 621°C-8h AC</td>
<td>(δ free), γ” and γ’ precipitated</td>
</tr>
<tr>
<td>conventionally Aged</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.3.** Heat treatment of Inconel718 notch tensile specimens. Adapted from [117]

**Figure 3.3.6.** The schematic illustration of notch tensile specimen. (Unit: mm)

Hydrogen charging of specimens was conducted at 300°C. The time needed for hydrogen to reach half the thickness of the specimen was calculated to be 21h using the equation \( x = \sqrt{2Dt} \). (\( x \) is penetration depth; \( t \) is charging time and \( D \) is diffusion coefficient) with and without hydrogen pre-charging. The notch tensile tests are conducted at room temperature with slow cross head speed of 1.4 \( \times 10^{-5} \) s\(^{-1}\) with and without hydrogen. The SEM fractography for each specimen, tested under pre-charging and no pre-charging condition, is presented in Figure 3.3.8. Similar to [110], the pre-charging results in surface cracking of the specimens. The pre-charged specimens show significant loss of NTS ratio irrespective of δ precipitation morphology. The binding energy of hydrogen atoms with δ phase is 30kJ/mol, which is much smaller than 58 kJ/mol, thus it is ambiguous to explain the exact HE mechanism associated with this incoherent phase. However, the effect of δ phase can be explained as: δ as being incoherent with γ matrix, results in induction of large strain between the two at interface when subjected to stress or load. This provides strong tendency of hydrogen trapping at the interface: thus, accumulated hydrogen
atoms at interface results in being attached to moving dislocations under stress. This slip process significantly reduces the ductility and fracture toughness of the interface site and encourages crack initiation. Still more work is required to clarify the actual effect of δ phase on HE sensitivity of Inconel 718.

(a) δ and hydrogen free and (b) δ free and Hydrogen pre-charged, both are higher solution treated and conventionally aged

(c) δ free and hydrogen free and (d) δ free and hydrogen pre-charged, both are higher solution annealed 1040°C 1h.

**Figure 3.3.7(a).** Fracture morphologies of SSR tested notch specimens [117].
Figure 3.3.7(b). (e) hydrogen free and (f) hydrogen pre-charged, both are conventionally aged. (g) Hydrogen free and (h) hydrogen pre-charged, both are conventionally annealed [117].

It has been suggested that notch tensile strength (NTS) of Inconel718 decrease significantly by hydrogen pre-charging regardless of the delta (δ) precipitation. However, dissolving delta (δ) particles results in decrease of loss of NTS caused by pre-charged hydrogen. It was recommended to use delta (δ) free Inconel718 for better hydrogen embrittlement resistance than conventionally heat treated inconel718 [117].
HEE is most severe in vicinity of room temperature for certain alloys like Inconel718 when exposed to high pressure hydrogen environment. However, over a wide range of temperature from cryogenic to around 800°C HEE is effective for number of alloys from nickel based to cobalt based. The data from past decades [129] [131-133] has shown that these index were obtained at two hydrogen pressure points of 34.5 and 60 MPa at room temperature. This invaluable database is presented in Table 3.4, showing collection of HEE index based on property ratios of notch tensile strength (NTS), reduction in area (RA) and percentage elongation (PE) for range of alloys, including Inconel718 (highlighted in yellow) in solution treated condition (at 955°C) with hydrogen pressure of 34.5 MP. The reason for such low NTS (0.53), RA (0.34) and PE (0.24) ratio is because of extensive precipitation of delta (Ni₃Nb) (see section 'Phases of Nickel Based Alloys' for detail). Typical strain rates used for SSRT were $8.3 \times 10^{-6}$/sec for smooth specimens and $8.3 \times 10^{-5}$/sec for notched specimens. The yield strength (YS), ultimate tensile strength (UTS) and notch tensile strength (NTS) were tested under in-air environment.

<table>
<thead>
<tr>
<th>Superalloys</th>
<th>HEE Index (ratio)</th>
<th>Hydrogen Pressure (MPa)</th>
<th>Strength in Air (MPA)</th>
<th>Alloy system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NTS</td>
<td>RA</td>
<td>Elong.</td>
<td>NTS</td>
</tr>
<tr>
<td>Hastelloy X</td>
<td>0.86</td>
<td>0.98</td>
<td>0.98</td>
<td>34.5</td>
</tr>
<tr>
<td>Hayness 230</td>
<td>0.76</td>
<td>0.41</td>
<td></td>
<td>34.5</td>
</tr>
<tr>
<td>Hayness 242</td>
<td>0.77</td>
<td>0.20</td>
<td></td>
<td>34.5</td>
</tr>
<tr>
<td>Inconel 100</td>
<td>0.30</td>
<td></td>
<td></td>
<td>34.5</td>
</tr>
<tr>
<td>Inconel625</td>
<td>0.76</td>
<td>0.36</td>
<td>0.36</td>
<td>34.5</td>
</tr>
<tr>
<td>Inconel700</td>
<td>0.32</td>
<td></td>
<td></td>
<td>69.0</td>
</tr>
<tr>
<td>Inco 706</td>
<td>0.82</td>
<td>0.54</td>
<td></td>
<td>48.3</td>
</tr>
<tr>
<td>Inconel713LC</td>
<td>0.38</td>
<td>0.42</td>
<td></td>
<td>41.8</td>
</tr>
<tr>
<td>Inco 718 (sol. t treat at 955°C)</td>
<td>0.53</td>
<td>0.34</td>
<td>0.24</td>
<td>34.5</td>
</tr>
<tr>
<td>InconelX-750</td>
<td>0.26</td>
<td></td>
<td></td>
<td>48.3</td>
</tr>
<tr>
<td>Inco 4005</td>
<td>0.64</td>
<td>0.21</td>
<td></td>
<td>34.5</td>
</tr>
<tr>
<td>Rene41</td>
<td>0.27</td>
<td>0.38</td>
<td>0.20</td>
<td>69.0</td>
</tr>
</tbody>
</table>
Table 3.4. HEE Index for superalloys at 24°C (Inconel718(highlighted in red)) under hydrogen pressure range 34.5 – 69 MPa and thermally charged at temperature 200°C. Adapted from [69].

NOTE: A number of superalloys are added in Table 3.0 for HEE index information.

The NTS, RA and PE ratio are calculated according to the equations:

\[
NTS_{ratio} = \frac{NTS_{in\ hydrogen}}{NTS_{in\ air\ or\ inert\ environment}} - 4.3
\]

\[
RA_{ratio} = \frac{RA_{in\ hydrogen}}{RA_{in\ air\ or\ inert\ environment}} - 4.4
\]

\[
PE_{ratio} = \frac{PE_{in\ hydrogen}}{PE_{in\ air\ or\ inert\ environment}} - 4.5
\]

The effect of heat treatments and product forms has profound impact on the ratio of NTS, RA and PE. This was evident from Table 3.0 and Table 3.4, that Inconel718 in wrought form with solution annealing temperature around 955°C give HEE index of 0.53 (highly embrittled). Further, Inconel718 with combination of five different heat treatments and product forms i.e. rolled bar, forging, plate, plate (weld or heat affected zone) demonstrated that for all heat treatments (A-E) plate form display (from NTS ratio) less dependency upon hydrogen than rolled bar and forging forms. As mentioned earlier, solution treatment around ~950°C give rise to extensive precipitation of delta δ (Ni₃Nb) along grain boundaries which result in fracture initiation and low NTS. Micro-structural analysis reveal for heat treatment A, discontinuous delta δ along grain boundaries is observed for plate, making it less embrittled by hydrogen. Whereas, same heat treatment A when performed on rolled bar and forgings resulted in continuous grain boundary delta δ which increase hydrogen embrittlement with low NTS ratio. The effect of other intermetallic phases such as M (C, N) in solutionised condition (around 1025°C) demonstrated high NTS ratio of 0.83. This increase in NTS ratio is because of the fact that delta δ along with γ'/γ'' dissolve back into the γ matrix. The precipitation and dissolution temperatures for different intermetallic phases present in Inconel718 were calculated using Differential Scanning Calorimetry (DSC) (see Appendix A) which were in good agreement with ThermoCalc/JMatPro phase simulations for 718.
3.9.3 Hydrogen Assisted Cracking Mechanisms

Different mechanisms have been proposed over the past century to describe hydrogen induced embrittlement (HIC) and the most common are described as below:

3.9.3.1 Hydrogen-enhanced Decohesion (HEDE)

The mechanism was first proposed by Pfiel [134] in 1926 then followed by Triano [135] in 1960 and Oriani [136] with co-workers [137-141]. These all basically states that hydrogen atoms at crack tip lowers the fracture energy and initiate cleavage like fracture. The reason behind is the stress intensity $\Delta K$ of the fracture which is reduced below the value at which dislocation emission occur blunting crack and stops cleavage like fracture [142]. Hydrogen atoms preliminary reside or accumulates within lattice or ahead of crack tip, Figure 3.3.8 (i) and (ii), result in reducing cohesive strength between the atoms or separation of atoms in front of crack tip and/or crack tip opening displacement (CTOD) which is about half of inter atomic spacing [69]. It is postulated that hydrogen damage occurs in fracture process zone when critical CTOD stress exceeds local interatomic bond strength due to presence of hydrogen atoms [136].

In one of the study [77] HEDE mechanism was explained as ‘HEDE occurs due to the increased solubility of hydrogen in tension field of an edge dislocation. There is a decrease in atom binding forces of the metal lattice, which results in premature brittle fracture. The brittle fracture may be in the form of either intergranular or transgranular cleavage.’ The fracture path (later described for HELP) depends upon the concentration of hydrogen sites whether close to crack tip, at intergranular positions or within lattice [69].

It is believed that hydrogen damage occurs in stress field surrounding the crack tip or matrix particle interface [43][44]. Figure 3.3.8(iii), where maximum tensile stress is observed. It is even seen that high concentration of hydrogen along with impurities are present at grain boundaries and decohesion process is highly likely e.g. for nickel element segregation of impurity (sulphur S) at grain boundary enhance decohesion process [143][144].

HEDE is emerging as the most likely mechanism happening in hydrogen assisted cracking of high strength steels that do not form hydrides. This could be because of the following reasons: i) large concentration of hydrogen accumulates in fracture process zone (FPZ) due to high crack tip stresses ii) hydrogen trapping along crack path. Still because of the lack of experimental evidence or support HEDE is considered ambiguous. Further, there is no direct experimental demonstrating evidence that atomic hydrogen lowers the interatomic force displacement relationship. Also, the amount of hydrogen that ingress the bulk of the metal lattice for bulk property measurement is orders of magnitude less than that projected to accumulate locally at the crack tip FPZ [77].
Figure 3.3.8: Schematic illustration of HEDE mechanism with breaking or weakening of interatomic bonds because of tensile separation i) when hydrogen presence in atomic lattice ii) hydrogen diffusion to crack tip iii) hydrogen presence between particle matrix interface. Image taken from [69]

3.9.3.2 Hydrogen-enhanced localised plasticity (HELP)

The mechanism is supported by the findings of Beachem, Birnbaum, Sofronis, Robertson et al based on changes in the dislocations pile ups with and without hydrogen and fracture surfaces showing high local plastic like deformation while observing through transmission electron microscopy [124][145-148]. Contradiction, still exist between the proposed HELP mechanism and actual hydrogen embrittlement. However, HELP mechanism is still debated over lack of supporting evidences [142].

It was proposed that high hydrogen concentration with high hydrostatic stresses around crack tip result in localised plastic deformation and/or localised micro-void coalescence (MVC). This increases localised plasticity but decreases overall ductility. Initially, fracture surface at microscopic scale appears to be localised plasticity of MVC and cleavage brittle facets at macroscopic scale but TEM studies reveal nano scale dimples within micro craters.

It is obvious that high local hydrogen concentration is required for operation of HELP mechanism both in Internal hydrogen embrittlement (IHE) and hydrogen environment embrittlement (HEE). In HELP dislocation maneuverability depends upon external stresses. Additionally [145][149], ‘hydrogen eases dislocation movement by shielding the dislocation stress fields against each other as well as against other grid defects. This local drop of yield stress
(YS) due to hydrogen causes local dislocation movement at low levels of shearing stress. Sliding localisation ocurleading to a micro-crack caused by the formation of micro pores and shearing action. Thus once the crack leaves the area of reduced yield stress, it will not propagate any further’ [77].

Fracture path (intergranular or transgranular) is associated to the position of the local hydrogen concentration ahead of crack tip within grains or close to grain boundaries. In Figure 3.3.9 plastic zone around crack tip under inert environment appear to be larger than that effected by high local concentration of hydrogen with high hydrostatic stress. Edge dislocations are shielded more than screw dislocations as stress field around edge dislocation enhances hydrogen atmosphere around them [69]. The studies [38] about different materials revealed that interstitial hydrogen atom increase crack propagation rate and edge dislocation propensity and decrease stacking fault energy. The last factor should reduce cross slip and enhance slip planarity. The initial TEM studies reveal that HE occur by completely dimpled fracture surface showing microvoid coalescence which led Beachem [145] to propose a new model for hydrogen assisted cracking based on solute hydrogen enhancing dislocation movement ahead of crack tip. TEM also reveals that dimples have variety of shapes, depths and sizes depending upon microstructure, composition, and nature of stress, environment and other variables [69].

![Figure 3.3.9](image-url)

**Figure 3.3.9.** Schematic illustration of HELP mechanism, where crack propagate with formation of void and their coalescence (MVC). In high hydrogen concentration (hydrostatic stresses) localised plasticity occurs ahead of the crack tip. Contrarily, large plastic zone with less strain localisation and more crack blunting without hydrogen resulting in ductile dimpled (deeper) fracture. Image taken from [69]
First proposed by Westlake [150] in 1969, fundamental principle involved is illustrated in Figure 3.4.0. Robertson et al [151-153] with extraordinary findings, where in controlled environment β-Ti was charged under in-situ transmission electron microscopy (TEM) and observation revealed small hydrides nucleation and coalescence to form larger hydrides. Metals which are potent hydride formers include Vanadium (V), Zirconium (Zr) and Titanium (Ti), which cause hydrogen absorption and then result in formation of brittle hydrides. With low concentration of hydrogen, below solid solubility limit, stress assisted hydride formation causes embrittlement which is enhanced by slow strain rate. With high level of hydrogen concentration above solubility limit brittle hydride formation occur which causes severe embrittlement enhanced by high strain rates, decreased temperature and presence of notches [154]. Moreover, metals like Niobium (Nb) and Tantalum (Ta) absorb hydrogen and causes severe hardening which results in embrittlement enhanced by increased rate of straining [151]. In further studies [142] it is also believed that presence of local stress intensities is critical to fracture process and high intensities facilitate HELP mechanism whereas low intensities result in formation of titanium hydrides.

**Figure 3.4.0.** Schematic explaining the mechanism of hydride induced embrittlement. Hydrogen diffusion to high hydrostatically stress regions, ahead of the crack tip where brittle hydride nucleates and grow, fracture in a cleavage like manner when reach a critical size resulting in crack arrest and blunting at hydride matrix interface. Image taken from [69]
In 1976 Lynch [155] [156] was the first to introduce the AIDE mechanism. The AIDE is highly influenced by the movement of dislocations, originating from crack tip. These dislocations move away from the crack tip under applied stress, which can be thought as slips. It is very important to recognize the criticality of dislocation emission from the crack tip under hydrogen adsorption. The dislocation nucleation stage involves the ‘simultaneous formation of dislocation core and surface step by cooperative shearing of atoms (breaking and re-forming of interatomic bonds) over several atomic planes’ [69]. The adsorption of hydrogen atoms accumulate over the moving dislocations which result in the weakening of interatomic bonds near the crack tip and over several atomic distances.

Further, when the stress is applied to the crack tip, along with dislocation emission micro-voids nucleate and grow ahead of the crack tip. This phenomenon has been illustrated in Figure 3.4.1. These voids nucleate and grow ahead of crack tip at secondary phase particles, slip band intersections and at several sites in plastic zone ahead of crack tip. It is very important to note that dissociation of hydrogen atoms and diffusion and adsorption up to crack tip is necessary for AIDE mechanism.

![Figure 3.4.1](image_url)

**Figure 3.4.1.** The schematic of AIDE mechanism illustrating hydrogen assisted cracking when hydrogen adsorption occurs at the crack tip, resulting in nucleation and emission of dislocation under stress applied. This results in the coalescence of voids with growth of crack in plastic zone.
ahead of crack tip. Whereas, some voids are extremely small present at nano-scale hence they are not apparent on fracture surface. Image taken from [69]

3.9.3.5 Mixed HE Mechanisms

All above mechanisms which have been described could occur simultaneously in many cases, Figure 3.4.2. The possible combination of AIDE, HEDE and HELP could be evident depending upon alloy composition, heat treatment, structure (micro and nano) and hydrogen concentration. The secondary phase particles present at the intergranular sites act as the trapping sites for hydrogen atoms which lowers the fracture energy by decreasing the strength of atomic bonds (HEDE) at particle matrix interface and further hydrogen localised plastic degradation with the help of HELP. As already mentioned, the AIDE could be thought of as mechanism occurring directly at the crack tip. On the other hand, hydride induced embrittlement (HIE) mostly occur at grain boundaries where brittle hydrides form, providing path for crack propagation.

Figure 3.4.2. Schematic illustration of HE mechanisms occurring simultaneously in a microstructure. Hydrogen induced cracking with assistance of AIDE, HEDE, HELP and HIE as shown in (a) and (b). Image taken from [69]
CHAPTER 4. Prediction of equilibrium phases and Coarsening of Gamma prime during ageing

It is necessary to possess understanding of the CRAs microstructure along with phases that strengthen the γ matrix. Thermodynamic calculations and kinetic simulations have become important in understanding material properties. In this chapter the equilibrium phases, which can exist in CRA’s 718, 945 and 945x, are predicted using the thermodynamic software packages JMatPro and ThermoCalc. ThermoCal (Ni database) and JMatPro (version 8.04 with NiFe database) had been used to calculate amount of equilibrium phases and dissolution temperature of phases i.e. solidus, liquidus and precipitation etc. The use of JMatPro was extended to calculate the size of the gamma’ (γ’) precipitates corresponding to number of hours of ageing temperature applied. The main reason of extracting equilibrium phase simulation was to observe whether any metastable or topological closed packed phases will precipitate in CRAs as per the standard heat treatments applied. These phases are critical for CRA’s strength and their vulnerability to hydrogen embrittlement (HE). The actual heat treatments applied to CRAs is presented in Table 4.0.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Alloy</th>
<th>Heat Treatment Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ST) S1</td>
<td>718</td>
<td>Standard ST at 1035°C - 2hr AC</td>
</tr>
<tr>
<td>(STA) S2</td>
<td>718</td>
<td>Standard STA at 1035°C - 2hr AC / 790°C-7hr AC (API Oil&amp;Gas Grade)</td>
</tr>
<tr>
<td>(NS) S3</td>
<td>718</td>
<td>1250°C – 2hr AC 790°C – 16hr AC</td>
</tr>
<tr>
<td>(NS) S3*</td>
<td>718</td>
<td>1250°C – 2hr AC</td>
</tr>
<tr>
<td>(NS) S4</td>
<td>718</td>
<td>1035°C - 1hr AC / 718°C-8hr then 621°C-8hr AC</td>
</tr>
<tr>
<td>(NS) S5</td>
<td>718</td>
<td>1035°C - 1hr AC / 955°C-8hr AC / 718°C-8hr then 621°C-8hr AC</td>
</tr>
<tr>
<td>ST</td>
<td>945/945x</td>
<td>1038°C 1hr WQ</td>
</tr>
<tr>
<td>STA</td>
<td>945/945x</td>
<td>1038°C 1hr WQ then 718°C 8hr FC + 621°C 8hr AC</td>
</tr>
<tr>
<td>AR</td>
<td>945/945x</td>
<td>As Received in bulk form</td>
</tr>
<tr>
<td>NS</td>
<td>945x</td>
<td>1250°C 1hr WQ then 718°C 8hr FC + 621°C 8hr AC</td>
</tr>
</tbody>
</table>

Table 4.0. Heat treatments given to CRAs 718, 945 and 945x specimens.

Note: Air cooling (AC); Water quenched (WQ); Furnace Cooling (FC); (ST) Solution Treated; (STA) Solution Treated and Aged; Non Standard (NS).

4.1. INCONEL718

4.1.1. Time Temperature Transformation (TTT) Diagram of Alloy718
The TTT diagram of Alloy718 shows predicted phases that could precipitate at different heating parameters depending upon span of heating treatment. A range of heat treatments applied can have variable phases in the microstructure at intergranular (grain boundaries) or at transgranular (within grains) positions. Each phase has its own
morphology (shape and size) depending upon the heat treatment applied. The solution treatments and ageing treatments applied to alloy718 samples in current work have been highlighted in TTT diagram, shown in Figure 4.1.0.

**Figure 4.1.0.** TTT diagram showing Gamma\(^{'}\) (\(\gamma^{'}\)), Gamma\(^{''}\) (\(\gamma^{''}\)), Delta (\(\delta\)), and Laves phase (except M (C, N) particles) which are predicted in the 718 samples as per heat treatment mentioned. SIGMA, ETA and MU phases are normally present at extended exposure to high temperatures (approximately close to 100hr).

**NOTE:** Heating parameters for API 6A718 and conventional double ageing is mentioned on TTT diagram.

4.1.2. Thermotech - Equilibrium Phase Simulations and Databases

It is important understand that NiFe-based superalloys behave in a more complex way than predominantly Ni-based superalloys. This is because the hardening mechanism in \(\gamma^{'}\)
matrix phase involve the metastable gamma’’ (γ’’) \( \text{Ni}_3\text{Nb} \) along with stable gamma’ (γ’) \( \text{Ni}_3 \) (Al,Ti). Thus NiFe-Super database is capable enough of handling these complex alloys for predicting both stable and metastable equilibrium states. In the literature available online, the thermotech [160][161] have number of databases for use with thermodynamical calculation software packages like JMatPro and Thermo-Calc. ‘Ni-DATA’ and ‘NiFe-Super’(subset of Ni-DATA) are the databases used for calculation of phase equilibria in Ni based and NiFe superalloys and believed to be the most reliable database. Hence to validate the simulations, it was compared with experimental data (Appendix A) which demonstrate that these databases operate close to expected experimental measurements. ‘NiFe-Super’ is designed specifically for Ni based superalloys containing high Fe content such as INCONEL718 (18wt%) and INCOLOY945 (22wt%) but is not available at University of Leicester. Where, only ‘Ni-Data’ database is available in ThermoCalc software and Ni-Fe database is available in JMatPro. According to NiFe-Super database, the phase percentage vs. temperature (°C) plot of Inconel718 has two conditions, as shown in Figure 4.1.1, first state is stable 718 where delta δ phase \( \text{Ni}_3\text{Nb} \) (orthorhombic structure) is formed and second state where metastable gamma’’ (γ’’) \( \text{Ni}_3\text{Nb} \) with body centred tetragonal structure is formed. As already mentioned earlier ‘chapter 2: section: 2.3.3’ that gamma’’(γ’’) is metastable phase which tend to be replaced by incoherent stable orthorhombic delta (δ) phase, \( \text{Ni}_3\text{Nb} \), after long term exposure to temperature above 650°C. Thus, to reproduce them in the Figure 4.1.1 (a) γ’’ phase was suppressed and δ phase was selected prior to running the simulation and in Figure 4.1.1 (b) δ phase was suppressed and γ’’ phase preferentially appears in the simulation. Similarly, the Figure 4.1.2 shows the thermodynamic simulation obtained using ThermoCalc ‘Ni-Data’ database, thus it is not very accurate in predicting the equilibrium phases present in Inconel 718 i.e. MC carbides not available in the selection list and metastable γ’’ phase not predicted though selected prior to running the simulation. The Figure 4.1.3 was obtained using JMatPro (NiFe Database) which was close approximation to the thermotech simulation (extracted from literature [160][161]), using NiFe-Super database, for the equilibrium phases present in the γ phase of Inconel718. More detailed analysis of phase simulation from ThermoCalc and JMatPro software packages under different database will be discussed in detail in terms of phase dissolution temperatures and amount of equilibrium phases at a specific temperature.
Figure 4.1.1. Predicted phases in INCONEL718 under stable and metastable states, showing in (a) that δ phase present in stable state while in (b) γ" in metastable state [162]. The vertical red dotted line shows melting point of MC carbides and represent the amount of liquid phase formed.

The dissolution temperature of delta δ phase extracted from Figure 4.1.1(a) is around 1000°C and γ" from Figure 6.0(b) is in the range 920-930 °C which is in good agreement with [16]. Other phases Gamma (γ), Gamma' (γ'), Liquid, M23C6, MC, Sigma, αCr have dissolution temperatures of ~1200°C, 900-920°C, ~1400°C, 690-750°C, ~1300°C, 810°C and 810°C respectively. If we observe the dissolution temperature of MC particles it is close to 1250°C. For this reason, non-standard solution treatment was added to dissolve back most of the MC carbides back into the matrix. As MC carbides are Nb based so γ matrix will be Nb rich. The
extra niobium available for γ’ precipitation might have the risk of forming delta δ or laves phase at intergranular positions depending upon span of ageing treatment. The ageing treatment of 16hr after high solution treatment results in continuous intergranular precipitation and will be observed later in chapter 5. Moreover, solution treatment at such high temperature had drawback of forming γ liquid phase of approximately 20-30 mole percentage (red vertical dotted line at1250°C). Other phases such as sigma and αCr are topological closed packed phases incoherent with gamma (γ) matrix and normally present in alloy after long exposure to high temperatures and are not observed in current studies.

4.1.3. ThermoCalc – Equilibrium Phase Simulation of Alloy 718 (Stable)

Figure 4.1.2. ThermoCalc simulation of stable alloy 718 showing amount of phases at specific temperature and their dissolution temperature. (‘Ni-Data’ Database)

The simulation in Figure 4.1.2 was obtained using optical emission spectroscopy (OES) result for Inconel 718 bolt at university of Leicester licensed software package named ‘ThermoCalc’. Due to unavailability of ‘NiFe-Super’ database, ‘Ni-Data’ database was used. The colour lines, shown in Figure 4.1.2, represent amount of different phases at a given temperature value. Each colour line is numbered and represent a phase (see colour scheme box at right). The dissolution temperature of each phase can be calculated at the intercept of colour lines with temperature axis (x axis). The simulation in Figure 4.1.2 was in good agreement with Figure 4.1.1(a) with respect to dissolution temperature of phases. It is important to note that prior to running the simulations in ThermoCalc both phases (γ” and δ) were selected but the δ phase appears in the simulation. As a reminder both γ” and δ have same composition Ni₃Nb but
different structure. The presence of incoherent delta $\delta$ phase (Line 1) makes alloy 718 to be considered as stable alloy. 'Ni-Data' database does not allow MC phase to add prior to running the simulations thus simulations do not show primary carbides (MCs) instead of which secondary carbides is added, commonly $M_{23}C_6$ (line 4) and $M_6C$ (line 7). MC carbides were added in JMatPro and presented in simulation shown in Figure 4.1.3(a). Their melting point computed was around 1250°C, as described earlier in Thermotech and ThermoCalc simulations, associated with the risk of forming liquid phase. Sigma and $\alpha$Cr were not added in the selected phase list prior to running simulation because of their presence in the alloy under excessive exposure to ageing temperature ((longer ageing), which was not the case with applied API 6A718 heat treatment and NS heating parameters (maximum ageing time was 16hr).
Figure 4.1.3. JMatPro simulation using ‘NiFe database’ of stable alloy 718 showing in (a) amount of phases at specific temperature and their dissolution temperature. The liquid phase is simulated and shown in (b). The vertical red dotted line is at the melting point of MC carbides and represent the amount of liquid phase formed.

4.1.4. $\gamma'$ Coarsening Theory and Simulations

As already mentioned earlier that nickel based superalloys (including Inconel718) are precipitation strengthened by fine dispersion of $\gamma'$ particles in $\gamma$ phase. These fine particles
[203] coarsen into lower density of larger particles with smaller interfacial area under ageing treatment. It has been demonstrated by Ardell et al [197-199] that in binary γ-γ' systems, the growth of γ' particles follow a diffusion controlled coarsening model where the average particle radius increases linearly with \( t^{1/3} \). The coarsening rate of γ' particles in nickel based superalloys has been calculated using the method based on model of ‘Lifshitz and Slyozov’[200] and Wagner [201]. A similar \( t^{1/3} \)law has been observed for alloys containing high volume fraction of γ' phase [202]. However, the main models for coarsening of γ' particles has been based on work of ‘Lifshitz and Slyozov’ and Wagner, and they proposed the following relationship [203]:

\[
\left[ \bar{r}_0^3 - \bar{r}_t^3 \right]^{1/3} = kt^{1/3} - 4.6
\]

Where k denotes as coarsening rate coefficient, \( \bar{r}_0 \) is the mean radius at \( t=0 \) and \( \bar{r}_t \) is the average radius at time \( t \) [203]. The k can then be redefined as:

\[
k = \sqrt{\frac{8D_{eff}\sigma V_m}{9RT}} - 4.7
\]

Where \( D_{eff} \) is the effective diffusion coefficient; \( \sigma \) is the matrix-precipitate interfacial energy per unit area which is the most critical input parameter calculated using the ‘back-calculations’ from the experimental coarsening data; \( N_\alpha \) is the total equilibrium mole fraction of solute in the matrix; \( V_m \) is molar volume of precipitate; \( R \) is gas constant and \( T \) is the absolute temperature. However, this equation was derived on assumption that \( N_\alpha \approx 0 \) and \( N_\beta \approx 1 \) (where \( N_\beta \) is the total mole fraction of solute is the precipitate) thus it does not take into account the significant ranges of solubility of solute in the matrix and precipitate [203]. Thus, for a general case the k becomes as follows:

\[
k = \sqrt{\frac{8D_{eff}\sigma V_m}{9G_m^{\beta}(N_\beta-N_\alpha)^2}} - 4.8
\]

Here, the \( G_m^{\beta} \) is the second derivative of the Gibbs energy of the γ phase with respect to composition. Therefore, the ideal solution for k becomes[203]:

\[
k = \sqrt{\frac{8D_{eff}\sigma V_m N_\alpha(1-N_\alpha)}{9RT(N_\beta-N_\alpha)^2}} - 4.9
\]

In binary alloys the estimation of diffusion coefficients and solute concentrations in the matrix and precipitate are easy to calculate but in multicomponent alloys like Inconel 718 the situation becomes far complex. As the parameters for k are inter-dependent upon each other.
In chapter 5 it has been found that double ageing produces hardness 10% higher (Specimens S4 and S5) than single ageing in API 6A718 heat treatment (S2_{API}). The hardness of any specimen is related to coarsening of $\gamma'$ and $\gamma''$ at their respective ageing temperatures. For this reason JMatPto simulations, which are based on models described in [200][201], were created to understand the coarsening of $\gamma'$ with ageing temperatures and compare with hardness, tensile and TEM experimental data in chapter 5. The simulation in Figure 4.1.4 demonstrates the ageing effect on the coarsening of $\gamma'$ for specimen S2_{API}. It is important to note that for less than 10hr of ageing the coarsening curve is nearly proportional and after that coarsening increases at a decreasing rate. The specimen was heat treated at 790°C for 7hr and the simulation represent the coarsening of $\gamma'$ up to around 20nm. This theoretical prediction was in good agreement with TEM data (chapter 5: section 5.4.2).

![Coarsening graph](image)

**Figure 4.1.4.** Effect of ageing at 790°C on $\gamma'$ size for API specimen S2_{API} which is solution treated at 1035°C for 2hr AC and for S3 specimen which was solution treated at 1250°C-2hr.

**NOTE:** Solution treated condition was added to JMatPro software prior to obtaining $\gamma'$ coarsening curve.

The change in solution treatment temperature from API to non-standard higher solution treatment does not affect the coarsening rate. The mean particle diameter of $\gamma'$ was
around 26nm for 16hr ageing of specimen S3. This theoretical prediction was close approximation of the mean γ' size in experimental TEM studies.

The simulations in Figure 4.1.5 show the effect of conventional double ageing (718°C and 621°C) on coarsening of γ' particles after solution treatment at 1030°C-1hr AC. Simulation (a) is related to ageing at 718°C (considering the small γ' particles of 1-2nm precipitated after solution treatment) and followed by (b) where second ageing at 621°C is performed. The consecutive effect of double ageing demonstrates that most of γ' coarsening occurs during the first ageing at 718°C (γ' particles reaches mean size of 10nm) and second ageing at 621°C consolidates the growth with adding a few fraction (0.15 nm) of a nano meter. However, independent ageing at 621°C does increase the size of γ' by few nano metres (1-3 nm), as shown in Figure 6.3 (c). Solution treatment at 1030°C-1hr followed by air cooling (AC) is taken into account prior to obtaining ageing simulation at 718°C. Actually, air cool will lead to precipitation of small γ' precipitates with mean size of 1-2 nm, so the simulation curve in 6.3 (a) starts from 1.5nm γ' size.
Figure 4.1.5. $\gamma'$ coarsening simulations for specimen S4 which goes under conventional double ageing after solution treatment at 1035°C. (a) $\gamma'$ coarsening at ageing temperature of 718°C. (b)
The γ' coarsening simulation at 621°C (after 718°C ageing) shows fraction increase (~0.15nm) in mean size. Whereas (c) showing independent effect of each ageing temperature on γ' coarsening after solution treatment.

It is to remind that γ' size which was obtained from Figure 4.1.5 for each ageing temperature was mean size and not the maximum size reached. It can be possible to have range of γ' particles ~5-20nm distributed throughout γ matrix of specimen S4 with a mean γ' size around 8-10nm. This was confirmed in TEM studies conducted on S4 where two populations of γ' observed: one between 1-10nm and the second around 40-50nm. There was a need to perform TEM at each individual ageing temperature to confirm the size of γ' as experimental evidence, as Whitmore et al [163] reported in his studies for alloy718plus. If from γ' coarsening simulations mean γ' size at each ageing temperature is computed then at 718°C it was ~10nm and at 621°C it was around ~2nm.

4.2. INCOLOY 945 and 945x

4.2.1. Time Temperature Transformation (TTT) Diagram of Alloy 945 and 945x

The time temperature transformation (TTT) simulation shown in Figure 4.2.1 demonstrate precipitation of different phases under different ageing time. One can predict from TTT diagram the phases that could be precipitate in 945 and 945x under conventional double ageing. TTT diagram predict phases that include γ', γ'', δ and laves phase. These phases are expected to be present in the structure under double ageing of alloy. However, practical experimental data (SEM and TEM) shows no evidence of γ'', δ and laves phase, chapter 6: Microstructural Analysis. In fact low content of Nb (3.11wt% in 945 and 4.14wt% in 945x) resist formation of δ phase at grain boundaries.

It was to note that for laves phase to form, Nb 10-12% is required in the matrix. Thus higher solution treatment close to melting point of alloy result in dissolution of NbC, γ' and γ'' back to matrix providing more Nb for laves phase. However, in order to avoid laves phase high temperature homogenization can be used to distribute Nb uniformly throughout the bulk γ matrix. After long term exposures at temperatures above 650°C results in γ' phase to be replaced by stable γ' hexagonal Ni₃Ti, ETA⁰ phase, as shown in TTT diagram, in form of coarse platelets in microstructure. This transformation is associated with considerable loss in strength and is always avoided. TTT diagram also shows that sigma phase is precipitated under long term ageing which is absent under standard ageing times.
Figure 4.2.1. Typical JMatPro (NiFe database) TTT diagram showing possible space for precipitation of phases under conventional double ageing (red arrow lines represent each ageing temperature) for 945 and 945x.

4.2.2. ThermoCalc – Equilibrium Phase Simulation of Alloy 945 and 945x

The phase diagram for alloy 945 and 945x was shown in Figure 4.2.2. All equilibrium thermodynamic phases were selected prior to running the simulation under Ni database. Stable delta δ phase forms preferentially than metastable γ” phase, like in alloy 718.
Figure 4.2.2. The phase diagram extracted from ThermoCalc for alloy 945 (a) and 945x (b). The phase diagram in (a) and (b) shows dissolution temperature of equilibrium phases (see colour lines with phases numbered).
The simulations shown in Figure 4.2.2 was obtained using optical emission spectroscopy (OES) of 945 and 945x (chapter 6: section 6.2.1) and putting in ThermoCalc (Ni-database). The colour lines are associated to each phase as shown in colour key at the right side of Figure 4.2.2. Each colour line represent amount of different phase at a given temperature value. The dissolution temperature of each phase can be calculated at the intercept of the colour line with temperature axis (x axis). As described earlier that alloy 945 and 945x because of low Nb content show resistance to the formation of grain boundary incoherent δ phase (Line 2). This was evident from SEM images of STA and AR specimen having no grain boundary precipitates, (chapter 6: section 6.3.2). Ni database was used for computing thermodynamic phase simulation but it does not show primary metal carbides (MC) or metal nitrides (MN) instead secondary carbides M₂₃C₆ (line 5) can be seen. They mostly reside at intergranular positions and were not observed in any of the specimens. 945 and 945x having Fe content 22.26 wt% and 14.40 wt% respectively in the matrix thus we see α-Fe (Line 1) and γ-Fe (Line 6) in the simulations. This was because Fe begin to change form α ferrite to γ austenite at ~790°C. As already described earlier sigma and αCr are not added in the selected phase list prior to running simulation because of their presence in the alloy under excessive exposure to high temperatures which was also not the case with provided industrial alloy 945 and 945x.

4.2.3. JMatPro– Equilibrium Phase Simulation of Alloy 945 and 945x

Whilst running JMatPro simulations NiFe database was used to simulate the equilibrium phases in 945 and 945x, Figure 4.2.3a and 4.2.3b. It was interesting to see that 945 had neither δ nor γ” phase. The primary strengthening phase simulated was γ’ along with MC carbides (solvus temperature around 1200°C]. Contrarily, 945x was simulated with two strengthening phases γ’ and γ”. The presence of metastable γ” Ni₃Nb could be because of extra niobium content in 945x than in 945. The laves phase simulated in both 945 and 945x could be treated as an error. The reason could be because laves phase require high Nb content availability in γ matrix. This was further clarified under microstructural analysis of 945x in chapter 6. The solid γ phase (matrix) in each alloy starts to form into liquid around 1100°C and turns into complete liquid state around 1350°C, shown in Figure 4.2.3(b) and Figure 4.2.4(b).
Figure 4.2.3. JMatPro (NiFe database) simulation of thermodynamic equilibrium phases in 945.
Figure 4.2.4. JMatPro (NiFe database) simulation of thermodynamic equilibrium phases in 945x.
### 4.2.4. γ' Coarsening Simulations

The hardness, strength and size of γ' precipitates is function of ageing time and are interrelated. The experimental size of γ' computed for each specimen using TEM was taken into account and compared with simulated coarsening of γ' as a function of ageing time.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>HT</th>
<th>HV5</th>
<th>YS(MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>945</td>
<td>ST</td>
<td>140 ± 5</td>
<td>330</td>
</tr>
<tr>
<td></td>
<td>STA</td>
<td>350 ± 2</td>
<td>980</td>
</tr>
<tr>
<td></td>
<td>AR</td>
<td>350 ± 2</td>
<td>985</td>
</tr>
<tr>
<td>945x</td>
<td>ST</td>
<td>155 ± 5</td>
<td>380</td>
</tr>
<tr>
<td></td>
<td>STA</td>
<td>434 ± 2</td>
<td>1100</td>
</tr>
<tr>
<td></td>
<td>AR</td>
<td>430 ± 2</td>
<td>1110</td>
</tr>
<tr>
<td></td>
<td>NS</td>
<td>296 ± 5</td>
<td>780</td>
</tr>
</tbody>
</table>

**Table 4.1.** Vickers hardness and mechanical properties of ST, STA and AR samples of 945 and 945x. HV5, YS and UTS corresponds to Vickers hardness at 5kgf, yield strength and ultimate tensile strength respectively.

The hardness for 945 and 945x ST samples was not surprising, which is because incomplete chemical ordering and small size of γ' precipitates contribute partially to the strength (330 MPa and 380 MPa) and hardness (140HV5 and 155HV5). The solvus temperature of γ' precipitates is less than solution temperature 1038°C resulting in dissolution back to the γ matrix, Figure 4.2.2. The average hardness for each sample obtained was mostly because of the presence of small size of γ' precipitates which were precipitated during water quenching and MC,Ns (NbC and TiN) that were precipitated randomly throughout the structure and some of which dissolve back into the matrix during solution treatment. This extra niobium and titanium diffusing back into the matrix would end up precipitating γ' during water quenching and two step ageing.
Figure 4.2.5. $\gamma'$ coarsening simulation of 945 and 945x STA samples at two step ageing: (a) at 718°C and (b) at 621°C, where starting point for 945 is 8.39nm and 945x is 9.73nm.

The hardness and strength values obtained for the AR and STA samples rely on volume fraction, size of $\gamma'$ precipitates, the lattice strain induce by $\gamma$-$\gamma'$ misfit and M C,Ns pinning the grain boundaries. The hardness values obtained while moving from one end of sample to the other were in the range 350HV5 ±5 for 945 AR/STA and ~430HV5 ±2 for 945x AR/STA. The slight variation in the hardness in each sample of the alloy might be because of first ageing at 718°C which led to finer precipitation of $\gamma'$ ~5nm at few places (also during air cooling $\gamma'<2$nm precipitates) and relatively coarser 10-20nm elsewhere. Moreover, the difference of hardness between the alloys could be because of the higher Nb and Ti in 945x, as described in chapter 6: section 6.4.2. The yield strenght 980MPa in 945 and 1100MPa in 945x is associated to the first isothermal ageing at 718°C where the maximum size of $\gamma'$ precipitates reaches to ~20-25nm.
Later consecutive ageing at isothermal temperature of 621°C led to complete chemical ordering within γ' with fraction increase in size. This was presented as JMatPro γ' coarsening simulation for each alloy under two step ageing, Figure 4.2.5(a)-(b). The experimental mean size of γ' computed for 945 and 945x (chapter 6: section 6.4.2) AR/STA samples were in close agreement with γ' simulations. It was evident that γ' precipitates of 1-2nm precipitated after solution treatment, therefore their initial size was taken into account prior to running ageing simulations. The simulations shows that mean size of γ' achieved was around 8.4 nm for 945 and 9.74nm for 945x after first ageing at 718°C for 8hr. Then after followed by consecutive ageing at 621°C for 8hr results in fraction increase (~0.20nm) in size of γ'. This was demonstrated in Figure 4.2.5 where coarsening of γ' under each ageing was reflected. It was reported in [163] that secondary ageing at 675°C after first ageing at 788°C results in nucleating finer γ' precipitates with mean size of less than 4nm and/or increasing size of pre-existing γ' precipitates by few nano meters. The later part might be the dominating factor in increase of hardness and strength because of faceted growth (resulting in complete chemical ordering). It has been reported for alloy718 [164] that solution heat treatment (1024°C-0.5h) and double ageing (718°C-8hr plus 621°C-8hr) of alloy718 led to uniform precipitation of γ' and γ'' throughout the matrix and achieve a hardness value of 423HV. The reason for precipitation of γ'' and high hardness value, when compared to 945 and 945x was because of high weight percentage of nickel (53wt%) and niobium (5wt%) in alloy718. These elements are the potent members of γ'' which enhances hardness and strength. 945x AR and STA samples were found deprived of having any γ'' but their hardness and strength was considerably greater than 945 AR/STA samples and even greater than Inconel718. As already mentioned this could be because of higher Ti and Nb within γ' precipitate with complete chemical ordering and more γ' edge definition.

In TEM examination of the alloys (945 or 945x) no γ'' was observed. The simulation shown in Figure 4.2.5 of γ' coarsening was extracted with the assumption that alloys have no γ'' in their structure. γ' precipitates on the other hand reaches maximum final size of around 20-25 nm in both alloys after two step ageing, shown in chapter 6: section 6.4.2. As already mentioned in precious section and by examination of yield strength and hardness of AR samples of each alloy, it can be said that same conventional double ageing had been conducted by the supplier. Figure 4.2.5 is a theoretical evidence showing that ageing at 718°C produce major γ' precipitates and ageing at 621°C consolidates the growth for each alloy. The secondary aging at 621°C help to achieve faceted growth by adding few fraction of increase in size, which increases hardness and yield strength of alloys. The effect of single and double ageing on morphology of γ' in 718plus waas studied using TEM and reported in [163]. It could be interesting to do TEM again
on both alloys to observe the individual effect of each ageing temperature after solution treatment. \( \gamma' \) coarsening simulation shown in Figure 4.2.6 demonstrate the effect of individual ageing at 621°C for 8hr which increases the mean size of \( \gamma' \) particle around \( \sim 3\text{nm} \) which was opposite to the fraction increase of \( \sim 0.20\text{nm} \) after consecutive double ageing. The individual effect of ageing at 621°C temperature after solution treatment at 1038°C was simulated in Figure 4.2.6. The individual ageing at 718°C for 8hr does not alter the mean size when compared with consecutive double ageing effect (Figure 4.2.5). Also prior to running the simulations small \( \gamma' \) precipitates of few nano meters (<2nm) after solution treatment at 1038°C were taken into account. These small size precipitates were clearly visible when TEM performed on ST samples. The theoretical simulations were close to experimental observations (TEM) and can be used as benchmark for comparison.

![Figure 4.2.6.](image.png)

Figure 4.2.6. The effect of ageing at 621°C on mean \( \gamma' \) coarsening after solution treatment (ST).
4.3. Chapter Summary

The precipitation and dissolution temperatures of phases in alloy 718, 945 and 945x was simulated using ThermoCalc and JMatPro. The simulations extracted for the coarsening of γ’ were used to compare with experimental TEM results. The following important points of the chapter are summarised as below:

1. The space for precipitation of secondary phases in alloys 718, 945 and 945x under standard heat treatment i.e. API 6A718 and conventional double ageing was presented as TTT diagram.
2. Dissolution temperature of secondary phases in each alloy were simulated in ThermoCalc (using Ni database) and JMatPro (using NiFe database).
3. Presence of metastable γ’’ phase makes alloy 718 and 945x metastable under Thermotech (using NiFe database) and JMatPro (using NiFe database) phase simulation respectively. Whereas, no metastable γ’’ phase observed for 718 and 945 under ThermoCalc and JMatPro phase simulations.
4. The γ’ coarsening simulation for alloy 718’s specimen S2_API simulate the mean size of around 20nm under API ageing at 790°C for 7hr. Whereas, the size simulated for non-standard heat treatments for specimens S3 and S4 would be comparable to TEM results.
5. The mean γ’ size simulated for 945 and 945x was around 8.40nm and 9.74nm respectively under two step ageing. The second ageing at 621°C consolidates the growth of γ’ precipitates by adding little fraction (~0.20nm) in size.
CHAPTER 5. Hydrogen embrittlement theory for existing CRA alloy - INCONEL 718

The microstructure of bolts strongly depend upon the manufacturing sequence. Normally the bolts are cold rolled and then heat treated. This manufacturing process had led to increase in hardness, lower ductility and more susceptibility to HE [64]. The reason for this abrupt change in mechanical and corrosive properties lies under the microstructure. Apart from apparently detrimental role of intergranular precipitates [64] transgranular nano precipitates might be the primary source for crack initiation and then under slip crack propagate as intergranular. It was therefore important to possess the understanding of structure if the manufacturing route is changed. In the manufacturing route heat treatment was performed first and cold rolling of threads at the end; applied to the API 718 CRA bolts. The micro and nano-structure at edge and bulk of bolt was investigated and compared with rectangular block (RB) of API 718. The morphological difference of nano phase at bulk and edge could help us to identify initiation point for hydrogen cracking and an effort was made to establish hydrogen assisted cracking (HAC) theory which could aid to analyse slow strain rate testing results under CP in future.

5.1. Introduction

5.1.1. Metallurgy of Inconel 718

The nominal composition of Inconel 718 in wt% is 52.50 - 18.50 Fe – 19 Cr – 5.10Nb – 3.0 Mo – 0.5 Al – 1.0 Ti – 0.08 C [16] [165]. The matrix is composed of face centered cubic (FCC) structure, nickel base austenitic phase, called gamma (γ). It has a large number of solid solution elements such as Tungsten (W), Molybdenum (Mo), Chromium (Cr), Iron (Fe), Aluminium (Al), Titanium (Ti) and Cobalt (Co). Al and Cr form Al₂O₃ and Cr₂O₃ protective oxide films respectively that increase corrosion resistance [33]. It is primarily strengthened by unique intermetallic, (L1₂ ordered) face centered cubic (FCC) phase, γ’Ni₃(Al, Ti, Nb), by interacting with dislocations [33]. This ordering places Ni at the face of each unit cell and Al, Ti or Nb at each corner. γ’ phase is more like spherical at low volume fraction and tend to be cubic at higher volume fraction depending upon heat treatment [34]. Hagel and Beattie [15] observe that γ are like spheres with 0-0.2% lattice mismatch, then cubes at mismatch around 0.5-1.0% and then plates at mismatch above about 1.25%. They are coherent precipitates with γ matrix and precipitates around 620°C. γ" phase supply additional strength and considered as main strengthening agent. They are body centered tetragonal (BCT) Ni₃Nb and precipitate in γ matrix around 720°C. Both γ’ and γ” have solvus temperature around 900-920°C [16]. However, γ” is metastable phase which tend to be replaced by incoherent stable orthorhombic delta (δ) phase, Ni₃Nb, after long term exposure to temperature above 650°C [19] [27] [37]. It precipitates normally between 650-980°C on grain boundaries with thin plates extending to
grains [14] and with solvus temperature between ~980-995°C. As both γ'' and δ phase are Nb based which implies that δ phase precipitation occurs with the loss of γ'' phase. Their morphology contribute to the loss of strength and hardenability because of depletion of γ'' and presence in the structure lead to increased susceptibility of hydrogen cracking with loss of fracture strain and notch tensile strength (NTS) [110][117]. In addition to these phases, blocky shaped carbides i.e. MC carbides, M being mostly Nb and Ti, are distributed homogeneously throughout the matrix [38][40][167]. Both δ and MC carbides inhibit grain growth and prevent grain boundary sliding. Nb plays a key role in making up all the phases present in alloy 718. It has been found that Laves phase requires 10-12% Nb; the delta δ phase requires 6-8% Nb; γ'' needs 4% Nb and γ' can form with Nb levels below 4%. The degree of Nb segregation during ingot or casting solidification depends on rate of cooling, the faster the cooling less the segregation. High temperature homogenization can be used to solution laves phase and distribute Nb uniformly throughout the bulk matrix [39]. Sigma phase has hexagonal geometry with composition formula (Cr, Mo),(Ni,Co), where x and y vary from 1 to 7; and generally grows through γ' particles. It has detrimental effect with plate like morphology. They are source for crack initiation and propagation leading to low temperature brittle fracture. It contain high amount of refractory elements sapped from γ matrix resulting in loss of solution strengthening [21].It should be noted that morphology of all phases mentioned above are dependent upon heat treatment.

5.2. Experimental Aim

It would be logical to further improve the alloy but oil grade 718 is finely balanced and small changes in chemistry to avoid δ or improve corrosion resistance have the risk of forming Laves phase [65]. This is highlighted in time temperature transformation (TTT) diagram of alloy 718 in chapter 4. The predicted phases that could be present in alloy at different heating parameters can be seen. The aim of the present work is to investigate oil grade alloy 718 heat treated according to API specification in two different product forms; as 'rectangular block' and CRA 'bolt' and then discussed and compared in terms of micro-structural phases and their vulnerability to HE. Non-standard higher solution treatment (1300°C) and slightly longer ageing condition was added to observe the effect on microstructure. Two other non-standard heating parameters with conventional double ageing added to observe their effect on microstructural and mechanical properties. The basic idea of selecting non-standard heating parameters was to characterise the evolution of second phase particles specifically γ', metastable γ'', stable δ and MC, Ns or any laves phase within grains and on grain boundaries. The grain size for each heat treatment was evaluated using light microscopy (LM) intercept
method. The identification and morphology of precipitates (micro and nano) was revealed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

5.3. Experimental Procedure and Method

5.3.1 Material

Inconel 718 in the product form as rectangular block (RB) (10 x 3 x 2 cm) and 3 bolts (Φ ~28 mm and length ~15 cm) were received in as received condition. They were heat treated according to API 6A718 specification. The optical electron spectroscopy (OES) was performed with thin off cut from the bolt and RB. The OES results were identical and are presented in Table 5.0.

<table>
<thead>
<tr>
<th>Element wt.%</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Al</th>
<th>Co</th>
<th>Cu</th>
<th>Nb</th>
<th>Ti</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>718</td>
<td>0.025</td>
<td>0.11</td>
<td>0.05</td>
<td>18.1</td>
<td>3.09</td>
<td>18.7</td>
<td>0.48</td>
<td>0.14</td>
<td>0.04</td>
<td>5.06</td>
<td>0.98</td>
<td>52.6</td>
</tr>
</tbody>
</table>

Table 5.0. Elemental composition of the as received alloy 718.

5.3.2 Sample Preparation

From rectangular-block small samples were prepared using spark erosion machine and heat treated at standard and non-standard heat treatments. The detail about heat treatment is shown in Table 5.1. The bolts were rolled to remove the threads and then solution annealed at 1030°C for 1 hr air cooled. The bolts were now turned into rolled bars of diameter ~22 mm. Standard heat treatment of API 6A718 is then applied to three of the rolled bars. After completion of the heat treatment cold rolling of threads were performed. Cross sectional off cuts of thickness ~2 mm and diameter ~22 mm were extracted from bolt for microstructural analysis.

<table>
<thead>
<tr>
<th>Alloy 718 Specimens</th>
<th>Product form</th>
<th>HT Condition</th>
<th>Heat treatment detail</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 x S1</td>
<td>Rectangular Block</td>
<td>Standard</td>
<td>1035°C - 2 hr AC</td>
</tr>
<tr>
<td>2 x S2</td>
<td>Rectangular Block</td>
<td>Standard</td>
<td>1035°C - 2 hr AC / 790°C - 7 hr AC (API Oil &amp; Gas Grade)</td>
</tr>
<tr>
<td>1 x S3</td>
<td>Rectangular Block</td>
<td>Non-Standard</td>
<td>1250°C - 2 hr AC 790°C - 16 hr and 25 hr AC</td>
</tr>
<tr>
<td>1 x S3*</td>
<td>Rectangular Block</td>
<td>Non-Standard</td>
<td>1250°C - 2 hr AC</td>
</tr>
<tr>
<td>1 x S4</td>
<td>Rectangular Block</td>
<td>Non-Standard</td>
<td>1035°C - 1 hr AC / 718°C - 8 hr then 621°C - 8 hr AC</td>
</tr>
<tr>
<td>S5</td>
<td>Rectangular Block</td>
<td>Non-Standard</td>
<td>1035°C - 2 hr AC / 955°C - 3 hr AC / 718°C - 8 hr then 621°C - 8 hr AC</td>
</tr>
<tr>
<td>4 x S6</td>
<td>Bolt</td>
<td>Standard</td>
<td>1035°C - 2 hr AC / 790°C - 7 hr AC (API Oil &amp; Gas Grade)</td>
</tr>
<tr>
<td>4 x S7</td>
<td>Bolt</td>
<td>As Received</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1. Alloy 718 specimens and their heat treated condition.
NOTE: The symbol ‘x’ represent the number of TEM samples extracted from each specimen.

(AC=Air Cool and WQ = Water Quench)

The thermal heat treatments, shown in Table 2, were performed on 718 specimens using standard workshop methods. The sample S1 was solution treated in furnace preheated to 1035°C for 2hr and then air cooled (AC) to room temperature. This was then taken out to prepare for micro-structural investigation, while the S2 sample was put in a furnace preheated to 788°C and single aged at this temperature for 7hr. S3 was higher solution treated at 1300°C for 2hr air cooled and then aged at 788°C for 16hr and 25 hr followed by air cooling (AC) to room temperature. S3* was higher solution treated at 1300°C for 2hr air cooled (AC) and water quench (WQ). S4 was solution treated at temperature similar to S1 and then followed by double ageing temperature: sample was put in a furnace preheated to 718°C for 8hr, then it was furnace cooled at 56°C/hour to 621°C, holding at this temperature for further 8hr and then extracted followed by air cooling. Same heat treatment has been applied to S5 except with one more intermediate step ageing at 955°C for 3hr after solution treatment.

The specimens which are observed under light and scanning electron microscope was grinded and polished (Table 5.2) using descending order of abrasive cloths up to finer grit size ~0.25μm. Specimens are then mounted with Bakelite (conductive resin) prior to grinding or polishing. Kallings reagent (100ml HCL, 100ml ethanol, 5g CuCl₂) was used to reveal the microstructure i.e. grain boundaries and metal carbides. Electrolytic etching was performed with 8ml H₂SO₄ and 100ml H₂O at 2V for 3sec to reveal δ/γ'/γ” precipitates. Confirmation of presence of these particles was performed in SEM (spot size 5 operated at 20KV and in backscatter electron (BSE) mode) with energy dispersive x-ray (EDX) spectroscopy. The average size of micro particles within grain and on grain boundary is measured by randomly considering approximately 50 particles.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Abrasive/Size (μm)</th>
<th>Load (N)</th>
<th>Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waterproof paper</td>
<td>P240-P1 200 Silicon carbide(SiC) paper</td>
<td>27</td>
<td>Until Plane</td>
</tr>
<tr>
<td>Polyester Cloth</td>
<td>6μm diamond with suspension</td>
<td>27</td>
<td>5</td>
</tr>
<tr>
<td>Polyester Cloth</td>
<td>3μm diamond with diamond suspension</td>
<td>27</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Description</td>
<td>Value</td>
<td>Range</td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------------------------------------------------------------</td>
<td>--------</td>
<td>-------</td>
</tr>
<tr>
<td>Polyester Cloth</td>
<td>1μm diamond with diamond suspension</td>
<td>27</td>
<td>4</td>
</tr>
<tr>
<td>Synthetic rayon medium-nap cloth</td>
<td>0.25μm with alumina OP-S suspension (0.06μm)</td>
<td>27</td>
<td>5-10</td>
</tr>
</tbody>
</table>

**Table 5.2.** Grinding and polishing scheme used in the experiment.

For transmission electron microscopy (TEM), apparatus JEOL 2100 at department of engineering of University of Leicester was used and operated at accelerating voltage of 200KV (beam current ~102μA) with spot size 1 and alpha angle 2. The mean size range of nano particles were calculated by randomly considering 50 particles and taking average. Two methods were adopted to prepare TEM electron transparent samples. The first is twin-jet electro polisher. The apparatus is shown in Figure 5.1.1a and Figure 5.1.1b. Thin foils were prepared from each characterisation specimen, which were mechanically grounded down to a thickness less than 100μm by silicon carbide papers (240-1200 grit). 3mm foils were punched and subsequently polished by struers twin jet electrolytic polishers using a solution of 450 ml methanol, 100 ml 2-butoxyethanol and 50ml perchloric acid. The polishing operation was performed at a voltage of 10-15V, current of ~45mA and polishing speed of ~4.5 for one minute or until the electrolyte penetrated through the thickness of the specimen and the hole is created in the middle of sample. Soon after that alarm comes up and the samples were taken out from the holder. They were rinsed in methanol and left on soft paper towels to dry.
Figure 5.1.0a. Voltage and Current control unit of the electro polishing machine.
Figure 5.1.1b. Sample or foil holder of the ‘struers’ twin jet electro polishing machine.

The second technique for TEM sample extraction was dual beam SEM/FIB lift out method. SEM was operated at 20KV with spot size 5 and ion beam was operated at 30KV with varying currents from 10pA to 7nA depending upon the preparation stage. The method is illustrated in Figure 5.1.2, where each image from (i) to (xii) reveal the key stages for acquiring TEM electron transparent foil from region of interest in the sample. TEM samples have been lift out from edge and bulk area of the bolt, schematic shown in Figure 5.1.3. Whereas, TEM sample from bulk of rectangular block was prepared using twin-jet electro polisher and from edge using FIB.

The following points below is the description of each stage:

i. This is the location of region of interest (RoI)

ii. Platinum layer of dimension 20 x 2 x 4 µm is deposited at 52°.

iii. Milling of trenches above and below the platinum deposit.

iv. Milling of ‘L’ cut at 7° and cleaning of trenches at 52°.

v. Tilting back to 7° to check the ‘L’ cut.

vi. Attaching the tungsten omniprobe needle with carbon deposition to the right side of the foil. The vertical cut (red dotted line) is made to extract the sample from trench.
vii. Foil attached with the omniprobe needle.

viii. Aerial view of the TEM copper grid where foil to be attached.

ix. Attachment of foil using C deposition to the 'I' shaped holder of TEM grid.

x. Attached foil with TEM grid at 'I' shaped holder.

xi. Ion beam image showing final thinning of the foil with reduced current.

xii. SEM image of electron transparent foil which is less than or ~100nm and ready for TEM imaging.
**Figure 5.1.2.** The images (i) to (xii) illustrate the method for preparing TEM electron transparent foil using focused ion beam (FIB) lift out technique.
**Figure 5.1.3.** Schematic showing the position of TEM samples extracted from rectangular block (*top*) and API bolt (*bottom*) using FIB technique. Two TEM samples were extracted from bulk and edge of the rectangular block and four TEM samples were extracted from shank edge, Shank bulk, thread edge and thread bulk of the API bolt.
The schematic of tensile specimen is shown in Figure 5.1.4. Two tensile specimens for each heat treatment were prepared using standard laboratory methods. The tensile specimens from bolt were extracted from the bulk. They were tested in tensile machine 'Tinius Olsen' at strain rate of 10mm/min.

![Schematic illustration of the tensile specimen (unit: mm).](image)

**Figure 5.1.4.** Schematic illustration of the tensile specimen (unit: mm).

Vickers hardness (HV) measurements were carried out at each characterisation specimens. Prior to hardness testing, samples were mounted in resin followed by grinding (240-1200 grit) and polishing up to 0.25μm with colloidal silica. Measurements were performed using diamond pyramid indenter with a force of 5-10 kgf (HV5/10). Set of values were recorded while moving from one end to other. The distance between each indent was kept approximately of more than 3d spacing, where d is indent diameter (either in x or y direction), to prevent overlap of strain fields.
5.4. Microstructural Analysis

API and non-standard heat treatments were applied to 718 specimens, which were extracted from rectangular block and CRA bolt (shown in Table 5.1). The microstructure results especially SEM and TEM were then compared together to analyse the effect of microstructure on mechanical properties and its vulnerability to HE. The HAC theory was then established as per CRA bolt’s microstructure.

5.4.1. Light and Scanning Electron Microscopy (SEM)

Light micrographs for each specimen are shown in Figure 5.1.5 – 5.2.1. The light images from bulk (shank and thread) and edge (shank and thread) section of the bolt were quiet similar and no significant change in grain size was observed. In order to have statistical approach towards grain size and particle size measurement at least 5 light and 5 SEM micrographs were considered. Twinning was observed in each specimen as highlighted in microstructures. It has always been recognized as plastic deformation mechanism for Inconel718 [168][169].

![Twinning microstructures](image)

Figure 5.1.5. Light microstructure of S1\textsubscript{API} (1035°C-2hr AC) showing grain size of 30-35µm
**Figure 5.1.6.** Light microstructure S2_{API} \((1035\degree C-2hr + 790\degree C-7hr)\) showing grain size of 30-35\(\mu m\).

**Figure 5.1.7.** Light microstructure of S3 \((1300\degree C-2hr + 790\degree C-16hr)\)\text{left} and S3\((1300\degree C-2hr + 790\degree C-25hr)\)\text{right} showing grain size in range 75-85 \(\mu m\). 25hr aged specimen clearly show continuous intergranular precipitation.

**Figure 5.1.8.** Light microstructure of S3*\((1300\degree C-2hr\ AC)\) showing grain size in range 75-85\(\mu m\).
**Figure 5.1.9.** Light microstructure of S4 (1035°C - 2hr AC/718°C-8hr then 621°C-8hr AC) showing grain size in range 55-65µm.

**Figure 5.2.0.** Light microstructure of S5(1035°C - 1hr AC / 955°C-3.5hr/718°C-8hr then 621°C-8hr AC) showing grain size in range 55-65µm. The images are at high magnification to see any accicular delta δ phase on grain boundaries.
Figure 5.2.1. Typical light microstructure showing equiaxed grains with size range of 30-40 µm from bulk and edge of the API bolt.
Typical scanning electron image from edge and bulk of CRA bolt, shown in Figure 5.2.2. Metal carbides and nitrides (M C,Ns) are distributed randomly at intergranular and transgranular positions from edge (shank and thread) to bulk (shank and edge) of the bolt. They are present in variable size range from 1-20µm. Metal carbides are identified as NbC and metal nitrides as TiN.

Figure 5.2.2. Typical SEM image showing random distribution of M C,Ns as bright particles from bulk to edge of CRA bolt.

The SEM image shown in Figure 5.2.2 is an overview of the bolt microstructure with M C,Ns precipitates (appearing as bright spots), distributed randomly throughout the structure. These precipitates were seen at shank edge, shank bulk, thread edge and thread bulk of the bolt. Grain boundaries were carefully examined at each of these locations and found as deprived of any continuous intergranular precipitation, shown in Figure 5.2.3(a-d). Composition spectrum are shown in Figure 5.2.3 (g) and (h) for metal carbides (white) and nitrides (black).
(a) Shank Bulk of API bolt

(b) Shank Edge of API bolt
(c) Thread Bulk of API bolt

(d) Thread Edge of API bolt
Figure 5.2.3. Typical SEM images (a-d) of API bolt showing no grain boundary precipitation at shank bulk, shank edge, thread bulk and thread edge. (e) and (f) showing white and black particles which are NbC and TiN respectively. Composition spectrums in (g) and (h) are of NbC and TiN respectively.
**Figure 5.2.4.** SEM images of specimen S1 API from RB which is solution annealed at 1035°C for 2hr AC. (a) and (b) showing M C, N's (NbC; TiN). (c) and (d) is high magnification of (a) and (b) respectively, as expected showing no grain boundary precipitation.
Figure5.2.5. SEM images of specimen S2 API from RB heat treated at 790°C for 7 hr, (a) and (b) showing M C, N’s (NbC_white and TiN_black). (c) and (d) high magnification of intergranular positions showing acicular (needle like) delta (δ) phase precipitation.
Figure 5.2.6. SEM images of specimen S3 for 16hr and 25hr ageing. (a) and (b) showing acicular delta phase (needle like) at grain boundaries extending to within grains because of ageing for 16hr. (c) and (d) showing continuous grain boundary laves phase. (e) EDS spectra of intergranular phase rich in Nb, Mo and Ti and (f) EDS spectra of $\gamma$ matrix.
Figure 5.2.7. SEM images of specimen S3*(1300°C 2hr-AC) (a) dark secondary electron image - showing random distribution of M C,N's throughout the microstructure which appear as bright spots. (b) and (c) as expected grain boundaries having with no second phase precipitation.
Solution treated specimen S3* at 1300°C AC results in dissolution of the carbides and some nitrides back into the matrix. Grain boundary precipitates if any also dissolve back into the matrix because of their solvus temperature less than 1000°C. This can be seen in Figure 4.5 (b) and (c) where grain boundaries have no second phase precipitation.

**Figure 5.2.8.** SEM images of specimen S4 (a) showing random distribution of M C,N's (NbC and TiN) throughout the microstructure which appear as black and white precipitates on grains and within grains. (c) and (d) showing discrete $M_{23}C_6$ precipitation on grain boundary.
Figure 5.2.9. SEM images of specimen S5 with additional intermediate ageing at 955°C for 3hr (a) grains overview (b) showing random distribution of M23C6, N's which appear as white (NbC) and black(TiN). (c) and (d) showing discrete grain boundary delta δ phase and M23C6.

It was observed that S4 and S6 (API bolt) have no delta δ phase (needle platelets) at the grain boundary but S4 has discrete M23C6. Whereas, S2API and S5 shown discrete delta δ phase precipitation at intergranular positions. For specimens S1 and S3* no intergranular precipitation was observed because solvus temperature of all second phases are below 1000°C. The solvus temperature of all second phases e.g. γ', γ'', M23C6 and MC, are calculated using ThermoCalc simulations, see chapter 4. The detail of this has been discussed in ThermoCalc and JMatPro simulations.
5.4.2. Transmission Electron Microscopy (TEM)

5.4.2.1. Morphology and Identification of nano precipitates

The TEM images of specimens from API bolt and rectangular block are shown in Figure 5.3.0 - 5.4.0. The morphology (shape and size) of nano precipitates examined under TEM were compared and confirmed with the established metallurgy of Inconel718, as described earlier ‘Metallurgy of Inconel718’. Along with morphology every nano phase has unique selected area diffraction pattern associated to its crystal structure, which were recorded as a confirmation of their existence in the $\gamma$ lattice. The bright spots are related to fcc $\gamma$ and slightly faint spots are associated to $\gamma'$. These faint spots where they appear to be elongated represent $\gamma''$ phase, e.g. see Figure 5.3.0 (f) diffraction pattern corresponding to $\gamma''$. Further, some EDS line scans (their length depending upon the size of nano phase) was run from $\gamma$ matrix to nano phase for extracting phase composition.
Figure 5.3.0. TEM images of API bolt from shank bulk (a and b) and shank edge (c and d). (a) Dark field imaging - overview of $\gamma'$ precipitates (appearing as black spheres) which are distributed randomly and $\gamma''$ in elongated disc shaped ranging between $\sim$30-50 nm in $\gamma$ matrix. (b) at higher magnification clearly shows $\gamma'$ in spherical shape around 30 nm and $\gamma''$ in elongated disc shaped ranging between $\sim$30-50 nm. (c) reveal the presence of $\gamma''$ 50-100 nm elongated discs and (d) at higher magnification. (e) and (f) showing selected area diffraction pattern (SADP) corresponding to $\gamma'$ and $\gamma''$ phase at shank bulk and shank edge respectively.
Figure 5.3.1. TEM images of API bolt from thread bulk (a and b) and thread edge (c and d). (a) overview of γ’ precipitates ~30nm appearing as black spheres and elongated disc shaped γ” ~50nm distributed randomly throughout the γ matrix. (b) at higher magnification. (c) showing γ’ in spherical shape around ~45 nm and γ” between 50-100 nm. (e) and (f) showing selected area diffraction pattern (SADP) corresponding to γ’ and γ” phase at thread bulk and thread edge respectively.
Figure 5.3.2. TEM images of AR bolt from shank bulk, shank edge, thread bulk and thread edge.

(a) Dark field imaging at shank bulk showing $\gamma'$ precipitates $\sim$30nm as black spheres and $\gamma''$ elongated disc shaped $\sim$50nm, distributed randomly throughout the $\gamma$ matrix. (b) Shank edge showing only $\gamma''$ between 50-100nm. (c) Thread bulk (similar to shank bulk) having $\gamma'$ precipitates $\sim$30nm and $\gamma''$ around 50nm. Whereas, (d) thread edge clearly shows $\gamma'$ in spherical shape around 50 nm and $\gamma''$ in elongated disc shaped ranging between 50-100 nm. (e) and (f) showing selected area diffraction pattern (SADP) corresponding to $\gamma$ matrix, $\gamma'$ and $\gamma''$. 
\( \gamma'' \) phase at thread bulk and thread edge respectively (shank bulk and shank edge had similar diffraction patterns).

**Figure 5.3.3.** TEM image of solution treated \((1035^\circ C \text{ 2hr \textendash AC})\) sample S1 from RB. (a) showing an overview of \( \gamma \) matrix. Bright field image (b) showing dense distribution of very small (appear white) \( \gamma' \) precipitates of about 1-2 nm. Whereas (c) is dark field image - at higher magnification with mottled appearance and (d) selected area diffraction pattern (SADP) corresponding to \( \gamma' \) and \( \gamma \) matrix.
Figure 5.3.4. TEM images of S2\textsubscript{API} from bulk and edge of RB, (a)-(c) Bulk - overview of \(\gamma'\) precipitates that are distributed homogenously throughout the matrix. (b) \(\gamma'\) precipitates between 10-20 nm were observed, Whereas, (c) is higher magnification of (b). (d) Showing strong selected area diffraction pattern (SADP) spots related to \(\gamma'\) precipitates and \(\gamma\) matrix. Edge - (e) and (f) showing \(\gamma'\) precipitates around 10-20 nm. (Note: Mean size of \(\gamma'\) precipitates \(\sim 15-20 \pm 5\) nm)
Figure 5.3.5. TEM images of sample S3 (16hr) from RB showing in (a) Bright field image - overview of spherical γ' precipitates (conglomeration of γ' precipitates can be observed) distributed homogenously throughout the γ matrix. Dark faint line around precipitates distinguish γ' from γ matrix. (b) γ' precipitates between 10-50 nm are recorded. (c) higher magnification showing variable size of γ' precipitates (d) strong selected area diffraction spots associated to γ' and γ matrix (Note: mean size of γ' precipitates recorded ~ 30 ± 5nm)
Figure 5.3.6. TEM images of solution treated sample S3* (1300°C – 2hr AC). Shown in (a) dense distribution of very small γ' precipitates of about 1-2 nm in diameter. (b) Selected area diffraction pattern (SADP) representing more of fcc γ matrix than γ'.
Figure 5.3.7. TEM images of S4 showing in (a) and (b) maximum γ' precipitate around 50nm in diameter and γ'' as elongated discs between 50-70nm. (c) at higher magnification clearly showing small γ' precipitates 1-10nm (red arrows) which nucleated during air cooling or second ageing. (d) showing selected area diffraction pattern (SADP) corresponding to γ matrix, γ' and γ'' phase.
5.5. Discussion

5.5.1. Effect of primary carbides and nitrides on grain size of Bolt and RB

Figures 5.2.2 – 5.2.9 shows the primary MC type carbides (white particles identified NbC) and MN type nitrides (black particles identified as TiN). They are observed in the microstructure of the Bolt (from bulk to edge of shank and thread) and RB specimens both in solution treated and solution treated plus aged condition. There was no significant change observed on the size and volume fraction of primary carbides and nitrides. In solution treated (S1 and S3*) and aged specimens (S2API, S3, S4, S5, S6 and AR) the population for carbides and nitrides was clearly visible. For a given location in each specimen the size range of 1-30µm and volume fraction of carbide and nitride are comparable with any slight difference might be because of the difference in heating parameters. The low volume fraction of carbides and nitrides (approximately <2%) with heterogeneous distribution at transgranular and intergranular positions have little influence on the mechanical properties (yield strength and hardness) of superalloys [170]. MC type carbides are major source of Nb for the solution treated specimens (S1 and S3*) to use during thermal ageing [170] and some of them dissociate to form intergranular secondary carbides $M_23C_6$ (refer to Figure 5.2.8 and 5.2.9 for S4 and S5). However, their presence at the grain boundaries helps to pin or hold the grain boundaries and restrain their growth. For specimens S3 and S3* higher solution treatment around 1250°C for 2hr was performed because of the higher solvus temperature of primary carbides (MC) but with risk of forming liquid phase between 20-30 mole percentage, as described in Chapter 4: section 4.1.3. The reason for selecting this non-standard solution treatment was to have low volume fraction of MC,Ns by dissolving NbC and TiN back into lattice and thus increasing the grain size when compared with S1API. The solvus temperature of nitrides was not calculated from the ThermoCalc simulations and they are believed to be very stable even temperatures close to the bulk melting point of $\gamma$ matrix. These carbides and nitrides are important for the grain size control during thermal ageing treatment.

No significant difference observed in grain size for S2API from RB and S6API from Bolt (shank and thread) and was in the range 30-40µm. The observation of the light microstructures, shown in Figure 5.1.5 - 5.2.1, for S1API, S2API, S6API and AR clearly indicated finer grains with grain size between 30-40 µm. This shows that RB and Bolt have the same grain size under API heat treatment. However, evolution of grain size was observed for non-standard heat treated specimens S4 and S5 (55-65 µm) to specimen S3 and S3* (75-85 µm). For S3 and S3* this might be due to the increase in solution treatment temperature from 1035°C to 1250°C, which results in the dissolution of carbides (as mentioned earlier) and some nitrides back into matrix. Whereas, for S4 and S5 the change of grain size could have been
because of double ageing after solution treatment. Which might have dissolved the primary carbides and as described earlier dissociate them to form intergranular $M_{23}C_6$. It has been observed as evidence that change in solution treatment and ageing process alter the carbides formation, which prevent to hold grain boundaries and allow grains to grow excessively large. It is worth noting that revealing the grain boundaries of solution treated specimens S1_{API} and S3* was not possible using swabbing or emersion in electrolyte and even after attempting electrolytic etching. The colloidal silica alumina suspension (0.06µm) found to be suitable for not only polishing but also slight etching of specimens. It was very useful specifically for revealing grain boundaries and helps in computing accurate grain size.

5.5.2. Effect of heating parameters on morphology of second phase of Bolt and RB

The second phase of the RB and Bolt microstructure include $\delta$ Ni$_3$Nb, $\gamma'$ Ni$_3$(Ti, Al, Nb) and $\gamma''$ Ni$_3$Nb In the literature [151][171][172][164] $\delta$ phase have needle like morphology, whereas $\gamma'$ and $\gamma''$ have spherical and compact disc shaped morphology respectively. S. Azadian et al [36] reported $\delta$ precipitation in Inconel 718 in wrought and spray formed versions in the temperature range from 700-1000°C. They concluded that the volume fraction of $\delta$ phase reaches to near maximum during 20h of ageing, whereas mean $\delta$-plate thickness changes with a standard deviation of 100nm under 100h of ageing. In the work presented here, when aged at API heat treatment (790°C for 7hr), S2_{API} from RB, precipitated not much but discrete $\delta$ phase at intergranular positions, as shown in Figure 5.2.5 (c) and (d). Whereas, S6_{API} (typical of bolt’s shank and thread microstructure) shows no intergranular $\delta$ precipitation, Figure 5.2.3. The precipitation and dissolution of $M_{23}C_6$ in 718 was predicted in ‘Themotech and ‘ThermoCalc’ simulations shown in chapter 4: section 4.1.2-4.1.3). The presence of $M_{23}C_6$ in S2_{API} might be because of single ageing which dissociate primary carbides (NbC) into intergranular carbides, chapter 2: section 2.3.4. Their absence from S1_{API} was an evidence that ageing S2_{API} at 790°C had resulted in formation of these carbides.

The morphology of $\delta$ as needles is evident from Figure 5.2.5 (S2_{API}; $\delta$ 1-2µm), Figure 5.2.6(b) (S3; $\delta$ 5-15µm) and Figure 5.2.9 (S5; $\delta$ 1-2µm). The laves phase present on grain boundaries in specimen S3(aged for 25hr), as shown in Figure 5.3.6(c) was because of the excess amount of Nb present in the y matrix for ageing from higher solution treatment at 1250°C. Ageing times of 16hr and 25hr were performed on specimens S3 and the result for 16hr ageing was in the form of needle like $\delta$ on grain boundaries extended to grains, whereas, for 25hr ageing continuous laves phase (rich in Nb) was observed on grain boundaries, see EDS spectra in Figure 5.2.6 (e). The main reason for performing higher solution treatment was to have more Nb and Ti content for the $\gamma'$ and $\gamma''$ precipitation and longer ageing (16hr) to see the effect on their coarsening behaviour under TEM. The non-standard heat treatments given to
RB was to observe the evolutionary effect on morphology of nano phases and to compare them with the API Bolt’s nano structure. Starting from the nano phases which were observed in RB; γ’ present in solution treated specimens S1 and S3, Figure 5.3.3 and 5.3.6, was in the range 1-2 nm. This small size precipitation of γ’ was because of air cooling after solution treatment. In specimen S2, Figure 5.3.4, after precipitation of γ’ during cooling from solution temperature results in growth and coarsening of γ’ at 7hr ageing. They found to be in spherical shape in size range of ~10-20 nm with a mean size of 15-18 nm. This small size precipitation of γ’ was because of air cooling after solution treatment. In specimen S2, Figure 5.3.4, after precipitation of γ’ during cooling from solution temperature results in growth and coarsening of γ’ at 7hr ageing. They found to be in spherical shape in size range of ~10-20 nm with a mean size of 15-18 nm. This small size precipitation of γ’ was because of air cooling after solution treatment. In specimen S2 API, Figure 5.3.4, after precipitation of γ’ during cooling from solution temperature results in growth and coarsening of γ’ at 7hr ageing. They found to be in spherical shape in size range of ~10-20 nm with a mean size of 15-18 nm, close to what was simulated in chapter 4: section 4.1.4. This single population of γ’ is contrary with the findings of Ding [173] who found two main populations in a plate of 718 solution treated at 1050°C-1hr AC followed by double ageing at 720°C-8hr and 650°C-8hr. Ding found primary γ’ of 25nm homogeneously distributed throughout the matrix and secondary γ’ of 100nm but with less number density. The difference in the size range of γ’ in S2 and Ding’s specimens is obviously because of difference in ageing parameters, as S2 was single aged. It could be that difference in ageing parameters not only influence the mean size but also the size range of γ’ particles. The effect of solution annealing temperature on the γ’ size range is also significant. The solution annealing or homogenization temperature of specimen S3 is 1250°C and after ageing for 16hr resulted in extended size range of γ’ population, which can be seen in TEM images in Figure 5.3.5. Nearly spherical γ’ precipitates in the size range 10-50 nm were observed. One of the reason for this significant increase in size of γ’ particles might be because of more Ti and Nb present in the matrix for γ’ precipitation. Metastable γ” Ni3Nb was not observed instead stable intergranular needles 5-15µm of δ Ni3Nb precipitated on grain boundaries extending to grains, Figure 5.2.6(b). Specimen S4 was conventional double aged after standard API solution treatment. The reason was to observe the effect on precipitation sequence and morphology of γ’ and γ” phases. It was expected to have both γ’ and γ” as main strengthening phases but the surprising factor was the size of the γ’ precipitates ~50nm and γ” 50-70nm Figure 5.3.7 (which is similar to S6 API and ARAPI specimen from Bolt). There were also small γ’ particles 1-5nm (indicated by red arrows) which precipitated after the second ageing step at 620°C during air cooling to room temperature. Thus γ’ particles are present in the range between 1-50nm along with metastable γ” which contribute to remarkable strength and hardness (discuss later).

Additional step ageing at 955°C for 3hr after solution treatment at 1035°C differentiate specimen S4 from S5. The reason was to deliberately generate δ at grain boundaries for S5, as shown in Figure 5.2.9 (c) and (d). S4 and S5 were double aged, we secondary carbides M23C6 were observed at intergranular postions for both specimens, Figure 5.2.8(c) and Figure 5.2.9(c)-(d). The difference in the ageing step results in increase of hardness value of specimen S5 up to 432 HV10 when compared to specimen S4 with hardness 408 HV05. This was
unexpected because precipitation of δ phase results in decrease in hardness, as described earlier 'Metallurgy of Inconel718'. One reason might be because more Ni and Nb from the γ matrix consumed up during intermediate ageing to form metastable γ'' particles along with some δ in S5. This excess Nb in the γ matrix because of solution treatment end up dissolving some of NbC back into the matrix, providing more Nb for γ'' precipitation during ageing process for both S4 and S5 but intermediate step ageing at 955°C form or coarsen existing metastable γ'' phase apart from forming δ at intergranular positions. The FIB specimen extracted from S5 failed during thinning procedure thus TEM imaging not performed on S5 thus a clear judgement cannot be made. However, γ' size for specimen S4 was computed using JMatPro coarsening simulations, chapter 4: section 4.1.4. A mean size of 10 nm is obtained and it is observed from simulations that ageing at 718°C increases the size of γ' precipitates significantly than ageing at 621°C. Ageing at 621°C consolidates the growth by adding few fraction of a nano-meter (0.15nm), described in chapter 4. It is mostly associated to the complete chemical ordering of elements within γ' particle which result in faceted growth. Consolidation of the shape of γ' precipitates or assist faceted growth, which significantly increases the strength of the alloy, as shown in theoretical simulation Figure 6.4 (b). This is nearly coherent with the results obtained from Whitmore et al [163], they concluded that most of γ' precipitated after single ageing (solution treatment at 975°C WQ then ageing at 788°C-4hr AC) were around 23.5 nm in diameter, and after double ageing (solution treatment at 975°C WQ then ageing at 788°C-4hr, WQ to RT then 675°C-8hr AC) they are some 14% larger at 28.0 nm diameter. Double ageing is not found to give rise to an additional population of γ' precipitates of comparable size to the first population. As mentioned earlier, during air cooling of the specimens γ' precipitates in the range of 1-2 nm (this is evident from Figure 5.3.3 and 5.3.6 of specimens S1 and S3* respectively). At early stages of precipitation during air cooling the chemical ordering within γ' is not complete which result in spherical shape. After ageing of specimens S2API and S3, bright contrasting lines are observed at the edges of the γ' particles, Figure 5.3.4 and 5.3.5, which tend to define the angular shape or faceted growth resulting in increase of hardness when compared with S1 and S3*.

TEM observation of the API bolt from shank (bulk and edge) and thread (bulk and edge) area reveal contrarily results from S2API of RB. Though the heat treatment applied to bolt and S2API was the same; It was interesting to see two phases γ' and γ'' existing together in bolt and just γ' in S2API. The γ' coarsening simulation predicted a maximum increase of ~20nm under API ageing at 790°C for 7hr. It was surprise in terms of γ' reaching ~50nm at thread edge along with metastable elongated discs of γ'' 50-100nm in size at edge of shank and thread area of bolt. The TEM images of the bolt from shank area, shown in Figure 5.3.0, reveal spherical γ'
maximum of 30 nm and elongated discs of γ'' 30-50 nm at bulk. The γ'' 50-100nm in size observed at edge of the shank with no γ' particles. The bulk of the thread has the same size of γ' and γ'' particle, Figure 5.3.1a-b, as bulk of the shank. Whilst, at edge of the thread the γ' size shoots up to ~50nm and γ'' around 50-100nm, Figure 5.3.1c-d. The nano phases observed in the AR specimen at thread and shank area of the bolt reveal similar structure to API heat treated bolt, Figure 5.3.2. It was now confirmed that AR bolt (S7) was heat treated according to API specification 6A718:2009 just as S2 API. The presence of γ'' makes 718 bolt metastable and also γ' particles which are reaching 50nm in size (at thread edge) might be to some extent makes bolt prone to HE failure under extreme stress conditions. The reason being metastable γ'' particles which share some common chemical properties with incoherent δ particles (discuss in detail next).

The bulk of the bolt (γ' ~30nm) reveal comparable TEM details with bulk of RB S2 API (γ' ~20nm) in terms of size of γ' but the presence of γ'' 30-50nm makes bolt 718 as metastable. It is important to consider Thermotech equilibrium phase simulations (chapter 4: section 4.1.2) where alloy718 was stated as ‘stable’ because of the presence of δ Ni₃Nb and ‘metastable’ because of γ'' Ni₃Nb in γ matrix. As both γ'' and δ are Nb based which implies that δ phase precipitation occurs with the loss of γ'' phase. The theory which support this state that γ'' as metastable phase tend to be replaced by incoherent stable orthorhombic δ phase after long term exposure to temperature above 650°C [168][164][47]. Whereas, the operating temperatures of the subsea bolts under CP stay in the range 4 – 80 °C. Sometimes under HTHP applications they might operate close to 200°C but that is still many less than 650°C. The operation of these bolts under service stress close to 70% of their yield strength could make this metastable phase vulnerable to HE. It has been reported in [110][117] about detrimental role of intergranular δ as making alloy susceptible to hydrogen embrittlement but the interaction of hydrogen with transgranular metastable γ'' has not been reported extensively. As a comparison between δ and γ'' it has been reported in [20], where Dai et al using the first principles total energy pseudo-potential method based on density functional theory stated that both γ'' and δ has covalent bonding between Ni-Ni atoms and a combination of covalent and ionic bonding between Ni and Nb atoms. There exist covalent bonding between Nb and Nb atoms in γ'' phase and no interaction was found between Nb and Nb atoms in δ phase. In addition, their results also indicated that both the phases are hard and have good ductility. Its already well established that presence of intergranular δ in the bolts microstructure without any doubt makes it susceptible to hydrogen embrittlement (HE). There might be one other reason for this susceptibility; this could be because of metastable γ' phase initiating hydrogen cracking process. As γ'' share some similar chemical properties with δ phase, reported in [20].
In the bolt extensive $\gamma''$ phase has been observed, some discs even exceeds 100nm limit, Figure-5.3.0c, 5.3.1c, 5.3.2d, at edge of shank and thread area of the bolt. These bolts under CP withstand stresses up to 70% of their yield strength and sometimes close to their yield strength under unexpected stresses. Considering this scenario, the presence of $\gamma''$ phase at the edge of shank and thread area of the bolt helps to trap hydrogen atoms (assuming the hydrogen entry into bolt from surface where edge is nearer and binding energy to $\gamma''$ is roughly same as delta ($\delta$) particles which is 30kJ/mol). The bulk modulus of $\gamma''$ and $\delta$ is 211GPa and 208GPa respectively, which make both phases as incompressible and hard phase. The structure difference between the two phases might also has the individual effect on their interaction with hydrogen atoms but this needs to be resolved as a future work by generating 718 specimens with desired microstructure: 

i) specimen having only $\gamma''$, this specimen can be extracted by doing extensive cold work prior to heat treatment.

ii) specimen having $\gamma' \sim 50$nm along with $\gamma''$; the specimen can be extracted from the edge of thread where $\gamma'$ size is around 50nm along with $\gamma''$ phase.

iii) specimen having $\gamma' \sim 20$nm with discrete intergranular $\delta$, this is actually S2API extracted from the rectangular block. Thus, the only sample which needs extra caution to machine is the ii) specimen because of the machining position as being at edge of thread. These Inconel 718 specimens in contrast to their micro and nano-structure if undergoes slow strain rate testing in CP could provide us with valuable data for resisting hydrogen embrittlement or to decrease bolts vulnerability to hydrogen induced cracking in service.

### 5.5.3. Hardness and Tensile data of Bolt and RB

The Table 5.3 shows the data obtained for each specimen from stress strain curves. The tensile specimens were extracted from bulk of rectangular block and bulk of bolt. The tensile data extracted from bolts and rectangular block was from single specimens because of the limited amount of material available for characterisation. Thus, single measurements for yield strength, ultimate tensile strength, percentage elongation and percentage reduction in area were calculated from the tested tensile specimens. The tensile specimens were machined from the bulk of bolt (AR bolt and S6API bolt), therefore the tensile data does not associate to the microstructure of the edge of the bolt. The uncertainty or error associated to these single readings were eliminated by comparing them with standard mechanical data available in Appendix B. Where standard mechanical data and OES composition limits from TWI industry is presented in tables. The yield strength according to first point of yielding for solution annealed S1API specimen extracted from stress strain curve is approximately 350 MPa and 0.2% offset yield strength is approximately 380 MPa. For API aged specimen (S2API) yield strength and 0.2% offset yield strength is approximately 840 MPa and 880 MPa respectively. Whereas, non-standard heat treatment given to S3 and S3* yields yield strength of 680MPa and 280 MPa.
respectively. For specimens S4 (YS ~ 910MPa) and S5 (YS ~ 910MPa) the yield strength was same and have 0.2% offset value of 920MPa and 940MPa respectively. S6<sub>API</sub> and AR specimen from bolt has the yield strength value of 880MPa and 0.2% offset value of 910MPa which vary significantly from RB specimen S2<sub>API</sub>. The ultimate tensile strength for solution treated specimen S1<sub>API</sub> is around 700 MPa and for all aged specimens (S2<sub>API</sub>, S4, S5, S6 and AR) it was above 1100 MPa. S3 and S3* has ultimate tensile strength of 860MPa and 550MPa respectively. Next, yield strength, percentage elongation, reduction of area and hardness of each specimen is compared and analysed in terms of micro and nano structure.

<table>
<thead>
<tr>
<th>Specimen and Shape</th>
<th>σ&lt;sub&gt;YS&lt;/sub&gt; (MPa)</th>
<th>σ&lt;sub&gt;YS&lt;/sub&gt; (0.2% Offset) (MPa)</th>
<th>UTS (MPa)</th>
<th>%EL</th>
<th>%RA</th>
<th>Vickers Hardness (HV) Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 RB</td>
<td>350</td>
<td>360</td>
<td>700</td>
<td>27.4</td>
<td>67.7</td>
<td>158±5 HV10</td>
</tr>
<tr>
<td>S2 RB</td>
<td>840</td>
<td>880</td>
<td>1240</td>
<td>31.4</td>
<td>50.8</td>
<td>340±2 HV10</td>
</tr>
<tr>
<td>S3 RB</td>
<td>680</td>
<td>700</td>
<td>860</td>
<td>22.3</td>
<td>55.3</td>
<td>258±10 HV10</td>
</tr>
<tr>
<td>S3* RB</td>
<td>280</td>
<td>290</td>
<td>550</td>
<td>24.6</td>
<td>64.1</td>
<td>185±10 HV10</td>
</tr>
<tr>
<td>S4 RB</td>
<td>910</td>
<td>920</td>
<td>1150</td>
<td>39.6</td>
<td>49.1</td>
<td>408±5 HV05</td>
</tr>
<tr>
<td>S5 RB</td>
<td>910</td>
<td>940</td>
<td>1170</td>
<td>30.5</td>
<td>48.0</td>
<td>432±5 HV10</td>
</tr>
<tr>
<td>S6 Bolt</td>
<td>885</td>
<td>920</td>
<td>1170</td>
<td>31.5</td>
<td>41.4</td>
<td>370±2 HV10 (Bulk)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>400±5 HV10 (Edge)</td>
</tr>
<tr>
<td>AR Bolt</td>
<td>880</td>
<td>910</td>
<td>1175</td>
<td>30.9</td>
<td>42.9</td>
<td>370±2 HV10 (Bulk)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>400±5 HV10 (Edge)</td>
</tr>
</tbody>
</table>

Table 5.3. Mechanical properties of solution treated and aged specimens of alloy718. σ<sub>YS</sub>, σ<sub>YS</sub>(0.2% offset), UTS, %EL, %RA and HV stands for yield strength, 0.2% offset yield strength, ultimate tensile strength, percentage elongation, percentage reduction of area and average vickers hardness respectively for each specimen.

Note: Values of σ<sub>YS</sub>, σ<sub>YS</sub>(0.2% offset), UTS, %EL and %RA for S6 Bolt and AR Bolt were extracted from single tensile specimen and represent the bulk of the bolt not the edge.
The hardness results for the solution annealed specimens S1 (158HV10) and S3* (185 HV10) were not surprising, as it was already known from thermodynamic simulations shown in chapter 4: section 4.1.2-4.1.3, that dissolution temperatures of δ, M_{23}C_6, γ' and γ'' is below solution temperature. These particles contribute to the strength and hardness of the alloy. Thus, yield strength of 340 MPa and 280 MPa observed for specimen S1 and S3* respectively. This yield strength and hardness is due to γ' precipitation (1-2nm) and MCN particles during air cooling after each solution temperature, which resist movement of dislocations. The hardness value of 185 HV10 for S3* is because of the dissolution of most of NbC precipitates back into matrix providing more niobium for γ' particles during air cooling. However, in order to avoid or at least minimise precipitation of MC and γ' particles during air cooling we could practice water quench (WQ) instead of air cool (AC). Specimens S1 and S3* as expected shows maximum percentage reduction in area (%RA) of 67.7% and 64.1% respectively, displaying increased ductility. This was because of dislocations traveling within γ lattice with minimum hindrance as the size of γ' particles were around 1-2nm.

The hardness and yield strength values for specimens (S2_{API}, S3, S4 and S5) obtained from RB rely on volume fraction and morphology of γ', γ'' and γ' - γ misfit. For S2_{API} the hardness values obtained were in the range 338-342 HV10 from edge to bulk of RB. The decrease in the hardness values when compared with specimen S6 and AR is because of the presence of γ' and γ''. The edge of shank and thread area had average hardness value of around 400HV, whilst bulk of shank and thread had average hardness of 370HV. As already described earlier about the nano-structure at the edge (γ' ~50nm and γ'' 50-100nm) and bulk (γ' maximum ~30nm and γ'' 30-50nm) of the bolt. It was interesting to note that γ'' were not present extensively at the bulk of of shank and thread and more predominant with γ' precipitation. Therefore, the primary reason for the hardness difference at the edge and bulk was clearly because of difference in the size of γ' precipitates and the extensive γ'' precipitation at the edge when compared to bulk, Figure 5.3.0-5.3.2. This also reflected at the yield strength with a value of 880-885MPa. The tensile specimens were extracted from the bulk of the bolt, thus this reflection was more of the bulk nano-structure. Both S6 and AR specimen have the same nano-structure at bulk and edge of the bolt. This confirms that AR bolts were heat treated according to API specification. Now if we compare S6_{API} with S2_{API} there was difference in yield strength of Δ40MPa and hardness of Δ30-60HV. This difference could be associated to the nano-structure (Figure 5.3.4) where single population of γ' 10-20nm precipitated in S2_{API}, whereas in S6_{API} γ' 30-50nm along with metastable γ'' 30-50nm precipitated in the bulk. Thus, resulting in the net decrease in hardness and strength between the two samples. This difference could even be
more associated to the lattice distortion during cold rolling of the bolts which results in γ” precipitation in the bulk along with edge. We know from Ni based superalloy metallurgy that anisotropic γ” discs form because of lattice mismatch between the BCT precipitate and the FCC γ matrix. Further, it has been examined that kinetics of formation of γ” is sluggish in Inconel718 (by observing S2-API and S3 under NS ageing of 16hr). This slower ageing characteristic of inconel718 resist strain age cracking in post weld heat treatment (PWHT) [174]. As we had seen earlier in Table 3.0 that different product form e.g. plate, rolled bar, welded plate etc, had an impact on the strength. This must be because of microstructure variation in different forms just like S2-API from RB and S6-API from bolt. This in turn makes alloy718 under CP more or less susceptible to HE depending upon the product form and microstructure. Considering the nano-structure of bolt, the presence of oversize γ’ precipitates ~50nm and elongated metastable γ” discs ~50-10nm (which contribute to remarkable strength of bolt) could assist shearing at matrix precipitate interface, whilst these bolts are subjected to stresses 70% of their yield strength or even more in service. The %EL for S2-API and S6-API was around 30 but the difference observed for %RA in area was noticeable. S2-API had %RA of ~50 and S6-API having ~41. The difference between the two reflects more ductility, which is directly related to the movement of dislocations in the γ matrix containing γ’ and γ” precipitates. It is reminded that %RA of S6-API is from the bulk area of the bolt from where the tensile specimens were extracted. This means that γ matrix having population of γ” (30-50nm) along with γ’ (~30nm) would resist movement of dislocations, as γ” precipitate in the matrix wherever there is localised lattice mismatch. It would have been more interesting tensile data if we had tensile specimens from edge of the bolt, where the size of γ’ precipitates was around 50nm and some γ” discs closer or even higher than 100nm.

It is to remind that single step ageing treatment at 790°C for 7hr is to increase sulphide stress cracking resistance and stress corrosion cracking (SCC) resistance while sacrificing strength and hardness. The other NS heat treatment applied to S4 was conventional double ageing heat treatment after standard API solution treatment. This led to γ’ and γ” precipitation (similar to what was observed for S6-API and AR specimens from bolt edge) but the second ageing at 621°C aided complete chemical ordering of the existing γ’ particles resulting hardness of 408HV. It is reported in [164][175] that solution heat treatment of Inconel 718 at 1024°C for 0.5h and double ageing (718°C-7hr and 621°C-8hr) led to uniform precipitation of γ’ and γ” throughout the matrix and achieve a hardness value of 423HV (close to hardness value of specimen S4 and S5). Whereas in specimen S6-API γ’ reaches to their maximum size around 50nm but without second step ageing at 621°C the hardness value was limited to around 400HV. S4 was also observed with spherical γ’ particles 1-2nm precipitated during second step ageing which
contribute to extra hardness and strength. As a comparison in terms of nano-structure yield strength value of 880 MPa corresponds to S6 API having γ’ size of 30nm and γ” 30-50nm (because the tensile specimens extracted from bulk of the bolt) as compared to yield strength of 910 MPa for S4. The yield strength of S6 API is associated to nano-structure at the bulk of the bolt. It was very important to have bolt’s structure with increased ductility and toughness for operation under extreme service stresses and corrosive conditions. Whereas, the nano-structure at the edge of bolt had oversize γ’ particles and presence of elongated metastable discs ~100nm at lattice mismatch regions. These nano phases morphology could prove to be deleterious for the bolts corrosion resistance under CP and service stresses. It is very likely that dislocations moving under stress assist shearing of these oversize γ’ precipitates and could initiate a crack at the matrix particle interface, supported by the findings [26][159][205] mentioned in section 2.3.6. Whereas, the bulk dislocations fail to shear γ’ particles and bow around them because of the size. No intergranular δ was observed for S6 API and AR but still the %EL recorded was around 30. It is reminded again that S5 was deliberately intermediate step aged at 955°C for 3hr to precipitate δ at intergranular positions. Hence, experimental value of 30.5 for %EL could relate to micro-structural features such as presence of δ which resulted in reduced ductility. This might suggest that γ” (30-50nm) contribute to remarkable strength of the bolt but in terms ductility they show similar pattern closer to δ phase. Similarly, specimen S4 having no δ at intergranular positions but with continuous intergranular secondary carbides (M23C6) have %EL of 39.6. The observed percentage reduction in area (%RA) for specimens S2 API, S4 and S5 does not vary much and little difference could be related to error in machining of gage diameter of tensile specimens. Whereas, S6 API and AR show similar values for the %RA but less than S2 API, S4 and S5 which was confusing as intergranular precipitation reduce ductility. There are other factors like strain rate which need to be considered for analysing tensile data. The cross-head speed used in tensile testing was around 10mm/min which was quiet fast. The cross-head speed should be around 7.5 x 10^-3 mm.min^-1 or strain rate of 3.33 x 10^-4 min^-1 (computed using the formula cross-head speed = gauge length (mm) x strain rate (min^-1)) which is slow enough to observe the effect of the nano-structure.

5.5.4. Hydrogen embrittlement susceptibility - γ’ size, metastable γ’’ and Dislocations

Presence of interstitial hydrogen found to be prejudicial for global performance and more specifically for mechanical properties such as ductility, strength and fracture toughness of the bolt. Hydrogen as being interstitial solute considered to be universally adverse. It basically lowers the fracture energy (reduce fracture toughness) of the crack and encourage
cleavage brittle fracture. The interaction of hydrogen atoms with second phase is important that need to be understood at an atomistic scale. A number of hydrogen embrittlement mechanisms have been proposed i.e. hydrogen enhanced localized plasticity (HELP)[124][148]; hydrogen enhanced de-cohesion (HEDE)[136][135]; hydride induced embrittlement (HIE)[151] and adsorption induced dislocation emission (AIDE), but these involve assumptions that limit their use and reliability and are discussed in detail under chapter 3: section 3.9.2. The data published in study [42][43] for the effect of hydrogen on properties of nickel base alloys including Inconel718 [44] suggest a detrimental role of second phase particles within grains and on grain boundaries. For this reason the effect of different heat treatments on the morphology of second phase and tensile properties were observed (under two different forms of 718) prior to actual slow strain rate testing under CP (future work).

![Figure 5.3.8. Alloy 718: (a) S3: 16hr ageing resulting in precipitation of needle-like delta phase and (b) showing increase in intergranular fracture with increasing grain boundary hydrogen concentration[118].](image)

The current investigation on alloy718 specimens, from RB and Bolt, under SEM and TEM had shown the morphology of second phase particles and their effect on tensile properties. As a reminder, it was reported in [176] that long exposure to high temperatures(~720°C) led to coarsening (spherical to cubic) of γ' and transformation of metastable γ'' (cubic) to stable delta δ particles (platelets) on grain boundaries. Anyways this excessive heat treatment is always avoided which make the alloy more prone to hydrogen embrittlement as can be seen in Figure 5.3.8(a), where δ particles were decorated on grain boundaries (similar to S3). They are always incoherent with the γ matrix; traps hydrogen
atoms and lower the fracture energy of the micro crack site. Stress intensity $K_{th}$ of the fracture site reduces below the value at which dislocations emission occurs and results in cleavage like fracture. Loss of ductility was mainly due to the absorption of hydrogen in bulk matrix particularly at delta ($\delta$) particles on grain boundaries resulting in nucleation and propagation of intergranular crack. It has been reported by Lassila and Birnbaum [118] that critical grain boundary hydrogen concentration has been indicated to be between 0.04 – 0.10 ppm, as shown in Figure 5.3.8(b). Cracks tend to initiate at intergranular positions where $\delta$ particles are present and was reported in [47] that crack propagate along $\delta/\gamma$ interface when tensile tests of alloy718 conducted in high pressure hydrogen. The grain boundaries of the bolt were found deprived of having continuous or even discrete $\delta$ particles but the presence of transgranular oversized $\gamma'$ particles and metastable elongated discs of $\gamma''$ at the edge of bolt could also prove to be vulnerable to hydrogen assisted cracking. These TEM findings for bolt’s microstructure at the edge and bulk depend on the diameter of the bolt. Less the diameter of the bolt less the structure variation from bulk to edge. RB undergoes less machining effect which does not effect the structure at bulk and edge, Figure 5.3.4 of S2 API. On the other hand rolling of bolts at the manufacturing level significantly alters the structure by inducing lattice mismatch regions. These regions are more at the edge than at the bulk, the reason is the extensive precipitation of $\gamma''$ discs at the edge of the bolt where their size even surpass 100nm limit. Similarly, the size of $\gamma'$ reaches 50nm limit which was way beyond predicted in the $\gamma'$ coarsening simulations under API ageing. As mentioned earlier, there was wide spread consensus among researchers over the theory that HE crack initiate at the matrix particle interface, and it has been postulated specifically for Inconel718 by Cassagne et al [44] that cracking mechanism was HEDE at grain boundary. The particle which was made responsible is intergranular $\delta$ phase but it could be possible that these overgrown $\gamma'$ and $\gamma''$ particles assist crack initiation under hydrogen atoms with high service stress level (70% of yield strength). In order to bring this hydrogen assisted cracking theory to a nutshell for API 718 bolt these $\gamma''$ particle are incompressible and hard phase (just like $\delta$ phase) and could assist crack initiation, The crack propagate transgranular preliminary and then as intergranular subsequently. On the hand the coarse $\gamma'$ particles could also initiate crack, as they get sheared by slip. Which is also similar to HEDE mechanism as these particles are coherent with the $\gamma$ matrix but depending upon their size, the misfit between $\gamma$-$\gamma'$ is critical for aiding de-cohesion process. The predicted equation for hydrogen embrittlement of CRA 718 bolts was created and presented in Figure 5.3.9.
Figure 5.3.9. The equation for the hydrogen assisted cracking of CRA 718 bolt. The schematic shows the factors which could act simultaneously and make bolt susceptible to HE.
Already described earlier, the size of the γ' particles at the edge of the thread area of the bolt was around 50nm. Upon close examination of γ' particles it was observed that there were γ' precipitates sheared into half. The reason for this could be threading of the bolt. During the threading process large number of dislocations move from edge to the bulk of the thread. These dislocations bow or cut depending upon the size of γ'. The critical diameter of the particle after

Examination of sheared single γ' precipitate ~50nm at thread edge

**Figure 5.4.0.** Examination of the sheared single γ' precipitate of size ~50nm at thread edge of bolt. (a) showing the distribution of γ' and γ'' precipitates. Whereas, (b) higher magnification of the selected sheared γ' precipitate showing dislocations network in between.
which cutting dominates is around 30nm. Thus $\gamma'$ particle in bolt larger than critical diameter undergoes cutting, shown in Figure 5.4.0(a). The sheared particle at high magnification reveal dislocation network in between (dark grey region in the middle). The disordering of crystallographic planes within the $\gamma'$ particle such that $\gamma$ matrix appear (shown as light grey region in Figure 5.4.0(b)). These particles along with many other, on edge of thread area, remain part of the $\gamma$ matrix when these bolts were used in service under CP. They could act as initiation point for hydrogen cracking if dislocations carrying hydrogen atoms move under stress. The matrix particle cohesive strength could in this case be reduced by hydrogen atoms resulting in HEDE and initiate transgranular crack which later grow as intergranular for ease of propagation.

Figure 8.1. Schematic (a) showing random distribution of $\gamma'$ and $\gamma''$ precipitates. Whereas in (b) dislocations travelling in pair carrying hydrogen atoms and passing through $\gamma'$ particles.

718 bolts under continuous cathodic protection hydrogen ingress occur by bulk diffusion from the surface. For localisation of hydrogen atoms along active slip planes very slow strain rates are necessary [110]. Figure 5.4.1(a) shows random distribution of $\gamma'$ and $\gamma''$ precipitates. The basic idea is to visualise the nano-structure close to the surface of the bolt with $\gamma'$ and $\gamma''$ precipitates in variable size, as shown in Figure 5.4.1(a). The dislocations generated in the bolt because of service stress carry hydrogen atoms (depending upon dislocation velocity) and interact with the $\gamma'$ particles. The size of $\gamma'$ particles along with stress field determine whether shearing will occur and/or dislocations bow around $\gamma'$ particles. The interaction of hydrogen atoms at atomistic scale is still a mystery to be solved but it was
reported in [110] that interaction of dislocations with obstacles i.e. precipitates or grain boundaries, lead to formation of two zones; enhanced plasticity zone blocked by previously hardened zone. The later zone is formed during in service at a local scale ahead of a defect, assuming the sheared γ' particle. Thus dislocation carrying hydrogen atoms piles up at the γ' particle which lowers the local fracture toughness (kIC). Crack tends to propagate by normal stress with decreasing de-cohesion energy of atoms by hydrogen adsorption. The transport of hydrogen atoms by dislocations, Figure 5.4.1(b), is considered to be localised process occurring at distance of few microns thus accelerating the formation of enhanced plasticity zone. Hydrogen embrittlement is characterised by change of fracture mode from partially or complete ductile to partially or complete brittle depending upon availability and ingress of hydrogen source. Hydrogen atoms segregate on moving dislocation and travel in the form of "Cottrell atmosphere". Hence, at low strain rates dislocation carries more hydrogen atoms resulting in notable hydrogen embrittlement as reported in [110]. Whereas, at significant high strain rates velocity of dislocation increases resulting in less segregation of hydrogen atoms thus de-cohesion energy of atoms uphold and hydrogen embrittlement is less pronounced.

The grain size is critical to the strength of alloy718, excessively fine grains decrease rupture strength whereas excessively large grains have lower tensile strength. It can be controlled by M C,Ns since they pin the grain boundaries and inhibit grain growth. These particles are potential source of hydrogen traps and in Inconel718 77-87 kJ/mol has been suggested as activation energy (Q) for hydrogen atoms to be trapped in carbide particles [122]. Activation energy of 58kJ/mol has been proposed as the criterion to determine whether the hydrogen already traps in a site can be released reversibly or not [123]. On the other hand the binding energy to delta (δ) particles is 30kJ/mol, which makes it less than 58kJ/mol [122]. Thus it is still confusing to understand the exact effect of δ on HE mechanism. However, presence of both δ [117] and MC carbides at grain boundaries is critical to hydrogen embrittlement (HE). As we observed solution treated specimens (S1, S3*) only contain NbC carbides and TiN nitrides distributed randomly throughout the bulk matrix. The mode of embrittlement solely from these particles can be evaluated using slow strain rate tensile tests under CP and in-air. On the other hand, hydrogen concentration at grain boundaries, irrespective of test temperature, strain rate and bulk hydrogen concentration, will be critical and need to be considered for fractography analysis. It was previously shown by Lassila and Birnbaum that diffusive segregation of hydrogen to grain boundaries in nickel controls the degree of embrittlement [118]. The behaviour of grain boundary carbides in nickel base alloys under hydrogen concentration led to reduce interfacial strength between matrix and grain boundary carbides. [177][178] It is therefore important to analyse slow strain rate tensile test results
under the light of trapping energy that control the fracture, characteristic distance and fracture toughness. The trapping energy controlling fracture must be linked to micro-structural features that are revealed using SEM (NbC and Ti N) and TEM (γ’ 1-2nm). A number of researchers found that the common microstructural trapping sites in alloy are grain boundary carbides [116], δ phase[117], grain boundary region [118], dislocations [119] and voids [118]. These findings are appreciated because the cracking phenomena mostly experienced under hydrogen environment was intergranular for the bolts. Whereas, the interaction of hydrogen atoms with transgranular γ’ and γ” precipitates needs to be addressed extensively because the cracking process could have primarily initiated from within the transgranular regions. The slow strain rate testing of specimens with targeted microstructure (from bolt’s: thread edge, shank edge and bulk) could gave us a realistic approach in analysing the effect of the morphology of nano phases with hydrogen atoms by considering HEEI (based on NTS and RA ratio) and fractography.
5.6. Chapter Summary

The CRA bolts after being given API heat treatment are used subsea for integration of flanges and critical well components. They are subjected to extreme stresses and corrosion thus cathodically protected (CP), exposing to the risk of hydrogen atoms being diffused from the surface of the bolts. The hydrogen atoms lowers the ductility and fracture toughness thus making the bolts susceptible to HE. It is therefore important to observe micro and nano structure of the bolt from edge to bulk.

Alloy 718 was received as rectangular block (RB) and subsea Bolts (Φ28mm) for structure analysis. The as-received (AR) bolts were heat treated according to API6A718 specification from the supplier. They were rolled again and heat treated as per API6A718 specification again before threads were machined. The new bolts had a diameter of around 22mm. API heat treatment and non-standard heat treatments were also given to specimens from RB. The micro & nano structure of specimens from RB (S1API, S2API, S3, S3*, S4 and S5) and bolt (S6 and AR) were compared together. It was observed that with no intergranular micro phase the nano-structure of the bolt under API ageing varied from edge to bulk. Whereas, the primary reason for adding non-standard higher solution treatment (for S3*), conventional double ageing (for S4 and S5) and longer API ageing (for S3) was to observe the morphological evolution (γ’ and metastable γ”) of the nano phases and its effect on hardness and yield strength. Whist, comparing these non-standard results (for specimens from RB: S3, S3*, S4 and S5) with API single ageing results (for specimens from RB: S2API; Bolt: S6 and AR). It was found that API single ageing on RB (S2API) gave 8-15% decrease in hardness and ~4.5% decrease in yield strength when compared to API (S6) and APIAR (S7) bolt.

The main results are summarised as below:

1. The nano-structure of specimens from API bolt (S6 and AR): The maximum size of spherical γ’ precipitates at bulk of the bolt were found 30nm with elongated discs of metastable γ” 30-50nm. Whereas, the shank edge had only γ” 50-100nm and thread edge had maximum γ’ around 50nm with γ” around 50-100nm. The hardness at the edge and bulk was 400HV and 370HV respectively. The tensile specimens were extracted from the bulk of the bolts and the yield strength of 880MPa represent bulk of bolt.

2. The nano-structure of API specimens from RB (S1API and S2API): During air cooling after solution treatment fine particles of γ’ around 1-2 nm precipitates in S1API. These small precipitates were evident under TEM. After API ageing on S2API for 7hr γ’ reaches 10-20nm in size. The size of the γ’ precipitates contribute to hardness of 340HV and yield
strength of 840MPa. The metastable transgranular γ" precipitates were not present which reduce the hardness and yield strength when compared to API bolt. Also the presence of intergranular discrete 1-2µm δ phase for specimen S2API results in decrease in hardness and strength.

3. The higher solution treatment at 1250°C was to dissolve back most of NbC and TiN back into the γ matrix thus providing more Nb and Ti for γ' and γ" precipitation. Whereas, S3 under longer ageing for 16hr reveal continuous intergranular needle like platelets of δ phase 5-15µm, extending from grain boundaries to within grains. The nano-structure had maximum size of γ' precipitates around 50nm with large inter-particle spacing. This results in the decrease of hardness to 258HV and yield strength to 680MPa.

4. The conventional double ageing after API solution annealing on S4 results in significant increase in hardness to 408HV and yield strength to 910MPa. The nano-structure reveal two populations for γ' precipitates: 1-10nm and 30-50nm in diameter. The small γ' precipitates might have precipitated during second ageing at 621°C as predicted in γ' coarsening simulations. Whereas, γ" as elongated discs were found of size 50-70nm. S5 was deliberately aged at 950°C to precipitate intergranular δ phase, evident under SEM. The higher hardness value of 432HV suggest that some pre-existed γ" discs also coarsen under 950°C (while some γ" discs got replaced by intergranular δ phase) resulting in increase in hardness.

5. The machining of threads after API heat treatment of bolts could lead to shearing of γ' precipitates at thread edge. These bolts when used in service could lead to hydrogen assisted cracking (HEDE). The initial cracking phenomena might commence as HEDE, at sheared γ' precipitate and matrix interface. These oversized γ' precipitates at thread edge could also be sheared in service when dislocations travelling under stress and carrying hydrogen atoms reduce the anti phase boundary energy barrier created by the first dislocation.

6. The trangranular metastable γ" precipitates makes alloy718 as metastable. The extensive precipitation of γ" at shank and thread edge of the bolt makes 718 bolt metastable. As these bolts are subjected to extreme stresses (70% or more of their yield strength) in service which might assist γ" to have properties similar to δ phase (both phases are hard and incompressible: bulk modulus of 208GPa for δ and 211GPa for γ"").

7. The hydrogen assisted cracking susceptibility of a bolt's structure depend on some factors which could lead to HE. These might occur simultaneously or in pair: i. CP under service stress, ii. Nanoscale oversized γ' precipitates, iii. Metastable transgranular precipitates and iv. Intergranular precipitates.
CHAPTER 6. Micro and Nano structure of New CRAs - INCOLOY 945 and 945x

New material for CRA bolts was introduced over the past decade. The micro and nano structure characterisation of these new alloys were not extensively carried out. The structure characterisation (similar to Inconel718 rectangular block) was conducted on 945 and 945x: which were received in the form of rectangular and cylindrical shape respectively. In order to obtain the effect of micro and nano structure on hydrogen cracking susceptibility it was important to understand the morphology of secondary phases that could be present in γ matrix. The aim was to observe whether any deleterious intergranular or metastable transgranular phases exist in the alloy. These two Incolloys are nickel based alloys with slight variation in composition than Inconel718. It would have been more relevant to 718 bolts if 945 and 945x alloys were also in the form of bolts.

6.1. Metallurgy - Incoloy 945 and 945x

The elemental composition of 945 and 945x has a vital role in resisting corrosion. As normally with any nickel based superalloy the matrix consists of a face centred cubic (FCC) structure called gamma (γ). The solid solution strengthening elements of gamma are chromium (Cr), iron (Fe), molybdenum (Mo), titanium (Ti), aluminum (Al) and cobalt (Co). The main strengthening precipitates are γ’ (Ni₃ Al,Ti,Nb) and γ’’(Ni₃Nb) having L₁₂ and DO₁₂ crystal structure respectively, a subject of numerous investigators [38][179-183]. γ’ is unique intermetallic phase which precipitates around 620°C and contributes to remarkable strengthening by resisting dislocation motion either through bypassing or particle cutting. As reported by Hagel and Beattie[15] that γ’ phase is coherent with the gamma matrix with 0.1% lattice (γ) mismatch as spheres, 0.5-1.0% mismatch as cubes and greater than 1.25% as plates. γ’ as A₃B phase where elements substituting A are Ni and Co and B are replaced by Ti, Al and Nb. Hume-Rotherys [17] stated that Ni₃Al is the most stable γ’ phase. Ni₅Ti, Ni₃Nb and Ni₃Ta with decreasing stability respectively. The nickel content above 42wt.% is generally needed for resistance to aqueous stress corrosion cracking [55] whilst molybdenum and chromium give the alloy general pitting corrosion resistance in reducing acid and alkali solutions [56][57]. Niobium, titanium and aluminium are the primary precipitation strengthening components [58]. Whilst titanium increases the strength and hardness of the alloy, an excessive amount is known to degrade micro-structural stability [59][185]. Aluminium increases the volume fraction of γ’ [11] which may be expected to increase hardness further but a high aluminium content reduces the lattice mismatch/coherency strain resulting in a net decrease in hardness. Metastable γ’’ [38][33][182][183][167][186] having body centered tetragonal structure (BCT) usually precipitates <650°C. The alloys normally exhibit precipitation of γ’’ under high coherency strains regions [184]. These are fine nano precipitates just like γ’ exhibiting high
hardening and strength but their length is approximately six times greater than their width. This metastable phase tends to be replaced by stable delta \( \text{Ni}_3\text{Nb} \) (\( \delta \)) phase when exposed to temperatures above 650°C for a longer time [19][27][37][187]. The presence of intergranular \( \delta \) platelets[36] having orthorhombic crystal structure results in loss of hardness and ductility[117].

945 and 945x are known for resisting formation of stable or metastable intergranular phase and the current study was conducted as verification of this. This could be because of lower content of Nb in the actual composition of the alloys when compared with Nb content in parent alloy Inconel718. Normally for nickel base alloys the carbon content is low. Carbon tends to react with refractory elements to form MC carbides that reside at the grain boundaries and within grains, where M being mostly Nb. In addition, Ti helps to form TiN: both MC carbides and TiN are beneficial for grain boundary strengthening, inhibit grain growth and reduce grain sliding beside their detrimental properties of decreasing ductility and toughness. There are few studies[59][185][188] which have been conducted on 945 and relatively new 945x. The relationship between microstructure and mechanical property for these alloys is not fully characterised as compared to other nickel based alloys. The aim of the current study was to investigate the microstructure at isothermal solution treatment, ageing and discuss their vulnerability to hydrogen embrittlement. The reason for higher strength of 945x was investigated and compared with 945. The main strengthening precipitate \( \gamma' \) have been examined in each alloy with their chemical constituents and compared with coarsening simulations.

### 6.2. Experimental Procedure

#### 6.2.1. Materials

The Incoloy 945 (140x110x24 mm) and 945x (25x25x36 cm) was supplied by 'Titanium Engineers' and 'C.H. Robinson Europe BV' respectively, under unknown heat treatment (HT) conditions. The alloys in as received condition will be termed as As Received (AR) alloys. The optical emission spectroscopy (OES) on thin off cuts from each alloy was conducted and the results are shown in Table 6.0.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Al</th>
<th>Cu</th>
<th>Nb</th>
<th>Ti</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>945</td>
<td>wt.%</td>
<td>0.01</td>
<td>0.1</td>
<td>0.07</td>
<td>20.5</td>
<td>3.2</td>
<td>22.2</td>
<td>0.17</td>
<td>1.95</td>
<td>3.11</td>
<td>1.55</td>
<td>47.04</td>
</tr>
<tr>
<td>945x</td>
<td>wt.%</td>
<td>0.01</td>
<td>0.08</td>
<td>0.04</td>
<td>20.2</td>
<td>3.2</td>
<td>14.4</td>
<td>0.15</td>
<td>2.09</td>
<td>4.14</td>
<td>1.57</td>
<td>53.9</td>
</tr>
</tbody>
</table>

**Table 6.0.** Elemental composition of as received 945 and 945x alloy.
6.2.2. Sample Preparation

The thermal heat treatments shown in Table 6.1 were performed on 945 and 945x. The samples were solution treated (ST) in an preheated furnace to 1038°C for 1hr and then quench with water to room temperature at cooling rate of 50°C/min. ST samples were then taken out to prepare for micro-structural investigation, while the remaining samples were solution treated plus aged (STA) in a preheated furnace to 718°C and aged at this temperature for 8hr. The samples were than furnace cooled (FC) at 56°C/hour to 621°C, holding at this temperature for further 8hr and then extracted followed by air cooling (AC). For every sample holes were drilled in reference pieces of nickel alloy and a type K thermocouple peened into each hole. These reference pieces were put in the furnace along with the actual samples. The temperature of the reference samples was noted and kept in record so that any change in actual and reference sample can be monitored. Alloy 945x was solution annealed at a higher temperature of 1250°C for 1hr, compared with standard solution treatment (ST) at 1038°C, then water quenched to room temperature followed by two step ageing similar to STA sample. The melting point of MC carbides is close to 1200°C [162]. As 945x has more Niobium (4.14wt%) and Nickel (53.9wt%) than 945 so the reason for higher solution annealing was to investigate whether it precipitates any secondary phase at intergranular regions and transgranular metastable precipitates at nano scale during two step ageing.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Alloy</th>
<th>Dimension</th>
<th>Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST</td>
<td>945/945x</td>
<td>14 x 10 mm</td>
<td>1038°C 1hr WQ</td>
</tr>
<tr>
<td>STA</td>
<td>945/945x</td>
<td>14 x 10 mm</td>
<td>1038°C 1hr WQ then 718°C 8hr FC + 621°C 8hr AC</td>
</tr>
<tr>
<td>AR</td>
<td>945/945x</td>
<td>14 x 10 mm</td>
<td>As Received</td>
</tr>
<tr>
<td>NS</td>
<td>945x</td>
<td>14 x 10 mm</td>
<td>1250°C 1hr WQ then 718°C 8hr FC + 621°C 8hr AC</td>
</tr>
</tbody>
</table>

Table 6.1. Solution annealed and ageing temperature of 945 and 945x specimens.

Note: Air cooling (AC); Water quenched (WQ); Furnace Cooling (FC); (ST) Solution Treated; (STA) Solution Treated and Aged; Non-Standard (NS).

Metallographic samples for light microscopy (LM) and scanning electron microscopy (SEM) (operated at 10KV; spot size 5; Backscatter electron mode) were prepared using standard mechanical polishing procedures. The specimen to be observed were grounded using silicon carbide papers from P240-P2500 grit and polished using descending order of abrasive cloths from 6μm up to finer grit size ~0.25μm. Kalling reagent etchant (100ml HCL, 100ml ethanol, 5g CuCl₂) and colloidal silica (0.06) was used to reveal the microstructure i.e. grain boundaries and metal carbides.

For transmission electron microscopy (see chapter 5: section 5.5)
Vickers hardness (HV) measurements were carried out at each sample to get an insight of morphology of γ’ precipitates. Prior to hardness testing specimens were mounted in resin followed by grinding (P240-P1200 grit) and polished up to 0.25μm. Measurements were performed using a diamond pyramid indenter with a force of 5 kgf (HV5). Set of values were recorded while moving from one end of the sample to other (unit: mm). The distance between each indent was kept approximately more than 3d spacing, where d is indent diameter (either in x or y direction), to prevent overlap of strain fields.

Tensile specimens from each alloy were machined as per the schematic shown in Figure 6.1.0. The specimens were tested using Instron tensile machine at a standard displacement rate (SDR) of $2.22 \times 10^{-4}$ sec$^{-1}$.

![Figure 6.1.0. Schematic illustration of tensile specimen. (unit: mm)](image)

Heat treatments have been carried out to observe the effect on morphology of precipitates at micro and nano scale. Hardness and yield strength are measured using standard laboratory methods. Scanning electron microscopy (SEM) with energy dispersive x-ray spectrometry (EDS) was conducted to reveal the composition of various phases. Scanning transmission electron microscopy (STEM) was used to identify and obtain the chemical constituents of nano precipitates.

### 6.2.3. 945 and 945x in the form of bolts

It would be more interesting to observe the structure of 945 and 945x alloys in the form of subsea bolts. The manufacturing route of the bolts could significantly alters the structure micro and nano at edge (thread and shank area) and bulk of the bolt: the threads would be machined after the final heat treatment. There was not enough material available for 945 to transform them into bolts and also the 945x was received late in the research project. Thus the possible investigation was to observe the structure of these newly developed alloys in the as received form under conventional double ageing. However, the effect of Nb content could be better reflected when these alloys are transform as bolts: the structure at thread, shank and bulk of the bolt under conventional double ageing could suggest their susceptibility to HAC.
6.3. Microstructural analysis

6.3.1. Grain size after heat treatments

Light microscope images were obtained for ST, STA and As Received (AR) samples of each alloy. Figure 6.1.1(a) is a typical of alloy 945 and 945x containing γ matrix with grains and grain boundaries. The nano scale γ' phase in γ matrix was examined for each sample of alloy under subsequent section. The initial metallography started with the use of kallings reagent (concentrated and dilute solution) with cotton bud swabbing which led to uneven revealing of the microstructure; some grains were etched while the other remains under etched with no clear distinction of grain boundaries. Colloidal silica 0.04µm was used as final polishing suspension, which not only polish but slightly etch and reveal grain boundaries. Grain size was evaluated using intercept method by considering 10 light micrographs of each sample. No significant variation of grain size observed with average grain size of 110µm was recorded for each standard alloy specimen. However, 945x NS sample due to solution treatment(ST) at 1250°C has increase in grain size with range 140-150µm and with intergranular phase, shown in Figure 6.1.1(b).

Figure 6.1.1. Typical LM image of alloy 945 and 945X containing γ matrix of grains, which are distinguished from each other by grain boundaries.
Figure 6.1.1. Light Microscopy (LM) image of 945x NS sample revealing continuous intergranular phase.

6.3.2. Morphology and distribution of M(C, N)s

The Figure 6.1.2 (a) and (b) shows the typical microstructure for both 945 and 945x. 10-15 micrographs (with a scale bar of 200µm) were taken for each sample from one edge to the other and examined methodically for the size of M (C,Ns). The experimental results for the average diameter of M (C,Ns) selected randomly from centre, mid-radius and edge from each alloy are presented statistically in Figure 6.1.1(c).
Figure 6.1.1(c). Average diameter of Ti N and Nb C particles in 945 and 945x aged alloys. The standard deviations value of measurements is shown as vertical error bars with mean diameter highlighted.

The black and white blocky shaped precipitates distributed randomly throughout the grains are identified as Titanium nitride (TiN) and Niobium carbide (NbC). Approximately 30-50 precipitates from each micrograph were selected at random to obtain size range of titanium nitrides and niobium carbides. TiN's appearing black were seen randomly distributed along the grain boundary and within the grains. The size of the nitrides and carbides was in the range between 1-20µm and 1-10µm respectively. Some few nitrides were also seen of size approximately 30µm. Twinning of grains has been observed in each of the specimen. No grain boundary precipitates observed for 945 in either solution annealed or aged condition but 945x in AR snd STA sample reveal intergranular precipitates as TiC. Grain boundaries have been observed from one edge to the other of each sample, to see if there are any discrete or continuous precipitations that could affect the tensile properties of the sample. Figure 6.1.2(c) shows the high magnification micrographs of the grain boundary for each sample. The grain boundaries show no precipitation of secondary phase i.e. delta δ or secondary carbides M₆C, M₂₃C₆ etc. EDS line scan of ~5µm along the grain boundary show no evidence of any grain boundary precipitation in 945. In 945 AR and STA sample EDS line scan perpendicular to grain boundary (moving from grain towards grain boundary and then moving away from grain boundary towards grain) was performed which reveal no difference in elemental peaks when compared with EDS line scan of matrix. This could be because of EDS spot size of 1µm that was used to detect any discrete intergranular precipitates. Thus, the EDS detector picks up surrounding signals from gamma γ matrix (reflected as high intensity peaks of Ni, Fe and Cr in EDS spectrums of grain boundary) apart from the spot under investigation. This resulted in grain boundary EDS spectrum be like transgranular matrix spectrum for any sample and one such γ matrix spectrum is shown in Figure 6.1.3(d). 945 whether in solution annealed or aged condition deprived of having any grain boundary precipitates apart from nitrides and carbides distributed randomly. Examination of grain boundaries of 945x in AR and STA samples reveal discrete 1-2µm intergranular precipitates, shown in Figure 6.1.2(c), identified as TiC. 945x ST sample less surprisingly reveal no intergranular precipitates as like 945 ST because of the higher solutionizng temperature above 1000°C which dissolve any intergranular precipitates back into the matrix.
Figure 6.1.2. (a) Showing typical a scanning electron image of 945 and 945x showing black TiN and white NbC distributed randomly throughout the microstructure and (b) showing conglomeration of Ti N(black) and Nb C(white) with dark elongated needles rich in Ti, Nb and Mo. (c) High magnification 5µm grain boundary images of each specimen revealing any intergranular precipitates present.

The as-received condition for each alloy was believed to be solution treated and double aged at a heat treatment not disclosed by the supplier. This was the reason AR samples were prepared from each alloy to characterise them individually. The microstructure shows the average grain size of about 110µm with random distribution of titanium nitrides and niobium carbides just like STA sample. Similarly for ST sample the solution treatment at 1038°C for 1hr had little effect on grain size and at dissolving metal nitrides and carbides back in to the matrix
because they are still appearing randomly throughout the structure. Figure 1.2(b) shows some precipitates that were conglomerated and identified using EDS in each of the alloy. Other than TiN and NbC there were dark elongated needles rich in Ti, Nb and Mo in all samples irrespective of the heat treatment applied. The EDS spectrums of each particle including one of the γ matrix (typical of 945 and 945x) is shown in Figure 6.1.3(i). The element sulphur appears in EDS spectrum of dark needles, shown in in Figure 6.1.3(i)(c), which should not be the actual case. Similarly carbon appearing in the spectrum (a), both are low atomic number elements with low atomic mass difficult to detect using EDS and could be treated as error.
Figure 6.1.3(i). Typical EDS spectrums of (a) NbC, (b) TiN, (c) dark elongated needle and (d) γ matrix.

As already described in chapter 5 solution annealing at higher temperature [162] 1250°C for 945x NS sample may have resulted in dissolving most of NbC and TiN back into the matrix providing more Nb and Ti for γ” and γ’ precipitation respectively (will discuss more in detail under subsequent section). SEM micrograph in Figure 6.1.3(ii)(a) shows intergranular laves phase rich in Niobium reveal by EDS spectra, Figure 6.1.3(ii)(b). For this reason the averaged grain size increases from 110µm (which was for 945/945x: AR, ST and STA samples) to 140-150µm as there were less NbC and TiN for pinning the grain boundaries.
6.4. γ' precipitates in 945 and 945x

6.4.1. Morphology and Distribution of γ'

The TEM images of 945 and 945x AR sample, as shown in Figure 6.1.4 left and right respectively, reveal dense homogeneous distribution of γ' phase. In dark field mode the γ' appears as bright spots. They appear more as spherical in 945AR to spheroid in 945x AR and are distributed throughout the matrix. In bright field imaging, Figure 6.1.4 – (left) 945 AR (b) shows contrast image of γ' with γ matrix. There are faint grey lines distinguishing the precipitates from the matrix. The use of diffracted beam for dark field imaging at higher magnification results in observing γ' phase as spherical precipitates around 4-8 nm and compact disc shaped around 10-25 nm, see (left) 945 AR (b) and (c). Selected area electron diffraction pattern at major zone axis [12̅3] yields a pattern associated with fcc γ matrix (primary spots) together with the secondary spots that are representative of γ' phase in (̅110). Similarly, for 945x AR the higher magnification (Figure 6.1.4 right (b) and (c)) shows γ' precipitation in (010) which are spheroid in shape ranging between 10-15nm and other as coalescence of 2-3 γ' precipitates 10-20nm. There were few precipitates which exceeds the 20nm barrier and were analysed under γ' size distribution.

The TEM images in Figure 6.1.5 shows the solution annealed and aged STA sample for 945 and 945x. The samples have homogeneous distribution of γ' as evident in Figure 6.1.5(a) (left and right). In bright field imaging mode the sample have a mottled appearance, Figure 6.1.5 945
STA (b), where γ' phase is not easily distinguishable from the γ matrix. Further, there is a faint dark line around these precipitates that can be associated with the lattice misfit of γ /γ'. The selected area diffraction patterns correspond strongly to the presence of γ' phase at (100) and (110) in 945 and 945x respectively. At higher magnification, (left) 945 STA (c), in bright field mode the γ' are like spherical, spheroid and coalesce (appearing as elongated) as black precipitates and approximately between 2-15nm in radius. Whereas, in (right) 945x STA (b) γ' are observed in dark field mode with much clear distinction and appear as embedded within the γ matrix. Upon closer inspection, the γ' precipitates appears to have faceted growth with edge definition when compared with 945 STA sample having less sharpening effect. This morphological difference could have profound effect on the strength of both alloys.

Figure 6.1.6 shows TEM images of solution annealed (1038°C-1hr WQ) 945 ST and 945x ST sample with γ' precipitation <2nm. In dark field imaging mode both samples show dense homogeneous distribution of γ' precipitates in range of 0.1-2nm but distinction of γ' from γ matrix is hard to detect. The electron diffraction pattern in (left) 945 ST is more associated with fcc γ lattice but however, due to presence of γ' in small size they are more coherent with matrix and not easily distinguishable. This is the opposite case for (right) 945x ST where upon higher magnification, see (b) and (c) clear distinction of γ' precipitates from γ matrix. This is further evident from the electron diffraction spots from the γ matrix and γ' precipitates. These very small precipitates give rise to secondary diffraction spots in selected area diffraction patterns, which is primarily associated with the presence of γ' phase in the matrix.
Figure 6.1.4. TEM images of 945 (left) and 945x (right) AR sample. Left: (a) Dark field imaging - overview of γ’ precipitates (appearing bright) which are distributed homogenously throughout the γ matrix with selected area diffraction pattern (SADP) corresponding to (110) γ’ phase. (b) Bright field mode showing contrast image of γ’ and γ matrix with faint line around precipitates distinguishing γ’ precipitates from γ phase and (c) at higher magnification clearly shows γ’ appearing black in spherical shape around 4-8 nm and in compact disc shaped ranging between 10-20 nm. Right 945x AR: (a) shows (010) γ’ precipitates as grey precipitates in dark field mode with the γ matrix appearing as dark grey. (b) and (c) corresponds to higher magnification, clearly showing γ’ in spheroid shape (10-15nm) and coalescence of γ’ 10-20nm.

Figure 6.1.5. 945 (left) and 945x (right) TEM images of solution treated and Aged sample showing in (a) overview of γ’ precipitates that are distributed homogenously throughout the γ matrix with strong diffraction spots from (100) and (110) related to γ’ precipitates respectively. Left 945 STA (b) mottled appearance of γ’ phase in bright field imaging and (c) higher magnification of (b) showing γ’ between 1-20 nm. Right 945x STA: (b) and (c) dark field imaging- higher magnification shows spherical (1-5nm), spheroid (5-15nm) and coalescence of γ’ precipitates (10-20nm) with clear edge definition.
Figure 6.1.6. 945 (left) and 945x (right) TEM image of ST sample showing (a) dense distribution of very small (appear white) γ’ precipitates of about 1-2 nm with weak super lattice reflection spots in selected area diffraction pattern (SADP), whereas images (b) and (c) shows γ’ precipitates at higher magnification for both 945 and 945x.

Around 400 γ’ precipitates were selected from 10 different nano-graphs or TEM images from each sample to do the morphological analysis using image J and the results showing γ’ size distribution in AR and STA samples is presented in Figure 6.1.7. The graph clearly indicates a peak position where the maximum number of γ’ precipitates are found in any sample. The distribution was not normal distribution as there are some secondary peaks at 0-5 nm, 10-15 nm and 15-20 nm for each alloy. The error bar associated to the distribution data is ± 0.5nm for each reading. The graph for 945 AR and STA samples represent the mean γ’ size range between 6-8 nm. Whereas, for 945x AR and STA samples the mean γ’ size range increases to 10-12 nm. It is important to note that the curves for AR samples nearly overlap STA curves for each alloy. It can be assumed that AR condition of each alloy undergoes the same heat treatment as per STA samples. It was found that a mean difference of ~4nm was recorded for the γ’ size between 945 and 945x under solution treated plus aged condition. It is important to consider here that mean γ’ size of each alloy does not allow us to predict their cutting or bowing phenomenen under service stress and CP, if these alloys are used as subsea bolts. Whereas, if these alloys are machined into bolts then the area at the edge of threads and shank could be critical (chapter 5: as like 718 bolts where nearly single size population of γ’ increases from 30nm at bulk to 50nm at thread edge). Thus taking into consideration the product form as rectangular and cylindrical blocks, the micro and nano structure (γ’ size range) of 945 and 945x could be different when machined as bolts after the ageing process. This way we could end up having γ’ population having nearly one single size and if heat treated after maching metastable
γ'' at the threads edge and shank area precipitate because of the amount of cold work the bolt has gone through. ST condition of each alloy have γ' size around 1-2 nm after water quenching, as shown in Figure 6.1.6(b) and (c).

![Figure 6.1.7. γ' size distribution in AR and STA samples of 945 and 945x.](image)

It can be stated that maximen γ' size and its physical definition in any alloy have a crucial role in their strength and hardness. As evidence, the clear edge definition and faceted growth of γ' precipitates in 945x (AR and STA samples) have significantly influence the mechanical properties. The γ' size distribution and TEM images reveal that higher strength version 945x have γ' size greater than 945. It was assumed that 945 will led to γ' precipitation only and 945x having more niobium content (close to Inconel718 5wt%) population of both γ'(Ni3Al, Ti) and γ''(Ni3Nb) was expected to appear in the γ matrix. It was interesting to see just γ' precipitates in the 945x γ matrix as main strengthening precipitate. In order to understand the variation in strength between the alloys there was a need to identify the γ' constituents in each alloy. For this to be resolved STEM EDS was used with a line scan across the γ' precipitate.

945x NS sample having non standard solution treatment at 1250°C 1hr WQ then followed by standard two step ageing was also observed under TEM. The reason for having higher ST was to dissolve back most of the metal carbides into the matrix providing more Nb for γ'' or intergranular δ precipitation. These particles were not observed and double ageing led to continuous intergranular phase called laves rich in Nb, reported earlier in Figure 6.1.3. The TEM
image of 945x NS sample, see Figure 6.1.8, shows only γ' precipitates 5-15 nm distributed randomly with greater interparticle spacing and ultimately with reduced strength and hardness. The metastable γ'' and intergranular δ was not seen in any of the sample. This attempt of performing non standard heat treatment was to verify that whether providing higher Nb to the γ matrix could led to γ'' metastable or intergranular stable δ phase.

6.4.2. Identification and Evolution of γ' in AR and STA samples

The AR and STA samples of 945 and 945x contains one main population of γ' precipitates which are present in spherical to spheroid shape. The size of the γ' precipitates depend upon the time of ageing and we can see significant variation in ST and STA samples. AR and STA samples for each alloy have approximately the same size of γ' size distribution population, reported earlier in Figure 6.1.7. The primary elements which are responsible for γ' precipitation are Ni, Ti, Al or Nb. It was reported in [58] that Nb, Ti and Al are added for precipitation strengthening. Ti with 1.55wt % and 1.57wt% increases the strength and hardness of alloy945 and 945x respectively and form part of γ' phase. Contrarily, increase in Al reduces the lattice mismatch/coherency strain [11] which decrease hardness of 945 and 945x thus 0.17wt% and 0.15wt% of Al is added respectively. As discussed earlier the amount of Nb that is present in 945 and 945x is around 3.11wt% and 4.14wt% respectively, when compared to parent alloys Inconel718 (5.06wt %) and Incoloy925 (0wt %). This reduction in Nb content aid to resist
precipitation of metastable $\gamma''$ ($\text{Ni}_3\text{Nb}$) and stable $\delta$ phase. This change in the chemistry results in precipitation of only $\gamma'$ phase at nano scale and was evident from the TEM images in Figure 6.1.4-6.1.6. It was further supported from the findings of Slama and Abdellaoui [24] who reported that $\gamma'$ appears before $\gamma''$ during isothermal ageing at 680°C. The authors Oradei-Basile and Radavich [189] and Brooks and Bridge [190] stated the fact that the precipitates $\gamma'/\gamma''$ are too small at the early stage and difficult to distinguish from each other. This can be seen in ST samples where dense distribution of $\gamma'$ precipitates of 1-2nm resulted even from water quenching, as shown in Figure 6.1.6. EDX scan at this magnification only reveal elemental composition corresponding to matrix which is associated to the increase coherency between $\gamma'$ and matrix. Auburtin et al [191] reported that they are uncertain of the precipitation sequence of $\gamma'$ and $\gamma''$ in any alloy; however, if the ratio $(\text{Al+Ti/Nb})$ is equal to 0.66 then $\gamma'$ and $\gamma''$ precipitates simultaneously at 550-660°C temperature range. Contrarily, 945 has ratio $0.55\left[(0.17+1.55)/3.11\right]$ and 945x has $0.42\left[(0.15+1.57)/4.14\right]$, it can be assumed that $\gamma'$ precipitates first in the sequence and continue to evolve ($\gamma'$ consolidates with addition of few fraction of nano-meter in size) under secondary ageing with faceted growth. It was reported in [163] for 718plus at relatively different ageing temperatures (788°C-4hr and 675°C-8hr), with the aim of observing the effect of each ageing temperature on the morphology of $\gamma'$ precipitates. The first ageing increases the size to $23 \pm 2.9$nm and after second ageing they are around $28 \pm 3.02$nm. The main difference between the two ageing temperatures is the morphology of $\gamma'$. The physical definition of $\gamma'$ is enhanced after two step ageing when compared with single ageing. Sometimes two or more $\gamma'$ precipitates coalesce to form elongated particles but these should not be confused with $\gamma''$ as they appear to look elongated platelets (see right Figure 6.1.4(b) and Figure 6.1.5(a),(b)).

STEM EDS point analysis from the $\gamma$ matrix and $\gamma'$ precipitate does not reveal reliable difference in composition peaks. The EDS counts received from $\gamma'$ were not actually from the core of precipitate instead mixed up with the $\gamma$ matrix. This was probably due to the spot size of 20nm used in the analysis and the precipitates size are mostly less than that. The element Cu with high wt% was observed because of the copper grid where the TEM sample reside. The EDS data of $\gamma'/\gamma'$ from each sample is presented in Table 3. As already expected elemental composition (wt%) of the $\gamma$ matrix of AR and STA samples shows significant increase of Ni, Fe and Cr as reflected in Table 2, whereas, Nb, Ti and Al were observed with low wt%. $\gamma'$ give elemental peaks of Nb and Ti but still Ni, Fe and Cr from $\gamma$ matrix were more prominent and the difference between the two EDS spectrums was hard to observe.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Method</th>
<th>Elements wt%</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDS</td>
<td>Cr</td>
<td>Fe</td>
</tr>
<tr>
<td>945</td>
<td>SEM</td>
<td>20.9</td>
<td>21.8</td>
</tr>
<tr>
<td>STA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>945</td>
<td>STEM</td>
<td>19.4</td>
<td>21.9</td>
</tr>
<tr>
<td>STA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AR</td>
<td>STEM</td>
<td>17.5</td>
<td>17.7</td>
</tr>
<tr>
<td>STA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>945x</td>
<td>SEM</td>
<td>19.3</td>
<td>15.0</td>
</tr>
<tr>
<td>945x</td>
<td>STEM</td>
<td>16.1</td>
<td>17.3</td>
</tr>
<tr>
<td>AR</td>
<td>STEM</td>
<td>6.5</td>
<td>10.8</td>
</tr>
<tr>
<td>STA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>STEM</td>
<td>6.1</td>
<td>10.5</td>
</tr>
</tbody>
</table>

**Table 6.2.** SEM-EDS and STEM-EDS results.

For more precise identification of γ' from γ, STEM EDS line scan was performed across the γ' precipitate and the counts received at the detector from elements normalised, as presented in Figure 1.9. The line scan across γ' shows Cr and Fe decreasing while Ni fairly remain constant. It was interesting to see 945x STA sample having more deflection in counts for Nb and Ti when compared with 945 STA sample. It was expected to have the same size of γ' precipitates distributed homogenously throughout the matrix in AR and STA samples. The small size of γ' precipitates spherical in shape <5nm were also observed along with large ones, Figure 6.1.9. These small precipitates are associated with natural cooling (air cooling) of the alloy after final ageing. Bright field TEM of 945AR sample Figure 6.1.4 (b)(left), demonstrate faint contrast around the edges of the γ' which can be associated to the lattice distortion or lattice misfit between γ and γ', which increase further as size of γ' increases. In 945x samples the γ' precipitates appear bright, see Figure 6.1.4 and 6.1.5, this can be due to the presence of higher atomic number element like Nb, which diffused at the edges of γ' precipitates to minimise elastic strain caused by the lattice misfit between γ' phase and γ matrix [163][192]. The presence of Nb is evident from the line scan of 945x STA reflecting a high Nb deflection along with Ti.
**γ’ in ST samples**

The EDS spectrum as shown in Figure 6.2.0 is of γ matrix and γ’ precipitates; as γ’ is of few nanometers in size so less Ti and Nb counts are observed and most counts were from γ matrix of Ni, Fe and Cr. It is clear that with solution annealing at 1038°C for 1hr results in dissolution of γ’ precipitates back into the matrix. However, during water quenching it is possible that small γ’ precipitates (more like ‘baby’ or ‘sub’ precipitates) <2nm emerge having morphology different from cuboid or sphere. The size of the γ’ are small which makes them appear as part of the matrix which is because at early stages of precipitation the chemical ordering within the γ’ precipitate is not strong enough to form spherical or cuboidal shape. This is why diffraction pattern is more related to γ fcc matrix but the presence of faint secondary spots along with
primary spots confirms $\gamma'$ precipitates in the matrix. It is also worthy to note that $\gamma'$ is fcc $L1_2$ structure where Ni atoms reside at the face centre and Ti, Nb and Al occupy the corners. Thus after two step ageing in STA samples $\gamma'$ undergoes complete chemical ordering in comparison to solution annealed condition [193] resulting in increase of strength and hardness. It is reported in [194] that Nb and Mo atoms appear bright while Ni and Cr atoms appear dark. As Cr possesses a low desorption field strength which leads to preferential desorption of Cr atoms [195] and this is why $\gamma$ matrix appears dark as having high quantity of Ni and Cr atoms, Figure 6.1.4 and 6.1.5.

![Line Sum Spectrum](image)

**Figure 6.2.0.** STEM EDS with a spot size of 10nm on ST samples showing combined elemental composition of the $\gamma$ matrix and $\gamma'$ precipitate.
6.5. Chapter Summary

Newly developed 945 and 945x alloys were received in the form of rectangular and cylindrical block respectively. They were heat treated by the suppliers but the details of heating parameters were not disclosed. Thus, they were heat treated again as per standard conventional double ageing but the as received samples were also prepared for micro and nano structure investigation. The AR and HT 945x was found to have 18.6% more hardness and 10.91% more strength than AR and HT 945. To understand this, the microstructure was investigated using SEM and TEM. 945x was expected to have metastable γ'' phase because of higher Nb content but found to have none. The coherent γ' precipitates responsible for precipitation hardening were observed in both alloys. The following key observations can be drawn from the chapter:

1. MC,Ns (NbC as white and TiN as black) are distributed randomly throughout the γ matrix with mean grain size of 110µm, measured for ST, STA and AR samples. 945 in any HT condition found deprived of having any intergranular precipitate; whereas, 945x found with (Nb,Ti)C as discrete intergranular precipitates.
2. 945x NS sample reveal continuous intergranular laves phase rich in Nb with γ' precipitates having large inter-particle spacing.
3. As expected small γ' precipitates <2nm in ST samples which precipitated during water quenching.
4. In AR/STA samples γ' precipitates around 10-20nm and some were 20-25 nm with some coalescence. Small γ' precipitates <5nm nucleated after final ageing at 621°C and during air cooling.
5. Mean γ' diameter of ~7nm for 945 and ~10nm for 945x recorded under γ' precipitates analysis, which was close approximation to JMatPro γ' coarsening simulations. The mean γ' size of 945 and 945x could not be used to predict their cutting phenomenon under slip, whereas maximum γ' size should assist.
6. STEM-EDS line scan across γ' precipitate reveal more Nb and Ti deflection in 945x than in 945. The γ' in 945x appear bright with faceted growth when compared to 945. This could be because of higher atomic number element Nb diffusing at the edges of γ' precipitates thus distinguishing them from γ matrix. This lead to high 0.2% yield strength (1100 MPa) and hardness (~430 HV5).
7. As γ' ageing simulation at 621°C (after ageing at 718°C) shows consolidation of γ' precipitates by little increase in mean diameter ~0.20nm, compare to 1.5-2nm increase after ST; this could be γ' undergoing complete chemical ordering for faceted growth.

8. The investigation of 945 and 945x in the form of subsea bolts could help us to understand the effect of Nb content on the micro and nano structure of the bolt at thread edge, shank edge and bulk of the bolt.
CHAPTER 7. Conclusions and Future Work

7.1. Conclusions

CRAs 718, 945 and 945x because of their high corrosion resistance and mechanical strength are used as bolts for integration of critical well components. These components are subjected to extreme corrosion and stress conditions under CP resulting in hydrogen ingress and HE. Thus it is a must requirement for oil and gas industries to have bolts of CRAs which can withstand corrosive stress environments. The micro and nano structure of the bolts could have significant susceptibility to HAC and thus needs to be investigated for better resistance to HAC failures.

The case studies reveal surface cracks under the head area (shank) and thread area of the bolts after being used under CP: which encouraged us to reveal the structure phases present at these particular positions. The aim was to identify the structure of the 718 bolt at bulk and edge under standard API heat treatment and compare it with 718 in the form of RB having same standard API heat treatment along with non-standard heat treatments. 945 and 945x (not in the form of bolts) were also added for investigation to observe whether the change in composition (wt% of Ni and Nb) could generate a structure less susceptible to HAC than 718. The role of intergranular precipitates for the susceptibility of HE has been well documented for the CRAs. Whereas, the effect of morphology of nano precipitates at transgranular regions is still unclear.

API heat treatment was applied to 718 alloy in the form of bolts (Φ28 and Φ22mm) and RB. The micro and nano structure of the API bolt and API RB was different in terms of size of γ', presence of metastable γ'' and intergranular precipitates. This significantly alters the hardness and yield strength properties between the two forms of 718 alloy. The γ' size of ~30nm and γ'' of 30-50nm at thread and shank bulk was recorded. Whereas, γ' found to be ~50nm at thread edge with γ'' elongated discs reaches 50-100nm at thread and shank edge. Only γ'' was observed at shank edge of the bolt. There were some regions where these metastable discs even surpass 100nm barrier. The extensive precipitation of γ'' on the edge of the bolt was because of the distortion (lattice mismatch regions) created by the rolling of the bolts at manufacturing level. On the other hand the API heat treatment given to RB had only γ' precipitates with an average size between 15-20nm. The γ' coarsening simulation under API ageing for 7hr gave the average size of γ' around 20nm which was in good agreement. The absence of metastable γ'' in RB makes it stable 718 alloy whereas its presence in 718 bolt makes it as metastable. This change of structure at nano scale leads to hardness of 340HV for RB and 370-400HV for API bolt from bulk to edge.

The non-standard heat treatments performed on the specimens from RB of 718 was to observe the effect on morphology of nano precipitates (γ' and γ''). It was observed in S4 that
double ageing after standard API solution treatment gives nearly same nano structure as we had for thread edge of the bolt but the second population of γ' of 1-10nm precipitated during second ageing at 621°C differentiate the two cases. This was the reason the hardness value computed for S4 was around 408HV as compare to 390-400HV for thread edge of bolt. Similarly, S3 with higher solution treatment (1250°C) gave γ' in the range between 10-50nm but with continuous intergranular δ phase. This variation in the size of the γ', presence of transgranular γ'' precipitates and intergranular δ precipitates in API bolt and API RB would help to assess their susceptibility to HE during SSRT.

The micro and nano structure between as-received (Φ28mm) and machined (Φ22mm) bolts was found to be same at edge and bulk area. The machining of threads of the bolt after the heat treatment had led to possible shearing of the γ' precipitates. The 50nm size precipitates were observed sheared at thread edge of the bolt. These precipitates could act as an initiation point for HEDE when these bolts are used subsea under CP and service stress.

945 and 945x have less Nb content than 718 which led to δ free structure. Metastable γ'' discs were also not observed in any of the alloy. Instead both alloys have γ' precipitates in the size range 5-25nm. The mean size of the γ' precipitates in both alloys computed experimentally were in good agreement with the γ' coarsening simulations. The mean γ' size of 945 and 945x could not be used to predict their cutting phenomenon under slip, whereas maximum γ' size should assist. Thus taking into consideration the product form as rectangular and cylindrical blocks, the micro and nano structure (γ' size range) of 945 and 945x could be different when machined as bolts after the ageing process. This way we could end up having γ' population having nearly one single size and if heat treated after machining metastable γ'' at the threads edge and shank area precipitate because of the amount of cold work the bolt has gone through. It was also found that high strength of 945x was because of the diffusion of the Nb in γ' precipitates (resulting in faceted growth with γ' precipitates appearing whitish) which had resulted in significant increase of hardness (430HV) and yield strength (1100MPa), as compared to 350HV and 980MPa for 945. Moreover, the presence of discrete intergranular precipitates (NbC and TiC) were observed in 945x but 945 found deprived of having any grain boundary precipitates. Investigation of 945 and 945x in the form of bolts could give better understanding of the effect of Nb content in precipitating oversize γ' or metastable γ'' precipitates.

7.2. Future Work

7.2.1. Slow Strain Rate Testing
A number of testing methods are available to access HE susceptibility and to quantitatively predict long term service behaviour. The most common methods which are used include constant
Load test, slow strain rate (SSR) and single edge notch bend (SENB) testing. The second method will be used to assess the susceptibility of alloys in the form of bolts (718/945/945x). It basically tests the material subjected to elongation at a constant rate and then load is varied to maintain constant extension rate. Critical strain rate for alloys usually reside in the range $10^{-3} \text{s}^{-1}$ to $10^{-7} \text{s}^{-1}$. The strain rate computed for testing of SSR specimens was $5.56 \times 10^{-6} \text{s}^{-1}$. During the extension process the specimens would be subjected to certain environment i.e. hydrogen charging under CP (3.5% NaCl). This method also evaluates the susceptibility of stress corrosion cracking (SCC), sulphide stress cracking (SSC) along with hydrogen embrittlement (HE).

Hydrogen environment assisted cracking (HEAC) laboratory testing is important in screening out 718, 945 and 945x alloys, in order to find which are more susceptible to HE. As the tests conducted at laboratory are short when compared with the life time of alloys that are to be assessed. It is therefore very important to consider the time span of the test and should be approximate representative of the actual HEE otherwise can lead to ambiguous predictions. Hydrogen ingress and transport within the structure is an important phenomenon that is time dependent (depending upon diameter of bolts). Hence, the fundamental question arises about the time span of the laboratory tests to ensure homogeneous ingress to the desired location of interest and should be true reflection of hydrogen concentration under service considering bolts of Φ28mm. Thus, it would be necessary to ensure steady state conditions for each laboratory test where generally longer time is needed to hydrogen charge specimens to steady state at normal temperatures. Already described earlier, using the equation $x = \sqrt{2Dh \cdot t}$, close approximation of hydrogen penetration depth ($x$) during cathodic charging can be calculated depending on hydrogen diffusion constant $D$ of the alloy under investigation and charging time ($t$).

HE susceptibility testing can be on smooth specimens or pre-cracked specimens. Smooth specimens are normally selected on the assumption that they are defect free and degrade after 90% of their service life. Sidewise, pre-cracked specimens (notched specimens) acknowledge the manufacturing or fabrication flaws of the material and their influence under hydrogen damage. We would be testing both smooth and notch specimens for each alloy: as informed that 945x in notch condition will behave strangely under SSRT. For this reason would add some smooth specimens for 945x along with notch.

Some case studies [110][117] of alloy Inconel718 (smooth and notched specimens but with nano structure different from API bolt) under SSR test has been mentioned with mechanical behaviour and fractography (section 3.9.1 and 3.9.2). The general trend reveals that hydrogen atoms lower the fracture energy and decrease fracture strain with crucial role of dislocations mobility. The mechanism involving hydrogen transport, in the form of 'Cottrell' atmosphere
dynamic strain aging: where hydrogen atoms pin to the dislocations and then unpin to get attach
to the subsequent dislocation), was first given by Bastein and Azou [157]. Tien et al [158]
investigate the critical dislocation velocity above which dislocation break free of hydrogen
atmosphere and is expressed as:

\[ V_{dc} = \frac{D.E}{30.b.K.T} \]

Where D is diffusion coefficient; E 0.3eV is binding energy of hydrogen atom to moving
dislocation, b is burgers vector, K is Boltzmann Constant, T is absolute temperature (K).
This critical dislocation velocity can be related to critical strain rate as:

\[ \varepsilon_c = \rho_m \cdot V_{dc} \cdot b, \text{ Where } \rho_m \text{ is mobile dislocation density.} \]

7.2.2. Heating Parameters for Slow Strain Rate specimens

The main challenge would be to generate the structure of SSR specimens as per different
positions (Bulk, Shank and Thread) of the bolt. One way is to extract small SSR specimens from
these positions. This would help to assess their susceptibility to HAC when the morphology of
nano phases (γ' and γ'') changes.

The γ' particles for API alloy718 (S2API) were found to be coherent with the γ matrix
because of size range (5-20 nm); but still small misfits could be an important anomaly to consider
for hydrogen embrittlement. In addition, dislocations and coherent precipitates (depending upon
morphology) are considered as reversible traps with binding energies typically between 4.8 and
14.5 kJ/mol [120][196]. Hence, heat treatment for alloy718 is crucial and determines the
morphology of second phase particles whether at grain boundary or within grains. Under
hydrogen environment morphological incoherency is associated with stress field between matrix
and particle interface which might assist to initiate crack, reduce fracture toughness and
encourage cleavage like fracture. It would be interesting to conduct the SSRT of API heat treated
(1035°C-2hr plus 790°C-7hr AC) samples extracted from the 718 bolt having structure similar to
shank bulk, shank edge, thread bulk and thread edge of the bolt. The non-standard heat treated
(1250°C-2hr WQ plus 790°C-7hr AC; 1035°C-2hr AC then 718°C-8hr FC to 621°C-8hr AC) SSRT
samples would then be compared with standard SSR samples in terms of effect of morphology of
γ' and γ'' precipitates on mode of HE. The SSRT sample extracted from shank edge of the bolt
could give the sole effect of the metastable γ'' precipitates under CP and in-air.

As described earlier that MC type carbides are potential hydrogen traps in Inconel718.
77-87 kJ/mol has been suggested as activation energy (Q) for hydrogen atoms to be trapped in
carbide particles. Hence, MC,Ns at intergranular and transgranular positions traps hydrogen
atoms and could play a crucial role in hydrogen cracking. Thus the solution treated samples of 718 (S\textsuperscript{1API}, S3), 945 and 945x (ST), where the size of nano precipitates are <2nm, could give the individual effect of M\textsubscript{C,Ns} on HE susceptibility under SSRT. Further, the reduction in non-standard ageing from 16hr to 7hr for sample S3 is to compare it with API 7hr ageing. Initially idea of longer ageing of S3 for 16hr was to have variable size range of γ’ in the matrix (10-50nm in S3), and to observe their effect with dislocations carrying hydrogen atoms during SSR testing but on the other hand Nb has been consumed up for precipitation of needle like δ phase (Ni\textsubscript{3}Nb) when aged for 16hr and continuous laves phase at grain boundaries when aged for 25hr. The presence of any second phase including δ has been well established and reported \cite{42-44,110} to be detrimental for the mechanical properties of Inconel718. Thus, if we reduce the ageing time from 16hr to 7hr for specimen S3 we could generate comparable microstructure for SSR testing between S\textsuperscript{2API} and S3 specimens: noting the fact that excess amount of Nb content still present in the matrix of S3 due to higher solution treatment.

As mentioned earlier, the reason for performing higher solution treatment at 1250°C was to dissolve back the M\textsubscript{C,Ns} in γ matrix (but with the associated risk of forming liquid phase of 20-30 wt%), thus providing more Nb and Ti for γ’ precipitation, this is evident from the size of γ’ for S3 and the continuous intergranular delta and laves phase (rich in Nb) when aged for 16hr and 25hr respectively. The mode of cooling after higher solution treatment for S3 and S3* will be changed from air cooling to water quench to avoid formation of carbides as much as possible. However, carbides were still observed under SEM for S3* WQ specimen but the grain size value 75–85 µm suggest a low volume fraction of carbides and nitrides which basically pin or hold the grain boundaries from growing excessively large.

Finally, the heating parameters for 945 and 945x would be solution treatment and double ageing as per given to specimens in chapter 6. The reason is because of the absence of metastable γ'' phase or intergranular δ phase.
References


Russell D.Kane Editor, 'Slow strain rate testing for the evaluation environmentally induced cracking', Research and engineering applications', ASTM 1916 Race Street, Philadelphia, PA 19103.


Appendix A

Differential Scanning Calorimetry (DSC) *(at 3, 10, 20k/min)*

Differential Scanning Calorimetry (DSC) was used at different ramp rates for measuring precipitation and solvus temperature of phases present in Alloy 718.<br/>

---

### INCONEL718 - Thermal arrests have been observed as ‘peak’ in DSC curves (Heating and Cooling) for precipitation and dissolution of γ', γ", δ phase, M (C, N)s, Liquidus and Solidus.

<table>
<thead>
<tr>
<th>Precipitates</th>
<th>γ*</th>
<th>γ**</th>
<th>δ</th>
<th>MC</th>
<th>T&lt;sub&gt;L&lt;/sub&gt;</th>
<th>T&lt;sub&gt;S&lt;/sub&gt;</th>
<th>γ*</th>
<th>γ**</th>
<th>δ</th>
<th>MC</th>
<th>T&lt;sub&gt;L&lt;/sub&gt;</th>
<th>T&lt;sub&gt;S&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating 1</td>
<td>1070</td>
<td>1335</td>
<td>-</td>
<td>-</td>
<td>~980</td>
<td>1080</td>
<td>1338</td>
<td>-</td>
<td>~620</td>
<td>840-880</td>
<td>970-980</td>
<td>1050-1190</td>
</tr>
<tr>
<td>Heating 2</td>
<td>1080</td>
<td>1348</td>
<td>-</td>
<td>-</td>
<td>~980</td>
<td>1080</td>
<td>1350</td>
<td>-</td>
<td>~620</td>
<td>840-890</td>
<td>Dissolve</td>
<td>1070-1210</td>
</tr>
<tr>
<td>Heating 3</td>
<td>1080</td>
<td>1358</td>
<td>-</td>
<td>-</td>
<td>~980</td>
<td>1080</td>
<td>1358</td>
<td>-</td>
<td>~625</td>
<td>840-890</td>
<td>Dissolve</td>
<td>1080-1190</td>
</tr>
<tr>
<td>Cooling 1</td>
<td>1344</td>
<td>1290</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cooling 2</td>
<td>1348</td>
<td>1300</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cooling 3</td>
<td>1364</td>
<td>1300</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Appendix B
As-received mechanical data and OES composition of Inconel 718 bolts.

Table 4 Rockwell C hardness measurements

<table>
<thead>
<tr>
<th>Stud</th>
<th>HRC Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>XT2 3.6 (Heat number 440662)</td>
<td>(42.0) 39.5 40.0 40.0 39.5</td>
</tr>
<tr>
<td>XT2 3.3 (Heat number 413023)</td>
<td>40.0 (41.0) 40.0 (41.0) 39.5</td>
</tr>
<tr>
<td>XT2 3.10 (Heat number 413023)</td>
<td>(40.5) 40.0 40.0 (41.0) 30.5</td>
</tr>
</tbody>
</table>

Table 5 Charpy-V notch results - Minimum value stated in API 6A 718: 81J

<table>
<thead>
<tr>
<th>Stud</th>
<th>CVN Values (J) - 2 specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td>XT2 3.5 (Heat number 440662)</td>
<td>77 82</td>
</tr>
<tr>
<td>XT2 3.10 (Heat number 413023)</td>
<td>69 67</td>
</tr>
<tr>
<td>XT2 3.3 (Heat number 413023)</td>
<td>66 66</td>
</tr>
<tr>
<td>XT2 AA5 (Heat number 440694)</td>
<td>(58) (57)</td>
</tr>
<tr>
<td>XT2 AA6 (Heat number 440694)</td>
<td>(48) (48)</td>
</tr>
<tr>
<td>XT2 AA3 (Heat number 440694)</td>
<td>(50) (52)</td>
</tr>
</tbody>
</table>

Table 6 Results of the tensile tests

<table>
<thead>
<tr>
<th>Stud</th>
<th>0.2% proof stress, MPa</th>
<th>UTS, MPa</th>
<th>Elongation, %</th>
<th>Reduction in area, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>XT2 3.7 (Heat number 413023)</td>
<td>960 1300</td>
<td>32.0</td>
<td>48.0</td>
<td></td>
</tr>
<tr>
<td>API 6A 718</td>
<td>Min. 627</td>
<td>1034</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>Max.</td>
<td>1090</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3 - Results of the OES analyses carried out on studs from XT2 (TWI Report S/12/05)

<table>
<thead>
<tr>
<th>Element wt%</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn+Ta</th>
<th>Mo</th>
<th>Ti</th>
<th>Al</th>
<th>C</th>
<th>Co</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>XT2 EE9 (heat number 940652)</td>
<td>53.7</td>
<td>18.25</td>
<td>18.22</td>
<td>5.07</td>
<td>2.90</td>
<td>0.99</td>
<td>0.55</td>
<td>0.023</td>
<td>0.04</td>
<td>0.08</td>
<td>0.07</td>
<td>0.006</td>
<td>&lt;0.003</td>
<td>0.01</td>
<td>0.0044</td>
</tr>
<tr>
<td>XT2 3.3 (Heat number 440628)</td>
<td>53.3</td>
<td>18.25</td>
<td>18.59</td>
<td>5.03</td>
<td>3.09</td>
<td>0.94</td>
<td>0.49</td>
<td>0.021</td>
<td>0.14</td>
<td>0.04</td>
<td>0.11</td>
<td>0.006</td>
<td>&lt;0.003</td>
<td>0.03</td>
<td>0.0027</td>
</tr>
<tr>
<td>XT2 3.10 (Heat number 413023)</td>
<td>53.52</td>
<td>18.16</td>
<td>18.66</td>
<td>5.07</td>
<td>3.08</td>
<td>0.94</td>
<td>0.50</td>
<td>0.022</td>
<td>0.14</td>
<td>0.04</td>
<td>0.11</td>
<td>0.007</td>
<td>&lt;0.003</td>
<td>0.03</td>
<td>0.0028</td>
</tr>
<tr>
<td>XT2 AA5 (heat number 440694)</td>
<td>53.60</td>
<td>18.20</td>
<td>18.31</td>
<td>4.90</td>
<td>2.97</td>
<td>0.97</td>
<td>0.54</td>
<td>0.01</td>
<td>0.04</td>
<td>0.07</td>
<td>0.09</td>
<td>0.006</td>
<td>&lt;0.003</td>
<td>0.01</td>
<td>0.0046</td>
</tr>
<tr>
<td>XT2 AA6 (heat number 440694)</td>
<td>54.10</td>
<td>17.14</td>
<td>18.37</td>
<td>4.96</td>
<td>2.96</td>
<td>0.99</td>
<td>0.53</td>
<td>0.025</td>
<td>0.04</td>
<td>0.07</td>
<td>0.10</td>
<td>0.006</td>
<td>&lt;0.003</td>
<td>0.01</td>
<td>0.0048</td>
</tr>
<tr>
<td>API 6A 718 Min.</td>
<td>50.0</td>
<td>17.0</td>
<td>-</td>
<td>4.87</td>
<td>2.80</td>
<td>0.80</td>
<td>0.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Max.</td>
<td>55.0</td>
<td>21.0</td>
<td>Bal.</td>
<td>5.20</td>
<td>3.30</td>
<td>1.15</td>
<td>0.60</td>
<td>0.045</td>
<td>1.00</td>
<td>0.35</td>
<td>0.35</td>
<td>0.010</td>
<td>0.010</td>
<td>0.23</td>
<td>0.006</td>
</tr>
</tbody>
</table>