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Effect of microstructure and alloy chemistry on hydrogen embrittlement of Precipitation Hardened Ni base alloys

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Abstract:

The sensitivity to hydrogen embrittlement (HE) has been studied in respect to precipitation size distributions in two nickel base superalloys, Alloy 718 (UNS N07718) and Alloy 945X (UNS N09946). Quantitative microstructure analysis was carried out by the combination of scanning and transmission electron microscopy and energy dispersive x-ray spectroscopy (EDS). While Alloy 718 is mainly strengthened by γ'' , and therefore readily forms intergranular δ phase, Alloy 945X has been designed to avoid δ formation by reducing Nb levels providing high strength through a combination of γ' and γ'' . Slow strain rate tensile tests were carried out for different microstructural conditions in air and after cathodic hydrogen (H) charging. HE sensitivity was determined based on loss of elongation due to the H uptake in comparison to elongation to failure in air. Results showed that both alloys exhibited an elevated sensitivity to HE. Fracture surfaces of the H pre-charged material showed quasi-cleavage and transgranular cracks in the H affected region while ductile failure was observed towards the centre of the sample. The crack origins observed on the H pre-charged samples exhibited quasi-cleavage with slip traces at high magnification. The sensitivity is slightly reduced for Alloy 718, by coarsening γ'' and reducing the overall strength of the alloy. However, on further coarsening of γ'' , which promotes continuous decoration of grain boundaries with δ phase, the embrittlement index rose again indicating a change of hydrogen embrittlement mechanism from hydrogen enhanced local plasticity (HELP) to hydrogen enhanced decohesion embrittlement (HEDE). In contrast, Alloy 945X displayed a strong correlation between strength, based on precipitation size, and embrittlement index, due to the absence of any significant formation of δ phase for the investigated microstructures. For the given test parameters, Alloy 945X did not display any

reduced sensitivity to HE compared to Alloy 718 when considering high strength conditions despite the absence of intergranular δ phase.

Keywords: Microstructure, Mechanical properties and Hydrogen embrittlement

1. Introduction

Precipitation-hardened (PH) nickel-base superalloys combine high strength, ductility with good formability, weldability and long-time microstructural stability at elevated temperatures. They derive their strength from the combination of solid solution and precipitation strengthening with the latter through formation of $L1_2$ -ordered γ' ($\text{Ni}_3(\text{Ti}, \text{Al})$) and/or DO_{22} -ordered γ'' (Ni_3Nb) in a face-centered-cubic (fcc) γ matrix. In addition, precipitation of grain boundary carbides contributes to creep strengthening. Importantly, γ'' is a metastable phase and a precursor for the more stable orthorhombic δ phase, which has the same stoichiometry as γ'' , but tends to be significantly coarser and incoherent with the matrix [1].

Alloy 718 (UNS N07718) was specifically developed for high strength and high temperature aeroengine applications by the formation of fine γ'' when heat-treated appropriately. It also displays good resistance to stress corrosion cracking [2]. Today, Alloy 718 is used far more widely, now also including applications in the oil and gas sector for high pressure, high temperature (HPHT) applications. However, corrosion processes can result in hydrogen ‘pick-up’ during service in these environments that may cause hydrogen enrichment in near-surface regions and, consequently, local embrittlement of the material [3].

To date, hydrogen embrittlement (HE) in PH nickel-base superalloys is mitigated by limiting the hardness to less than 40 HRC or 388HV [4]. This is achieved in Alloy 718 by over-aging the material, which results in the reduction of γ'' volume fraction and the formation of δ phase. However, work by L. Liu et al. has highlighted potential deleterious effects of δ formation as the δ /matrix interface can initiate transgranular fractures and micro-cracks, as well as promoting susceptibility of the alloy to HE by a mechanism that remains to be identified [5].

HE has been strongly linked with hydrogen segregation towards dislocations and hydrogen transport in the form of a Cottrell atmosphere around these dislocations, thereby reducing the stress field associated with a dislocation ^[5,6]. Hence, by the presence of hydrogen the elastic interaction between dislocations is reduced resulting in a lower critical stress level at which dislocations become glissile ^[7,8]. Such behaviour, in conjunction with enhanced strain localisation, is believed to promote HE during slow strain rate testing.

Further, the accumulation of hydrogen at precipitates is generally considered to promote micro-void initiation via the fracture of particles or the weakening of particle-matrix interfaces ^[5,9]. Recently, it has been demonstrated that both γ'' and δ precipitates play significant roles in altering the HE sensitivity of PH nickel base alloy ^[1,3,5]. Hydrogen induced cracking was shown to occur at δ or $\gamma'-\gamma''$ /matrix interfaces promoting the formation of planar cleavage micro-facets on the fracture surfaces of hydrogen embrittled specimens ^[5,10].

It is also well established that the overall strength of an alloy does affect HE. Hydrogen diffuses towards high tri-axial stress states found ahead of a crack tip or notch. In the case of high strength alloys, the propensity for hydrogen-enhanced cracking is exacerbated by the reduction in distance between the crack tip and the peak point of tri-axial stress state ahead of crack tip ^[11].

Carbide particles have been seen to enhance HE sensitivity and promote micro-void initiation at their interface with the matrix, which then leads to dimples on the fracture surface ^[12]. In PH nickel-base superalloys, carbides are primarily found in the form of NbC carbides and ((Nb,Ti)C, N) carbonitrides. It has been suggested that these carbides are irreversible hydrogen traps ^[5,13,14] and Robertson suggested that hydrogen solubility was strongly affected by the presence of fine precipitates and elements in solid-solution within the matrix of Alloy 718 ^[13].

Without the addition of atomic hydrogen, PH nickel-base superalloys display ductile fracture. In contrast, HE related fracture modes are varied, ranging from intergranular to transgranular modes with cleavage facets or ductile character ^[5,15]. In addition, the transgranular facets seems to be roughened by slip steps, which is an indication of failure by separation along preferential slip bands ^[16].

Overall, the assertion that precipitates enhance HE susceptibility is not well understood. Therefore, the aim of this study is to provide further insight into the role of microstructural features and strength on HE sensitivity by using two PH nickel-base superalloys (Alloy 718 and Alloy 945X), each being subject to different cooling rates from solution temperature followed by aging. In contrast to Alloy 718, Alloy 945X has a reduced level of Nb in order to minimize the formation of δ phase. Both PH nickel base superalloys were pre-charged with hydrogen via a cathodic charging process, prior to conducting slow strain rate tensile testing in air at room temperature. The HE sensitivity of these Ni-alloys was assessed based on the loss of ductility by comparing strain to failure of the hydrogen pre-charging specimen to its strain to failure of the uncharged in air. The mechanistic understanding of hydrogen embrittlement is discussed in terms of the potential role of hydrogen on enhanced slip localisation.

2. Experimental procedure

2.1 Materials

Alloy 718 and 945X were supplied as forged bars in an annealed plus aged condition with their chemical composition given in Table 1. Of particular note is that Alloy 945X has lower Nb (γ'' and δ stabiliser) but higher Ti (γ' stabilisers) content than Alloy 718 in order to reduce susceptibility of δ phase formation without compromising strength. To understand the influence of different microstructural conditions on HE sensitivity, both alloys were annealed at 1040°C followed by either cooling at slow, intermediate or fast cooling rate. The cooling rates employed were 5 K/min (controlled Slow Cooled, SC), 16-10 K/min (Furnace Cooled, FC) and 260 K/min (Air Cooled, AC), respectively. All samples were subsequently aged in accordance to API6A718 standard aging treatment for 718 and 945X^[17]. Alloy 718 was aged at 774 °C for 6 hours and then air cooled to room temperature. Alloy 945X was aged in two stages: firstly at 706 °C for 6 hours and then cooled to 607 °C at 0.5 °C per minute, and in the second stage, it was maintained at 607 °C for 18 hours following which air cooled to room temperature.

2.2 Hydrogen Charging

Hydrogen was introduced into the material at 80°C by electrochemical charging in a sodium chloride (NaCl) aqueous solution for 7 days. A three-electrode electrochemical cell system was used and the relevant reactions were as follows:

As a consequence of the water electrolysis, hydrogen ions were produced at the counter electrode i.e. the specimen surface. Some of the nascent hydrogen were adsorbed into the specimen surface and permeated into the bulk of the specimen. The remaining unadsorbed hydrogen recombined at the metal surface to form hydrogen gas which was not available for entering the specimen. The hydrogen penetration depth was estimated to be $\sim 140 \mu\text{m}$ by diffusion calculations using hydrogen diffusion coefficients from ^[1]. The electrochemical potential of the sample (working electrode) was measured with respect to saturated calomel reference electrode (SCE) and the sample was maintained at a constant cathodic current density of 7.7 mA/cm^2 . The reference electrode is normally ionically connected within the three-electrode cell *via* a porous frit to the solution in which the other electrode is immersed and connected to a potentiostat to monitor the change in the potential of the working electrode. All specimens and holders, except for the surfaces intended for charging, were coated with a thermally resistant and non-conducting lacquer to prevent the formation of a galvanic cell and to confine the hydrogen charging to the gauge section.

2.3 Characterisation of mechanical properties

Slow strain rate tests (SSRTs) were performed in air at room temperature (20°C) on both uncharged and hydrogen charged samples that were prepared using NACE standard for sub-size tensile specimens with a cylindrical gauge diameter of 3.81 mm and a gauge length of 25.4 mm. Loading was carried out using Instron® 5569 testing machine equipment with a 50 kN load cell at a strain rate of 10^{-6} s^{-1} . After hydrogen charging, the specimens were mechanically loaded within an hour to prevent hydrogen desorption. The amount of hydrogen in the hydrogen pre-charged (7 days) Alloy 718 samples and 945X were evaluated, immediately after taking the sample from the electrochemical bath and after leaving the sample in air for 10 h, using melt extraction method, and the hydrogen content appeared to remain constant. Hence, the specimen transfer time is assumed to be relatively short for these alloys. For each heat treatment conditions, three tensile specimens were tested to verify the reproducibility of the results.

HE susceptibility was quantified by means of an embrittlement index (EI) related to the loss of the elongation to failure:

$$EI = \frac{\varepsilon_n - \varepsilon_{HC}}{\varepsilon_n} \quad (\text{Eq. 4})$$

where ε_n and ε_{HC} are, respectively, the elongation to failure of the H-free and the hydrogen charged tensile specimens. The higher the EI, the higher the susceptibility to HE for the considered alloy. The fracture surfaces of the failed samples were investigated *via* FEI Quanta 650 scanning electron microscope (SEM).

2.4 Microstructural analysis

The microstructures of the solution-treated, as well as the aged samples, were characterised *via* energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and transition electron microscopy (TEM). SEM samples were prepared by conventional grinding and polishing using colloidal silica solution (OPS). TEM investigations were carried out on 3 mm disc samples, ground to approximately 120 μm thickness before electro-polishing using a Struers Tenupol-5 at -30°C and a voltage of 17 V in a solution of 100 ml perchloric acid and 900 ml methanol. Macro-hardness values for each condition were recorded using a Vickers hardness tester at 10 kg.

3 Results

3.1 Microstructural evolution

First, a detailed SEM analysis was undertaken on both alloys in the as-received (AR) and heat treated conditions using the backscattered electron detector. Additionally, SEM analysis under immersion mode was used to reveal γ' precipitates, see Figure 1a. Figure 1 focuses on Alloy 718 and shows evidence of discontinuous precipitation of δ phase decoration of grain boundaries for all four conditions. The δ phase appeared significantly coarser in the SC-aged material (see Figure 1d) compared to the FC-aged and AC-aged as well as the AR, see Figure (1 a, b, c). In the case of SC-aged, the SEM images also revealed some relatively coarse intergranular precipitation, most likely to be γ'' , see Figure 1d. As the aging treatment was the same for the three heat treated samples, Figure 1 (b-d) shows a significant effect of the cooling rate after solution annealing at 1040°C on δ phase formation and size of γ'' . Figure 2 displays typical SEM images of Alloy 945X for AR condition and solution annealed subject to the three different cooling rates after solution annealing at 1040°C and aging. All

conditions exhibited clean grain boundaries with no obvious evidence of δ phase precipitation.

Figure 1 SEM micrographs of precipitation hardened 718 (a) AR showing δ phase and γ' , (b) AC cooled and aged (c) FC and aged, (d) 5°C/min and aged showing γ'' (white circle).

Figure 2 SEM micrographs of Alloy 945X (a) AR showing no evidence of δ phase, (b) AC cooled and aged (c) FC and aged, (d) 5°C/min and aged.

For detailed dimensional characterisation of γ'' , dark field TEM imaging was carried out on both alloys and their different conditions. Figure 3 presents representative dark field images for Alloy 718. A typical selected area diffraction pattern is also presented and shows the expected super-lattice spots of the coherent γ'' phase on the $\langle 001 \rangle \gamma$ zone axis (see Figure 3a inset). The images show evidence of ellipsoidal disc shaped morphology and all three variants of γ'' . Figure 3d shows evidence of a bi-modal γ'' distribution, i.e. large (primary) and small (secondary) γ'' precipitates. Similar bi-modal γ'' precipitate distributions were observed by Rezende et al. ^[18] and Miller et al ^[19]. SC-aged samples also showed evidence of γ'' precipitate free zones near grain boundaries with more δ phase formation, see inset of Figure 3d. In the case of Alloy 945X, the dark field TEM images generally exhibit similar features as that of Alloy 718, but the size of γ'' was significantly smaller, see Figure 4.

Figure 3 Selected area diffraction pattern and TEM micrographs showing γ'' of Alloy 718 for different processing conditions (a) AR with $\langle 001 \rangle$ zone axis subset (b) AC and aged, (c) FC and aged, (d) $5^\circ\text{C}/\text{min}$ and aged with δ phase subset.

Figure 4 TEM micrographs showing γ'' of Alloy 945X for different processing conditions (a) AR (b) AC and aged, (c) FC and aged, (d) 5°C/min and aged.

A quantitative analysis of the size (length along the major axis) of several hundred γ'' precipitates for each microstructural condition of 718 and 945X was performed. Figure 5a compares the precipitate length distribution of the three heat treatment conditions and the as received condition of Alloy 718. The SC-aged condition displays a wider size distribution than the other three microstructures with a significant skew towards lengths exceeding 80 nm. In addition, there is a slight trend of increasing particle length distribution, notably SC > FC > AC > AR conditions. Figure 5b compares the precipitate length distribution in different processing conditions and as-received condition of Alloy 945X. Again, the SC-aged showed a wider size distribution than the other two microstructures (AC and AR). As with Alloy 718, Alloy 945X shows a slight tendency for γ'' coarsening with decreasing cooling rate.

However, a comparison of Figure 5a and b shows that the mean precipitate length of Alloy 718 is about twice or three times as large as that of Alloy 945X when comparing the same solution annealed conditions.

Figure 5 γ'' size distributions for different processing conditions of (a) Alloy 718 and (b) Alloy 945X.

In general the carbides and nitrides found in both alloys were unaffected by the additional solution anneal heat treatment and aging as the temperatures of these heat treatments were well below the solvus temperature of both types of precipitates ^[18]. EDS analysis showed strong signals of Ti and Nb in the carbides and nitrides, which were dispersed within the grains and along the grain boundaries. The carbides seem to preferentially nucleate at pre-existing TiN particles and so they are referred to as carbo-nitrides, see the EDS maps and line scan in Figure (6a, b). The figures show that the carbides have mixed compositions, with Ti and Nb as the major elements and Mo and Ta as minor elements.

Figure 6 Energy dispersive x-ray spectroscopy (EDS) analysis showing line scan and elemental maps (a) line scan showing TiN encircled by NbC, (b) maps showing Nb, Ti (C, N) and (c) maps showing Nb, Ti, Mo(C).

3.2 Mechanical properties

The 0.2% proof strength and ultimate tensile strength (UTS) properties determined by SSRT for the non-hydrogen charged (NHC) and hydrogen-charged (HC) conditions are presented in Figure 7a and b. With regards to Alloy 718, the additional heat treatment generally resulted in significant reduction in the 0.2% proof stress and UTS, while the different cooling rates during the additional heat treatments only had a minor effect on proof stress and UTS. In contrast, the cooling rates had effect on the 0.2% proof stress and UTS for 945X. In the case

of Alloy 718, the lowest strength values were observed for the condition with the lowest cooling rate. It is worth pointing out here that the AR condition represents a maximum strength condition optimised for aero-engine applications ^[20]. When comparing Figure 7a and b, the strength (UTS) of Alloy 945X, in its AR condition, was 61 ± 5 MPa lower than AR condition of Alloy 718. For Alloy 945X, the additional heat treatment had a strengthening effect when the material was cooled slowly from solution annealed (5K/min and FC) and a weakening effect when AC was applied. In both alloys, the hydrogen charging only slightly reduced the 0.2% proof strength but had a more pronounced effect on UTS.

Figure 7 0.2% proof/ yield strength (YS) and ultimate tensile strength (UTS) of non-charged (NHC) and H pre-charged (HC) specimens of (a) 718 and (b) 945X using SSRT at room temperature.

Figure 8 Elongation of non-charged (NHC) and H pre-charged (HC) specimens of different microstructural conditions of (a) Alloy 718 and (b) Alloy 945X when SSR tested at room temperature.

Figure 8 shows that in Alloy 718 without hydrogen charging, the elongation to failure of all four microstructural conditions is very similar whereas for Alloy 945X some variations are observed. It is also evident from Figure 8 that all the hydrogen pre-charged specimens showed substantial loss of elongation indicating embrittlement. In the case of Alloy 718, the hydrogen embrittlement susceptibility improved from the microstructural conditions - 718 AR, AC-aged, FC-aged but dropped for SC-aged to the same level as the AC-aged. For Alloy 945X the greatest hydrogen embrittlement susceptibility was found for the FC and SC conditions. While the elongation to failure values had greatly reduced after hydrogen charging, the relative trends comparing the different microstructures were retained in Alloy 945X. The embrittlement indexes (EI) for the different microstructures of Alloys 718 and 945X were calculated using Eq. 4 and are shown in Table 2 and plotted in Figure 9 as a function of 0.2% proof strength. The data show that regardless of alloy chemistry and microstructure, significant loss of ductility was observed with no benefit from the absence δ phase in the case of 945X. Moreover, Figure 9 shows that EI does strongly correlate with strength, reaching values of 90%, when the 0.2% proof strength is increased to 1100 MPa.

Hence, both alloys, with their various microstructure variants, exhibit a relationship between strength and HE, which is in agreement with previous works ^[11,21].

Figure 9 Variation of embrittlement index (EI) as a function of 0.2% proof strength of Alloys 718 and 945X.

The effect of mean precipitate length of γ'' on embrittlement index of Alloys 718 and 945X is presented in Fig. 10. It can be clearly seen that one has to consider the two alloys separately here. For Alloy 718, the embrittlement index drops significantly from close to 90% to 50% when the precipitate length of γ'' increases from about 14 nm to 42 nm. However, a further increase seems to increase the embrittlement index to ~65%. In 945X, the embrittlement index

seems to increase sharply with increasing γ'' length, which is in contrast to Alloy 718. In order to check the consistency of this observation; an additional two-stage heat treatment was carried out at 735°C/6hr/0.5°C/min/635°C/18hr/air cooled. In this way the γ'' was further coarsened to 32 nm. It can be seen from Figure 10 that the EI remained high despite large precipitate size.

Figure 10 Effect of mean precipitate length of γ'' on EI of Ni Alloys 718 and 945X.

3.3 Effect of carbides

The SEM micrographs in Figure 11a and b show examples of fracture surfaces observed for Alloys 718 and 945X following slow strain rate testing. In both cases the FC-aged condition displays a significant presence of voids, most likely originating from second phase particles, in this case (Nb, Ti) CN type precipitates.

The SEM image of the cross section of hydrogen charged Alloy 718 specimen subjected to 3% strain (interrupted SSRT test) is presented in Figure 11c and d. The figure shows the formation of micro voids and cracks in the vicinity of coarse intergranular carbide particles, Figure 11c. While hydrogen is known to cause intergranular failure, involving crack initiation

and propagation along grain boundaries in many metals and alloys ^[22,23]. The crack originating from intergranular carbide grows into the grain boundary with the aid of hydrogen segregated at the grain boundary as in Fig 11c. However, the intragranular carbides presented a different behaviour as shown Figure 11d. The figure shows cracking of the intragranular carbides, with no evidence of the crack propagating into the γ matrix.

Figure 11 SEM micrographs of fractured surfaces for alloys FC and aged. (a) dimples originating from carbides in 718, (b) dimples originating from carbides in 945X (c) cracked carbide at the grain boundary showing micro-crack propagation in alloy 718, (d) matrix cracked carbides in alloy 718.

3.4 Fractography

The representative SEM fracture surfaces of Alloys 718 and 945X are presented in Figures 12. All non-hydrogen charged specimens fractured *via* ductile micro-void coalescence (MVC) as observed in Figures 12a and 12d. In contrast, the transgranular facets with its surface roughened by slip steps indicate that failure might occur by separation along some slip bands in the hydrogen charged specimens, as shown in Figure 12b and 12e. In addition, the hydrogen-charged samples exhibited mixture of intergranular and transgranular fracture

modes in the region where hydrogen was present, as presented in Figure 12g. The central region of fracture surface in the hydrogen charged samples displayed dimple fracture mode (see Figure 12c and 12f) as in non-hydrogen charged specimens (see Figure 12a and 12d). This observation indicates an absence of hydrogen in the central region of the hydrogen charged specimens and this is expected following the hydrogen penetration depth of $\sim 140\ \mu\text{m}$, obtained by diffusion calculations using hydrogen diffusion coefficients from ^[1]. The annular radius of outer quasi-cleavage ring observed on the fracture surface using SEM was $\sim 250\ \mu\text{m}$. The difference in penetration distances obtained is due to enhanced diffusion of hydrogen by dislocation motion ^[24]. The non-charged samples presented shallow dimples, while the region where hydrogen was present in the hydrogen-charged samples showed quasi-cleavage morphology, with few noticeable dimples. Similar morphology was observed by Liu et al ^[5] and Miller et al ^[18].

Figure 12 First column of SEM micrographs shows fracture surfaces of Alloy 718 AR specimens (a) outer region of non-charged, ductile fracture with dimples, (b) outer region of charged, quasi-cleavage fracture with tear ridges and slip lines, (c) central region of fracture surface of hydrogen charged specimens showing ductile fracture. The second column shows fracture surface of 945X SC and aged specimens (d) outer region of non-charged, ductile fracture with dimples, (e) outer region of charged, quasi-cleavage fracture with tear ridges and slip lines, (f) central region of fracture surface of hydrogen charged specimens showing ductile fracture, (g) intergranular and transgranular fracture facets in the outer region of a hydrogen charged specimen.

4. Discussion

Susceptibility of Ni-alloys to HE is expected to depend on factors such as microstructural features affecting hydrogen transport properties and deformation mode in the presence of hydrogen. The hydrogen diffusivity of age-hardened Ni alloys is significantly reduced by enhanced hydrogen trapping at precipitate-matrix interfaces when compared with the hydrogen diffusivity of solution annealed Ni alloys ^[25–27]. According to previous H permeation experiments, the binding energy of H for δ phases in Alloy 718 is higher than that of γ'' . The same study also identified γ'' in Alloy 718 as a reversible trap at 80 °C ^[25]. It is well known that the PH Ni-alloys promote strain localisation due to the presence of coherent, nano-scale precipitates ^[28,29]. In addition to this, the interaction of diffusible hydrogen with dislocation motion and precipitates further enhances the strain localisation, and this induces slip along a particular plane in Ni-alloy single crystal ^[30] and in Ni-base superalloy 718 ^[31].

4.1 Mechanical properties

The effect of strength on susceptibility to hydrogen embrittlement was clearly demonstrated for both alloys in the present study for the given hydrogen charging parameters and loading conditions, see Figure 9. It is particularly noticeable that the ‘low strength’ (AC, FC, SC 718 with 0.2% proof strength 900 ± 25 MPa) conditions tested in the present work exhibit a lower embrittlement index compared to high strength Alloy 718 (AR), even though all the other variations of Alloy 718 contained δ phase. This appears to be in contrast to results of previous studies, ^[1,3,5,16], which suggested that δ phase was the main cause of hydrogen

embrittlement. Hence, the reduction in strength seems to be a more dominant factor mitigating HE than that of the δ phase does promote HE. The discrepancy between the present work and the work reported by Liu et al [5] may be attributed to several factors, namely, the difference in hydrogen pre-charging conditions, test conditions, and heat treatment conditions. The most important reason is likely to be the considerable difference in size distribution of precipitates between the present work and [5]. Hence, it might be more sensible to compare precipitation size of alloy 718 with their embrittlement index as shown in Figure 13a. It shows that initially an increase of the γ'' length leads to a reduction in the EI. However, around a γ'' length of 40 nm and a partial decoration of δ phase at the grain boundaries (see Figure 13b), the EI starts to increase again despite the 0.2% proof stress continuing to fall. In order to extend the γ'' size range in Figure 13 an additional ageing heat treatment was carried out on Alloy 718 SC at 802°C for 8 h (in contrast to 774°C for 6 h) followed by air cooling. In this way the proof strength was further reduced by coarsening of γ'' and the continuous decoration of δ phase at all the grain boundaries as shown in Figure 13c. It can be seen from Figure 13a that this microstructure showed a dramatic increase in the EI, close to that of as-received microstructure of Alloy 718 despite a much lower yield strength. Hence, there is a critical size of γ'' beyond which the continuous decoration of δ phase decorating grain boundaries ensues and it affects the HE resistance significantly.

Figure 13 (a) Variation of embrittlement index and 0.2% proof strength of alloy 718 with average precipitate length (γ'') and (b) SEM micrograph of alloy 718 (SC) with partial decoration of δ phase at grain boundaries (GB), (c) SEM micrograph of Alloy 718 with significant coarsening of γ'' and continuous decoration of δ phase decoration at GB.

Alloy 945X also showed dramatic decrease in susceptibility to hydrogen embrittlement with decreasing 0.2% proof stress, Figures 9, however, the susceptibility increased with increasing γ'' length, Figure 10. The 0.2% proof strength of alloy 945X increased with an increase in γ'' length. This observation reveals that all microstructures developed are in underaged condition. Hence, the synergistic effect of planar deformation promoted by high strength underaged condition and ingressed hydrogen results in enhanced susceptibility to HE [31]. Generally, the Alloy 945X (SC and FC and aged, with 0.2% proof strength in the excess of 1000 MPa) showed high EI values, similar to Alloy 718 AR, which is best related to the high strength of Alloy 945X. In the light of the evidence provided here one can, therefore, suggest that the strength itself markedly affected the resistance to hydrogen embrittlement, particularly for microstructures with relatively low content of δ phase. However, there is

clearly an optimum microstructure for Alloy 718, i.e. coarse γ'' and δ phase still being below a critical size, at which the EI reaches a minimum. The strength of Alloy 945X mainly derives from strengthening precipitates γ' and γ'' which are reversible traps according to [25]. The effect of strength on the embrittlement can be explained by the reduction of plastic zone size ahead of the crack tip and higher crack tip stress. These factors seem to increase the tendency for hydrogen accumulation in this region and causes early failure [11]. However, it is important to keep the amount of δ phase relatively low, since increasing amount of δ phase could potentially change the failure mechanism and eventually enhance the susceptibility of the alloy to HE.

The morphology of the fracture close to the surface of the specimens of the non-hydrogen charged and hydrogen charged Alloy 718 and Alloy 945X, Figure (12a, b) and Figure 12 (d, e), respectively, showed significant differences due to the uptake of hydrogen. In the case of the non-charged surface, the dominant fracture mode was shallow dimples, indicating ductile fracture. In contrast, the charged samples showed quasi-cleavage with smooth facets. These observations are similar to the work of Hicks and Altstetter [32], where these smooth facets were related to flat planar facets on $\{111\}$ planes. Liu et al. [5] and Rezende et al. [18] have also reported such facets in hydrogen charged samples. The central region of the tensile specimens, for charged Alloys 718 and 945X in Figure 12(c) and 12(f) respectively, present a fracture mode with a mix of quasi-cleavage micro-facets and intergranular fracture, with discrete regions and shallow dimples on some grain facets, indicating significant ductile fracture. The similarity in the morphology of the dimples in the outer region of non-charged specimens and the central region of the charged was evidenced, which is expected since hydrogen penetrated only around $\sim 250\ \mu\text{m}$.

4.2 Hydrogen embrittlement mechanism

Several theories have been proposed to explain the HE phenomenon; mostly, hydrogen-enhanced localized plasticity (HELP) [7,33–35], hydrogen-enhanced de-cohesion (HEDE) [36–38] and adsorption induced dislocation emission (AIDE) [39,40] mechanisms are invoked to explain the observation of failure modes in Ni alloys failed in hydrogen environment. In simple terms, HELP mechanism describes the failure/cracking owing to the increased multiplication of dislocations at the localised region along with the enhancement of dislocation motion and micro-void formation at the intersection of dislocations in the

presence of hydrogen. Further, the suppression of cross-slip leads to the macroscopic reduction in ductility and a presence of quasi-brittle fracture features. In contrast, HEDE mechanism defines the failure or cracking due to the reduction in cohesive strength of lattice under hydrogen. AIDE describes the failure due to dislocation emission induced cracking by the adsorbed hydrogen at the surface. It is prudent to say that all of these mechanisms are operating simultaneously, for example, the observation of slip traces on some of the intergranular facets where the effect of HELP cannot be ruled out, in addition to HEDE [38,41]. These mechanisms are controlled by hydrogen trapping characteristics of precipitates and second-phase particles lead to crack nucleation and propagation [42–44]. Notwithstanding the mechanisms, highly localised hydrogen concentration and high stress concentrations are essential for HE crack initiation [5], and accelerated transport of hydrogen to propagating crack tips is a prerequisite for crack propagation..

The fracture features of hydrogen embrittled surfaces in Figure 12e exhibited evidence of slip, dimples and tear ridges. Also, a minor reduction in 0.2% proof strength was observed in all conditions. These features are all evidence of dislocation activity as previously reported in [31,45,46]. The distinct fracture modes, between the outer regions with hydrogen and inner region without hydrogen, indicate enhanced dislocation activity by hydrogen. Similar observation have also been reported by other researchers [22,31,33]. However, the present work also demonstrates that if the γ'' is sufficiently coarsened in Alloy 718, which inevitably also results in significant δ formation and coarsening, the HEDE mechanism might become the more dominant factor in terms of HE.

5. Conclusions

Two PH nickel base super-alloys (alloy UNS N07718 and alloy UNS N09945X) were studied to elucidate the role of microstructural condition on susceptibility to hydrogen embrittlement. The Alloy 718 microstructures were composed of γ' , γ'' and δ phase precipitates, whereas γ' , γ'' and no δ phase were observed in Alloy 945X. The following conclusions are made based on the experimental results:

- Both alloys showed significant hydrogen embrittlement after hydrogen charging but the microstructure sensitivity to HE was slightly different when comparing both alloys

- It was demonstrated that there is an optimum microstructure in terms of the embrittlement index at which the γ'' had been coarsened to reduce the strength of the alloy without intergranular δ phase, noticeably affecting the embrittlement index. When further coarsening γ'' and δ resulting in a further reduction of the yield strength, the embrittlement index increased dramatically indicating a change of the hydrogen embrittlement mechanism. It is suggested that at this stage HEDE becomes more dominant than the HELP mechanism.
- Alloy 945X showed a more simple relationship between γ'' size or 0.2% proof stress and embrittlement index. Here, the embrittlement index clearly increased as the material became stronger. As there is no evidence of significant δ formation in Alloy 945X, it is suggested that the HELP mechanism dominates in the HE process for the tested microstructures of Alloy 945X.

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