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An Investigation into the

Effects of Hydrogen on the Fracture and

Deformation Behavior of Alloy X-750

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ABSTRACT

This study investigated the effect of hydrogen on the fracture of a nickel-base superalloy, Alloy X-750 in the solution treated and aged (HTH) condition. The effect of hydrogen was examined through tensile testing and fracture toughness testing incorporating observations from scanning electron microscopy and light microscopy. The elongation for tensile specimens tested at $3.33 \times 10^{-4} \text{ s}^{-1}$ was reduced from 21% for noncharged specimens to 7.3% for 5.7 ppm hydrogen and was further reduced to 3.5% for 65 ppm hydrogen. The fracture surface for all specimens was intergranular ductile dimples with minimal transgranular dimple fracture. The elongation further decreased as the strain rate was decreased for the hydrogen-charged specimens while for the noncharged specimens no strain rate effect was observed. Prestraining prior to charging dramatically decreased elongation after hydrogen charging, though in all cases the flow stress was achieved prior to failure. This showed plastic deformation was required for failure. The intergranular failure mechanism in Alloy X-750 was a microvoid initiation process at grain boundary carbides followed by void growth and coalescence.

The effect of hydrogen was also investigated through fracture toughness testing. A model based on a strain modified critical stress criterion was shown to correlate the fracture behavior as a function of hydrogen well. The fracture toughness of the noncharged specimen was $147 \text{ MPa}\sqrt{\text{m}}$ and decreased to $52 \text{ MPa}\sqrt{\text{m}}$ at a rapid

loading rate and further decreases the toughness to $42 \text{ MPa}\sqrt{\text{m}}$ for a slow loading rate. This is consistent with the need for hydrogen diffusion to the hydrostatic stress field or a stress field due to a dislocation pile-up in front of the crack.

The effect of hydrogen on the deformation behavior was studied in order to determine how a change in the deformation behavior affected the fracture behavior. The effect of hydrogen on the activation area was examined through stress relaxation testing and strain rate change tensile testing incorporating observations from transmission electron microscopy on the dislocation substructure. The activation area was slightly decreased for specimens which contain hydrogen. This change was small and would be expected to have only minor affects on embrittlement.

The embrittlement phenomenon may be explained by a reduction of the interfacial strength of the carbide-matrix interface due to hydrogen with possible secondary effects of HELP (hydrogen enhanced local plasticity) and a local hydrogen pressure at the carbide-matrix interface reducing the void initiation strain.

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1.0 INTRODUCTION

Iron-base and nickel-base superalloys used in nuclear reactor environments must possess high strength, relaxation resistance, and good corrosion properties ((1),(2)). One such alloy used for fastener applications is Alloy X-750. Alloy X-750, an age-hardenable high-strength austenitic Ni-Cr-Fe alloy, is widely used in both pressurized water and boiling water nuclear reactors ((1),(2)). A typical operating environment for these applications is in water at temperatures on the order of 300°C.

Over the past two decades, cracking of Alloy X-750 has been observed in nuclear reactor environments((1),(2),(3)). Due to these failures, work has focussed on determining the effect of heat treatment and metallurgical structure on stress-corrosion-cracking (SCC) resistance. The early Alloy X-750 components were heat treated to maximize high-temperature creep resistance as originally developed for aerospace applications. This heat treatment, termed AH, consisted of an equalization at 890°C for 24 hours, air cooling, and an age at 704°C for 20 hours. The subsequent microstructure was susceptible to both low-temperature ($< 100^{\circ}\text{C}$) and high-temperature ($> 200^{\circ}\text{C}$) SCC in primary water environments. The AH microstructure consisted of both fine (20 nm) and coarse ($1\mu\text{m}$) intragranular γ' precipitates and MC type carbides(4). A microstructure that is much more resistant to SCC was later developed, as demonstrated by extensive testing (4). This

treatment, referred to as HTH, included a solution anneal at 1093°C for 1 to 2 hours followed by rapid cooling and an aging treatment at 704°C for 20 hours.

Alloy X-750 is susceptible to two types of cracking, large crack growth rates below 100°C and slow crack growth rates observed above 200°C((4),(5)). The low-temperature cracking phenomenon appears to be hydrogen-enhanced cracking ((4),(5)). The high-temperature cracking also appears to be enhanced by hydrogen, though this is still controversial. While there exists extensive databases on the high-temperature cracking process in nuclear reactor primary water(1),(2),(3) a basic mechanistic understanding is lacking. There has been no model developed for the low temperature cracking of this alloy. Despite demonstrated effects of hydrogen on iron-base and nickel-base alloys, there has been little effort to understand how the hydrogen affects the fracture behavior in this alloy system and how to correlate the fracture behavior with the microstructure. It is the purpose of this work to investigate how hydrogen influences the fracture and deformation behavior of HTH Alloy X-750 at low temperatures as well as to develop a model to describe the fracture behavior for low temperature cracking. This increased understanding of the mechanism of hydrogen-enhanced fracture at low temperatures will help in the future design of alloys.

The testing to understand the effect of hydrogen on the fracture behavior was oriented toward determining the micromechanism of fracture, how hydrogen affects

this mechanism, and development of a model to describe the fracture. This fracture behavior study incorporated test results from fracture-toughness specimens, as notched bend bars, and uniaxial tensile specimens. Gas phase hydrogen charging was used to achieve a uniform hydrogen concentration for testing. The hydrogen assisted fracture was very sensitive to loading rate as well as temperature. Therefore these two parameters were examined. The role of temperature and loading rate were to alter the hydrogen transport and trapping phenomena thereby increasing the local hydrogen concentration at the fracture initiation site. Prestrain experiments were also used to increase the flow stress and evaluate the effect of yield strength on embrittlement. By understanding how altering the yield strength affected fracture, the critical fracture parameter may be determined and be used to develop the model. In cleavage fracture of steels it has been shown that a material must deform plastically in order to initiate a cleavage crack (17). In order to determine if this same effect is observed in the intergranular fracture of X-750, the flow stress was increased by prestraining the specimen prior to hydrogen charging. It was determined that the onset of fracture could be altered.

The testing to understand the role of hydrogen in altering the deformation behavior was oriented toward determining how deformation is related to the fracture behavior. The effect of hydrogen on the deformation behavior of this alloy was examined using tensile testing, strain rate change testing and stress relaxation testing techniques. These techniques were used to elucidate the activation area of the

material. The activation area may be related to the thermally activated deformation processes, which are the processes that hydrogen may affect. Also the effect of hydrogen on the localization of deformation was studied by analyzing the surface slip steps on a flat polished tensile specimens.

In summary, the main goals of this work were:

- 1) To characterize the effect of hydrogen on the fracture behavior of the Alloy X-750 and to relate this behavior to a model that describes the fracture behavior. This includes the determination of the micromechanism of fracture.
- 2) To characterize the effect of hydrogen on the deformation behavior and determine how this relates to the embrittlement phenomenon.

2.0 LITERATURE REVIEW

2.1 MATERIAL CHEMISTRY AND MICROSTRUCTURE

Alloy X-750 is a nickel-base superalloy that is strengthened by the precipitation of γ' . The chemistry and microstructure of superalloys are important factors in determining their resistance to environmentally enhanced fracture(6). Within-specification variations of bulk material chemistry have been shown to have a significant impact on the degree of embrittlement due to hydrogen effects of the austenitic nickel-base and iron-base alloys (6). Alloy X-750 is comprised of many elements. The nominal chemistry is shown in TABLE 2.1.1 from Reference (7). The rationale for the addition of the elements is given below.

TABLE 2.1.1: NOMINAL COMPOSITIONS OF X-750 (wt. %)

	Ni	Cr	Fe	C	Mn	Cu	Al	Ti	Si	S	Nb+Ta
Nom.	73	15.5	7.0	.04	.5	.2	.7	2.5	.2	.005	1
Min	70	14	5				.4				
Max		17	9	.08	1	.5	1				

The first category of elements are those that favor the FCC austenitic matrix. These include Ni, Cr, and Fe. The second category of elements are those that partition to the γ' to form the Ni_3X precipitate. These include Al, Ti, Nb, and Ta.

Ta is only a trace element and is not intentionally added. The third category of elements are B and C (8). These elements segregate to the grain boundaries to decrease the susceptibility to creep rupture and intergranular fracture. These elements may also form grain-boundary precipitates, carbides and borides. The carbides and borides are formed with Cr, Ti and Nb. A detailed characterization of the constituents in Alloy X-750 is given below.

a) Nickel matrix (γ) : This is a continuous FCC nickel-base matrix. Analysis of AH material showed that this is an FCC lattice with $a_0=3.57\text{\AA}$ (9). The composition of the matrix is given in TABLE 2.1.2 from Reference (9). This is similar to what was determined for the heat studied for this program as discussed in the results section.

TABLE 2.1.2: COMPOSITION OF THE MATRIX (wt. %)

Ni	Cr	Fe	Al	Ti	Nb+Ta
75	16.3	7.5	.3	.4	<.2

b) Gamma prime precipitates (γ') : The initial microstructural studies on Alloy X-750 were reported by Raymond in 1967(10). Raymond showed that the strengthening phase in X-750 was γ' with an $L1_2$ structure and that the precipitate was fully coherent with the matrix.

The measured lattice parameter was 3.598Å, based on an analysis of AH material(9). The composition of the γ' precipitates, developed from AH data are presented in TABLE 2.1.3 from Reference (9).

TABLE 2.1.3: γ' COMPOSITION IN ALLOY X-750 (wt %)

Ni	Cr	Al	Ti	Nb+Ta	Fe
77	2.1	3.3	11	4.7	1.9

The γ' phase is a cuboidal precipitate that is coherent with the matrix. The misfit between the matrix and precipitate, given by $\delta = (a_{\gamma'} - a_{\gamma})/a_{\gamma}$, is 0.78% for AH at room temperature. This is consistent with the work of Symonds(11) on precipitate morphology, which showed that precipitates with misfits up to 0.3% are spherical and when the misfit is over 0.3% and less than approximately 0.75%, the precipitates take on a cuboidal shape.

c) Carbides (MC and $M_{23}C_6$) : The primary carbides in this material are the MC carbides where the M is Ti or Nb. The lattice parameter of this phase is approximately 4.4Å depending on the Ti:Nb ratio, with a NaCl structure (13). These are the carbides that form at high temperatures and are considered to be very stable (8). The majority of the carbon is in the form of primary carbides which are found both as intergranular and intragranular precipitates. The secondary carbides,

$M_{23}C_6$, are precipitated on grain boundaries during the aging process. The solvus temperature for the carbides is 870°C. The major constituent in the secondary carbides is chromium. While the typical morphology for these carbides is globular, there have been instances where cellular carbides were observed (12). The precipitation of the $M_{23}C_6$ carbides may result in a chromium depleted zone adjacent to the boundaries, depending on the thermal-mechanical processing(12). The lattice parameter for the $Cr_{23}C_6$ carbides is 10.638Å, three times that of the nickel matrix(13). These intergranular carbides are semicoherent with one boundary and usually incoherent with the other. The growth of the carbides is mainly in the grain in which the carbide is incoherent.

2.2 THE MICROMECHANISMS OF FRACTURE

The fracture behavior of materials at less than 0.5 of the melting temperature may occur by cleavage, interfacial decohesion, ductile fracture, or some combination of these mechanisms. As will be discussed in the following section hydrogen may enhance any one of these mechanisms. Transgranular cleavage was not shown to be relevant to this system and was not discussed. Therefore interfacial separation and ductile fracture are reviewed. The fracture of this material is by intergranular microvoid coalescence in which a majority of the failure strain is the strain needed to initiate the voids. This initiation strain was related to the strength of the carbide-matrix interface.

2.2.1 The Phenomenon of Ductile Fracture

The characteristics of ductile fracture are well established(14)(15). In most materials, including the intergranular fracture behavior of this material, ductile fracture occurs by the initiation, growth and link-up of the voids. The link-up stage may be either by void coalescence or by local fracture between voids. An extensive review of ductile fracture will not be given, since there have been many reviews on ductile fracture with the most recent by Garrison and Moody (14) and Van Stone et al. (15). A review will be given here of the aspects that are directly related to the fracture processes observed in X-750.

The modelling of the fracture process requires an understanding of the controlling parameters. The void initiation, growth, and coalescence process observed in materials is determined by the local stress at the void initiating particle which is a function of the applied stress and the local stress due to dislocation pile-ups. A review of the models that describe this work will be provided. In a material like HTH Alloy X-750 that fails by ductile intergranular fracture with extensive networks of discrete grain boundary carbides, void initiation is a key component and has been modeled using both stress and energy criteria as will be described.

Void initiation may occur by either the decohesion of a particle with the matrix or the fracture of the precipitate. The carbides are very fine in HTH Alloy

X-750, less than $0.3\text{ }\mu\text{m}$ and do not appear to fracture based on the plateau etching and sectioning experiments performed in this work. Therefore, only decohesion at the carbide-matrix interface will be reviewed. The initiation of voids at second phase particles has been shown for numerous systems including internally oxidized copper (16), high strength steels (17) and aluminum alloys (18). It has also been shown that intergranular voids may initiate due to slip band intersections with the grain boundary (19). The strain at which a void initiates at a particle is dependent on the stress state. It was shown by Cox and Low(17) that as the stress state is changed from uniaxial to triaxial using notched tensile specimens, the strain to initiate voids decreased. A similar effect was noted by French and Weinrich(20) who showed that the strain to initiate voids increased as a hydrostatic pressure was superimposed on the uniaxial stress up to a critical hydrostatic stress when the effect of hydrostatic stress appeared to diminish. It was suggested by Van Stone et al. (15) that for high hydrostatic stresses, a critical stress is no longer a valid initiation criterion and a strain modified stress criterion should be used. It was further observed that the smaller inclusions initiated voids at higher strains. Chen suggested that it is not the void initiation that is affected by the stress state but the void growth(21). It has been shown for many other systems that voids initiate sooner for large inclusions ((16),(23)). While many parameters seem to affect the void initiation process, the strain appears to be a key factor and was determined to be the fundamental parameter required when modelling the fracture behavior.

2.2.2 Modeling Ductile Fracture

Void initiation in this material is due to the separation of the interface between the carbide particles and the γ matrix. In order to develop fracture models and determine what microstructural features may affect the fracture process, the models that describe the void initiation processes were reviewed. Gurland and Plateau(22) first developed a void initiation criteria based on the fracture of a particle. They assumed that the elastic energy released from the fracture of the particle had to exceed the surface energy of the newly formed surfaces. With that assumption, Gurland and Plateau (22) developed the following equation:

$$\sigma = \frac{1}{q} \left[\frac{E\gamma}{d} \right]^{\frac{1}{2}} \quad (2.2.1)$$

where :

- q is the stress concentration factor
- E is the modulus of elasticity
- γ is the surface energy of the particle
- σ is the critical stress for particle cracking
- d is the grain size.

Other models developed to describe void initiation were based on work hardening theories. Dislocation loops were hypothesized to result from tensile

stresses at the particle-matrix interface. The first such model was that of Ashby (24). This model was not used since the dislocations do not loop around the carbide particles, though it should be noted, that a similar approach may be used for the grain boundary carbides except the local stress due to dislocations would be from a dislocation pile-up and not the dislocation loop. One important contribution of the model developed by Ashby is that the strain to initiate a void was proportional to the cohesive energy of the interfacial bond.

Rosenfield(25) suggested that the stress state is important and the combination of the local and far-field stresses should be included to develop a complete model. The tensile stress at the particle is the sum of the stress developed from dislocations, as proposed by Ashby, the local stress intensification, and the hydrostatic stress. Later, the work of Argon et al.((26),(27)) and the work of Goods and Brown(28) incorporated this idea into the modeling.

Argon et al.((26),(27)) assumed that a void initiated when the radial stress at the particle-matrix interface exceeds the fracture stress. They suggested that the interfacial stress must be equal to or greater than the sum of 1.5 to 2 times the shear yield stress and the hydrostatic stress for a nonhardening material. They then extended this idea to include hardening materials by using the tensile flow stress in the region of the particle instead of the shear yield stress. The work of Goods and Brown (28), which extended the work of Brown and Stobbs (29), used an equation

very similar to the one developed by Rosenfield. Their equation was:

$$\sigma_I = \sigma_c + \sigma_f + \sigma_H \quad (2.2.2)$$

where σ_I was the interfacial fracture stress, σ_c is the local stress due to dislocations, σ_f is the local flow stress, and σ_H is the hydrostatic stress. Ashby (24) suggested that σ_c was proportional to the square root of the plastic strain. Also, the flow strength was described by a the plastic strain. This work suggested that strain was an important parameter in determining the void initiation event and that a strain modified critical stress criterion should be used. The critical strain may be dependent on the stress state since hydrostatic stress reduces the strain needed for void initiation but this is not always the case. This is why void initiation and fracture modeling is sometimes proposed as the strain-modified critical stress criterion.

In the models that describe the void initiation due to decohesion at an interface, the bond strength of that interface controls the fracture process. This has been shown for a number of systems. In an Fe-40%Ni base alloy with 1.6 wt. % Al_2O_3 , the cohesive strength was close to zero and the fracture strain was 21% (30). The addition of 5% Mn increased the cohesive strength to 80 mJ/m² and the fracture strain increased to 36%. The addition of 5% Mo and 10% Cr increased the fracture strain to over 50% while the cohesive energy in these systems was over 1000 mJ/m² (30). A similar effect was observed when Cr was added to thoriated nickel (31). Impurity segregation to the carbide-matrix interface has been shown to reduce the

strain to nucleate voids(32)(33). In steels, it was shown that segregation of impurity elements to the carbide-matrix interface decreases the strain required to initiate voids(32). This was conclusively shown in a study of the temper embrittlement of a low alloy 300M steel in which the heat treatment that caused P segregation to the carbide matrix interface, as determined by Auger microscopy, reduced the strain to initiate the voids(33).

2.3 THE EFFECT OF HYDROGEN ON THE FRACTURE OF NICKEL AND NICKEL-BASE ALLOYS

There have been a number of studies that investigate the effects of hydrogen in metals as reviewed by A. W. Thompson and I. M. Bernstein(6) and a variety of mechanisms have been proposed to explain the embrittlement phenomenon(34)(35)(44). The effects in different systems vary widely and therefore it would be incorrect to assume one single mechanism for the phenomena of hydrogen embrittlement. Furthermore, in one system hydrogen may have multiple effects and the mechanism that causes fracture is controlled by the energetics and kinetics of the phenomenon. In this review, three of the four most-likely mechanisms applicable to this material-environment system will be discussed. These are hydrogen-enhanced localized plasticity (HELP), hydrogen degradation of cohesive energy, and hydrogen pressurization. Hydrogen-related phase changes, e.g., hydride formation, were not discussed since they are not applicable to the nickel-base system being studied at the relatively low hydrogen fugacities. The mechanisms of decohesion, hydrogen enhanced plasticity, and hydrogen bubble formation will then be related to the problem at hand, the hydrogen enhanced cracking of Alloy X-750. A theory proposed for Alloy X-750 was a methane bubble formation (61). The evidence from the work presented in this paper does not support a methane bubble formation theory. Though the formation of a local hydrogen pressure at grain boundary particles is discussed as a possibility as was

first proposed by Zapfee and Sims (34). The enhanced mobility of dislocations due to hydrogen was first theorized and experimentally shown to occur in steels by Beachem (35). This mechanism was demonstrated by fractographic techniques and in-situ environmental-cell TEM. The HELP mechanism was experimentally verified for pure nickel ((36), (37)) and precipitation strengthened superalloys, which may be either polycrystalline (38) or single crystals (39). The work on polycrystals showed that in some instances the failure was near the grain boundary, not exactly on the boundary (38), suggesting a mechanism based on shear fracture failure enhanced by hydrogen. The HELP mechanism suggested that the fracture occurred by very localized plasticity but the details of this mechanism were not fully understood. Other investigators supported a model in which hydrogen promotes shear localization ((40),(41)).

A more fundamental understanding of the HELP phenomena was developed through stress-relaxation testing of nickel specimens with various amounts of either carbon or hydrogen(42). The effect of carbon in solid solution was to increase the resistance of the material to thermally activated deformation and to decrease the activation area. The relaxation behavior of specimens with hydrogen was enhanced. The activation area was slightly increased when hydrogen was added.

The stress relaxation of Alloy X-750 without hydrogen has been examined (43). An increase in plastic strain resulted in a decrease in the activation area. This

was explained by increased dislocation-dislocation interaction. As strain was increased, the dislocation density was increased and the spacing between the dislocations decreased. As the spacing between dislocations decreased, the distance a mobile dislocation can travel without intersecting other dislocations would then decrease. An important area lacking in the work on correlating the stress relaxation to an increase in dislocation density is the corresponding experimental evidence on the deformation structure. Preliminary evidence is presented in this document.

The decohesion mechanism in which hydrogen decreases the cohesive energy between atoms and promotes a more brittle transgranular fracture was originally proposed for steels by Troiano (44) and furthered by Oriani (45). The work here utilizes the idea of hydrogen reduction of the cohesive energy, but differs from the earlier work in that the reduction in cohesive strength was related to the carbide-matrix interface. The reduction in cohesive energy between atoms is particularly important when the strain to initiate voids is a large fraction of the failure strain as was discussed by Thompson for steels(46). It was shown that the effect of hydrogen acted to alter the strain for void initiation event which resulted in reduced ductility. Also, Thompson showed that the critical fracture criterion was neither stress nor strain controlled but appeared to be controlled by a combination of stress and strain, $\sigma\epsilon^{1/2}$. It was shown by Lewandowski and Thompson (47) that even for cleavage fracture, some amount of plasticity was required to initiate the cleavage crack. Using double notched bend specimens, they showed that the crack would initiate at

sites closer to the notch tip than the peak stress location. The decohesion mechanism for nickel was further supported by the investigations on impurity effects. Latanision and Oppenhauser reported that impurities affect the SCC resistance of nickel-base alloys(48) by acting as hydrogen recombination poisons. This hypothesis was examined by Jones and coworkers who studied the effect of S, P, and Sb on the SCC resistance using a straining electrode test ((49), (50)). The results indicated that S was the most effective segregant in reducing the SCC resistance of nickel-base alloys. Sb was approximately half as effective as S and P had only a small effect. Jones et al. suggested that the recombination poison theory was not completely accurate since P was also a strong recombination poison. The possibility of decohesion is further supported by the work of Lassila and Birnbaum on nickel. They showed that sulfur segregated to the boundaries causes intergranular cracking without any external environmental effect (51).

There are many similarities when comparing the intergranular fracture of the nickel- base alloys and the iron-base alloys. The key factor controlling the intergranular fracture in iron base-alloys is the grain-boundary composition as discussed by Briant (52). One of the best studied intergranular fracture phenomena, with and without hydrogen, is the temper embrittlement of steels. In the case of no dissolved hydrogen, the intergranular fracture was shown to be caused by the segregation of impurity elements such as phosphorus, tin, and antimony (53) which is similar to what was discussed above for nickel-base alloys. It was further shown

that in a gaseous hydrogen environment, the crack path would change from transgranular to intergranular when the material was aged to enhance the impurity segregation. Yoshino and McMahon performed a similar test on HY130 steel in H_2SO_4 that showed the crack path for stable crack growth changed from transgranular to intergranular when the steel was step cooled to allow segregation as compared to quenched (no segregation)(54). These results further support the role of impurities and the possibility of a grain boundary decohesion mechanism playing a role.

As was previously stated, it is important to understand the interaction of hydrogen with dislocations and how that relates to the embrittlement process. Wilcox and Smith observed that the hydrogen embrittlement in pure nickel was maximized at $-50^{\circ}C$ and was enhanced by the occurrence of grain-boundary shear and serrated yielding (55). This work also showed that the activation energy for crack growth in pure nickel at low temperatures was 28.5 kJ/mol. It was shown by Boniszewski and Smith (56) that hydrogen interacts with dislocations and that the brittle fracture is intergranular. They described a model based on Cottrell atmospheres to describe the interaction between the hydrogen and dislocations, realizing that under typical testing conditions hydrogen can not escape from the dislocation atmosphere. It was shown that when specimens were tested at high strain rates at room temperature, the ductility of hydrogen charged specimens was

similar to that for noncharged specimens. As the strain rate was decreased the ductility in the noncharged specimens did not change while the ductility for the hydrogen charged specimens decreased. A decrease in the test temperature had the same effect as an increase in the strain rate. At liquid nitrogen temperatures, there was only a small decrement in ductility due to hydrogen. This appears to show that hydrogen in solution is not enough to cause intergranular fracture in nickel but that dislocation-hydrogen interaction is important. One such interaction is local hydrogen pressurization. A model has been developed to describe the increase in local pressure at inclusions due to dislocation transport of hydrogen(70). The functional forms of the equations were compared to experimental data and showed a very good correlation. The analysis may be applicable to the intergranular fracture of X-750 since it is noted that the initiation sites are carbides at the grain boundaries and the fracture morphology is a dimpled surface.

The discussion so far has separated the decohesion and HELP mechanisms, this is not necessarily the case. The testing by Lassila and Birnbaum showed that a decohesion mechanism and a HELP mechanism may work together to embrittle nickel (51). They showed that either hydrogen with no sulfur or sulfur with no hydrogen can cause intergranular fracture in nickel. They concluded that HELP near the grain boundaries and sulfur induced decohesion were primary factors in the intergranular fracture of nickel.

Alloy 600, an alloy very similar to Alloy X-750 but without the Ti, Nb, or Al, showed that the least-sensitized grain boundaries appeared to be the most susceptible to stress-corrosion cracking (58). Recent testing of Alloy 600, a Ni-Cr-Fe alloy, has shown that the deformation behavior is directly related to the SCC behavior(57). More-recent testing of Alloy X-750 has also shown that the sensitized boundaries are the least susceptible to stress corrosion cracking in a strongly reducing environment (4). This may be related to site competition between the hydrogen and carbon on the boundaries or the carbides acting as dislocation nucleation sites thus reducing the localization of plasticity. The thermomechanical history of the of nickel-base alloys is important in modifying the resistance to hydrogen embrittlement by altering the deformation characteristics and the morphology of the grain boundary precipitates. It has been shown that Alloy 600 is much more resistant to stress corrosion cracking than Alloy X-750 (61). A possible explanation of this is the increased planarity of the slip when the same material is strengthened by fine coherent precipitates. The increased planarity is caused from the shearing of the precipitates. The precipitate shearing results in slip planes that have less resistance to glide and therefore dislocation motion is enhanced on those planes. Furthermore, the aging of the alloy is important. It has been shown that the embrittlement of A-286, an austenitic iron-based alloy that is strengthened by γ' , is decreased as the mismatch between the precipitates and the matrix is increased and when γ' transforms to η (59). It should also be noted that there is a large strength difference between Alloy 600 and X-750, which may be important in altering the

susceptibility to hydrogen embrittlement. If the fracture criterion is a decohesion of the grain boundaries which requires a critical stress to fracture the boundary, then larger strains may be needed in Alloy 600 for fracture as compared to X-750 since A600 is a lower yield stress material. The decohesion mechanism may also be used to explain the role of carbides. In Alloy 600 it was shown by Bruemmer (60) that the carbides are sources of dislocations. In the absence of carbides the local stress may be higher since plastic deformation is difficult, thus making decohesion easier.

Shen and Shewmon, on both Alloy X-750 and Alloy 600, suggested that the intergranular stress corrosion cracking is due to the formation of methane bubbles on the grain boundaries. Once initiated it is assumed that the fracture occurs by the bubbles growing together (61). While TEM replicas show grain boundary features that could be due to fine bubbles on the boundaries, the present work shows the same small features after the material is strained at room temperature where the formation of methane would not be expected. Furthermore, there is a continuum of microvoid sizes from no hydrogen to large quantities of hydrogen in the alloys. Finally, as was discussed in this work, there was no sharp transition in the embrittlement behavior of this material in changing from low to high temperature testing suggesting that the failure mechanism was the same at all temperatures.

2.4 GENERAL CHARACTERISTICS OF DEFORMATION

HTH Alloy X-750 is strengthened by precipitation of fine γ' , in a nickel matrix. Since the γ' precipitate is an $L1_2$ -type phase, it is necessary for dislocation pairs to travel through the precipitate so that the second dislocation may restore the order that the first dislocation destroyed. For the first dislocation of the pair to enter the precipitate, the applied stress must overcome the antiphase boundary energy (APBE) of the precipitate (62). The shearing of the precipitate occurs by two $a/2 \langle 110 \rangle$ dislocations along a $\{111\}$ plane separated by a distance controlled by the APBE.

2.5 EFFECTS OF ALLOYING ADDITIONS ON THE DEFORMATION BEHAVIOR IN PRECIPITATION STRENGTHENED NICKEL-BASE ALLOYS

In the review article by Brown and Ham (63) a detailed discussion is given on the strengthening mechanisms in Ni-Al, Ni-Al-Ti and Ni-Al-Cr alloys. That review provided much of the information discussed in the strengthening mechanism analysis. When Ti is added to a Ni-Al alloy, the Ti substitutes for Al while the structure remains $L1_2$. The effect of Ti is to both increase the coherency strain and to increase the antiphase boundary (APB) energy. In Alloy X-750 the Ti:Al ratio in γ' is 2:1. The effects of both coherency strain and changes in antiphase boundary energy were studied in a Fe-Cr-Ni-Al-Ti alloy as reported by Brown and Ham (63). The addition of Cr to Ni-Al-Cr alloys decreased the misfit strain as well as the APB energy. A comparison of the APB energy for γ' in a Ni-Al-Cr system was measured by Hornbogen and Mukherjee(64) and by Glieter and Hornbogen(65) where the average APB energy was 97mJ/m^2 while for Ni-Al systems the APB energy is approximately 145 mJ/m^2 . From this and other work Brown and Ham concluded that the Cr may substitute for either the Ni or Al atoms and effectively reduce the degree of order and subsequently the APB energy. Therefore, the elements that are very important in controlling the role γ' plays are titanium and aluminum. Further discussion on the strengthening mechanisms in HTH Alloy X-750 are given in Appendix 2. The analysis was performed in order to determine the relative magnitude of the strengthening mechanisms.

2.6 THERMALLY ACTIVATED GLIDE OF DISLOCATIONS

The function of hydrogen in altering the deformation behavior is to alter the thermally activated deformation processes. The interaction of hydrogen with dislocations may be investigated by analyzing the thermal component of dislocation glide. It is generally recognized that dislocation glide is a dynamic phenomenon that can be described by the Orowan equation

$$\dot{\epsilon} = \rho_m b \bar{v} \quad (2.6.1)$$

where $\dot{\epsilon}$ is the plastic strain rate, ρ_m is the mobile dislocation density and $\bar{v}$ is the average dislocation velocity. The average dislocation velocity is described by the general equation for a thermally activated process:

$$\bar{v} = \bar{v}_0 \exp - \left[\frac{(\Delta H_0 - \int b \Delta A d\sigma)}{k T} \right] \quad (2.6.2)$$

where,

ΔH_0 - thermal activation enthalpy required for activation at zero applied stress

ΔA - activation area

b - Burgers vector

k - Boltzman's constant

T - temperature ($^{\circ}\text{K}$)

$\bar{v}_0$ - constant related to the atomic vibration frequency

As a dislocation moves through the lattice there are two types of obstacles acting to retard motion of the dislocation. These are:

- 1) Long-range obstacles, which are considered athermal obstacles, i.e., thermal fluctuations do not enhance the motion of dislocations past these obstacles
- 2) Short-range obstacles where dislocations may bypass the obstacle by a thermally activated process.

The mechanism of low-temperature deformation is thermally activated glide phenomenon which is described by Equations 2.6.1 and 2.6.2. A physical picture of this process is described below. As a dislocation moves from one equilibrium position to the next it passes through a region of higher energy. The activation area is a descriptive parameter that is related to the size of the obstacle that must be overcome. As has been pointed out in the literature there are many obstacles that range in size from b^2 to $10,000 b^2$ (68). These obstacles are normalized to the Burgers vector to relate them to physical barriers. Table 2.4.1 lists some typical activation areas.

**TABLE 2.6.1: ACTIVATION AREA FOR THERMALLY
ACTIVATED GLIDE (68)**

MECHANISM	RANGE OF ACTIVATION AREA normalized by the square of the Burger's vector
Peierls-Nabarro (friction) stress	10-100
Intersection of forest dislocations	50-10000
Nonconservative motion of jogs	50-10000
Cross-slip	10-100
Climb	1

Further insight into the deformation characteristics of this alloy and how hydrogen affects these characteristics can be determined by analysis of the activation area.

Stress-relaxation and strain rate change testing provides data that allows the determination of the activation area for the thermally activated glide process. This method has been used to study the activation area and the effect of hydrogen and carbon on deformation of pure Ni (42). Furthermore, activation-area characterization for Alloy X-750 in the temperature regime of interest has been reported (43). That study was performed on specimens using the strain-rate-change tensile test technique. The study described herein incorporates TEM analysis and slip line analysis on polished tensile specimens to better define the deformation structure as a function of hydrogen concentration

3.0 EXPERIMENTAL PROCEDURE

3.1 MATERIAL CONDITION

3.1.1 As received material

One heat of Alloy X-750 was used for this study. The material was vacuum induction melted (VIM), vacuum arc remelted (VAR) and hot worked at 1094°C followed by air cooling. Next, the material was given a high temperature solution anneal for 1 hour at 1094°C and again air cooled. The final step was an age-harden at 704°C for 20 hours followed by air cooling to room temperature.

The heat chosen for this work was used because it had the unique property of failing by intergranular fracture even without dissolved hydrogen. This material has an elongation of 20% at room temperature while similar heats that fail by predominantly transgranular fracture failed at elongations of approximately 24%. This suggests that the grain boundaries in this heat were slightly more susceptible than the grain interior when no hydrogen was present. An Auger analysis of the heat used showed more sulfur and boron segregated to the grain boundaries as compared to other heats.

3.1.2 Hydrogen Charging

The hydrogen-containing specimens used to evaluate the effect of hydrogen concentration on the fracture and deformation behavior were gas-phase hydrogen charged per the following method. Specimens, hydrogen analysis blanks, and tantalum hydride were placed in an oxygen free high conductivity (OFHC) copper chamber. Each specimen and hydride was weighed then inserted into the copper chamber. Once closed, the copper chamber was sealed in an Alloy X-750 compression fitting. The complete chamber was heated to 704°C for 1.5 hours. This allowed the metal hydride to decompose creating a high partial pressure of hydrogen gas. The partial pressure of hydrogen in the chamber was varied by changing the volume of the TaH and thus increasing the free volume in the chamber. An increase in the free volume in the chamber resulted in a decrease of the hydrogen partial pressure. After sufficient time for the specimens to achieve a uniform equilibrium hydrogen concentration was achieved, the chamber was cooled quickly. The specimens were then removed, and stored below 0°C. Alloy X-750 blanks were analyzed for hydrogen concentration to check for the efficiency of the hydrogen-charging process. The hydrogen concentration was measured by use of a LECO hydrogen analyzer model RH404, which used induction heating to quickly heat the specimen and then measured the conductivity of the evolved gas to determine the hydrogen concentration. The hydrogen concentrations that resulted from the charging were between 5 ppm and 65 ppm (by weight).

The majority of tensile specimens, compact tension specimens, and bend specimens were charged in a high-pressure hydrogen autoclave. The autoclave was cleaned with deionized steam and then water at 360°C. The specimens were then cleaned and inserted into the autoclave. Prior to the hydrogen gas entering the autoclave it was purified by running the gas line through a liquid nitrogen bath that condensed all gas impurities. The maximum pressure used was 5,000 psi hydrogen at 360°C which resulted in a hydrogen concentration of 65 ppm. Specimens were charged in the autoclave for 3 weeks. This was twice the time needed for diffusion of the hydrogen through the specimen and should assure a uniform hydrogen concentration. A second charging run was performed at 315°C and 3000 psi hydrogen in order to obtain a different hydrogen concentration, 40 ppm, for the testing of compact tension specimens and allow for a study of hydrogen concentration on the fracture toughness properties. This low-temperature charging, at or below 360°C, was utilized to avoid the possibility of recovery processes occurring.

3.2 Microstructural Characterization

3.2.1 Metallography

Metallography was performed on specimens that were mounted in bakelite. Mounting was followed by sequential grinding on 240, 320, 400, and 600 grit silicon carbide papers. The samples were then polished using 6 μ m and 1 μ m diamond polishing compound. The primary etchant for optical microscopy was 2% bromine in methanol.

3.2.2 Transmission Electron Microscopy (TEM)

Further characterization of the microstructure was possible through the use of transmission electron microscopy. The foils were prepared by cutting the gage section of the tensile specimens into 0.4 mm slices using a diamond wafering blade. These slices were then electropolished in a 10% HCl/methanol solution at room temperature to a thickness of 0.150 mm. Three millimeter discs were punched from the 0.150 mm slices. The discs were then electropolished using a dual jet electropolisher in a solution of 55% methanol, 35% butyl cellosolve and 10% perchloric acid at a temperature of -20°C and a voltage of 13.0 volts in a Fischione dual jet electropolisher. These foils were used for both the deformation study and to characterize the effect of the fine microstructure on the fracture behavior. The aspects of microstructure that may be important were the dislocation morphologies, the carbide size, shape, and distribution, and the γ' precipitate size, volume fraction, shape, and distribution. Foils were taken from specimens deformed to plastic strains of 0%, 0.5%, and 2.5% to characterize the effect of strain and microstructure on the dislocation substructure. Measurements of dislocation spacing were also used to approximate the antiphase boundary energy.

3.2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used for both microstructural analysis and fractography. Both the carbide morphology and distribution were characterized. The fractography was used to determine the microstructural features that were important in understanding the fracture micromechanisms. Comparing the fractographic features on matching fracture halves was used to better characterize the fracture mechanism. Other techniques such as plateau etching (69), fracture face fractography, and microstructure fracture surface fractography (from sectioning), were employed.

3.2.4 γ' Analysis

The deformation behavior of superalloys was dependent upon the character of the strengthening phase. In the case of Alloy X-750 the material was strengthened by γ' . Therefore, to determine the interaction of the microstructure with dislocations it was important to characterize the γ' . The most accurate method of determining the lattice parameter and the volume fraction of γ' , a technique involving anodic dissolution of the matrix and subsequent filtering out of the γ' , as described in Ref (9). The specimen was suspended in water-base solution containing 1% citric acid and 1% ammonium sulfate with an applied current density of 100 mA/cm². Most of the γ' remains adhered to the specimen surface following

dissolution and was removed using a rubber spatula. Some of the γ' was also suspended in solution, therefore the solution was filtered. By comparing the weight of the γ' recovered to the amount of material dissolved, the weight fraction of the γ' was calculated. It should be noted that this weight includes the carbides since they do not dissolve during the dissolution process. The exact volume fraction of γ' was then determined by subtracting the weight fraction of primary carbides and Cr_{23}C_6 as determined by a separate analysis. The lattice parameter of the γ' was determined by X-ray diffraction analysis. This can be compared to the lattice parameter of the matrix, also determined by X-ray techniques. The separated γ' was chemically dissolved in a 20% HCl/water solution and analyzed by ICPS (Inductively Coupled Plasma Spectroscopy). The chemical composition of the matrix also was determined by using ICPS on the filtrate from the γ' dissolution process. The carbide analysis consisted of an anodic dissolution in a 10% HCl/methanol solution which dissolved everything except the carbide particles. Using energy dispersive X-ray spectroscopy of the carbides the weight fraction of Cr, Ti, and Nb was determined. Assuming the carbide composition was either Cr_{23}C_6 or $(\text{Ti,Nb})\text{C}$ the weight fractions of the two types of carbides were determined. Back calculation of the chemistry matrix was performed by subtracting the chemistry of the γ' precipitates from the overall chemistry. The agreed well with the chemistry analysis of the matrix and supported the use of the electrolytic separation technique.

3.3 MECHANICAL TESTING

3.3.1 Testing to Determine Fracture Mechanisms

Round uniaxial tensile testing was used to study the effect of hydrogen on the fracture process. These tests were analyzed to determine:

- 1) % reduction in area (% RA)
- 2) % fracture strain (plastic strain to failure)
- 3) % RA loss due to hydrogen : $100 \times (1 - (\text{RA in Aggressive Env} / \text{RA in Neutral Env}))$
- 4) Yield Strength
- 5) True Fracture Stress

In order to define the mechanism, an important question was whether the fracture criterion occurred at a critical stress, critical strain, or some combination thereof. The testing described below was developed to answer this question as well as the microstructural feature controlling the fracture behavior.

3.3.1a Uniaxial Tensile Specimens Tested to Fracture

Subsize tensile specimens were tested at room temperatures with varying amounts of dissolved hydrogen. These tests used cylindrical subsize specimens fabricated according to ASTM E8 with a nominal gage diameter of 0.635 cm. The rate controlling parameter for hydrogen enhanced fracture may be a thermally

activated event. In order to understand the effect of thermal activation, the testing was performed at room temperature at different strain rates as well as subzero and elevated temperatures.

3.3.1b Uniaxial Tensile Specimens Strained Prior to Hydrogen Charging

In a fracture process that includes void initiation and growth or that relies on hydrogen interaction with dislocations, plasticity was required for the embrittlement. This testing was to confirm that plastic deformation was required for the fracture in hydrogen charged specimens. Specimens were strained to 1.6%, 5%, and 10% plastic strain prior to hydrogen charging thereby increasing the stress required for plastic flow, the flow stress. This technique was used to define the parameter that controls fracture. A comparison was made of the prestrain load, the fracture load, and the fracture strain after charging. The effect of loading rate on these parameters was also investigated. If the pretrained specimens fail during loading at the same stress as the unstrained specimens, this would suggest that a critical stress was the appropriate failure parameter. If the specimens fail after some amount of plastic deformation, the correct failure criteria may relate to some plastic strain increment after charging.

3.3.1c Single Edge Notch Bend Specimens

The hydrogen charged single edge notched bend (SENB) specimens were tested at room temperature at a loading rate of 0.005 cm/min. The notch root radius was 0.25 mm with an included angle of 45°. The thickness was 5.6 mm with a width of 102 mm and a span of 408 mm. The applied loads ranged from the fracture load to 87% of the fracture load. After loading, the specimens were sectioned along the midplane of the thickness and metallographically prepared and examined. These specimens were then serial ground and polished at 0.25 mm intervals. The purpose of the sectioning was to observe the location of crack initiation.

3.3.1d Fracture Toughness Testing

To understand how both hydrogen and microstructure affect the fracture in these materials, fracture mechanics specimens, 1 cm thick compact tension specimens, were employed. It was discovered that a valid J test was not possible on the noncharged specimens using this size specimen due to crack tunnelling. In order to obtain valid J tests on the noncharged specimens, 0.6T specimens (1.52 cm thick) with a 20% side groove were tested. The larger side grooved specimens were required due to excessive tunnelling when the side grooves were not present. Specimens were precracked at a frequency of 30 Hz at a final K_{max} of 16.5 MPa $\sqrt{m}$

and required between 200,000 and 400,000 cycles to reach the desired crack length. After precracking selected specimens were hydrogen charged per the method described in the hydrogen autoclave and loaded in displacement control. The specimens tested were listed in Table 3.3.1d.1. The loading rates were varied in the charged and noncharged specimens to determine if there was an effect of loading rate. If hydrogen diffusion to the hydrostatic stress region or hydrogen-dislocation interaction were important, then a slower loading rate should produce a lower fracture toughness value. The fracture toughness of the hydrogen-charged specimens was determined by using linear-elastic fracture toughness testing while for the noncharged specimens elastic-plastic fracture toughness testing was employed. The hydrogen-charged 0.4T compact tension specimens tested at room temperature were loaded using rates that varied by a factor of 15. The tests were run according to ASTM E399-90 to determine K_{Ic} . Noncharged specimens were tested using ASTM E399-90 as well as ASTM E813-81. ASTM E813-81 was used instead of the more-recent E813-89 since the methodology used to develop a procedure for estimating K_{Ic} from J_{Ic} was established using analysis procedures that are consistent with ASTM E813-81. The method for calculating the J integral used the 1989 specification while the calculation of J_{Ic} used the 1981 specification. This is because the calculation of J itself has been better refined since that time. It should be noted that K_{Ic} if computed using J_{Ic} as determined from ASTM E813-89, is 5% higher than the value calculated per the 1981 standard. It was not possible to perform a J test on the hydrogen-charged specimens. Once cracking initiated in the hydrogen

charged specimens, during the hold prior to the unload portion stable cracking was observed due to a hydrogen enhanced cracking phenomenon.

TABLE 3.3.1d.1

Precracked Compact Tension Specimens Using Various Loading Rates

	<u>Hydrogen Charged</u>	<u>No Hydrogen</u>
<u>Strain Rate</u> (cm/min)	0.025, 0.0025, 0.0005	0.025, 0.008
<u>Loading Rate</u> (MPa√m/min)	33, 3, 0.6	33, 11

Two 0.4T compact tension specimens that were bolt loaded, constant displacement, after hydrogen charging were used to determine the threshold stress intensity factor for crack growth of internally charged specimens. The specimens were precracked prior to hydrogen charging. After hydrogen charging, one specimen was loaded to 52 MPa√m and one to 58 MPa√m. The crack growth was monitored using AC potential drop as described in ASTM E647. The potential drop crack lengths were compared to values determined from destructive examinations at the end of the precrack, start of test, and at the end of the test. The final crack length was determined by tinting in air at 400°C. The bolt was removed prior to heat tinting. Most of the cracking was observed in the first 5 hours, the specimen was run for 300 hours to confirm that the stress measured was a real threshold value.

3.3.2 Testing to determine Deformation Characteristics

It was important to understand the deformation characteristics of the material and how they relate to the fracture process. There were two methods that effectively elucidate the controlling mechanisms. The first was a study of the surface slip bands on a polished flat uniaxial specimen. The second was a more extensive study of the deformation, which includes its localization and character. These features were revealed using specimens that have been strained to various strain levels and analyzed with the transmission electron microscope as discussed previously. These results contribute to an understanding of the deformation stages that lead to fracture.

3.3.2a Uniaxial Tensile Specimens Tested to Fixed Deformations

The uniaxial tensile testing was also performed on specimens not strained to failure. These specimens were used for the transmission electron microscopy in order to determine the dislocation morphology.

No Hydrogen	Hydrogen Charged
Room temperature 0.5% ϵ , 2.5% ϵ	Room temperature 0.5% ϵ , 2.5% ϵ

The above tests used round subsize specimens according to ASTM E8 with a nominal gage diameter of 0.635 cm with a gage length of 2.54 cm.

3.3.2b Flat Uniaxial Tensile Specimens

Flat uniaxial tensile specimens with a gage length of 1.25 cm, 0.25 cm wide and 0.175 cm thick were used to understand the deformation character. The specimens were polished to a metallographic finish prior to hydrogen charging. These specimens were extended to plastic strains between 2.5% and 8%. Light and scanning electron microscopy were used to determine the character of the slip. The bands were described as fine or coarse bands and as planar or wavy slip. This technique allows bulk samples to be described which reduces the possibility of being misled by studying small areas by transmission electron microscopy.

3.3.2c Stress-Relaxation Testing

Round uniaxial tensile specimens were used for the stress relaxation testing. The load and strain were each recorded as a function of time. Throughout the test the strain was monitored using a digital volt meter to ensure that the strain was constant.

The stress-relaxation testing was performed on specimens at room temperature. The possibility of interaction of carbon and hydrogen at dislocations

prevents the testing at temperatures higher than room temperature. Stress relaxation was performed on specimens with and without internally charged hydrogen at various strain levels. The stress relaxation was performed on a servohydraulic machine with the capabilities for strain and stroke control. The elastic compliance of the system including the specimen was 29GPa while the modulus of the specimen was 213GPa. This was achieved by having no more than 15 cm between the specimen and the servohydraulic valve and no more than 15 cm between the specimen and the load cell and mount. The stress relaxation was performed at strain levels from 1% through 21% plastic strain.

The stress-relaxation test was run under constant strain conditions so that the increase in plastic strain and plastic strain rate are equal to and opposite in sign to the elastic strain and elastic strain rates. The elastic strain was calculated by dividing the change in stress by the elastic modulus. The elastic strain rate was given by the change in elastic strain divided by the change in time. Stress relaxation testing was able to give the change in plastic strain rate as the stress was changing while the material maintains a constant structure.

3.3.2d Strain-Rate Change Testing

Round uniaxial tensile specimens were used for the strain-rate change (SRC) testing. The SRC testing was performed using a servohydraulic MTS system in strain control. The load, strain and time were recorded using a data acquisition system. The SRC testing was performed on specimens with and without internally charged hydrogen at room temperature. The strain-rate changes were performed at plastic strain levels of 1% and 2% for all specimens and up to 20% for noncharged specimens. The strain-rate change testing was another method to determine activation areas. In this test the strain rate applied to the specimen was increased or decreased by at least one order of magnitude. This change in strain rate gives rise to a change in load. These data were then analyzed using the same method as described for stress relaxation testing. There are two methods that were used to determine the change in load due to the change in strain rate. The first method calculates the change in load based on the instantaneous change in load. The second method extrapolates the load strain curve back to the strain where the rate was changed. A comparison of these two methods was made in the results and discussion section as well as a comparison to the stress relaxation testing.

4.0 RESULTS AND DISCUSSION

4.1 MICROSTRUCTURAL CHARACTERIZATION

The bulk composition was:

CHEMICAL ANALYSIS

Major Elements (wt %)

Ni	Cr	Nb + Ta*	Ti	Al	Fe	C	B
71.17	15.46	1.00	2.67	0.76	8.33	0.072	0.006

Minor Elements (wt. %)

Mn	Si	S	Co	P	V	As	Cu
0.10	0.11	.001	0.07	.007	0.02	< 10 ppm	0.01

* - tantalum is a trace impurity and not intentionally added with the niobium

The mean intercept grain size of this material was determined to be 125 μm as shown in Figure 4.1.1. There were small discrete carbide precipitates decorating the grain boundaries as depicted in the TEM micrograph of Figure 4.1.2. This carbide, from TEM diffraction patterns, was M_{23}C_6 . There were also primary carbides and nitrides, $\text{M}(\text{C},\text{N})$, aligned along the rolling direction. The metal constituent in the primary carbides and carbonitrides were approximately equal amounts of Nb and Ti, as determined from SEM energy-dispersive X-ray

spectroscopy. The lattice parameters of the primary carbides and further confirmation of their structure was determined from X-ray diffraction.

The technique of dissolving the matrix, subsequent filtering of the γ' and carbides and ICPS (Inductively Coupled Plasma Spectroscopy) analysis of the filtrate was used to determine the matrix composition. The matrix composition was:

Chemistry of Matrix

	Ni	Fe	Cr	Al	Ti	Nb
wt. %	72.7	8.4	16.7	0.37	1.2	0.6
at. %	70.5	8.6	18.3	0.78	1.4	0.37

The matrix was enriched in Cr and depleted in Al, Ti, and Nb as compared to the chemistry of the overall alloy. This was expected since the Al, Ti, and Nb partition to the γ' precipitates.

Figure 4.1.1 Microstructure of
HTH Alloy X-750

Figure 4.1.2 Grain Boundary Carbides
of HTH Alloy X-750

Figure 4.1.3a
Fine Scale Microstructure
Bright Field of γ'

Figure 4.1.3b
Fine Scale Microstructure
Dark Field of γ'

The strengthening phase in this alloy was γ' . Due to the relatively low misfit, the γ' was expected to be a coherent phase. The size of the γ' ranged from 10 to 25 nm with an average of 20 nm. A rounded cuboidal shape was observed, which was consistent with the previous discussion of obtaining a cuboidal structure when the misfit was between 0.3% and 0.75%. As discussed in Appendix 2, the majority of the strengthening was from antiphase boundary strengthening with additional strengthening caused by the coherency strain of the precipitates.

Using the technique of separating the γ' by anodic dissolution and then by comparing the weight of the γ' recovered to the amount of material dissolved, the volume fraction was 0.13. This weight included the carbides since they do not dissolve during the dissolution process. A second dissolution process to dissolve all constituents except the carbides resulted in a weight fraction of carbides of 0.004. Therefore, the weight fraction of the γ' was 0.126. X-ray diffractometry of the extracted γ' showed no evidence of the metal. The lattice parameter of the γ' was 3.592Å. X-ray diffractometry of the matrix resulted in a lattice parameter of 3.569Å.

The chemical composition of the γ' was determined using ICPS as displayed in TABLE 4.1.1.

TABLE 4.1.1 Chemistry of γ'

	Ni	Fe	Cr	Al	Ti	Nb
wt. %	74.8	2.9	4.1	3.4	11.8	2.9
at. %	70.4	3.0	4.3	7.0	13.6	1.7

The chemistry of the γ' , assuming the Cr partitions equally to the Ni and Al

lattice sites as was described by Brown and Ham was

$(\text{Ni}_{0.93}, \text{Fe}_{0.04}, \text{Cr}_{0.03})_3(\text{Al}_{0.27}, \text{Ti}_{0.55}, \text{Nb}_{0.08}, \text{Cr}_{0.10})$. It was assumed that the Cr segregates equally to the Ni and Al sites since the Cr decreased the antiphase boundary energy.

4.2 Tensile Testing

The heat chosen for the mechanical testing was used because it had the unique property of failing by an intergranular mode with no dissolved hydrogen.

The tensile properties were evaluated to determine the effect of hydrogen concentration, strain rate, and temperature on the embrittlement process. The tensile properties were displayed in Table 4.2.1.

TABLE 4.2.1 TENSILE PROPERTIES OF HTH ALLOY X-750

Hydrogen Concentration (wppm)	Yield Stress (MPa)	True Fracture Stress (MPa)	Fracture Strain (%)	Reduction in Area (%)	% RA loss	Strain rate (s ⁻¹)	Temp. (°C)
0	861	1399	13.5	14	0	3.33x10 ⁻⁴	-196
0	814	1482	23	24	0	3.33x10 ⁻⁴	-25
0	819	1375	21.2	22.1	0	3.33x10 ⁻⁴	25
0	809	1424	22	24	0	3.33x10 ⁻⁵	25
0	800	1385	21.5	—	0	3.33x10 ⁻⁴	65
0	766	1359	23	26	0	3.33x10 ⁻⁴	175
0	735	1378	30	—	0	3.33x10 ⁻⁴	285
5.7	801	1088	7.3	13.9	37	3.33x10 ⁻⁴	25
18	803	1009	4.3	11.5	48	3.33x10 ⁻⁴	25
52	806	942	2.5	8.4	80	3.33x10 ⁻⁵	25
65	902	1447	13.5	14	0	3.33x10 ⁻⁴	-196
65	837	1039	5.0	12	50	3.33x10 ⁻⁴	-25
65	837	997	3.5	7.4	69	5.00x10 ⁻⁵	-25
65	817	1022	4.7	—	—	3.33x10 ⁻³	25
65	806	983	3.5	8.6	62	3.33x10 ⁻⁴	25
65	806	930	2.6	8.9	60	3.33x10 ⁻⁵	25
65	810	902	1.6	5.2	75	3.33x10 ⁻⁶	25
65	793	958	3.6	—	—	3.33x10 ⁻⁴	65
65	751	948	6.5	15	42	3.33x10 ⁻⁴	175
65	725	1145	13.5	—	—	3.33x10 ⁻⁴	285

The hydrogen had very little effect on the yield strength of the alloy. This was most likely due to the rate at which the tensile testing was conducted, which was from $3.33 \times 10^{-3} \text{ s}^{-1}$ to $3.33 \times 10^{-6} \text{ s}^{-1}$. As will be seen in a later section of the paper, the hydrogen affected the relaxation behavior. This was due to the slower strain rates resulting from the relaxation experiment.

The hydrogen had very little effect on the work hardening characteristics of this material. The work hardening exponent, n , was defined by the following equation:

$$\sigma = K \epsilon_{pl}^n \quad (4.2.1)$$

where σ was the true stress and ϵ_{pl} was the true plastic strain. The work hardening coefficient was a function of strain. For specimens that were not hydrogen charged at low strains the work hardening coefficient was 0.07 while at strains greater than 3% the strain hardening coefficient was 0.20. The strain hardening of the specimens charged with 5.7 ppm hydrogen was 0.05 at low strains and was approaching 0.20 for strains greater than 2%. The specimens with 65 ppm hydrogen had strain hardening exponents on the order of 0.05 for the first 2% plastic strain. The specimen failed at 2.5% strain and therefore it was not possible to determine the strain hardening exponent for large strains. A comparison of the true-stress versus true-plastic strain for the specimens tested was given in Figure 4.2.1.

THE EFFECT OF HYDROGEN ON THE TRUE-STRESS TRUE-STRAIN BEHAVIOR OF HTH ALLOY X-750

Figure 4.2.1

There was little effect of temperature on the shape of the stress strain curve as shown in Figure 4.2.2. Increasing the test temperature resulted in a shift of the stress-strain curve to lower stresses while the work hardening characteristics in the low stress regime remained constant. The work hardening was slightly higher in the high strain regime at the elevated temperature as compared to ambient temperature. The shift in the stress-strain curve was proportional to the change in the modulus with temperature. This was consistent with the equations developed in the appendix on the strengthening mechanisms which show that the strengthening mechanisms are proportional to the modulus.

The elongation was dramatically decreased by increasing hydrogen concentration. The elongation was 21% with no hydrogen and decreased to 7.3% with only 5.7 ppm hydrogen and was further reduced to 3.5% with 65 ppm hydrogen at 3.33×10^{-4} and room temperature. The decrease in the strain to failure and failure stress is portrayed in Figure 4.2.3. This material shows predominantly intergranular fracture in the noncharged state; the effect of hydrogen was to decrease the macroscopic strain to failure. A phenomenological view of the fracture process is that at some hydrogen concentration or temperature, the grain boundary carbide interface becomes weaker than the grain interior and the intergranular process becomes predominant. In the case of this alloy system at all temperatures tested, the failure mode is primarily intergranular. As explained above, it is expected that the decrease in ductility occurs due to the reduction in grain boundary carbide interface

strength. This is further supported by the fact that no void initiation was observed on noncharged specimens sectioned after 4% strain while charged specimens failed at strains as low as 1.6%. This does not preclude the idea that void growth characteristics are also altered. Though, changes in the void growth characteristics are not expected to alter the failure behavior to the extent observed. It should be noted that even at the highest hydrogen concentrations there is some amount of transgranular fracture. This suggests that some grain boundary carbides are more resistant to fracture possibly due to the grain boundary carbides being semicoherent with both grains instead of only one of the boundaries. A schematic representation of the effect of hydrogen on the grain boundary carbide strength is displayed in Figure 4.2.4. The effect of hydrogen was shown to be reversible. A hydrogen charged tensile specimen was annealed at 360°C in argon for three weeks prior to testing. This specimen showed the same properties as the noncharged specimen.

THE EFFECT OF TEMPERATURE ON THE TRUE-STRESS
TRUE-STRAIN BEHAVIOR OF HTH ALLOY X-750

FIGURE 4.2.2

EFFECT OF HYDROGEN ON THE FAILURE CRITERIA

FIGURE 4.2.3

SCHEMATIC REPRESENTATION OF THE EFFECTS OF
HYDROGEN ON THE STRENGTH OF THE GRAIN BOUNDARY
AND THE GRAIN INTERIOR

FIGURE 4.2.4

No effect of changing the strain rate was observed on the tensile behavior of the noncharged specimens. As shown in TABLE 4.2.1 the fracture stress and elongation showed no noticeable change as the strain rate was decreased for noncharged specimens. There was a small effect of strain rate on the elongation to failure for the hydrogen charged specimens. The elongation was decreased from 4.7% to 1.6% for a specimen with 65 ppm hydrogen as the strain rate was decreased from 3.33×10^{-3} to $3.33 \times 10^{-6} \text{ s}^{-1}$ at 25°C . This difference shows the need for hydrogen diffusion in the embrittlement of this superalloy. The trend of increasing the strain rate was the same as decreasing the temperature while the magnitude of the embrittlement as measured by the elongation to failure due to strain rate changes are smaller than those of changes in the temperature. The effect of strain rate on the elongation to failure was analyzed using a relationship of the form:

$$\varepsilon_f = A(\dot{\varepsilon})^B \quad (4.3.2)$$

where A is 0.12 and B is 0.153 for 65 ppm hydrogen over the range of strain rates tested. Evaluation of this equation to determine the strain rate required to have no embrittlement results in a strain rate of 30 s^{-1} . It should be noted that this equation does not show a plateau in the embrittlement once the strain rate drops below a critical value. In order to determine if such a phenomenon exists, testing at much lower rates would be required.

The effect of temperature is represented schematically in Figure 4.2.5. Over a large part of the temperature range tested, there was only a small effect of temperature on the tensile properties of the noncharged specimens. Though, at -196°C , the noncharged specimen did show a decrease in the ductility. There was a large effect of temperature on the hydrogen charged specimens. As the temperature decreased below 65°C , the ductility of the hydrogen charged specimens increased while that of the noncharged specimens was decreased. In fact, at -196°C and a rate of 3.33×10^{-4} , hydrogen did not degrade the mechanical properties. Therefore, the role of hydrogen diffusion or hydrogen interaction with dislocations may be a key component in the phenomena of hydrogen embrittlement. The diffusion of hydrogen to the high hydrostatic stress region could not explain these results either. If hydrogen diffusion to the hydrostatic stress region ahead of the crack tip controlled the fracture process, then one would expect that the specimen with 65 ppm hydrogen tested in liquid nitrogen would be embrittled at least as much as the specimen with nominally 5.7 ppm hydrogen tested at 25°C . The strain rate used for the testing at -196°C was much faster than the critical strain rate for the dislocation to break away from the hydrogen atmosphere.

EFFECT OF TEMPERATURE AND STRAIN RATE ON THE
FRACTURE ON CONDITION HTH ALLOY X-750

Hydrogen charged 3.33E-4/s $\square$ Hydrogen charged 3.33E-5/s $\triangle$ Hydrogen charged 3.33E-3/s $\circ$
 Hydrogen charged 5E-5/s $-$ No Hydrogen 3.33E-4/s $-*$ Hydrogen charged 3.33E-6/s $\blacktriangle$

FIGURE 4.2.5

The following equation describes the critical strain rate where hydrogen is capable of diffusing fast enough to move along with the dislocation.

$$\dot{\epsilon} = \rho_H b v_c \quad (4.2.3)$$

where v_c - critical dislocation velocity to break away from Cottrell atmosphere
 b - Burger's vector
 ρ_H - mobile dislocation density to transport hydrogen

The equation used for determining the critical velocity was previously developed in Reference (70). This equation is:

$$\bar{v}_c = \frac{D_H}{kT} \cdot \frac{E_B}{30 b} \quad (4.2.4)$$

where D_H - hydrogen diffusion in cm^2/s
 E_B - binding energy of hydrogen to the dislocation
 k, T - Boltzman constant and absolute temperature, respectively
and the other constant are described above.

In order to analyze the effect of temperature, the hydrogen diffusion equation must be known as well as the binding energy for hydrogen to the dislocations. A binding energy from 0.1 to 0.2 eV has been reported (66). A conservative estimate of 0.2 eV was used. The hydrogen diffusion equation was developed in Appendix 1. The

hydrogen diffusion equation is:

$$D_H = 0.016 \exp \left[\frac{-49,000}{R T} \right] \quad (4.2.5)$$

where R is in J/mol and T is in degrees Kelvin.

At -196°C, assuming a dislocation density of $10^8/\text{cm}^2$, the critical strain rate is $10^{-36}/\text{s}$. Therefore, at -196°C, the hydrogen was not expected to move with the dislocation. At room temperature the critical strain rate was 6×10^{-3} for a dislocation density of $10^8/\text{cm}^2$. Hydrogen was expected to diffuse with the dislocations at the strain rates used in this experiment for room temperature and above. At -25°C, the critical velocity was 1×10^{-4} which is near the fastest strain rate tested at that temperature, and it is expected, within the approximations in the calculation, that hydrogen would diffuse with the dislocations. The lack of degradation at -196°C may also be partially caused by the embrittlement mechanism being hydrogen enhanced local plasticity (HELP). As discussed above, there is no interaction between the hydrogen and mobile dislocations at this temperature.

Another factor that must be accounted for when analyzing this data is that the minimum in ductility occurs at a higher temperature in X-750 than in pure nickel. This may be due to the lower diffusivity of hydrogen in the alloy as compared to pure nickel (67). A minimum in ductility as a function of temperature suggests that there are two competing processes that influence the embrittlement. The first

process is hydrogen diffusion which is enhanced as the temperature is increased. As diffusion is increased, more hydrogen is supplied to the dislocations or the location of crack initiation. The second process is the trapping of hydrogen at dislocations or precipitates. The fraction of trapped hydrogen is decreased as temperature is increased. In order to separate these two processes, the strain rate was normalized by the diffusivity for the specimens with 65 ppm hydrogen. The results are displayed in Table 4.2.2

TABLE 4.2.2 EFFECT OF STRAIN RATE AND TEMPERATURE ON
THE FRACTURE BEHAVIOR

failure strain for hydrogenated (65 ppm)	failure strain for noncharged	Strain rate (s ⁻¹)	Temp. (°C)	Diffusivity (cm ² /s)	strain rate/ Diffusivity
14	14	3.33x10 ⁻⁴	-196	7.1x10 ⁻³⁷	4.7x10 ³²
5	23	3.33x10 ⁻⁴	-25	7.8x10 ⁻¹²	4.3x10 ⁷
3.5	23	5x10 ⁻⁵	-25	7.8x10 ⁻¹²	6.4x10 ⁶
4.7	21	3.33x10 ⁻³	25	4.2x10 ⁻¹⁰	7.9x10 ⁶
3.5	21	3.33x10 ⁻⁴	25	4.2x10 ⁻¹⁰	7.9x10 ⁵
2.6	21	3.33x10 ⁻⁵	25	4.2x10 ⁻¹⁰	7.9x10 ⁴
1.6	21	3.33x10 ⁻⁶	25	4.2x10 ⁻¹⁰	7.9x10 ³
3.6	21	3.33x10 ⁻⁴	65	4.3x10 ⁻⁹	7.6x10 ⁴
6.5	23	3.33x10 ⁻⁴	175	3.1x10 ⁻⁷	1.1x10 ³
13.5	30	3.33x10 ⁻⁴	285	4.2x10 ⁻⁶	8.0x10 ¹

A comparison of specimens that have the same ratio of strain rate to diffusivity reveals that as the temperature is decreased, the embrittlement was slightly more severe. This is observed by comparing specimens at -25°C and 25°C as well as specimens at 25°C and 65°C . The effect of trapping on embrittlement is more pronounced at over 65°C . In those cases, the diffusion is much quicker than at 25°C yet the embrittlement is less severe. Above 65°C the ductility of the noncharged specimens was slightly increased while the ductility of the hydrogen charged specimens, as portrayed in Figure 4.2.5, was substantially increased. As has been discussed in previous papers ((72),(70)) hydrogen transport by dislocations may be important.

The effect of testing at 175°C was to slightly increase the ductility of the noncharged specimens and to substantially increase the ductility of the hydrogen charged specimens as displayed in Table 4.2.2. This suggests that diffusion was not the only factor that must be incorporated into understanding the hydrogen enhanced fracture. The trapping at grain boundary carbides may also be very important since the embrittlement occurred at temperatures as high as 285°C where there is limited interaction with dislocations(71). Trapping of hydrogen at precipitates has been observed to continue over 300°C (73).

Therefore, hydrogen trapping at precipitates may be a key component in the hydrogen embrittlement of this alloy with hydrogen transport to local areas of stress

concentration and hydrogen interaction with dislocations may also be contributing factors in the embrittlement.

The effect of hydrogen appears to reduce the strain required to initiate microvoids while there may be secondary effects on the void growth properties. These voids link together to form microcracks. The microcracks were internal to the specimen. One tensile specimen that was hydrogen charged to 65 ppm hydrogen and strained at $3.33 \times 10^{-5} \text{ s}^{-1}$ was unloaded just prior to failure. As noted in Figure 4.2.6, the grain boundaries were separating and appear as a microcrack. In Figure 4.2.6b, inside of the crack ductile ligaments are still intact. The fracture of these ligaments is the void coalescence event.

FIGURE 4.2.6a Microcrack Nucleation
in a Hydrogen Charged Tensile Specimen

↑
↓
tensile
axis

FIGURE 4.2.6b Microcrack Nucleation
in a Hydrogen Charged Tensile Specimen

The fracture morphology of all the tensile specimens was examined using the scanning electron microscope. In noncharged specimens tested at 25°C the grain-boundary facets were covered with well formed microvoids as depicted in Figure 4.2.7. These intergranular facets contain ledges which were the result of nonuniform deformation consisting of channels of dislocations. Hydrogen charged specimens tested at 25°C resulted in reduced ductility as compared to the noncharged specimens. The addition of hydrogen resulted in less well defined microvoids as depicted in Figure 4.2.8. Hydrogen acted to decrease the strain needed to initiate the defects. Once initiated, the coalescence process may have been either grain-boundary decohesion or by localized strain. Either coalescence process would result in minimal macroscopic strain. Fractography of secondary cracking of the hydrogen charged specimen tested at 25°C showed that the initiation sites for the microvoids were the grain-boundary-carbide particles. Figure 4.2.9 depicts a void that initiated around a carbide particle. An analysis of matching fracture halves showed that in the noncharged specimen the voids initiated around a particle and then grew due to gross plastic deformation. The resulting fracture surface was like those of the typical ductile dimple fracture. Hydrogen charged specimens also showed the typical ductile dimple fracture surface. Sectioning of tensile specimens in which the straining was stopped just prior to failure has shown cracks on the order of one to two grains. This suggests that the fracture was not a initiation controlled event.

The fracture morphology of the tensile specimens tested at 285°C for both the hydrogen charged and the noncharged specimens was a mixture of intergranular facets containing fine dimples and a small amount of transgranular dimpled fracture surface. The fracture morphology for the noncharged specimens is shown in Figure 4.2.10 and the morphology for the hydrogen charged specimens is displayed in Figure 4.2.11. There is no noticeable fractographic difference between these two specimens while the elongation of the noncharged specimen was twice that of the hydrogen charged specimen. This further supports the premise that the role of hydrogen is to reduce the strain to initiate the voids while the strain for growth was not altered. Also, the void size of the hydrogen charged and noncharged specimens are the same, the hydrogen is not affecting the number of void initiation sites. This was expected since in the noncharged case the void spacing is approximately the same as the carbide precipitate spacing. Therefore, most of the precipitates are already involved in the fracture process. Fractography was performed on the specimens tested below 0°C as well. The specimens did not exhibit any difference between the hydrogen charged and noncharged specimens continuing to support the role of hydrogen altering the void initiation process.

Figure 4.2.7a Fractography of
Noncharged Specimen Tested at 25°C

Figure 4.2.7b Fractography
of Noncharged Specimen Tested at 25°C

Figure 4.2.7c Fractography of
Noncharged Specimen Tested at 25°C

Figure 4.2.7d Fractography
of Noncharged Specimen Tested at 25°C

Figure 4.2.8a Fractography of Hydrogen Charged Specimen Tested at 25°C

Figure 4.2.8b Fractography of Hydrogen Charged Specimen Tested at 25°C

Figure 4.2.8c Fractography of Hydrogen
Charged Specimen Tested at 25°C

Figure 4.2.8d Fractography of Hydrogen
Charged Specimen Tested at 25°C

Figure 4.2.9 Fractography
of Hydrogen Charged Specimen
Void Nucleating at $M_{23}C_6$ particle

Figure 4.2.10a Fractography of Noncharged Specimen Tested at 285°C

Figure 4.2.10b Fractography of Noncharged Specimen Tested at 285°C

Figure 4.2.11a Fractography of Hydrogen
Charged Specimen Tested at 285°C

Figure 4.2.11b Fractography of Hydrogen
Charged Specimen Tested at 285°C

The use of the prestraining the specimens, i.e. cold working, prior to hydrogen charging was discussed previously as an experimental method that may contribute to the understanding of the fracture mechanism. It was necessary to determine if the prestrain affected the solubility of hydrogen and would then produce a "different" starting material. Hydrogen analysis was performed on specimens that were hydrogen charged at 360°C after prestraining. The results were shown in Table 4.2.3. There was no effect of prestrain observed on the hydrogen solubility. There have been studies which show that dislocations trap hydrogen in the nickel base alloys with a binding energy near 0.1 electron volts (eV)(71). Using the this binding energy, the calculated trapped hydrogen was below the sensitivity of the equipment.

TABLE 4.2.3 EFFECT OF STRAIN ON HYDROGEN SOLUBILITY

Strain prior to hydrogen charging	0%	1%	10%	20%
Hydrogen solubility at 360°C and 5000psi H ₂ (ppm)	65	65	64	66

Table 4.2.4 displays the data on the specimens that were strained prior to hydrogen charging and subsequently strained to failure as well as illustrated in Figure 4.2.12.

TABLE 4.2.4 EFFECT OF STRAIN PRIOR TO HYDROGEN
CHARGING ON FRACTURE STRAIN

Strain rate (s ⁻¹)	Strain prior to H charging	True Stress prior to H charging (MPa)	Hydrogen concentration (ppm)	Plastic Failure strain after charging	True Failure stress after charging
3.33x10 ⁻⁵	0	0	65	2.5%	930
3.33x10 ⁻⁵	5%	1030	65	0%	1035
3.33x10 ⁻⁵	10%	1186	65	0%	1166
3.33x10 ⁻⁴	0	0	65	3.5%	983
3.33x10 ⁻⁴	1.6%	871	65	2.5%	980
3.33x10 ⁻⁴	5%	1019	65	0.6%	1041
3.33x10 ⁻⁴	10%	1182	65	0.2%	1170

THE EFFECT OF PRESTRAIN ON THE FRACTURE STRESS

FIGURE 4.2.12

The specimen prestrained to 1.6% plastic strain failed at an additional 2.5% plastic strain after hydrogen charging. The final failure stress was the same as the failure stress for the nonprestrained specimen while the total strain, prestrain added to the strain after charging, was slightly higher than the nonprestrained specimen. This suggests that a critical stress was needed for fracture. The specimen prestrained to 1.6% showed a yield point phenomenon after the hydrogen charging. This is to be expected since the temperature for hydrogen charging is in the range where Alloy X-750 exhibits dynamic strain aging. At both strain rates used, the specimens that were prestrained to 5% or 10% failed near the final stress where the prestraining was stopped. At the lower strain rate, 3.33×10^{-5} , the specimens exhibited no gross plasticity once this load was reached. At the higher strain rate the specimen exhibited some macroscopic plasticity once the prestrain final load was achieved, though the load never exceeded the final prestrain load. In all cases prestraining increased the critical fracture load. This study shows that in the presence of hydrogen some local plastic deformation was essential for the onset of intergranular fracture and that high loads may be achieved by a specimen as long as plastic yielding does not occur. A critical stress criterion alone would then not describe the fracture process. Since the specimens at the lower strain rate did not fail until the new flow stress was achieved, this implies that at least local grain boundary plasticity is required. The failure criteria may then be that both a critical stress must be achieved as well as a critical strain. This is similar to what was shown by Lewandowski and Thompson (47), that even for cleavage fracture, some

amount of plasticity was required to initiate the cleavage crack. Using double notched bend specimens, they showed that the crack would initiate at sites closer to the notch tip than the peak stress location. It was further shown that the fracture stress was temperature dependent and that strain was important for the fracture. Since no gross plasticity was noted in these specimens, there would have been little transport of hydrogen due to dislocation motion. This suggests that the time dependence may be due to hydrogen diffusion and not dislocation sweeping.

Figure 4.2.13 Fractography of Hydrogen
Charged Specimen Prestrained 10%

4.3 Rising Load Tests of Notched Bend Specimens

SENB (Single Edge Notch Bend) specimens were loaded in three point bending. The nominal stress at maximum load was 860 MPa while a slight deviation from linearity of the load-displacement curve occurred at 750 MPa. Fractography of the failed specimen showed that the predominant fracture mode was intergranular. Serial grinding of specimens loaded to nominal stresses of 800 MPa and 822 MPa revealed the initiation of cracking occurring between 0.127 mm and 0.177 mm ahead of the notch tip. It should be noted that there was a small ductile tear at the notch tip in these cases, the length of this transgranular crack was approximately 0.01 mm. Assuming that the crack length was the length of the crack plus notch length, the applied stress intensity factor was $64.5 \text{ MPa}\sqrt{\text{m}}$ which would generate a plastic zone size on the order of 0.33 mm with the maximum stress at 0.02 mm ahead of the crack tip according to the work of Rice and Johnson (81). Since the crack started well ahead of the notch or crack tip, the fracture was controlled by the notch stress field which continues to support a failure criterion based on achieving both a critical stress and strain. If a critical strain criterion controlled the fracture, initiation of a microcrack would be expected to initiate on the grain boundaries at the notch tip where the strain was maximized; this was not observed. If the fracture were purely stress controlled, the fracture would be observed at .25 mm ahead of the notch tip where the stress was maximized; this was not observed. These results suggest it was a combination of the stress and strain. Figure 4.3.1 shows the initiation event occurring ahead of the notch tip.

Figure 4.3.1b Etched
Micrograph of Crack Initiation

Figure 4.3.1a As-Polished
Micrograph of Crack Initiation

In order to analyze the data, the finite element work of Griffiths and Owen was used (74). While the geometries of the two specimens were slightly different, the notch radius and the notch angles were the same. The elastically calculated stress concentration factors for the geometry used in this work and in the work of Griffiths and Owen were similar. The finite element method (FEM) showed that the stress was maximized at approximately 0.25 mm ahead of the notch tip. The stress at the surface for the nominal applied stresses of 800 MPa to 822 MPa was 980 MPa while at approximately 0.25 mm ahead of the notch tip the stress increases to 1570 MPa and at 0.125 mm the stress was 1440 MPa. The strain on the other hand decreases from 1.4% at the notch tip to 0.4% at 0.125 mm ahead of the notch tip. This suggests that for modeling the fracture phenomena, a critical strain of 0.4% may be used. The work of Griffiths and Owen assumed a plain strain stress state, which was not the case at hand. Thus, their work was only used qualitatively. The strain distribution would be different in a plane stress condition.

4.4 Fracture Toughness Properties

As stated in the procedure, the fracture toughness of the hydrogen charged specimens was determined by using linear-elastic fracture toughness testing while for the noncharged specimens elastic-plastic fracture toughness testing was employed. The results from the fracture toughness testing were displayed in Table 4.4.1. The fracture toughness testing of the hydrogen charged specimens resulted in valid K_{Ic} values as determined by ASTM E399-90, there were two tests used to determine

fracture toughness values for the noncharged material, the first displays K_Q from ASTM E399-90 and the second determines K_{Jc} as determined from ASTM E813-81 as well as a K_Q from ASTM E399-90. It should be noted that when K_{Jc} was computed using J_{Ic} as determined from ASTM E813-89, the calculated fracture toughness was 5% higher. The specimen for the J-integral testing were the 20% side-grooved 0.6T compact tension specimens. This specimen design resulted in valid J_{Ic} tests.

TABLE 4.4.1 FRACTURE TOUGHNESS PROPERTIES OF HTH ALLOY X-750

Hydrogen conc. (ppm)	Loading Rate (cm/min)	Loading Rate (MPa√m/min)	K_{Ic} or K_Q (MPa√m)	Valid per ASTM E399	K_{Jc} (MPa√m)	Valid per ASTM E813
0	0.025	33	98	No (size requirements)	--	--
0	0.005	7	101	No (size requirements)	147 ($T_r=23$)	Yes
40	.0025	3	53	Yes	--	--
65	0.025	33	52	Yes	--	--
65	0.0025	3	45	Yes	--	--
65	.0005	0.7	42	Yes	--	--

The fracture toughness was dramatically decreased by hydrogen charging the specimens. The fracture toughness dropped from 147 MPa√m with no hydrogen to as low as 42 MPa√m with 65 ppm hydrogen.

The loading rate also affected the toughness of the hydrogen charged specimens. The change in fracture toughness due to a change in loading rate was small compared to the change in fracture toughness due to hydrogen charging. As shown in TABLE 4.4.1, K_{Ic} decreased from 52 MPa√m when loaded quickly to 42 MPa√m when loaded at a slower rate. The loading rate effect may have been caused by hydrogen diffusion to the hydrostatic stress region at the tip of the crack and hydrogen interaction with dislocations. No such strain rate effect was observed on the noncharged specimens for the rates investigated.

In Alloy X-750 the fracture toughness of specimens, K_{Ic} , was approximately the same as the threshold value determined from a threshold test from a bolt-loaded hydrogen-charged specimen. The fracture toughness of a specimen with 40 ppm hydrogen was 53 MPa√m. A specimen with 40 ppm hydrogen was quickly bolt-loaded to 57 MPa√m. The crack growth rate was initially 2.5×10^{-6} m/s but rapidly decreased to 2.5×10^{-8} m/s at 49 MPa√m and at 48 MPa√m no cracking was observed. The 48 MPa√m was slightly below the observed fracture toughness measured on the rising load specimen at 0.0025 cm/min. The reason for the lower threshold was again based on the increased time for hydrogen diffusion to the local

fracture site and increased interaction of hydrogen with dislocations and other defects.

Scanning electron microscopy of the fracture surface of specimens was used to analyze the fracture morphology. In noncharged specimens there was a mixture of transgranular and intergranular fracture morphologies. The grain-boundary facets were covered with well formed microvoids as depicted in Figure 4.4.1. The transgranular areas were also covered with well formed microvoids, though much larger than the intergranular voids also depicted in Figure 4.4.1. Hydrogen charging the specimens resulted in reduced toughness as described previously. The fracture surface was completely intergranular. The addition of hydrogen appears to have also slightly reduced the size of the intergranular voids as depicted in Figure 4.4.2. The presence of hydrogen may have been to decrease the strain needed to initiate the defects. Once initiated, the voids acted as local stress concentrators. The increased stress then would have resulted in localized deformation and growth of the voids.

Figure 4.4.1b Fractography
of Noncharged Specimen
Interggranular dimples

Figure 4.4.1a Fractography of
Noncharged Specimen
Transgranular dimples

Figure 4.4.2 Fractography of
Hydrogen Charged Specimen
Intergranular dimples

4.5 STRESS-RELAXATION TESTING AND STRAIN RATE CHANGE TESTING

The plastic deformation of materials consists of both an athermal component and a thermally activated component that may be described by the Arrhenius type equation:

$$\dot{\epsilon} = \dot{\epsilon}_0 \exp - \left[\frac{(\Delta H_0 - \int b \Delta A d\sigma)}{k T} \right] \quad (4.5.1)$$

where

ΔH_0 - thermal activation enthalpy required for activation at zero applied effective stress,

ΔA - activation area,

b - Burgers vector,

k - Boltzman's constant, and

T - temperature ($^{\circ}\text{K}$),

and the numerator in the exponential was the total activation enthalpy for a given stress.

Differentiation of the logarithmic form of the equation, assuming $\dot{\epsilon}_0$ was not a function of stress, results in the following equation for constant dislocation substructure and density of mobile dislocations:

$$\frac{\partial \ln \dot{\epsilon}}{\partial \sigma} = \frac{b \Delta A}{k T} \quad (4.5.2)$$

Therefore, stress-relaxation and strain rate change testing were used to determine the effect of hydrogen on the activation area.

TABLE 4.5.1: Activation Area for Specimens Not Hydrogen Charged

Plastic Strain (%)	True Stress (MPa)	Activation Area Normalized by b^2 Stress Relaxation	Activation Area Normalized by b^2 Strain Rate change (instantaneous load)	Activation Area Normalized by b^2 Strain Rate Change (regressed load)
1	869	144	109	189
2	925	140	83	152
7	1076	90	69	138
11.4	1088	65.4	52	90
14	1263	65.9	-	-
16	1276	57.8	47	83
21	1309	50.6	-	-

TABLE 4.5.2: Activation Area for Specimens Hydrogen Charged (65 ppm)

Plastic Strain (%)	True Stress (MPa)	Activation Area Normalized by b^2 Stress Relaxation	Activation Area Normalized by b^2 Strain Rate change (instantaneous load)	Activation Area Normalized by b^2 Strain Rate Change (regressed load)
1	890	110	75	119
2	934	98	62	115

The activation areas for noncharged, Table 4.5.1, and hydrogen charged, Table 4.5.2, using three different methods have been analyzed. The first method utilizes stress relaxation testing as displayed in Figure 4.5.1a. The second and third methods use strain rate change testing to analyze the activation area as displayed in Figure 4.5.1b. The second method calculates the activation area using the instantaneous change in load when the strain rate was changed. The third method back extrapolates the change in load from the slope of the load strain curve after the specimen has come to steady state conditions at the new strain rate. The activation area as determined from method [2] results in the lowest activation area while method [3] results in the highest activation area, and the stress relaxation technique results in an activation area between methods [2] and [3]. The difference in these techniques may be explained by understanding how the internal structure changes during the test. The lowest activation area, and the most accurate, was determined at a constant internal structure as described by method [2]. Method [1] allows for

some change in internal structure during the relaxation such as pinning dislocations during the test. Method [3], due to the extrapolation, uses two different structures, the steady state structures for the two rates.

Stress-relaxation testing at room temperature was performed on specimens that had been deformed to plastic strain levels from one to ten percent with hydrogen concentrations to 65 ppm. The activation area as a function of strain was calculated and the results are shown in the following tables.

TABLE 4.5.3: Activation Area for Hydrogen-Charged Specimens

Plastic Strain (%)	Activation Area Normalized by the Burger's vector (5.7 ppm)	Activation Area Normalized by the Burger's vector (18 ppm)	Activation Area Normalized by the Burger's vector (65 ppm)
1	124	112	110
2	114	102	98
7	83.6		
10	71		

EFFECT OF HYDROGEN ON RATE OF STRESS RELAXATION

(Initial Strain: 2%; 25 C)

FIGURE 4.5.1a

STRAIN RATE CHANGE EXPERIMENTS ON
HYDROGEN CHARGED AND NONCHARGED SPECIMENS

FIGURE 4.5.1b

The results show that the activation area decreases slightly with the addition of hydrogen to the specimen and that the rate at which the hydrogen-charged specimens relaxed was slightly greater than the noncharged specimens as displayed in Figure 4.5.1a. The change in activation area due to hydrogen was extremely small. The measured change in activation area due hydrogen was smaller than the observed change in activation area by changing the technique used to measure the activation area. It is not expected that the effect of hydrogen on the deformation properties as measured by activation area would be large enough to alter the fracture behavior.

The plastic strain of the material was given by the equation:

$$\varepsilon_{pl} = \rho bx \quad (4.5.3)$$

where x was the average distance moved by dislocations and the other terms have been described previously. The thermally activated relaxation phenomenon in these specimens was caused by the intersection of single or superdislocations with the channels. As pointed out by Conrad(68), the activation area for this mode of deformation was proportional to the spacing between the dislocations within the shear band. For a uniform distribution of dislocations, the spacing of the dislocations was proportional to the inverse of the square root of the dislocation density. The equations that describe this concept may be written as:

where l_{disl} is the dislocation spacing and α and β are a constants.

Combining the above equations, the result is:

$$l_{disl} = \frac{\alpha}{\sqrt{\rho}} \quad (4.7.4)$$

$$\Delta A = \beta l_{disl}$$

$$\frac{1}{\Delta A} \propto \sqrt{\epsilon} \quad (4.5.4)$$

A plot of $b^2/\Delta A$ vs. the square root of the plastic strain, Figure 4.5.2, shows that the activation area for hydrogen-charged specimens was consistently lower than the activation area for noncharged specimens, though the difference was very small. It should be noted that there is no observable difference in $b^2/\Delta A$ as the strain increased between the charged and noncharged specimens decreases. This was consistent with the work of Sirois et al. on Ni (42). It remains uncertain whether hydrogen causes localization of that plasticity. Though as was discussed in the section on fractography, even without hydrogen there were slip steps on the fracture surface which were indicative of strain localization through fracture.

EFFECT OF STRAIN AND HYDROGEN ON THE ACTIVATION AREA OF ALLOY X-750

FIGURE 4.5.2

4.6 ANALYSIS OF THE DEFORMATION STRUCTURE

The deformation structures of specimens with 0% strain, 0.5% plastic strain and 2.5% plastic strain were analyzed using transmission electron microscopy. In order to better understand the deformation behavior, flat polished specimens were strained to 2%, and the intersection of the slip bands with the surface was examined.

The dislocation density for specimens with 0% plastic strain was very low. The hydrogen charging at 704°C did not appear to alter the dislocation structure or the size of the precipitates. No effect would be expected since prior to hydrogen charging the material was aged at 704°C for twenty hours. Deformation analysis was performed using a g of (220).

Application of 0.5% plastic strain to noncharged and hydrogen charged specimens resulted in nonuniform deformation consisting of channels of dislocations. Both types of specimens consisted only of localized strain as depicted in Figures 4.6.1. In these specimens it did not appear that hydrogen altered the deformation substructure.

At 2.5% plastic strain, the noncharged specimen continued to show mostly bands of localized strain with some uniform strain developing across the specimen, Figure 4.6.2. The dislocations still traveled in pairs suggesting that the precipitates

continued to be sheared at this higher strain. The hydrogen charged specimen also contained mostly localized strain and the dislocations continued to move in pairs, Figure 4.6.3. The differences in dislocation substructure were minor at this strain level. This suggests that changes in the deformation behavior were not responsible for the embrittlement observed.

The specimens that the foils were made from were strained at a rate of $3.3 \times 10^{-5} \text{ s}^{-1}$. The yield and strain hardening behaviors were not strongly affected by the hydrogen at this rate and a change in dislocation substructure was not be expected. It is important to note that even without hydrogen, Alloy X-750 deforms by localized flow.

There were two factors that would affect the localization of strain in nickel base alloys. These are:

- 1) shearing of ordered precipitates
- 2) decreasing stacking fault energy

The deformation behavior of HTH X-750 consists of shearing γ' precipitates by dislocations moving in pairs, i.e., as superdislocations. This mode of deformation was expected to result in dislocation channeling. Brown and Ham(63) discussed the phenomenon of dislocations cutting an ordered precipitate and in effect reducing the cross sectional area of the precipitate. A model describing the reduction in the

stress needed to move a dislocation along a band that has already been sheared was developed by Hornbogen(82). This model incorporated the reduction in the critical resolved shear stress (CRSS) along a given slip plane due to the cutting of coherent cuboidal precipitates with straight dislocations. The resulting equation for CRSS was:

$$\Delta\tau(n) = \frac{\sqrt{3}}{4} \frac{\gamma_{apb} d_{\gamma'}}{b D_{spacing \gamma'}} \left[1 - \frac{n b}{d_{\gamma'}} \right] \quad (4.6.1)$$

In this equation, $\Delta\tau(n)$ was the critical resolved shear stress on a given slip plane after n dislocations sheared the plane, γ_{APB} was the antiphase boundary energy, $d_{\gamma'}$ was the edge size of the γ' precipitates, $D_{spacing \gamma'}$ was the spacing of the γ' precipitates and b was the Burgers vector. The above explanation assumed that one of the controlling strengthening mechanisms was due to creation of an antiphase boundary (APB). In order to confirm this, the strengthening mechanisms in HTH were analyzed. Using the work of Brown and Ham (63), the majority of the γ' strengthening was due either to strengthening by creation of an antiphase boundary or due to the coherency strain around the precipitates. Approximately 70% of the strength of this material was a result of the creation of an antiphase boundary while a majority of the remaining strength was due to the coherency strain around the particle. The complete analysis of the strengthening mechanisms was given in Appendix 2. This analysis was used to determine qualitatively what controls the strengthening.

The second phenomenon that results in increased slip planarity was a decrease in the stacking fault energy of the material. In face centered cubic (FCC) materials such as nickel, a single dislocation wants to split into two partial dislocations in which the sum of the Burger's vectors was equal to the initial dislocation but the sum of the energy was less. Upon splitting into two partial dislocations there was an area between the dislocations which does not have the correct stacking of close-packed planes. The incorrect stacking was termed a stacking fault. The energy of this fault draws the two partial dislocations together while the stress fields of the dislocations repel the two partials. As the stacking fault energy was decreased the partial dislocations move farther apart, which make cross-slip more difficult. For the dislocations to cross onto another plane the two partials must come together. Therefore without the ability to cross-slip, the deformation would be more localized. While in materials that were not strengthened by precipitation this may be the source for planar slip, it was expected that the shearing of precipitates plays a dominant role in the slip planarity in precipitation hardened materials such as HTH X-750.

At small strains dislocations move along a single slip plane. This type of planar deformation was very similar to the Stage I deformation in a single crystal. This stage of deformation was best described by a power law relationship between stress and strain with a very low work hardening rate. This phenomenon may be related to HTH since the large grained material may behave like single crystal

material at relatively low strains.

At higher strains, the strain-hardening rate dramatically increases. This may be described by a linear strain-hardening rate. This linear work hardening rate appears similar to stage II deformation in single-crystal specimens. Again at these low strains it may still be expected that HTH behaves similar to a single crystal where the strain compatibility with other grains was not existent. While there has been considerable theoretical and experimental work to describe the mechanism of hardening in Stage II, there was not a generally agreed upon theory(83). It should be noted that the work hardening rate in Stage II deformation has been reported in the literature to be between $G/300$ and $G/200$ (83), where G was the shear modulus. In Alloy X-750 the linear portion of the stress-strain curve as measured in this work has a slope of $G/185$. This slope was similar to the slope of single-crystal specimens and supports the idea that most of the deformation is consistent with the type of deformation observed in Stage II. It has also been discussed for other FCC polycrystalline materials that Stage II begins at approximately 2% strain as was seen in this alloy (84). Furthermore, the extent of Stage II strain was dependent on the stacking fault energy and the APB energy. The extent of Stage II decreases as the stacking fault energy increases, which in turn controls the propensity for cross slip in the alloy. Due to the complications arising from interaction of strain compatibility with other grains it was not possible to determine if and when Stage III dynamic recovery would begin in this material.

Figure 4.6.1a
Hydrogen Charged Specimen
0.5% Plastic Strain

Figure 4.6.1b
Hydrogen Charged Specimen
0.5% Plastic Strain

Figure 4.6.2a
Noncharged Specimen
2.5% Plastic Strain

Figure 4.6.2b
Noncharged Specimen
2.5% Plastic Strain

Figure 4.6.3a
Hydrogen Charged Specimen
2.5% Plastic Strain

Figure 4.6.3b
Hydrogen Charged Specimen
2.5% Plastic Strain

Observations from the flat tensile specimens showed that the deformation behavior of the charged and noncharged specimens were mainly by localized deformation, though it appears that the noncharged specimens have a higher tendency for slip localization as compared to the hydrogen charged specimens. The noncharged specimens showed slip mainly on a single slip system, Figure 4.6.4, while the hydrogen charged specimens showed slip on two and in some cases three slip systems, Figure 4.6.5. This supports the premise that hydrogen enhances local slip, i.e. slip at a crack tip with high hydrogen levels, but does not support the premise that hydrogen enhances the localization of slip. This work supports the reduction in the activation area when hydrogen is present in the material. In the presence of hydrogen, more slip systems are activated, thus reducing the mean free path between dislocations. A decrease in the mean free path would then decrease the activation area. It should be noted that these changes are small. This assumes that the thermally activated process is the intersection of individual dislocations with a forest of dislocations. In Figure 4.6.5a, it was observed that there was grain boundary fracture at the boundary in the direction of the slip line. This suggests that in some instances, the grain boundary fracture may be near boundary fracture. This supports the HELP mechanism for fracture. Though, this may only be a surface phenomena and may not occur in the bulk of the specimen. For, fracture was observed along slip traces on the surface that were not observed during sectioning experiments. It was also expected that the surface traces may show different effects than the internal deformation due to the difference in strain

compatibility at the surface. While these results are consistent with the activation area, the enhanced dislocation motion on more slip planes suggests that hydrogen may make dislocation motion easier, though the quantification of this phenomena appears to show the effect as small. Thus, it is not expected to affect the fracture process to a large extent.

Figure 4.6.4a Surface Slip Lines on
Noncharged Specimen, 2% Plastic Strain

Figure 4.6.4b Surface Slip Lines on
Noncharged Specimen, 2% Plastic Strain

Figure 4.6.5a Surface Slip Lines on
Hydrogen Charged Specimen, 2% Plastic Strain

Figure 4.6.5b Surface Slip Lines on
Hydrogen Charged Specimen, 2% Plastic Strain

4.7 DISCUSSION ON THE MECHANISMS OF HYDROGEN EMBRITTLEMENT IN HTH ALLOY X-750

The hydrogen embrittlement in HTH Alloy X-750 involves the initiation and growth of grain boundary voids. In the literature review there were three mechanisms that describe the processes by which hydrogen may degrade the ductility of nickel-base alloys. This work shows that the predominant fracture mechanism is the decohesion mechanism, reduction of the bond strength between the grain boundary carbides and the matrix, while the HELP mechanism may be functioning in a minor role. The hydrogen pressure mechanism can not be discounted, but it is felt that it plays a minor role.

The microvoid initiation sites appear to be the grain boundary chromium carbides as were determined from the size and the spacing of the microvoids and the plateau etching results. The final void size did not appear to be affected by the hydrogen while the failure strain was reduced from over 20% to under 2% suggesting that the role of hydrogen was to decrease the void initiation strain. Though, it was also possible that the growth rate of the voids was increased. There did not seem to be any discernible difference in the void growth process due to hydrogen and this would have a small effect. Though, it is important to note that since void growth and coalescence is required for fracture, plastic deformation was essential for fracture as was exhibited by the prestrain experiments.

The degradation of properties as high as 285°C does not support a mechanism in which the embrittlement is totally controlled by the interaction of dislocations with hydrogen. Since the embrittlement was observed as high as 285°C where dislocation trapping is not very effective at this temperature with an activation energy of 0.1 eV (71), the trapping at grain boundary carbides may be very important. Further, the experiments where the specimens were prestrained to 10% prior to hydrogen charging show little macroscopic ductility in a uniform hydrogen concentration and do not support a mechanism in which hydrogen is altering the dislocation mobility.

As the temperature was decreased below 25°C, the ductility of the hydrogen charged specimens increased while that of the noncharged specimens decreased. In fact, at -196°C, hydrogen did not degrade the mechanical properties. It should be noted that the diffusion of hydrogen to the high hydrostatic stress region and a reduction in the cohesive energy of the carbide-matrix interface could not explain these results. Separate tensile testing at 25°C of a specimen charged with only 5.7 ppm hydrogen failed at 7.3% elongation. If diffusion to the hydrostatic stress region described the fracture process, then it would be expected that the specimen with 65 ppm hydrogen tested in liquid nitrogen would be embrittled at least as much as the specimen charged to 5.7 ppm hydrogen. This suggests some thermally activated component is required for the embrittlement. The thermally activated component required for the embrittlement may be a combination of dislocations sweeping

hydrogen to the void initiation site as well as hydrogen diffusion to this site. As shown previously in the results section, the diffusion of hydrogen is too slow to have any interaction of hydrogen with dislocations at this temperature.

A reduction in the cohesive energy of the carbide-matrix interface or a local hydrogen pressure at the carbide-matrix interface are supported by these results. In either of these cases, the strain to initiate the voids would be decreased and the macroscopic strain to failure would also be decreased. It is envisioned that the role of the local hydrogen concentration and the interaction of hydrogen with the bonding is to reduce the effective surface energy, γ_{SE} . γ_{SE} is defined as $\gamma_s + \gamma_p$, where γ_s is the surface energy and γ_p is the plastic energy used in creating the new surfaces. The magnitude of the degradation and the kinetics of the embrittlement process appeared to be controlled by the diffusion of hydrogen and the interaction with the dislocations.

The strain for void initiation at the carbide particles, due to the strong bonding of the carbide-matrix interface and supported by sectioning experiments of tensile specimens, suggests that the strain to initiate voids when hydrogen is not present was much higher than the failure strain for the hydrogen charged specimens. This justifies the assumption that the primary role of hydrogen is in decreasing the void initiation strain. It should be noted that hydrogen may also act to increase the void growth rate. An increased growth rate may be due to either a local hydrogen

pressure in the void increasing the local stress or by hydrogen increasing the localization of deformation. While altering the void growth behavior may be enhancing the embrittlement process, this would only be a secondary effect.

The relation between the changes in ductility and the fracture topography for ductile fracture for void initiation was discussed by Thompson (75). Thompson discussed two ways ductility could be altered by modifying the void initiation event. One method was to reduce the strain to initiate the void while maintaining a constant density of void nuclei. The other method was to keep the initiation strain approximately constant and to increase the number of void nuclei. In the first case, the void size should not be affected while the fracture strain should be reduced. This is what was observed in the testing discussed in this paper. The second possibility would result in a decrease in void size as well as in ductility. In this material, a majority of the possible void nucleating particles appear to initiate the voids even in the noncharged state. This is shown by the average void size without hydrogen being approximately $0.4\ \mu\text{m}$ and the grain boundary carbide size between $0.1\ \mu\text{m}$ and $0.3\ \mu\text{m}$. The final void size in the specimens charged with hydrogen was also approximately $0.4\ \mu\text{m}$. There appears not to be a single mechanism for the embrittlement. A reduction in the cohesive energy of the carbide-matrix interface are consistent with the results while the HELP mechanism plays a minor role. The build up of a local hydrogen pressure at the carbide-matrix interface is also a possibility. In these cases, the macroscopic strain to initiate the voids would be

decreased. It is also expected that the void initiation strain without hydrogen is well over 3% strain which further supports the reduction in void initiation strain as the embrittlement phenomena.

The prestraining experiments showed that the material can sustain high loads without fracture as long as no plasticity develops. Though once the macroscopic flow stress was achieved, internal voids initiate and rapidly grow. In a fracture process that includes void initiation and growth, plasticity was required. The necessity for plasticity was confirmed in the prestrained hydrogen charged specimens. The specimens that were prestrained to 5% or 10% plastic strain failed near the flow stress, i.e., the final prestraining stress. The fracture strain of the nonprestrained specimens was 2.9%. The specimens exhibited limited plasticity once the prestrain final load was achieved. This suggests that while stress was important in the fracture process, fracture can not occur unless there was some plastic strain. A model to describe this fracture process must include a critical strain criterion as well as achieving a critical stress. It will be shown below that the limiting criterion was the critical strain for fracture at cracks. This result seems similar to the results obtained on the cleavage cracking of iron specimens (76) as briefly reviewed below.

Iron specimens with a range of grain sizes were tested at -196°C (77°K) in tension and compression (76). Yielding in all cases preceded fracture. In

particular, for large grain sizes, the fracture stress in tension was equal to the yield strength in compression. These results led to the conclusion that yielding was necessary to produce a cleavage crack nucleus. The micromechanistic model states that a slip band of length equal to the grain size is needed to create a local stress concentrator so that the local stress exceeded the critical fracture stress. The cleavage process described here was an initiation controlled event. An analysis developed by Stroh (77) and expanded upon by Smith and Barnby (78) on the relative energies for crack initiation and growth showed that once energy for the initiation event was obtained, unstable growth may follow depending on the results of the relative fracture energies of the initiation and growth processes.

The local embrittlement may be partially caused by a local hydrogen pressure at the carbide particles. The concept of hydrogen being transported in the form of Cottrell atmospheres was first suggested by Bastien and Azou (72). Temperature affects hydrogen transport by dislocations in two ways. First, as temperature was decreased there was a greater affinity for hydrogen to the dislocations and therefore more hydrogen may be trapped. Second, as temperature was decreased, the diffusion rate was decreased and therefore less hydrogen was able to diffuse to the dislocations and be transported to the initiation sites. The reduced diffusivity also results in a lower critical strain rate at which point the dislocation breaks away from the Cottrell atmosphere. Since at -196°C hydrogen diffusion was too slow for hydrogen segregation to the dislocations and transport by the dislocations, no effect

of hydrogen was expected and none was observed. Once the dislocations have transported the hydrogen to the grain boundary, the grain boundary carbides have a stronger attraction to the hydrogen than the dislocations. This may lead to a local pressure of hydrogen also enhancing the formation of voids. It should be noted that the prestrain experiment does not support a hydrogen transport mechanism by dislocation sweeping since macroscopic plasticity was not observed in the prestrained specimens. Another mechanism in which the hydrogen could be increased is due to the locally high stress at the matrix-precipitate interface. The stress would be high at the interface due to the carbide particle remaining elastic while the surrounding matrix deforming plastically. In this case the stresses created by the different strengths are large enough to nucleate dislocations(24). It is also possible that the two mechanisms are complimentary, the decohesion mechanism as well as the HELP mechanism may be occurring. Part of the time dependence of the embrittlement phenomenon would be the time required for hydrogen to diffuse to the dislocation pile-ups at the carbides. This could then explain the results.

The results of stress relaxation testing demonstrate the role of hydrogen in deformation. Hydrogen enhances the rate of stress relaxation to a small extent. Strain rates below 10^{-6} show that hydrogen increases the mobility of dislocations. Enhanced dislocation motion may reduce the macroscopic strain needed to reach the critical stress necessary for intergranular fracture. The crack growth may be enhanced from the increased dislocation mobility since voids ahead of the crack tip

may be easier to initiate. The role of the hydrogen enhanced plasticity in this system was minor. It appears that the major role of hydrogen was to decrease the cohesive energy of the carbide-matrix interface. This was further supported by the tensile tests in which the yield strength was not altered by hydrogen while the embrittlement was severe. It does appear that hydrogen interaction with dislocations was important since no embrittlement was observed at -196°C .

4.8 A MODEL TO CORRELATE THE MICROSTRUCTURE AND THE FRACTURE TOUGHNESS

Correlating the fracture toughness to microstructural features was a key component to both alloy development and micromechanical modeling of fracture. The model presented below describes a possible void initiation process, which was taken to be the critical fracture event. Void initiation was discussed previously as being at grain-boundary carbides which was supported by fractography and serial grinding and polishing. From the analysis of the notched specimen, it appeared that a critical strain criterion described the cracking phenomenon. For fracture to occur at a critical location, a critical strain must be exceeded. It is shown below for fracture in the precracked specimens that fractured occurred when a critical strain was achieved. This criterion states that for fracture to occur, the effective plastic strain, ϵ_p , must exceed a critical value, ϵ_c , over a characteristic fracture distance, r_c , for a given stress state, (effective stress/hydrostatic stress). The strains ahead of a crack may be described by the solutions of Hutchinson (79) and Rice and Rosengren (80) when the distance was between 2 and 8 crack-tip-opening displacements, δ_t . This solution is for small scale yielding while large scale geometry changes as modeled by Rice and Johnson could be more appropriate. For the work described here, the results for small scale yielding are not substantially altered by the use of the small geometry change (SGC) solutions. Further, there is not a closed form solution for the large geometry change (LGC) analysis. The HRR solution for strain

is given by:

$$\epsilon_p = \alpha \epsilon_y \left[\frac{J}{\alpha \epsilon_y \sigma_y I_N r} \right]^{\frac{N}{N+1}} \tilde{\epsilon}_p(\theta, N) \quad (4.8.1)$$

In the previous equation:

α is a constant approximately 1,

ϵ_y is the yield strain, related to yield stress through the elastic modulus, E ,

σ_y is the yield stress, 790 MPa for this material,

J is the J-integral,

N is the work hardening exponent, $N=16$ for X-750,

I_N is an integration constant weakly dependent on strain hardening, $I_N=4.5$ for X-750,

r is the distance from the crack tip, and

$\tilde{\epsilon}_p(\theta, N)$ is an angular factor for the equivalent plastic strain, at $\theta=45^\circ$, $\tilde{\epsilon}_p=0.1$.

In terms of linear elastic fracture mechanics, the J-integral may be rewritten in terms of K , the linear elastic stress intensity factor:

$$J_I = \frac{K_I^2}{E} \quad (4.8.2)$$

Equation 4.8.1 may then be rewritten as:

$$\epsilon_p = \alpha \epsilon_y \left[\frac{K^2}{\alpha \epsilon_y \sigma_y I_N r E} \right]^{\frac{N}{N+1}} \bar{\epsilon}_p(\theta, N) \quad (4.8.3)$$

With $N=16$, one may assume $N/(N+1) \approx 1$, Equation 4.8.3 simplifies as:

$$\epsilon_p = \left[\frac{K^2}{\sigma_y r E} \right] \left[\frac{\bar{\epsilon}_p(\theta, N)}{I_N} \right] \quad (4.8.4)$$

When $\epsilon_p = \epsilon_c$ at $r=r_c$ the stress intensity factor is equivalent to the critical fracture toughness, K_{Ic} , as shown below.

$$K_{Ic} = \sqrt{\epsilon_c \sigma_y r E} \sqrt{\frac{I_N}{\bar{\epsilon}_p(\theta, N)}} \quad (4.8.5)$$

Incorporating the constants for I_N and $\bar{\epsilon}_p$, the equation becomes

$$K_{Ic} = 6.7 \sqrt{\epsilon_c \sigma_y r E} \quad (4.8.6)$$

The critical fracture strain is expected to be a function of both the hydrogen concentration and the stress state. The testing of round uniaxial tensile specimens at room temperature and a strain rate of $3.33 \times 10^{-5} \text{ s}^{-1}$ resulted in the critical strain for 65 ppm hydrogen of approximately 0.025. The critical strain for 40 ppm hydrogen was approximately 0.031. This failure strain was approximated since the crack tip strain rate was approximated and stress state effects are not known. The failure strain for the noncharged specimen was 0.21.

The final parameter that must be incorporated into the model is the critical distance. This distance was chosen to be $10\ \mu\text{m}$ as a fitting parameter. This distance is much larger than the carbide spacing and much smaller than the grain size. This distance may be related to the distance of a location of a "weaker" carbide-matrix interface on an average basis. The predicted fracture toughness for the specimen with 65 ppm hydrogen was $43\ \text{MPa}\sqrt{\text{m}}$ and for 40 ppm was $48\ \text{MPa}\sqrt{\text{m}}$. For the noncharged specimen, the predicted toughness was $125\ \text{MPa}\sqrt{\text{m}}$. These numbers are near the measured values and suggest that this critical strain model correctly correlates the fracture behavior for a large range of hydrogen concentrations, 0 to 65 ppm. This supported the use of the critical strain parameter as the fracture criterion. The critical strain criterion was supported below by showing that the critical fracture stress observed in the uniaxial tensile specimens and the notched-bend specimens was achieved at much lower stress-intensity values than observed for failure.

The critical stress criterion was described below. This criterion states that for fracture to occur, the maximum stress, σ_1 , must exceed a critical value, σ_{fs} , over a characteristic fracture distance, r_c , for a given stress state, (effective stress/hydrostatic stress). The stresses ahead of a crack may be described by the solutions of Hutchinson (79) and Rice and Rosengren (80) when the distance was between 2 and 8 crack-tip-opening displacements, δ_t :

In this equation:

$$\sigma_1 = \sigma_y \left[\frac{K^2}{\alpha \sigma_y^2 I_N r} \right]^{\frac{1}{N+1}} \bar{\sigma}(\theta, N) \quad (4.8.7)$$

α is a constant approximately 1,

σ_1 is the maximum principal stress

σ_y is the yield stress, 790 MPa for this material

K is the linear elastic stress intensity factor

N is the work hardening exponent, $N=16$ for X-750 at low strains

I_N is an integration constant weakly dependent on strain hardening, $I_N=4.5$ for X-750

r is the distance from the crack tip

$\bar{\sigma}_p(\theta, N)$ is an angular factor for the maximum principal stress, at $\theta=0^\circ$, $\bar{\sigma}_p=1.8$

The above equation may be rewritten in terms of the stress intensity factor being the dependent parameter,

$$K_I = \sqrt{I_N r \left[\frac{\sigma_1}{\bar{\sigma} \cdot \sigma_y} \right]^{N+1}} \sigma_y \quad (4.8.8)$$

With $N=16$, then one may assume $1/(N+1) \approx 1/N$, letting $\sigma_1 = \sigma_{fs}$ at $r=r_c$ the stress intensity factor was equivalent to the critical fracture toughness, K_{Ic} , as shown below.

$$K_{Ic} = \sqrt{I_N r \left[\frac{\sigma_{fs}}{\bar{\sigma} \cdot \sigma_y} \right]^N} \sigma_y \quad (4.8.9)$$

Incorporating the constants for I_N , $\bar{\sigma}_p$, the fracture stress from the notched specimens and yield stress, the equation becomes

$$K_{Ic} = \sqrt{4.5 \cdot 70 \times 10^{-6} \left(\frac{1681}{2 \cdot 790} \right)^{16}} \cdot 790 \quad (4.8.10)$$

which results in a fracture toughness value of 22 MPa $\sqrt{m}$ using the same distance as in the critical strain criterion. If both a critical stress and a critical strain are required for failure, the critical stress was achieved well before actual fracture at the critical distance of 10 μ m. Since the 10 μ m was a fitting parameter, one may determine the critical distance assuming only a critical stress was required for failure. The maximum stress achieved in the notched bend specimen at failure was reached at distances of beyond 0.5 mm. This distance is physically unrealistic for a fracture criterion. This supports the critical strain criterion since the critical distance for a strain criterion is physically realistic while that for a critical stress criterion is not realistic and not supported by experimental evidence. It should be noted that in the above analysis for stress and strain the small scale yielding approximations of the HRR solutions were used. This work was used since the results were given as a closed form solution. In the actual case, there are large geometry changes which result in the solutions not being valid near the crack tip, a distance less than 2 crack tip opening displacements (CTOD). In the case at hand, the critical distance is 2 CTODs and there is little error in the equations. The error in the estimates was determined by comparing these results to those of the large geometry change analysis of Rice and Johnson (81).

5.0 SUMMARY

This study investigated the effect of hydrogen on the deformation and fracture of a nickel-base superalloy, HTH Alloy X-750. The effect of hydrogen was examined through stress relaxation experiments, tensile testing, and fracture mechanics testing, as well as analysis by transmission electron microscopy, scanning electron microscopy and optical microscopy. The following conclusions were drawn from the experiments:

- 1) The fracture mechanism was initiation of voids at grain boundary carbides followed by void growth and coalescence.
- 2) Plastic strain was required for fracture as observed from prestrained specimens. Prestraining prior to charging drastically decreased elongation. Specimens strained to either 5% or 10% plastic strain followed by charging and then strained at a rate of $3.33 \times 10^{-5} \text{ s}^{-1}$ showed no gross macroscopic plasticity and did not fail until the maximum prestrain load was achieved. When strained at a higher strain rate, $3.33 \times 10^{-4} \text{ s}^{-1}$, a small amount of elongation was noticed prior to failure. This was consistent with the need for plastic deformation to cause fracture.

3) A model was developed to correlate the microstructure to the fracture toughness behavior. The model was based on the need for a critical strain at a characteristic distance. The model uses the strain distribution developed from the work of Hutchinson and Rice and Rosengren. The model was able to correlate the effect of hydrogen concentration on the fracture toughness behavior. The critical distance was $10\mu\text{m}$.

4) Diffusion of hydrogen was essential to cause the embrittlement of the material. The need for diffusion may be required to allow hydrogen to interact with dislocations or to decrease to the high stress region at a dislocation pile-up. Elongation slightly decreased as the strain rate decreased for hydrogen charged specimens while no strain rate effect was observed for the noncharged specimens. This was consistent with the need for hydrogen interaction with dislocations or hydrogen diffusion. Hydrogen did not embrittle the material at -196°C . Testing at -196°C was a method used to separate the effect of uniform hydrogen and the hydrogen that was transported to the grain boundary by diffusion and dislocation transport. In this test the critical velocity of the dislocations was exceeded and the dislocations broke away from the Cottrell atmosphere. This shows that some amount of hydrogen diffusion and most likely interaction with dislocations was needed for hydrogen embrittlement.

5) Hydrogen trapping at dislocations or grain boundaries was required to cause the embrittlement of the material. The tensile specimens were less embrittled at 175°C and 285°C than at room temperature. At this temperature, the diffusion was faster than at room temperature while the trapping was less effective. This shows that trapping was also necessary for the embrittlement of the alloy. Since embrittlement was observed to 285°C, trapping at carbide particles may be important since the binding energy of hydrogen to dislocations is 0.1 eV.

6) Stress-relaxation and strain rate change testing have shown that hydrogen in the matrix slightly decreases the activation area for thermally activated glide. The difference in activation area due to hydrogen was less than the difference in activation area observed by changing the analysis technique. The decrease in activation area is consistent with the polished flat tensile specimens which showed hydrogen increased the number of operative slip systems, thereby decreasing the mean free path between dislocations. Again, this effect was small and would only be a minor effect in the embrittlement Alloy X-750.

7) It appears that the strain rate change test technique was the best method to determine activation area, though with stress relaxation testing a better understanding of the change in strain rate was obtained.

8) Prestraining of up to 20% prior to hydrogen charging at 360°C had no measurable effect on hydrogen solubility. This was consistent with reported literature values of 0.1 eV for the binding energy of hydrogen to dislocations. This suggests that it was not the trapping of hydrogen at the dislocations itself that was important but possibly the transport of hydrogen by the dislocations.

9) The role of hydrogen appears to decrease the cohesive strength of the grain-boundary carbide-matrix interface resulting in easier initiation of voids. Once initiated, very little void growth is required for fracture.

10) The HELP mechanism may play a role in the fracture process, though it does appear to be a minor role.

11) Hydrogen may affect the growth behavior of the voids. Though this is a secondary effect. Hydrogen may enhance plasticity, thus resulting in faster void growth rates. A local hydrogen pressure may also increase the growth rate by increasing the local stress.

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7.0 SUGGESTIONS FOR FUTURE WORK

The majority of work in the present study incorporated mechanical testing and fractographic evidence to understand and model the fracture behavior of Alloy X-750. While a quantitative model was developed to describe the fracture process, work on quantifying some of the parameters may be useful. This work quantified the void size, the particle size was not well quantified. Transmission electron microscopy of extraction replicas may be useful in quantifying the local strain.

The work in this program suggests that hydrogen may alter the plastic behavior including strain localization. Further work on this effect may help define the role of hydrogen in changing the deformation behavior. The present program focussed mainly on fracture with limited work on deformation.

The present program used only one heat treatment, the peak aging treatment. Studies on the SCC behavior of this alloy have shown that overaging decreases the susceptibility to SCC. In order to better develop a correlation between SCC and hydrogen embrittlement a study looking at the effect of aging on the embrittlement would be needed. This work would also lead to a better understanding of the interaction of deformation and the fracture behavior.

APPENDIX 1

HYDROGEN DIFFUSION AND TRAPPING IN CONDITION HTH ALLOY X-750

A1.1 INTRODUCTION

The hydrogen embrittlement of Alloy X-750 requires the diffusion of hydrogen. The need for hydrogen diffusion is exemplified by the lack of embrittlement observed at -196°C. The concept of hydrogen embrittlement being dependent on the transport of hydrogen by dislocations was first proposed by Bastien and Azou (1) with a model developed by Tien et al (2). In order to apply this model to the hydrogen embrittlement of X-750, the diffusion equation must be determined. The diffusion of hydrogen in Alloy X-750 has been extensively studied at ambient temperature ((3),(4)) as well as temperatures over 600°C (5).

The ambient temperature results were developed from permeability testing of Alloy X-750. There was no work performed above ambient temperature and no temperature dependency could be evaluated (3),(4). The binding energy of hydrogen to the γ' was determined from the room temperature permeability testing (3). The

calculated binding energy was 7400 cal/mol with an effective diffusivity of 1.3×10^{-10} cm²/s (3). The effective diffusivity determined by Latanision and Kurkela (4) also for ambient temperature was 5.3×10^{-11} . Permeability studies of Ni270 in the cold worked condition and the annealed condition were also studied (4). This work also showed less than a factor of 2 decrease in diffusivity for an 80% cold worked material.

The elevated temperature gas phase permeation testing (5) resulted in a diffusion equation:

$$D_H = 0.016 \exp \left[\frac{-12,500}{R T} \right] \quad (\text{A1.1})$$

where R is in cal/mol, T is in degrees Kelvin and D_H is in cm²/s.

The elevated temperature work did not incorporate the effect of trapping on the diffusivity. The purpose of this work was to determine the diffusivity in temperature ranges where the trapping of hydrogen by γ' precipitates may be important. This was done by gas phase charging cylindrical specimens and measuring the overall hydrogen remaining in the specimens after various times at temperatures low enough to allow trapping to interact with the hydrogen diffusion.

The binding energy of hydrogen to γ' precipitates was also evaluated using solubility experiments. A comparison of the solubility of hydrogen in aged material

and solution annealed material was examined. The result was compared with literature values for γ' precipitates.

A1.2 EXPERIMENTAL PROCEDURE

Cylindrical rods of Condition HTH Alloy X-750, 0.232 cm diameter by 1.8 cm long, were gas phase hydrogen charged in an autoclave at 5,000 psi hydrogen for 3 weeks at 360°C. Once removed from the autoclave, the specimens were stored in liquid nitrogen. The specimens were then sealed in glass tubes in an argon atmosphere after evacuating and backfilling the bulbs with argon 3 times prior to sealing. The specimens were then inserted into the furnaces at either 204°C or 315°C. The test matrix is shown below.

Time (hrs) at 204°C	1,8.5,30, 100
Time (hrs) at 315°C	1,8.5,30

The specimens were water quenched after removal from the furnace and stored in liquid nitrogen until the specimens were analyzed for hydrogen concentration. The hydrogen concentration was measured by use of a LECO hydrogen analyzer model RH404 which uses electrical current to quickly heat the specimen and then measures the conductivity of the evolved gas to determine the hydrogen concentration.

A1.3

The solubility of solution annealed specimens was compared to the solubility of solution annealed and aged specimens. A comparison of the overall hydrogen concentration of the aged vs. annealed specimens was then used to determine the trapping energy at the γ' -matrix interface.

A1.2 DIFFUSION RESULTS AND DISCUSSION

The equations that describe the diffusion through a cylinder were derived in Crank (9) and are reviewed here for the specific case of a solid cylinder with uniform initial concentration. The governing differential equation is:

$$\frac{\partial C_H}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[r D \frac{\partial C}{\partial r} \right] \quad (\text{A1.2})$$

This equation may then be solved for nonsteady-state conditions. Crank developed a plot showing the amount of diffused substance out of the cylinder normalized by the initial concentration vs. the normalized parameter given by $(Dt/a^2)^{1/2}$, where D is the diffusion constant, t is the time, and a is the radius.

The results of the desorption study are shown below. The data from the experiment are concentration and time. The dimensionless parameter, Dt/a^2 is then determined from Crank (7). The diffusion constant is then easily determined. The results are shown below in Table A1.2.1a for the 204°C experiment and Table A1.2.1b for the 315°C experiment.

TABLE A1.2.1a. Hydrogen Desorption Study at 204°C for a 0.232 cm Cylinder

with initial Concentration of 65 ppm

Concentration (ppm)	time (sec)	$(Dt/a^2)^{1/2}$ from p. 72 Ref.8	D (cm ² /sec)
58	3600	.058	5.0×10^{-8}
38	3.06×10^4	.21	7.7×10^{-8}
18	1.08×10^5	.4	8.0×10^{-8}
3.4	3.6×10^5	.67	6.7×10^{-8}
		Average	6.9×10^{-8}

TABLE A1.2.1a. Hydrogen Desorption Study at 315°C for a 0.232 cm Cylinder

with initial Concentration of 65 ppm

Concentration (ppm)	time (sec)	$(Dt/a^2)^{1/2}$ from p. 72 Ref.8	D (cm ² /sec)
29	3600	.28	1.2×10^{-6}
5.2	3.06×10^4	.61	6.5×10^{-7}
1.5	1.08×10^5	.76	2.9×10^{-7}
		Average	7.1×10^{-7}

An equation for the diffusivity of hydrogen in Alloy X-750 was determined using the average values for diffusivity at 204°C and 315°C. The activation energy is an exact fit with only two temperatures used to develop the equation. This resulted in an equation for hydrogen diffusivity of:

$$D_H = 0.016 \exp \left[\frac{-49,000}{R T} \right] \quad (A1.3)$$

where R is in J/mol, T is in degrees Kelvin, and D_H is in cm^2/s .

A check on this equation is to compare the results to the room temperature diffusivity as determined in the literature. At room temperature, the calculated diffusivity is 4.2×10^{-11} from equation (4). The measured values at room temperature, as discussed previously, are $1.3 \times 10^{-10} \text{ cm}^2/\text{s}$ and 5.3×10^{-11} . The equation developed here extrapolates to room-temperature values that are in reasonable agreement with other studies for the hydrogen diffusion in this material.

A diffusion study also was performed on specimens that were strained 20% prior to hydrogen charging. The hydrogen concentration of the strained specimens was within 10% of the hydrogen concentration in unstrained specimens on specimens that were given the same time and temperature as the nonstrained specimens. This suggests that there was no observable effect of trapping at dislocations on the hydrogen diffusivity. This test does not show how the effect of dislocation sweeping may effect the hydrogen transport.

A1.3 SOLUBILITY RESULTS AND DISCUSSION

The hydrogen level in the solution annealed material was 55 ppm (3162 appm) and in the aged material was 65 ppm (3737 appm). The total hydrogen in one cubic centimeter is equal to the sum of hydrogen in solution and the trapped hydrogen as described by the following equation:

$$C_H \times (\text{total sites}) = C_{H_0} \times (\text{total sites} - \text{trapsites}) + C_{Ht} \times (\text{trap sites}) \quad (\text{A1.4})$$

where C_H is the total hydrogen concentration

C_{H_0} is the hydrogen concentration in the absence of traps

C_{Ht} is the hydrogen concentration at traps

The γ' in this system is a saturable trap. The number of trap sites can be calculated making the assumption that the trap is only at the interface. With a weight fraction of γ' of 12.5%, the volume fraction is 13%. The size of the γ' particles is approximately 20nm and there are two octahedral sites per cube face. These numbers result in a trap density of 6×10^{20} traps/cm³. The density of octahedral sites is 9×10^{22} , the total number of lattice positions hydrogen takes. Substituting these numbers into Eqn. A1.4 results in a concentration of hydrogen on the γ' interface is then 86250 appm.

The equation used to describe trapping is:

$$C_{Ht} = C_{Ho} \exp \left[\frac{E_b}{RT} \right] \quad (A1.5)$$

where E_b is the binding energy of hydrogen to γ' and the other terms have been described. The calculated binding energy was 4200 cal/mol. If the binding energy were 7900 cal/mol as reported in the literature, the traps would be saturated in our samples and the overall hydrogen concentration would be 180 ppm. Thus the value of 7900 cal/mol was too high. In the literature on Alloy 903 (8), an austenitic iron-based superalloy, Moody reported a binding energy of 4600 cal/mol. The precipitates in Alloy 903 are similar to X-750, both being coherent 20 nm diameter γ' precipitates. This is in very good agreement with the value of 4200 cal/mol determined in our samples.

A1.4 CONCLUSIONS

The effect of γ' is to trap the hydrogen at the precipitate matrix interface. The binding energy is approximately 4200 cal/mol which is similar to the results on Alloy 903 but only half that of the reported work of Alloy X-750. The analytical treatment of hydrogen diffusivity shows that the diffusivity is similar to that developed for Alloy 718 and is much slower than pure nickel.

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APPENDIX 2

STRENGTHENING MECHANISMS IN CONDITION HTH ALLOY X-750

A.2.1 Introduction

The following analysis of the strengthening mechanism was performed to determine the role of precipitates and therefore to better understand the interaction of hydrogen with the dislocations. This analysis is not intended to be exact due to the uncertainties in measuring the antiphase boundary energy and the lattice parameters, though for the purpose of qualitative analysis of the strengthening mechanisms, it was sufficient. There are many ways in which precipitates may strengthen a material. For the nickel-base superalloys strengthened by a low volume fraction of coherent γ' precipitates, the majority of strengthening is from the coherency strains around the precipitate and the energy to form antiphase boundaries. To determine the mechanism of precipitate strengthening in Condition HTH Alloy X-750 some basic physical parameters are needed. The parameters are:

- a) the particle size
- b) the volume fraction of particles
- c) the lattice parameter of the matrix
- d) the lattice parameter of the gamma prime
- e) the antiphase boundary energy
- f) the shear modulus

Analysis of dislocations in slightly deformed tensile specimens made it possible to approximate the APB energy. The measurement of the APB energy from measuring the spacing of dislocations is very approximate. The effect of part of the dislocation being outside of the precipitate as well as the exact nature of the dislocation are not taken into account. The spacing of the dislocations is inversely proportional to the APB energy. Also, the spacing of the dislocation pair is important in determining what equation is to be used to calculate the strengthening due to the creation of an APB. The average spacing between super-dislocations was approximately 18 nm. The antiphase boundary energy may then be estimated from the following equation:

$$\gamma_{APB} = \sqrt{6} \frac{T}{x} \quad (A2.1)$$

where x is the spacing, T is the dislocation line tension, and γ_{APB} is the antiphase boundary energy. According to the work of Brown and Ham(1) and Raynor and Silcock(2) the APB energy is approximately 250 mJ/m². In order to determine the APB energy from this work, the dislocation line tension must be estimated. The deWit-Koehler model for dislocation line tension, assuming a square lattice spacing of the precipitates, is:

$$T = \frac{G b^2}{8 \pi} \ln\left(\frac{\lambda}{b}\right) \quad (A2.2)$$

where λ is the particle spacing and the other terms have been defined previously. It should be noted that the deWit-Koehler model is an approximation and better calculations may be made by determining the dislocation character. With the

assumption of the square lattice spacing, the average distance between two precipitates is given by:

$$\lambda = \left[\frac{\pi}{6f} \right]^{\frac{1}{2}} d \quad (\text{A2.3})$$

where f is the volume fraction of precipitates, which is approximately 12.5% for this system, and d is the particle diameter, which is approximately 20×10^{-9} m. Therefore the average distance between two precipitates is 4.18×10^{-8} m. The shear modulus, G , is 7.9×10^{10} Pa and the burgers vector is 2.54×10^{-10} m. Therefore, the line tension as given by equation (2) was roughly 1.18×10^9 Pa-m. The APB energy, as given by equation (1) is then approximately 245 mJ/m². This is consistent with the results from Brown and Ham (1).

A2.2 Calculation of Strengthening from γ'

The work discussed in this section follows closely the discussion of Brown and Ham (1) on the strengthening mechanisms. There are two equations that may be used to calculate the strength due to the creation of APB's. The first is for the spacing of the dislocations being smaller than the size of the γ' particles which is the case at hand. Therefore, the equation to be used in the determination of the strength due to the creation of an APB is:

A2.3

$$\Delta \tau_{APB} = \frac{\gamma}{2b} \left[\left[\frac{\left(\frac{8}{3}\right) \gamma d f}{\pi T} \right] - f \right] \quad (A2.4)$$

Using constants developed above, the increase in the critical resolved shear stress was estimated to be 190 MPa. In order to relate the CRSS to polycrystalline tensile strength, a Taylor factor of 3.0 was used (3). This results in the strengthening due to the creation of an APB on the order of 570 MPa.

The strengthening due to the misfit strain is the other major contributor to the strength. The equation discussed by Brown and Ham (1) which is used in this analysis, was:

$$(\Delta \tau)^2 = \left(\frac{35}{4}\right) \frac{G^3 \varepsilon^3 b^5 n_v \left(\frac{d}{2}\right)^4}{T^3} \quad (A2.5)$$

In the previous equation n_v is the number of precipitates per unit volume.

Incorporating all the assumptions described above, n_v may be calculated by:

$$n_v = \frac{3f}{4 \pi r^3} \quad (A2.6)$$

Substitution of equation (A2.6) and equation (A2.2) into Eqn (A2.5) results in the following equation to estimate the increment in strength in which all the quantities are known:

$$\Delta \tau = 41 \pi G |\varepsilon|^{\frac{3}{2}} f^{\frac{1}{2}} \left(\frac{d}{b}\right)^{\frac{1}{2}} \left[\ln\left(\frac{\lambda}{b}\right)\right]^{-3} \quad (A2.7)$$

All of the quantities in equation (A2.7) are known or can be estimated in order to approximately determine the strengthening due to coherency strains. The X-ray diffraction analysis described above results in a misfit, $\delta = (a_{\gamma'} - a_{\gamma})/a_{\gamma}$, of 0.68%. The misfit strain for spherical precipitates was derived by Eshelby to be $2\delta/3$, which is 0.41%. This is an approximate solution for the γ' , the derivation of the conversion of δ to strain was developed by Eshelby (4) for spherical particles. Substitution of the misfit strain into equation (A2.7) results in a strengthening of 60 MPa. Again converting this number to that for polycrystalline material the resulting strength was approximately 180 MPa. The strengthening due to the formation of the APB is greater than the strengthening due to coherency strains. The important point of calculating the relative strengths due to the different strengthening mechanism is to obtain a better understanding on how the structure is controlling the deformation behavior. The theoretical framework for combining different strengthening mechanisms to obtain an estimate of total strength is not well developed (5). As it will not add anything to this outcome of this work, it was not pursued. The strengthening due to other mechanisms, e.g., solid-solution strengthening and grain-boundary strengthening was not taken into account, but again for the purpose of this work it was not considered necessary.

A2.3 Conclusions

These results show that the majority of the strengthening is caused by the formation of antiphase boundaries with some additional strength from the coherency

strains between the γ' and the matrix. This analysis was performed to determine the relative strengths of the strengthening mechanisms. These were order of magnitude approximations. The APB energy using this technique can not be closely determined. Thus the value for the strength from this calculation is approximate. The misfit between the precipitate and the matrix were determined with more precision, but the equation used to determine the strength was developed for spherical particles and thus is approximate for the rounded cuboidal precipitates observed in this work.

A2.4 References

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