Hydrogen Impact on Materials and Design:

Assessment of material qualification subject to hydrogen combustion environments

CAP 3119

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Contents

Executive Summary

The adoption of hydrogen as an aviation fuel will bring a wide range of technological challenges in aircraft components. Foresight will help avoid future difficulties in certifying hydrogen fuelled aviation gas turbines. From a Materials and Design perspective, Hydrogen is well known to degrade the mechanical properties of structural alloys, including nickel, titanium, aluminium and steel [1], by suddenly reducing their strength and ductility; this phenomenon is known as Hydrogen embrittlement and is a form of stress-induced fracture, causing metal alloys to suddenly crack or fail under stress values below the yield stress and without prior signs of damage. Hydrogen can also influence other material damage processes relevant to aviation materials, such as accelerating mechanical fatigue or increasing creep deformation rates. Hydrogen in both gaseous (H_2) and atomic (H) form is highly mobile, especially at high temperatures, and it is very likely that H will absorb and interact with materials used in combustion chambers and downstream components of gas engines. Despite the above-mentioned material degradation processes when exposed to gaseous H_2 there is little information on whether existing alloys used in gas turbines could fail prematurely, *i.e.* well before their specified lifetime, under Hydrogen combustion environments.

Qualification methods and **certification specifications of materials used in combustion engines currently do not consider the presence of hydrogen** [2]. On-going assessment of material compatibility with Hydrogen has mainly used existing information and research from other industries, including Space as well as Oil and Gas, where H-metal interactions leading to Hydrogen embrittlement can happen. Hydrogen has been used as a fuel in rockets for over 50 years, but the in-service conditions do not represent the more demanding requirements for modern aeroengines; aircraft follow more complex mission profiles, for which temperatures and mechanical loads inside gas turbines can fluctuate more abruptly, as well as components demanding much longer service lifespans (Figure 0.1) [3,4]. However, existing industrial demonstrator programmes cannot provide accurate information of the fundamental limits of material tolerance to Hydrogen under H_2 combustion environments that are needed to define accurate regulatory frameworks for the safe use of Hydrogen in aviation. First principles studies are needed to isolate and identify the critical physical processes leading to hydrogen absorption and embrittlement, as well as to unveil other material damage processes that are unique to hydrogen combustion conditions.

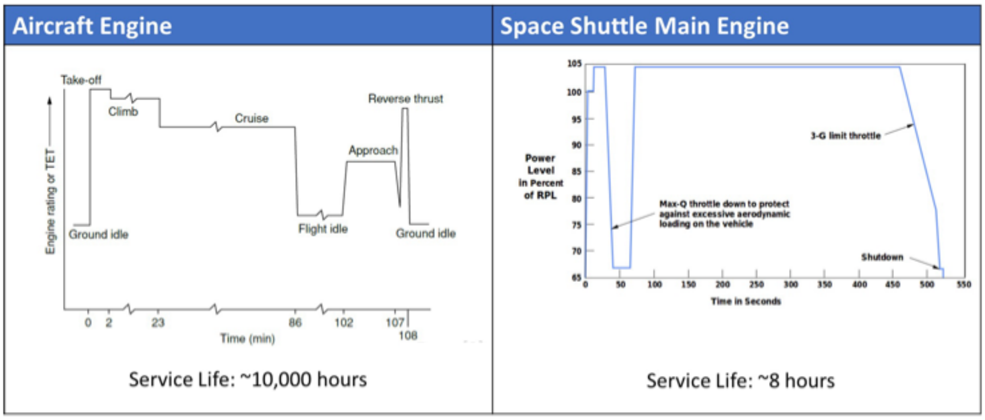

Figure 1 Comparison between mission profiles and service lifetimes of aircraft and rocket engines illustrating the markedly different specification requirements expected for materials. Figures modified from [3,4].

Supporting the H_2 challenge regulator gap: This work has addressed the core question: "How to qualify new materials for safe H_2 aviation?" through the delivery of highly novel and unique scientific evidence of the main material changes when alloys are exposed to a Hydrogen flame. **This work shows that H_2 has the potential to adversely affect material properties, and it is the first step towards fully unveiling the impact of H_2 on materials used in combustion chambers.** Section 1 presents the scientific and technological background leading to the present work. Section 2 describes in detail the Experimental programme, including the Methodology, Results and Discussion. Section 3 discusses the implications of the findings towards promoting standards for best practices on material handling and testing, as well as proposed changes in certification requirements of alloys used in gas turbine combustion chambers subject to Hydrogen flame charging. Section 4 presents the Outlook and recommended further work identified as key to define a more comprehensive regulatory framework on material qualification for safe H_2 combustion engines.

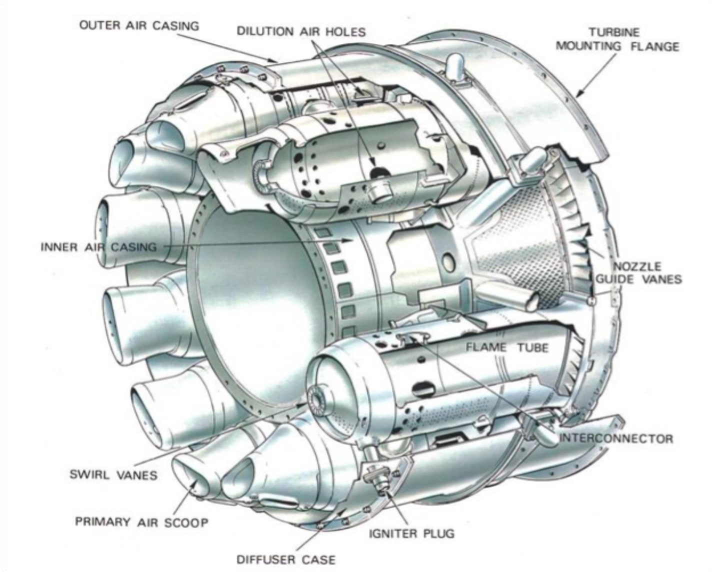

Figure 2 Schematic of a turbo-annular combustion chamber in a jet engine made from Nickel-based superalloys [5].

Project activities

As part of the experimental programme, *the first task (1)* consisted of exposing high-temperature Nickel superalloys to a H_2 flame at various temperatures and times to map the H content inside alloys vs various combustions conditions. Following flame exposure, materials were taken to a Thermal Desorption Analysis (TDA) machine to measure the hydrogen content within each sample. TDA is an experimental technique that measures the hydrogen desorption rate from a material at a constant heating rate and it can be used to characterise the diffusion profiles of H inside alloys; understanding hydrogen diffusion within alloys is the first step to address hydrogen embrittlement and design against it. The Nickel-based superalloy Inconel 718 was chosen for the study as it is the most used material in high-temperature components. The results show that **Hydrogen accumulation inside Inconel 718 increases with flame exposure time and temperature**, confirming easy H absorption during representative H_2 combustion conditions.

In addition, a number of test pieces were pre-oxidised to study how the surface condition of a combustor component can affect the H absorption and desorption behaviour. This is because **oxidation is ubiquitous to industrial combustion environments and its impact on H flow into alloys was unclear.** It is demonstrated that oxides play a dual role in the H mass flow, where pre-oxidising the samples can facilitate H absorption but at the same time oxides prevent H desorption, acting as surface barrier, within the first 4-6 hours of flame exposure. These findings confirm that **oxidation during H_2 combustion will be key in controlling alloy's overall H content and mechanical integrity.** The results also imply that new regulations will be needed towards how surface barriers can interact with H in Nickel-based superalloys.

Hydrogen was also introduced in materials using electrochemical charging at room temperature to compare their hydrogen diffusion and absorption behaviour against H_2 flame charged conditions. Electrochemical charging is one of the most common methods to introduce H inside alloys, but it is later shown that the results do not reflect the H-metal interaction behaviour under combustion conditions, including H absorption, diffusion and desorption rates within the alloy. Prior to electrochemical charging, materials were heat treated in an air furnace to mimic the thermal history during the H_2 flame experiments. The TDA results showed that the Hydrogen diffusion profiles in the flame-exposed materials are markedly different than the electrochemically charged samples; H remains inside the H-flame charged alloys for a wide temperature range up to 900 ^{o}C - indicating slower H diffusion and desorption behaviour- whereas most H is released below 500 ^{o}C in the sample electrochemically charged-confirming more rapid diffusion and desorption as temperatures increase. **The results demonstrate that existing testing methods for Hydrogen embrittlement do not represent in-service combustion conditions of aeroengine materials.**

Task 2 involved **tensile testing** of materials following H_2 flame exposure and electrochemically charging to **compare their mechanical response and confirm H**

embrittlement. The results were also compared against H-free materials to understand the relative impact of H on the same alloy. **It is shown that exposing Ni-based superalloys to a Hydrogen flame can cause significant degradation to their mechanical properties by reducing more than 50% their tensile ductility**. Material analysis in *Task 3*, via **detailed microscopic studies using Scanning Electron Microscopy, confirmed H embrittlement** and strain localisation close to the fracture surface, as consequence of most H remaining diffusible inside the sample. The results also showed that although the flame and electrochemically charged samples showed similar reduction in ductility, the micrometric distribution of strain during deformation showed significant differences between them. These **findings suggests that flame charged materials could also fail prematurely under other deformation modes, including mechanical fatigue.**

Recommendations

The results are used to **propose standards for best practices to study materials under H_2 combustion environments,** where a workflow and relevant suggestions for material handling are provided to **avoid surface contamination with hydrogen and promote consistency in material analysis and quality control against hydrogen embrittlement.**

In addition, the results are used to define **relevant modifications to the "Certification Specifications and Acceptable Means of Compliance for Engines"** by the **UK Civil Aviation Authority (CAA)** to incorporate the impact of H_2 on Materials and Design.

- Proposed modifications in "*CS-E 70 Materials and Manufacturing Methods*" state the requirement of demonstrating proper screening of material tolerance to Hydrogen Embrittlement, as well as to avoid surface contamination of components with hydrogen that could produce high variability in quality control metrics against hydrogen embrittlement or increase the likelihood of prematurely promoting hydrogen embrittlement.
- On "*CS-E 90 Prevention of Corrosion and Deterioration"* it is identified that maximum hydrogen absorption rate into materials must not exceed values that could promote hydrogen embrittlement and that each engine component and each item of equipment that shows susceptibility to Hydrogen embrittlement must be protected from hydrogen absorption and deterioration.
- Similarly, for "*CS-E 100 Strength*", since hydrogen embrittlement occurs under applied mechanical loads, it is advised that the stresses developed in the engine must be correlated with the possible hydrogen absorption rates in materials to identify critical stresses leading to Hydrogen embrittlement.
- Lastly, it is recommended that evidence of how hydrogen may affect other mechanical properties (not just embrittlement) is provided to demonstrate the impact of H_2 on assumed material characteristics.

The results help to provide a starting model for regulatory framework on H-flame charged gas turbine combustion chamber Nickel-based superalloys. The **recommended further work** follows from the **gaps identified to define more precise guidelines for certification specifications**. These include,

- for "*CS-E 70 Materials and Manufacturing Methods", s*tudy the impact of H in other deformation and damage mechanisms during and following H flame charging, conduct prolonged and cyclic combustion tests and a more detailed mapping of H combustion conditions. These are to identify material limits against hydrogen embrittlement and understand how H affects known mechanical requirements for Nickel-based superalloys.
- In addition, conducting similar studies in other Nickel-based superalloys with different chemical composition and method of manufacturing will help to identify possible differences in hydrogen embrittlement and support compliance requirements on "*AMC E 70 Castings, Forgings, Welded Structures and Welded Components".*
- *On "CS-E 90 Prevention of Corrosion and Deterioration",* it is recommended to conduct a more detailed analysis of oxidation evolution and its impact on H recombination at the surface. In addition, conduct combustion trials on thermal barrier coated (TBC) alloys commonly used in combustors. Most alloys are protected against corrosion using TBCs and these could have similar complex effects as oxides. The proposed activities will be critical to identify if there are self-protecting mechanisms inherent to materials/surface barriers against hydrogen accumulation and/or embrittlement.
- Lastly, on "*CS-E 100 Strength*", it is recommended to develop machine prototypes for in-situ mechanical characterisation while conducting H flame charging. Understanding the effect of simultaneously H charging and mechanically loading materials could provide more accurate insights of how hydrogen embrittlement could develop during engine operation.

Chapter 1

Introduction and Literature Review

Adopting Hydrogen as fuel is one of the most viable solutions for eliminating CO_2 emissions in aviation but it will bring a wide range of challenges for materials used in aircraft components. Hydrogen is well known to degrade the mechanical properties of structural alloys by reducing their strength and ductility without prior signs of warning; this phenomenon is known as Hydrogen embrittlement [1,6]. Hydrogen can also influence other material damage processes relevant to aviation materials, such as accelerating fatigue or increasing creep deformation rates [7]. Hydrogen in both gaseous (H_2) and dissolved (H) form is highly mobile, especially at high temperatures, and it is very likely that H will absorb and interact with Nickel-based superalloys, materials used in combustion chambers and downstream components of gas engines. Material failure may only require a having few tens of parts per million (ppm) of H inside alloys.

Despite the well-known material-related challenges when exposed to gaseous H_2, there is little information on whether exiting alloys used in gas turbines could fail prematurely under H_2 combustion environments. The authors have previously found preliminary evidence of rapid Hydrogen absorption in aerospace alloys when they are exposed to a H/NH_3-containing flame [7]. This report now focuses on studying with more detail the mechanisms of H flame charging and how material conditions affect H absorption; this is to later study the phenomenon of hydrogen embrittlement as it could be one of the most critical material failure mechanisms inside a combustion chamber. The remaining of this section presents main challenges in existing literature to study hydrogen embrittlement in high-temperature alloys used in gas turbines, including the widely referenced work by NASA, that need addressing to support the definition of regulatory frameworks on material qualification for H_2 combustion.

Studying Hydrogen Embrittlement in high-temperature materials for gas turbine engines

One of the most cited works on the impact of H_2 in high-temperature environments is a report prepared by **NASA** in 1973 [3]. It is a very detailed study of the influence of high temperature H_2 gas on the mechanical properties of alloys commonly used in the rocket industry of that era; properties included hydrogen embrittlement, creep, fatigue and fracture toughness. It is a very valuable source that confirms the presence of hydrogen embrittlement in many commonly used gas turbine alloys. This **report was tailored for the very specific requirements of a rocket engine**, with special focus on materials for fuel lines and other components in contact with hot, gaseous H_2 at high pressures. Additionally, the experimental campaigns in the report focused on a timescale consistent with the operation of a single-use rocket engine, or heavily refurbished before every mission as in the case of a space shuttle. The **time scales considered are significantly**

shorter than the tens of thousands of hours of intense operation expected from materials inside a typical turbofan jet engine powering a commercial flight.

Commonly used methods in existing literature to introduce hydrogen into metals and study H Embrittlement are electrochemical [9] (cathodic) or gaseous charging [10], but we will show in this report that these do not reproduce the hydrogen diffusion behaviour and material surface changes occurring during H_2 combustion. Electrochemical hydrogen charging is the most used hydrogen charging experimental method. This technique comes in two main forms: For cathodic charging, samples are placed in an electrolyte and cathodically polarised, initiating a hydrogen evolution reaction at the sample surface. During electrolysis, variables including temperature (typically less than 300^{o}C), electrolyte, charging currents and charging time amongst other things affect the final hydrogen concentration. The large number of variables that must be controlled results in a wide range of hydrogen concentration measured by different authors [10]. Another common method of testing hydrogen-metal interactions is using a double-cell electrochemical hydrogen charging method, or a Devanathan-Stachurski dual battery [11].

This test measures the hydrogen permeability through the metal membrane. It is a common method of measuring the hydrogen diffusion coefficient through metals, especially at room temperature. H_2 gas charging is the second common method of introducing H in metals. Thin specimens are placed in a pressure vessel filled with H_2 gas, usually at high temperatures [9,10]. This technique is especially useful for materials with low hydrogen diffusivity like stainless steels and nickel alloys as the tests are normally conducted above room temperature, as with NASA’s report, as well as for characterising the hydrogen attack phenomenon common in the chemical -especially petrochemical- industry [11]. Thermal Desorption Analysis (TDA) is also used to measure the hydrogen content following charging. TDA is an experimental technique that measures the hydrogen desorption rate from a material at a constant heating rate and it can be used to characterise the diffusion profiles of H inside alloys; **understanding hydrogen diffusion within alloys is the first step to address hydrogen embrittlement and design against it.** H-charged materials are then mechanically tested, typically under tensile or cyclic loading, to verify loss of ductility or early fracture. Advanced microscopy methods, including Scanning Electron Microscopy (SEM) and Transmission EM, are used to analyse the fracture surface and localised material changes at the micron- and nano-scales.

Missing gaps to support material qualification for H_2 combustion

Qualification methods of materials used in combustion engines currently do not consider the presence of hydrogen. On-going assessment of material compatibility with Hydrogen has mainly used existing information and research from other industries, including Space as well as Oil and Gas, where H-metal interactions leading to Hydrogen embrittlement can happen. Hydrogen has been used as a fuel in rockets for over 50 years, but the in-service conditions do not represent the more demanding requirements for modern aeroengines [3]; aircraft follow more complex mission profiles, for which temperatures and mechanical loads inside gas turbines can fluctuate more abruptly, as well as components demanding much longer service lifespans [3,4] (Figure 0.1). When trying to employ existing data from previous works, such as NASA's report [8], neither electrochemical nor high-pressure gas charging methods can replicate the expected conditions of H_2 combustion environments, where material changes such as oxidation happen at high temperatures, as well as H absorption and diffusion being much faster. Electrochemical and gas charging may be appropriate for pre-screening studies, e.g. for material selection, but they are not sufficiently accurate to predict the possible H embrittlement behaviour of materials used in H_2 combustion components. This information will be critical to define comprehensive regulatory frameworks that cover the most critical operating environments induced by H_2.

In Brief: Data and understanding on material testing from other industries is not easily transferable to long-term H_2 combustion.

This work therefore addresses the core question: "*How to qualify new materials for safe H_2 aviation?*" with focus on materials used in H_2 combustion chambers. The authors successfully achieve this by using a one-of-a kind H_2 combustion test rig where metallic test pieces can be directly exposed to different H_2 flames to allow hydrogen absorption and alloy interactions under more realistic combustion environments. This work demonstrates that H_2 has the potential to adversely affect material properties, and it is the first step towards fully unveiling the impact of H_2 on materials used in combustion chambers. The work also shows that the direct transfer of data created using conventional H charging methods, i.e. electrochemical charging, has limited applicability to combustion environments; careful attention must be paid when defining requirements for material qualification relying on these methods. The outcomes are successfully applied to propose inclusions of Hydrogen Embrittlement within existing regulatory frameworks for the safe use of Hydrogen in aviation, as well as to propose standards for best practices to handle H-flame charged materials for gas turbines.

Chapter 2

Experimental Work

This section presents a case study of how exposing a Ni-based superalloy, Inconel 718, to a pure hydrogen flame can lead to significant material changes and hydrogen embrittlement. Inconel 718 was selected due to its high-strength, corrosion-resistance, and wide application in aviation. The chemical composition is shown in Table 1. It is a nickel-chromium alloy widely utilised across various industries due to its exceptional mechanical properties and ability to withstand extreme environments. Its applications include components for liquid-fuelled rockets, rings, casings, and various formed sheet metal parts for aircraft and land-based gas turbine engines, as well as cryogenic tanks. It is also used for fasteners and instrumentation parts [13]. This study explores the physical phenomena occurring under H_2 combustion environments, as H absorption, diffusion and desorption inside the alloy changes with surface oxidation. The H desorption and embrittlement behaviour in the flame charged specimens were compared against the same material but using electrochemical charging to introduce H in the alloys; this is to contrast how the present findings on H_2 combustion compare with current knowledge in the field using conventional methods for introducing hydrogen into alloys.

Methodology and Materials used

The work has been conducted using UCL’s state-of-the-art bespoke H combustion rig and material characterisation facilities (Fig. 3). The H absorption rate in the H-flame exposed alloys has been characterised using various initial surface material conditions.

Table 1 Chemical composition (wt.%) of Inconel 718 used in this work

Type	Ni	Cr	Fe	Nb	Mo	Ti	Al	Co	Cu
Sheet	Bal.	18.66	17.11	5.22	2.91	0.94	0.57	0.23	0.18
Round	Bal.	17.37	19.9	5.21	3	0.98	0.45	0.04	0.01

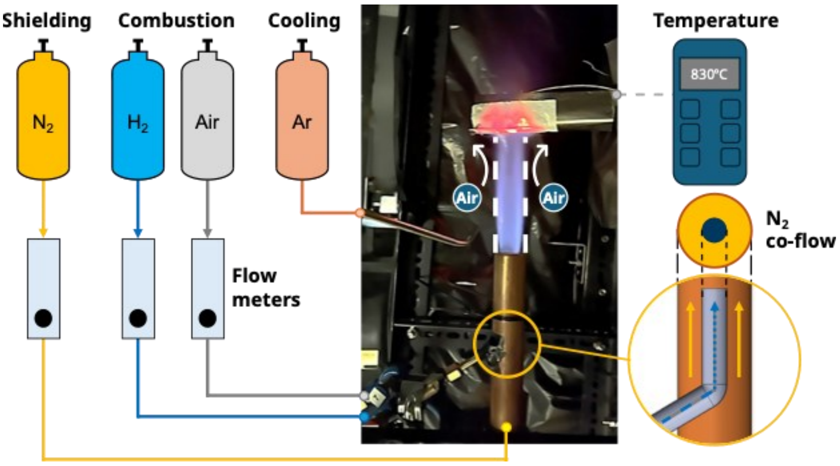

Figure 3 Schematic of premixed-flame combustion setup. Gas flow rates are set and monitored with flow meters. N co-flow shields the flame from atmospheric air.

The tests involved using thin sheets of Inconel 718 and thicker, round specimens of the same material; both sets of samples were prepared in polished and pre-oxidised conditions. Samples were exposed to a pure hydrogen flame in fuel-rich conditions for between 1 hours and 8 hours. Samples were mounted in an insulating fibre holder and placed above the flame's nozzle. At the back of the sample, a thermocouple continuously measured the alloy's temperature during the combustion tests. While this temperature may deviate from that temperature at the front of the sample, this effect is not significant for the (thin) sample sections used in the experiments. Hydrogen gas and air were sourced from commercial suppliers and the H_2/air flow rates were precisely set using flow meters. A stream of nitrogen gas surrounded the nozzle to shield the flame from surrounding atmospheric air. This prevented the reactive gas mixture to be diluted by outside air and ensured hydrogen-rich conditions at the sample surface. High-pressure argon gas was used to rapidly cool down the sample following flame extinguishment; this is to quickly lower the alloy's temperature and decrease the hydrogen diffusivity to limit its desorption from the hot material while cooling. Argon does not introduce hydrogen into the sample as other gases might do. The combustion tests were conducted at two sample temperatures of 690 °C and 835 °C; these are slightly above the service temperatures of Inconel 718 to study more extreme in-service environments. Following exposure to the H_2 flame, the amount of hydrogen inside the samples was evaluated using thermal desorption analysis (TDA) and later linked to material's mechanical performance using tensile testing. The loss in ductility following H_2 flame charging was also compared to samples that were electrochemically charged, as well as H-free reference samples. Scanning electron microscopy (SEM) was used to evaluate microstructural changes in H combustion samples compared to H-free specimens; energy dispersive X-ray (EDX) in the SEM was used to characterise oxide scales formed in hydrogen-rich and hydrogen-free environments. Electron backscatter diffraction analyses (EBSD) gave insights into the microscopic dislocation density distribution and aided in quantifying hydrogen embrittlement via estimating (micron-scale) strain localisation.

Results, Discussion and key scientific findings

The hydrogen absorption data for Inconel 718 at different temperatures and surface conditions is presented below. In all cases, a substantial H uptake of several parts per million (ppm) can be seen, but the amount of H absorbed vary significantly depending on alloy's initial surface condition. Figures 4 and 5a) show that for both temperatures pre-oxidised samples exhibit higher H content than the oxide-free samples with the same thermal history. It is worth noting that that despite the high temperatures, the H absorption rate changes with time and testing conditions; especially at lower temperatures (690 ºC), the H (increase) absorption rate continues beyond the duration of a single-flight in a typical rocket engine (Fig. 4).

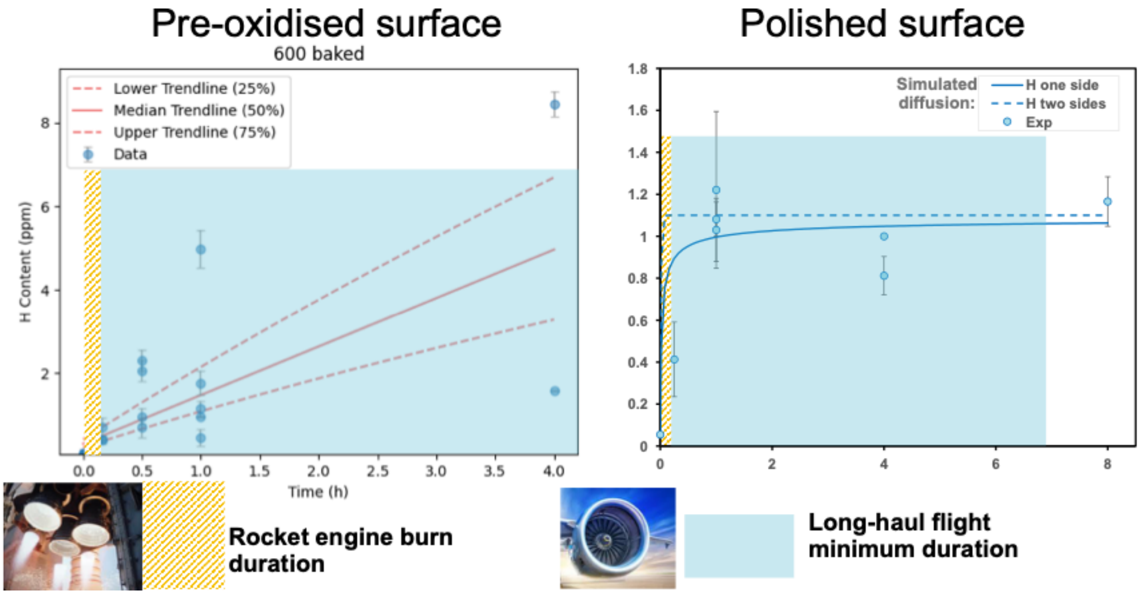

Figure 4 Difference in total H uptake up to 8h between pre-oxidised material and oxide-free (polished) surface conditions. Flame exposure at 690°C.

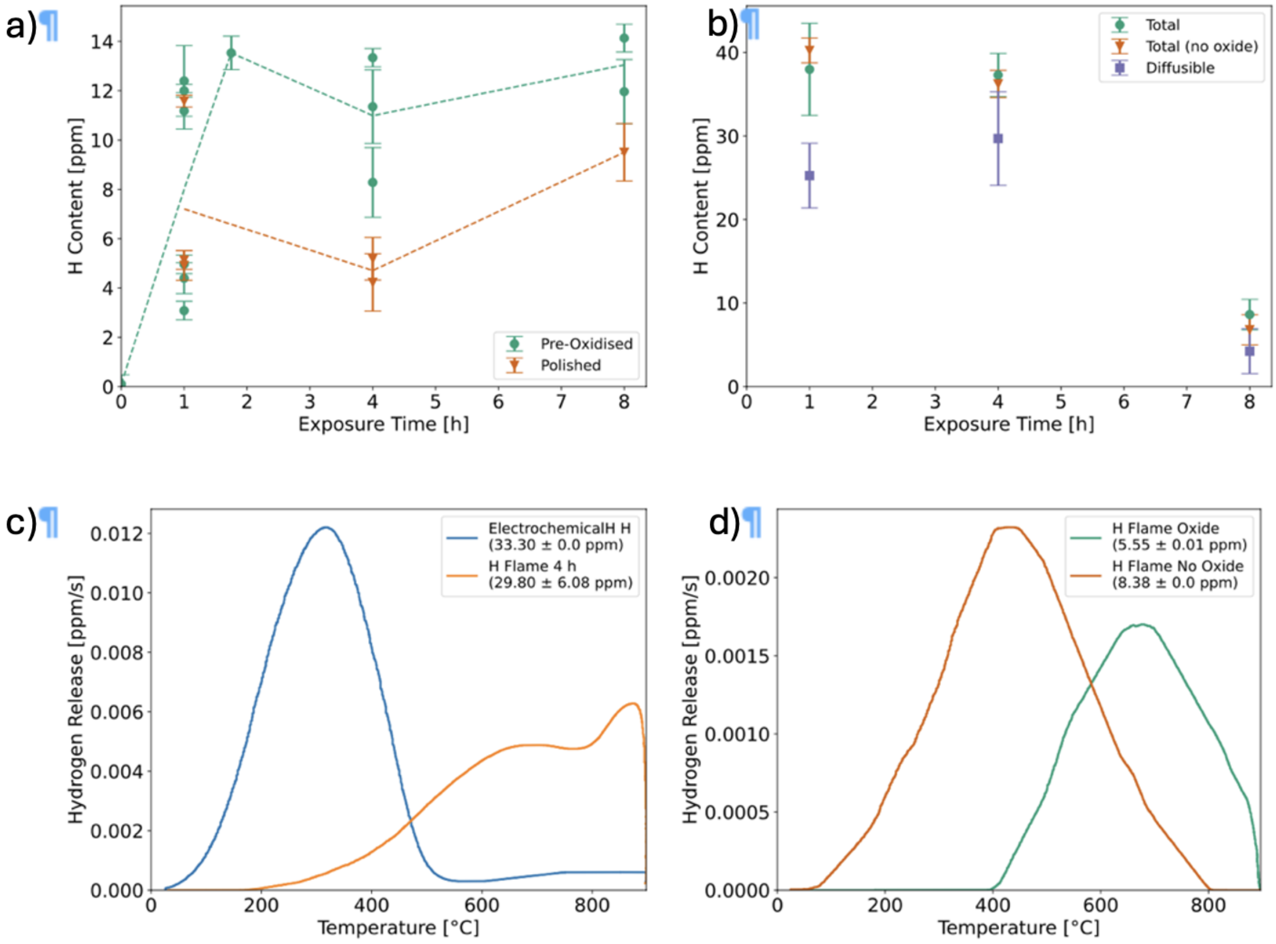

Figure 5 a) Total H uptake over time for pre-oxidised and polished samples; b) individual H content breakdown. c) Comparison in H desorption between alloy exposed to H flame vs electrochemically charged. d) TDA of sample with oxide and with oxide layer removed.

Further investigations were made using thin sheet samples (having a higher surface area per unit volume) to better capture surface-related effects. Figure 5b) shows the location of hydrogen in the tested samples by measuring the total hydrogen in the oxide containing samples (green dots), and by removing the oxide layer after flame exposure (orange dots); it is observed that removing the oxide changes very little the total H content in the samples. Additionally, a decrease of H content between 4 and 6 hours is noted. This drop is observed in several repeated tests and will be further commented while discussing the evolution of the oxide structure during combustion. **A conclusion can be drawn that most of the H is located inside the samples, not oxides, and this H can contribute to the embrittlement process.** The content of H released while heating up to 900°C shows that most of the hydrogen becomes diffusible in the operation range of combustor materials (purple dots), further confirming its potential impact on mechanical properties.

Detailed investigation of the thermal desorption curves shown in Figure 5c) indicate that during the TDA test most of the H in the H-flame charge sample (orange line) is released at high temperatures showing two distinct peaks at approximately 600 °C and 870 °C. Comparing the flame charged sample to the one charged electrochemically (no surface oxidation, blue line) it becomes clear that while the total amount of H released up to 900°C is similar, the desorption profile is dramatically different. The result of electrochemical charging shows that most of the H is diffusible or weakly trapped. Further analysis (of the thicker sample again) shows that after removing the oxide, the temperature of desorption drops significantly from 650 °C to 400 °C (Fig. 5d). This brings the conclusion that the hydrogen inside the alloy is mainly diffusible and desorbs faster without the presence of the oxide. This information is crucial for understanding H embrittlement. Most authors agree that the diffusible (mobile) H causes the embrittlement [6].

At the same time, usually having H in diffusible form causes natural desorption, lowering the total H content inside the alloy. The data presented above not only shows that oxides can promote H uptake but also contain the H inside the alloy, expanding significantly the temperature window of high concentrations of diffusible hydrogen that can promote embrittlement. **This observation demands further work in understanding the oxide evolution and its interaction with H uptake and surface recombination.**

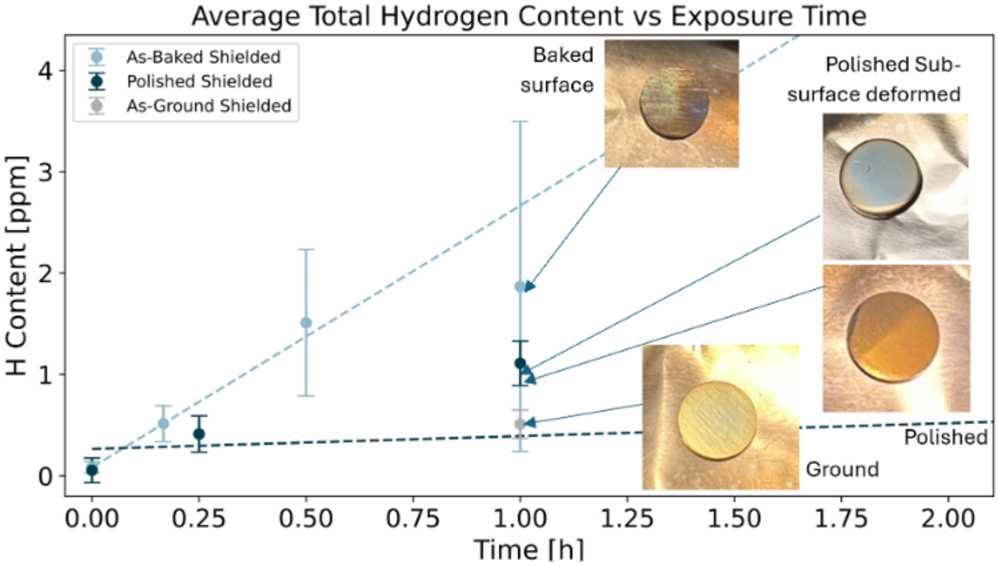

Figure 6 Differences in oxide evolution and H uptake depending on surface preparation. Flame exposure at 690°C.

Figure 6 illustrates the impact of the initial surface preparation on the surface appearance due to oxidation occurring. It shows that the pre-oxidised (baked) surface promotes the highest H uptake, which **corroborates the conclusion that the initial surface condition of materials is a key determining factor controlling the rate of hydrogen uptake in the alloy**. Section 3.1 will provide recommended standards for material handling to minimise the impact of surface changes in analysis materials for H_2 flame charging. Further oxide analysis is provided next.

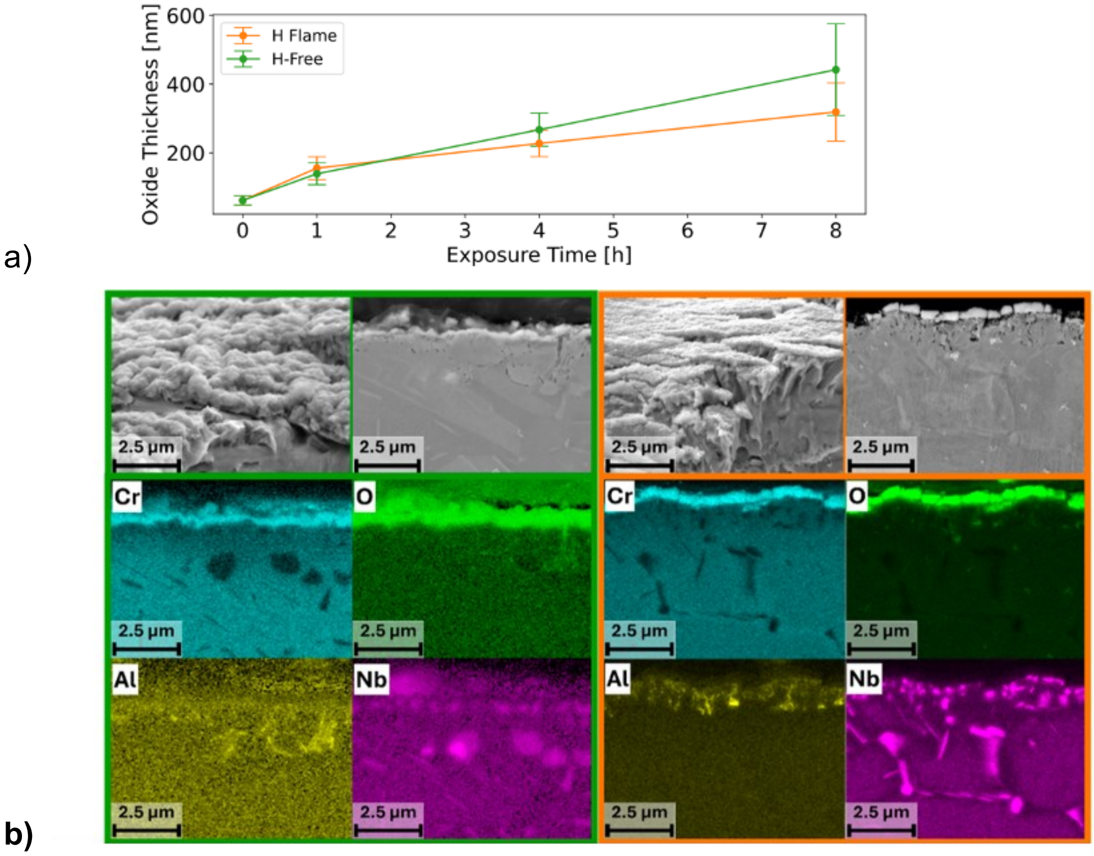

Figure 7 SEM analysis of surface oxide scale evolution measuring a) oxide thickness. b) Surface chemical analysis using EDX of sample exposed to 8 hours.

In Brief: Surface Oxides (and palpably other barrier coatings) can control H absorption into metallic components and possibly

The oxidation evolution analysis (Figure 7) between the H-flame charged samples and samples exposed in air at the same temperature showed apparent similarities. The oxide growth rate shown in Figure 7a) is similar in both cases, yet comparing the surface morphology and the cross section, substantial structural differences can be identified in Figure 7b). The most important difference being the presence of cracks through the surface. As expected in both cases, the main elements in the oxide layer are chromium and oxygen. Additionally, Nb-rich particles are observed in the oxide and an Al-rich phase is present below. The exact structure of the baking oxide used in the pre-oxidation case was too thin to characterise it using SEM and EDS. The structure of this oxide can be assumed from the literature. An oxide, created during baking at approximately 550°C is expected to be mainly NiO [3]. During flame exposure at 835°C, the most probable structure of the oxide layer consists of primarily Cr_2O_3. A hypothesis can be postulated that NiO could degrade after 6-8 hours of combustion changing the chemical interactions with H and also fragmenting the layer, leading to additional H desorption. This hypothesis can potentially explain the drop in H content shown in Figure 5b). A detailed study dedicated to tracking the surface changes is needed to confirm this theory.

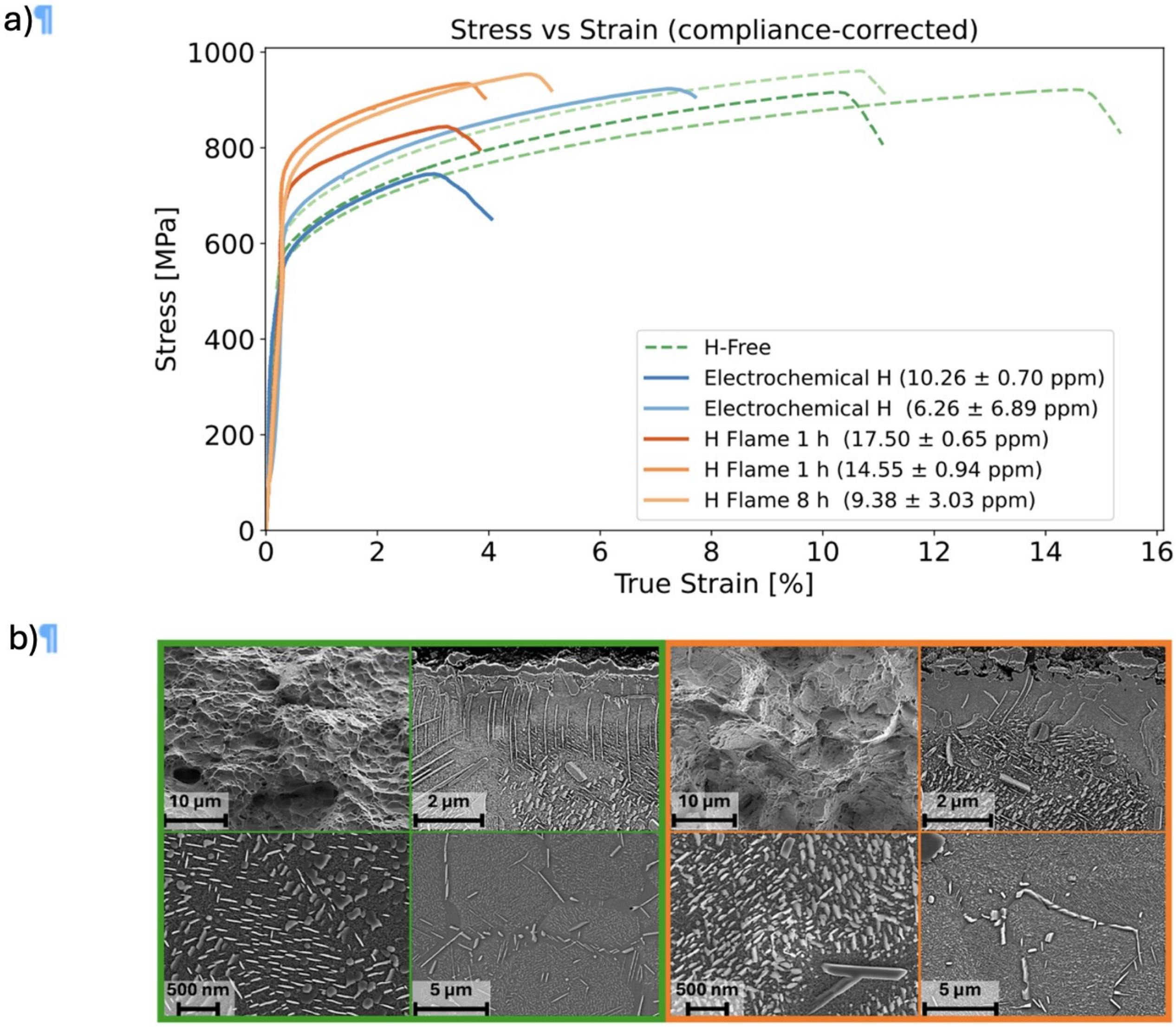

Figure 8 a) Stress-strain curves of H-free, electrochemically charged and H-flame exposed samples. b) SEM analysis of materials following mechanical testing.

In Brief: Hydrogen absorption causes significant drop in tensile ductility in aerospace alloys.

Figure 8a) shows the stress-strain curves and b) SEM analysis showing the detrimental impact of hydrogen in alloy's mechanical properties and microstructural changes. The most significant effect of exposing the Inconel 718 samples to the H_2 flame is the substantial drop in plastic elongation during the tensile tests for all the H containing samples vs the H-free samples subjected to the same thermal history. Interestingly, electrochemically and flame charged samples showed a similar drop in ductility. This further supports the theory that H in the flame charged samples is contained in the core rather than deeply trapped. Figure 8b) presents the fracture surface and the microstructure for both cases. Despite microstructural similarities with just the oxide being different, the fracture surface (upper left corner) shows distinct ductile character for the H-free samples and more brittle behaviour in the case of flame exposed sample.

Figure 9 below shows an SEM-EBSD study of localised strain and Geometrically Necessary Dislocation density (GND) illustrating the differences in micro-strain distribution close to the fracture surface of the deformed samples. The data shows significant differences in the micro-deformation behaviour in both uniform deformation and necking part. In the flame charged sample, the necking region shows large strain localisation -well defined areas with fairly low (blue) and high (green to yellow) dislocation density. As for the uniform deformation analysis, the electrochemically charged sample has the largest strain concentration with regions of almost no deformation (blue) and regions with highest strain localisation (green to yellow); the reference sample shows homogeneous strain distribution and the flame charged sample contains regions of localised strain concentration with a noticeable amount of plastic deformation.

The results also suggest that the tensile tests, while sufficient to demonstrate the occurrence of significant hydrogen embrittlement, are not enough to predict changes in other properties. Especially properties that are linked to localised deformation like mechanical fatigue, could show significant differences in local and global mechanical performance between (H-free) reference, H$_2$ flame and electrochemically charged samples.

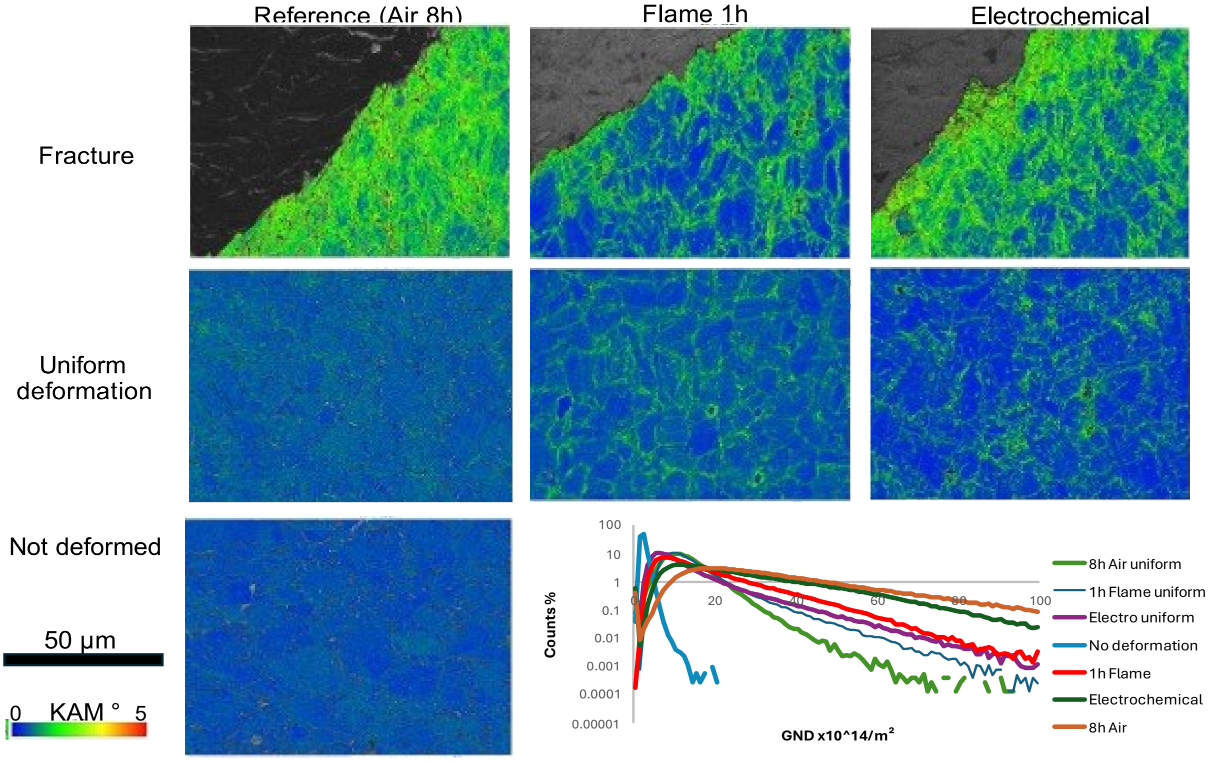

Figure 9 Strain distribution close to fracture surface between H-free sample (orange) and 1h flame (blue): a) Kernel Average Misorientation (KAM) map and b) Geometrically necessary dislocation (GND) density distribution calculated from EBSD maps.

Exposing Ni-based superalloys to a Hydrogen flame can cause significant degradation to their mechanical properties. This work has highlighted several H_2 combustion-specific material damage behaviour:

In Brief: Both methods for introducing H show similar loss of tensile properties but there are microscopic differences that could lead to premature failure under different deformation modes like fatigue.

No H	H Flame charging	Electro-chemically charged
Strain is homogeneously distributed	Mixed regions	Strain is mostly localised

- Hydrogen accumulation inside Inconel 718 increases with flame exposure, confirming easy H absorption during H_2 combustion.
- Surface oxides play a dual role in the H mass flow, where pre-oxidising the sample can facilitate H uptake but at the same time prevents H desorption. The composition of the oxide seems to impact the absorption and recombination kinetics. These findings indicate that oxidation during H_2 combustion is key in controlling alloy’s overall H content and mechanical integrity.
- Pre-existing or forming oxides in the sample prevent the desorption of otherwise mobile (diffusible) hydrogen. Thermal desorption analysis showed that hydrogen in the flame-exposed material remains inside the alloy for a wide temperature range up to 900 °C. This contrasts with the sample electrochemically charged with H, where most H is released below 500 °C.
- Mechanical testing confirmed Hydrogen embrittlement occurs in materials following exposure to H_2 flames as consequence of most H remaining diffusible in the sample. The damage mechanisms are consistent with H-enhanced localised plasticity.
- **The results demonstrate that existing knowledge of H diffusion and embrittlement, and experience from other industries where oxidation does not happen, is not directly transferable to H combustion conditions.**

Chapter 3

Implications for material qualification

Standards for best practices to study materials under H_2 combustion environments – Do’s and Don’ts

Investigating hydrogen evolution in metals, especially in H combustion environments requires highly rigorous procedures to ensure consistency in the measurements. Hydrogen is present in several items commonly used in laboratories and testing facilities, like gloves, plastics, oils, lubricants, and the investigator himself. Contamination with Hydrogen is extremely easy to happen.

Even if standard material preparation methods to study H embrittlement are followed from other industrial applications, there are two main mechanisms of contamination that can jeopardise accurate material analysis during Hydrogen combustion:

- Introducing additional H from contaminated samples (for example handling with nitryl gloves) will artificially increase the H content in the test pieces
- Modifying the surface of metals, e.g. by poor surface finish, will change the kinetics of H-material interactions and possibly promoting faster H absorption

To avoid these issues, a list of practical recommendations is given below:

- Use proper material handling procedures to avoid surface contamination:
  - Touching sample surfaces with nitryl or latex gloves can falsify the total hydrogen measurement by inflating it by several parts per million (ppm). Using clean metal tweezers is recommended.
- Apply surface cleaning procedures where needed:
  - Ultrasonic cleaning for 15 minutes in acetone, followed by 1 minute in propanol, rinse with propanol and drying with compressed air (oil and water droplets free).

Figure 10 below shows an example of the apparent total H content in a sample can change depending on the method for material preparation before H combustion. Here, the sample was delivered in the form of a 0.25mm thick sheet. Despite looking clean, it still held a significant amount of lubrication used during the manufacturing process. The first step was to do ultrasonic cleaning on the sample with acetone for 15 minutes. The total H test revealed significant drop of released hydrogen. This is because in this kind of melt extraction test, the whole available hydrogen is released in the gas form. This consists of diffusible hydrogen, trapped hydrogen, as well as any hydrogen from surface contaminations like hydrocarbons. Since acetone is known to leave residual H, following ultrasonic cleaning and acetone drying, another sample was further cleaned for 1 minute in propanol sprayed with fresh propanol and cleaned with dry (oil-free) compressed air. The total hydrogen content measured from the new sample further decreased H content to less than 1 ppm. This cleaning routine is sufficient to reliably measure the hydrogen content in most cases. If the sample undergoes a H charging test, a “baking” step can be applied to release more H and further standardise the baseline values. It needs to be reminded that handling need to be done with a set of tools (like metal tweezers) that would not introduce any surface contamination. For example, handling a baked sample with pair of new nitryl gloves would bring the apparent total H content to around 5ppm just by introducing surface contamination.

Tip: Be aware of any potential surface contamination sources. Even handling samples with standard nitryl gloves can artificially increase H readings. Use dedicated procedures that minimise surface contact when handling test pieces before and after testing.

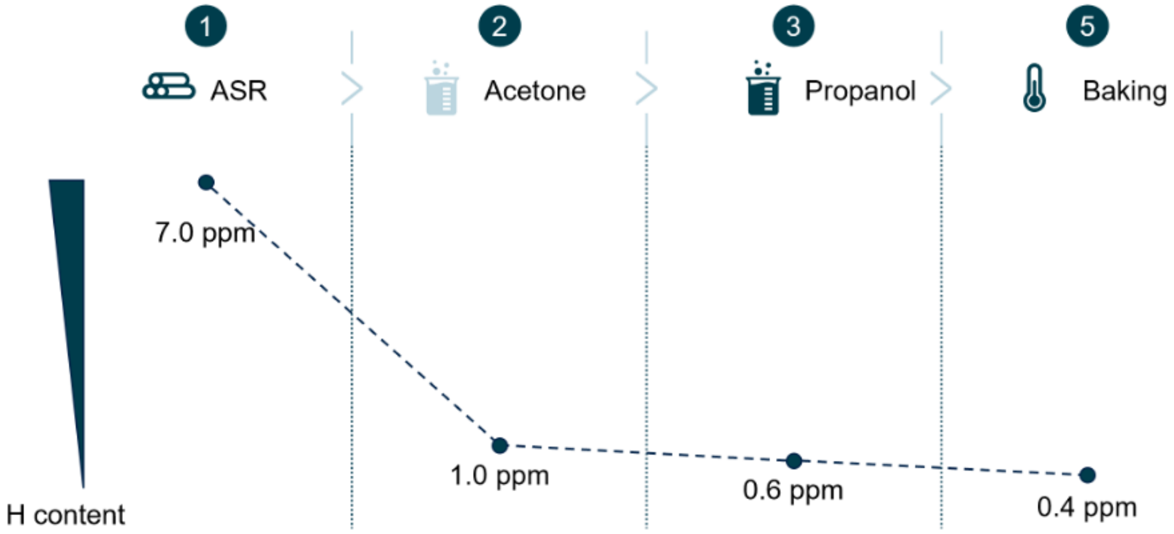

Figure 10 Example of sample of residual hydrogen before H combustion testing.

The optional step 5 of baking is intended for reference sample preparation. For proper understanding of the H uptake during the combustion tests, it is usually required to remove Hydrogen coming from previous preparation processes. Baking allows to ensure that all the non-deeply trapped Hydrogen comes from the charging method applied. The bake-off time and temperature need to be set based on the component size, H diffusivity in the material and the thermal stability of the microstructure of the sample. Handling a sample should only be done with tools (like metal tweezers) that do not introduce any surface contamination. Hence before the H uptake test, the surface needs to be brought to the condition representative for operation, e.g. by mechanically grind off the oxide. Even having a thin oxide of tens of nm (or possibly smaller) can heavily modify the H-metal interaction during combustion.

In Brief: It is necessary to distinguish the H introduced by surface contamination and that present inside the alloy.

Towards defining certification requirements for Hydrogen flame charged gas turbine combustion chamber Nickel-based superalloys

Pertinent certification specifications and acceptable means of compliance require the inclusion of possible Hydrogen embrittlement and other forms of H-related damage in materials used in gas turbine combustion chambers and downstream components. This section covers proposed modifications (highlighted in blue) to relevant requirements in the UK Civil Aviation Authority Certification Specifications for Engines [2,14]. This is only a starting point, and further work is needed to develop more comprehensive recommendations.

Gas turbine combustion chambers are constructed from forged and/or rolled rings that are then machined and drilled. The rings can be partly coated with barriers to increase thermal strength. Nickel-based superalloy is used to resist a combination of creep, pressure loading, high cycle and thermal fatigue.

CS-E 15 Terminology

Hydrogen embrittlement - means a form of stress-induced fracture, causing metal alloys to suddenly crack or fail under stress values below the yield stress and without prior signs of damage. The hydrogen accumulation rate inside materials as a result of being exposed to hydrogen flames must be kept below a critical threshold where hydrogen embrittlement could happen. In addition, hydrogen can affect other properties of superalloys, including creep and fatigue and evidence must be available to demonstrate the impact of H_2 in the assumed material characteristics.

CS-E Requirements Pertinent to Hydrogen Flame Charged Combustion Chamber Materials

CS-E 70 Materials and Manufacturing Methods

(a) The suitability and durability of materials used in the Engine must be established on the basis of experience or tests. The assumed design values of properties of materials must be suitably related to the minimum properties stated in the material specification.

(b) Hydrogen flame charged combustion chamber materials may be susceptible to hydrogen embrittlement and suitable tolerance to hydrogen must be stated in the material specification.

(c) Manufacturing methods and processes must be such as to produce sound structure and mechanisms which retain the original mechanical properties under reasonable service conditions. Handling of material during assembly must be such that surface contamination with hydrogen is avoided to reduce variability in quality control metrics against hydrogen embrittlement or reduce the likelihood of prematurely promoting hydrogen embrittlement.

In addition, Acceptable Means of compliance “AMC E 70 Castings, Forgings, Welded Structures and Welded Components” must be adapted to address manufacturing and material compliance methods of hydrogen combustion engines and demonstrate suitability of materials against hydrogen embrittlement.

CS-E 90 Prevention of Corrosion and Deterioration

(a) Each Engine component and each item of equipment must be protected from corrosion and deterioration in an approved manner.

(b) Materials which will render the Engine inherently self-protecting against corrosion, without the use of internal and external corrosion inhibitors, must be used wherever possible.

(c) The maximum hydrogen absorption rate into materials must not exceed values that could promote hydrogen embrittlement under most severe operating conditions conforming to those established by satisfactory practice for the material involved.

(d) Each engine component and each item of equipment that shows susceptibility to Hydrogen embrittlement must be protected from hydrogen absorption and deterioration in an approved manner.

CS-E 100 Strength

(a) The maximum stresses developed in the Engine must not exceed values conforming to those established by satisfactory practice for the material involved, due account being taken of the particular form of construction and the most severe operating conditions. Where a new type of material is involved, evidence must be available to substantiate the assumed material characteristics. For Turbine Engines, due consideration must be given to the effects of any residual stresses in Engine Critical Parts.

(b) The stresses developed in the Engine must be correlated with the possible hydrogen absorption rates in combustion engine materials to identify critical stresses leading to Hydrogen embrittlement.

(c) Apart from mapping critical operating conditions in (b), evidence of how hydrogen may affect other mechanical properties must be available to demonstrate the impact of H_2 in the assumed material characteristics. Maximum stress and hydrogen values must be defined conforming to those established by satisfactory practice for the material involved, due account being taken of the particular form of construction and the most severe operating conditions.

Chapter 4

Outlook and recommended further work

Existing industrial gas turbine demonstrator programmes cannot not provide accurate information of the fundamental limits of material tolerance to Hydrogen that are needed to define comprehensive regulatory frameworks for the safe use of Hydrogen in aviation. First principles studies, like the present work, are needed to isolate and identify the critical physical processes leading to hydrogen absorption and embrittlement, as well as to unveil other material damage processes that are unique to hydrogen combustion conditions. Having access to such understanding will help regulatory bodies to make informed and unbiased decisions on certification requirements on any future H_2-powered combustion technology.

The present work has demonstrated the adverse impact of H on materials used in combustion chambers, via showing hydrogen embrittlement in H flame charged Inconel 718. The results helped to provide a starting model for regulatory framework on H-flame charged gas turbine combustion chamber Nickel-based superalloys. However, further work is required to help providing more precise guidelines for certification specifications. These include:

- CS-E 70 Materials and Manufacturing Methods
  - Study the impact of H in other deformation and damage mechanisms during and following H flame charging; these can include fatigue and creep. This is not only to identify material limits against hydrogen embrittlement but also how H affects mechanical requirements for Nickel-based superalloys.
  - Conduct Prolonged and cyclic combustion tests to represent variable engine operating conditions. It is well known that cyclic loading, either thermal or mechanical, accelerates material failure (e.g. monotonic tensile vs fatigue deformation) and a similar behaviour may be observed for H-flame charging due to the dynamic behaviour of hydrogen absorption and desorption observed.
  - Conduct a more detailed mapping of H_2 combustion conditions and expand the comparison between flame and electrochemical charging. This is to develop a more comprehensive understanding of how the H charging method affects material properties. The differences and implications on strain localisation found between flame and electrochemical charged failed samples need to be better understood.

In Brief: It is necessary to find self-protecting mechanisms for existing and new materials against H-induced degradation.

- AMC E 70 Castings, Forgings, Welded Structures and Welded Components
    - Conduct a similar study in other Nickel-based superalloys, apart from Inconel 718, with different chemical composition and method of manufacturing to identify possible differences in hydrogen embrittlement
- CS-E 90 Prevention of Corrosion and Deterioration
    - Further expand the study of altering material's surface condition. Specifically, conduct a more detailed analysis of oxidation evolution and its impact on H recombination at the surface. The work provided seminal scientific conclusions, but more detailed studies are needed to properly explain the chemo-physical processes affecting H absorption when in contact with oxides, which could promote complex catalytic reactions.
    - Conduct combustion trials on thermal barrier coated (TBC) alloys commonly used in combustors. Most alloys are protected against corrosion using TBCs and, based on the present results, TBCs could have similar complex effect than oxides. Identifying if TBCs either delay or accelerate H absorption/desorption -or have no influence on H flow at all- will be crucial to understand more realistic in-service conditions for combustor materials leading to hydrogen embrittlement.
    - The previous activities will be critical to identify if there are self-protecting mechanisms inherent to materials/surface barriers against hydrogen accumulation and/or embrittlement.
- CS-E 100 Strength
    - Develop a prototype for in-situ mechanical characterisation while conducting H flame charging. Mechanical tests conducted in the present work were conducted following H flame charging, *i.e.* ex-situ, and understanding the effect of simultaneously H charging and mechanically loading materials could provide more accurate insights of how hydrogen embrittlement could develop during engine operation
    - Combustion chamber differential pressure depends on the engine cycle pressure ratios but the sizing case is with the aircraft flying low and fast on a cold day. This is suggested as a static load test case.

APPENDIX A

Nomenclature

Absorption the process where a substance (hydrogen) is dissolved into the bulk of material

Adsoprtion the process where molecules adhere to the surface of a material

Core (matrix) the internal part or bulk of a metal component

Creep time-dependent deformation of materials at elevated temperatures and constant mechanical stress

Desorption the release of previously adsorbed substances from a surface

Diffusible hydrogen atomic H dissolved in the metal lattice that is mobile and is usually associated with H embrittlement

EBSD Electron Backscatter Diffraction is a SEM based technique for materials characterisation. At each pixel the indexing of the diffracted pattern provides information about the phase and the crystallographic orientation of each microstructural constituent. This provides very detailed information about metal (or other crystalline material) microstructure and localised deformation.

EDX (EDS) Energy Dispersive X-ray (Spectrometry) is a technique for determining the elemental makeup and composition of materials in the Scanning or Transmission Electron Microscope (SEM/TEM).

Fatigue deformation mode consisting of material weakening induced by cyclic mechanical loading resulting in failure under stresses below the fracture stress under a single load

Fracture toughness engineering metric of the amount of stress required to propagate uncontrollably a preexisting crack or flaw

GND (Geometrically Necessary Dislocations) are a subset of dislocations within a crystal lattice that produce a net lattice curvature, rather than cancelling each other’s rotation. By examining the density and distribution of GNDs, local (micron-scale) plastic deformation can be quantified, offering insights into how the material accommodates strain at the microscopic level. EBSD technique can be used to quantify the GND in a crystal.

H atomic hydrogen; dissolved in metals or adsorbed and split on the surface or hydrogen radicals (highly reactive single atoms present in gas state)

H_2 molecular hydrogen; gas form or adsorbed at the surface but not split into atomic H

High Temperature Hydrogen Attack high temperature process consisting of H recombination with carbon inside alloys causing embrittlement due to the formation of methane (CH_4) gas bubbles. The **Nelson curves** are used to visually represent boundaries for maximum temperature and hydrogen partial pressure values where hydrogen attack can occur. This curve delineates the region of safe use for steels.

Hydrogen charging introducing H into metals to estimate its influence on the mechanical properties of alloys

Hydrogen embrittlement sudden decrease of ductility and mechanical strength without prior warnings caused by the dissolved, usually diffusible (not trapped) H

Hydrogen permeability measure of the rate of hydrogen atoms to diffusion through a metal section

Hydrogen trapping process where hydrogen atoms become localized at specific sites within a material, such as defects, dislocations, or precipitates, which reduces their mobility and mitigates their potential to cause embrittlement.

Hydrogen uptake process of accumulation of hydrogen in metal as an effect of the difference between absorption and desorption

KAM Kernel Average Misorientation is a method similar to measuring Geometrically Necessary Dislocations (GND) that used to visualise the local deformation of the crystal lattice. It calculates the average misorientation angle between a point of interest and its neighbouring points in a defined kernel.

Oxide layer of corrosion products forming on the metal surface during combustion

SEM Scanning Electron Microscopy

TDA (TDS) Thermal Desorption Analysis or Thermal Desorption Spectroscopy (for setups with detector using spectroscopy) is an experimental method where the desorption of H is measured during heating in protective atmosphere or vacuum. This method allows to quantify hydrogen diffusion and trapping.

Weak traps (reversible traps) the trapping sites that can easily release H with relatively small increase of temperature or mechanical loads.

APPENDIX B

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