AEROSPACE TECHNOLOGY INSTITUTE

Hydrogen Capability Network

University of Sheffield

Cryogenic Hydrogen Materials

Global Research Landscape

May 2025

About

This report is authored by the University of Sheffield with support from Oxford Research and Development Limited, in response to the Hydrogen Capability Network's Global Capability Research Tender for the topic of **Fundamental Research into Material Behaviour in Cryogenic Hydrogen Environments.**

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About the Aerospace Technology Institute

The **Aerospace Technology Institute (ATI)** is an independent organisation that works alongside government and industry to transform UK aerospace through technology and innovation. The ATI is funded equally by the **Department for Business and Trade (DBT)** and by industrial recipients of project grants who pay a small levy. ATI projects are chosen and overseen through close collaboration with Innovate UK and DBT.

As well as running this portfolio of R&T projects, the ATI conducts strategic research projects to help define and answer systemic questions of value to the UK aerospace sector. In 2022 the ATI published the findings of the **FlyZero** project, which concluded that liquid hydrogen is the most viable zero-carbon emission fuel with the potential to scale to larger aircraft.

The ATI Programme has made several investments in liquid hydrogen technologies to support the next generation of zero-carbon aircraft. The **Hydrogen Capability Network (HCN)** was launched in April 2023 funded by the Department for Business and Trade, to progress key recommendations from FlyZero which will enable the aerospace sector to deliver liquid hydrogen research and development (R&D).

About the University of Sheffield

The **University of Sheffield** is one of the biggest and best providers of engineering research and education in the UK. A member of the Russell Group of leading UK research universities, Sheffield has an outstanding performance for excellent teaching and research confirmed by international independent assessments. It is ranked top 100 in the Times Higher education World University Rankings 2025, and one of the top ten UK universities for engineering teaching and education. The faculty of engineering hosts an extensive range of expertise, with four academic schools incorporating three interdisciplinary programme areas for all engineering disciplines.

Hassan Ghadbeigi is a professor of Structural Integrity in Manufacturing and the deputy lead for Manufacturing and Structural Integrity research group at the School of Mechanical, Aerospace and Civil Engineering. His research is focused on manufacturing processes and the effects on structural integrity of materials and components. The team behind this report has further expertise in cryogenic testing, composite materials manufacture and design.

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Disclaimer and Funding Acknowledgement

This work was carried out by the **University of Sheffield** with support from **Oxford Research and Development Limited**, funded by the **Aerospace Technology Institute's Hydrogen Capability Network (HCN)**.

The report is based on reviews of published information available before February 2025. Although every effort has been made to ensure it reflects a comprehensive review there will be research that was not available in the public domain, unable to be translated to English or not published due to commercial or security restrictions. The ATI does not accept liability for any errors, omissions or misleading statements and no warranty is given or responsibility accepted for any actions users may take based on the content of the report. The ATI reserves the right at any time to make changes to the material, or discontinue the report, without notice.

Cryogenic Hydrogen Materials Summary

The Aerospace Technology Institute's (ATI) FlyZero project concluded that liquid hydrogen (LH2) is the most viable zero-carbon emission fuel for future larger aircraft. The FlyZero reports highlighted technologies which would be required to enable such aircraft to become a reality and the gaps in liquid hydrogen capability. The technological change to a liquid hydrogen architecture is revolutionary and the cryogenic hydrogen storage and fuel system faces great disruption. To get to a certifiable, commercially viable system design it requires a breadth of knowledge relating to cryogenic hydrogen that does not currently exist within the sector. As such, the Hydrogen Capability Network (HCN) has identified three key areas which need to be supported:

- Fundamental research into material behaviour in cryogenic hydrogen environments.
- Fundamental research into cryogenic hydrogen thermofluids behaviour.
- Fundamental research into cryogenic hydrogen health and safety.

Workshops on these three topics were held, to identify subtopics that were of particular interest to both industry and academia. The HCN commissioned global landscaping projects to investigate the current state-of-the-art fundamental research on these subtopics in each of the three key areas, and a report has been written by academic experts on each of them. Each report highlights the global research status and gaps in which research and development is needed to enable the liquid hydrogen aircraft of the future.

This report addresses the materials topic. The scope is to document global cryogenic hydrogen low (1-3) technology readiness level (TRL) materials research to identify: global capabilities and work underway, critical research gaps and potential partners for future collaboration.

To develop and certify future hydrogen powered civil aircraft, materials will need to be selected and validated for the entire liquid hydrogen fuel system, from storage tank through to heat exchangers, as illustrated in Figure 1. These will operate at temperatures down to 20 Kelvin (-253°C), with some surfaces hydrogen exposed, and with a wide range of mechanical and temperature cycling requirements depending on the position in the fuel system. The combined exposure of materials to hydrogen and to cryogenic temperature cycling creates particular materials challenges, with considerations including hydrogen embrittlement, internal stresses, and substantial physical and mechanical properties variation, and permanent modification due to temperatures approaching absolute zero.

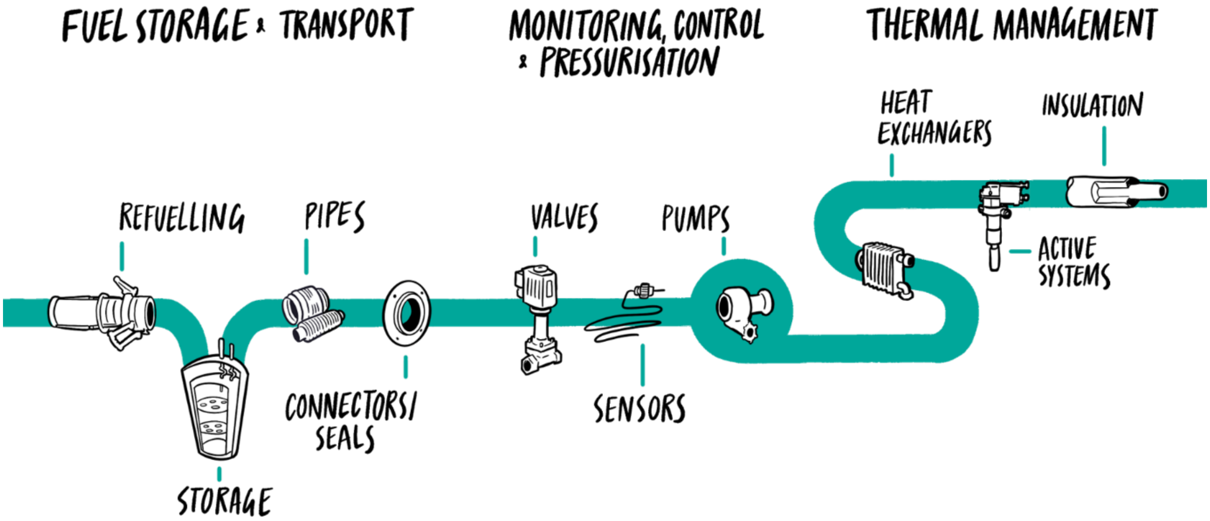

FIGURE 1: THE CRYOGENIC HYDROGEN STORAGE AND FUEL SYSTEM, SHOWING EXPECTED KEY COMPONENTS (ATI HCN).

The combined effects of cryogenic temperatures and hydrogen exposure are not necessarily the same as testing for each effect separately, as the kinetics of hydrogen transport through materials also changes significantly at cryogenic temperatures. Differential thermal contraction combined with temperature dependent stiffening of materials also becomes a significant concern, particularly at regions of high internal stress, or at interfaces between dissimilar materials. Ultimately, these various considerations and their underpinning data need to be combined in models to allow aircraft developers to simulate components and systems during the design process. Any such models need to be validated with robust materials data taken in representative conditions.

This report focuses on the global research landscape for acquisition of materials properties data required for development of the cryogenic hydrogen storage and fuel system. The purpose is to inform the UK aerospace industry and the wider UK cryogenics and hydrogen research sectors of research capability outside of the UK, Figure 2. This in turn will allow the UK research sector to consider gaps in UK capability, which may impact on competitiveness of the UK aerospace sector in realising liquid hydrogen fuelled civil aviation. In turn, this may inform strategies to collaborate or to compete, to close critical capability and knowledge gaps.

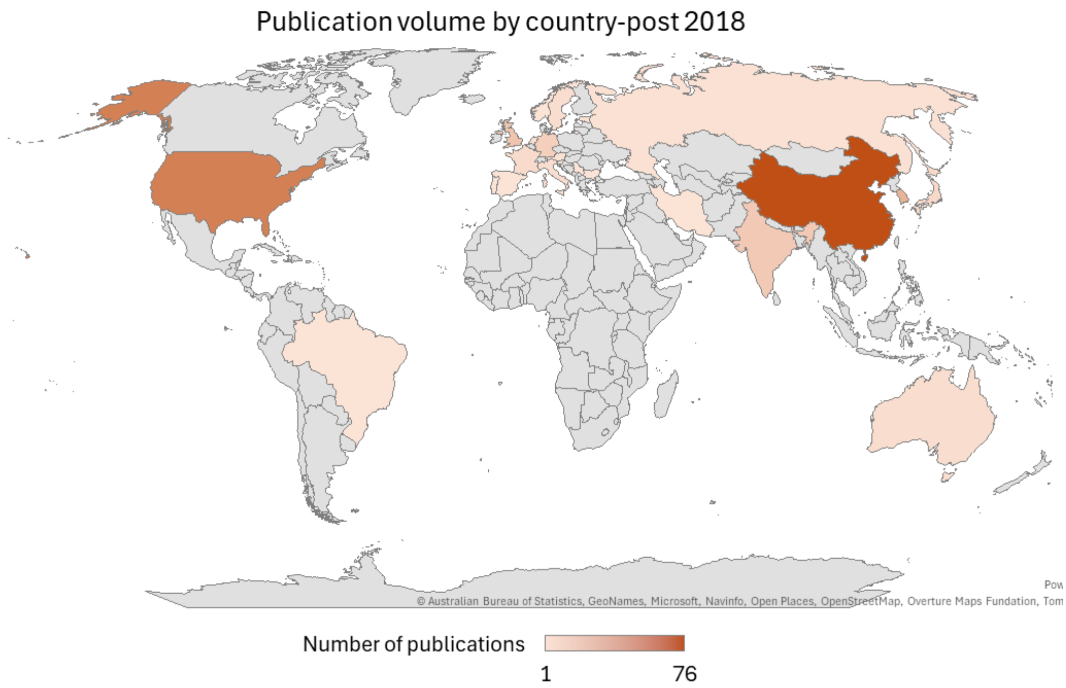

FIGURE 2: RELATIVE CUMULATIVE VOLUME OF LIQUID HYDROGEN RELEVANT MATERIALS TESTING RELATED PUBLICATIONS, BY COUNTRY, SINCE 2018, INDICATING RELATIVE LEVELS OF CURRENT RESEARCH CAPABILITY

Top 6 Global Research Gaps

1. For metals, data on the combined impacts of fatigue cycles and thermal cycles in cryogenic hydrogen is lacking. Whilst 316L Stainless Steel has a long history of use in liquid hydrogen systems, data on lightweight alloys is less mature.
2. There is a global lack of capability for long term or accelerated ageing studies for liquid hydrogen compatible materials.
3. There is extremely limited capability globally to acquire data on mechanical properties at liquid hydrogen relevant temperatures, and even more limited capability to do this in cryogenic hydrogen. Equipment and methods are not standardised.
4. For composites, comprehensive knowledge of the relationship between reinforcement structure, composition and macroscopic properties at cryogenic temperatures is lacking, making extrapolation to components more challenging due to impact of 3-dimensional form.
5. Modelling to link materials test data to component performance and service life at cryogenic temperatures is immature. Standardised data to validate models is also lacking.
6. The relationship between manufacturing parameters and mechanical properties becomes more pronounced at cryogenic temperatures, where material behaviour is more sensitive to microstructural features.

This report is structured into sections, first covering the fundamental materials science by materials groupings (metals, composites, and sealing materials) and then covering the various aspects of global know how and capability across mechanical properties testing, LH2 relevant hydrogen loading methods, hydrogen transport properties, tribology and thermal properties. Progress in modelling and service life prediction is also covered. Within each section a summary is provided on the current maturity of knowledge, the key research gaps (including capability gaps) and key global research centres. This is backed up by around 400 individual literature citations, providing readers with routes to further explore topics of specific interest.

An overview of the patent landscape provides an indication of global pre-commercial activity on liquid hydrogen, indicating strong dominance of Asia, with the UK currently in 7th place behind China, South Korea, Japan, USA, Germany and France, but starting to ramp up. Ramp up in Asia is at least 5 years ahead of other regions, driven by a strong interest in liquid hydrogen as an internationally shippable energy carrier, and for use in ground transport applications. This may create learning and collaboration opportunities for aerospace, along with potential competition due to transferability of capability.

Contents

Acronyms

BCC:	Body Centred Cubic
CCH2:	Cryo-Compressed Hydrogen
CF:	Carbon Fibre
CP:	Specific Heat Capacity
CRFP:	Carbon Fibre Reinforced Polymer
CryoH2:	Cryogenic Hydrogen (liquid or gaseous)
CTE:	Coefficient of Thermal Expansion
FCC:	Face Centred Cubic
FRP:	Fibre Reinforced Polymer (composite)
GF:	Glass Fibre
GRFP:	Glass Fibre Reinforced Polymer
H2:	Hydrogen
HCP:	Hexagonal Close Packed
HEA:	High Entropy Alloys
ILSS:	Interlaminar Shear Strength
IPSS:	In Plane Shear Strength
K:	Degrees Kelvin
LHe:	Liquid Helium
LH2:	Liquid Hydrogen
LN2:	Liquid Nitrogen
TC:	Thermal Conductivity
TRL:	Technology Readiness Level

1. Introduction

The Aerospace Technology Institute's (ATI) FlyZero project concluded that liquid hydrogen (LH2) is the most viable zero-carbon emission fuel with the potential to scale to larger aircraft. Amongst the many reports published, FlyZero identified a UK gap in LH2 capability. At the same time, the ATI published the UK aerospace technology strategy, Destination Zero, which identified that the UK could grow its market share from 13% to nearly 18% by 2050, as aircraft fleets transition towards zero-carbon emission technologies.

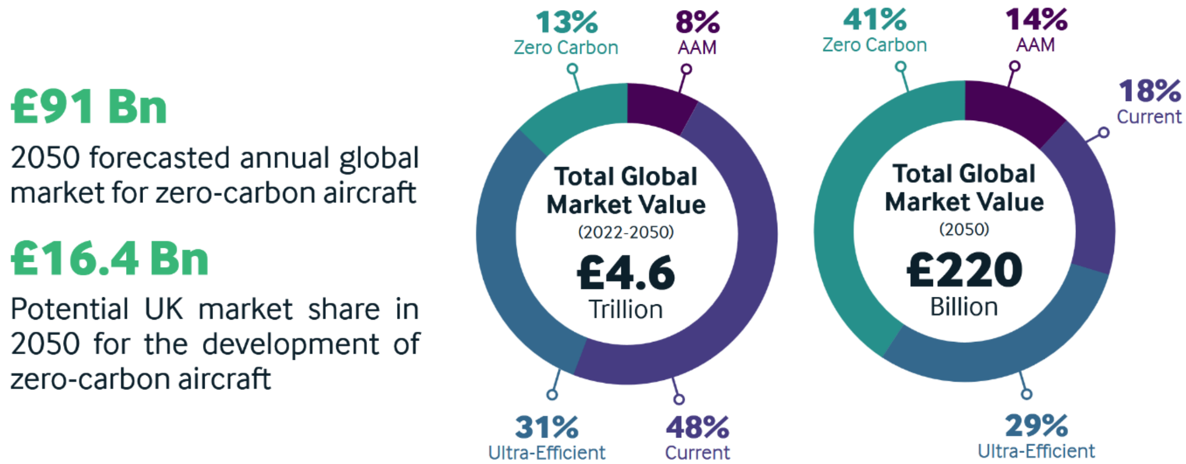

FIGURE 1-1: UK OPPORTUNITY SIZING, FROM "ATI HYDROGEN CAPABILITY NETWORK – SECURING LIQUID HYDROGEN CAPABILITY IN THE UK, MAY 2024".

Although the date for realising this market projection is likely to be later than currently published, the potential opportunity for hydrogen aircraft remains. Achieving this market share is contingent on continued investment in technology development, regulation, and infrastructure. Hydrogen aircraft deliveries are forecast to create a global market opportunity of £34bn by 2050. Having identified that other countries are already planning, or have commissioned, facilities and initiatives to support their domestic supply chain, in 2023 the ATI set up the Hydrogen Capability Network (HCN).

The HCN project aims to make recommendations on strategic interventions and what is required to maximise UK industry competitiveness in the emerging liquid hydrogen-powered flight market. Over the past 24 months, the HCN team has connected with over 260 stakeholders from across the UK. This has included 90+ face-to-face discussions and site visits; and over 100 attendees from 44 unique organisations to ATI's testing, research, and skills workshops. The HCN ran a first UK Cryogenic Hydrogen Research Conference in January 2025, with over 150 attendees from academia and industry.

1.1. Purpose of Study

The ATI HCN, through a series of well attended workshops, have reviewed and helped to co-ordinate UK fundamental research capability in support of developing Liquid Hydrogen fuelled civil aircraft. An interactive summary of UK capabilities can be found on the ATI HCN website and in the accompanying report *Cryogenic Hydrogen Materials Research Workshop Summary, August 2024 [1]*.

The purpose of this global landscape study is to extend beyond the review of UK capability to inform the HCN, UK aerospace industry and the wider UK cryogenics and hydrogen research sectors of research capability outside of the UK. This in turn will allow the UK research sector to consider gaps in UK capability which may impact on competitiveness of the UK aerospace sector in realising liquid hydrogen fuelled civil aviation. In turn, this may inform strategies to collaborate or to compete to close critical knowledge gaps, Figure 1-2. This global landscaping study report has been prepared by The University of Sheffield in conjunction with specialised R&D consultancy Oxford Research and Development Ltd, on behalf of the Aerospace Technology Institute's Hydrogen Capability Network (ATI HCN).

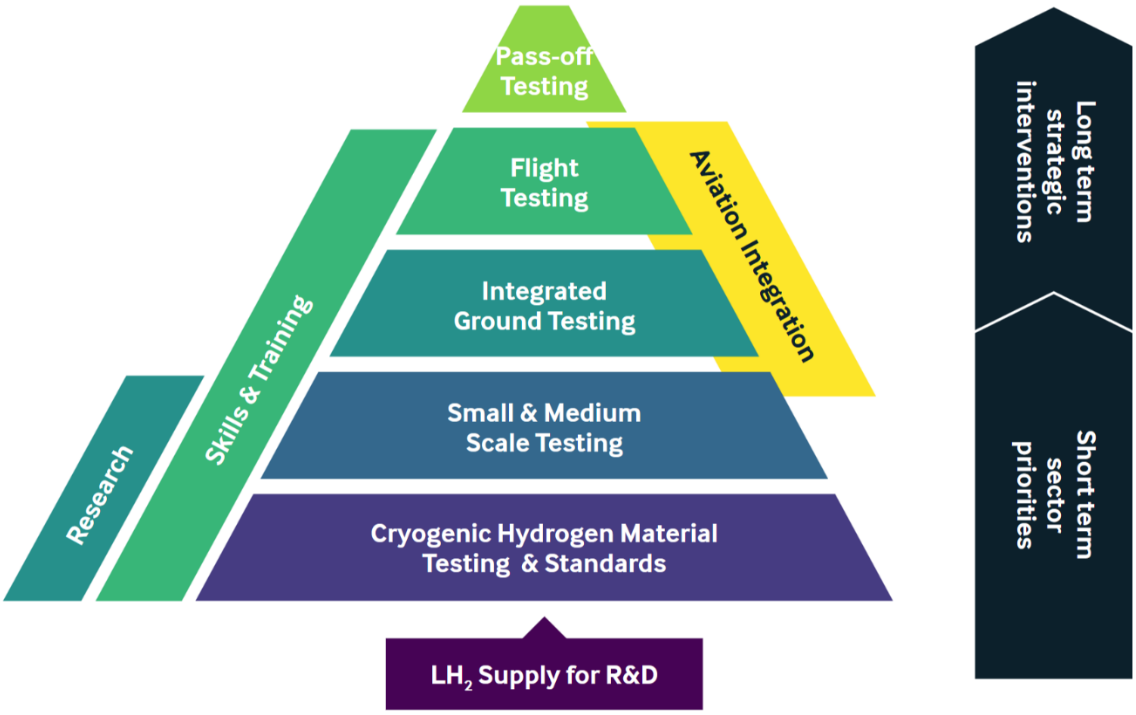

FIGURE 1-2: SHORT AND LONG TERM PRIORITIES AND INTERVENTIONS, FROM "ATI HYDROGEN CAPABILITY NETWORK – SECURING LIQUID HYDROGEN CAPABILITY IN THE UK, MAY 2024".

This study considers the global position, both as a whole and regionally, of fundamental science behind cryogenic hydrogen (cryoH2) effects on materials. The focus is on low TRL fundamental capabilities including expertise and capability across both experimental testing and modelling. Liquid hydrogen fuel systems are likely to contain hydrogen at temperatures ranging from 20 Kelvin (-253 Celsius) upwards. Whilst there is no formal definition of the temperature range covered by the word "cryogenic", for the purposes of this study, we have focused predominantly on test systems and data which achieve minimum temperatures below around 100 Kelvin (-173 Celsius). This study focuses on measurements of physical properties, mechanical properties and hydrogen transport properties that lead to a fundamental understanding of material performance and the ability to model this. Testing or modelling at the component or system level is outside of the study scope.

The study summarises capability in non-commercial research centres, focusing on published work in the period from January 2018 to September 2024 to identify current or at least recently active non-commercial centres of capability and know how. Alongside a review of active organisations and their research focus, a wider review of the historic body of knowledge and key gaps (of relevance to cryogenic hydrogen fuel system materials) is also reported on. Looking at these together, key gaps have been identified that without intervention, may impact development of cryogenic hydrogen fuel systems for civil aviation.

Aerospace relevant materials that have been considered include metals, composites and sealing materials. Cryogenic behaviour considers mechanical, thermal, tribology and hydrogen transport properties.

This report prioritises research on materials behaviour when exposed to a combination of both hydrogen and cryogenic temperatures. For some materials or their use cases, published research combining both hydrogen exposure and cryogenic temperature test conditions was minimal, in which case recent research capability and historic knowledge on materials behaviour at cryogenic temperatures without hydrogen has been included.

2. Global Drivers for LH2 Materials Compatibility Research

Research into liquid hydrogen compatibility of materials dates back to at least the early 1930's, with Prof De Haas and Sir Robert Hadfield [2] publishing a study on mechanical properties of forty one different metals and their alloys, at liquid hydrogen cryogenic temperatures. Globally, there are currently four main application areas of interest for liquid hydrogen compatible materials – space propulsion, bulk hydrogen maritime shipping, heavy ground transport (road and rail) and civil aviation.

Space propulsion was arguably the first substantial application of liquid hydrogen, with activity scaling up during the 1960's space race. Much of the global liquid hydrogen infrastructure in the USA still relates to the space sector and some of the ground-based installations carry many years (in some cases decades) of real-life ageing and learning, albeit for a very limited materials selection. While space-flight launch vehicles provide some learning, the short operational life of these means that usability of data for civil aviation applications is limited.

Recent development of liquid hydrogen compatible systems for marine transportation of hydrogen, particularly by South Korea and Japan, and related activity in China, has been the next major area of interest. The ramp up in research and development (R&D) for this application, along with associated heavy ground transport use cases, has led to a large body of publication (and patent) activity from Asia, ramping at least 5 years ahead of civil aviation interest. A 2023 report [3] from the Korean Register and associated academic paper [4] summarises the current state of knowledge and gaps in research related to materials compatibility for liquid hydrogen for marine applications. Two experimental liquid hydrogen ships, the Japanese Suiso Frontier (LH2 tanker) and the Norwegian Hydra (LH2 fuelled) are already commissioned based on known LH2 compatible materials.

While maritime applications focus on metal (as the weight advantage of composites is of lower relevance), heavy ground transport applications have increased the focus on lightweight materials including composites. LH2 fuelled buses and refuelling infrastructure is already being rolled out in South Korea, where the world's largest hydrogen liquefaction plant was recently commissioned for this purpose.

The more recent research scale up for LH2 fuelled civil aviation, predominantly focused in Europe and the USA, brings an even greater focus on lightweight materials, such as alloys and in particular composites.

Together, research relating to these four sectors provides the current body of knowledge and capability landscape on materials compatibility for liquid hydrogen applications.

3. Overview of the Hydrogen Cryogenic Materials Research Landscape

Globally, research publications of relevance to liquid hydrogen materials properties at cryogenic temperatures is widespread, Figure 3-1, with the highest levels of activity in the USA and Asia, particularly China, South Korea and Japan.

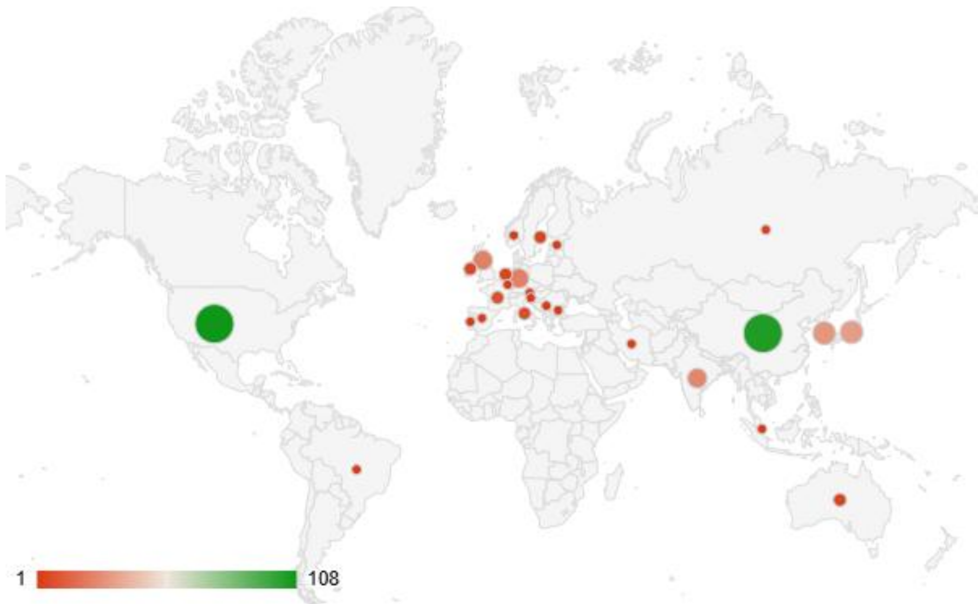

FIGURE 3-1: HEATMAP, SHOWING LEVELS OF IDENTIFIED LIQUID HYDROGEN MATERIALS PROPERTIES TESTING RELEVANT PUBLICATIONS, BY COUNTRY, INDICATING OVERALL RELATIVE LEVELS OF ACTIVITY.

Papers reviewed in this study cover a period from 1904 to September 2024. There has been a significant increase in identified relevant publications over the last decade, even considering the skewing of this review's searches towards more recent references (Figure 3-2).

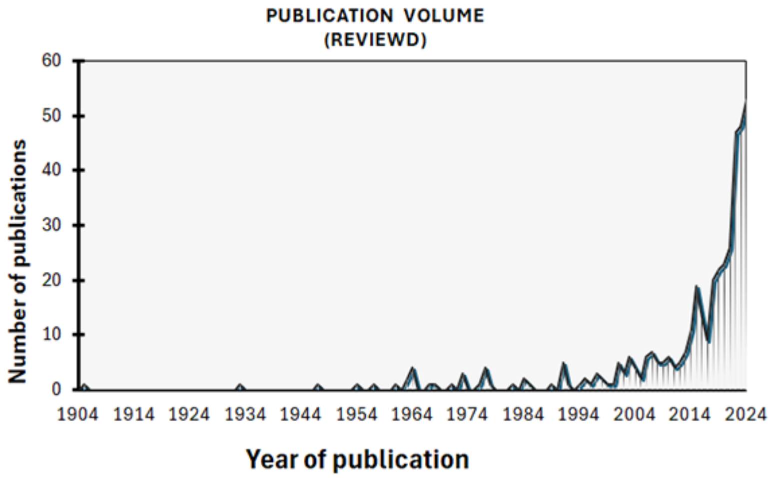

FIGURE 3-2: CHRONOLOGICAL DISTRIBUTION OF OVER 400 HIGH RELEVANCE PAPERS REVIEWED IN THIS REPORT.

Publications were split by those published before 2018 and those published after 2018. Papers published after 2018 were used to indicate overall levels of recent activity, likely to indicate the presence of current research capability. Historically, the USA dominated the identified liquid hydrogen materials properties relevant publications. Figure 3-3 shows that since 2018, China dominates the publications space, with the USA falling to second place, followed by South Korea and the United Kingdom. It should be noted that these statistical results are based on identified publications and did not include publications where there was not an English language translation.

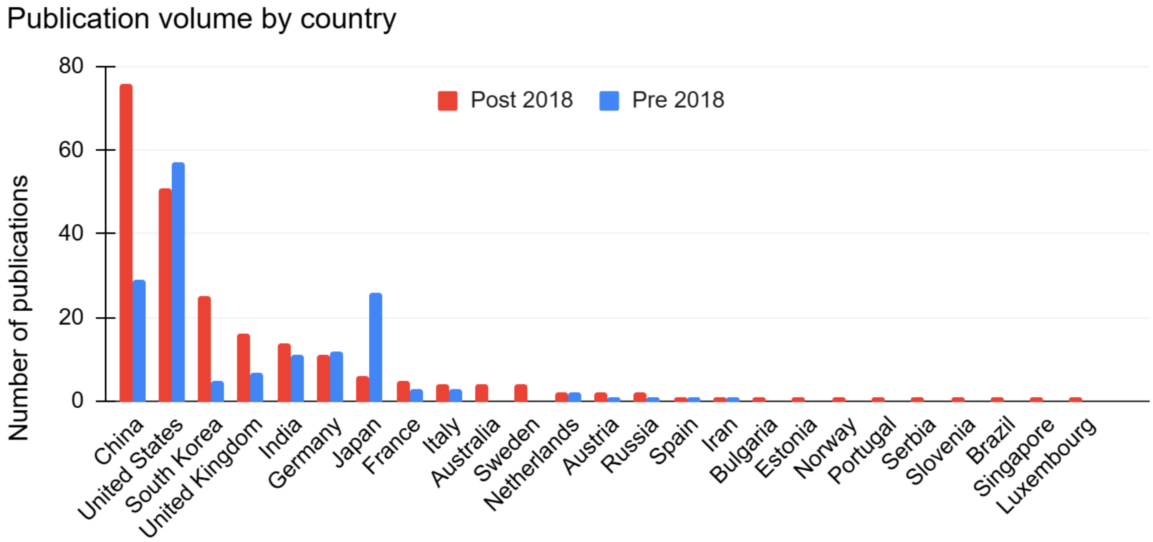

FIGURE 3-3: DISTRIBUTION OF REVIEWED PAPERS BY COUNTRIES BY TIME BRACKET (PRE 2018, POST 2018)

Liquid Hydrogen related patent applications provide an indication of levels of conversion of fundamental research into pre-commercial R&D activity. Identified patent publications have increased fivefold since 2018. Figure 3-4 shows the heat map of top 7 countries in LH2 related patent application indicating that China has significantly dominated recent patent activity, with South Korea, Japan and the USA following. Patent activity ramp up in Asia precedes that in the USA and Europe by at least 5 years, driven by interest in liquid hydrogen as an importable energy carrier and for road transport applications. The UK is in 7th place on the patent league table. The lower ranking of USA and UK patent activity versus research paper publication rankings possibly suggests a lower level of commercial exploitation of the fundamental materials and cryogenics research base in these countries.

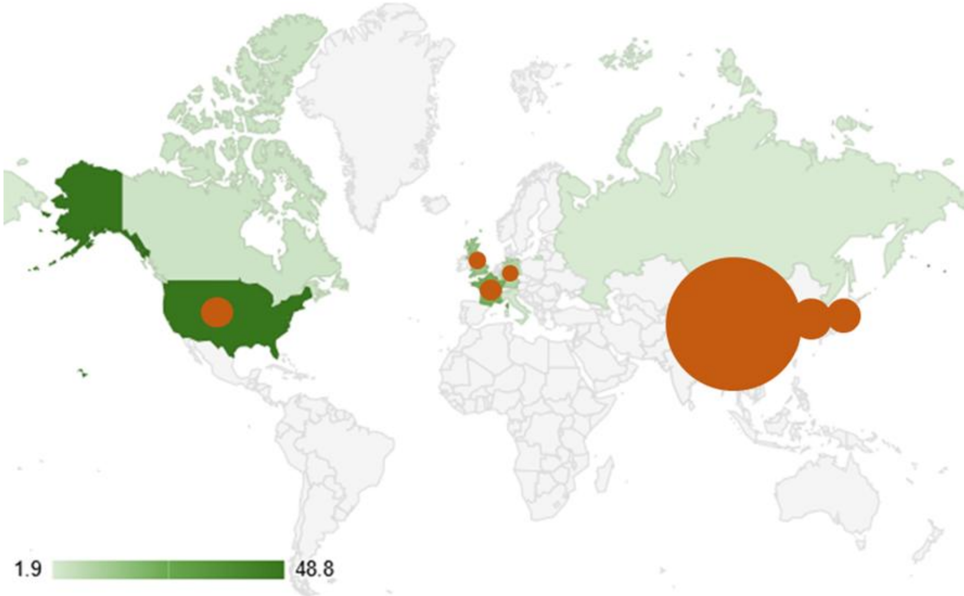

FIGURE 3-4: HEATMAP OF TOP 7 COUNTRIES WITH LIQUID HYDROGEN PATENT APPLICANTS 2018 – 2024 (CIRCLE AREA INDICATES CUMULATIVE PATENT FAMILIES) AND AEROSPACE MANUFACTURING GLOBAL RANKING (TOP 7) BY TRADE BALANCE 2021 [5] (SHADING, $BN).

Each section of the report includes a summary of overall knowledge maturity and key gaps. A high-level summary is provided below.

Knowledge Maturity Summary

- Testing of material mechanical properties at cryogenic temperatures is challenging even without the additional consideration of hydrogen, variables are more difficult to control, data is more difficult to acquire and sample access is challenging, with low test throughput.
- Research capability in Asia, particularly China, South Korea and Japan, driven by non-aviation applications, currently exceeds capability in Europe including Great Britain. USA research capability is currently dominated by space applications. Capability in Asia and the USA is potentially transferable to civil aviation applications.
- Liquid hydrogen materials compatibility challenges are new to the aviation sector but are not new to other sectors. There is a significant body of historic knowledge both on cryogenic performance and hydrogen compatibility, although there remain significant shortfalls in aerospace relevant materials data.
- Some standards exist for cryogenic materials testing of metals, but these have not been extended to include LH2 exposure or to cover composites.
- 316L stainless steel historically dominates as the material of choice, with lower cost metals being explored for shipping applications and lighter weight materials being explored for land transport and civil aviation applications.
- Cryogenic temperature operating conditions significantly alter material properties in a complex nonlinear manner. Data taken at ambient or elevated temperatures cannot be extrapolated to cryogenic temperatures.

- Cryogenic temperature exposure permanently alters the structure of a wide range of materials including composites and metals, introducing new hydrogen trapping centres in some metals. Thermal cycling history of a material is important.
- Hydrogen exposure alters the properties of materials to varying levels. Hydrogen mobility significantly reduces at cryogenic temperatures, creating more complex considerations including the impact of temperature cycling profiles on service life.
- The combined impact of these conditions at all relevant temperatures is required for materials selection and certification for cryogenic hydrogen storage and fuel system for civil aviation.
- Compared with mechanical property testing, physical property testing of materials at cryogenic temperatures is likely to be more consistent between labs, due to the wide adoption of Quantum Design Physical Properties Measurement Systems (QD PPMS).

Key Identified gaps:

- For metals, data on the combined impacts of fatigue cycles and thermal cycles in cryogenic hydrogen is lacking. Data on lightweight alloys is particularly lacking.
- There is a global lack of capability for long term or accelerated ageing studies for liquid hydrogen compatible materials.
- There is extremely limited capability globally to acquire data on mechanical properties at liquid hydrogen relevant temperatures, and even more limited capability to do this in cryogenic hydrogen.
- Equipment and methods are not standardised and can significantly impact results.
- For composites, comprehensive knowledge of the relationship between reinforcement structure, composition and macroscopic properties at cryogenic temperatures is lacking, making extrapolation to components more challenging due to impact of 3-dimensional form.
- Modelling to link materials test data to component performance and service life at cryogenic temperatures is immature. Standardised data to validate models is also lacking.
- The majority of currently available test data is short term and has been acquired at liquid nitrogen temperatures (77K) or above. This is not representative of the aircraft fuel system use case.
- There is a low level of standardisation of test methods for measurement of mechanical properties at cryogenic temperatures between laboratories – equipment is custom designed with a wide range of cooling, test frame integration and measurement methods.
- Whilst there is some limited data and capability for cryogenic temperature testing of materials previously exposed to hydrogen at room or elevated temperatures, there is minimal evidence linking impact of these accelerated exposures to long term cryogenic hydrogen exposure.
- Multi-physics modelling capability linking physical and mechanical property test results to material micro and meso scale structure at cryogenic temperatures is relatively immature.

4. Fundamental Behaviour of Materials Under Cryogenic and Liquid Hydrogen Conditions

This section covers the current landscape of materials science research relating to key materials groupings. It focuses specifically on fundamental research into the interaction of materials with liquid hydrogen or with hydrogen at cryogenic temperatures.

4.1. Fundamental science behind behaviour properties of metals

Metals are the most extensively studied and most used materials in both cryogenic systems and hydrogen systems. There are two main considerations for cryogenic hydrogen storage and fuel system designers in the choice of metals and assessment of design limits. Firstly, metals are known, to varying extents, to become embrittled on exposure to hydrogen. Secondly, the mechanical properties of metals change significantly at cryogenic temperatures. These two separate mechanisms for material property changes cannot be assumed to be independent, and the aircraft designer will need detailed knowledge of the impact on material properties and lifetime caused by cryogenic cycling in hydrogen.

This section considers global capabilities to perform the fundamental cryogenic hydrogen mechanical testing of these materials (Figure 4-1), alongside the historic body of knowledge and key gaps of relevance to aerospace.

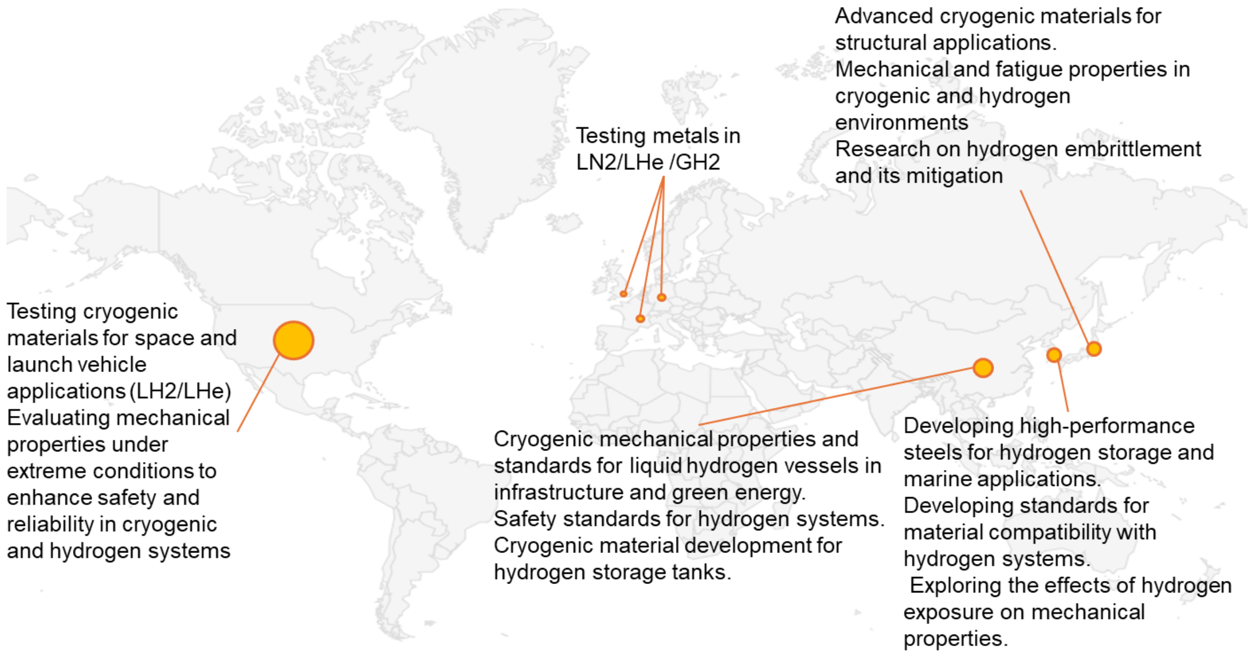

FIGURE 4-1: GLOBAL LANDSCAPE OF RESEARCH INTO FUNDAMENTAL BEHAVIOUR OF METALS UNDER LH2 AND CRYOGENIC CONDITIONS (THE SIZE OF THE MARKERS REPRESENTS THE RESEARCH CONTRIBUTION OF EACH REGION)

Knowledge Maturity Summary:

- NASA, mainly and US-Airforce have established substantial historical experience in testing various metallic alloys, with different heat treatment conditions, under cryogenic and specifically LH2 conditions including uniaxial and bi-axial testing [6-8].
- There are several systematic studies conducted and/or commissioned by NASA to identify the best combination of materials for space applications.
- The majority of existing liquid hydrogen systems utilise stainless steels, with 316L grade being the material of choice, due to its excellent cryogenic properties and low hydrogen embrittlement susceptibility. Aluminium alloys have also been considered for cryogenic hydrogen systems.
- Bespoke cryostats were developed for static and cyclic tests on welded sections in LH2, LHe and GH2 [9]. Smooth, notched, and weld sections of more than 29 alloys from Aluminium Alloys (series 2000, 5000 and 7000), Stainless Steels (SS), Ti-based, Ni-based and Mg- based alloys at LN2, LHe and LH2 have been tested and results have been made publicly available recently.
- In the recent years, there have been many research activities in Asia, mostly China, South Korea, Japan and India on LH2 and GH2 applications for marine and land transport [10-14].
- Ni and nickel equivalent (Nieq) content of steel-based alloys is the key parameter to determine their suitability for cryogenic applications such that above a threshold of 11%, hydrogen presence does not affect mechanical properties across temperature ranges [15].
- FCC crystal structures are the most suitable when performance in the cryogenic and LH2 conditions is of interest, and BCC structured materials must be avoided.

Key Research Gaps:

- Critical assessment of hydrogen effects at cryogenic temperatures.
- Lack of data and understanding about fracture behaviour in cryogenic hydrogen environments and fatigue performance due to thermal cycling for metallic materials.
- Lack of detailed technical information and performance data for GH2, Cryo-compressed H2 (CCH2) and LH2 storage tanks relevant to aviation applications.
- Lack of research on development of new alloying systems for high strength cryogenic applications suitable for LH2 service condition for aviation application.
- Lack of long-term performance and failure data for hydrogen storage systems under service conditions related to aviation operating conditions.
- Lack of standardised testing protocols for hydrogen embrittlement and cryogenic thermal cycling to create comparable and reproducible data.

Key Research Groups

TABLE 4-1: KEY RESEARCH INSTITUTES AND COUNTRIES ACTIVE IN FUNDAMENTAL RESEARCH ON BEHAVIOUR OF METALLIC MATERIALS IN CRYOGENIC AND LH2 CONDITIONS

Institution	Country	Topic
NASA	USA	Design of cryostats for LN2, LHe and LH2 testing of standard materials under various loading and processing conditions. Testing cryogenic materials for space and launch vehicle applications. Evaluating mechanical properties under extreme conditions to enhance safety and reliability in cryogenic and hydrogen systems.
State Key Laboratory of Technologies in Space Cryogenic Propellants, Chinese Academy of Sciences	China	Reviews of metallic materials for hydrogen storage applications. Research on cryogenic mechanical properties and standards for liquid hydrogen vessels. Liquid hydrogen applications in infrastructure and green energy. Safety standards for hydrogen systems. Cryogenic material development for hydrogen storage tanks.
Korean Institute of Machinery and Materials	South Korea	Investigating hydrogen embrittlement in austenitic stainless steels. Developing high-performance steels for hydrogen storage and marine applications. Developing standards for material compatibility with hydrogen systems. Exploring the effects of hydrogen exposure on mechanical properties.
University of Tokyo	Japan	Research in advanced cryogenic materials for structural applications. Evaluating tensile behaviour in cryogenic and hydrogen environments. Assessing fatigue and impact properties of stainless steels under hydrogen exposure. Studies on mechanical properties of austenitic steels in liquid hydrogen. Research on hydrogen embrittlement and its mitigation.

Narrative

Metals are likely to be used for hydrogen contacting surfaces throughout the liquid hydrogen fuel system, potentially including the storage technologies [7]. Cryogenic environments pose unique challenges to performance of metals, particularly for applications involving liquefied and cryogenic gaseous hydrogen (LH2, cryoH_2). The mechanical, thermal, and metallurgical properties of metals must be carefully evaluated to ensure safety and functionality.

Metals exhibit distinct mechanical behaviours under low-temperature conditions, which are heavily influenced by their crystal structures [2, 16]. These differences play a critical role in determining their suitability for engineering applications that demand resilience in extreme environments. The main considerations for metals in LH2 fuel systems include hydrogen embrittlement, permeability, and capability to withstand very low temperatures [17]. Hydrogen embrittlement (HE) occurs when hydrogen atoms infiltrate the structure of metallic materials, leading to a reduction in strength, ductility, and toughness. This results in rapid crack growth and catastrophic failure under stress.

Research on the mechanical properties of metals at cryogenic temperatures started by the early work of Dewar and Hadfield [16] testing different metals in liquid air, followed by the pioneering work of DeHaas and Hadfield testing 41 different alloys at liquid hydrogen conditions [2]. This was followed later by a systematic campaign for the race in space by U.S. institutes including NASA, Department of Defence and Energy in 1950-1976 [7, 8, 18, 19]. In recent years, post-2018, the interest on LH2 applications and relevant fundamental research in properties of metals has dramatically increased in Asia with institutes such as the Chinese State Key Laboratory of Technologies in Space Cryogenic Propellants [20], University of Tokyo (Japan) (e.g. [17]) and Korean Institute of Machinery and Materials (South Korea) [13] playing an active role in developing knowledge in the field (Figure 4-2). In this context, cryo mechanical properties of alloys including stainless steels, Aluminium alloys, Titanium alloys, Copper alloy, Nickel and Manganese alloys have been widely investigated [6, 8, 9, 19, 21-33]

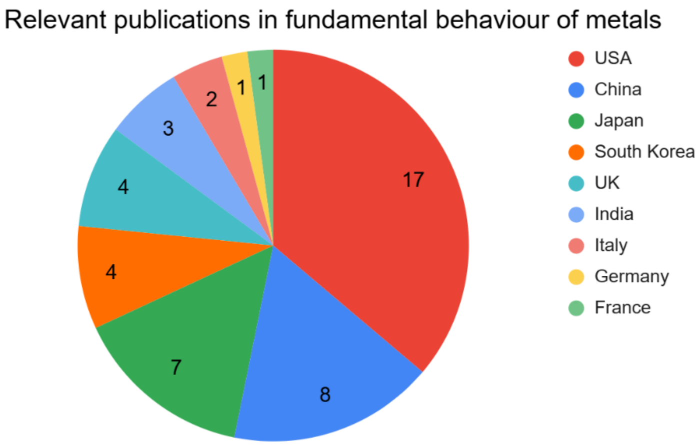

FIGURE 4-2: REVIEWED PUBLICATIONS RELATED TO THE FUNDAMENTAL BEHAVIOUR OF METALS UNDER CRYOGENIC AND LH2 CONDITIONS DEMONSTRATING THE GLOBAL TREND AND LEADING COUNTRIES

Recent review papers by various teams e.g. at the University of Southampton (UK), Sandia National Laboratories (US) and Liquid Propulsion Systems Centre (ISRO) highlight challenges in developing metallic alloys (e.g. steel and aluminium alloy) and their properties and performance in cryogenic and hydrogen applications [21-25]. Many metals, including stainless steels and aluminium alloys, exhibit cryogenic strengthening when subjected to LN2, LHe and LH2. However, prolonged exposure to liquid or gaseous hydrogen can degrade materials, e.g. due to the hydrogen embrittlement (HE) leading to the loss of ductility [34], the extent of which is linked to chemical and metallurgical properties of the used materials [35][36]. This underscores the need for meticulous material technology selection to develop metals with as high impact energy and resistance to hydrogen embrittlement, even under cryogenic temperatures and LH2 conditions, for aerospace applications [20, 37].

The material performance in cryogenic temperatures and in the presence of Hydrogen, either in gaseous (GH2), cryo-compressed (CCH2) or liquid (LH2) forms are reported be affected by the crystal structure [38], chemical composition and alloying elements and stress state at the presence of notches and other stress risers [20, 39, 40]. This is particularly important for aircraft internal components as well as associated external structure for the delivery of LH2 to the aircraft system.

Crystal structure and low temperature behaviour

The crystal structure of metals plays a significant role in their resistance to hydrogen embrittlement and their properties at low temperature. It is already known that , face-centred cubic (FCC) structures, such as austenitic stainless steels, aluminium, and copper alloys, are more suited for LH2 applications due to their lower susceptibility to hydrogen-induced cracking [4, 9, 41]. These alloys are demonstrated to have increased strength while retaining their ductility at LH2/LHe exposure temperatures as well as minimal fatigue life loss. On the other hand, body-centred cubic (BCC) metals, including carbon steel and low-alloy steels, are reported to be not suitable for low temperature applications due to severe loss of ductility linked to the lower activation energy making it easier for hydrogen atom to diffuse in the structure [38]. Historic research by US aerospace corporation [33], Japan's National Institute for Materials Science [11] as well as recently published data from State Key Laboratory of Technologies in Space Cryogenic Propellants in China [20, 42] and NASA [27] demonstrated that Hexagonal-Closed-Packed metals such as Ti-alloys show similar behaviour as FCC metals at lower temperatures with slightly reduced ductility and increased strength. Therefore, any alloying element that destabilises these structures could degrade mechanical properties of the metals at cryogenic temperatures. Although the literature covers properties of the studied conventional alloys, there is a gap in the knowledge about new generation alloys, along with a wider gap relating to the longevity of all alloys under the performance conditions related to the aerospace applications.

Effects of chemical composition and materials systems

Alloying elements significantly impact the low-temperature behaviour of metals. This effect is directly linked to the family of alloy being investigated as well as their crystal structure. The following sections provide the overall landscape for various alloys commonly used for cryogenic and LH2 application in this respect.

Aluminium Alloys

Aluminium alloys are amongst the very earliest adopted by NASA for the space missions and DoE-USA investigated their use for the storage and transfer of cryogenic gases and liquids due to their minimal susceptibility to hydrogen embrittlement which is partially linked to the FCC crystal structure of Al-alloys.

Various grades of Al-alloys have already been tested and analysed since the 1960's [6, 9, 17, 29]. These include different alloys from 2000 series [9, 20, 29, 40], 5000 series [40, 41], 6000 series [9, 21, 34] and 7000 series [20, 21, 29, 34]. Newer generations of 2000 series alloys have attracted more attention in recent years to better understand their fundamental behaviour under cryogenic and liquid hydrogen conditions suitable for aerospace, marine and land applications [13, 20, 21, 43].

The main failure mechanisms of Al-alloys, despite a low hydrogen solubility, include cracking at defects and precipitates, particularly at cryogenic temperatures, and stress corrosion cracking in hydrogen charged materials [34]. Aluminium alloys are leading candidates for LH2 storage tank construction, and are considered satisfactory for LH2 application as their usage effectively eliminates the hydrogen embrittlement [9]. Common alloys include 2219, 2029, and 2195, which are employed in space rockets like the Long March 5 and NASA's space systems [20], due to limited susceptibility to embrittlement combined with lightweight properties. However, care must be taken considering their lower yield and ultimate strength compared to other materials. An extensive review by Key Laboratory of Nuclear Materials and Safety Assessment, Shenyang (China) [43] highlights that despite little sensitivity to hydrogen embrittlement and cryogenic temperatures, current Al-alloys lack of strength for high-stress level structural applications necessitate further development in materials design and selection, specifically for structural element of hydrogen energy systems and LH2 storage.

The yield and ultimate strength of aluminium alloys (e.g., 2011, 2024, 6061, and 6063) generally decrease in liquid hydrogen compared to air and liquid helium testing conditions [9]. They maintain moderate ductility, with elongations up to 10% at both 20K and 4K cryogenic temperatures, which remains relatively stable across all environments, with only minor variations. On the other hand, the 5000 series alloys are characterised by excellent ductility at cryogenic temperatures, with elongation increasing at lower temperatures due to the stability of their microstructure. Alloys such as Al-5052, Al-5086, and Al-5456 exhibit progressively higher strength while maintaining good ductility, making them reliable for cryogenic applications [40, 41].

The NASA report on Safety Standards for Hydrogen and Hydrogen systems, reveals that in almost all the historically tested Al-alloys, the Charpy impact strength is not severely decreased at cryogenic temperature of LH2/LHe [9]. One exemption is the 2020 alloy that has lower ductility and is susceptible to notch embrittlement at subzero temperatures [29]. The difference between ultimate tensile strength and yield strength of Al-2219 [40], Al-6000 series and Al-7060 alloys [21] are reported to be reduced due to cryogenic strengthening effects in LH2 (20K). Tensile tests of different Al-7000 series alloys in LN2/LHe/LH2 by NASA [29] indicated that they are the strongest in the family of Al-alloys and their strength is directly linked to the alloying elements such as zinc and copper. The Al-7002 alloy offers a favourable combination of strength and ductility at subzero/LH2 temperatures and better resistance to notch embrittlement compared to other alloys including any of 2000 series alloys.

Despite the extensive research on conventional and relatively new Al-alloys, including 2219, for storage applications for LH2, these are mostly limited to the static properties and fracture strength and very little is known on the behaviour of these alloys under cyclic loading at cryogenic or LH2 conditions.

Nickel Alloys

Pure nickel shows reduced ductility in hydrogen, with a significant drop in reduction in area (79% in helium vs. 54% in hydrogen) and elongation (47% in helium vs. 25% in hydrogen) [9]. This reflects nickel's susceptibility to hydrogen embrittlement. However, nickel-based alloys, such as Inconel X, K-Monel, Waspaloy, and Rene 41, are excellent candidates for cryogenic applications due to their superior strength and toughness at temperatures approaching absolute zero - they maintain high strength and elongation (≥10%) at cryogenic temperatures, though aging treatments enhance strength while reducing ductility. Nickel alloys failure is accelerated by crack propagation because of hydrogen adsorption at crack tips, especially in liquid conditions [34]. Inconel 700 and Hastelloy X exhibit reduced ultimate strength and ductility in hydrogen, though Hastelloy X shows less sensitivity to environmental changes compared to Inconel.

A recent review paper [20] and NASA's research in the 1960s [9] indicate that alloys like Inconel 718 show excellent cryogenic impact toughness, resistance to hydrogen embrittlement, and strength retention across air, helium, and hydrogen. However, ductility is severely impacted in LH2, with elongation dropping from 25% in air to 9%.

Stainless and other families of steels

Austenitic stainless steels are the most widely studied materials for the cryogenic applications. Austenitic stainless steels, such as grades 304L, 316 and 316L [6, 9, 26, 31, 43], 202 and Carpenter 20-Cb [29], are commonly used due to their FCC structures, which enhance toughness and resistance to embrittlement even at cryogenic temperatures under LH2 conditions [2]. In reviewing the standards and materials for liquid hydrogen vessels by researchers in Zhejian University-China, materials such as S31608-LH are identified to have superior mechanical properties, stability under cryogenic conditions, and resilience to hydrogen embrittlement compared to standard austenitic stainless steels [37].

Austenitic stainless steel (such as 304L, 304, 316L) is significantly stronger (tensile and yield) up to 2.3X at cryogenic temperatures. Plastic strain-induced martensitic transformations at 20K contributed to strength enhancement but reduced ductility (~27% reduction in fracture strain) [44] [38]. However, the proof strengths of most of conventional austenitic stainless steels (types 304, 304L, 316, 316L, 321 and 347) are approximately half the values of the ultimate tensile strengths in LH2 conditions [21]. Joint research by Nippon Steel and National Institute for Materials Science-Japan [45] reports that the tensile properties and plastic behaviour of conventional austenitic stainless steels used for cryogenic and LH2 systems (316L, 316 LN, JIS SUS304L), differ significantly at LHe and LH2 conditions. A comprehensive review of cryogenic and hydrogen related properties of high strength alloys is reported by Yokohama National University-Japan [46]. The test environment and temperature have a clear impact on the fracture mechanics, highlighting the need for the material characterisation to be conducted at the service conditions and environment, i.e. LH2, to fully understand the fundamental response of the materials. Korean researchers in Pusan University and Korea Research Institute of Standards and Science demonstrated that Charpy impact strength of austenitic stainless steels (316, 316L, 304) decreases consistently with temperature drop (from 300K to 77K) [38, 47], however it does not show a significant change at LH2 and LHe conditions [9].

The cryogenic properties of austenitic stainless steels are directly linked to their capability in retaining the austenite phase stability [33]. Ni and nickel equivalent (Ni_{eq}) is a critical factor in hydrogen environment embrittlement of stainless steels [43, 48] due to austenite stabilisation effect that reduces strain-induced martensite formation, which is a primary site for hydrogen embrittlement [38]. A nickel content range of 10.5–21 wt.% , together with higher Mn (3.75%) are particularly critical to mitigate hydrogen embrittlement in hydrogen-exposed environments that require austenite stability down to 77K, such as for pumps, valves compressors, piping and fittings, and other cryogenic handling equipment [15, 33]. In contrast, N results in higher strength, but reduces stacking fault energy, and hence increased brittleness at LH2 and cryogenic conditions. Therefore, N containing alloys, e.g. 316LN and 304LN, should be used with caution. Higher Ni content can also affect the fatigue performance of these alloys with 301 and 304L performing moderately well at 77K but exhibiting significant reductions in fatigue life at 20K and LH2 conditions [33]. Fatigue life can significantly increase at 77K under strain-controlled loading system, at low strain values. However, as the strain level increases, this effect diminishes. The enhanced performance is attributed to a pronounced hardening effect at cryogenic temperatures [49] as well as reduction in cyclic softening for 77K conditions due to the constrained dislocation motions [49].

The research by Korea Research Institute of Standards demonstrated that the hydrogen effect on austenitic stainless steels is temperature dependent and hydrogen embrittlement (HE) susceptibility peaks at 223K but disappears below 123K due to limited hydrogen diffusion [10]. Increased susceptibility to hydrogen embrittlement (HE) at intermediate temperatures (50K to 200K), is attributed to enhanced hydrogen diffusion and stress localisation at these temperatures. Below 50K, the HE effects diminishes due to reduced hydrogen mobility, even as strain-induced martensitic transformation remains active [14]. Pre-charged (electrochemically charged) 304L and 316L stainless steel showed surface cracking and reduced strain-hardening rates at cryogenic temperatures and hydrogen charging altered the fracture morphologies and reduced ductility, but brittleness did not drastically increase at cryogenic temperatures [13]. Subsurface crack fatigue initiation in the high-cycle regime is very common for high-strength alloys at cryogenic temperatures (LN2 and LHe) and microcrack growth and coalescence can be mitigated through microstructure [46, 50].

Different cryogenic environment, across liquid nitrogen, helium, and hydrogen, affect the tensile strength and ductility of 304L and 316L stainless steels in various extent. A greater strength loss is observed for 304L in cryogenic hydrogen and helium than 316L. Generally, 304L loses strength and ductility more rapidly by temperature drop than 316L [51]. The fatigue strength of 304L is also decreased at lower temperatures with a significant reduction in the number of cycles to failure specially in high cycle regimes [21]. Interest in 304L has been largely due to lower costs compared with 316L.

Titanium and Magnesium alloys

Systematic research by NASA showed that the composition of various titanium alloys plays a key role in their cryogenic properties, including at LH2 conditions, and ductility of alloys such as Ti-6Al-4V, Ti-5Al-2.5Sn drops significantly below 77K [6]. New family alloys with extra low interstitial-element content (ELI with alpha or alpha-beta structures exhibit good ductility and notch toughness at temperatures as low as 20K. However, BCC beta-phase alloys like Ti-13V-11Cr-3Al are more prone to embrittlement at lower temperatures [29]. Alpha titanium alloys are well-suited for low-temperature applications where weight considerations are critical. Their combination of low density and high strength allows for the construction of lighter structures with equivalent load-bearing capacities compared to heavier materials like austenitic stainless steels [29]. The elongation and impact and fracture toughness of Ti-alloys decreases at cryogenic temperature, therefore, low temperature alloys have been designed with optimised interstitial elements (oxygen, hydrogen, nitrogen, and carbon), which reduce ductility and increase notch sensitivity and with reduced Al content, including OT4, BT5-1, α-Ti alloy TA7 ELI and α + β alloy TC4 ELI [20]. There is little information about fatigue life or the performance of Ti alloys under varying cryogenic conditions.

Limited data suggests magnesium alloys, such as LA-91 and LA-141, offer low density and acceptable ductility at cryogenic temperatures down to 20K. Both alloys retain their ductility at LH2 conditions, and their properties are enhanced by lithium additions.

High Entropy Alloys for cryogenic applications

In addition of conventional alloys, high-entropy alloys, i.e. alloys which have similar quantities of different metals, as opposed to traditional alloys which are mostly one metal, are increasingly used for challenging applications due to the opportunity to tune their performance for specific applications including at cryogenic temperatures [52]. At 77K, typical HEAs like CoCrFeMnNi show yield strength around 600 MPa, tensile strength of 1100 MPa, and elongation reaching 90%. These values represent improvements of 71%, 69%, and 38% respectively compared to room temperature performance. At cryogenic temperatures, the stacking fault energy decreases significantly, enabling both twinning-induced plasticity (TWIP) and transformation-induced plasticity (TRIP). These mechanisms contribute to exceptional work hardening and delay the onset of necking, resulting in improved ductility despite the low temperatures.

The fracture toughness of HEAs ($Al_{0.1\text{-}0.3}CoCrFeNi$) are particularly noteworthy, exceeding 200 MPa√m at 77K as demonstrated in Fig. 19 of [52]. the toughness of HEAs is found to be maintained or even improved at cryogenic temperatures, which is unusual compared to conventional alloys that typically become more brittle at low temperatures.

4.2. Fundamental Science behind behaviour properties of coatings

In order to extend the choice of materials available to designers of cryogenic hydrogen storage and fuel system, coatings may be considered. These may include hydrogen barrier coatings intended to protect hydrogen susceptible materials from hydrogen contact or coatings designed to protect bearing surfaces from wear. In either case there are considerations specific to the cryoH_2 applications, in particular, the resilience of the coating to blistering under repeated cryogenic cycling (including due to differential thermal contraction). The potential for hydrogen localisation at the coating / base material interface, particularly around defects, further complicates matters. This section focuses on the current state of research relating to coatings specifically in LH2 cryogenic environments.

FIGURE 4-3: GLOBAL LANDSCAPE OF RESEARCH INTO FUNDAMENTAL BEHAVIOUR OF COATINGS IN LH2 CONDITIONS (THE SIZE OF THE MARKERS REPRESENTS THE RESEARCH CONTRIBUTION OF EACH REGION)

Knowledge Maturity Summary:

- Whilst there has been significant recent research into hydrogen permeation barrier coatings for room temperature hydrogen applications, little was found looking at the use of these coatings in liquid hydrogen conditions.
- 316L stainless steel tubing has long-term real-time performance evidence in liquid hydrogen systems, without requiring coatings. The historical motivation to develop hydrogen barrier coatings may therefore be limited.
- Use of aluminium, titanium or other alloys may be of interest to aerospace as a lightweight alternative to stainless steels. Minimal research was found exploring coatings for these materials in cryogenic hydrogen conditions.

Key Research Gaps:

- Testing the long-term integrity of hydrogen permeation coatings with lightweight aerospace alloys, in liquid hydrogen thermal cycling conditions.
- Testing the impact of defects and damage to hydrogen permeation coatings, such as scratches and pinholes, on the long-term integrity of coatings for metals in liquid hydrogen thermal cycling conditions.
- Development and testing at cryogenic temperatures of hydrogen barrier coatings for additive manufactured metal components for use in LH2 fuel systems.
- There is interest in additive manufacturing for more complex metal components such as heat exchangers, which may be candidates for barrier coatings. Minimal research was found exploring cryogenic hydrogen performance of such coatings.

Key Research Groups:

TABLE 4-2: KEY RESEARCH GROUPS ACTIVE IN COATING MATERIALS

<table>
<tr><th>Institution</th><th>Country</th><th>Topic</th></tr>
<tr><td colspan="3">No research groups were found with significant current activity relating specifically to testing of coatings for metals in LH2 applications. The testing of cryo-mechanical and hydrogen transport properties of the coated materials is largely the same as for uncoated samples. Facilities with the capability to test the bulk materials are therefore likely to have the capability to perform testing of the coated materials, although in some cases, collaboration may be required to access SIMS or equivalent techniques to determine the depth profile of hydrogen through the coating. Cryogenic transfer of samples between facilities may therefore be required.</td></tr>
</table>

Narrative

For room temperature hydrogen applications, there has been significant recent interest in hydrogen permeation barrier coatings for embrittlement prevention in metals [53-55]. There has however been minimal published work on the suitability of these coatings for cryogenic hydrogen applications. This gap may be in part due to the need to adapt existing infrastructure to handle hydrogen in the wider hydrogen economy prompting interest in coatings, versus the ability to specify hydrogen resilient materials in new hydrogen aviation systems. For piping applications, uncoated 316 stainless steel has a long history of use with liquid hydrogen, with some ground based LH2 installations in constant use since the Apollo missions. Ultra thin walled stainless steel cryotube is readily available, lightweight and has additional mechanical properties desirable for aerospace applications. The motivation to develop and test coated alloys may therefore be more limited, particularly considering the potential for adequate performance from some newer generation alloys in an uncoated state.

Possibly the most relevant recent research is from a South Korean team [56] who report a limited performance impact of coating 304 stainless steels with PTFE, ahead of room temperature hydrogen pre-charging followed by cryo-mechanical testing at 77Kelvin. 304 grade stainless steel is potentially a lower cost option for liquid hydrogen applications, but potentially with reduced hydrogen resilience. Due to its lower cost, it is of interest for bulk storage and shipping, a focus area in South Korea, but likely of less interest for on-aircraft applications.

Nonetheless, for liquid hydrogen aviation applications, there may be future interest in coatings for metal substrates in two main areas. Firstly, for cryogenic sliding or rolling metal contact surfaces, there may be a need for friction and wear reducing coatings – this is covered in the tribology section.

Secondly, complex components such as for use in heat exchangers and pumps are candidates for additive manufacturing methods. A discussion of various additive metal manufacturing techniques explored by NASA and of potential relevance to aviation LH2 applications can be found at [57]. There may be concerns over permeability of these materials, particularly for sintered powder processing methods, resulting in a potential need for cryogenic hydrogen permeability barriers. Examples of development of additive manufactured metal components for cryogenic applications include various NASA programmes developing 3-D printed liquid hydrogen and liquid oxygen rocket engine turbopumps [58, 59] where process induced porosity is noted, although coating systems are not discussed.

Little research of relevance was found in the literature, either recently or historically, indicating that the study of hydrogen barrier coatings for additive manufactured metal parts for LH2 applications is currently immature. Overall, minimal relevant activity was found relating to coatings for metals in LH2 environments.

4.3. Fundamental science behind behaviour of joints in metals

In future LH2 fuel systems for civil aviation applications there are likely to be a large number of joints, with a design choice between permanent methods and re-makeable mechanical. This section covers the landscape of fundamental research relating to the behaviour of permanent joints in metals at cryogenic and LH2 conditions, across a range of aerospace relevant materials and joining methods.

FIGURE 4-4: GLOBAL LANDSCAPE OF RESEARCH INTO THE BEHAVIOUR OF METAL JOINTS FOR CRYOGENIC AND LH2 APPLICATIONS

Knowledge Maturity Summary:

- Widescale applications for LNG along with LH2 for the space sector mean that the cryo-mechanical properties of welds in materials such as austenitic stainless steels, Ni-alloys and aluminium alloys are well investigated, with limited work including hydrogen effects.
- For austenitic stainless steels, cryo-mechanical properties research covers 304L, 308L, 316L and 316LN grades welded with tungsten inert gas, plasma arc, gas tungsten arc, submerged arc, electron beam and laser beam methods.
- Research on cryo-mechanical properties of austenitic stainless steels welded with different filler materials includes austenite stabilisers such as Ni and Mo, and more recently, high entropy alloys.
- Some research exists on welding dissimilar materials using friction stir welding, including oxygen free high conductivity copper to 316L stainless steel, aluminium and titanium alloys, this included measurement of cryogenic thermal conductivity of the weld, indicating superior performance vs other explored methods.
- Research on cryo-mechanical properties of welded aluminium alloys covers select grades within 2000, 5000 and 7000 series, including friction stir welding, dual laser beam, tungsten inert gas, variable polarity tungsten inert gas arc and gas tungsten arc. Joined 2219 grade is widely reported to have superior cryo-mechanical performance.

Key Research Gaps:

- Most of the literature is focused on LN2 conditions, and at best LHe, with very little resources available about the properties of the weld performance in LH2 conditions.
- High cycle fatigue data for cryogenic temperatures of 77K and below are scarce.
- There is little information about the failure and fracture modelling of the welded sections at LH2 and CryoH_2 service conditions.
- No research was identified that investigated the longer-term effect of environmental hydrogen embrittlement of welds during cryogenic hydrogen exposure.

- There appears to be a general assumption that hydrogen embrittlement does not dominate at LH2 temperatures due to low hydrogen mobility, however this may not take account of slow migration effects or of thermal cycling during service.

Key Research Groups

TABLE 4-3: KEY RESEARCH GROUPS ACTIVE ON UNDERSTANDING THE BEHAVIOUR OF METAL JOINTS FOR CRYOGENIC AND LH2 APPLICATIONS

Institution	Country	Topic
State Key Laboratory of Technologies in Space Cryogenic Propellants, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences	China	Different welding methods, cryogenic properties, different alloys, HEA/SS/Al (LN2/LHe).
Shanghai Jiao Tong University	China	Different welding methods, cryogenic properties, different alloys, HEA/SS/Al (LN2/LHe).
Harbin Institute of Technology	China	Different welding methods, cryogenic properties, different alloys, HEA/SS/Al (LN2/LHe).
Liquid Propulsion System Centre, I.S.R.O.	India	Laser and FS welding for Al-Li alloys, similar and dissimilar, cryogenic mechanical properties (LN2/LHe).
Vikram National Space Centre	India	Various welding technologies for Al-Li alloys, similar and dissimilar, cryogenic mechanical properties (LN2/LHe).
NASA	USA	Fusion and TIG welding and the cryogenic properties of convectional alloys for aerospace (LN2/LHe/LH2).
Pusan National University	South Korea	Laser and FS welding, HEA and SS, similar and dissimilar welds, cryogenic properties (LN2/LHe).
Yeungnam University	South Korea	Laser and FS welding, HEA and SS, similar and dissimilar welds, cryogenic properties (LN2/LHe).

Narrative

Several welding and joining methods have been used to link different components in cryogenic and hydrogen, including LH2 applications, for aviation and space applications. Historically, NASA have been leading the research in this filed [29, 33, 60] due to the space projects, however, recently most of the research publications are originated from China, Korea, Japan and India that is aligned with the other topics related to the LH2 and cryogenic research for transport and space applications. Figure 4-5 illustrates the contribution of different countries in this field, demonstrating research domination by Asia, specifically since 2018.

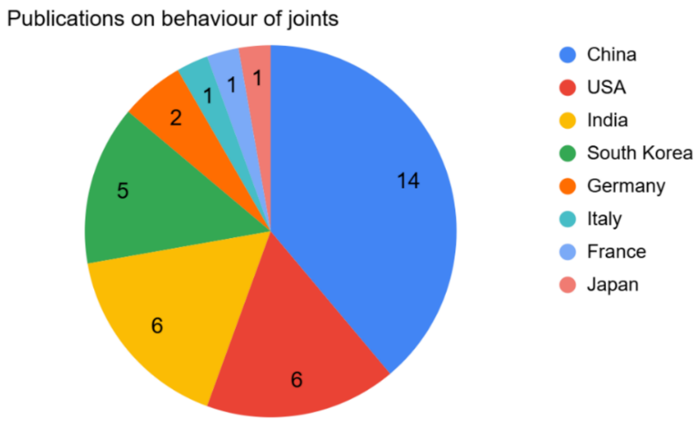

FIGURE 4-5: CONTRIBUTION OF DIFFERENT COUNTRIES IN FUNDAMENTAL RESEARCH ON THE BEHAVIOUR OF JOINTS FOR CRYOGENIC AND LH2 APPLICATIONS (ALL THE REVIEWED LITERATURE)

NASA's historic and comprehensive research programme covers various welding techniques including Tungsten inert gas (TIG) welding, electron beam welding and fusion welding of different alloys, such as Ti-based alloys, Nickel alloys, Stainless steels, Aluminium alloy, and their corresponding mechanical properties at cryogenic temperatures [6, 19, 29, 30, 60]. It was demonstrated that welding these alloys does not result in significant property degradation if contamination is carefully avoided, further enhancing their appeal for structural applications in cryogenic environments [29].

Austenitic Stainless steels weldments

There is a large body of research dedicated to weldments from austenitic stainless and their mechanical and fracture properties at cryogenic applications [61-67]. The properties at cryogenic temperatures are dependent on the chemical composition and welding method [68]. The higher ferrite content and increased precipitate formation leads to a lower tensile strength (R_m) and impact toughness in submerged arc welding (SAW) joints at temperatures as low as 77K compared to the plasma arc welding (PAW) + gas tungsten arc welding (GTAW) joints while the mechanics of failure in 304L, 308L, 316L are found to be different [61-63]. GTAW welded 316LN sections was also found to be more ductile at LN2 and LHe testing conditions compared to the materials welded by electron beam welding (EBW) [64], although limited research is reported for the testing at LH2 environment. However, a recent research by State Key Laboratory of Technologies in Space Cryogenic Propellants, Chinese Academy of Sciences [65] demonstrates that although the strength of the weld and base metals in laser beam welded (LBW) 316LN is similar at room and 4K, the fracture toughness of former is reduced to about 90% of the base metal at LHe conditions. Although, no data is available for the presence of Hydrogen at the cryogenic temperature and its effect on the weld/base metal properties.

Dissimilar materials

In order to join different structures with dissimilar materials for cryogenic applications, austenitic stainless steels are welded with different filler materials using fusion based methods such as TIG, LBW, SMAW [65-67, 69-74]. The performance of the weld sections at cryogenic environment, mostly reported for LN2 and LHe testing conditions, are linked to the austenite stabiliser elements in the filler such as Ni and Mo [66, 67, 72, 73]. Recently published literature by Korean [75] and Chinese researchers [70] demonstrated that the austenitic stainless steels can be successfully welded with advanced alloys, such as high entropy alloys, and demonstrate a reliable performance at cryogenic temperatures, albeit the available data only covers testing temperatures as low as 77K. Additionally, At cryogenic temperatures down to 77K, the low cycle fatigue life of 9% Ni steel welded joints improved due to higher fatigue strength, with fractures shifting from the fusion area at room temperature to the weld seam [76].

Welding oxygen free high conductivity (OFHC) copper and 316L with electron beam was found to be a reliable method with the joint structure retained as well as its leakage resistance down to 4K [77]. Thermal conductivity of the joints are critically important for the LH2 applications and it was shown that between Al, Ti and steel alloys thermal hysteresis effects are more pronounced for the aluminium alloy joints [78]. Additionally, thermal conductivity of the dissimilar joints was reduced with temperature. To reduce the thermal conductivity issues, gold-plating was suggested and proved to be effective between Al/Cu connections [79]

Friction stir welding (FSW) is preferred to other welding method for welding of dissimilar materials as it prevents the weld section softening**,** results in very fine grains and single FCC solid solution phase [80] in the weld. This leads to a significantly higher strength, and moderately lower elongation, at LN2 cryogenic conditions compared to their room temperature properties [81, 82] due to significantly finer twin structures and improved plasticity mechanisms by e.g. enhanced dislocation densities. Friction stir-welded dissimilar metals showed to be a good candidate for the pipework when tested by thermal shock and helium leak methods [83].

Aluminium alloys

Aluminium alloys exhibit varying suitability for cryogenic conditions based on their series. The 2000 and 7000 series, reliant on precipitation hardening, suffer strength and ductility losses when welded due to grain boundary segregation [33]. Aluminium alloy AA2219 is reportedly being investigated for the fabrication of the liquid hydrogen (20K) and liquid oxygen (90K) [84, 85] systems. The strength of 2219 alloy welded by dual laser beam welding increased when tested at cryogenic temperature due to severe grain size reduction due to cryogenic testing temperatures. [86]. A friction stir welded joint of the same alloy [87] led to a more uniform deformation with increased ductility of the weld zone at 77 K. It was also found that variable polarity tungsten inert gas arc welding (VPTIG) has similar effect on the produced welds with 20% increase in fracture toughness and plasticity metrics at 77K, but yet weaker than the base metal [88].

In contrast to LBW and VPTIG, the weld was found to be stronger and less ductile in FSW [81]. Similar observations were made for the GTAW sample tested at 77K [84], however no significant grain size effect on the mechanical properties of weld and the base metal was observed. Recently published research from Vikram Sarabhai Space Centre (India) reported that the performance of dissimilar friction stir welded samples (between 2195 (Al-Cu-Li) and 2219 (Al-Cu) alloys) and single material 2219 improves as temperatures decrease from room temperature down to 20K [85, 89, 90], hence making the FSW a preferred choice for LH2 applications, compared to LBW.

When compared to traditional TIG welding, friction stir welding showed higher tensile strength at all temperatures, better ductility, superior fracture toughness, particularly in the weld nugget zone and more consistent properties across the weld [89]. the Friction stir welding was successfully used to weld two different aluminium alloys - AA2219 (Al-Cu alloy) and AA5083 (Al-Mg alloy) - which was notable because combining copper and magnesium-containing aluminium alloys typically causes weldability problems [90]. Similar elements in the filler wire (AA2319, titanium and zirconium) helped to refine the grain and achieve a fine equiaxed grain structure in the weld. As opposed to the other reports [85], failures consistently occurred in the partially melted zone (PMZ) on the AA2219 side, despite this being a stronger alloy. Interestingly, the similar AA2219-AA2219 welds showed better improvement at cryogenic temperatures compared to the dissimilar joints and the grain orientation of AA2219 significantly affects failure location. Additionally, the produced welds were not sensitive to repair welding cycle retaining their properties and failure location at the expense higher porosity compared to the original weld.

The 5000 series, which relies on solid solution strengthening, shows better retention of properties after welding. Despite this, all aluminium alloys are susceptible to notch embrittlement at low temperatures, necessitating careful design considerations [33].

Nickel based and Magnesium alloys

Magnesium alloys, such as LA-91, exhibit low density and good ductility at cryogenic temperatures due to lithium additions. Welding reduces ductility and strength, with beta-phase alloys like LA-141 being more affected. These alloys are recommended for low-stress, weight-critical applications in unwelded configuration [6, 19, 29, 30, 60].

Nickel based metals are insensitive to the welding methods as similar microstructures are reported for Gas Tungsten Arc Welding (GTAW), and Shielded Metal Arc Welding (SMAW) while Submerged Arc Welding (SAW) generates significantly larger grains, hence less favourable cryogenic properties [91]. Welding does not significantly impair mechanical properties of Ni-alloys in the solution-treated condition but leads to reduced ductility and strength in age-hardened materials due to grain boundary particle segregation.

4.4. Fundamental science behind behaviour properties of composites

With the need for lightweight cryogenic hydrogen storage and fuel system for aircraft applications, composites are candidate materials for liquid hydrogen fuel tanks and for mechanical support structures throughout the fuel system. This will result in the need for aircraft designers to understand the impact of cryogenic thermal cycling on these mechanical structures over the full-service life of the aircraft. This section focuses on fundamental materials science research landscape, Figure 4-6, on the use of existing and novel composite materials at cryogenic temperatures and where relevant, with exposure to hydrogen.

FIGURE 4-6: GLOBAL LANDSCAPE OF RESEARCH INTO BEHAVIOUR OF COMPOSITES IN CRYOGENIC AND LH2 APPLICATIONS

Knowledge Maturity Summary:

- Due to interest in using composites as structural materials in the shell of LH2 fuel tanks, there is a maturing body of knowledge on their cryogenic performance.
- Cryogenic temperatures are known to increased strength and Young's modulus [92-94], reduce ductility and toughness (due to resin embrittlement) [95], and change fracture behaviour and surface morphology [95].
- Thermal expansion mismatch between fibres and resin leads to residual stresses, resulting in formation of microcracks during thermal cycling [95, 96]. Microcracks are influenced by layup, ply thickness and load case and lead to reduced strength and increased permeation.
- Interfacial Properties and Delamination are impacted by changes in fibre-matrix interface strength at cryogenic temperatures. Fatigue delamination growth rates are reduced at cryogenic temperatures.
- Several studies have focused on novel composite materials for cryogenic applications, including use of graphene and 3D printed composites [97].
- Exploration of materials for liner-less composite tanks has begun. PE films heat pressed between layers of CF before resin impregnation significantly reduce permeation after thermal cycling, increase tensile strength by 22% and reduce cryogenically induced delamination defects [56, 98].

Key Research Gaps:

- A comprehensive understanding of the relationship between microstructure and macroscopic properties at cryogenic temperatures is still lacking.
- Accurate prediction and mitigation of residual stresses in complex composite structures at cryogenic temperatures remain challenging.
- More detailed understanding of interfacial behaviour and the effect of CTE mismatches on overall composite performance is needed.

- Systematic investigation of advanced composite materials tailored for cryogenic applications is ongoing.
- The anisotropic nature of composites and their complex internal structures including thermal properties mismatches make modelling at cryogenic temperatures challenging. Integrated micromechanical and macro-mechanical modelling [99] addressing challenges in simulating thermomechanical behaviour linking manufacturing and operation [94] are still immature.
- Development of predictive models for microcrack formation and propagation at cryogenic temperatures and their influence on permeation is crucial.

Key Research Groups

TABLE 4-4: KEY RESEARCH GROUPS ACTIVE ON UNDERSTANDING THE BEHAVIOUR OF COMPOSITES

Institution	Country	Topic
NPL	UK	Mechanical testing of fibre-reinforced polymer matrix composites at cryogenic temperatures: Requirements for mechanical test capability at-269°C (4K).
Washington State University	USA	Experimental Analysis of Cryogenic Hydrogen Leakage in Additively Manufactured Hydrogen Tanks. High(er) TRL capabilities: testing of additively manufactured pressure vessel in LH2.
National Institute of Technology, Rourkela	India	Influence of graphene in thermoset composites for toughness and permeation applications. Recent advancements in interface engineering of carbon fibre reinforced polymer composites and their durability studies at different service temperatures.
Department of Aerospace Engineering, Mississippi State University	USA	Permeation properties in in fatigue before and after impact of CFRP pressure vessels in LN2. Gas permeability mitigation of cryogenically cycled stitched composites using thin plies.
College of Aerospace Engineering, Chongqing University	China	Incorporation of phosphorous flame retardant (DOPO) and brominated epoxy resin (EX48) in composites for oxygen tank at cryogenic temperatures.
Institute of Advanced Structure Technology, Beijing Institute of Technology	China	Enhancing cryogenic mechanical properties of epoxy resins toughened by biscitraconimide resin. The temperature-dependent properties of epoxy-functionalised graphene oxide/epoxy nanocomposites: insights from simulation and experiment.

Institution	Country	Topic
Key Laboratory of Technology on Space Energy Conversion, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing,	China	Enhanced cryogenic mechanical properties of carbon fibre reinforced epoxy composites by introducing graphene oxide. Cryogenic damage mechanisms of CFRP laminates based on in-situ X-ray computed tomography characterisation.

Narrative

Cryogenic temperatures have a profound impact on the behaviour and properties of composite materials, presenting both challenges and opportunities for their use in LH2 fuel systems. Composites have been used for several decades as low thermal conductivity structural materials in cryogenic applications, such as support structures for superconducting magnets, with G10 glass reinforced composites being a popular choice. More recently interest in use of composites in LH2 storage vessels has significantly increased research on cryogenic properties of a wide range of composite materials.

At cryogenic temperatures, composite materials exhibit significant changes in their mechanical properties. Notably, there is an increase in strength and Young's modulus [97], attributed to reduced molecular mobility and increased density of the polymer matrix. However, this improvement comes at a cost, as the ductility and toughness are reduced due to resin embrittlement. This leads to changes in fracture behaviour and surface morphology, often resulting in more catastrophic failure modes [95].

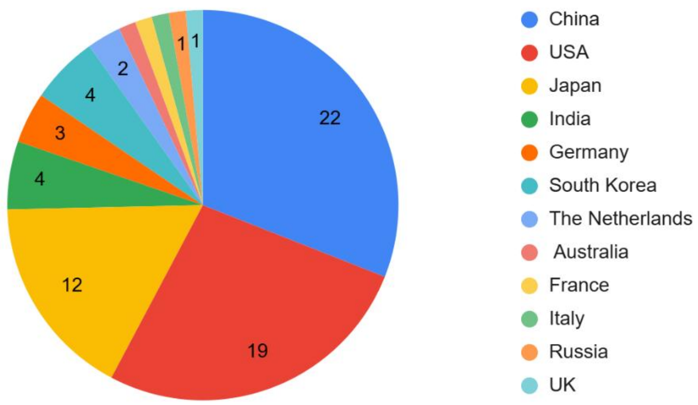

FIGURE 4-7: TOTAL NUMBER OF REVIEWED PAPERS AND LANDSCAPE ON FUNDAMENTAL PROPERTIES OF COMPOSITES FOR CRYOGENIC AND LH2 CONDITIONS

An overview of historic research on the influence of cryogenic temperature on mechanical properties is offered in a comprehensive 2020 literature review (Bath, UK) [94] - key material property changes and references are summarised below.

TABLE 4-5: CRYOGENIC MECHANICAL PROPERTIES OF COMPOSITES BY RESIN AND REINFORCEMENT TYPE

Resin Type	Reinforcement	Fibre Type	T (K)	Property Change	Reference
Epoxy (CU-125 NS)	Carbon Fibre (T700)	UD	123	E1T↑16%, XT↓9%	[100] https://doi.org/10.1016/j.compstruct.2005.11.031
Epoxy (DGEBA)	Carbon Fibre	UD	123	E2T↑, YT↑	[101]
Epoxy (DGEAC)	Carbon Fibre (T700)	UD	77	XT↑, YT↑	[101]
Epoxy (DGEAC)	Carbon Fibre (T800)	UD	77	XT↑, YT↑	[101]
Epoxy (DGEBF)	Carbon Fibre (T700)	UD	93	E1T=, E2T↑49%	[102]
Epoxy (E618)	Carbon Fibre (TC-33)	UD	77	E1T↑, XT↑20%, 1T↑	[103]
Epoxy (RIM135)	Carbon Fibre (T300)	3D MWK (Type A)	77	EF↑50%, E1T↑47%, XF↑81%, XT↑58%, 1T↑8%	[104] https://doi.org/10.1007/s12221-015-1349-2
Epoxy (R118)	Carbon Fibre (T300)	Woven	77	EF↓11%, XF↓8%	[105] https://doi.org/10.1016/j.compositesa.2019.02.012
Epoxy (R118) + GO	Carbon Fibre (T300)	Woven	77	EF↓2%, XF↓1%	[105]
Epoxy (R608)	Carbon Fibre (M40)	UD	77	XF↑, XT↑	[106]
Epoxy (828)	Carbon Fibre (HM50)	UD	77	E1T↑36%, XT↓10%, 1T↓53%	[107]
Epoxy (862)	Carbon Fibre	Woven	77	EF↓4%, E1T=, XF↓4%, XT↓3%	[108]
Epoxy (977–2)	Carbon Fibre (IM7)	UD	77	E2T↑37%, YT↑12%	[109]
Epoxy (977–3)	Carbon Fibre (IM7)	UD	77	E2T↑21%, YT↑29%	[110]
Epoxy (3633)	Carbon Fibre (T800H)	Woven	4	E1T↑8%, E2T↓2%, 12↑49%	[111]
Epoxy (3633)	Carbon Fibre (T800H)	Woven	77	XT↓15%	[112]
Epoxy (3633)	Carbon Fibre (T800H)	Woven	77	XT↓5%, YT↓20%	[112]
VE	Carbon Fibre	UD	173	EF↑, XF↑55%, F↑	[113]

Resin Type	Reinforcement	Fibre Type	T (K)	Property Change	Reference
Epoxy (DGEBA)	Glass Fibre (E-glass)	3D MWK (Type D)	77	E1T↑83%, XT↑104%, 1T↑	[104]
Epoxy (DGEBA)	Glass Fibre (G-11)	Woven	77	E3T↑75% (Type A), ZT↑80% (Type B), 3T↓	[114]
Epoxy (DGEBA)	Glass Fibre (SL-ES30)	Woven	77	EF↑25%, E1T↑31%, E2T↑14%, XF↑94%, XT↑94%, 12↑36%	[114]
Epoxy (E51)	Glass Fibre (E-glass)	UD	77	E1T↑, XT↑30%, 1T↑	[103]
Epoxy (EL-762H)	Glass Fibre (G-11)	Woven	4	E1T↑28%, XT↑94%, 12↑33%	[115]
Epoxy (EL-762H)	Glass Fibre (G-11)	Woven	20	E1T↑27%, XT↑92%, 12↑28%	[115]
Epoxy (EL-762H)	Glass Fibre (G-11)	Woven	77	E1T↑22%, XT↑91%, 12↑28%	[115]
Epoxy (ML-506)	Glass Fibre	UD	213	E1T↑24%, E2T↑, XT↑12%, YT↑, 1T↓14%, 2T↓	[116]
Epoxy (RIM135)	Glass Fibre (E-glass)	3D MWK (various types)	77	EF↑100% (type A), XF↑89% (type A), F↑ (types B and C)	[117]
Epoxy (828)	Aramid Fibre	UD	77	E1T↑33%, XT↓13%, 1T↓52%	[107]
Epoxy (862)	Aramid Fibre	Woven	77	EF↓1%, E1T↓5%, XF↓2%, XT↓2%	[108]
Epoxy (1266)	Zylon	UD	77	E1T↑8%, XT↑30%	[118]
BMI (QY9611)	Carbon Fibre (ZT7H)	UD	153	E1T↓5%, E2T↑24%, XT↓24%, YT↓31%, 1T↓, 2T↓	[119]

Resin Type	Reinforcement	Fibre Type	T (K)	Property Change	Reference
BMI (QY9611)	Carbon Fibre (ZT7H)	UD	153	E2T↑24%, XT↓18%, 2T↓, 21↑52%	[120]
BMI (5250–4)	Carbon Fibre (IM7)	UD	77	E2T↑9%, YT↑12%	[109]
BMI (5250–4)	Carbon Fibre (IM7)	UD	77	E1T↑1%, E2T↑15%, 12=, 23=	[121]
PEEK	Carbon Fibre (AS4)	UD	4	E1T↑11%, E2T↑41%	[122]
PEEK	Carbon Fibre (AS4)	UD	77	E1T↑10%, E2T↑34%	[122]
PES	Carbon Fibre (C30 S003/6 APS)	Short fibre	77	EF↑, E1T↑, XF↑, XT↑, F↑, 1T↑	[123]
PI (AFR-PE-4)	Carbon Fibre (T650)	UD	77	YT↑	[124]
PI (PETI-5)	Carbon Fibre (IM7)	UD	4	E1T↓8%, E2T↓10%, XT↓22%, YT↓77%	[125]
PI (PETI-5)	Carbon Fibre (IM7)	UD	77	E1T↓4%, E2T↓14%, XT↓16%, YT↑23%	[125]
PEEK	Glass Fibre	Chopped fibres	20	EF↑14%, E1T↑57%, XF↓15%, XT↑44%, 1T↓20%	[126]
PEEK	Glass Fibre	Chopped fibres	77	EF↑7%, E1T↑35%, XF↓7%, XT↑38%, 1T↓13%	[126]
PP	PP	Woven	77	EF↑114%, XF↑34%, F↓50%	[127]

Nomenclature:

E1T, E1C	Longitudinal tensile and compressive moduli
E2T, E2C	Transverse tensile and compressive moduli
Eabs	Absorbed impact energy
EF	Flexural modulus
ε1T, ε2T	Longitudinal and transverse tensile strains to failure
εF	Flexural strain to failure
G12	Shear modulus
GIC, GIIC	Mode I and II fracture toughness
I	Impact strength
ILSS, IPSS	Interlaminar and intraply shear strengths

XT, XC	Longitudinal tensile and compressive strengths
XF	Flexural strength
YT, YC	Transverse tensile and compressive strengths

Tension

At lower temperatures, the Young's modulus and tensile strength of polymer matrices increase due to reduced chain mobility, leading to higher stiffness. Cryogenic temperatures can arrest stress relaxation, further enhancing stiffness [128-131]. However, individual carbon fibres, already highly crystalline due to manufacturing, show minimal modulus improvement at low temperatures [132, 133].

Carbon fibres tend to crack at cryogenic temperatures, whereas glass fibres exhibit increased elongation due to crack accumulation acting as stress relief [134]. Kevlar fibres demonstrate excellent creep resistance at 4.2K [135].

In composite laminates, fracture behaviour changes with temperature, with lower temperatures leading to cleaner fracture planes [Fig. 1]. Poisson's ratio generally decreases with temperature due to increased stiffness, but some studies report increases due to variations in longitudinal and transverse modulus [94, 111, 115, 136, 137].

Compression

At cryogenic temperatures, the compressive modulus and strength increase, while failure strain decreases due to reduced polymer chain mobility [138]). Kevlar fibres show low compressive strength due to weak matrix adhesion, while boron fibres perform better due to larger diameters. Increased matrix stiffness enhances fibre support, leading to improved compressive properties and shifting failure from kinking to fracture [139-141].

Three-point bending tests show better compressive performance with reduced temperature, though failure mechanisms vary. CFRP composites shift from kinking to crack failure, while GFRP shows increased cracking at -196°C [113]. Braided composites offer enhanced properties and near-zero thermal expansion through optimised braid angles [117, 142]. Pinned specimens exhibit greater compressive and bearing strength [143]. These findings highlight the importance of selecting optimal fibre-matrix combinations for cryogenic applications.

Shear

The shear behaviour of fibre-reinforced composites is primarily dictated by the matrix properties. As the matrix stiffens and strengthens at cryogenic temperatures, the shear stress–shear strain response becomes more linear due to the suppression of nonlinearity in the resin's behaviour [112]. Fractographic analysis reveals that at lower temperatures, fracture surfaces exhibit finer and more densely packed cusps, indicating brittle failure.

The fibre-resin interface significantly affects interlaminar shear strength (ILSS). Woven Kevlar composites display lower ILSS than carbon fibre composites at −196°C and −100°C due to the poor adhesion between Kevlar fibres and resin [143] . Glass fibre composites exhibit higher ILSS than carbon fibre composites at −100°C. However, contradictory results exist regarding CFRP laminates, with some studies reporting no improvement in ILSS at lower temperatures.

Research on interlaminar shear strength at cryogenic temperatures presents varied findings. While most studies indicate increasing ILSS with decreasing temperature, a few observed a decline[144-146]. One study found a reduction in in-plane shear strength (IPSS) for bismaleimide (BMI) resin-based composites at −120°C [119]. In another study ILSS at 20K was lower than at room temperature [147], and further reductions were observed at 4K compared to 77K [148]. This suggests that ILSS may initially increase with decreasing temperature but decline near absolute zero due to thermal stress effects.

Fatigue properties

The mechanical fatigue strength of composites is generally enhanced at lower temperatures compared to room temperature, primarily due to increased resin strength and improved fibre-resin interface strength. Research indicates that as the temperature decreases, fatigue performance improves, with a notable increase in fibre tensile modulus contributing to this effect, especially at 77K [149]. Toughened epoxy and thermoplastic resins exhibit greater fatigue resistance than their brittle counterparts. However, the rate of crack propagation can rise when temperatures drop from 77K to 4.2 K, likely due to reduced fracture toughness of the resin [150, 151].

While open hole tensile fatigue tests demonstrate that fatigue life increases with decreasing temperature, this trend may reverse if the load rate is heightened [152]. Notably, fracture analysis reveals that at room temperature, fibre surfaces are often devoid of resin debris, indicating low interfacial strength, whereas at lower temperatures, fibres remain coated in resin, signifying improved interfacial adhesion [153, 154]. These findings underscore the complexity of composite behaviour under varying thermal conditions and highlight the necessity for targeted testing to accurately assess performance.

Thermal fatigue testing of composites is essential for assessing not only their strength and stiffness but also critical factors like permeability, outgassing, and vacuum effects [155, 156].

These tests typically encompass cycle counts ranging from 10^1 to 10^5, reflecting various operational scenarios such as the refuelling of Composite Overwrapped Pressure Vessels (COPVs) in reusable launch vehicles (RLVs) and the service life of satellites. However, studies extending beyond 10^4 cycles haven't been explored due to the complexities/costs involved in thermal cycling experiments [94]. Crack formation can occur even after the first cycle [157], with factors such as higher temperature differences and cooling rates contributing to increased crack density. Composites with tougher resins, lower coefficients of thermal expansion (CTE), and improved surface characteristics demonstrate enhanced resistance to crack development [158]. The mechanical properties of these materials can vary significantly during thermal cycling, exhibiting patterns of increase followed by decrease and eventual plateauing with increasing the number of cycles [159, 160] , yet the correlation between mechanical properties and crack density over cycles remains an area needing further investigation.

Thermal expansion in composites at cryogenic temperatures

Thermal expansion significantly affects the mechanical properties of composites at cryogenic temperatures. The difference in the coefficient of thermal expansion (CTE) between fibres and resins creates residual stresses that influence material behaviour. At macroscale, these stresses are typically analysed at the ply level, which is sufficient for predicting thermal effects during cooldown from cure to room temperature. However, in extreme cases, such as liquid helium composite overwrapped pressure vessels (LHe COPVs), where ΔT can reach 450°C, excessive thermal strain may lead to matrix cracking even without mechanical loading.

At microscale, the thermal expansion of fibres varies in different directions [161]. In the longitudinal direction, aramid and most carbon fibres expand upon cooling, while glass and basalt fibres contract. Carbon fibres expand transversely, while aramid, glass, and basalt fibres contract [149, 162]. This disparity creates complex stress states when combined with the resin. The contraction of the resin and the transverse expansion of carbon fibres generate compressive stresses at the fibre-resin interface, increasing adhesion and improving mechanical properties at cryogenic temperatures.

Furthermore, internal CTE variations exist within fibres themselves. Carbon fibres consist of a core with negative CTE and an outer shell with positive CTE. At cryogenic temperatures, the contraction of the outer layer and expansion of the core induce cracks in the outer shell, increasing surface roughness. This roughness enhances mechanical interlocking at the fibre-matrix interface, further strengthening the composite material [163-165].

The influence of microcracking on permeability and leakage

Leakage of liquid hydrogen (LH2) in unlined storage vessels results from microcracks forming interconnected pathways, distinct from permeation, which involves overall gas transport through the material. Differential thermal expansion effects play a crucial role in matrix microcracking, affecting leakage susceptibility. Factors such as composite material, lay-up, temperature, thermal cycles, and mechanical loading influence leakage behaviour [166].

Research indicates that while crack density increases with decreasing temperature and thermal cycling, further cooling may reduce leakage due to limited molecular motion. Microcracks are less problematic than long cracks or delamination, provided they do not interconnect to form leakage paths [167].

Studies on LH2 permeability are limited, with most experiments conducted using liquid nitrogen. PEEK CFRP after thermal cycling and was found to have increased leakage rates [168]. Another study [169] observed that ply orientation affects leakage, with 30° plies showing higher permeability than 45° or 60° due to crack length and connectivity . Quasi-isotropic laminates have been shown to have higher crack density and leakage than cross-ply designs [157].

Woven ply composites exhibit lower permeability than UD ply composites, even after cryogenic cycling. Dispersion of plies of different orientations reduces leakage by preventing crack propagation, while nano-particles at ply interfaces do not significantly mitigate leakage [170].

Manufacturing processes also impact leakage rates, for example, a study evidenced that laminates produced via automated tape placement had higher leakage than those cured in an autoclave due to greater post-manufacturing defects [171].

In their review paper, Sápi et al. recommend using toughened epoxies, BMI resins, or thermoplastics to minimise matrix cracking and leakage [94]. Metal-composite tanks with metal liners effectively prevent leakage but increase manufacturing complexity, weight and introduce further challenges around thermal contraction and expansion mismatches. Non-metallic barrier layers, such as NASA's polyethylene terephthalate film, have been integrated into composite tanks to mitigate leakage while maintaining lightweight properties.

4.5. Fundamental science behind behaviour and properties of sealing materials

In a future liquid hydrogen fuelled aircraft, there will be the need to join cryogenic components within the fuel system. Some mechanically connected joints are likely to be required for maintenance or ease of assembly and these will require sealing to prevent hydrogen leakage. This section focuses on the materials research landscape relating to joint sealing (i.e. gasket) materials relevant to liquid hydrogen. It also considers the research landscape on materials for dynamic seals such as sliding seals in cryogenic hydrogen valves - although wear properties of materials are covered in the section on tribology.

FIGURE 4-8: GLOBAL LANDSCAPE OF RESEARCH INTO BEHAVIOUR OF SEALING MATERIALS FOR CRYOGENIC AND LH2 APPLICATIONS

Knowledge Maturity Summary:

- NASA have established substantial historical experience and reliability practice notes / lessons learned on use of seals in liquid hydrogen launch vehicle applications [172-178]. Deflection activated pressure assisted coated metal seals are mature technology.
- High nickel content steel alloys coated with a thin layer of PTFE or plated with gold, silver, rhodium, indium, palladium, lead, copper, nickel, or aluminium have provided good sealing properties at elevated as well as cryogenic temperatures.
- NASA have developed qualification practices [179] for cryogenic liquid hydrogen joints which may be adaptable to aviation applications, where qualification is of the entire joint system [172].
- The use of clamped gasket seals is well established in the wider cryogenics sector [179-182], including for industrial scale hydrogen liquefier applications. Gasket materials are typically single or combined metals such as stainless steel, copper, Monel 400 or indium, with indium having specific benefits [179].
- Most elastomers undergo a glass transition at low temperatures making them unsuited to cryogenic gasket applications.

- Thin solid PTFE gasket seals are an exception and are established in the wider cryogenic sector for service temperatures down to 5 Kelvin. NASA has completed testing for CryoH_2 applications [175] although the extent of testing in CryoH_2 is unclear. Noted concerns include compression setting of PTFE during repeated thermal cycling.
- There is some limited recent activity exploring PEEK materials for sliding seals, indicating performance is already degraded at LN2 temperatures - the research did not include H2.

Key Research Gaps:

- Research gaps are predominantly around long-term performance.
- Minimal published activity was found on long term sealing properties of sliding and other dynamic seal materials for cryogenic hydrogen - this is particularly relevant for fuel system valves close to the LH2 storage vessel exit (see also tribology section).
- Long term ageing of single material gaskets under cyclical thermal and mechanical loading, in CryoH_2 environments, may be a gap.
- Long term coating integrity of coated gaskets when exposed to cryogenic hydrogen may also be a gap.
- Influence of H2 at cryogenic temperatures on long term plastic deformation of strained spring gasket materials may also be a gap, although NASA have medium term / cyclical testing data.

Key Research Groups

TABLE 4-6: KEY RESEARCH GROUPS ACTIVE ON UNDERSTANDING THE BEHAVIOUR OF SEALING MATERIALS FOR CRYOGENIC AND LH2 APPLICATIONS

Institution	Country	Topic
Polymer-tribology group, Division of Machine Element, Luleå University of Technology, Luleå.	Sweden	PEEK based composite mechanical and tribology (wear resistance) properties for cryogenic valves, bearings and gaskets.
CEMMPRE, Department of Mechanical Engineering, University of Coimbra	Portugal	Peek based composite mechanical and tribology (wear resistance) properties for cryogenic valves, bearings and gaskets (collaboration with Lulea above).
NASA Kennedy Space Center Merritt Island, Florida.	USA	Development of apparatus for testing of leak rates of fittings down to 20 Kelvin before and after launch vibration profiles using helium. Note: focus is on the overall fitting performance not the materials science.

Narrative

The use of gasket materials for sealing mechanically clamped cryogenic joints is well established in the space applications [172-178] and wider cryogenics industry [179-182].Figure 4-9 shows the contribution of different countries and the number of reviewed paper from each region in the field. This provides a wide menu of cryogenic and hydrogen demonstrated materials and materials combinations, along with geometries. NASA have developed qualification methods for liquid hydrogen gasket joints and lessons learned documents which are likely to provide lessons relevant to aerospace. Deflection activated pressure assisted coated metal seals are a mature technology for cryogenic hydrogen in space applications. High nickel content steel alloys coated with a thin layer of PTFE or plated with gold, silver, rhodium, indium, palladium, lead, copper, nickel, or aluminium have provided good sealing properties for space missions, including at elevated as well as cryogenic temperatures. The research in LH2 specific gasket materials appears to have peaked in the 1970's being led by NASA, during development of the space shuttle. Joint seal failure is more likely to stem from the overall joint system design (including the combination of gasket, surface preparation and clamping design) than from an inadequacy in current understanding of gasket materials, although longer term compatibility testing of materials combinations (including coating or plating integrity) for specific aerospace applications is still likely to be required. The level of data available from the space industry on long term cryogenic cyclical testing in hydrogen of nickel-based steels used in deflection activated pressure assisted coated metal seals requires further investigation. Industrial scale hydrogen liquefaction plants and their associated pipework and storage vessel connections are also increasingly established, and whilst specific performance data was not located in the literature, it is likely that qualification data of potential relevance to aerospace applications may be available via the supply chain.

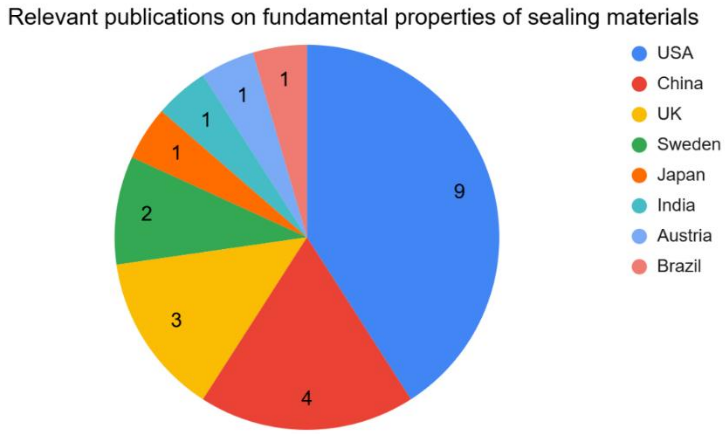

FIGURE 4-9: TOTAL NUMBER OF PAPERS AND LANDSCAPE ON FUNDAMENTAL PROPERTIES OF SEALING MATERIALS FOR CRYOGENIC APPLICATIONS

Aerospace relevant research gaps therefore relate more to the long-term ageing of the specific joint and gasket geometry under aerospace specific cyclical $CryoH_2$ conditions, at representative static and dynamic deformations.

Knowledge on polymer materials for seals, including on moving joints such as ball valves operating long term in liquid hydrogen is less advanced, possibly due to the suitability of PTFE coated metals for current applications. In addition, valve designs for cryogenic applications may move the sliding seal away from the lowest temperature zone. A body of knowledge on materials properties of polymers at cryogenic temperatures is summarised in the 2013 book "Polymers at Cryogenic Temperatures" [183]. Recent work is more limited and includes a collaboration between University of Lulea (Sweden) and University of Coimbra (Portugal) [184, 185] exploring the mechanical properties of four grades of commercially available PEEK composites with various fillers (carbon fibres, graphite, PTFE), for cryogenic sealing applications (with testing in LN2), including for sliding seals (e.g. valves). This included ageing in LN2 for 5 months. Dynamic mechanical analysis was performed on a Tritec 2000 DMA (Triton Technology, Ltd., UK) in a temperature sweep mode starting from 103K up to 573K at a mechanical frequency of 1 Hz. A wide array of non-cryogenic materials analysis was also conducted on the aged materials. It is not clear which tests were done at which collaborator. Conclusions were that cryogenic ageing reduces fracture toughness over time, but toughness increases with reduced test temperature, whilst temperature also impacts on wear mechanisms. None of the recent identified work included hydrogen exposure.

There is a significantly wider body of knowledge and ongoing activity (see for example [186-193]) on hydrogen induced degradation and permeation of elastomer sealing materials at non-cryogenic temperatures. Due to the general incompatibility of elastomers with cryogenic temperatures, and the likely change in permeation dynamics at cryogenic temperatures, this however has low relevance to seals in the cold parts of liquid hydrogen fuel systems.

Some further information on potential sliding seal materials is included in the section on tribology, which focuses more on wear properties than sealing properties.

5. Impact of Manufacturing and Processing Route on Mechanical Properties of Metals

Manufacturing and processing routes are known to impact on the cryogenic and LH2 performance of metals. Several manufacturing routes could be used to produce hydrogen system components for LH2 applications in the aviation industry, and understanding LH2 and cryoH_2 performance impacts from processing is equally as important as the selection of material grade. This section provides a brief review of the effects of the main processing operations on properties of metals at cryogenic and LH2 conditions. The references show the distribution of research across different countries and institutions over time, from early US-dominated research to more recent international contributions, particularly from Asian institutions.

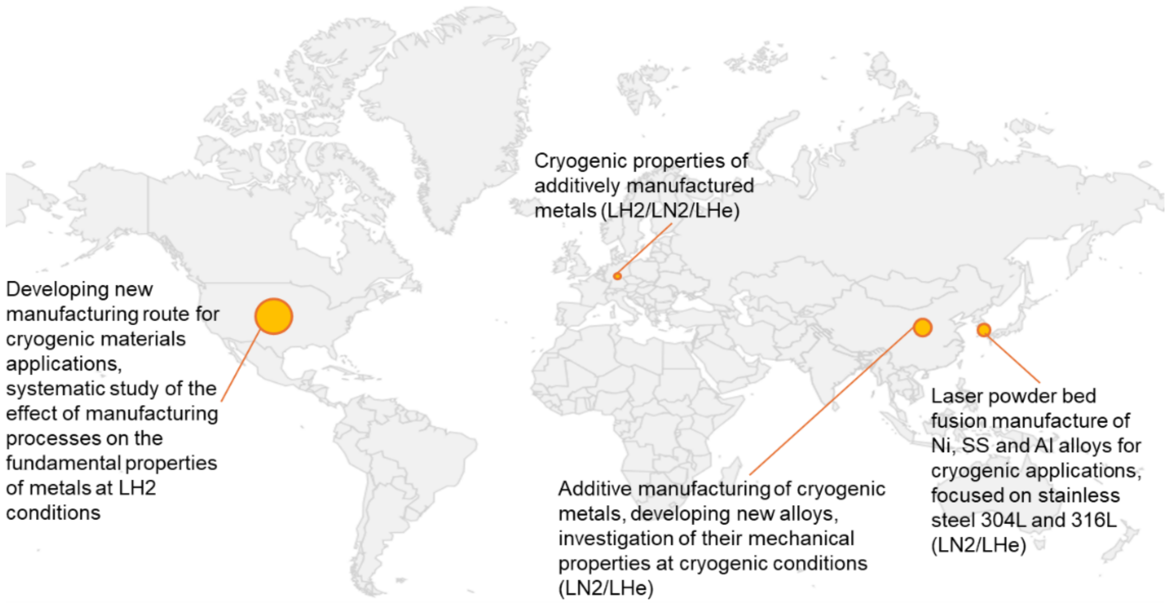

FIGURE 5-1: GLOBAL LANDSCAPE OF RESEARCH INTO THE EFFECT OF IMPACT OF MANUFACTURING AND PROCESSING ROUTE ON MECHANICAL PROPERTIES OF METALS

Knowledge Maturity Summary:

- NASA has advanced several novel and commonly available alloys through the use of additive manufacturing (AM), utilising integrated computational materials engineering [194, 195] with many of the alloys are being commercially produced for LH2 and cryogenic applications.
- The effect of cold forming on the mechanical properties of main alloys including 3xx austenitic stainless steel at cryogenic and LH2 temperatures are investigated to a limited extent, mainly by NASA [6, 19, 29, 172] [7, 12, 13], and it is demonstrated that based on the alloying family, the plastic deformation has limited effect on the hydrogen diffusivity and mechanical properties as long as the stable phase of FCC remains.
- There is an increased uptake of using AM processes and advanced computation materials engineering techniques to develop new family of alloys with tuned mechanical properties at cryogenic and LH2 conditions.
- Cryogenic deformation processing can be an effective strategy for optimising high entropy alloys (HEA) properties for low-temperature applications. The combination of

cold working and the inherent characteristics of HEAs results in materials with exceptional strength-ductility combinations at cryogenic temperatures [52].

- AM facilitates the use of novel alloying composition with enhanced mechanical and thermal properties for extreme conditions.

Key Research Gaps:

- There is limited information about the manufacturing route on the properties of metals at LH2 conditions.
- The effect of surface processing, including machining and forming, on the materials performance in the LH2 and GH_2 conditions are not known.
- The AM materials developed for cryogenic and LH2 applications, either conventional or new alloys, are mostly studied with respect to their hydrogen embrittlement at room temperature, with very few studies found for tests below 77K.
- There is very limited knowledge available on the mechanical properties of AM built parts in LH2/LHe/LN2 conditions despite the significant body of research on hydrogen induced cracking and embrittlement [196] for static and cyclic loads [197, 198] of these materials.
- There is still a need for new alloys for LH2 conditions as their development and characterisation of their properties in this harsh environment is missing.

Key Research Groups

TABLE 5-1: KEY RESEARCH GROUPS ACTIVE ON THE EFFECT OF IMPACT OF MANUFACTURING AND PROCESSING ROUTE ON MECHANICAL PROPERTIES OF METALS

Institution	Country	Topic
US government agencies (NASA, Aerospace Corporation)	USA	Developing new manufacturing route for cryogenic materials applications, systematic study of the effect of manufacturing processes on the fundamental properties of metals at LH2 conditions.
University of Science and Technology Beijing	China	Additive manufacturing of cryogenic metals, developing new alloys, investigation of their mechanical properties at cryogenic conditions.
Korea Institute of Industrial Technology	South Korea	Laser powder bed fusion manufacture of Ni, SS and Al alloys for cryogenic applications, focused on stainless steel 304L and 316L.
Material testing institute Stuttgart / Karlsruhe Institute of Technology	Germany	Cryogenic properties of additively manufactured metals.

Narrative

The main manufacturing processes studied for current applications include conventional sheet and bulk metal forming [199], e.g. roll forming, deep drawing, extrusion or the combination of them as well as additive manufacturing operations [194]. The conventional operations result in alteration of microstructural morphology of the metals [199] and hence affect their micro-mechanical properties at critical conditions including cryogenic temperatures. There are several research outputs by NASA demonstrating that as a metal's strength increases - whether through temperature reduction, cold working, heat treatment, or alloying - it typically becomes more brittle and more sensitive to notches [6, 33, 200]. This has recently been followed by activities in countries such as South Korea (Korean Institute of Industrial and Technology), China (University of Science and Technology Beijing) and Germany (Karlsruhe Institute of Technology), as is shown in Figure 5-2, with most of research focused on manufacture and processing of materials for cryogenic and LH2 applications for marine and land transport.

Cold working effect

The material's interaction with hydrogen differs under static and dynamic deformations. Research groups in Kyushu University (Japan) and Central South University of China have reported that plastic deformation and pre-straining could decrease the hydrogen diffusivity [201, 202] under static loading whilst elastic deformation has no significant effect, however, elastic deformation was the dominant mechanism in increasing the permeation rate under cyclic loading.

Cold-working, specifically when it is conducted at cryogenic condition e.g. cryogenic rolling [52], results in refined microstructures, improving mechanical strength, however the material may exhibit more pronounced surface cracking under LH2 and cryogenic conditions [6, 29, 30]. The embrittlement severity in hydrogen environments increases with greater cold-working percentages, whilst annealed materials demonstrate better resistance to embrittlement compared to cold-worked ones.

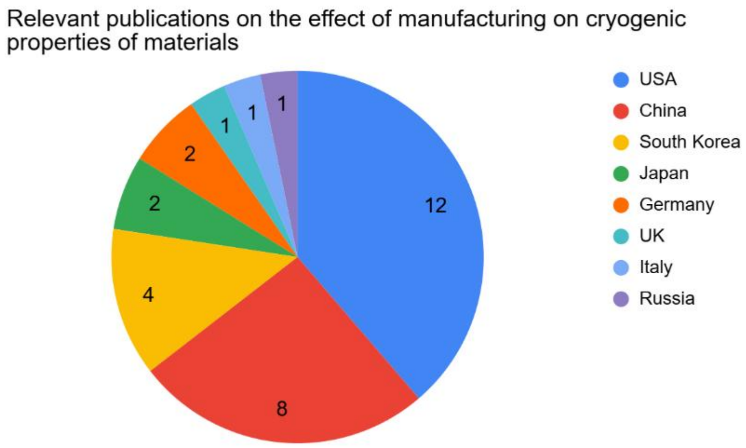

FIGURE 5-2: TOTAL NUMBER OF REVIEWED PAPERS AND LANDSCAPE ON THE EFFECT OF MANUFACTURING ON CRYOGENIC PROPERTIES OF MATERIALS

There is a large body of research on the effect of cold working on austenitic stainless steels, such as 301 and 304L, showing enhanced cryogenic properties mostly due to the stability of the austenite and preventing martensitic transformation that is demonstrated to be the main mechanism in retaining the strength and ductility at cryogenic and LH2 conditions [9, 15, 33, 34, 197, 200]. However, the orthotropy of mechanical properties is severely increased at the cryogenic and LH2 testing conditions [200]. In some alloys, e.g. 202, the cold working increases the yield strength at the expense of reduced ductility, however the ductility reduction becomes negligible compared to the annealed materials [29]. Ni-alloys such as Haynes 25 keep their excellent strength and ductility at LH2 testing condition to a certain extent and then become brittle at about 40% CW [33].

Additive Manufacturing:

Additive manufacturing (AM) methods fundamentally influence how materials perform in extreme cold environments [197]. The key effects manifest differently across major material classes. Several processes, such as Laser Powder Bed Fusion (L-PBF), Directed Energy Deposition (DED) have been used to produce materials and compare their mechanical properties and hydrogen performance with conventionally rolled or forged alloy [195, 203, 204]. Although, most of research is focused on austenitic stainless steel (e.g. 304L [205], 316L [197]) as they are proven to be suitable candidates for such applications [6, 29, 30, 33], NASA has been involved in maturation of metal additive manufacturing and developing new alloys for space and hydrogen application such as GRCop-42, GRCop-84, NASA HR-1, GRX-810, and C-103 [195].

Comparing DED with conventionally rolled plate of 304L stainless steel, AM process can significantly improve a material's resistance to hydrogen embrittlement. The AM specimens maintained mechanical integrity, showing minimal property reduction and preserving ductile fracture characteristics. Conversely, rolled specimens experienced dramatic mechanical property collapse, transitioning from ductile to brittle failure modes [206].

Processes such as L-PBF also provide an opportunity to develop new grades of alloys by strategically substituting manganese for nickel to find an alternative for 304L to reduce materials costs without compromising mechanical integrity [207] or generating new materials based on the concept of High Entropy Alloys with tuned thermo-mechanical parameters [52, 195, 202, 208]. In a study by Northwestern Polytechnical University (China), in contrast to conventional alloys, it is shown that in L-PBF produced CrMnFeCoNi HEA, the strength and ductility significantly increases at 77K compared to the room temperature [208], but there is limited knowledge available about their performance at LH2 conditions. Another example developed by NASA [194, 195] is GRCop-42 and LP-DED NASA HR-1 with increasing mechanical properties and thermal conductivity by decreasing temperature as well as comparable fatigue life at 77K. Type 316L stainless steel exhibits superior hydrogen embrittlement resistance compared to conventionally manufactured variants in GH2. This improved performance was attributed to L-PBF's unique microstructure featuring homogeneous elemental distribution and the stability of FCC crystal [208, 209].

In titanium alloys (Ti6Al4V), powder-based AM creates a refined lamellar microstructure that surprisingly improves hydrogen embrittlement resistance at room temperature compared to conventional manufacturing. The rapid cooling during AM leads to better control of hydride formation at phase interfaces when exposed to liquid hydrogen temperatures (20K) [197]. The mechanical strength of LPBF produced Ti6Al4V samples are shown to increase at LN2 testing condition with a slight reduction in strain at fracture [210]. For austenitic stainless steels (316L, 304L), AM produces unique cellular substructures that inhibit martensitic transformation at cryogenic temperatures, leading to better mechanical properties [197]. However, hydrogen charging could lead to marginal softening and reduction of strength in L-PBF 316 stainless steel [211].

In nickel-based superalloys like IN718, L-PBF samples followed by direct aging demonstrated a higher strength at the expense of lower hydrogen embrittlement resistance compared to the homogenised and aged samples. This is linked to precipitation along the grain boundaries when testing at room temperature as the AM process creates critical interfaces between different phases that determine hydrogen interaction. The interfaces between Laves phase/matrix in as-built conditions and γ-matrix/δ phase after heat treatment become crucial sites affecting material behaviours at cryogenic temperatures [197, 212].

A key finding is the importance of post-processing. The Hot Isostatic Pressing (HIP) process helps eliminate manufacturing-induced porosity, which becomes particularly problematic at extreme low temperatures where any defect can initiate failure [194].

5.1. Research into materials properties enhancement using cryogenic processing

There is a mature body of materials science that relates to the use of cryogenic temperature exposure (typically 77K) to permanently modify the physical properties of metals. This stems from advanced materials research for aerospace and cutting tool applications. While materials have traditionally been modified by cryogenic cycling for use in applications at non-cryogenic temperatures, the research into the fundamental mechanisms leading to cryogenic modification of metals is relevant to metals enduring exposure to cryogenic temperature cycles. This section reports on the latest findings on the effect of cryogenic processing on properties of materials relevant to LH2 and cryogenic applications.

FIGURE 5-3: GLOBAL LANDSCAPE OF RESEARCH INTO MATERIALS PROPERTIES ENHANCEMENT USING CRYOGENIC PROCESSING

Knowledge Maturity Summary:

- Cryogenic treatment (CT), in all forms including shallow, medium and deep cryogenic treatment (SCT, MCT and DCT respectively) is a well-established post processing in the field of manufacturing and enhancing wear and cutting performance of metals.
- There is significant evidence that the enhanced properties are mostly due to the dislocation freeze, grain refinement and homogenous distribution of fine carbides (for ferrous alloys) or secondary precipitates in the nonferrous alloys.
- The duration of cryogenic treatment and the warming up/cooling cycles are critical parameters to control the process.

- Cryogenic treatment often replaces the conventional heat treatment operations, and it is well stablished almost everywhere from North America to Southeast Asia.

Key Research Gaps:

- Little is known about the effect of CT on the mechanical properties at cryogenic and LH2 conditions.
- Despite demonstrated benefits, challenges persist in standardising protocols and understanding universal transformation mechanisms across diverse material systems, presenting compelling opportunities for future interdisciplinary research in materials science and advanced manufacturing technologies.
- limited research on different materials is available, and extensive research is required to investigate CT of materials with poor weldability.
- Further investigations are required to study mechanisms of structure-properties of alloys processed by DCT at LH2 service conditions and to develop the required knowledge for design, modelling and simulation tools.
- Various research groups were identified working on the effect of cryogenic treatments on mechanical properties of metals, welds and additively manufactured new alloys. However, none was specifically working at LH2 conditions and most focused on LN2 temperatures.
- There is limited knowledge on whether the cryogenic cycling actually has some healing effect which counteracts deterioration due to fatigue.

Key Research Groups

TABLE 5-2: KEY RESEARCH GROUPS ACTIVE ON UNDERSTANDING MATERIALS PROPERTIES ENHANCEMENT USING CRYOGENIC PROCESSING

Institution	Country	Topic
Harbin Institute of Technology	China	Effect of cryogenic treatments on mechanical properties of novel AM and conventional alloys and weldments for cryogenic applications.
Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Beijing	China	Effect of cryogenic treatment on metal composites.
Dr B R Ambedkar National Institute of Technology	India	Enhancing mechanical and wear resistance of metals with cryogenic treatment.
Louisiana Tech University	USA	Improving machining performance and wear resistance of cutting tool materials and other metals for aerospace applications.

Narrative

As early as 1937, reports of the positive benefits of cold treatments on tool performance were made [213-215], which was due to the microstructural changes encouraging the conversion of residual austenite into martensite and forming uniformly dispersed carbide precipitations [216].

Historically, cryogenic treatments have been used to improve mechanical, wear and cutting performance of cutting tools in manufacturing industries [215, 217-219]. Cryogenic treatment is a well-established practice in this context [215, 218], however there is a significant gap in identifying the effect on properties of materials when subjected to cryogenic temperatures after their treatment as well as their properties in cryogenic temperatures. The body of research on cryogenic treatments of materials is of significance to LH2 aerospace fuel systems, because the deep cryogenic thermal cycling that will be experienced by system materials has strong analogies to the cycles used for deliberate properties manipulation, albeit that cycling in the range from 77K (LN2) to 20K (LH2) is less well explored.

Cryogenic treatments are performed by submerging materials for a long duration of time in cryogenic fluids like helium [220], hydrogen, nitrogen, oxygen and methane [23, 214, 221-223]. The cryocooling and subsequent warming cycles routine play a crucial role on the achieved properties of materials [213]. It can be classified as cold (223–193K), shallow cryogenic (SCT) (193–113K) and deep cryogenic treatment/treated (DCT) with temperature range of 113–77K (using liquid nitrogen) [3]. Many review papers have already published the effect of CT on mechanical properties of various materials e.g. [23, 213-215, 217, 224-227].

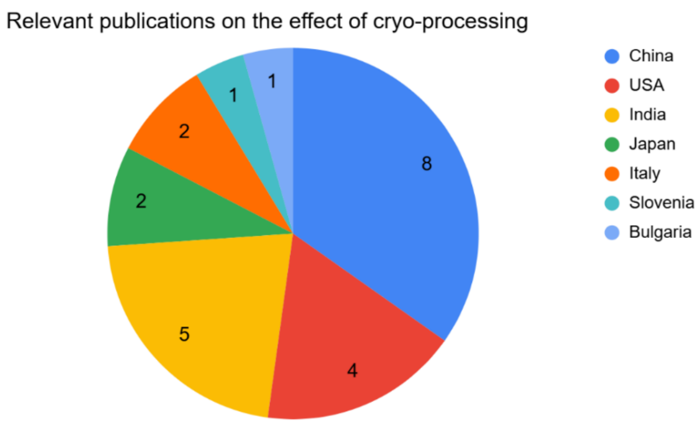

FIGURE 5-4: TOTAL NUMBER OF REVIEWED PAPERS AND LANDSCAPE ON THE EFFECT CRYO-PROCESSING ON PROPERTIES AT CRYOGENIC AND LH2 CONDITIONS

Effects on mechanical properties

Deep cryogenic processing was found to improve wear resistance (up to 200% [226]), dimensional stability [228, 229], and mechanical properties across different materials including metals, polymers, and composites produced by various operations [214] by refining and stabilising crystal lattice structures and achieving more uniform carbon particle distribution throughout the material [226]. The DCT is shown to be more effective than conventional heat treatment and SCT [23] in reducing residual stresses (up to 85% less in high-alloyed ferrous alloys) [228], improved hardness, with effects becoming more pronounced with longer aging times [222], and yield strength of alloys [23, 214, 222, 226, 230] while tensile strength of Al-Sic alloy showed minimal changes after DCT [222].

The improved mechanical properties also applies to alloys produced by L-PBF for conventional [230] and high entropy alloys [231, 232] and Al-alloys [23] due to the hardness improvements by increased precipitation and more uniform distribution of strengthening phases. Various CT have shown to significantly improve fatigue properties of Al-alloys [23, 214] as a result of increased resistance to crack propagation. It should be noted, however, that the CT after solution and aging treatment are shown to have minimal effect on the mechanical properties of Al-alloys [213].

The CT could lead to grain size reduction [23, 52] by as much as 58% while improving the wear rate by 30% through fine-grain and second-phase particle dispersion strengthening mechanisms to achieve a strength-ductility trade-off AM built HEAs.

Significant service life improvements are reported for industrial tools, gears, brake rotors, automotive and aerospace engine components, composites, medical devices, dental materials, and surgical implants subjected to CT [214, 233]. This could be that the process induces complex metallurgical transformations, including retained austenite to martensite conversion, ultra-fine carbide precipitation, and refined grain structures, which collectively contribute to remarkable improvements in mechanical characteristics [23, 214, 226]. It is demonstrated that deep cryogenic treatment can be applied as single step or a cyclic process and the latter is demonstrated to significantly reduce residual stresses in laser melting deposited (LMD) high entropy alloys [232].

In steels, CT promotes several important transformations: It converts retained austenite into martensite, encourages the formation of fine carbide particles, and creates a more uniform distribution of carbides throughout the material matrix. These changes are typically more pronounced with deep cryogenic treatment (DCT) compared to shallow cryogenic treatment (SCT) [225]. DCT creates a finer martensitic matrix compared to conventional heat treatment (CHT) with approximately 30% more sub-micrometre precipitated carbides, with a more homogeneous distribution throughout the material [228].

Effects joints

The effects of cryogenic treatment on joint properties can vary significantly depending on the specific materials involved and the joining process used. For interference fit joints, a higher load-bearing capacity is achieved by cryogenically treating the components before assembly [221]. This improvement stems from enhanced hardness and wear resistance resulting from the transformation of retained austenite to martensite. For electron beam welded joints, particularly in titanium alloys like Ti-6Al-4V [234, 235], cryogenic treatment reduces both longitudinal and transverse residual stresses in the welded area. The hardness in the welded zone typically increases compared to the base metal due to changes in the quantity, size, and morphology of the α and β phases. For friction stir welded joints, deep cryogenic treatment (DCT) creates a more uniform and coherent microstructure for aluminium alloys like 2219-T87 [236], 7050-T7451 [237] as well as significant improvement in strength and ductility of the weldments. This also was observed for Ti-6Al-4V alloy [234] where DCT was more effective in FSW compared to TIG. This improvement occurs through three main mechanisms: grain-boundary strengthening, substructure strengthening, and aging precipitation strengthening. These changes result in better overall joint properties. Despite the other report, a report from NASA [238] indicates that the CT has minimal effect on mechanical strength and high cycle fatigue life of Variable Polarity Plasma Arc (VPPA) welded samples while reducing the residual stress.

6. Mechanical and Physical Properties Test Capabilities

This section covers the current landscape of test methods and capability. It focuses specifically on capabilities relating to Mechanical Properties testing, hydrogen loading, tribology, thermal properties and hydrogen transport properties, at cryogenic temperatures of typically below 100K, preferably down to 20K.

6.1. Mechanical properties testing methodologies relevant to cryogenic and liquid hydrogen environments

Mechanical properties testing equipment designed to operate at LH2 relevant temperatures of 20K to 300K is significantly more complex than equipment designed to operate at ambient temperatures. Complexities in equipment also mean complexities in test methods, with additional variables to control, wider systemic error considerations and significantly more challenging operational considerations, including throughput. There is currently no “off the shelf” system for cryo-mechanical properties testing, although a range of “home grown” solutions are available across the world. Most commonly these operate at liquid nitrogen temperatures (>77K), although a small number of institutions are now extending the temperature range down to 20K. This section reviews the current landscape in terms of test equipment and methods.

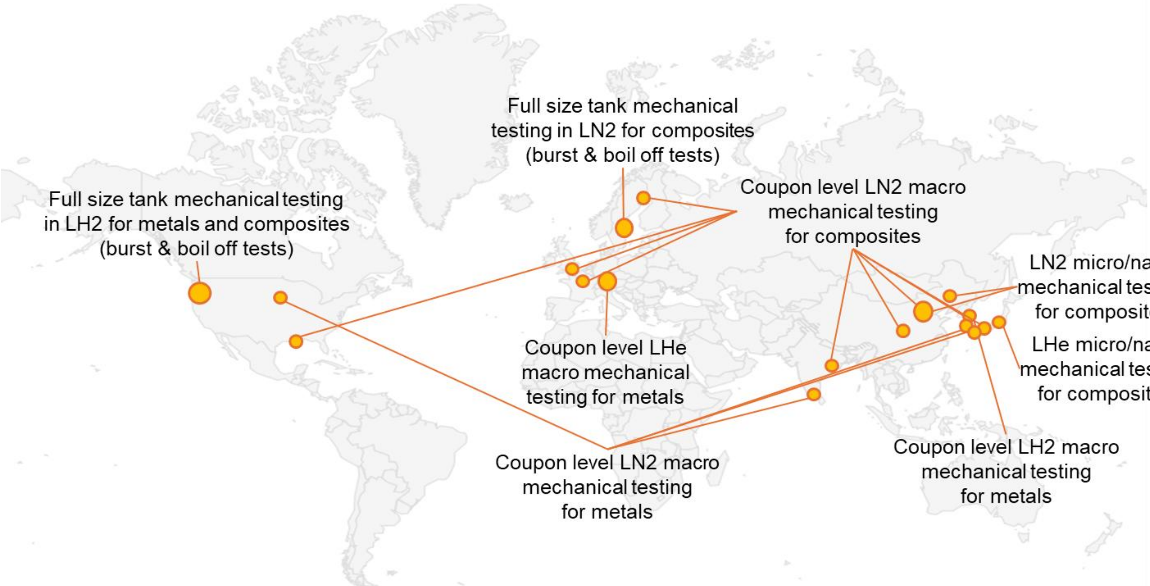

FIGURE 6-1: GLOBAL LANDSCAPE OF RESEARCH INTO RESEARCH RELATED TO MECHANICAL PROPERTIES AND TESTING RELEVANT TO CRYOGENIC AND LH2 CONDITIONS

Knowledge Maturity Summary:

- Metals have dedicated standards for cryogenic temperatures including in LHe and other cryogenic conditions but not including LH2 [239-241].
- NPL has done significant work on mechanical testing methods at cryogenic temperatures [242, 243].

- A wide range of equipment designs have been implemented depending on the temperature targeted, cooling methods, measurement methods and other design choices [244].
- Depending on equipment design, samples can be immersed in LN2, sprayed with LN2, in vacuum (conductively cooled), in N2 gas, in helium exchange gas, in H2 gas or in LH2.
- CERN designed a cryostat bespoke to tensile testing[245] based on the suggested materials in [244] and ASTM E1450 was used to validate the cryostat design.
- A small number of organisations have commissioned LH2 immersion cryo-mechanical testing capabilities including in situ hydrogen liquefaction to simplify logistics.

Key Research Gaps:

- There is no standard for robust control and conduct of mechanical tests at the LH2 conditions. This includes equipment design, cooling procedure and rates, temperature maintenance, etc, echoing [242].
- No dedicated composite standards for working at cryo-temperatures, research use normal room temperature standards (tension: ISO 527-4, [243] compression ISO 14126 , ILSS, ASTM D2344 [240] Flexure, ASTM D 7264 [246] or no standards at all [247].
- Instrumentation standardisation when testing composites at cryogenic temperatures is non-existent and usually substituted by its metal counterparts [241, 248].
- Guidelines about design of experimental setups to alleviate the coefficient of thermal expansion are very limited [241, 248-251].
- Gripping mechanisms, optimised by type of sample, dimensions, transferability of the data at sub/full scale transitions have not been covered in the literature. There is a large gap between available standards for metals [241, 248] and composite materials [94, 252].

  Although several types of instruments including extensometers [94, 149] and strain gauges are used, there is little standard calibration practice to 20K.

Key Research Groups

TABLE 6-1: KEY RESEARCH GROUPS ACTIVE ON MECHANCIAL PROPERTEIS AND TEST METHODOLOGIES

Institution	Country	Topic
NPL	UK	Gaseous and LN2, tension compression composites and metals.
Washington State University	USA	LH2, full tank size burst and boil off testing composites & metals. Fatigue testing with integrated LH2 liquefier.
Korea Institute of Machinery and Materials	South Korea	LH2, LHe, LN2, Cryogenic fracture toughness ASTM E1820 tension, (ASTM E1450) for metals tension test specimens in ASTM E8/E8M.
Key Laboratory of Technology on Space Energy Conversion	China	Flexure, ILSS on modified CFRP LN2.

Institution	Country	Topic
RISE Research Institutes of Sweden	Sweden	Full size tank mechanical testing in LN2 (burst & boil off tests) composites.
Tokyo University of Agriculture and Technology, Tokyo	Japan	Bespoke rig, Tension not standardised dimensions (120 mm length, 3 mm width). Ability to observe through OM and Micro CT in situ. LN2, LHe Metals.
Energie Technologie (Kiwa group)	Germany	Cryogenic tensile, fatigue, creep & fracture mechanics testing to 20K, covering composites and metals, in LH2.

Narrative

Mechanical tests have been developed and conducted at various cryogenic environments including liquid air, CCH2, LN2, LHe and LH2 [2, 6, 7, 13, 16, 26, 28-30, 35, 253]. The majority of systems are limited to LN2 temperatures. Whilst historically achieving LH2 relevant temperatures required a supply of liquid helium or liquid hydrogen, over the last 15 years, "cryofree" systems, based on mechanical cryocoolers incorporating closed helium loops, are now the norm. These can typically operate from <4.2K to 300K, although mechanical cryocoolers optimised for higher cooling power and efficiency at 20K are also available, enabling more rapid cooldown, potentially improving throughput. In these systems the sample can be in a vacuum environment [42, 254], conduction cooled through the grips, or in some cases, the sample chamber can be flooded with gas. The lack of standardised cooling methods and the absence of consistent protocols makes it difficult to compare results across different studies and laboratories.

Test apparatus has been used to conduct slow strain rate tensile tests [4, 11-13, 45, 255, 256] , conventional tensile, compression and shear tests [14, 29, 257] , Charpy impact tests [12, 38, 47] and cryogenic indentation on metallic materials [258]. The cyclic tests under strain and force controlled, Low Cycle Fatigue and High Cycle regimes are reported to be conducted by NASA and associated teams as early as 1950's [6, 26] and more recently by other researchers [4, 45, 49, 255, 259].

Different stress states are replicated in various sample geometries including smooth tensile [6, 26], notched tensile [6, 29], and biaxial testing to ensure various stress states are replicated in the working environment conditions [6]. However, most experimental results related to the LH2 conditions are originated from USA with some recent activities in Asia as it is demonstrated in the pie-chart of Figure 6-2.

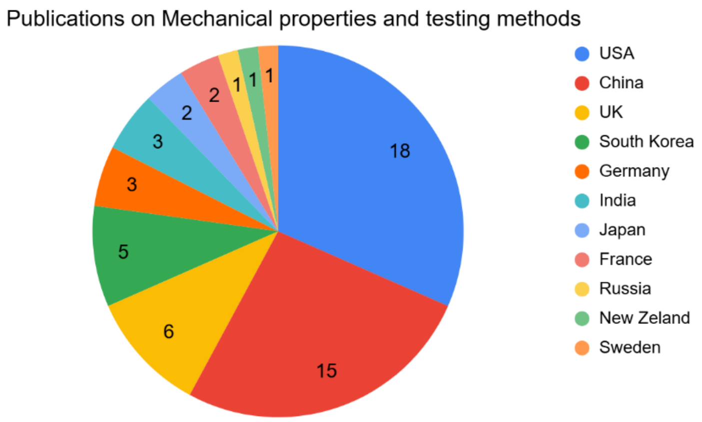

FIGURE 6-2: TOTAL NUMBER OF REVIEWED PAPERS AND LANDSCAPE MECHANICAL TESTING AND METHODS RELEVANT TO CRYOGENIC AND LH2 CONDITIONS

Despite all the developments in this regard, several challenges and gaps persist in this critical area of materials science, with currently no standardisation between labs:

Cryostat Design and Cooling Method

A wide range of cooling methods have been adopted in the literature cited above, but there has been little or no systematic research into the impact of the cooling method on the mechanical property test results. Parameters such as cool downtime and thermal shock are likely to lead to variations in internal stress levels after cooling, and whether the sample is in a hydrogen, helium, nitrogen or vacuum are likely to impact on hydrogen desorption, impacting final results. Thermal leakage through grips is also likely to impact sample temperature. For composites in particular, the very low thermal conductivity means that indirectly cooled systems are likely to read incorrect and inconsistent sample temperatures.

Sample Self Heating

Consistency of temperature throughout the sample is a concern specific to cryogenic testing. Specific heat capacity at LH2 temperatures is extremely low, so a small amount of frictional heating as material is elongated or starting to fracture will have a more substantial impact - this is not generally reported on. The impact of this will vary widely between directly cooled (e.g. immersion) and indirectly cooled sample cryostat designs.

Gripping Methods and Standards for Composites

The effectiveness of gripping methods for testing composites at cryogenic temperatures has not been systematically researched. This lack of comprehensive study hinders the development of reliable testing procedures for these increasingly important materials in extreme cold environments.

Measurement Techniques

Whilst contact-based measurement techniques dominate the literature on cryogenic testing, there is a notable lack of standardisation in this area. Moreover, non-contact optical methods for quantifying deformation and failure are scarcely used, despite their potential advantages in avoiding interference with the material's behaviour at extremely low temperatures.

6.2. Systematic Studies of The Impact of Hydrogen Loading Methods on Cryo-mechanical Materials Properties.

Hydrogen loading methodologies in relation to cryo-mechanical testing is a more complex area than it may first appear. This is because of significant reduction in hydrogen mobility at cryogenic temperatures, the potential for changes in trapping due to the reduced thermal kinetics, along with the potential creation of new trapping centres resulting from cryogenic thermal cycling. Internal material stresses due to thermal contraction create further questions regarding potential mechanistic differences depending on the temperature and method of hydrogen loading. There are therefore conflicting considerations of test time vs accurate replication of the real-world hydrogen distribution that would be present from long term CryoH_2 exposure. This section focuses on current systematic research into the impact of hydrogen loading methods on cryogenic materials properties, particularly mechanical properties. Figure 6-3 shows the global landscape of research into this topic.

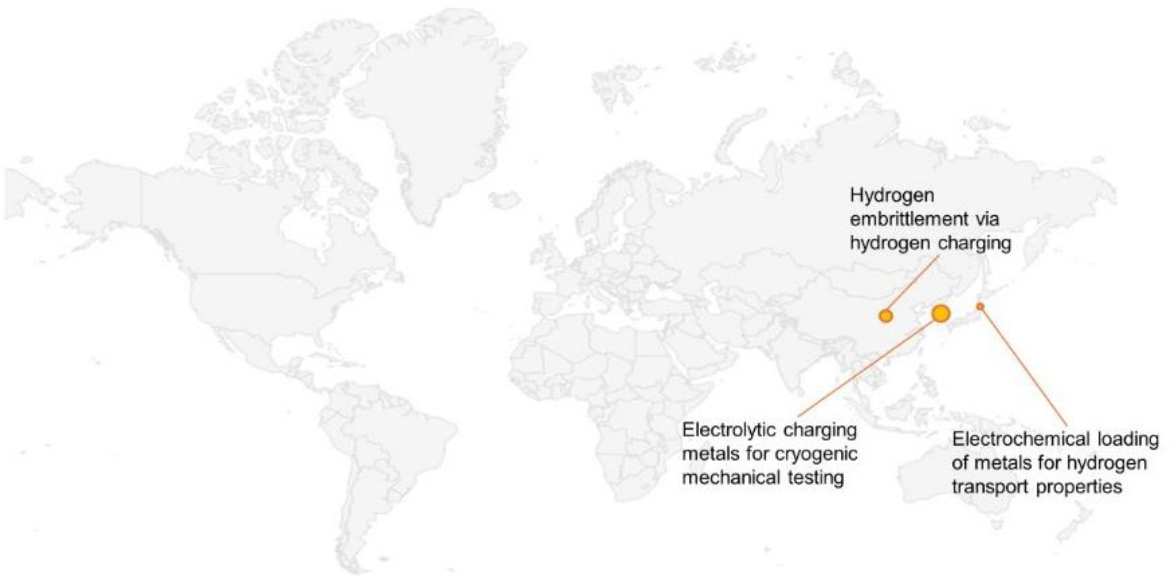

FIGURE 6-3: GLOBAL LANDSCAPE OF RESEARCH INTO THE IMPACT OF HYDROGEN LOADING METHODS ON CRYO-MECHANICAL PROPERTIES OF MATERIALS

Knowledge Maturity Summary:

- Research of hydrogen diffusion and embrittlement at non-cryogenic temperatures is mature [39, 260].
- ISO Standards are available for evaluating hydrogen embrittlement of metals, and mechanical properties of metals a non-cryogenic temperatures detailing loading methods.
- Two main methods used for hydrogen loading a sample are high pressure/high temperature and electrolytic loading [10, 13, 47, 56, 261].
- Hydrogen mobility at cryogenic temperatures is significantly reduced resulting in very significantly longer periods to reach equilibrium, meaning that short term exposure is unlikely to represent long term hydrogen distribution.
- Short term embrittlement studies have typically been conducted with samples pre-loaded with hydrogen and then cooled.

Key Research Gaps:

- Systematic studies on the impact of loading temperature on mechanisms of hydrogen embrittlement over the long term are lacking – with short term studies not accounting for long term slow hydrogen migration through stress gradients.
- There is a lack of research into long term hydrogen equilibriums in CryoH_2 exposed materials, including impacts of thermal cycling.
- Investigation of hydrogen loading composite materials are limited to transport properties (permeation) of hydrogen.
- Testing involving long term exposure of hydrogen on materials at cryogenic temperatures is generally lacking.

Key Research Groups

TABLE 6-2: KEY RESEARCH GROUPS ACTIVE ON THE EFFECT OF HYDREOGEN LOADING ON CRYOMECHANICAL PROPERTIES OF MATERIALS

Institution	Country	Topic
Pusan National University	Korea	Electrolytic loading of metals and cryogenic testing.
Korea Research Institute of Standard and Science (KRISS)	Korea	High temperature/high pressure hydrogen loading material and mechanical testing at cryogenic temperatures.
Beijing Institute of Technology,	China	Hydrogen charging methods on hydrogen distribution in high entropy alloys.
Sandia National Laboratories	United States	Hydrogen embrittlement, hydrogen loaded samples on mechanical performance.

Narrative

The use of metals for hydrogen applications has long been established, along with methods for evaluating hydrogen embrittlement in metals at non cryogenic temperatures. ISO 16573-2:2022 specifies the methodologies for assessing hydrogen embrittlement in steel. Two primary hydrogen loading methods are outlined: electrochemical loading (electrolytic loading) and high-temperature/high-pressure loading. To determine the hydrogen content in the material, thermal desorption analysis is used. Both electrochemical loading (electrolytic loading) and high-temperature/high-pressure loading involve accelerated hydrogen loading into materials to evaluate hydrogen embrittlement, making them the most utilised approaches. Both methods are presented in ISO standards as being equally valid methods of evaluating hydrogen embrittlement. Neither method is readily adaptable to cryogenic H2 soaking and there has been very little systematic research into their applicability to LH2 and CryoH_2 applications.

Recent studies conducted by researchers at Pusan National University (Korea) and the Korea Research Institute of Standard Science represent the latest advancements in mechanically testing hydrogen-loaded steel samples. Pusan National University employed electrolytic loading, while the Korea Research Institute used high-pressure/high-temperature loading. These studies primarily focus on hydrogen embrittlement and resultant mechanical properties at cryogenic temperatures. Findings indicate that hydrogen embrittlement is mitigated at cryogenic temperatures due to reduced hydrogen diffusion [262, 263].

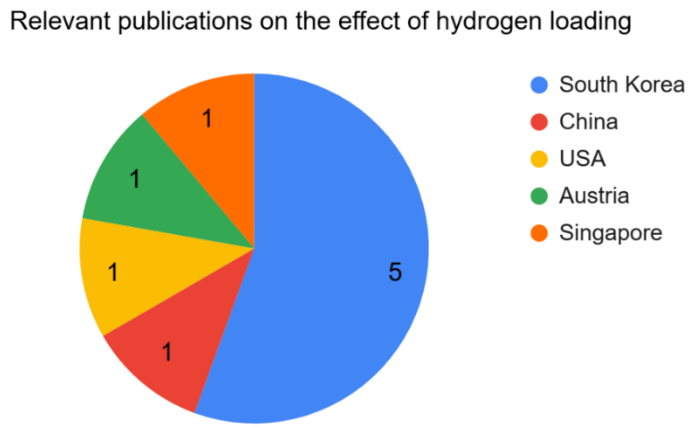

FIGURE 6-4: TOTAL NUMBER OF REVIEWED RECENT PAPERS AND LANDSCAPE ON THE EFFECT OF HYDROGEN LOADING ON THE PROPERTIES OF MATERIALS HIGHLIGHTING THE EXTENT OF RESEARCH ON THE TOPIC IN ASIA COMPARED TO THE REST OF THE WORLD

This body of research provides an initial understanding of hydrogen-loaded samples at cryogenic temperatures. However, the testing at cryogenic temperatures was short in duration and therefore further investigation is required to comprehend how cryogenic hydrogen migrates over the long term and localises in materials exposed to LH2, or thermally cycled in CryoH_2.

ISO 16573-2:2022 recommends storing samples in LN2 to prevent hydrogen desorption, although controversially, cycling some metals down to LN2 temperatures is well known to change the microstructure (see the sections on Transport Properties Research and on Research into Materials Properties Enhancement using Cryogenic Processing).

A systematic study is necessary to identify the most representative methods for hydrogen loading and mechanical testing at cryogenic temperatures. To validate accelerated loading methodologies long-term exposure studies under real-world conditions are likely to be required.

Such studies would likely begin by investigating the diffusion of hydrogen into materials at cryogenic temperatures. Subsequent or parallel steps likely need to expose the material over a very long period in a variety of unstressed and stressed configurations, including the effect of thermal cycling and at a range of intermediate temperatures. Different methods may be required for metals, composites, and polymers due to differing failure mechanisms.

6.3. Tribology – Research into wear properties of materials surfaces in cryogenic and hydrogen environments

Generally, within the field of cryogenics, due to the inability to use lubricating oils and greases, sliding surfaces are avoided where possible. There may still be a need for some sliding cryogenic surfaces in future cryogenic hydrogen storage and fuel system, for example, shut off valve(s) close to the outlet of the liquid hydrogen tank, or bearings in hydrogen fuel pumps (if required). This section considers the current research landscape, as demonstrated in Figure 6-5, and briefly considers the historic body of knowledge relating to sliding surfaces in cryogenic hydrogen environments. Challenges for cryogenic sliding surfaces include lubrication, along with changes in friction and wear properties with low temperatures. For liquid or cryogenic gaseous hydrogen applications, this is further complicated by potential for washing away of any lubricious films created by wear debris between sliding surfaces.

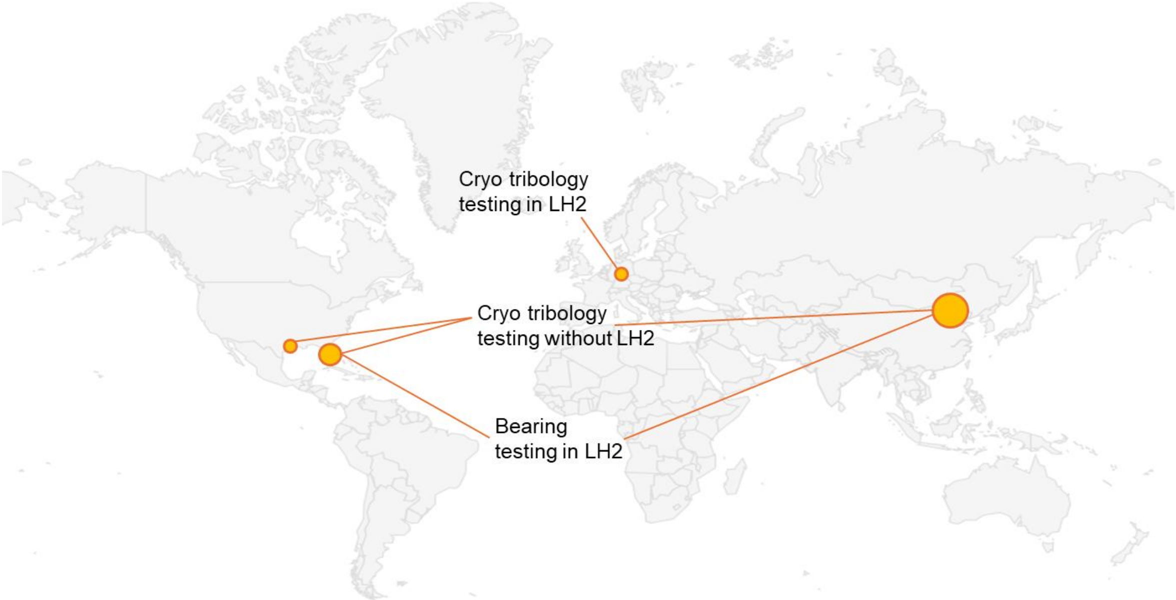

FIGURE 6-5: GLOBAL LANDSCAPE OF RESEARCH INTO RESEARCH ABOUT CRYO TRIBOLOGY

Knowledge Maturity Summary:

- There is a substantial body of research, both historical and recent, into tribological performance of materials at cryogenic temperatures, predominantly >77K and typically not involving H2.
- Numerous facilities globally have capability to measure tribology parameters at cryogenic temperatures, typically LN2 cooled.
- Knowledge and capability cover metals, polymers and some composites. Recent publication activity appears to be concentrated in China.
- Cryogenic tribometers are commercially available for operation down to 153K [264], with custom research systems also operating with samples in LN2 [265, 266]. The availability of cryogenic tribometers with LH2 capability is extremely rare, potentially limited to BAM [266] in Germany.
- There is extensive research on rocket turbopump bearings and sliding seals utilising LH2. The operating conditions and service life are however significantly outside of aircraft relevant parameters.

Key Research Gaps:

- Systematic research on the long-term impact of a combination of hydrogen and cryogenic temperatures on the friction and wear performance of materials is minimal.
- Standardisation of laboratory test methods for measurement of tribology properties of sliding material interfaces, particularly in CryoH_2 wetted applications, is lacking.
- Despite a wide body of literature on cryogenic tribology, there is limited capability and data relating to aviation relevant liquid hydrogen test environments.

Key Research Groups

TABLE 6-3: KEY RESEARCH GROUPS AND ASSOCIATED, TOPICS IN TRIBOLOGY AND WEAR PROPERTIES RELATED TO CRYOGENIC AND LH2 CONDITIONS

Institution	Country	Topic
Federal Institute for Materials Research and Testing (BAM), Berlin	Germany	Cryogenic tribology of materials in liquid hydrogen environments. Multiple test systems reported with LH2.
State Key Laboratory of Tribology, Tsinghua University, Beijing	China	Cryogenic performance of bearings at cryogenic temperatures (93-293K) and heavy loads. Without LH2.
Key Laboratory of Science and Technology on Wear and Protection of Materials, Lanzhou	China	Cryogenic tribology focusing on fundamental processes. Likely without LH2.
University of Florida	United States	Cryo-tribology to 103 Kelvin using liquid nitrogen (with Sandia National Laboratories). Without LH2.
Key Laboratory of Modern Design and Rotor-Bearing System, Xi'an Jiaotong University.	China	Cryogenic tribology of bearing surfaces including novel superconducting bearings. Possibly without LH2.
Centre of Advanced Lubrication and Seal Materials, Northwestern Polytechnical University	China	Cryogenic tribology with focus on metals and microstructure down to 153K. Without LH2.
Thayer School of Engineering, Dartmouth College, Hanover	US	Access to cryo tribometer and research into cryogenic wear of stainless steel, LN2 system down to 115K. Without LH2.
Hefei University of Technology	China	Development of a novel reciprocating cryogenic tribometer with Liquid Nitrogen Immersion. Without LH2.
Texas A&M University, Texas	United States	Cryo tribology of coatings down to c200K. Development of 3d printed ceramic vacuum cryo-tribometer to 77K. Without LH2.

Narrative

The first reported cryogenic tribotester was developed at the NASA Lewis Research Centre in the 1950's [267] and extensive activity continued later during the development of sliding labyrinth seals and silicon nitride bearings during development of the Space Shuttle. The majority of research utilising LH2 (or LN2 for convenience and experimental safety) has focused on high speed bearings and labyrinth shaft seals for rocket turbopumps, a summary of historical progress can be found in chapter 4 of the 2013 book Tribology: Fundamental and Advancements [268]. Capabilities for testing turbopump bearings and seals with LH2 are established in at least the US, China, Europe [268], Japan and Russia. A summary of more recent studies can be found in the references of [269].

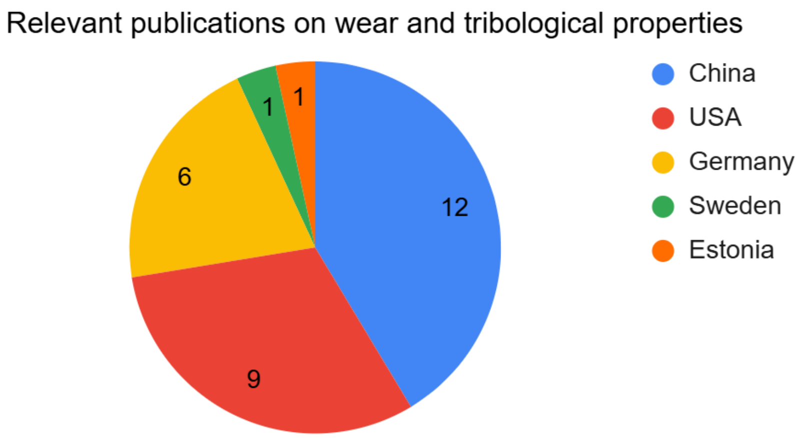

FIGURE 6-6: TOTAL NUMBER OF REVIEWED RECENT PAPERS AND LANDSCAPE ON TRIBOLOGY AND WEAR PROPERTIES OF MATERIALS UNDER CRYOGENIC AND LH2 CONDITIONS

Due to the extreme conditions, bearing testing may be conducted in-situ using prototype turbo pumps (outside of academic research organisations), although some work has been done using custom laboratory bearing testers in liquid nitrogen [270] or in liquid hydrogen [271]. Rocket turbo pumps are designed with extremely high rotation speeds (c100,000rpm), extremely high hydrogen (and/or oxygen) throughput, leaky wetted seals and short component lifetimes, so the results may be of limited relevance to the likely components in an aviation cryogenic hydrogen storage and fuel system. For example, re-usable space shuttle turbo pumps were considered to have a long service life, being rated for 7.5 hours and a more typical single use launcher may have a rated life of just 0.5 hours.

There has been significant academic research into the impact of cryogenic temperatures on the friction and wear properties of materials, however this is typically in vacuum environments. A historical summary including lead institutions and research topics can be found in Figure 1 of [272]. There are potentially three significant variables that call into question the usability for LH2 aviation fuel systems of cryogenic test data not involving hydrogen. Firstly, the impact of adsorbed hydrogen on the material properties, such as embrittlement, mean that the material surface itself may be modified by the hydrogen environment. Secondly, the passing of gaseous or liquid hydrogen over or around the wear surfaces may modify the processes leading to formation of solid lubricious films between surfaces. Thirdly, friction and wear properties are significantly dependent on both the contact pressure and the sliding speed, meaning that generalised testing is unlikely to extrapolate to specific LH2 aviation fuel system applications.

Test systems are available operating with liquid nitrogen, including commercial systems. A novel reciprocating liquid nitrogen immersion tribometer was recently developed in China [273]. A 3D printed ceramic cryo-tribometer focusing on rapid cool down to accelerate sample throughput was recently developed at Texas A&M university USA [274] – the sample was at liquid nitrogen temperatures and not wetted.

The most relevant recent work [266, 275] appears to be from BAM in Germany, who tested the tribology of pure and graphite filled polymers in liquid hydrogen. This work concluded that the presence of liquid hydrogen impacted the cryogenic tribology of the tested polymers. Historically, the team at BAM have developed three liquid or gaseous hydrogen capable cryo-tribometers and have studied a wide range of materials, including diamond like carbon coatings, steels, solid lubricants and polymers. This research indicates that results taken in vacuum cannot be assumed to read across to liquid hydrogen environments.

For metals, whilst there has been historic research into the friction and wear properties at cryogenic temperatures, along with limited recent activity [276-278] no recent activity has been found on the impact of hydrogen on those properties. A recent US-China collaboration [265] developed a new cryogenic tribotester (77 Kelvin) and studied its application to the wear of AISI316 stainless steel – a common candidate material for liquid hydrogen applications. Whilst this research did not include hydrogen, it did include testing with liquid nitrogen wetted surfaces, which may give some insights into the impact on flushing of lubricious wear films by liquid cryogens.

For composites and polymers, there is activity both historic and recent on the impact of cryogenic temperatures on friction and wear properties [185, 279-293], however, there is extremely limited current activity looking at the impact of a combination of hydrogen and cryogenic temperatures on these properties. A summary of historic work can be found in the 2013 book Polymers at Cryogenic Temperatures[294].

For ceramics, in addition to work on turbo pumps for space applications, the tribology performance of ceramic bearings at cryogenic temperatures for other applications is an area of some limited ongoing research. Specifically, collaboration[295] between Shenyang Jianzhu University (China) and the State Key Laboratory of Tribology at Tsinghua University, Beijing (China) recently focused on the cryogenic performance of Si_3N_4 fully ceramic bearings. The work did not include hydrogen.

6.4. Thermal Properties Research

The thermal properties of materials used in aerospace are critical to calibrating computational models of components and systems to account for thermal expansion related stresses, conductive heat loads through structures and thermal lag during temperature excursions. This section highlights recent experimental studies on the thermal properties of such materials at cryogenic temperatures. Additionally, it provides an overview of the established research landscape for materials, such as metals, that have been extensively studied under cryogenic conditions. The thermal properties discussed include specific heat capacity (CP), the coefficient of thermal expansion (CTE), thermal conductivity (TC), and, where applicable, thermal diffusivity.

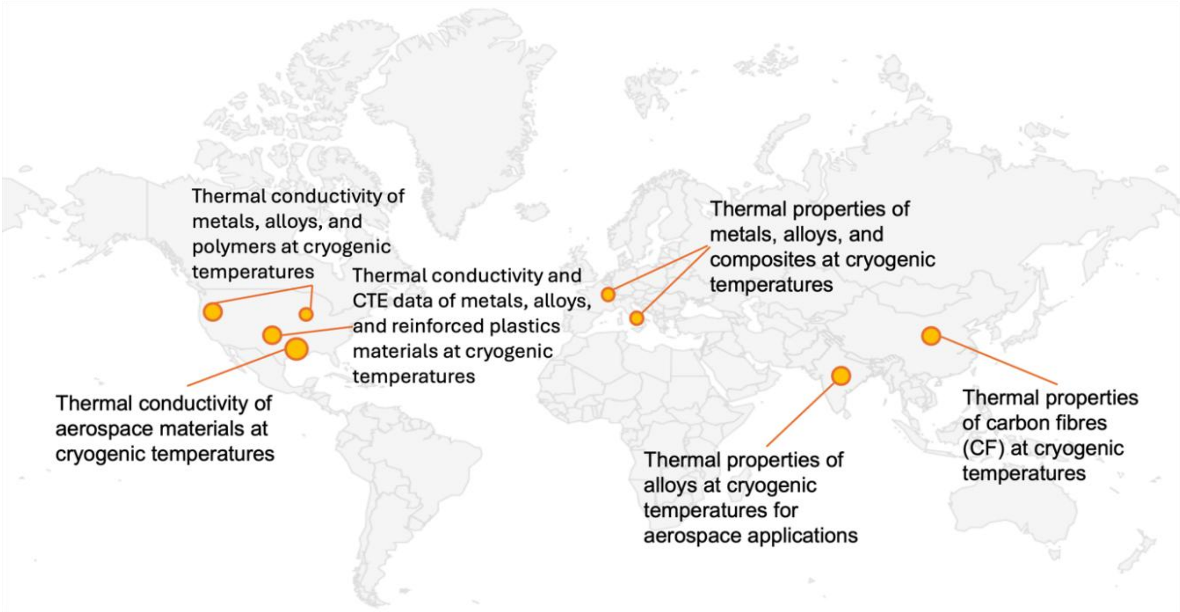

FIGURE 6-7: GLOBAL LANDSCAPE OF RESEARCH INTO THERMAL PROPERTIES AT CRYOGENIC AND LH2 CONDITIONS

Knowledge Maturity Summary:

- There is extensive published material on thermal properties of common materials of interest for cryogenic systems, particularly metals.
- Whilst not universally used, the Quantum Design (QD) Physical Property Measurement Systems (PPMS) has become the de facto standard tool for measurement of thermal properties at temperatures down to <4K. It is mature technology with off the shelf probes and application notes defining methods.
- In Europe and the USA, Karlsruhe Institute of Technology (KIT), CERN, and the Electro-mechanical Testing Group at the National High Magnetic Field Laboratory (NHMFL) [296-298] are amongst institutes performing thermal properties testing (1.4K-room temperature).
- NASA has documented cryogenic thermal conductivity of metals, alloys, polymers, and composites (<4K–room temperature) [263, 299] [300] [300].

Key Research Gaps:

- Due to the wide availability of QD PPMS machines, major gaps in cryogenic thermal properties measurement capability were not found.
- For metals, the literature is often unclear on exact experimental set up, method and specific material manufacturer and processing. Limited repeat test work is therefore likely to be required on common materials to produce fully traceable results.
- For more exotic metal alloys, primary testing may be required.
- For composites, the manufacturing process is likely to have a more substantial impact as properties will vary depending on exact weave, ratio of resin / polymer to reinforcement and orientation. Primary measurements are likely to be required to accurately calibrate modelling.
- The impact on cryogenic thermal properties from absorbed hydrogen is a gap likely requiring further investigation and possibly testing.

Key Research Groups

TABLE 6-4: KEY RESEARCH GROUPS ACTIVE ON THERMAL PROPERTIES OF MATERIALS AT CRYOGENIC AND LH2 CONDITIONS

Institution	Country	Topic
NASA Kennedy Space Centre Merritt Island, Florida	USA	Extensive testing of thermo-physical properties of various materials usually via calorimetry tests, but there are options for LN2 dipping and cryocoolers.
National High Magnetic Field Laboratory (NHMFL), Tallahassee, Gainesville and Los Alamos	USA	NHMFL perform critical current test measurements on superconducting materials and is equipped with a QD PPMS (4.2K-room temperature; 0-9T magnetic field) measuring specific heat capacity, thermal conductivity, Seebeck coefficient, electrical resistivity, and coefficient of thermal expansion.
Key Laboratory of Lightweight Multi-functional Composite Materials and Structures, Beijing Institute of Technology	China	The laboratory focuses on developing advanced lightweight composites, optimising structures for performance and durability, creating materials for extreme environments and energy applications, and designing multi-functional and smart materials.
Karlsruhe Institute of Technology (KIT)	Germany	KIT has three research groups, one of which (CryoMaK) is a large cryogenic material testing laboratory for mechanical and thermal property measurements.
CERN, Esplanade des Particules 1, P.O. Box 1211, Geneva 23	Switzerland	CERN is one of the world's largest systems that extensively uses cryogenics, and includes cryogenic physical properties testing capabilities.
Indian Space Research Organisation. Department of Space Applications Centre (SAC)	India	Thermo-mechanical characterisation of metals, alloys, and composite materials.

Narrative

Thermal properties of materials change significantly as temperatures approach absolute zero. For example, even at 20K, the specific heat capacity (CP) of many metals is two orders of magnitude lower than at room temperature, whilst coefficient of thermal expansion (CTE) typically bottoms out at near zero by around 20K. Thermal conductivity (TC) behaviour is sometimes more complex, for example in copper and some aluminium alloys, initially increasing with reducing temperatures and then dropping, whilst in others the TC does not peak up and instead drops steadily from around 70 Kelvin. These effects create unique challenges for modelling of aircraft components subjected to cryogenic temperature cycling, as the thermal properties change significantly and non-linearly with temperature, impacting how heat is retained and flows through the materials during cycling (including thermal lag) and how the material expands and contracts, impacting internal stress strain maps. A thorough understanding of thermal properties across the full range that a cryogenic structure is exposed to is therefore required to develop complete component and systems models.

Literature containing cryogenic measurements of CTE, TC, CP and/or thermal diffusivity date back to before the 1950's [301-303]. Thermal properties at cryogenic temperatures have been documented not only for metals, but also for reinforced composites, polymers (i.e., PEEK) and various resins, of potential relevance to aviation applications [94, 304-308] from various countries and research groups. Figure 6-8 shows the number recent and historic paper reviewed on the topic according to their country of origin. Books and guidelines are available containing collated literature values [309, 310]. More recent publications for example from CERN include thermal insulators and composite materials [311] tailored for cryogenic systems. There are however inconsistencies in literature values and precise techniques and grades of materials (including manufacturer and processed state) are often not specified. It is therefore likely that for aerospace modelling leading to certification, repeat measurements using the exact grade and processed state of material may be required. Literature values, particularly for common metals, are however likely to be adequate for initial model development activities.

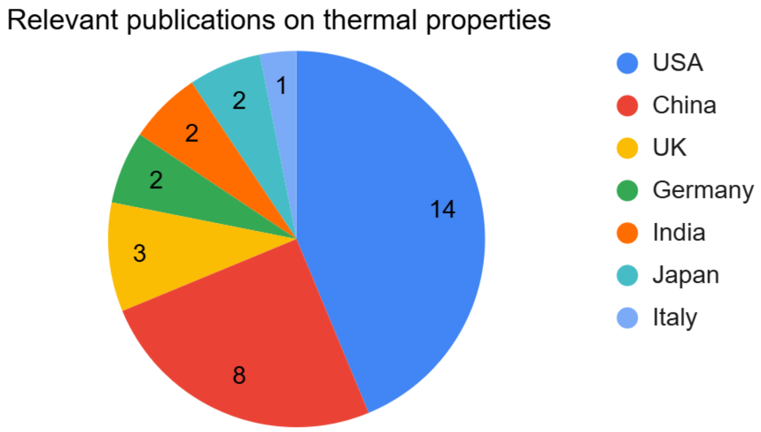

FIGURE 6-8: TOTAL NUMBER OF REVIEWED PAPERS AND LANDSCAPE ON THERMAL PROPERTIES OF MATERIALS AT CRYOGENIC AND LH2 CONDITIONS

Some recent material specific studies include: polyimide (PI) and SiO_2 nanocomposites tested for cryogenic CTE at 300K and 92K using LN2 [312]; CTE, CP, TC and thermal diffusivity of Invar, Kovar, and Silvar alloys measured at -150C for space applications [313]; micro-fibreglass wool material tested via LN2 boil-off calorimetry [314]; Thermal diffusivity, specific heat capacity, and thermal conductivity of carbon fibres measured using electrothermal techniques down to 10K, highlighting expansion mismatch effects [315];and, thermal conductivity of composite CFRP laminates along with separate values for the epoxy and carbon fibres [316].

For composites both the measurement of thermal properties and the use of the measurement in modelling are significantly more complex, due to the anisotropy of the materials and the significant impact of manufacturing process, including localised variations in structure. Whilst the literature does cover a range of composite materials, the sheer number of permutations and combinations of binder and reinforcement materials, weaves and layer structures, means that the requirement to make primary measurements on material systems of interest is almost inevitable.

For aerospace cryogenic hydrogen storage and fuel system, the metal components in particular will be soaked in hydrogen. The impact of absorbed hydrogen on cryogenic thermal properties appears to be a significant gap, with some literature focusing on metal hydrides, but not on absorbed hydrogen in structural materials. The collapse of thermal properties at low temperatures means that hydrogen loading impacts could be more significant and this may therefore require further investigation.

Whilst some results have been measured using custom cryogenic systems, the Quantum Design (QD) Physical Property Measurement System (PPMS) is now a well-established and reliable tool [317-320] for measuring TC, CP, CTE and other thermo-physical properties. The PPMS is widely used by researchers globally across a temperature range of 1.8K to 300+K [321-325]. Older models use liquid helium and the more recent installed base are “cryofree” utilising mechanical cryocoolers and a closed helium loop – the sample is in a separate sample tube. Currently, outside of the UK, Karlsruhe Institute of Technology (KIT), CERN, and the Electro-mechanical Testing Group at the National High Magnetic Field Laboratory (NHMFL) [296-298] perform thermophysical tests (1.4K-room temperature).

Use of PPMS systems (including application notes) means that there is a relatively low technical barrier to obtaining additional datasets, and a significant potential for standardisation of these measurements using the existing installed base. Pre-loading samples with hydrogen at room temperature could provide a route to rapidly exploring impact of hydrogen on the cryogenic thermal properties.

6.5. Hydrogen transport properties research

Hydrogen can permeate through most materials and can concentrate within materials, such as at grain boundaries and localised deposits in metals, potentially causing embrittlement and degradation of the structural integrity. This section focuses on measurement of transport properties, which provides information on how hydrogen migrates within materials, as well as its absorption and desorption. Transport properties change at cryogenic temperatures, both due to reduced thermal energy resulting in reduced mobility and also due to changes to materials from cryogenic temperature cycling, both due to thermal contraction related strain fields and from permanent structural changes. For future liquid hydrogen fuelled aircraft, a knowledge of H2 transport properties at cryogenic temperatures will inform materials selection along with design requirements such as wall thickness and use of permeability barriers such as coatings.

FIGURE 6-9: GLOBAL LANDSCAPE OF RESEARCH INTO RESEARCH RELATED TO THE HYDROGEN PERMEABILITY AND TRANSPORT PROPERTIES AT CRYOGENIC AND LH2 CONDITIONS

Knowledge Maturity Summary:

- There are established methods for hydrogen permeation testing at room temperature.
- Cryogenic permeability testing has been performed utilising modifications to ASTM D1434 -82/ISO 15105 [326] for thin samples. Test gases used include helium and hydrogen, helium is used due to ease of detection and safety, although its transport properties differ from hydrogen.
- Mature methods with potential applicability to bulk transport properties such as diffusivity and trapping include TDA, XPS-SIMS and neutron radiography, although use to date for $CryH_2$ applications appears very limited.
- Permanent changes to some metals due to cryogenic thermal cycling have been shown to introduce new hydrogen trapping sites when exposed to hydrogen at room temperature.

Key Research Gaps:

- There is no standardised testing method for cryogenic permeation testing.
- The impact on H2 cryogenic transport properties (mobility and localisation) from thermal contraction / expansion induced strain fields does not appear to be significantly researched.
- Testing of transport properties for specific aerospace candidate materials during repeat thermal cycling is not well researched. The dynamics of absorption, desorption, mobility and localisation during repeated thermal cycling, including hold times at flight vs ground based cycle elements, may require additional testing and modelling.
- There is a strong overlap between this and mechanical testing (which shows the structural impact of hydrogen localisation) – testing may therefore be required to understand mechanical property changes revealed through mechanical testing of H2 cryogenically cycled materials.

Key Research Groups

TABLE 6-5: KEY RESEARCH GROUPS ACTIVE IN RESEARCH RELATED TO THE HYDROGEN PERMEABILITY AND TRANSPORT PROPERTIES AT CRYOGENIC AND LH2 CONDITIONS

Institution	Country	Topic
Washington State University (HYPER)	United States	Cryogenic hydrogen permeation metals, Liquid hydrogen testing.
Mississippi State University	United States	Cryogenic hydrogen permeation, composites.
Research Centre for Hydrogen Industrial Use and Storage Kyushu University (HYDROGENIUS)	Japan	Cryogenic Hydrogen permeation, high pressure hydrogen, thermal desorption analysis.
Technische Universität Dresden, Institute of Lightweight Engineering and Polymer Technology	Germany	Hydrogen permeability of thermoplastic composites and liner systems.

Narrative

Hydrogen transport within materials changes with reduction of temperatures due to the combination of temperature dependent hydrogen absorption, desorption and mobility (reducing with lower temperatures, [327, 328], changes to material structure through cryogenic cycling and thermal contraction related internal strains.

Hydrogen transport properties of materials at non-cryogenic temperatures are typically determined using two complementary methods, high pressure hydrogen permeation (HPHP) and thermal desorption analysis (TDA)[329]. There is a large body of research in different countries, as shown in Figure 6-10, focusing on this topic that are reviewed in this section.

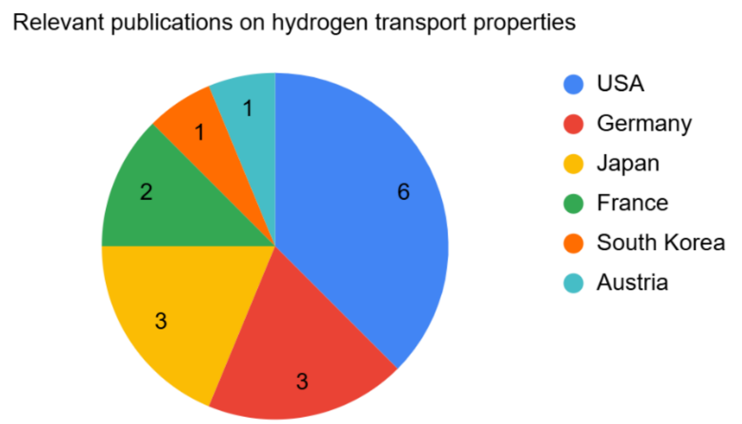

FIGURE 6-10: TOTAL NUMBER OF REVIEWED PAPERS AND THEIR LANDSCAPE RELATED TO THE HYDROGEN TRANSFER PROPERTIES IN MATERIALS

HPHP is commonly used on thin films and composites where the permeability rate is sufficient to be measured directly[330]. HPHP involves a test chamber divided by the sample, with one side exposed to high-pressure hydrogen and the other maintained at low pressure or vacuum. The hydrogen flux through the material is measured using either pressure sensors, mass spectrometry or using gas chromatography. These tests can be carried out according to ASTM D1434/ISO 15105 standards. Helium is commonly used instead of hydrogen as it is safer, although its transport properties differ from hydrogen. These methods can be adapted for direct cryogenic permeation measurements, particularly of composites. Low perfusion rates in metals at cryogenic temperatures make the technique less suited to metals, although use with thin samples is possible. Whilst hydrogen permeability tests are well-established, no standardised methods currently exist for conducting permeation testing on samples at cryogenic temperatures. As a result, researchers often adapt existing high-pressure high-temperature (HPHP) testing methodologies for cryogenic conditions by integrating the testing setup with a cryostat or connecting it to a cryocooler. This approach enables testing at temperatures ranging from 20K to 77K [327, 331, 332].

TDA methods heat a hydrogen loaded sample (more typically a metal) through a temperature ramp, typically from room temperature to 900 Kelvin, although the range varies between equipment. TDA measures the hydrogen desorbed from the surface, using mass spectrometry or gas chromatography to detect the free hydrogen gas molecules [36, 333]. Samples are typically hydrogen loaded by placing the sample in a high-pressure hydrogen environment, possibly at elevated temperature, or by using electrolytic loading [13, 36, 334]. From the desorption measurement vs temperature, the permeability coefficient, diffusion coefficient and absorption can be calculated along with binding energies at trap sites. TDA is commonly used for metals or material samples where HPHP test time would be unfeasible. Whilst TDA is unsuitable for directly measuring the transport properties of hydrogen at cryogenic temperatures, it may be applicable to measuring the amount of hydrogen absorbed during long term storage of samples in LH2 or $CryoH_2$ and any permanent changes to trap sites due to cryogenic cycling.

Other methods of detecting hydrogen in a material include XPS-SIMS, which enables determination of the hydrogen loading within the surface layer of a material[335]. Neutron radiography/ tomography has also been applied to determination of hydrogen concentrations deeper in a material and can provide three dimensional images of hydrogen localisation with resolutions of 20 – 30 microns [336, 337]. As it is non-destructive and presents a relatively low heat load to a sample, it may be applicable to determination of hydrogen transport properties in situ at cryogenic temperatures. Due to slow diffusion at cryogenic temperatures through metals in particular, short term laboratory tests with cryogenic hydrogen exposure are however unlikely to represent the long term distribution of hydrogen in a system exposed either to LH2 or regularly thermally cycled in $CryoH_2$.

For metals The transport of hydrogen at cryogenic temperatures is significantly lower compared to room temperature due to the reduced molecular diffusion rate and decreased kinetics [327]. For systems under long term $CryoH_2$ exposure they are however likely to eventually come to some form of equilibrium distribution. It is however known that for many metals, the structure of the material changes due to cryogenic cycling, even when that is only to LN2 temperatures. The induced permanent changes to material structure have recently been observed to create new hydrogen trapping centres in high Cr ferrous alloys, as detected by TDS [338]. It may be more likely that transport properties studies are therefore more appropriate as part of an investigation of mechanical property changes in CryoH_2 cycled metals, particularly of those that are not typically associated with LH2 systems.

For composites, micro cracking during cryogenic thermal cycling becomes a specific concern for permeability of unlined hydrogen contacting structures. Gas permeation of composites are also highly influenced by their layup, thickness, materials, load case and manufacturing defects. An extensive review of research into the key parameters that influence the cryogenic gas permeability of composites, along with summaries of test methods can be found in [339]. For composites, cryogenic thermal cycling typically induces microcracks in the material, which can significantly increase permeation rates. Analysing these changes helps in estimating the material's potential service life and its suitability for applications in CryoH_2 environments [326, 327, 339, 340].

7. Modelling, Simulation and Service Life Prediction

Methodologies and recent advances in simulations targeting the behaviour of materials at cryogenic temperatures or liquid hydrogen impact on materials that could be used in aviation are described in this section. The developed models' final focus is usually at the component level, often aiming to bridge from limited laboratory testing of materials properties to final component performance. The complex interaction of physical and mechanical properties, which change rapidly and non-linearly with cryogenic temperatures, makes modelling of cryogenic behaviour more challenging. The addition of property modifying hydrogen further complicates modelling.

7.1. Modelling focusing on meso-scale materials behaviour

Meso-scale modelling is defined as the creation of solid mechanical models which mimic the substructure of a material, such as the modelling of systems combining individual grains, fibres or other discontinuities as separate linked material domains. The focus of this section is on modelling that explains the cryogenic behaviour of materials at scales ranging from microns to millimetres. This includes models that provide a fundamental understanding of hydrogen interactions within material structures at cryogenic temperatures. It encompasses multi-physics modelling of hydrogen transport, including its migration influenced by concentration, temperature, strain gradients, solubility, and bonding potential, as well as its effects on localisation within material microstructures under cryogenic conditions.

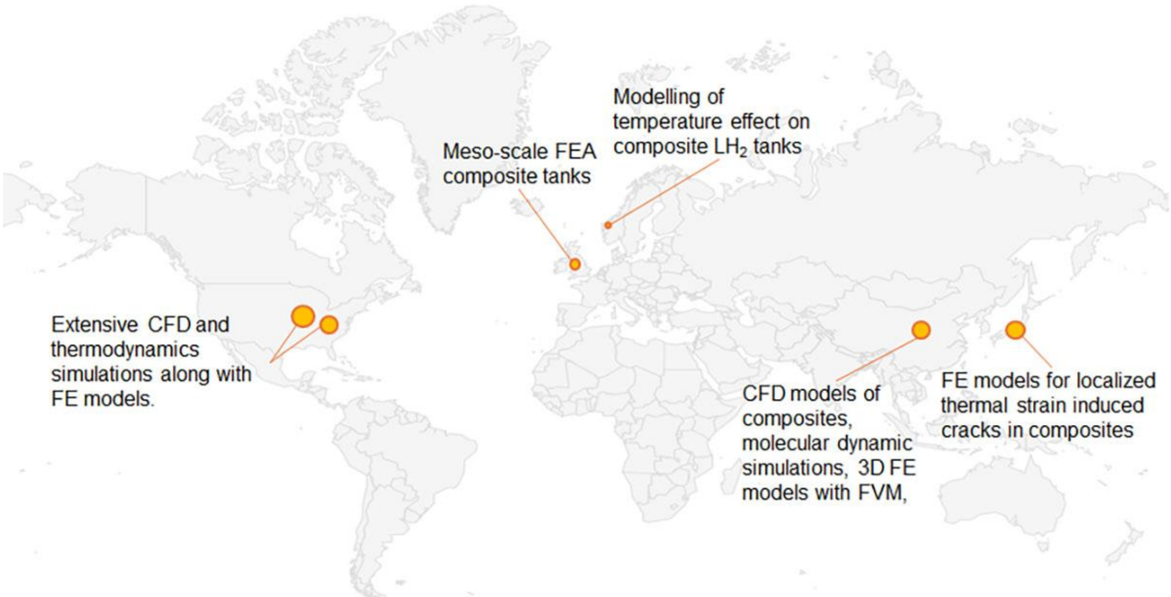

FIGURE 7-1: GLOBAL LANDSCAPE OF RESEARCH INTO MESO SCALE MODELLING OF MATERIALS BEHAVIOUR AT CRYOGENIC AND LH2 CONDITIONS

Knowledge Maturity Summary:

- Modelling of molecular and micro scale interactions between hydrogen and metals at non cryogenic temperatures is maturing and is focused mainly on understanding the mechanisms of hydrogen embrittlement.

- There has been limited development of FE models relevant to composite LH2 fuel tanks for aviation applications investigating thermal stress induced microcracking [341] [342] at meso scales.
- Molecular dynamics (MD) simulations have been used to analyse the effectiveness of fillers in epoxy nanocomposites at temperatures down to 4K [343].

Key Research Gaps:

- Modelling relating to the effects of cryogenic temperatures on composite structures at the micro to meso scale is maturing but no consistent approach has emerged.
- Modelling relating to the combined effects of cryogenic temperatures and hydrogen on composites is very immature.
- Modelling relating to the combined effects of cryogenic temperatures and hydrogen on metals is very immature.
- Availability of experimental data to validate models across cryogenic temperature ranges is lacking.

Key Research Groups

TABLE 7-1: KEY RESEARCH GROUPS ACTIVE ON MESO SCALE MODELLING OF THE EFFECT OF HYDROGEN ON PROPERTIES OF MATERIALS

Institution	Country	Topic
Tokyo University	Japan	Use of finite element modelling to understand localised thermal strain induced micro cracking behaviour in composites at 30K.
NASA, Glenn Research Centre Cleveland, Ohio, United States.	United States	Extensive fluid mechanics and thermodynamics simulation along with FE models.
Key Lab of Aerospace Advanced Materials and Performance, Beihang University	China	Modelling of temperature dependent properties of epoxy based nanocomposites down to 4K using molecular dynamics simulation.
Cranfield University	UK	FEA modelling of composite LH2 tanks.
TU Delft	Netherland	Limited simulation work on impact of cryogenic temperatures on composite LH2 tanks.
Various – see review papers.	Globally	Modelling of hydrogen embrittlement mechanisms in metals, excluding cryogenic temperatures.

Narrative

There is a growing body of published literature on mesoscale modelling extending to macroscale modelling on the interaction between hydrogen and materials, but with significant gaps around performance at cryogenic temperatures. Extending models to LH2 relevant cryogenic temperatures, particularly for models where temperature is a dynamic variable, will further complicate efforts due to the non-linear impact of temperature on a wide range of physical and mechanical parameters.

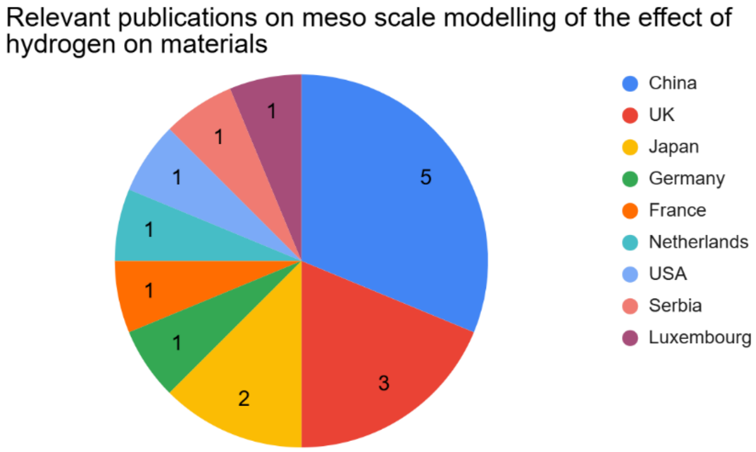

FIGURE 7-2: TOTAL NUMBER OF REVIEWED PAPERS AND THEIR LANDSCAPE ON MESO SCALE MODELLING OF THE EFFECT OF HYDROGEN ON MATERIALS

Modelling methods for metals and for composites appear to be substantially different, due to the significantly different structures and different key concerns, focusing on hydrogen embrittlement in metals and focusing on pressure and thermally induced micro cracking in composites.

Metals

For metals, publications relating to meso scale modelling of hydrogen interactions have to date not significantly focused on cryogenic temperatures. This is likely due to the relative immaturity of the modelling, the focus on understanding the fundamental mechanisms of hydrogen induced embrittlement, and that CryoH2 has until recently been a very limited niche where, due to the widescale use of 316L stainless steel, embrittlement has not been a significant concern. For example, of over 100 experimental and analytical journal papers published since 2020 that cited a 2016 review [344] of “Hydrogen Embrittlement of Industrial Components: Prediction, Prevention, and Models”, none of the titles were found to relate to cryogenic modelling. Only three were focused on modelling and / or experimental understanding of temperature effects [345-347]. It was interesting to note that the number of papers citing this review increased steadily from 20 in 2021 to 33 in 2024, indicating an increasing interest and maturity in modelling of hydrogen interactions, particularly relating to embrittlement. It is possible that elements of some of these modelling techniques could in the future be applied to modelling the combined effects of cryogenic temperatures and hydrogen interactions.

A small selection of examples of modelling work at non cryogenic temperatures includes University of Oxford (UK) who published[348] progress towards a physics based model of hydrogen in metals focusing on Discrete Dislocation Plasticity (DPP) and Crystal Plasticity (CP). Swansea University (UK) working with Fraunhofer (Germany) have historically developed a meso-scale microstructural finite element model to simulate hydrogen diffusivity along grain boundaries in polycrystalline materials, showing a significantly higher grain boundary diffusion rate compared to lattice diffusion in nickel [349]. BAM Federal Institute for materials research and testing (Germany) developed a mesoscale numerical model to simulate hydrogen-assisted cracking in duplex stainless steel using ANSYS [350]. Their model qualitatively captured crack initiation and propagation, identifying critical areas in ferrite under high hydrogen concentrations.

Composites

For composites, the concerns focused on by modelling appear to be more about structural integrity reduction resulting from cryogenic and pressure cycling, rather than the interaction with hydrogen itself. A recent review paper discusses advancements in the modelling relating to composite pressure vessels and includes somewhat limited references to cryogenic modelling [351]. Whilst numerous teams have focused on high pressure storage vessels, for example [349, 350, 352-354] ,work on modelling cryogenic behaviour is less mature.

A recent Masters thesis from TU Delft describes a study considering the impact of LH2 on the material behaviour, however it makes assumptions for input material parameters (due to lack of data), such as CTE, permeability, etc. [355]. A very recent paper from Tokyo University (Japan) focuses mainly on experimental work on microscopic damage at cryogenic temperatures and also includes limited FE modelling to estimate thermal stresses using experimental data for CTE at 30K and 290K [339]. Cranfield University has developed FEA models of LH2 fuel tanks destined for large aircraft and investigated the stress distribution at critical loading conditions [341]. Beihang University (China) has developed models of temperature dependent properties of epoxy based nanocomposites down to 4K using molecular dynamics (MD) simulations with good correlation to experimental results [356].

7.2. Modelling focusing on multi scale impact of hydrogen and cryogenic temperatures on materials behaviour.

This section focuses on multi-scale, multi-physics modelling, with a main emphasis on techniques for bridging and combining micro- and meso-scale modelling and extending their application to macro scale design challenges. The ability to use models to simulate mechanical performance of complex components will allow interpolation and potentially extrapolation from more limited CryoH2 test data, enabling higher confidence design decisions. Models, if fully validated, may also contribute to certification data. Figures 7-3 and 7-4 show the heatmap of the activities and their associated countries and the total number of recently published papers (post 2018) reviewed.

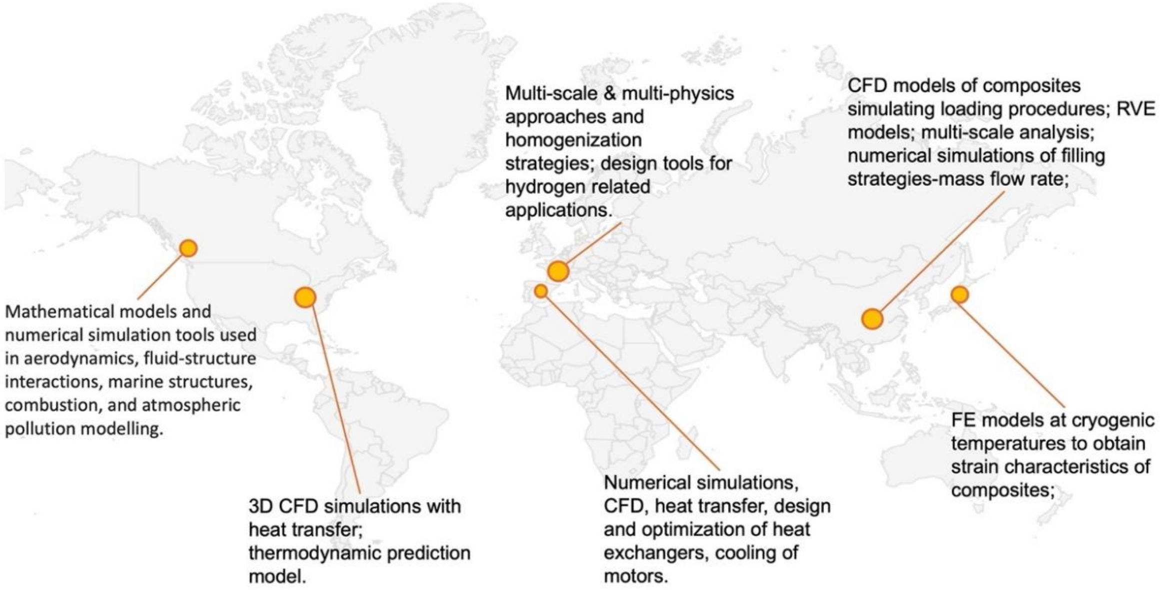

FIGURE 7-3: GLOBAL LANDSCAPE OF RESEARCH INTO MULTISCALE MODELLING OF THE EFFECT OF HYDROGEN AND CRYOGENIC TEMPERATURES ON BEHAVIOUR OF MATERIALS

Knowledge Maturity Summary:

- There is a mature body of knowledge and significant ongoing activity on development of multiscale multiphysics models of hydrogen embrittlement mechanisms and failure modes in metals at non-cryogenic temperatures, although a universal model remains elusive.
- There is a maturing body of knowledge and significant ongoing activity on development of multiscale multiphysics models of cryogenic performance of composite materials, excluding the impact of hydrogen.
- Modelling of composites at cryogenic temperatures has been extended to full tank scale.
- The boundary between meso scale and multiscale modelling is blurred.

Key Research Gaps:

- Whilst there has been significant progress on multiscale modelling of composite structures at cryogenic temperatures, a universally agreed approach has not yet been established. Modelling techniques are at varying stages of validation.
- Multiscale models relating to mixed material boundaries (such as for metal lined composite tanks) appear less mature.
- Multiscale models relating to metals in cryogenic hydrogen environments and which incorporate hydrogen transport changes due to thermal stresses are at a low stage of development.
- Limited data exists on hydrogen transport, embrittlement, and fracture at CryoH2 relevant temperatures – this will be required to calibrate and validate models.

Key Research Groups

TABLE 7-2: KEY RESEARCH ORGANISATION ACTIVE ON MULTISCALE MODELLING OF THE IMPACT OF HYDROGEN AND CRYOGENIC TEMPERATURES ON MATERIALS

Institution	Country	Topic
Max Planck-Institute	Germany	Multiscale modelling of hydrogen transport and segregation in steels, focusing on embrittlement, not at cryogenic temperatures.
Georgia Institute of Technology	USA	Hydrogen transport and trapping in metals linking to mechanical failure, not at cryogenic temperatures.
East China University of Science	China	Hydrogen assisted fracture model for metals, not at cryogenic temperatures.
Pacific Northwest Laboratory	USA	Modelling of composites at cryogenic temperatures for LH2 storage vessels.
Sandia National Laboratories	USA	Modelling of composites at cryogenic temperatures for LH2 storage vessels.
Tohoku University	Japan	Modelling of carbon nanotube reinforced plastics at cryogenic temperatures.
Leibniz Universität Hannover.	Germany	Modelling of composites at cryogenic temperatures for LH2 storage vessels.
NASA, Glenn Research Centre, United States.	USA	Extensive 3D computational FE models using FLUENT to incorporate heat transfer into their models.

Narrative

Research in multiscale modelling spans various disciplines, including solid mechanics, fluid mechanics, materials science, physics, mathematics, and chemistry. Some recent publications focus on modelling and simulating hydrogen transport and its effects in polycrystalline and nanopolycrystalline materials [357-359]. These studies collectively highlight the critical influence of microstructural features, such as grain boundaries, triple junctions (TJs), grain boundary affected zones (GBAZ), and grain size, on hydrogen transport, diffusion, and segregation. Models focusing on metals tend to differ significantly from those focusing on polymers. As Figure 7-4 shows, research groups in China are the most active in this field.

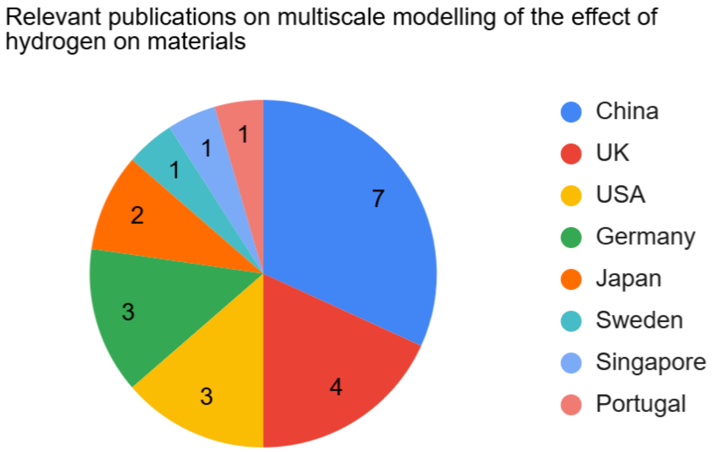

FIGURE 7-4: TOTAL NUMBER OF REVIEWED, RECENTLY PUBLISHED, PAPERS AND THEIR LANDSCAPE ON MULTISCALE MODELLING OF THE IMPACT OF CRYOGENIC AND HYDROGEN ON BEHAVIOUR OF MATERIALS

Metals

As with meso scale modelling of hydrogen interaction with metals, much of the multiscale modelling is focused on hydrogen embrittlement and there is considerable overlap due to the phenomena initiating at the molecular level, but influenced by parameters such as stress derived at both the macroscopic and microscopic levels, and then once initiated, spreading to the macroscopic level. A 2024 comprehensive review of hydrogen embrittlement [360] includes a summary of the current state of knowledge, including mechanistic understanding, experimental evidence and modelling attempting to link the two. Over the last 150 years there have been over 6000 papers on hydrogen embrittlement and a universal theory and model remains elusive. The extensive list of 931 references presents a good starting point for understanding of both the level of challenge and the state of the art across the overall field of hydrogen embrittlement, including multiscale modelling. None of the references included cryo or temperature in their titles and the challenges of extending the knowledge base to liquid hydrogen applications is only mentioned in passing.

Specific examples of recent activities include Max Planck-Institute reporting on multiscale modelling of hydrogen transport and segregation in polycrystalline steels, with a focus on understanding embrittlement [361, 362]. University of Manchester (UK) recently report on simulating hydrogen-controlled crack growth using a coupled chemo-mechanical model [363]. Georgia Institute of Technology (USA) have developed models of dislocation-mediated hydrogen transport and trapping in face-centred cubic metals [364]. School of Mechanical and Power Engineering, East China University of Science are developing a hydrogen assisted fracture model taking account of coexistence of hydrogen enhanced plasticity and decohesion [365]. Chengdu Technology University (China) have developed multiscale modelling of hydrogen induced cracking in reactor vessels [366]. None of these focus on cryogenic temperature interactions.

Composites

For composites, as for meso scale modelling, multiscale modelling focuses more on the impact of stress induced by combined external forces and thermal contraction than it does on the direct impact of hydrogen. Modelling of relevance to LH2 fuelled aircraft structures is more mature than for metals. Again, meso scale and multiscale modelling overlap significantly. Recent examples of multiscale modelling activity include:

Pacific Northwest Laboratory (USA) have developed models combining constitutive modelling and FEA applied to cryo-compressed hydrogen storage vessels [367]. Sandia National Labs (USA) have recently studied models for polymer based composite cryogenic hydrogen storage technologies [368]. College of Aerospace Engineering, Chongqing University (China) have completed experimental and multiscale modelling on the impact of cryo thermal cycling on carbon reinforced epoxy composites [369]. Dalian University of Technology (China) have developed models incorporating fibre / matrix interfaces based on self consistent clustering analysis, including cryogenic performance [370, 371]. Shanghai Jiao Tong University (China) have developed multiscale models to study progressive damage in linerless composite cryotanks [372].

Tohoku University (Japan) have developed multiscale simulations of tensile properties of carbon nanotube reinforced polymer composites at cryogenic temperatures [373]. University do Porto (Portugal) have progressed end to end simulations of composite structures to link manufacturing processes to structural performance of cryogenic tanks [374]. Okyama University (Japan) has explored micro to macro scale modelling of long carbon fibre reinforced plastics at cryogenic temperatures [348, 375]. Zhejiang University (China) have developed multi-scale failure analysis models for cryogenic pressure vessels incorporating both thermal stress and mechanical stress [376]. Leibniz University (Germany) has explored models linking the dynamic forces from LH2 fill volume and temperatures on composite tank structures [377]. Empire State University (USA) has developed thermodynamic and molecular level simulations focused on nanocomposites [343, 378].

7.3. Service life prediction, including cyclical loading impacts

This section focuses on any published research which specifically looks to combine materials cryogenic properties testing (coupon level) results and modelling to predict service life of cryogenic hydrogen materials. The emphasis is on fundamental approaches towards utilising these towards the certification of cryogenic hydrogen aircraft components, including experimental calibration and validation of models extending to simple (2D) geometry systems (e.g. coupons). The distribution of such activities and the global landscape is presented in Figure 7-5 whilst Figure 7-6 shows the breakdown of recently published paper and reviewed on this topic.

FIGURE 7-5: GLOBAL LANDSCAPE OF RESEARCH INTO SERVICE LIFE PREDICTION OF MATERIALS AND COMPONENTS USED FOR CRYOGENIC AND LH2 APPLICATIONS

Knowledge Maturity Summary:

- Washington State University (USA) has developed a cryogenic accelerated fatigue tester allowing for tensile, compressive and fatigue testing at >20Hz, of polymer composites and incorporating an in-situ hydrogen liquefier. Limited other systems exist at <20Hz.
- Some relevant ASTM standards exist for stress and fatigue testing at cryogenic temperatures for metals.
- There has been some work to understand the impact of thermal cycling on composite structures for LH2 storage tanks, this has been both at the system level and coupon level, with work aiming to link these.
- There is a strong body of evidence from NASA in particular on the long term performance of 316L stainless steel in ground based liquid hydrogen storage applications, with some storage tanks in operation since the Apollo missions.

Key Research Gaps:

- The long term impact of the compounding effect of hydrogen exposure, cryogenic thermal cycling and flight relevant fatigue cycling is not well published.
- Whilst some stainless steels have long term history of use evidence for LH2 applications, the body of evidence for lightweight alloys is somewhat weaker.
- There is a lack of standardisation of and limited equipment available to conduct high cycle fatigue testing in CryoH2 conditions.
- Uncertainty quantification across the full cryo-mechanical properties testing and simulation chain is relatively immature.
- There is a lack of consensus on basic measurement instrumentation during cryo-mechanical (fatigue) testing, with clip on extensometers, strain gauges, digital image correlation (DIC) and optical fibres under consideration, due to all methods having compromises. This lack of standardisation may hinder transferability of results.
- A consensus model of flight cycle dynamic thermal and mechanical loadings will be required in order to define standardised testing and modelling / analysis.

Key Research Groups

TABLE 7-3: KEY RESEARCH ORGANISATION ACTIVE ON PREDICTING SERVICE LIFE OF COMPONENTS AND MATERIALS FOR CRYOGENIC AND LH2 APPLICATIONS

Institution	Country	Topic
Washington State University	USA	Cryogenic hydrogen testing of ageing including high frequency fatigue testing using a test system with integrated hydrogen liquefier. Composites focus.
Korea Institute of Machinery and Materials	South Korea	Investigations of ageing including cryogenic fracture toughness testing, focusing on metals down to LN2 temperatures.
National Institute of Technology, Rourkela	India	Mechanical ageing properties (ILSS, bending) of composites soaked in LN2.
Mississippi State University	USA	Ageing microcrack related gas permeability and mitigation strategies for composite fuel tanks, including test capabilities at LN2 temperatures.
Islamic Azad University, Tehran	Iran	Studies of impact properties of composites following cryogenic thermal ageing.

Narrative

Thermal fatigue and cryogenic effects are typically studied by immersing materials in liquid nitrogen [12, 240, 246, 379] or liquid hydrogen [12] for varying durations, either once [240, 246] or repeatedly [380]. This approach allows researchers to simulate extreme low-temperature conditions and assess material behaviour under cryogenic environments. Whilst some ASTM standards exist for stress and fatigue testing at cryogenic temperatures for metals [381-383] , there are currently no comprehensive established standards for fatigue testing at these extreme conditions, such as SN curves, Basquin slopes, or the limit of elasticity. This lack of standardisation presents a challenge for researchers and engineers working in the field of cryogenic materials.

The reproducibility of test instrumentation at cryogenic temperatures is an area that also requires further attention. Optical sensors [384], including fibre optic systems, have been investigated to operate at cryogenic temperatures and offer benefits such as compact sensing, EMI insensitivity, and intrinsic safety. However, the absolute accuracy and reproducibility of these instruments at extremely low temperatures require further investigation.

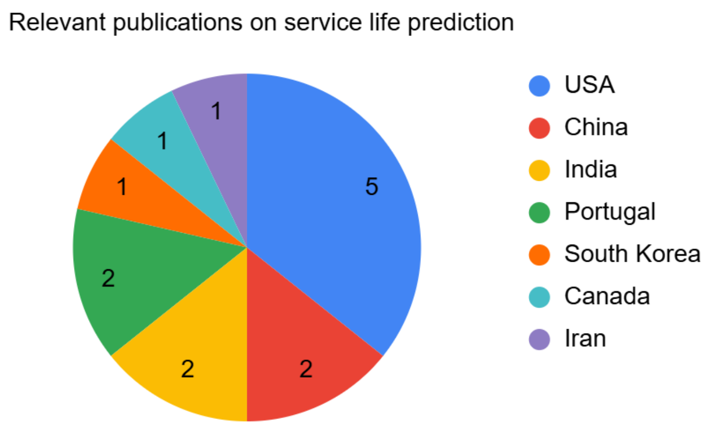

FIGURE 7-6: TOTAL NUMBER OF RECENTLY PUBLISHED AND REVIEWED PAPERS ON SERVICE LIFE PREDICTION OF MATERIALS AND COMPONENTS AT CRYOGENIC AND LH2 CONDITIONS

There is a notable lack of understanding regarding operational conditions at higher TRL, particularly for liquid hydrogen applications, including:

- Thermal considerations for LH2: The behaviour of materials and systems when exposed to LH2 (20K) is not as well understood as those in LN2 (77K) stemming from a general lack of capabilities due to much higher H&S requirements for LH2 testing.
- Service and maintenance requirements: The maintenance policy for cryogenic systems is critical for their reliability. Key factors include preventive maintenance routines, spare parts management, and performance indicators.
- Long-term effects: There is limited data on the long-term behaviour (weeks, months) of materials and components under CryoH2 conditions, which is crucial for predicting the lifespan of systems operating in these environments.

To address these gaps, researchers are developing specialised testing equipment and methodologies. For example, Washington State University (USA) have developed a Cryogenic Accelerated Fatigue Tester [385] allowing for tensile, compressive, and high-frequency (extending beyond 20Hz) fatigue testing of polymer composites. The system incorporates a mechanical cryocooler and includes the ability to liquefy hydrogen to a bath surrounding the sample.

For metals, work has focused more on lower cost stainless steels for shipping and ground applications than on lightweight alloys for aerospace. 316L stainless steel has a very long history of safe use for LH2, for example at NASA, 316L lined LH2 storage tanks have been in continuous use since the Apollo missions. For 304L stainless steel, Korea Institute of Machinery and Materials have confirmed that the effect of hydrogen embrittlement is negligible at LH2 temperatures, with cryogenic temperature effects dominating [12]. This is even when the materials are hydrogen charged for 30 days at elevated temperature and pressure, due to slow permeation through stress fields at temperatures below 123K. This presents a natural mitigation for liquid hydrogen systems, as hydrogen mobility is low when thermal contraction stresses are high, and hydrogen mobility is high when thermal contraction stresses are relieved. From a practical measurement point of view, the Korean team also found that limitations in crack length estimations at cryogenic temperatures led to variability in fracture toughness determination, and propose alternative methods.

For composites several research groups [246, 380]report on ageing and have observed an initial significant increase in strength at cryogenic temperatures (without hydrogen), followed by a sharp decline. Afterward, the strength stabilises. Research at the National Institute of Technology (India) has also focused on reinforcing carbon fibre composites with carbon nanotubes, and reinforcing Glass Fibre composites with short carbon fibres, yielding relative resilience improvements after thermal cycling in LN2 (excluding hydrogen) [240, 246]. A recent study at Mississippi State University (USA) focused on gas permeability (due to microcracking) mitigations for composite fuel tanks subjected to repeated fill / empty cycles, although the application was re-usable space launch vehicles, so cycling was minimal compared to aerospace needs [332]. Recent studies at Washington State University (USA) focused on additive manufacturing of LH2 fuel tanks including coupon studies, burst testing with hydrogen leakage as an end point - poor adhesion between metal and composite resulted in significant permeation after a few cycles [331].

Overall, it is clear that across both metals and composites, a complex mixture of parameters impact ageing of materials in LH2 systems. Ageing models based on ambient temperature effects may not translate to cryogenic temperatures, due to different mechanisms dominating at different temperatures and the non-linear nature of these parameter interplays vs temperature. In the case of systems that regularly cycle between cryogenic and ambient temperature regimes, the challenge of service life prediction is further complicated.

Uncertainty Quantification

Uncertainty quantification bridges testing and modelling, leading to assessment of confidence levels in the output results resulting from uncertainties throughout the analysis chain. Uncertainty analysis specific to measurement and modelling of LH2 materials is not strongly addressed in the literature. For many modelling studies, information including boundary conditions and materials properties are taken from online resources, if available, e.g. [29, 30, 33] wherein limited detailed uncertainty analysis of data is available. As testing and modelling for aerospace design to certification activities increases, it is expected that activities relating to uncertainty quantification will increase.

Examples of recent activities where uncertainty quantification was explored include Okayama University (Japan) [375], where the team analysed the variability in inputs (e.g. material properties), refined models based on observed discrepancies and quantified the impact of uncertainties on tensile strength predictions. They compared analytical predictions to experimental results at different temperatures and modified the compound law to include residual stress and tensile strength variations–previously not considered. Similarly, in a study at Leibniz University (Germany) [377], researchers addressed uncertainty through analysis of variable environmental and operational conditions, sensitivity studies, and design approaches for developing a design tool for cryogenic hydrogen tanks; they found that a universal solution in overall tank design is more challenging compared to kerosene tanks. Experimental parameters and design, including temperature fluctuations resulting from the choice of cooling medium and method, have been shown to significantly influence current uncertainty assessment methods [251].

8. Patent Landscape

Global liquid hydrogen patent activity has been analysed to provide an indicator of regional research and development levels which may, as inventions progress through development and into certification, drive demand for additional materials development and testing. Additional patent searches have been conducted to explore levels of patent publications relating to Physical Properties Cryogenic Measurement equipment and methods of relevance to liquid hydrogen materials.

8.1. Liquid Hydrogen Patent Activity Levels by Country

The heatmap of top 7 countries for liquid hydrogen related patent activities is shown in Figure 8-1. The annual patent family publication trends are plotted in Figure 8-2 where it demonstrate a significant increase since 2020.

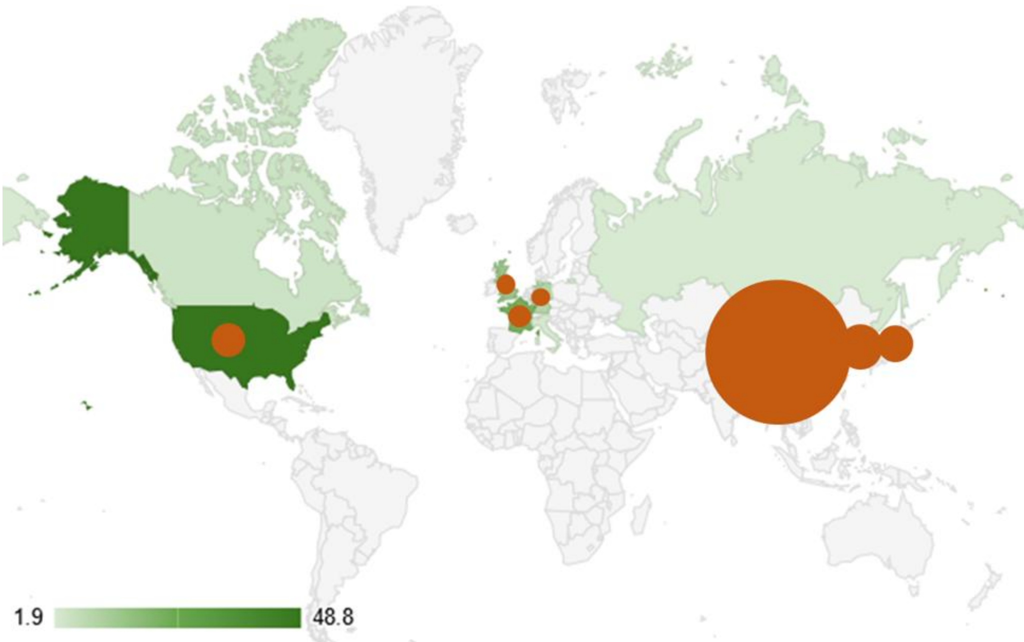

FIGURE 8-1: HEATMAP OF TOP 7 COUNTRIES WITH LIQUID HYDROGEN PATENT APPLICANTS 2018 – 2024 (CIRCLE AREA INDICATES CUMULATIVE PATENT FAMILIES) AND AEROSPACE MANUFACTURING GLOBAL RANKING (TOP 7) BY TRADE BALANCE 2021[5] (SHADING, $BN).

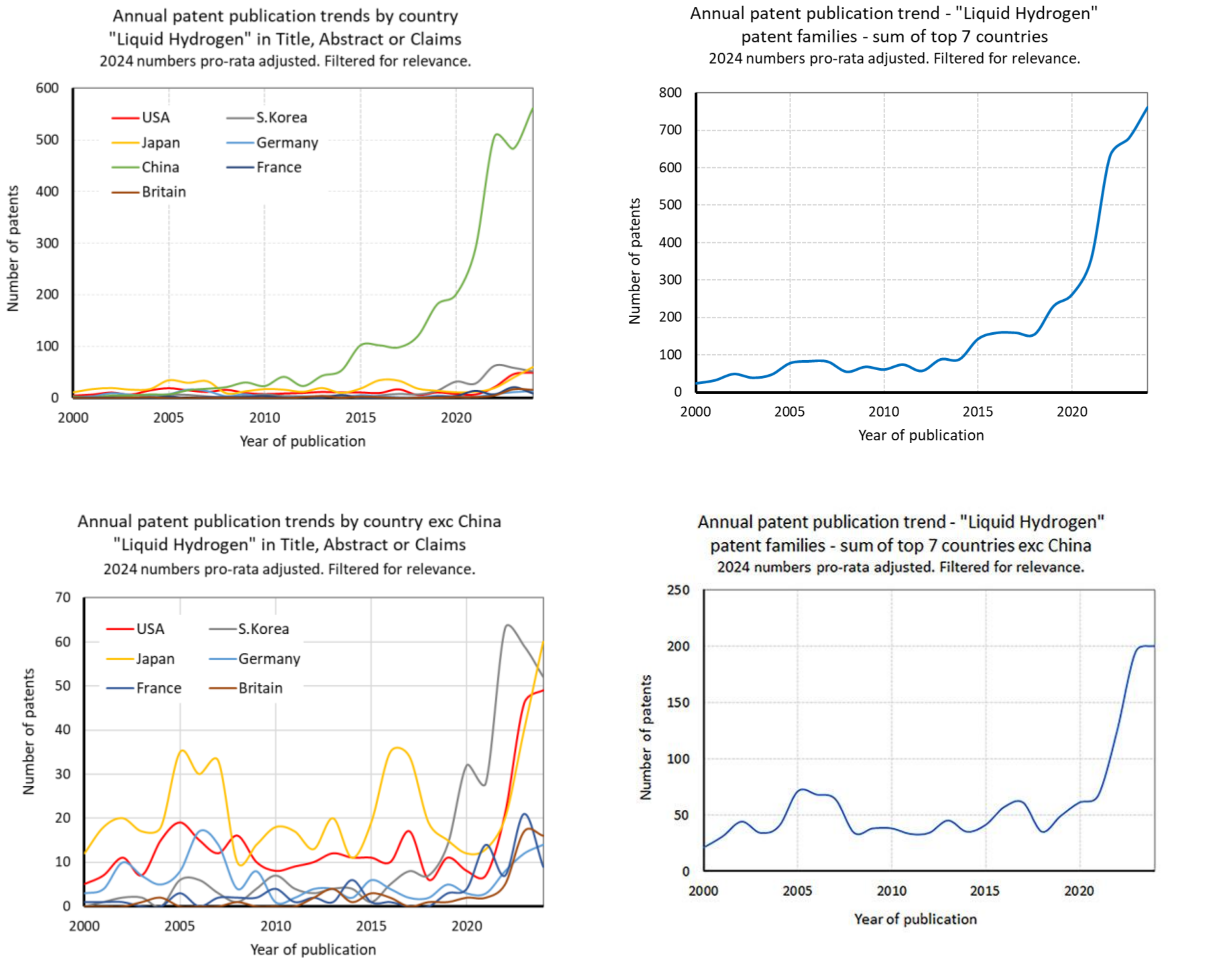

FIGURE 8-2: ANNUAL LIQUID HYDROGEN PATENT FAMILY PUBLICATIONS TREND 2000 TO 2024 – TOP 7 COUNTRIES

Headlines

- Liquid Hydrogen patent family publications increased fivefold 2018 to 2024, driven mainly by activity in Asia, although activity in other regions is also ramping up.
- China's ramp up started 7 years ahead of most other countries and dominates. South Korea also ramped up earlier than the rest of world, with Japan and the USA following.
- Europe is trailing, with France and Germany in the top six based on cumulative publications.
- Great Britain is in 7th place based on cumulative publications, but is starting to ramp up.
- Accelerated roll out of non-aerospace LH2 applications in Asia has strongly influenced the increase in patent activity - this may facilitate earlier access to ageing data for some materials.

Key organisations were identified by manual analysis of results by applicant country. Applications from companies within a group were manually merged to identify the most prolific groups and it is shown in Table 8-1.

TABLE 8-1: KEY APPLICANT ORGANISATION BY COUNTRY 2000 – 2024.

USA	South Korea	Japan
General Electric	Daewoo Ship Building	Toyota Motor Co
General Motors	Hylium Industries	Kawasaki Heavy Ind
Boeing	Korea Inst Mach & Material	Mitsubishi Heavy Ind
Air Liquide	Samsung Heavy Ind	Kobe Steel
Air Prod & Chem	Korea Adv Inst Sci & Tech	

Germany	France	Great Britain
Linde	Air Liquide	Airbus
Airbus	SNECMA	Rolls Royce
Bayerische Motoren	Airbus	Zero Avia
	Ariane	

China
Beijing Inst Aerospace Testing Tech
Zhangjiagang Res Inst Hydrogen Energy Co
Bayerische Motoren
Univ Xi An Jiaotong
Jiangsu Guofu Hydrogen Energy Equip Co
Technical Inst Physics & Chemistry CAS
China Petroleum & Chemical Corp

Narrative

The World Intellectual Property Organisation (WIPO) "patent landscape reports and global directory of patent landscape studies"[386] was checked for relevant landscape reports and none were found covering relevant recent patent activity specific to liquid hydrogen. Patent publications related to liquid hydrogen were therefore searched through the European Patent Office global patent database of over 150 million patent records, and analysed to indicate the top 7 applicant countries, along with the overall trend in patent publications. The level of liquid hydrogen patent activity globally was low (compared to other sectors) until 2014 and has increased eightfold since, with a fivefold increase since 2018. China stands out significantly as the leader in liquid hydrogen patent activity, with South Korea, the USA and Japan following. Identified levels of activity in Germany, France and Britain have also increased above historical levels.

Limitations in patent database searching (in particular differences in EPO data completeness for Asian filings), along with distortive Chinese government subsidies for patent filing (which were reformed in June 2021[387]), mean that the comparative levels of patent publications should be treated with caution. That said, this analysis indicates a very clear and sharp ramp up, considering that the Chinese incentives were in place long ahead of the ramp and that the subsidy induced ramp in the wider Chinese patent landscape started earlier. The dip in Chinese patent publications in 2023 is likely to be an after effect of the subsidies, but the continued (prorata) climb in publications in 2024 suggests continued post subsidy ramp up. Growth in publications outside of China follows a similar, although delayed ramp up.

Considering the R&D activity to patent publication lag, this analysis suggests a sharp ramp up in R&D activity from around 2015. This is consistent with the increasing global interest in liquid hydrogen as a renewable energy carrier across the heavy transport, refuelling station logistics, and energy export application spaces in Asia, along with more recent ramp up of interest for aerospace applications in Europe and the USA. It is also apparent that the UK, whilst lagging behind the global leaders, has more recently started to mobilise.

South East Asia activity driven by non-aerospace applications.

Analysis of lead applicants indicates that sector interest in LH2 varies significantly by region. China has interests both in aerospace (driven historically by its space programme), and in liquid hydrogen as an energy carrier for non-aerospace applications. South Korea and Japan, who currently have low aerospace economic output[5], have strong interest in liquid hydrogen to facilitate energy imports from Australia[388], alongside power, industrial and transport applications.

In October 2018 Japan's **Mitsubishi Heavy Industries** announced [389] capital investment in H2U Investments, a leading Australian Developer of hydrogen projects. In March 2023, Japan announced investment of $2.35Bn in the world's first liquid hydrogen supply chain[390], a collaboration between J-Power and Sumitomo Corporation. **Japan Suiso Energy**, comprising **Kawasaki Heavy Industries** and **Iwatani Corporation** will build the commercial scale Liquid Hydrogen facilities in Australia. This follows on from the world's first sea shipment of bulk liquid hydrogen in February 2022, on the Suiso Frontier liquid hydrogen tanker.

In South Korea, planned government spending on hydrogen projects exceeded $700M in 2021 with a further $2.3Bn committed in 2022 to establish a hydrogen vehicle market [391]. The South Korean Hydrogen Economy Plan aims for 6.2 million FCEV's by 2040, along with 1200 hydrogen refuelling stations, targeting 310 by 2022 [392]. Heavy transport is a key focus for Liquid Hydrogen, with targets for 40,000 hydrogen buses and 30,000 hydrogen trucks. **SK E&S Co** completed the world's largest hydrogen liquefaction plant in May 2024 [393], capable of supplying 5000 Liquid hydrogen buses. The first liquid hydrogen bus refuelling station was completed [394] in July 2024, with **Air Liquide** [395] as a partner - a further 39 stations are planned by 2026. Korea joins 8 other countries, including USA and Japan in operating hydrogen liquefaction facilities. **Lattice Technologies** are leading a project to progress liquid hydrogen shipping [396] using novel composite material lattices, in collaboration with Korea Advanced Institute of Science and Technology (**KAIST**) [397]. In 2021, fifteen major Korean companies formed a hydrogen business council with members pledging $37.3Bn in the sector by 2030 [398]. Members with potential interest in Liquid Hydrogen include **Hyundai** (fuel cell powered vehicles), **SK** (LH2 infrastructure for import and supply for vehicle refuelling), **Samsung** (Refuelling infrastructure), **Doosan Heavy Industries** (fuel cells, storage, drones, LH2), **Hyundai Heavy Industries** (technical guidelines for H2 production safety), **Hyosung** (built world's largest liquid hydrogen production plant) and **ILJIN** (mobile storage, refuelling).

Whilst recognising the more stringent demands of the aerospace sector, these parallel liquid hydrogen activities may indicate wider collaboration opportunities related to materials research and testing. Due to the accelerated nature of non-aerospace roll out, particularly in South Korea and Japan, this may also facilitate earlier access to real world ageing data for some materials.

8.2. Patent landscape - Physical properties cryogenic measurement

Levels of patent activity relating to novel approaches for measuring physical properties, as shown in Figure 8-3, provides potential indications of levels of activity (novel equipment or method development), suggesting advancement of and interest in research methodologies. This in turn may provide a macroscopic indication of research activity beyond status quo techniques.

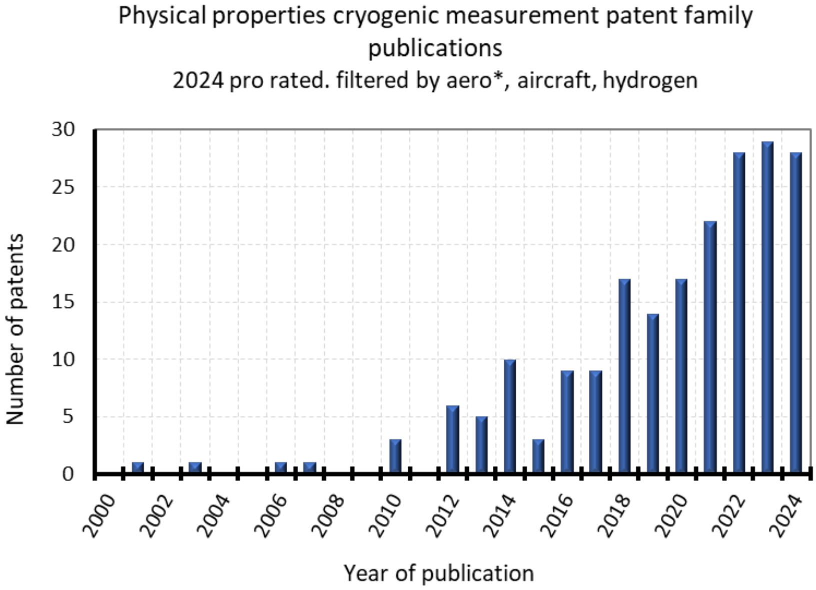

FIGURE 8-3: GLOBAL PATENT PUBLICATIONS TREND – PHYSICAL OR CHEMICAL PROPERTIES MEASUREMENT (CPC G01N) INVOLVING APPLICATION OF TENSILE OR COMPRESSIVE FORCES (G01N3/08) OR PERFORMING TESTS AT HIGH OR LOW TEMPERATURES (G01N3/18) OR BY MECHANICAL METHODS (G01N19/00) - INCORPORATING CRYO* OR LOW TEMPERATURE OR LIQUID HYDROGEN IN TITLE, CLAIMS OR ABSTRACT, NARROWED TO THOSE THAT MENTION AERO*, AIRCRAFT OR HYDROGEN ANYWHERE IN THE PATENT TEXT.

Headlines

- Levels of method and equipment patents has increased steadily since 2010, relating to cryogenic and/or low temperature physical properties measurements of potential relevance.
- Overall levels of patent activity remain low, as may be expected for such a specialised topic.
- Chinese applicants dominate, accounting for 90% of publications sifted for close relevance. Activity is dispersed, suggesting relatively widespread capability across Chinese labs.

TABLE 8-2: KEY APPLICANT ORGANISATIONS BY COUNTRY 2018 – 2024.

USA	South Korea	Japan
GOFF OMEGA HOLDINGS TEXAS A & M UNIV SYS ATSP INNOVATIONS INC	KOREA RES INST CHEM	IWATANI INT CORP

Spain	Russia	China
AIRBUS OPERATIONS SLU	Saratov State University	Univ Jilin Univ Qingdao Sci & Tech China Univ Sci & Tech Yangtze Adv Mat Inst Univ Jiangsu Sci & Tech Univ Southeast Univ Shenyang Aerospace Univ Nanjing Sci & Tech Univ Chongqing Tech Inst Phys Chem Cas Songshan Lake Mat Lab

Narrative

To explore the publication trend of relevant patents, searches were conducted including the combined term Cryo* AND "low temperature", along with filtering to only include CPC codes of high relevance to physical and mechanical properties measurement and search strings related to specific properties of interest. The search was further narrowed to only identify patents where the author identified (anywhere in the patent text) applications related to aero, aircraft or liquid hydrogen. This limitation removed a high number of low relevance publications from the analysis, although it is recognised that it may have removed a smaller number of more general cryogenic equipment patents with some relevance to liquid hydrogen applications. Overall, the level of patent publications has increased steadily since around 2010, from a very low starting point.

The search was narrowed to Jan 2018 – Sep2024 to examine recent activity in more depth – resulting in a list of 148 patent families. These were individually reviewed for relevance and 79 high relevance results were carried forwards for further geographical analysis of relevant organisations.

The vast majority of the 79 high relevance patent families were from Chinese applicants, with just 2 from the USA and 1 each from Japan, Korea, Russia and Spain. The Chinese patent publications are predominantly domestic only. Chinese institutes were incentivised to file patents until June 2021, through generous government subsidies. The subsidy scheme however started significantly before the ramp up of patent activity, suggesting that the increase in activity may genuinely reflect an increase in research focus (with a rush to file before subsidy reduction in 2021 potentially skewing up the peak of publications in 2022/2023).

In the period since 2018 over 50 Chinese organisations, mostly academic, proceeded to publication of high relevance patent filings, indicating widespread cryogenic properties research capability across Chinese organisations. Of these, around 40 had one patent publication, 8 had two publications, 4 had three publications. Whilst the exceptionally niche nature of many of these patent applications would not be considered of patent interest to organisations outside of China (and would instead be published or held as a trade secret), the overall level of research activity is of interest.

Outside of China, the levels of patent publications per year remain extremely low, suggesting limited commercial opportunities in developing cryogenic materials properties measurement systems. This is in line with the small and highly specialised market for this equipment, and the propensity for custom builds, either within research institutions or by custom order to a specialised cryogenics company.

9. Conclusions, Reflection and Recommendations

Although new to civil aerospace, liquid hydrogen has been used in other industries for some time and there is an existing body of evidence on materials compatibility but limited to a very small selection of materials. The wider industry has predominantly used 316L stainless steel, which has an excellent combination of hydrogen compatibility and cryogenic temperature compatibility. The main reason to consider other materials for aerospace applications is weight, although the well evidenced history of use of ultra-thin wall 316L stainless steel tubing, bellows (required to compensate for thermal contraction and expansion) and heat exchangers in cryogenic applications means that the weight difference may not be as significant as it first appears. Differential thermal expansion between dissimilar materials at joints and interfaces further steers material choices, considering the propensity of nature's smallest molecule to escape through the smallest of defects.

Lightweight alloys have also been explored and used for liquid hydrogen applications, such as for tank liners in composite LH2 fuel tanks for space applications, albeit with shorter lifetime requirements. Polymer / resin based composite materials are mainly considered for non-hydrogen wetted structural applications, such as the structural shell of LH2 storage tanks, or for thermally insulating support structures for other system components. Cryogenic testing of composites is typically without hydrogen, although in the event of seal or liner failure, or fugitive hydrogen permeation, wetting may occur and therefore some testing in hydrogen is likely to be required.

The main knowledge gaps that could delay development of LH2 fuelled civil aircraft appear related to longer term reliability of selected materials systems in aerospace specific conditions. Shorter term test considerations relate to the lack of standardised test data for mechanical properties at cryogenic temperatures, the relatively unexplored impact of repeated thermal cycling on these, and the impact of hydrogen exposure on these.

Based on a review of over 400 publications, this report provides an overview of current global capabilities, the state of global knowledge maturity and identified gaps. Considering those gaps alongside the outputs of ATI HCN industry prioritisation surveys, the authors consider the following as priority focus areas for further work. This list is not definitive, and other activities are likely to be required in the short to medium term.

1. A shortlist of priority candidate materials, including processed state, is urgently required in order to focus testing – especially considering the significantly lower throughput of mechanical property tests at LH2 temperatures (currently a maximum of one test at one condition per day, although a focus on development of load locks could increase this).
2. For metals, particularly lightweight alloys, data on the combined impacts of fatigue cycles and LH2 temperature thermal cycles, ideally in cryogenic hydrogen, is lacking. Equipment for these studies is exceptionally limited globally, and thermal cycling will result in very low throughput. Consideration should be given to developing test capacity in the UK.
3. Long term real time ageing data is lacking on the impact of cyclical CryoH2 exposure on most metals at most cryogenic temperatures. Material conditioning systems are not yet defined, particularly considering thermal cycling and mechanical loading. The conditioning itself is likely to require significant time to conduct – eventually years. Defining and beginning this conditioning activity on a plethora of destructive test samples is therefore relatively urgent.

4. Short-term and long-term ageing data is lacking on coating integrity for metals when exposed to hydrogen and repeat cryogenic thermal cycling. Investigation of candidate hydrogen barrier coating compatibility is likely to be a priority to enable material selection.
5. Correlation evidence between accelerated hydrogen loading (pressure and temperature, or electrolytic) and natural loading during long term cryogenic cycling is lacking. A systematic study is required to close this gap. The current assumption is that accelerated loading is likely to provide a worst-case scenario, but this appears unproven.
6. Development of a consensus full-service life thermal cycling profile will enable development of representative conditioning protocols and standards.
7. LH2 gasket seals are mature technology, however, the level of evidence relating to long term performance, in particular loss of spring performance through thermal cycling in hydrogen, of deflection activated coated metal seals, warrants early investigation.
8. For composites, the complex interactions of anisotropic thermal and mechanical properties, and the likely changes in structure around three-dimensional forms, makes correlation between coupon testing and final structure much more challenging. Further development of improved cryo-mechanical test systems and standards focused on composites, and on modelling of anisotropic behaviour, is required to inform designs. The alternative is to rely on testing at component or system level.
9. Failure mode testing of proposed polymer / resin-based composites with exposure to cryoH2 may be required as part of material selection, to ensure no catastrophic loss in structural properties in the event of hydrogen leakage.
10. Modelling development is required to enable cryogenic conditions to be better incorporated into design simulations. It is unclear that a universal Multiphysics model is essential (linking hydrogen migration and localisation to mechanical property changes and physical properties, across the full range of temperatures and length scales). A simpler and adequate approach may be to separate these considerations, although that approach may increase test requirements. Further activity is required in order to develop a pragmatic route that enables design activities whilst minimising risk.
11. Physical properties measurement can most easily be standardised on the Quantum Design Physical Properties Measurement System, based on existing test methods. This testing is relatively quick to conduct, due to the ability to acquire multiple data points during temperature ramps. Methods should be standardised ahead of confirmatory testing of aerospace candidate materials.

10. Appendix 1: Research Methodologies

Methodology: Literature reviews

Prior to starting a literature search the keywords were agreed. It was agreed that the search would be done utilising Google Scholar (in a custom range), Scopus, Web of Science, IEEE Xplore, and ScienceDirect (Elsevier). Specifically, the years in between which the search would be done were 2018 and 2024 in order to identify recent activity in the expectation that capability is more likely to still exist at the identified institution. The 'include citations' filter was also enabled to help with relevance and significance of the papers found.

Primary search terms were determined based on the proposal outline. The main objective was to provide an overview of the global hydrogen research landscape, with a focus on materials, liquid hydrogen, and cryogenic testing, highlighting the leading institutions within the scientific community. The primary search term used to generate the final dataset was "hydrogen liquid cryogenic testing".

A Python script was developed to facilitate the analysis and generate a structured, spreadsheet-like output of the relevant data. The script used the specified search term as input and tracked key metrics, including the number of publications, citation counts, and publication trends from 2018 onwards. Additionally, it identified and recorded leading authors or research groups, affiliated institutions, publication venues, abstracts, paper titles, and publication years.

An initial search conducted without the Python script yielded a large volume of irrelevant results, making it difficult to isolate relevant publications. However, applying a year range filter significantly narrowed the results to a few hundred. The Python script was then employed to generate the first draft of the spreadsheet, which identified approximately 200 papers relevant to the search term "hydrogen liquid cryogenic testing".

Upon building up the first draft of the spreadsheet it was necessary to manually review all the papers and identify in which of the following categories they fell:

- Metals: Bulk: Fundamental materials science
- Composite: Bulk: Fundamental materials science
- Sealing Material: Fundamental science
- Metal Coatings: Fundamental science
- Testing mechanical properties (static/quasi-static/high cycle)
- Testing - Tribology
- Testing - Thermal properties
- Transport properties
- Modelling - Materials: Multi-scale, multi-physics
- Modelling - Materials: Meso scale
- Service life prediction/cyclic loading impact
- Uncertainty quantification/qualification
- Hydrogen Charging (methods)
- NDT (for hydrogen presence in materials)

Following the initial landscape search, sections were assigned to individual authors. The initial circa 200 papers were categorised using an A/B/C grading system for each relevant category, where A indicated the highest relevance and C the lowest. Some papers were assigned an "A" in multiple categories, such as testing and modelling, reflecting their significance in more than one area. This grading system helped streamline the report structure, making it easier to draft the initial version. During this process, it became evident that the Python script had not fully captured the breadth of scientific research in certain fields, leaving some areas underrepresented. Updated searches were conducted to include the category name alongside "liquid hydrogen" and "cryogenic."

Each team member conducted a targeted search for their respective chapter, focusing initially on publications released after 2018, including working up the citations trees to find more recent relevant publications and down the reference trees. This approach yielded additional relevant publications.

In order to assess the wider knowledge maturity in each category, the author conducted a further literature search, combining intelligent specific search terms, reference tree analysis and citations tree analysis. This was not intended to be a definitive review of the historic literature, but more to focus on key publications, including review papers, pointing the reader to information sources that can be a starting point for further reading. This process was iterative, also yielding additional recent (post 2018) papers. This additional search highlighted areas with extensive literature, including well-cited papers, books, book chapters, guidelines, and other resources, ensuring a comprehensive overview of the research landscape in each field.

Literature review disclaimer and limitations:

The literature search prior to 2018 was non-exhaustive and aimed primarily to provide an overview of the maturity of the historical knowledge base only. The initial search terms were limited and did not fully capture the breadth of scientific research across certain fields. Due to the limitations of search tools and issues with open access, the statistical data presented should be used for indicative trend analysis only, rather than as absolute values. Search tools may have missed relevant results, particularly for papers that were not open access or hosted on entirely different platforms, such as those specific to Russian or Chinese databases. Business critical or financial decisions should not be based on the indicative literature research data provided in this report.

Methodology: Patent Search - Tools

In order to gain insights into the relative levels of global activity in Liquid Hydrogen research and development, a patent search was conducted utilising the European Patent Office global database of over 150 million patent documents, accessed via the EspaceNet search engine using advanced mode searching combined with offline analysis of downloaded patent data. “Patent families” searching was used as this provides a more accurate indication of R&D activity, as a single family can spawn a varying number of territorial applications.

Methodology: Liquid Hydrogen Global Patent Landscape

Primary search terms were explored and refined based on an analysis of results. Initially two search terms were explored “Liquid Hydrogen” and [Cryogenic AND Hydrogen]. The latter term returned large numbers of irrelevant results which were hard to separate out, so the exact phrase “Liquid Hydrogen” was used. It is recognised that this may miss some results, however, it is expected that the majority of patents specifically targeting liquid hydrogen applications would include the phrase. In addition, the search was narrowed to inclusion of the search term in the title, abstract or claims to focus in on patents specifically targeting liquid hydrogen applications.

Following manual review of a random selection of patents returned by the simple search phrase, the following exclusion terms were added to reduce the number of irrelevant patents:

=“Liquid Hydrogen” NOT (chloride OR fluoride OR bromide OR hydrogenated OR ammonia OR geological OR cement)

In order to prevent skewing of data by only searching within specific CPC classifications, the search was initially conducted across all classifications and then the returned classification codes individually reviewed for potential relevance. The following codes were excluded due to low relevance:

A61xx, B01Dxx, B01Jxx, B60Lxx, C01Bxx, C02xx, C25xx, F02Cxx

The final search phrase was therefore:

ctxt = "liquid hydrogen" NOT ctxt any "chloride fluoride bromide hydrogenated ammonia geological cement"

CPC main groups: ~~C25B1~~ ~~AND~~ ~~F02C3~~ ~~AND~~ ~~A61L2~~ ~~AND~~ ~~C01B2203~~ ~~AND~~ ~~B01D53~~ ~~AND~~ ~~B60L58~~ ~~AND~~ ~~B60L50~~ ~~AND~~ ~~A61L2202~~ ~~AND~~ ~~C25B9~~ ~~AND~~ ~~C02F1~~ ~~AND~~ ~~B01J23~~ ~~AND~~ ~~C25B15~~ ~~AND~~ ~~B01J19~~ ~~AND~~ ~~B01J2219~~ ×

It is apparent that the EPO search engine refined its search results when the request was narrowed to individual countries, returning significantly lower levels of hits compared to its automated country breakdown of the initial global search. These lower level country specific returns were small enough to allow random manual checking of lists of specific patent families vs returned statistics, across a sample of countries, confirming significantly greater accuracy. Country based searches were then used for detailed country by country analysis. Earlier statistical results from initial broad searches (where returns were in the thousands) were discarded. Levels of publications associated with each country should still be considered as indicative only. It should also be noted that the Chinese Patent Office frequently omits the “applicant country” data field from its reporting to the EPO and an applicant country search therefore significantly under reported patent filings from Chinese organisations. *WIPO hydrogen patent landscape report[386]* indicates that Chinese applicants predominantly file in China and as numbers of Chinese filings from other countries are low, a workaround was used, searching for all initial filings at the Chinese Patent Office and then removing overseas applicants.

Filter data (lists) for each country were individually downloaded from the EPO system and combined within a spreadsheet for more detailed trend analysis. Data on numbers of patents for 2024 was pro-rated due to the partial recording year (x12/9).

Methodology: Physical Properties Cryogenic Measurement Patent Search

The same basic methodology was utilised for searching the patent landscape for Physical Properties Cryogenic Measurement equipment and methods. The main difference in methods was that CPC codes were included in the search term to narrow to only report ones of high relevance, rather than utilising a wide search and then excluding CPC codes of low relevance. An initial wide search was used to identify exemplar patents of strong relevance and these were then used to reveal the CPC codes of high relevance. CPC code lists were then reviewed to identify the most appropriate hierarchical level of code required to capture relevant publications whilst excluding those on irrelevant topics. A complex search term combining CPC codes along with grouped text string inclusions and exclusions was developed to maximise relevant patents whilst excluding those of low relevance.

The final search term was:

cl any "g01n3/18 g01N3/08 G01N19/00" AND (ctxt any "cryo*" OR ctxt=("hydrogen" prox/distance<1 "liquid ") OR ctxt = "low temperature") AND (ctxt any "indentation impact tensile fatigue stress strain creep mechanical fracture friction tribology" OR ctxt = "thermal effusivity" OR ctxt = "thermal diffusivity" OR ctxt = "thermal conductivity" OR ctxt = "transport properties" OR ctxt = "heat capacity") AND nftxt any "aero* aircraft hydrogen"

The final limiting term eliminated a large number of search hits. Whilst its use may have removed equipment or method patent families which could potentially be utilised for aerospace applications, it narrows the search to patents where the author explicitly identified aerospace or hydrogen applications anywhere within the patent text.

Initial Results with this term added (01Jan2000 to 30Sep2024) = 197

Initial Results with this term removed (01Jan2000 to 30Sep2024) = 1013

Results were downloaded to a spreadsheet for more detailed analysis.

The search was then limited to the date range 01Jan2018 to 30Sep2024 to explore more recent activity returning 148 patents which were manually reviewed for relevance. Of these 79 were found to be of high relevance, of which 71 were from Chinese applicants. More detailed country graphical analysis was not conducted due to the very low numbers of patents from outside of China.

Patent search disclaimer and limitations:

Patent searches were non-exhaustive and were intended to provide an indication of geographical activity levels and highly patent active organisations within those geographies. Patent searching utilised publicly available published patent data sources and search engines, which may be incomplete or inaccurate. Search terms were limited and it is likely that these will have not identified some relevant patent filings and may have classified some low relevance patents as relevant. There will be a variable lag between filing of any patent and publication, and the patent data therefore lags activity. Due to search tool limitations, statistical data should be used for indicative trend analysis only and not for absolute values. Search tools may exclude results where an English translation such as a machine translation is not available on the database and may fail to identify multiple documents as being within the same patent family. Business critical or financial decisions should not at all be based on the indicative patent landscape data presented herein.

11. List of Figures

12. List of Tables

13. References

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