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The challenges of hydrogen and metals

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1. Introduction

The challenge of hydrogen and metals, and in particular the phenomenon now known as “hydrogen embrittlement” (HE) [1], is both a very old and a very new problem. It was reported first, to the Royal Society, in 1874 [2]. The question became of interest to metallurgists, chemists and physicists in the decades following the 1920s; and although much research was done and many *mechanisms* of HE were proposed, there has been no consensus. There may or may not be one single phenomenon that lies behind HE. While industry developed means of avoiding the catastrophic consequences of sudden failure due to hydrogen ingress in metals, the problem lay dormant at the end of the previous century. It came very much to the fore in the current one for two reasons.

- (i) Steelmakers developed ultra high strength steels; the yield strength of automotive body structural components, chassis legs, intrusion bars, increased by as much as a factor of three over a decade. Steels with tensile strengths as high as 2 GPa are now available to the automotive sector that are essential in meeting targets on CO₂ emissions through vehicle weight reduction; but these cannot be put into use until the problem of HE is finally solved and the pernicious effects of hydrogen are ameliorated. A similar situation applies in the offshore wind turbine industry. Repair of such plant is extremely expensive and difficult due to its location, but rolling contact fatigue failure of bearing steels due to HE severely limits the lifetime of the drivetrain. In the following proceedings numerous other examples will be found in which hydrogen is limiting and curtailing the deployment of modern metals, including zirconium, titanium and nickel based alloys.
- (ii) Society has begun to appreciate that one solution to the problem of climate change brought about by CO₂ emissions is to implement the “hydrogen economy”. Examples of this, decarbonising the gas grid by replacement of the domestic supply with hydrogen (figure 1), and the use of hydrogen as an automotive fuel (figure 2) were both presented in the first session of the Meeting.

In the last few years a number of consortia of industry and academia have been formed, in particular to investigate the fundamental issues behind HE and to embark on the design of alloys, especially steels, that are resistant to hydrogen. These include the HYDRAMICROS [4] and MultiHy [5] projects in Framework Programme 7, of the European Commission; and the EPSRC funded Programme Grant: hydrogen in metals—from fundamentals to the design of new steels (HEmS) [6]. It is under the aegis of this latter programme that the present Meeting was conceived and planned.

2. Motivation and scope of the Scientific Meeting

In view of the above it seemed timely to organise a Scientific Discussion Meeting, broadly interdisciplinary, in order to bring interested parties together to discuss possible solutions to the alloy design problem and to materials and societal issues thrown up by the emerging hydrogen economy. From the outset we determined on a number of principles.

- To achieve a *balance* of delegates, speakers and panelists from across government, industry and academia.
- To devote a sizeable portion of the content to the role of hydrogen in corrosion.
- To allow the greatest possible time for discussion and networking; and to foster a full engagement of early career researchers as it is they who will lead the efforts going forward to solve the current economic and technical problems that face society.
- In the manner of historic conferences of the 50s and 60s to record, transcribe and publish all of the discussions.

To this latter end, we planned as a central feature of the Meeting an extended panel discussion on the *mechanisms of hydrogen embrittlement in steels*. Initially it was questioned whether the

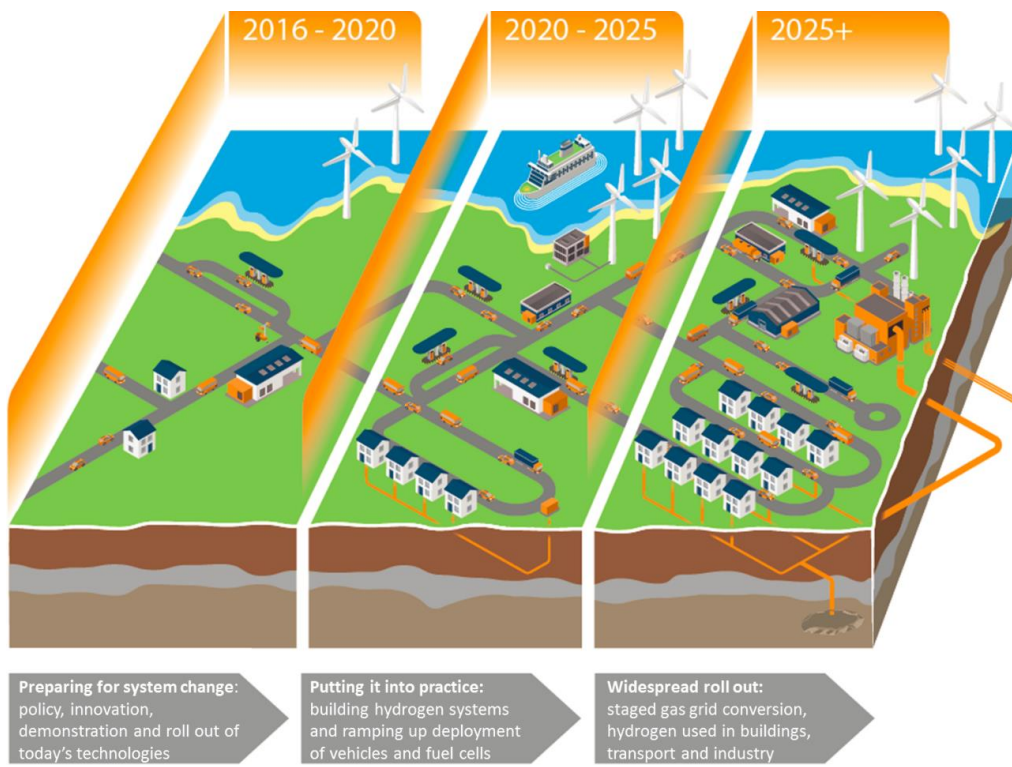


Figure 1. A pathway for development of hydrogen and fuel cells in the UK energy system [5]



Figure 2. Hydrogen powered car. Image courtesy of BMW Group.

Community really needs to *know* what are the mechanisms if the chief aim is amelioration; but the consensus is very clear—even after decades of research there is a woeful lack of understanding of the fundamental science that lies behind the hydrogen problem. And industry and academia are in agreement that until such understanding is reached there can be nothing more than an *empirical* approach to the engineering issues. Many established principles and conventional wisdom must be challenged. We do not list them here as they become evident in what follows. However two central questions emerged: (i) how can elastic screening lead to enhanced localised plasticity and how can that in turn lead to brittle failure? and (ii) if hydrogen is feeding into a crack tip, how can it influence the behaviour of a crack whose speed exceeds that of diffusing hydrogen?

We chose to distribute the subject matter into five conventional sessions (conventional except that a third of each speaker's time was given over to discussion), two panel discussions and a poster session.

Session 1: *Political, economic and environmental concerns*, Chair Dr Vigdis Olden (Sintef, Trondheim, Norway)

Mr Dan Sadler (Northern Gas Networks, UK) *Decarbonising the UK Gas Network—The H21 Project*

Prof. Nigel Brandon OBE FREng, (Imperial College London) *Clean energy and the hydrogen economy*

Dr Salim Brahimi (Industrial Fasteners Institute, USA) *Effect of material characteristics on hydrogen embrittlement failures of high strength steel fasteners*

Session 2: *Hydrogen transport and trapping: from quantum effects to alloy design*, Chair: Dr Pedro Rivera (Department of Materials, University of Cambridge)

Dr Tilmann Hickel (Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf) *The first principles approach: insights into hydrogen trapping by microstructures in steels*

Dr Jutta Rogal (Ruhr University Bochum, Germany) *A kinetic Monte Carlo approach to diffusion controlled thermal desorption spectroscopy*

Prof. Reiner Kirchheim (University of Göttingen) *The physics of hydrogen transport and trapping in metals*

Dr Frantz Martin (CEA Saclay, France) *Isotopic tracing of hydrogen transport and trapping in nuclear materials*

Session 3: *Hydrogen in steels*, Chair Prof. Mark Rainforth FREng (Department of Materials, University of Sheffield)

Dr Richard Thiessen (thyssenkrupp Steel Europe) *Hydrogen related challenges for the steelmaker*

Prof. Norman Fleck FREng FRS (University of Cambridge) *Hydrogen embrittlement in structural steels*

Ms Tarlan Hajilou (Norwegian University of Science and Technology, NTNU, Trondheim) *Hydrogen embrittlement investigated by novel critical experiments*

Dr Vigdis Olden (SINTEF Materials and Nanotechnology, Trondheim) *Hydrogen induced stress cracking in steels—examples of failures and numerical modelling*

Prof. Hisao Matsunaga (Kyushu University) *Effects of hydrogen on fatigue crack growth in steel*

Session 4: *Mechanisms of hydrogen embrittlement in steels: panel discussion*, Chair: Prof. Adrian Sutton FRS (Department of Physics, Imperial College London). Panelists: Prof. Afroz Barnoush (Norwegian University of Science and Technology, NTNU, Trondheim), Prof. David Dye (Department of Materials, Imperial College London), Prof. Xavier Feaugas (Université de la Rochelle, France), Prof. Hisao Matsunaga (Kyushu University, Japan)

Session 5: *Hydrogen effects in corrosion*, Chair: Prof. Afroz Barnoush (Norwegian University of Science and Technology, NTNU, Trondheim)

Prof. Mary Ryan FEng (Imperial College London) *High resolution imaging in corrosion studies*

Prof. Philippe Marcus (CNRS-Chimie ParisTech, France) *Atomic level characterisation in corrosion studies*

Dr Helmuth Sarmiento Klapper (Center for Materials Research, Baker Hughes) *Hydrogen embrittlement—the game changing factor on the applicability of Nickel alloys in oilfield technology*

Session 6: *Hydrogen effects in non-ferrous alloys*, Chair: Prof. Mike Finnis (Departments of Materials and Physics, Imperial College London)

Dr Ben Britton (Imperial College London) *Hydrides and zirconium—a micromechanics story*
Prof. Xavier Feaugas (Université de la Rochelle) *Hydrogen effects and hydride formation in Zr and Ti alloys*

Dr Tamara Chapman (Rolls-Royce plc) *The role of hydrogen in stress corrosion cracking—a titanium alloy case study*

Prof. Dave Rugg (Rolls-Royce plc) *Hydrogen in titanium and zirconium—an industrial perspective*

Session 7: *Future directions: panel discussion*, Chair: Prof. Tony Paxton (Department of Physics, King's College London). Panelists: Prof. Mary Ryan FEng (Department of Materials, Imperial College London), Ms Yung Deng (Norwegian University of Science and Technology, NTNU, Trondheim), Mr Jon Saltmarsh MA (Cantab) MBA (Department of Business, Energy and Industrial Strategy, London), Dr Tilmann Hickel (Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf)

Full details of the programme, and audio recordings of the talks, will be found at the Royal Society's web pages [7].

On 14th December 2016, in her keynote speech to the Policy Exchange event, *The Heat Summit*, Baroness Neville-Rolfe DBE CMG, Commercial Secretary to the Treasury, pointed to a "... radical possibility; replacing natural gas with hydrogen in the gas grid." Our Meeting opened with a description of this by Dan Sadler of the Northern Gas Network. He was seconded to DECC/BEIS in the previous year and is the author of the H21 report which, in the words of Jon Saltmarsh (BEIS) "... is the most comprehensive review of the feasibility of using hydrogen to decarbonise the UK gas grid published to date." Briefly, H21 is an engineering and economic feasibility study of the practicality, impact and consequences of converting the City of Leeds from the natural gas to a hydrogen supply. Hydrogen will be obtained from natural gas using a carbon neutral extraction route and distributed through the city's low pressure main; the problem of hydrogen damage to the high pressure metal pipework still needing to be resolved. Hydrogen will be stored in salt caverns. The session, *Political, economic and environmental concerns*, continued with a talk by Prof. Nigel Brandon FEng OBE, recently appointed Dean of the Faculty of Engineering, Imperial College London. He gave a broader description of the hydrogen economy encompassing both energy and transport. The same session concluded with a talk by Dr Salim Brahimi who was elected Chairman of the ASTM International Fasteners Committee in 2012. He is also the founder and president of IBECA Technologies Corp. and Research Manager at the McGill Hydrogen Embrittlement Facility, Montreal. Among other things Dr Brahimi was involved in the investigation of the failure of bolts on the Cheesegrater Building in London. As reported by the *Telegraph* on 14th January 2015, "The company [British Land] said the investigation had concluded that a process known as *hydrogen embrittlement* had caused the bolts to become brittle and fracture." In a slightly more hysterical vein on 6th November 2014 the *Express* screamed, "Two steel bolts *the size of a human arm* have broken off from the Cheesegrater skyscraper in London—with one crashing to the ground below. Sam Jones, who works for an insurance company based in the City, also told The Evening Standard: It's terrifying. They may say it's structurally safe but if someone was hit they would have died, plain and simple."

A central issue in the prevention of HE is the notion of immobilisation of hydrogen by deep traps, designed into the microstructure [9]. These are usually transition metal carbides, many of which already play a vital role in strengthening: for example, interphase precipitates in microalloy steel. The principal outstanding questions here are, (i) how the hydrogen reaches the deepest traps if the activation barrier is, as typically found in quantum mechanical calculations, greater than 1–2 eV; (ii) whether hydrogen resides at the matrix particle interface, or deep within the particle [10]; and perhaps most importantly, (iii) how microstructural traps can provide protection against continuous ingress (for example during rolling contact fatigue or cathodic “protection”) since they will eventually all become filled.

There followed two sessions on hydrogen in steels. A highlight of the contributed talks, and indeed of the Meeting, by general agreement, was the description of the “novel critical experiments” by the two young PhD candidate researchers Ms Tarlan Hajilou and Ms Yung Deng, led by Prof. Afrooz Barnoush of NTNU. In the words of Prof. George Smith FRS this was a “stunning piece of work”.

Following these two sessions we moved to the role of hydrogen in corrosion. Prof. Mary Ryan FEng, the Shell/RAEng Research Chair at Imperial College London, gave the opening talk, in particular addressing corrosion induced failure and consequent toxicity in cobalt surgical implants [11, 12]. Prof. Philippe Marcus, Director of Research at CNRS and Professor at the Ecole Nationale Supérieure de Chimie de Paris, provided a detailed description of the state of the art in electrochemical scanning electron microscopy. This is a genuine breakthrough in characterisation since it is now possible to make atomic scale imaging under electrochemical conditions *in situ* rather than *post mortem*. Finally in this session, Dr Helmuth Sarmiento Klapper, Baker Hughes Enterprise Research, Germany, gave an industry perspective on hydrogen embrittlement of nickel base alloys in the oil and gas sector. It is an interesting contrast to note that the δ -phase which is deleterious to high temperature superalloys in the aerospace sector is a beneficial microstructural element to the down-hole materials engineer.

The final session of contributed papers was on non ferrous alloys, in particular titanium and zirconium. These are stable hydride formers and so the mechanisms of hydrogen failure are very different compared to steel. As Prof. Xavier Feaugas pointed out in his talk, the interplay of hydrogen with oxygen is of central importance. Indeed the role of oxygen is itself very intriguing, in its effects on plasticity. There is clearly an effect on the core structure of dislocations with oxygen effecting a planar to non planar core transformation with a consequence that a dislocation will “jump” over several Peierls valleys in between locking events induced by oxygen. There is considerable complexity in the crystallography, habit plane and orientation relations in hexagonal metal hydride morphology which Prof. Feaugas describes in detail in his paper. There followed two talks from Rolls-Royce plc, by Dr Tamara Chapman and Prof. Dave Rugg on failure analysis and component integrity. The case study of “blue spot” on titanium alloy turbine discs is an exemplary instance of industry–academia collaboration, in which modern characterisation and analysis led to a detailed understanding of the materials chemistry with the combined outcomes of a seminal PhD thesis and considerable financial advantage to the Company.

It is this remarkable range in scope from atomic scale experiment and theory to the performance of turbofan engines, and the range of interests from Government policy, through academia to industry that highlights the vast influence that the smallest atom holds over the modern world.

3. Thanks

We have received many complimentary remarks following the Meeting to the effect that it was original, stimulating and productive. This success is largely due to the labours of those who have supported the organisers. While we determined the programme and selected the topics, speakers and panelists, the organisation was conducted by Catriona Ross, Senior Scientific Programmes Officer of the Royal Society, whom we thank for meticulous attention to detail and professionalism. These proceedings are appearing well within six months of the Meeting thanks

to the prompt responses of the authors, most of whom provided manuscripts in advance of the event, and to the very rapid and efficient management of the publication by Bailey Fallon, Commissioning Editor, *Philosophical Transactions A*.

We owe a particular debt to the student and post doctoral *scribes* who took copious notes during the sessions and later on transcribed from the audio recordings to produce manuscripts of the seven discussion papers which appear in this volume. The scribes are, Yi-Sheng Chen (Department of Materials, University of Oxford); Felicity Dear (Department of Materials, Imperial College London); Dr Henry Lambert (Department of Physics, King's College London); Mitesh Patel (Department of Physics, Imperial College London); E. Luke Simpson (Department of Physics, King's College London); Guy Skinner (Department of Physics, King's College London) and Miles Stopher (Department of Materials, University of Cambridge).

A particularly thankless task was to act as microphone handler, although this was an essential duty since it was necessary to obtain clear audio records from which to transcribe the Discussion papers. Microphone handlers were, Dr Lefteri Andritsos (Department of Physics, King's College London); Dr David Bombac (Department of Materials, University of Cambridge); Lisa Claeys (Department of Materials, Textiles and Chemical Engineering, Ghent University); Emilie Van den Eeckhout (Department of Materials, Textiles and Chemical Engineering, Ghent University); Peng Gong (Department of Materials, University of Sheffield); Charles Harper (Department of Engineering, University of Cambridge); Chiara Liverani (Department of Physics, Imperial College London) and Dr Sebastián Echeverri Restrepo (SKF Engineering and Research Centre, Nieuwegein, The Netherlands).

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