September 01, 2020

Maths, Physics & Chemistry

Enabling a hydrogen-fueled future

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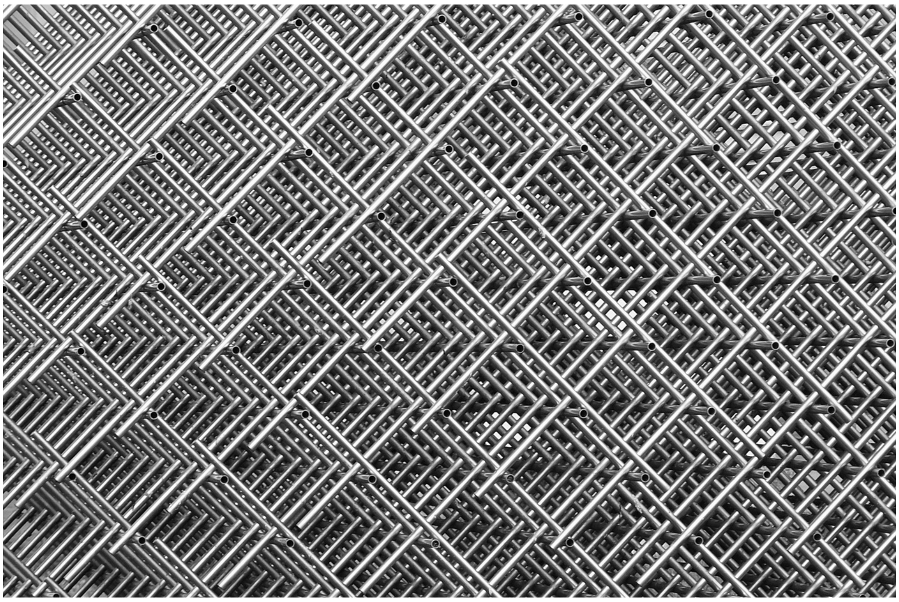
This Break was edited by Max Caine, *Editor-in-chief* - TheScienceBreaker

ABSTRACT

Hydrogen embrittlement is an obstacle for using metals in hydrogen fuel technologies. We found the origin of this effect by using a customized state-of-the-art microscope to directly observe hydrogen at both defects and an incoherent interface between internal carbides and the surrounding steel.



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Due to its nature as a clean fuel, there has been substantial interest in recent decades in developing hydrogen fuel cells and storage technologies. However, this ‘hydrogen economy’ is currently limited by the fact that hydrogen is known to significantly reduce the toughness of steels. This phenomenon is known as hydrogen embrittlement, and it leads to premature fracture. This situation prevents the use of existing steel pipes and transport vessels for gas transportation and storage in a future hydrogen economy, affecting its financial viability. The phenomenon of hydrogen embrittlement has been known for more than a century. However, the exact origin and effective solutions against such embrittlement are yet to be found. Our work focused on observing the precise behaviour of hydrogen in steels at an atomic scale. Using a state-of-the-art atom probe microscope coupled with a custom-developed sample preparation technique, we set out to understand the specific mechanisms responsible for hydrogen embrittlement of steel as well as to highlight a concrete pathway to solve this problem.

Hydrogen embrittlement involves hydrogen interactions with different material defect types across multiple-length scales. It has been suspected for many years that hydrogen embrittlement of steels arises from the attraction of hydrogen to defects in steels, particularly to the dislocations and grain boundaries that exist in all metals. In the presence of hydrogen defects such as grain boundaries become more sensitive and less tolerant to stress loading and will eventually fail under stress. Although this hypothesis was presented over 50 years ago, there had been no direct evidence of the suspected hydrogen-defect combinations in the intervening years. This lack of evidence arises from the difficulty of accurately detecting and locating the atomic positions of hydrogen in steels. Accordingly, our first aim is to provide a more sophisticated insight into this problem by determining precisely which microstructural features within steels interact with hydrogen and are responsible for fracture initiation. Secondly, we wanted to explore the nature of hydrogen interactions with carbide precipitates, since these microstructural features have been proposed as internal traps for hydrogen that can minimize its interactions with defects and prevent embrittlement. This type of information is of importance for metallurgical engineers when designing new alloys that are resistant to hydrogen embrittlement.

To observe hydrogen in steel microstructures, we used a microscopy technique called atom probe tomography (APT). APT is a powerful technique that gives exquisite 3D maps showing the positions of atoms within a selected volume of matter. Whilst similar in resolution to the more widely understood technique of transmission electron microscopy, APT allows near atomic-scale information about the arrangement of matter within a needle-shaped sample. APT determines this information via a process that involves the field evaporation and direct detection of atoms, including hydrogen, from the needle sample by using time of flight and position-sensitive detectors. Although hydrogen can be easily detected in APT, it is prevalent in the APT vacuum chamber. Therefore, researchers can never be sure whether the hydrogen detected arises from the sample or the microscope chamber itself. Additionally, due to its rapid rate of diffusion through bulk metals, there is further uncertainty about the whether the measured locations of hydrogen after slow APT sample handing procedure is an accurate reflection of its exact position within the steel samples. In order to get around this issue, we loaded our specimens with deuterium, a naturally rare isotope of hydrogen, which is able to be unambiguously detected and serve as a marker for the hydrogen distribution. We also developed a customized cryogenic sample-transfer (cryo-transfer) method. Such a method allowed us to plunge-freeze the steel samples after deuterium loading and keep them at -150 °C throughout the entire sample handling procedural chain. This protocol allowed us to 'freeze' the hydrogen in place before APT observation, ensuring that the measured location is a true reflection of the hydrogen location without significant diffusional movement.

The efforts allowed us to successfully demonstrate that the hydrogen atoms in steels localize at grain boundaries and dislocations, as shown in the top and bottom figures, respectively. Both of the right figures are 2-D slices from their corresponding 3-D visualizations at the left, showing the locations of hydrogen (red) at the grain boundaries/dislocations with carbon decorations (blue). These results were the first-ever observations of hydrogen at these microstructural features, providing direct evidence in support of the existing theories of hydrogen embrittlement and settling a long-term debate regarding hydrogen embrittlement mechanisms with substantial experimental evidence. We also found hydrogen atoms at the interface between carbide precipitates and the broader steel matrix. This exciting result demonstrates that carbide precipitates can be utilized to trap damaging hydrogen, providing a clear design pathway via the incorporation of such carbide precipitates into the engineering design of steels in order to create new materials that are highly resistant to hydrogen embrittlement. We believe this technique can be further applied for our understanding of how hydrogen behaves in other essential engineering materials, such as pearlitic steels, superalloys or aluminium alloys. More broadly, this cryogenic workflow could enable the analyses to the atomic structure of vitrified organic materials or even aqueous solutions. Such endeavours open up the powerful technique of atom probe to the chemical and life sciences field, complementing recent developments in cryo-electron microscopy and providing unprecedented 3D information about the composition of the hidden machinery of life.