
# RESPUESTAS DESDE EL ACERO PARA LOS MATERIALES ESTRUCTURALES EN UNA ECONOMÍA DE HIDRÓGENO

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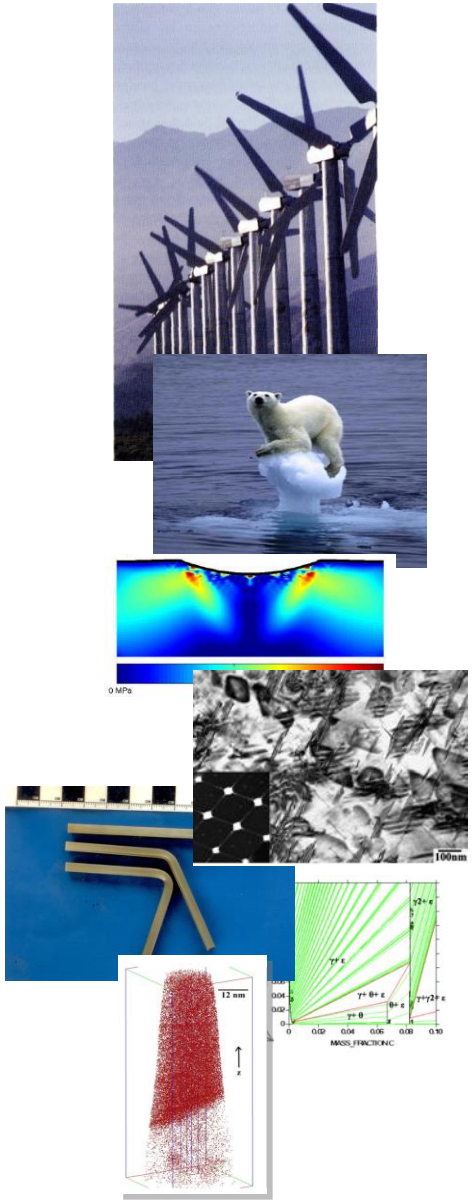

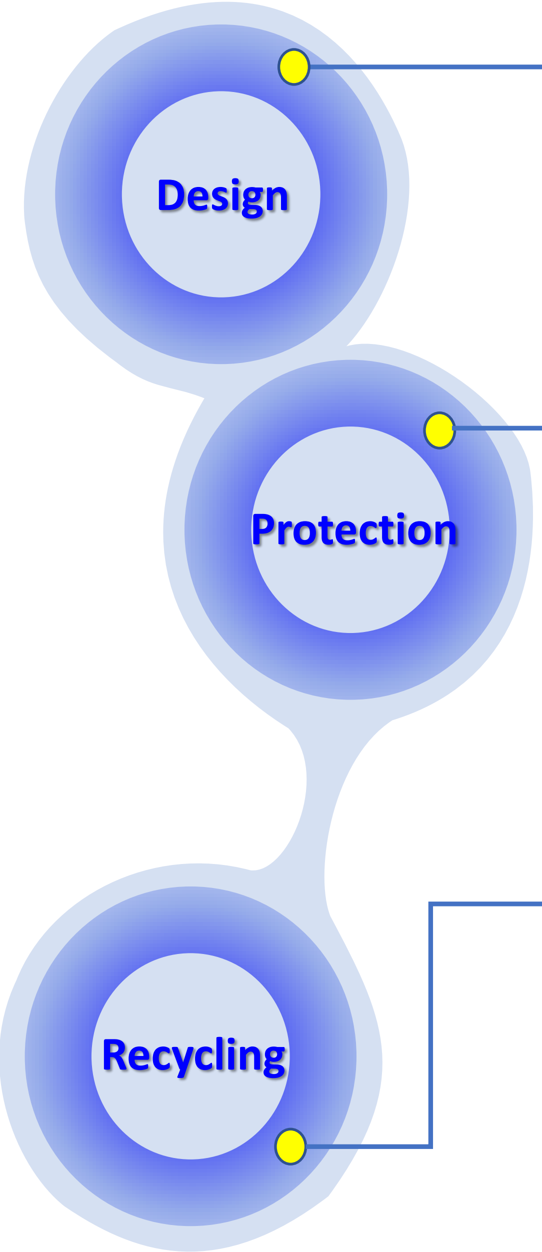


**Design and processing** of advanced metallic materials for transportation and construction.
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Development of **eco-innovative technologies** for the environment, recycling of materials and energy recovery.

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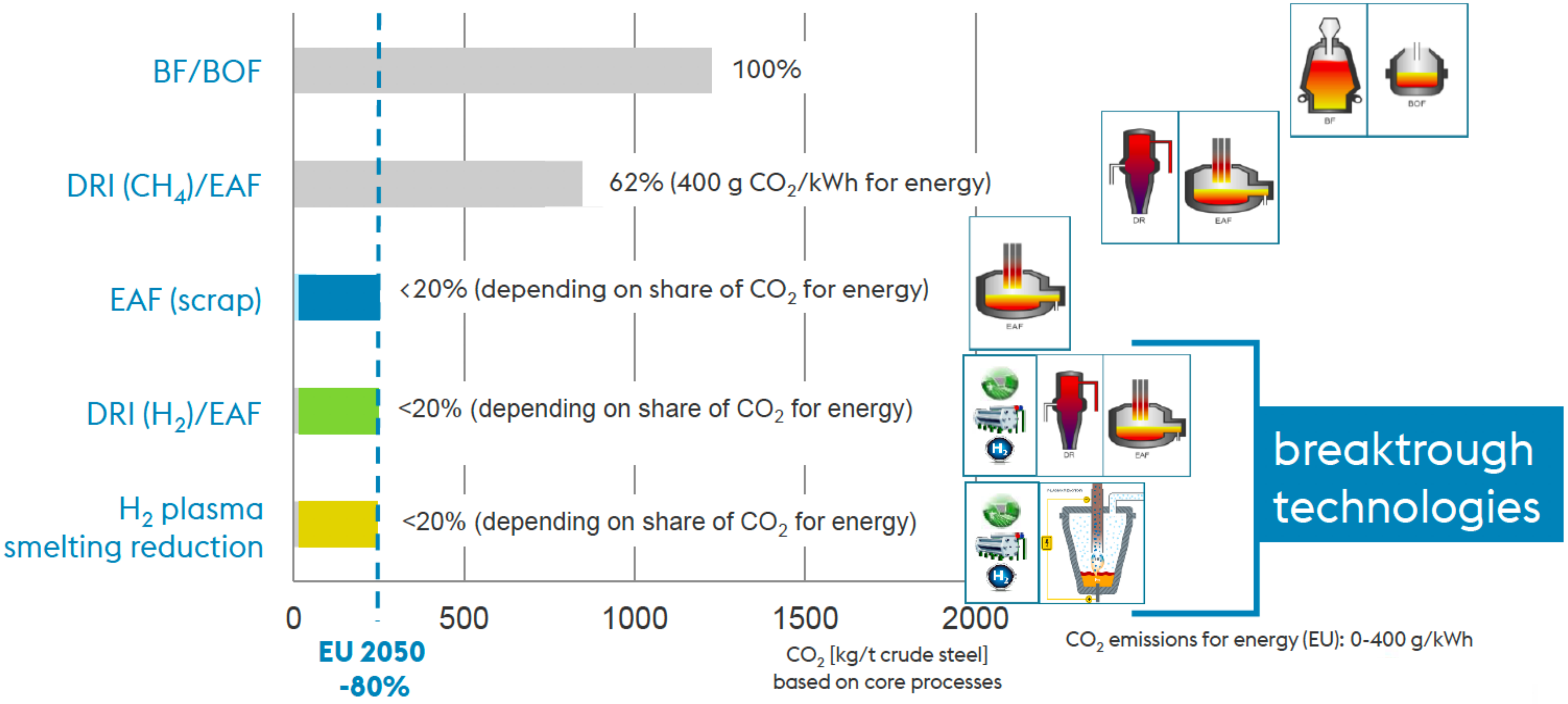
# Decarbonization of Steel Industry

Proposal from CENIM


- ❑Reduction of iron ore with $H_2$ strategies
- ❑Application of $H_2$ in EAF
- ❑Evaluation of $H_2$ in the value of chain of Steel produced with low $CO_2$ emissions
- ❑Alliance within CSIC for $H_2$-production

# Decarbonization of Steel Industry



# CLEAN STEEL

## Steel is vital to the EU's economy

### STEEL FOR CLIMATE CHANGE MITIGATION AND SUSTAINABLE GROWTH

**EU Steel research:**

| | |
|---|---|
| RFCS | ~150 running projects on steel processes, products and applications |
| SPIRE | Projects with cross-sectorial perspective |
| GREEN STEEL FOR EU | Technology roadmap & funding analysis to decarbonise steel industry |

**EU Steel production:**

**168 million tons/year**
second largest producer in the world
(10% of global production)

**166 billion €/year**
= 1.3% total EU GDP

**320.000 people employed** directly
+ 2.6 million EU jobs supported

Steel industry responsible for **20% to 25%** of Industrial $CO_2$ emissions in EU (ETS)

# Steel Decarbonization Roadmap

| | Breakthrough low-$CO_2$ technologies | Description | Development period | Actors involved | Estimated emission mitigation (compared to BF/BOF) | Estimated TRL |
|---|---|---|---|---|---|---|
| The Hydrogen path | **SALCOS** | Hydrogen-based DRI-EAF steelmaking. | 2017 - 2019 | Salzgitter AG, Fraunhofer | ~82% CO2 operated 55% H2<br>~95% CO2 operated 100% H2 | 1 - 3 |
| | **SUSTEEL** | Based on hydrogen-based DRI-EAF steelmaking (Hydrogen Plasma Smelting Reduction: HPSR process). | 2017 - 2019 | Voestalpine Group, K1-MET, Center, Primetals, MUL | not published any emission reduction values | 1 - 3 |
| | **HYBRIT** | Direct reduction of iron into steel using with hydrogen and renewable energy | 2018 - 2024 | SSAB, LKAB, Vattenfall | 95% | 2 - 4 |
| | **Carbon4PUR** | Based on transformation of the flued gas streams (containing CO2/CO) from the energy-intensive industries | 2017 - 2020 | Covestro, ArcelorMittal, Dechema | 20% – 60% | 2 - 4 |
| | **Steelanol** | Industrial waste gases into liquid fuels, through biotech solutions | 2018 - 2020 | ArcelorMittal, Primetals, Lanzatech, E4tech | 65% | 4 - 6 |
| | **Carbon2Chem** | utilisation of industrial waste gases | 2017 - 2030 | ThyssenKrupp AG, Fraunhofer, Max Planck Institute | n. a. | 2 - 4 |
| | **FReSMe** | captures CO2 from steel production for production of methanol fuel to be utilised in the ship transportation sector. | 2016 - 2020 | TataSteel, SSAB | n. a. | 3 - 5 |
| | **Hisarna** | New type of furnace in which iron ore is directly injected | 2017 - 2020 | TataSteel, Rio Tinto, ArclorMittal, ThyssenKrup, Voestalpine, Paul Wurth | 35% with scrap<br>80% with CCS | 4 - 5 |
| | **SIDERWIN** | electrolysis, transforming iron oxide | 2017 - 2022 | ArcelorMittal | 87% | 4 - 5 |
| | **IGAR** | Process integrated CO2-capture through top-gas recycling in a blast furnace. | Start 2020 | ArcelorMittal | n. a. | n. a. |
| | **PEM** | melting of low-quality scrap with metallurgy/natural gas | Start 2020 | ArcelorMittal, SMS Group | n. a. | n. a. |

# Steel Decarbonization Roadmap

## COST

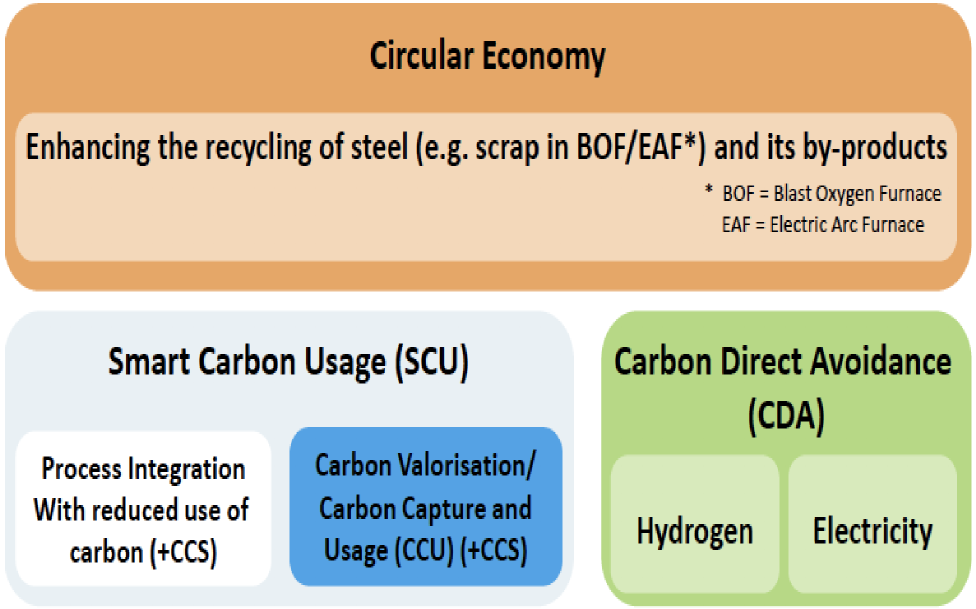
**<u>Current blast furnace requirements (all costs are approximate)</u>**

Oil – 81 kWh. Cost approximately €4. (Assumption: 8 liters of oil at a price of around $0.5/litre)
Coal – 5,510 kWh. Cost approximately €96. (Assumption: coking coal of 24 MJ/kg at $130/ton, $1.10=1€)
Electricity – 235 kWh. Cost approximately $11 (Assumption NordPool price of €45/MWh)
**Total energy and reducing agent cost per ton steel = €111**
Price of allowances per ton $CO_2$ from €5 up to €30
**Total cost per ton steel including $CO_2$ allowances = €121 - €171**

**<u>Hydrogen direct reduction route (all costs are approximate)</u>**

Graphite - 45 kWh. Cost €6. (Graphite, small flakes, $550 ton, energy value 32.8 MJ/kg)
Biomass fuel – 560 kWh. Cost €5 (Same price as low carbon content coal)
Electricity – 3,488 kWh. Cost €157. Assumption (NordPool price of €45/MWh)
**Total energy and reducing cost per ton steel = approximately €168**
Price of allowances per ton $CO_2$ from €5 up to €30
**Total cost per ton steel including $CO_2$ allowances = €169 - €171**

# EP-PP-CLEAN-STEEL-2019 - Research on reduction of C02 emissions in steel production



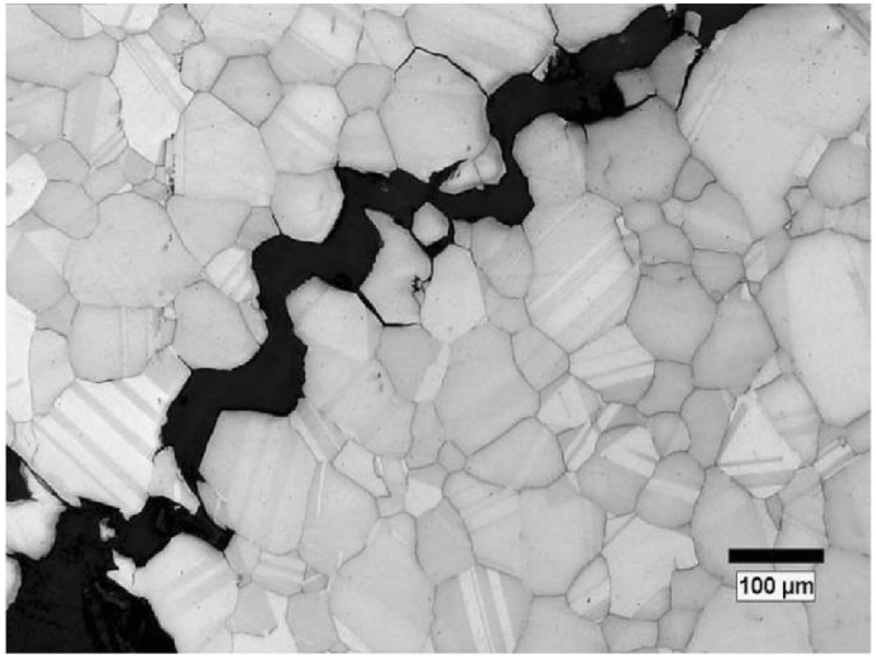

SPECIFIC OBJETIVES

1. Fostering the Smart use of carbon usage (SCU) technologies in steelmaking routes
2. Enabling steel production through CDA technologies
3. Developing deployable technologies to improve energy and resource efficiency (SCU Process Integration)
4. Increasing the recycling of steel scrap and residues to increase smart resources usage and further support a circular economy model in EU
5. Demonstrating clean steel breakthrough technologies contributing to carbon neutral steelmaking
6. Strengthening the global competitiveness of the EU steel industry

# CENIM/CSIC Project added value

# H2 embrittlement

In the year 1875, Johnson [1] revealed extraordinary changes in the toughness and breaking-strain of iron that was immersed temporarily in acid for just a few minutes. He further observed that the change is not permanent since "with the lapse of time, the metal slowly regains it original toughness and strength".




Since the early days of metallurgy it is known that:

1. it is hydrogen that embrittles steel, not the acid;
2. that the hydrogen is nascent, not molecular;
3. it is diffusible hydrogen that embrittles, so the phenomenon is reversible;
4. that stronger steel is more susceptible to embrittlement than softer versions.

Nice review by H.K.D.H. Bhadeshia, ISIJ Int. 56 (2016) 24-36

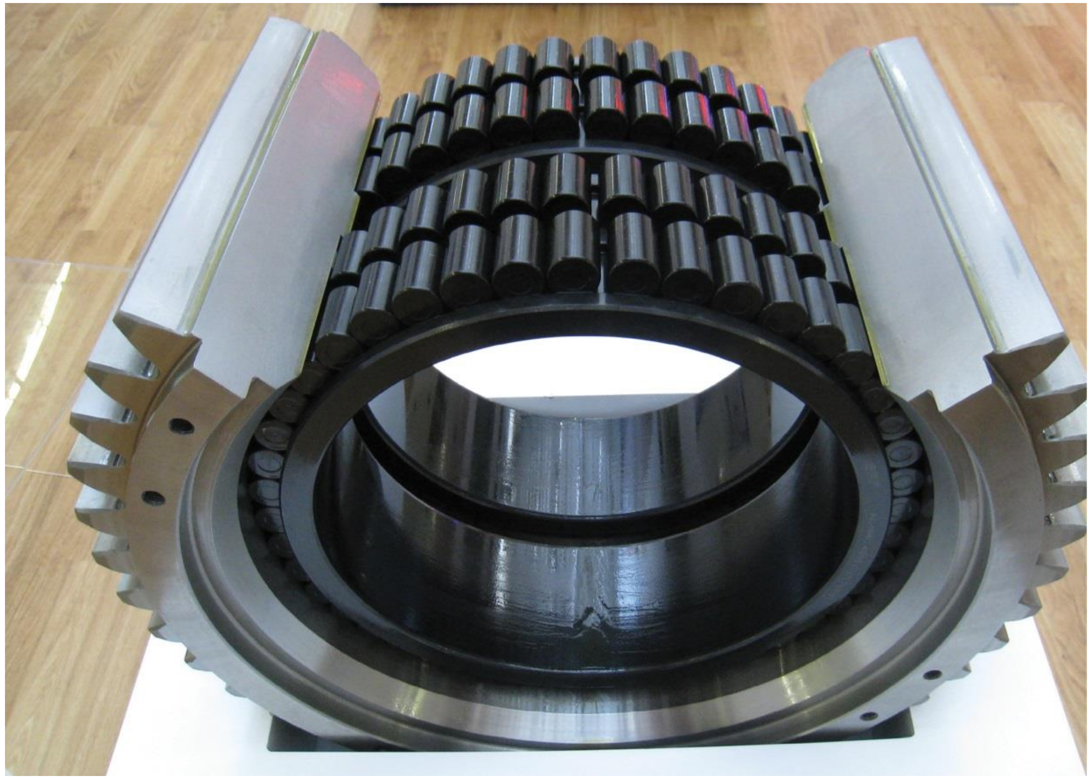
[1] W. H. Johnson: Proceedings of the Royal Society of London, 23 (1875) 168–179.

# Methods that resist hydrogen embrittlement

**Black oxide coating**

The inmersion of bare Steel in alkaline solution to promote the formation of hematite/magnetite layer in the Surface. The original goal of the black oxide coating was to provide some resistance to atmospheric corrosion and this function can be enhanced by immersion of the component in hot oil because the thin oxide film, typically 1-3 µm, can otherwise be permeable.

Black oxide has been applied to wind turbine bearings in an attempt to reduce the occurrence of axial cracks [1]. One interpretation is that the oxide retards the diffusion hydrogen into the steel.

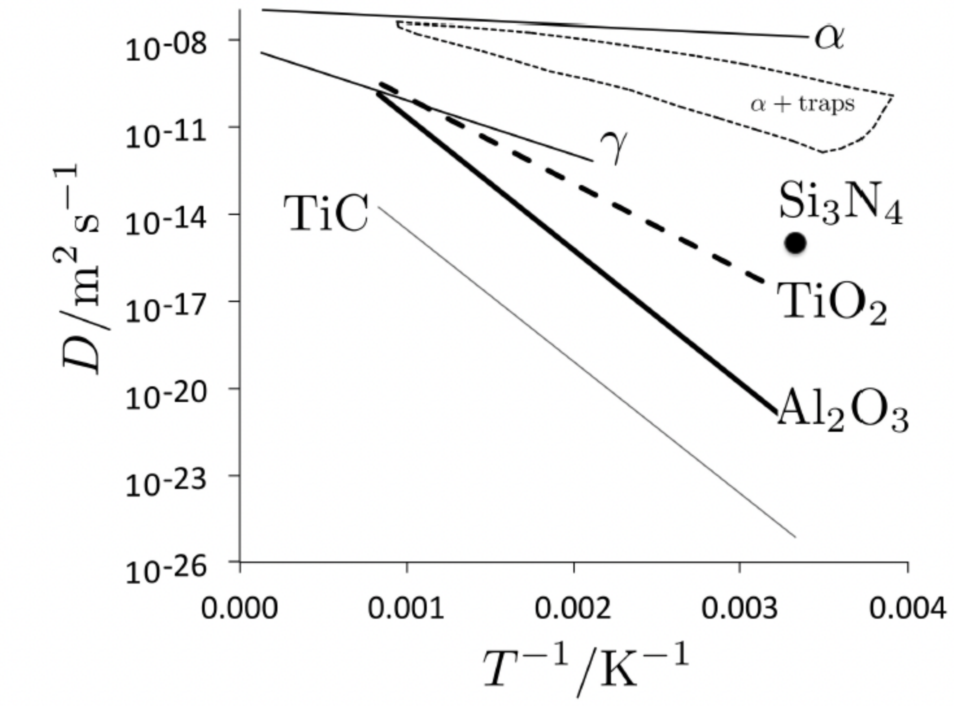


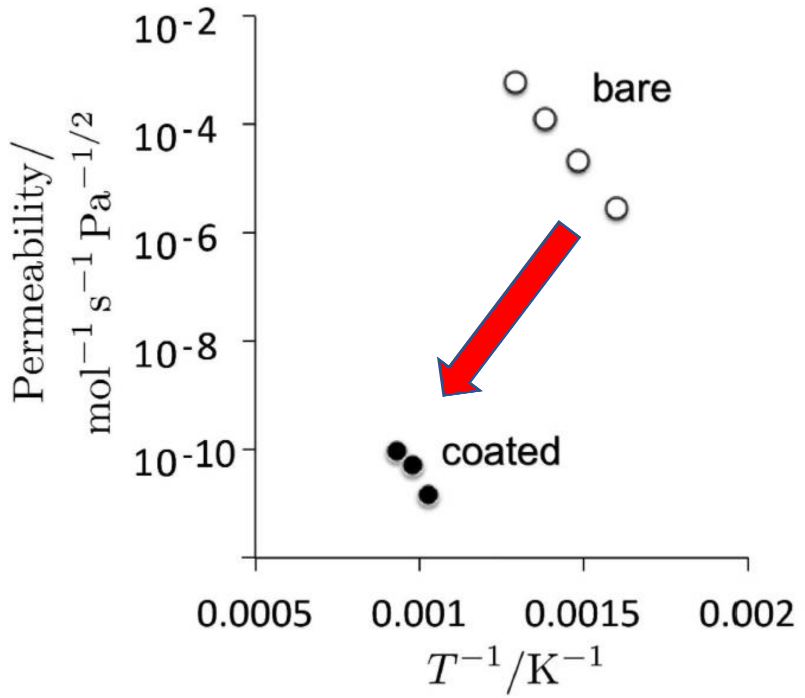
[1] R. Errichello, S. Sheng, J. Keller, A. Greco: Wind turbine tribology seminar: Tech. Rep. DOE/GO-102012-3496 February 2012: U. S. Department of Energy: Golden, Colorado, USA (2012)..

# Methods that resist hydrogen embrittlement

**Hard coatings**

Hard coatings such as alumina, TiC, TiN, $TiO_2$, BN, $H_3PO_4$ glass, $Cr_2O_3$ and WC, all are in principle formidable barriers to the permeation of hydrogen, although the actual performance depends on the structural integrity and defect structure of the coating



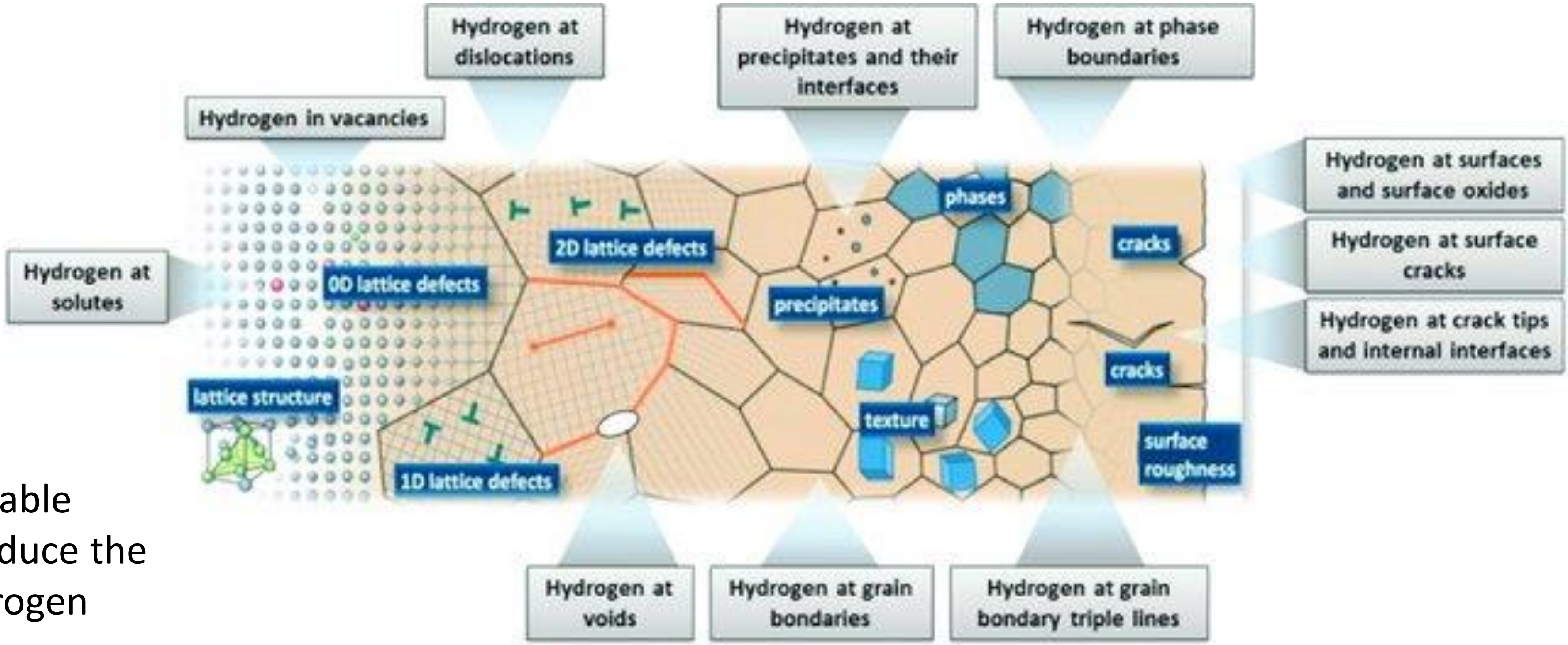




1 µm thick layer of crystalline α-alumina deposited using a plasma technique, on a reduced-activation tempered-martensitic steel has been shown to reduce the permeation flux by a factor of $10^3$[1]


[1] D. Levchuk, F. Koch, H. Maier, H. Bolt: Journal of Nuclear Materials, 328 (2004) 103-106.

# Methods that resist hydrogen embrittlement

**Hydrogen Trapping**




Given that it is diffusible hydrogen that is damaging to steel, any method that renders it immobile should mitigate its effects.

The general and physically justifiable consensus is that strong traps reduce the susceptibility of the steel to hydrogen embrittlement.

The presence of traps does increase the saturation hydrogen content of the steel but this trapped hydrogen is innocuous.

# Methods that resist hydrogen embrittlement

## Hydrogen Trapping: Substitutionally-Alloyed Carbides and Nitrides

As an example, it is illustrated the trapping capacity of engineered desing Steel novel steel has been designed for use in the oil and gas industry, displaying properties comparable with the currently available F22 grade

MATERIALS SCIENCE AND TECHNOLOGY
https://doi.org/10.1080/02670836.2018.1475919

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Designing steel to resist hydrogen embrittlement: Part 1 – trapping capacity

T. I. Ramjaun[a], S. W. Ooi[a], R. Morana[b] and H. K. D. H. Bhadeshia[a]

[a]University of Cambridge, Cambridge, UK; [b]BP Exploration, Sunbury-on-Thames, UK

Extracting resources from deep oil and gas reservoirs can be an attractive prospect that presents significant technical challenges for the industry. Deeper reservoirs require materials that can **perform at higher operating temperatures and pressures**. Simply increasing steel strength for such sub-sea applications is not appropriate because **the accompanying microstructure exacerbates the susceptibility to hydrogen embrittlement**.

# Methods that resist hydrogen embrittlement

**Hydrogen Trapping: Substitutionally-Alloyed Carbides and Nitrides**

The carbide particles that precipitate at temperatures where substitutional solutes such as molybdenum, vanadium, niobium and titanium become mobile over length scales of a few nanometres are particularly interesting from the point of view of hydrogen trapping.

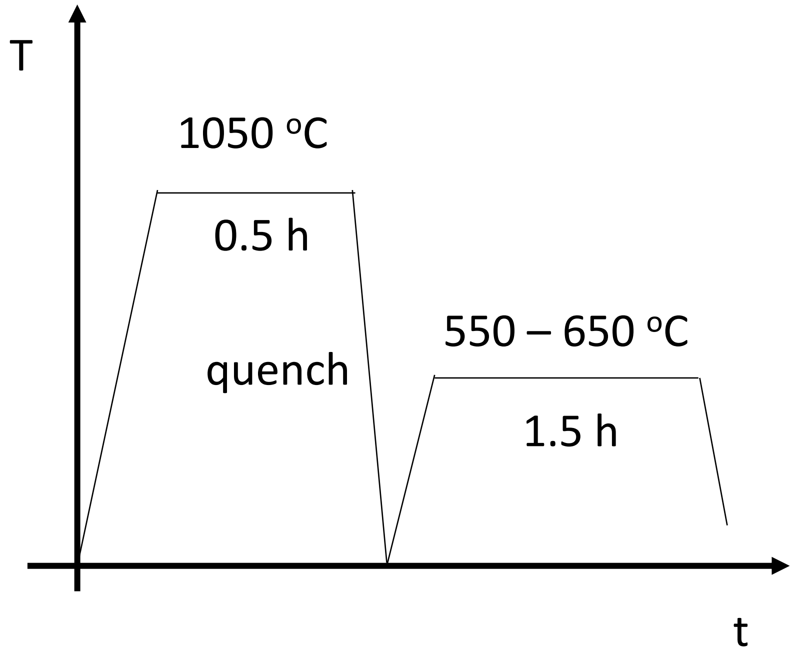
Vanadium based carbides have long been known to be effective in mitigating hydrogen-induced delayed fracture in strong bolting steels. it has been demonstrated that the state of coherency with the ferrite influences the hydrogen trapping capacity, emphasising the role of the strain fields around the carbides.

# Methods that resist hydrogen embrittlement

**Hydrogen Trapping: Substitutionally-Alloyed Carbides and Nitrides**

There are several reasons why a secondary-hardening system would be the preferred microstructure. Foremost, the strength needed is readily generated due to the precipitation of Mo and V-rich carbides. The particles serve an additional vital purpose, if the heat treatment is controlled so that they are small enough to be partially coherent with the matrix, the resulting strain fields can interact with the hydrogen and trap it so that it can no longer do harm.

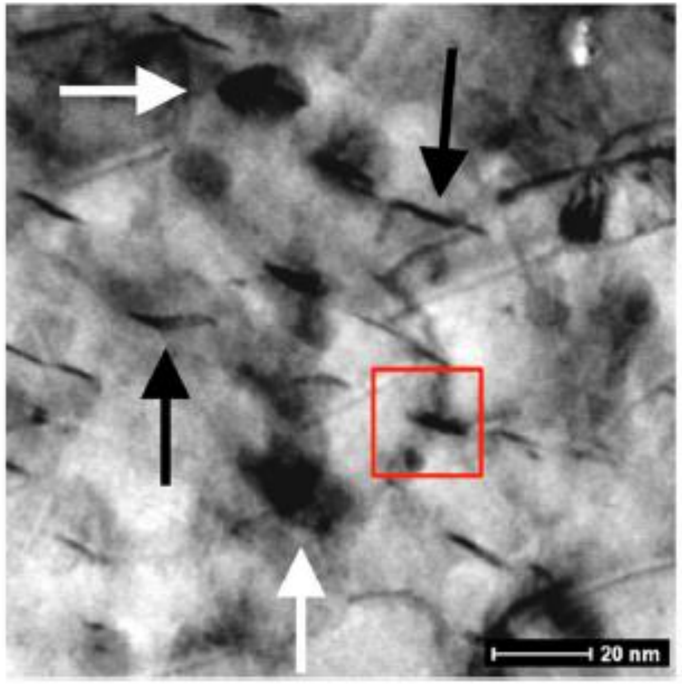
| Alloy | C | Mn | Mo | Cr | V | Nb |
|---|---|---|---|---|---|---|
| With V | 0.5 | 0.3 | 0.7 | 1.0 | 0.3 | 0.03 |
| Without V | 0.39 | 0.82 | 0.16 | 1.11 | - | 0.03 |

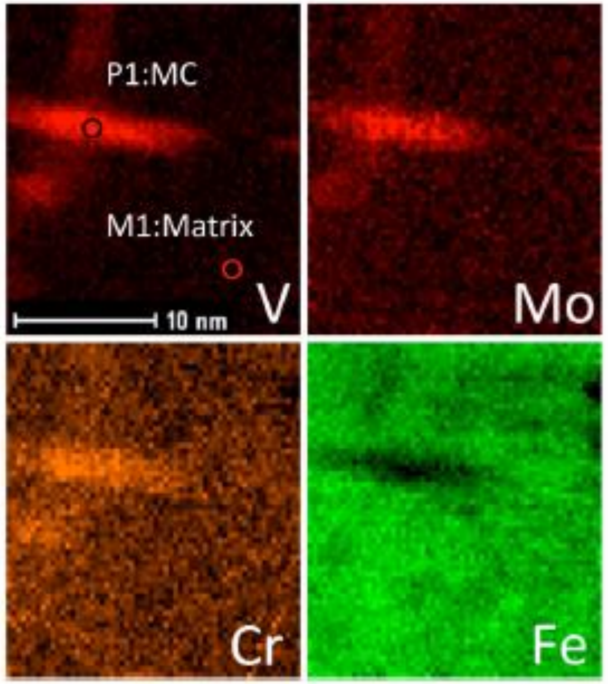


# Methods that resist hydrogen embrittlement

**Hydrogen Trapping: Substitutionally-Alloyed Carbides and Nitrides**

Transmission electron microscopy (TEM), show precipitates within the martensite laths and also at the lath boundaries. These fine platelet Cr-, V- and Mo-rich precipitates are less than 20 nm in length and 5 nm in thickness

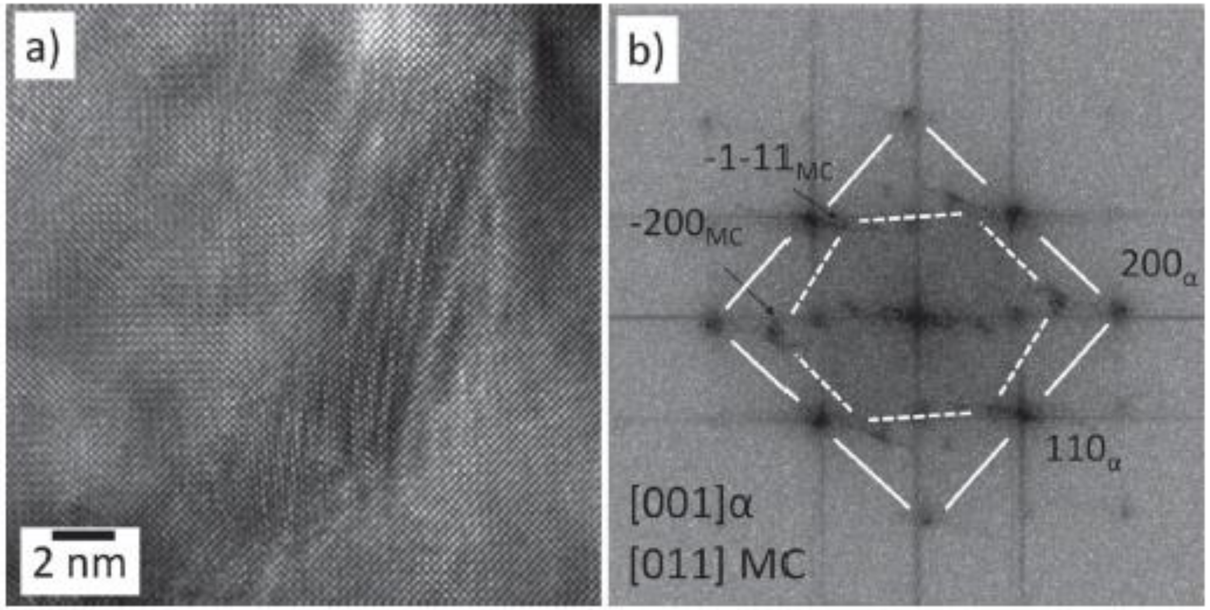



Fine V–Mo–Cr-rich carbides observed in sample tempered at 600 $^{o}C$ for 10h.

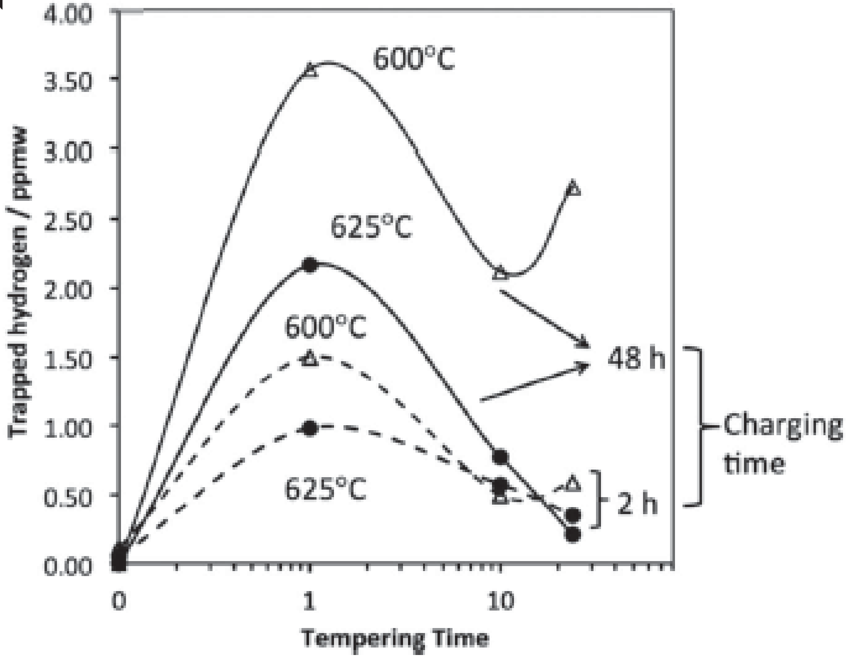
# Methods that resist hydrogen embrittlement

**Hydrogen Trapping: Substitutionally-Alloyed Carbides and Nitrides**




MC precipitate observed after tempering at 600°C for 10h; (a)HRTEM image (b) FFT diffractogram of (a) showing that the alloy carbide possesses Baker and Nutting orientation relationships with martensite lath.

Thermal desorption data: **total trapped hydrogen** indicates that extended hydrogen charging times are required to achieve saturation as the hydrogen trapping capa



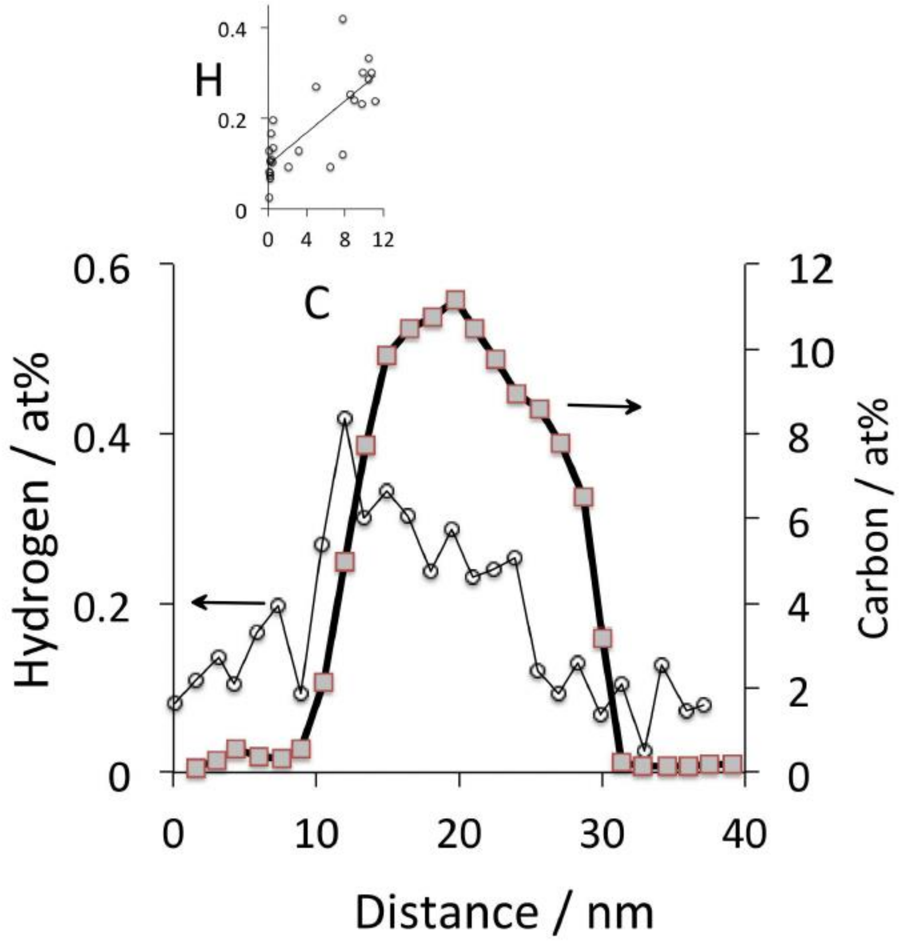
# Methods that resist hydrogen embrittlement

**Hydrogen Trapping: ε-Carbides**

Coherent ε-carbides ($Fe_2C$) are likely to be hydrogen traps and even form a compound $Fe_2HC$, in addition to acting as a trap via its coherency strain fields.

Atom-probe tomography has revealed the segregation of hydrogen to ε-carbide, and the data seem to suggest that the hydrogen is in fact inside the carbide particles.

On the other hand, incoherent precipitates such as cementite, represent ineffective traps for hydrogen.



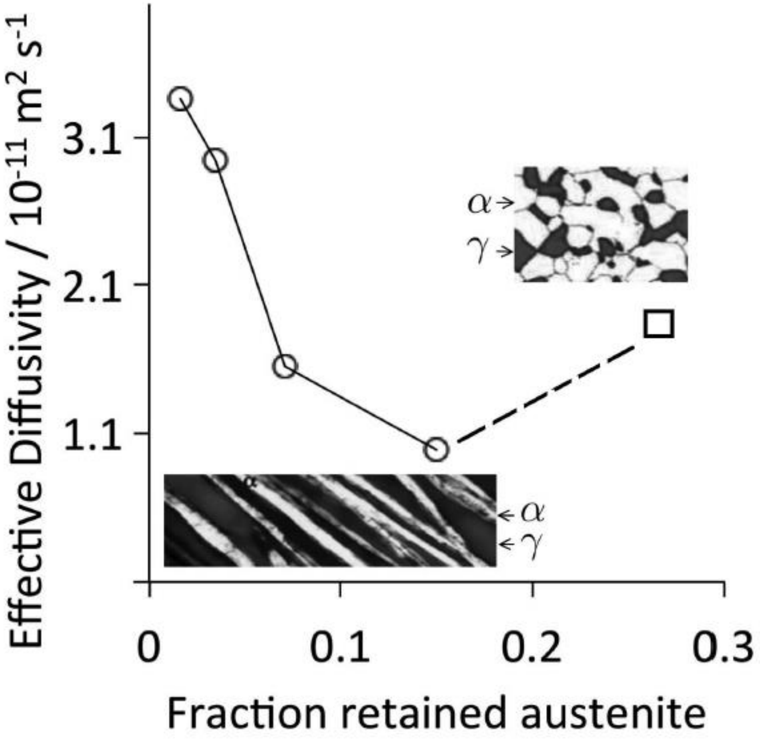

Atom probe data taken across an ε-carbide particle in a hydrogen-containing steel. (After X. Zhu, W. Li, T. Y. Hsu, S. Zhou, L. Wang, X. Jin: Scripta Materialia, 97 (2015) 21–24.)

# Methods that resist hydrogen embrittlement

**Hydrogen Trapping: retained austenite**

Retained austenite is able to act as a trap for several:

- The solubility of hydrogen is greater in that phase
- The low rate at which hydrogen can diffuse in austenite
- The γ/α interface is a strong trap so that once the hydrogen enters the austenite, it is more difficult for it to leave it [1]
- Retained austenite also reduces the overall diffusivity and permeability of hydrogen through the Steel [2]



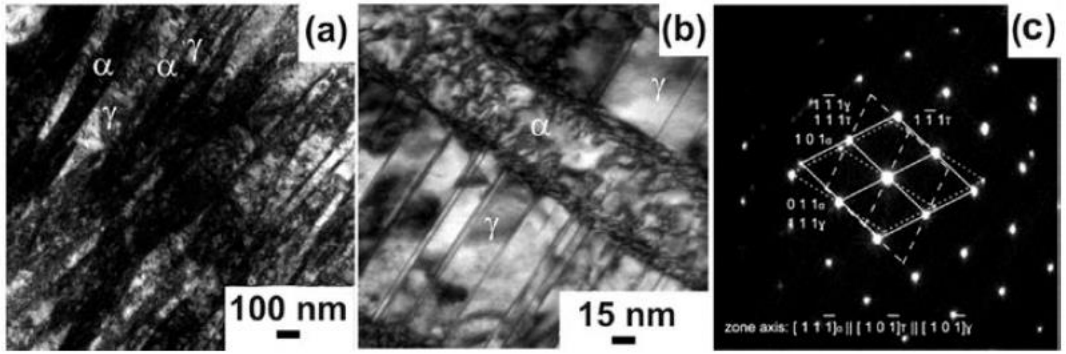

The diffusion coefficient for hydrogen through nanostructured bainite (circles) and a different duplex Steel where the austenite does not percolate (square). After [2].


[1] A. Turnbull, R. B. Hutchings: Materials Science & Engineering A, 177 (1994) 161–171.

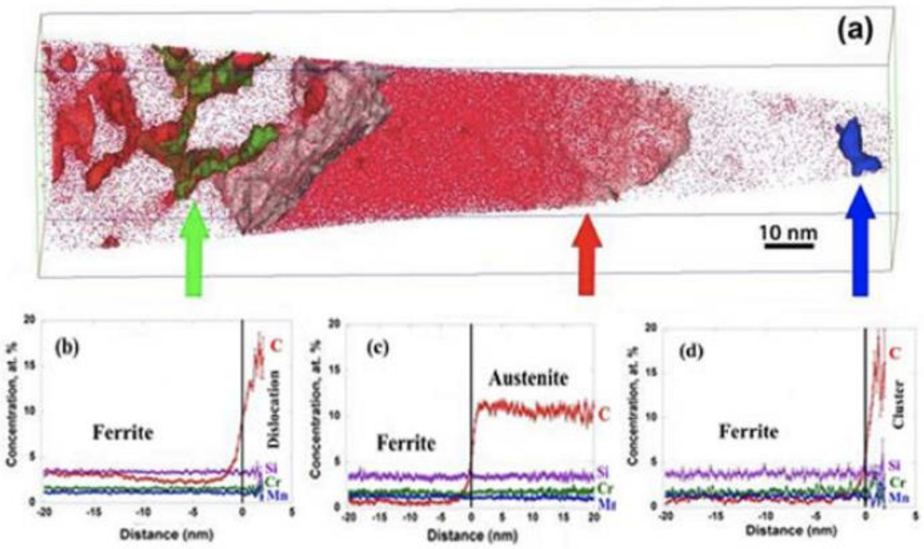
[2] L. C. D. Fielding, E. J. Song, D. K. Han, H. K. D. H. Bhadeshia, D. W. Suh: Proceedings of the Royal Society of London A, 470 (2014) 20140108.

# Methods that resist hydrogen embrittlement

**Hydrogen Trapping: retained austenite**




TEM images of nanostructured bainite transformed at 200 ºC for 10 days: (a) general microstructure; (b) nanoscale twins in retained austenite; (c) corresponding diffraction pattern. α is bainitic ferrite, and γ is austenite. **CENIM, Tohoku University (Japan) and National Taiwan University Collaboration.**

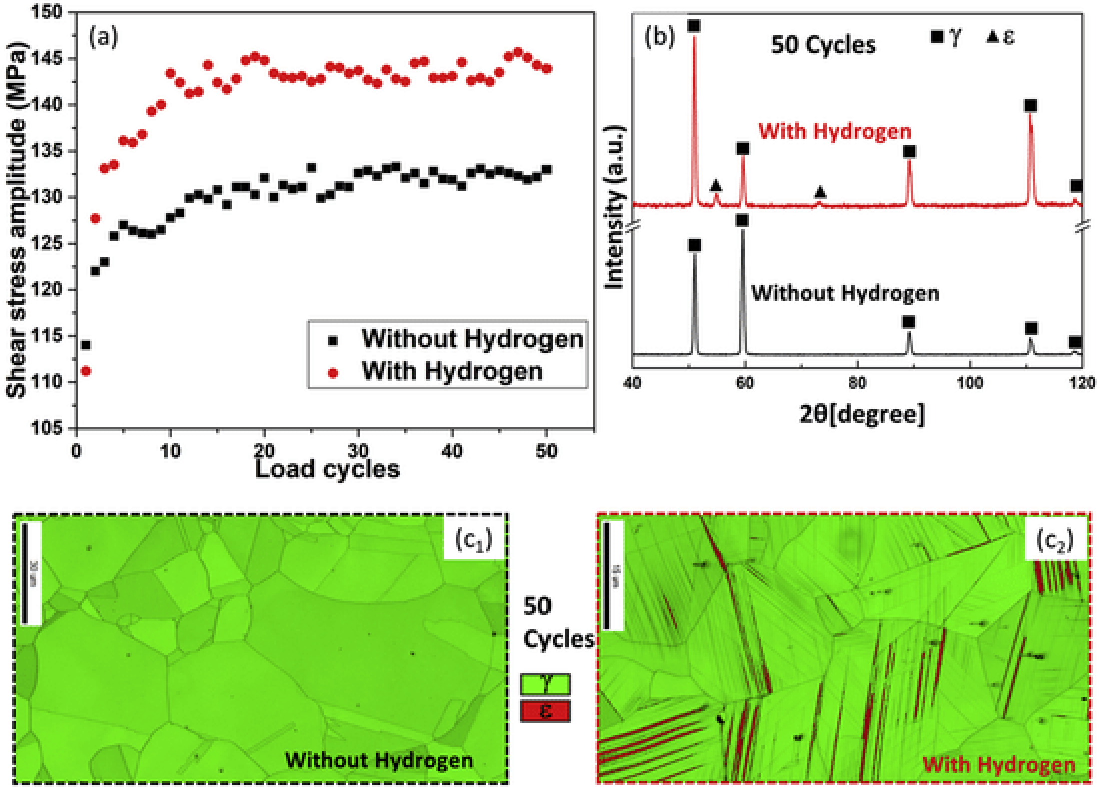



Atom probe tomography results on (a) carbon iso-concentration surfaces at 8 at. % C superimposed with the carbon atom map, and proximity histograms across (b) a dislocation network, (c) a ferrite/austenite interface, and (d) a carbon cluster in bainitic ferrite after transformation at 200ºC in a nanocrystalline bainitic steel. **CENIM and Oak Ridge National Laboratory Collaboration funded by the Office of Basic Energy Sciences, US Department of Energy.**

# Methods that resist hydrogen embrittlement

**Hydrogen Trapping in austenitic stainless steels**

Due to their high nickel and molybdenum content, 316L-type steels has high stacking fault energy; a feature that promotes cross slip and is generally associated with superior hydrogen compatibility.




Technical Reference on Hydrogen Compatibility of Materials

Austenitic Stainless Steels:
Type 316 (code 2103)

Prepared by:
C. San Marchi, Sandia National Laboratories

Editors
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B.P. Somerday
Sandia National Laboratories

The decrease of the Stacking Fault Energy (SFE), induced by hydrogen in austenitic stainless steels, was always invoked to explain the formation of {epsilon}-martensite at room temperature during cathodic charging of hydrogen.
(A. Inoue, Y. Hosoya, and T. Masumoto, Trans. ISIJ. 19, 170 (1979).)

# Conclusions

That hydrogen embrittles iron, both austenitic and ferritic, is in no doubt and it does so at incredibly low average concentrations. It has been known since 1875 that it is diffusible hydrogen that is harmful. The conventional wisdom is that diffusion is necessary so that the hydrogen can concentrate at stress concentrations such as the tips of sharp cracks and therefore has greater consequences than indicated by a low average concentration

Many coatings exist that have been demonstrated to reduce either the outgassing of hydrogen in vacuum systems, or as diffusion barriers to the ingress of hydrogen. However, the choice of coatings available decreases when the coating has to perform multiple functions, for example to resist abrasion and impact.

Some phases within steels can actually soak-up hydrogen, for example the retained austenite may be the most promiscuous hydrogen sink. Retained austenite can have a different function, that of acting as a diffusion barrier to hydrogen in predominantly ferritic steels. However, its volumen fraction must be above a percolation threshold so that the ferrite is microscopically isolated.

The actual trapping capacity from the vanadium carbides is in fact much greater than any other of thre traps mentioned. The strain fields around coherent precipitates acts as effective traps for hydrogen. The microstructure consisting on a dispersion of fine plateshaped V–Mo–Cr-rich carbides in a martensitic matrix combine both strength and resistance to hydrogen embrittlement.



April, 1937, Net Paid Daily Circulation: 357,857

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## Zep Crash Shocks World

(Story on page 2)



Hindenburgh Zeppelin Crash, 1937