Fighting corrosion through industry/academia collaborations.

The Chevron and Woodside Chair in Corrosion Story.

Mariano Iannuzzi, Sofia Hazarabedian, Kod Pojtanabuntoeng, and Andy Viereckl.

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Industry/Academia Collaborations — The Good.

High Strength Low Alloy Steels for Sour Service.

Self-inhibiting insulations — Preventing CUI using active corrosion protection.

Age-hardened Nickel Alloys — Effect of Thermomechanical Processing.

Hydrogen Induced Stress Cracking of 25Cr SDSS.

Industry/Academia Collaborations — The Bad and the Ugly.

Conclusions.

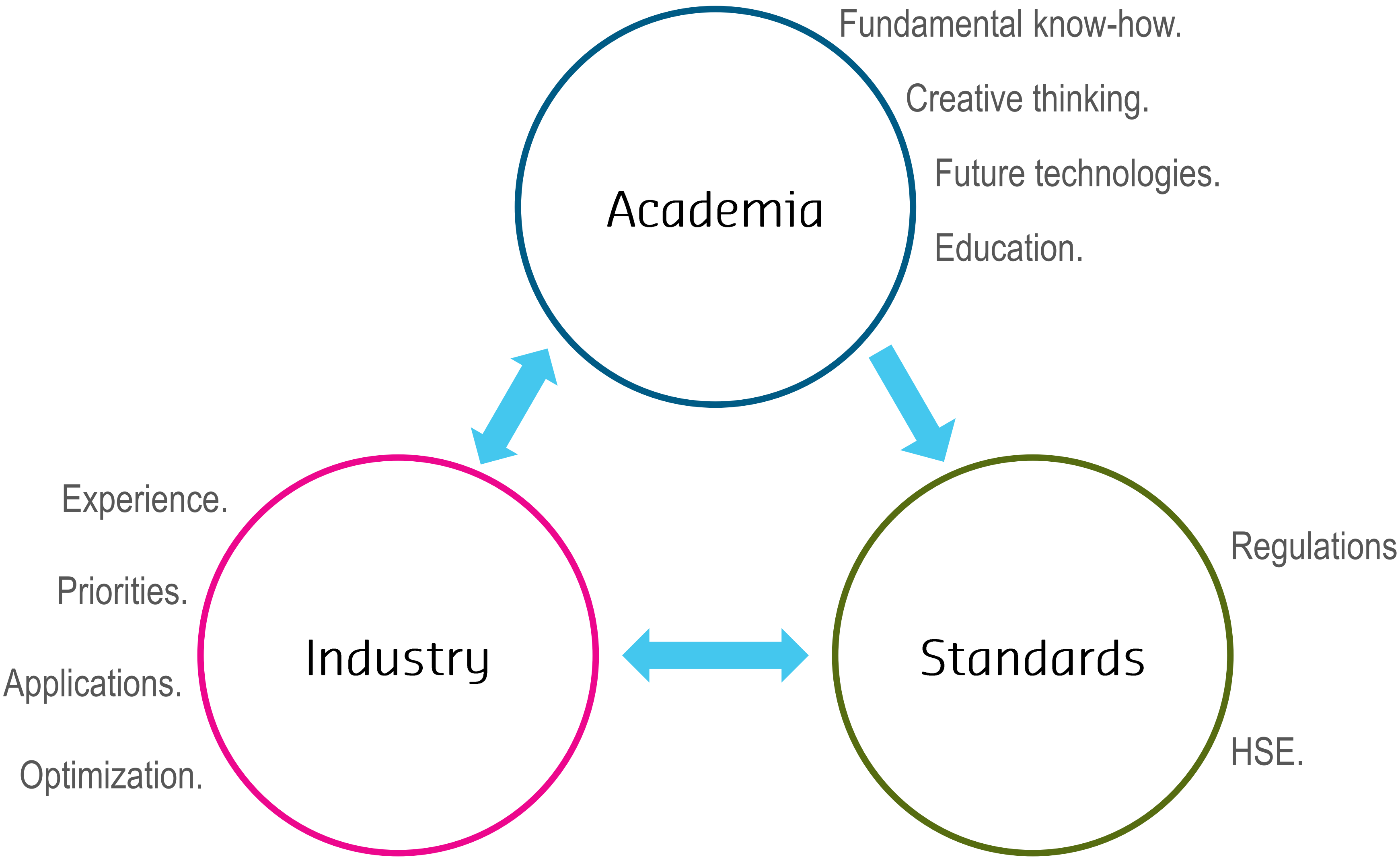
Industry/Academia Collaborations

The Good.

The best approach to solving a problem is to look at it from multiple perspectives.

Image Credits: LINK.

Industry-Academia partnerships create a virtuous innovation cycle.



"My team has created a very innovative solution, but we're still looking for a problem to go with it."

We work together with industry in solving challenging, and recurring corrosion and materials issues.

Identify most pervasive problems.
High return, improved safety, quick turnaround.

Perform "jugular experiments."
Move decision process in a cost-effective way.

Research & Development.
Evaluate new technologies or solutions further.

Implementation.
New product or technology introduction cycle.

Admittedly, materials and corrosion are not considered necessarily the primary cost drivers.

However, cumulative advancements across the value chain can lower cost, improve on-time delivery, increase reliability, ensure safety, etc.

Silver Bridge collapse. On December 15, 1967, the 1460-foot suspended portion of the Silver Bridge collapsed due to environmentally assisted cracking. More than 30 vehicles plunged into the water and 46 people died as a result. LINK.

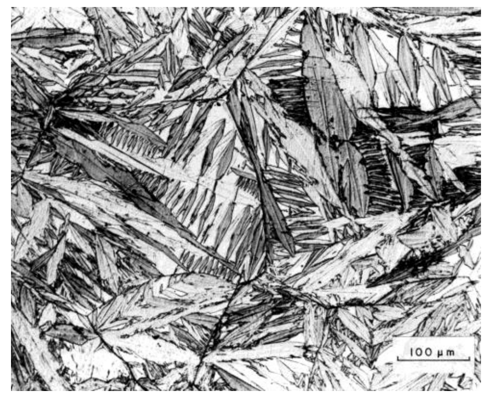
We favor a reverse multi-scale approach to R&D:

Field

First, we focus on problems that affect, e.g., production and fabrication.

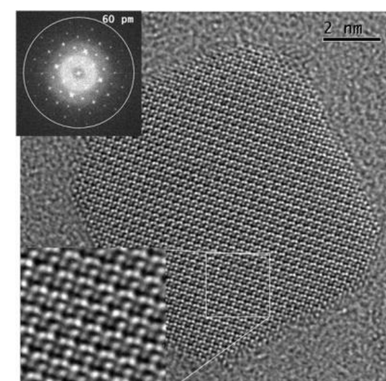
Fabrication

µm



Microstructure

<nm



Lattice

Then, we proceed to define the best experimental approach to address the problem in the most time and cost effective way.

Together with Chevron and Woodside, we identified three strategic areas to prioritize R&D.

Pushing boundaries
High Strength Materials.
Corrosion Resistant Alloys.

Design optimization
New technologies &
Solutions.

Prevention
Corrosion management.

After a series of technical workshops, we established five Strategic Research Themes.

The themes cover different corrosion and materials topics, addressing some of the most costly (and rewarding) challenges.

- High strength low alloy steels for sour service.
- Preventing CUI by Self-inhibiting insulations.
- Iron contamination of stainless steels.
- Boundaries of CRAs for seawater service.
- Age-hardening nickel alloys: TMP & Hydrogen

Hight Strength Low Alloy Steels

Challenging ISO 15156.

Project goal

The goal of this project is to qualify High Strength Low Alloy (HSLA) steels that are commercially available for intermediate sour service with improved strength (SMYS>100ksi), toughness, hardenability, and fatigue life compared to conventional steels used for pipelines and heavy forgings.

Overcome ISO 15156 Restrictions.

State-of-the-art: low alloy steels for sour service equipment:

Heavy Forgings

Yield strength rarely exceeds 80–85 ksi (550–586 MPa) for HSLA steels in sour service.

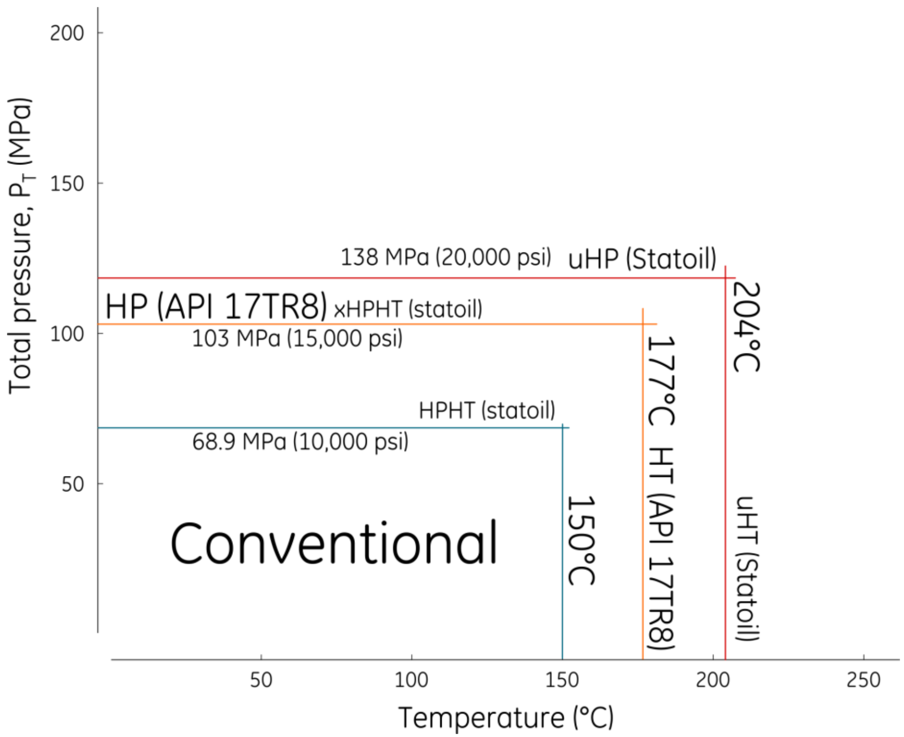
Line Pipe

The most common line-pipe steel grade is API X65, with an SMYS = 65 ksi (448 MPa)

Materials used in the **Oil & Gas industry** can face some of the **most challenging environments**.

The development of unconventional oil reserves will benefit from a new generation of low alloy steels.

HPHT: P > 103 MPa, T > 177 °C



Arctic fields: T < -60 °C

Photo credit: https://bit.ly/2FaWMYj

The target mechanical and technological properties of our ideal HSLA steel are:

Specified Minimum Yield Strength

690 – 725 MPa (100-105 ksi)

“Good” weldability

High Hardenability

H >> 12 cm (5 inch)

Intermediate Sour Service

Excellent Toughness

CVN = 100 J @ -60 °C
DBTT = -60 °C

CVN: Charpy V-notch impact energy.
DBTT: Ductile-Brittle Transition Temperature.

Commercial HSLA steels used in other industries.

Their nickel content = 2.0 to 4.0 wt.%.

Shipbuilding steel

HY-100
HSLA-100

Pressure vessel/structural steel

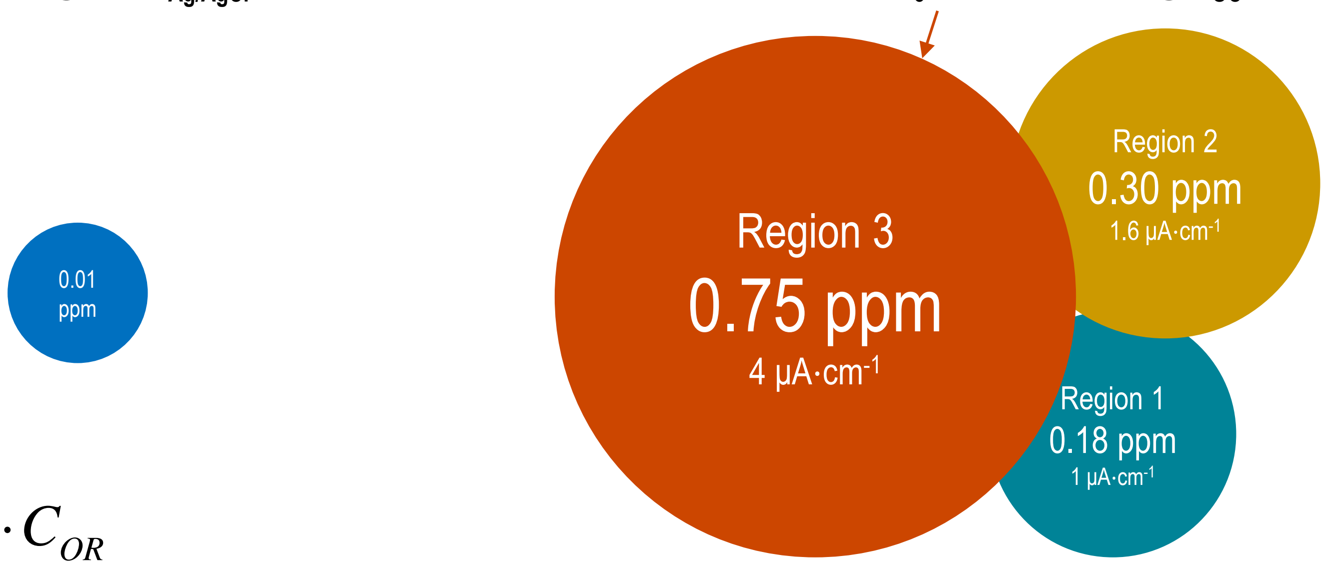
P690 QL2
S690 QL

Nuclear Industry: A508 Gr.4N

In O&G environments, H_2S acts as a hydrogen recombination poison, the amount of hydrogen entering the steel by corrosion at the open circuit potential (E_{OC}) in a sour environment is much higher than, e.g., that caused by the external cathodic protection system.

The sub-surface H concentration in the lattice and trap sites (C_{OR}) was found to be >70 times higher in the presence of H_2S than in samples cathodically polarized to -1.1 VAg/AgCl in seawater.

Cathodic protection	**Sour service**
Seawater @ -1.1 $V_{Ag/AgCl}$	**5% NaCl + 0.5% CH_3COOH pH = 2.7 @ E_{OC}**



$D_{EFF} \approx 7\cdot10^{-6}\ cm^2\cdot s^{-1}$

$$J_{SS} \cdot L = D_{EFF} \cdot C_{OR}$$

- B.J. Berkowitz, H.H. Horowitz, Journal of The Electrochemical Society 129, 3 (1982): p. 468-474.
- H. Husby, P. Wagstaff, M. Iannuzzi, R. Johnsen, M. Kappes, Corrosion 74, 7 (2018): p. 801-818.
- M.J. Cancio, B. Giacomel, G. Kissner, M. Valdez, F. Vouilloz, "High Strength Low Alloy Steel for HPHT Wells," Offshore Technology Conference-Asia, paper no. OTC-24746-MS (Kuala Lumpur, Malaysia: Offshore Technology Conference, 2014).

In 2018, we engaged with steel producers worldwide.

Our goal was to partner with vendors, learning from their steel-making expertise on promising HSLA steel families.

- Japan Steel Works (Japan)
- Siderforgerossi (Italy)
- JFE (Japan)
- Brück Forgings (Germany)

JSW
THE JAPAN STEEL WORKS, LTD.

SFRG

JFE

BRÜCK®

We traveled the world to find the finest HSLA steels!

We found extraordinary hospitality and a keen interest in the research.

Samurai Sword Museum
Japan Steel Works.

Siderforgerossi Headquarters
Arsiero, Italy.

Japan Steel Works partnership.

THE JAPAN STEEL WORKS, LTD.

JSW will initially provide 4 forged plates of ASTM A508 Gr. 4N

C %	Mn %	Si %	P %	S %	Cr %	Ni %	Mo %	Cu %	Al %
0.23	0.2-0.4	0.4	0.02	0.02	1.5-2.0	**2.8-3.9**	0.4-0.6	0.25	0.025
Ti %	**V %**	**Nb %**	**Ca %**	**B %**			**SMYS (KSI)**		**CE %**
0.03	0.03	0.01	0.015	0.003			100		**0.9-1.1**

Example of a 128 ton component made from **ASTM A508 Gr. 4N.**

Girth welding operation!

Siderforgerossi partnership.

SFRG will initially provide 2 forged bars of S690 QL

C %	Mn %	Si %	P %	S %	Cr %	Ni %	Mo %	Cu %	Sn %
0.13	0.70	0.33	0.006	0.004	0.47	0.83	0.52	0.09	0.006
Al %	**Ti %**	**V %**	**Nb %**	**Zr %**	**B %**	**Ca %**	**N %**	**Nb %**	**CE %**
0.038	0.001	0.005	0.001	0.001	0.0005	0.0003	0.0083	0.002	**0.507**

The project is divided in two Phases:

The Scope of Work combines fundamental and applied research.

HSLA steels for sour service applications

Phase 1

- **Commercial HSLA steel grades – "As received."**
- **HSC under cathodic protection.**
- **SSC under simulated H_2S conditions.**

Phase 2

- **Research-grade low alloy steels.**
- **Optimize microstructure through heat treatment.**
- **Sour service performance with differing Ni contents.**

HSC: Hydrogen Stress Cracking & SSC: Sulfide Stress Cracking.

The Curtin Corrosion Centre has just commissioned a unique EXTREME Laboratory, which allows testing in pure high-pressure H_2S, H_2S mixtures, and hydrogen gas.

The EXTREME Laboratory is the only one of its kind in Australia, and one of the few in the world.

Proof Rings, Slow Strain Rate Testing, and Custom rigs.

H_2 Research
Microbial Corrosion & Hydrogen Embrittlement.

High pressure autoclave testing.

Self-Inhibiting Insulations

Preventing CUI using active protection.

Current mitigation strategies are unsatisfactory.

A definitive solution to Corrosion Under Insulation (CUI) shall include an active corrosion protection strategy.

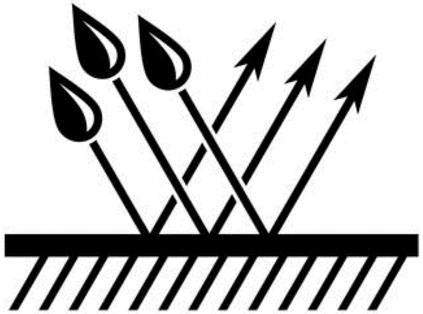
Inhibitors – A possible approach.

According to Fitzgerald et al., CUI management accounts for up to 10% of the total maintenance budget.[1]

Traditional CUI management plans include:

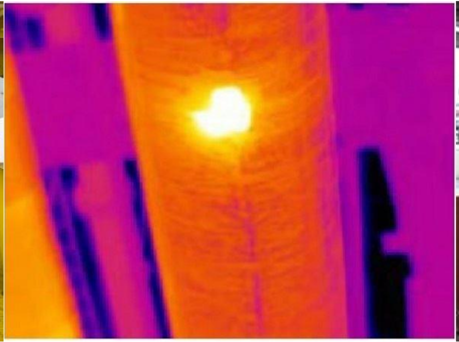
Exclude Water

NDE Inspections



123rf.com

Coatingsystems.com



Corrosionpedia.com

G. Hart, Insulation.org, 2014

Organic coatings

Repair

[1] B.J. Fitzgerald, S. Winnik, J. Prot. Coatings Linings. April (2005) 52–57.

Preventing water from entering insulated systems has been proven to be an unreliable strategy.

Although protective coatings can be effective when properly specified and applied, coatings degrade over time (on average 5 to 13 years).

Inspection and maintenance are vital to minimize risks, but insufficient.

NACE SP 0198: corrosion inhibitors and cathodic protection are less effective than coatings.

https://info.aerogel.com/hubfs/Corrosion%202%20(2).jpg

In this project, we aim at answering key decisive questions:

Can the service life be extended?

Can CUI risks be minimized?

Can the inspection frequency be reduced?

Can coating repairs be postponed?

Project goals

Assess commercially available chemical treatments for CUI that can provide active corrosion protection to insulated carbon steel.

Identify critical functions governing inhibition efficacy; e.g., pH neutralizing effects, film forming, and precipitating effects.

We identified two chemical treatment options that provide corrosion protection by two different mechanisms.

Silicate-containing insulations
(Calsil, Expanded perlite).

6 month test duration. Sweating condition 7 °C to 18 °C.

A. Kulprathipanja, M. Jones, K. Melton, The comprehensive results from "real-world" corrosion under insulation test protocols, 2018.

Volatile corrosion inhibitor.

5 days test duration. 8h@45°C + 8h@25°C. 20 mL 200 ppm NaCl solution every 48 h

B. Bavarian et al., "" Protection Effectiveness of Vapor Corrosion Inhibitor for Corrosion Under Insulation" CORROSION 2015, Paper No. 5448.

D. Shong, "Understanding Insulation Chemistry Proven to Inhibit Corrosion Under Insulation (CUI)," Corrosion 2017, paper no. 8876.

The are no published track records regarding CUI mitigation.

Other questions raised are inhibitor depletion & replenishment frequency, effectiveness on corroded CS, and compatibility with operating conditions.

Silicate-containing insulations
(Calsil, Expanded perlite).

pH neutralizing effects

Precipitation of $Fe_2(SiO_3)_3$

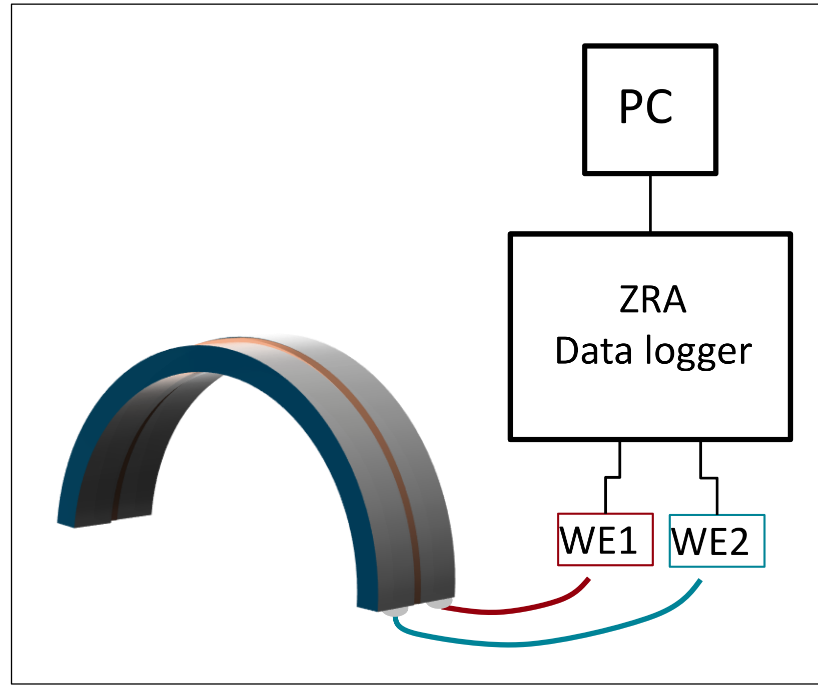
Water industry & concrete reinforcement.

Volatile corrosion inhibitor.

Film forming corrosion inhibitor (Alkyltriazole)

Packaging industry.

Preliminary tests were conducted at 80ºC pipe temperature, mineral wool insulation saturated with synthetic seawater.

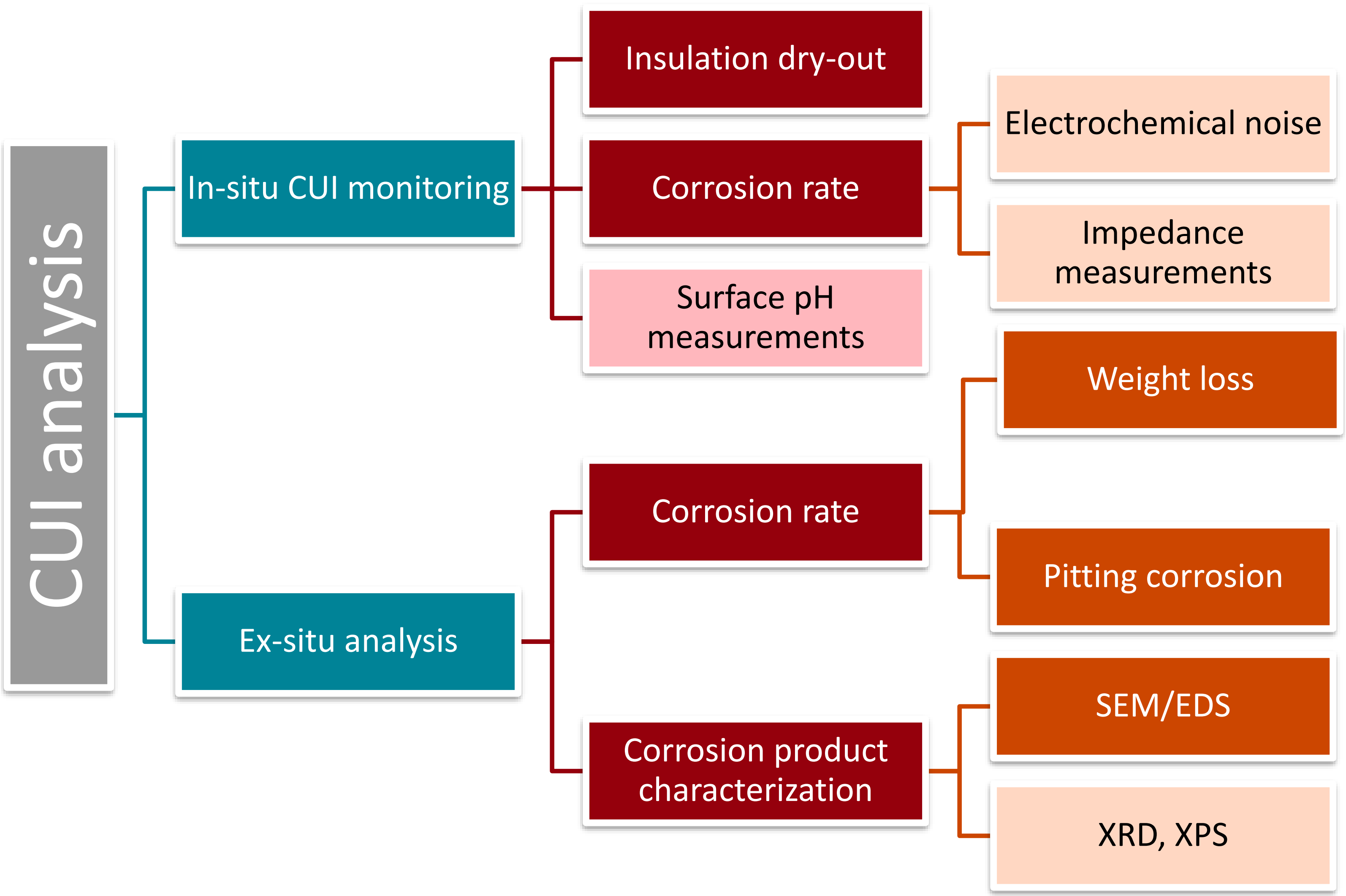


Test duration: 7 d

Assessment: Electrochemical noise technique (sampling frequency 2 and 5 Hz).

Potentiostat and Zero Resistance Amperemeter.

We modified CUI test protocols for studying the performance of chemical treatments in situ.

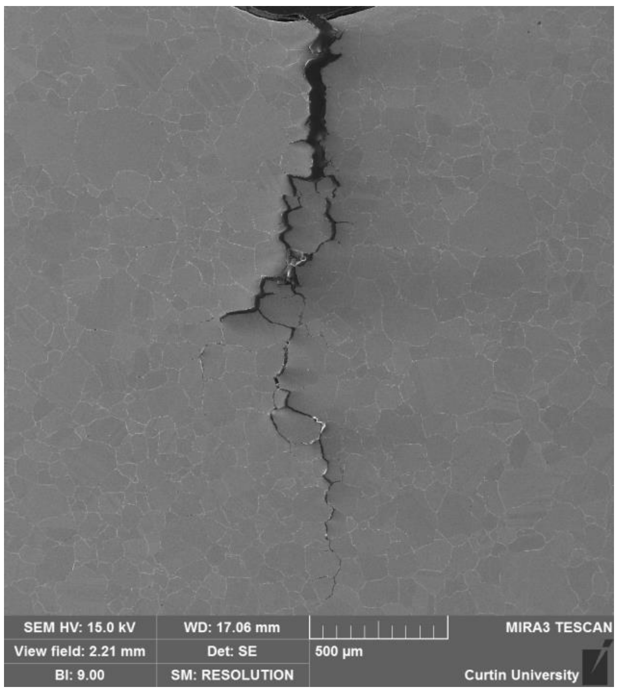


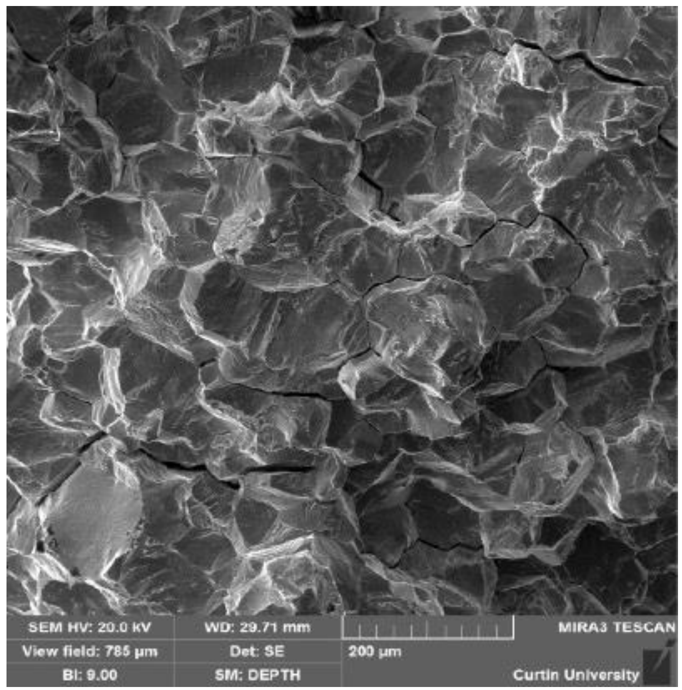
Age-hardened Nickel Alloys

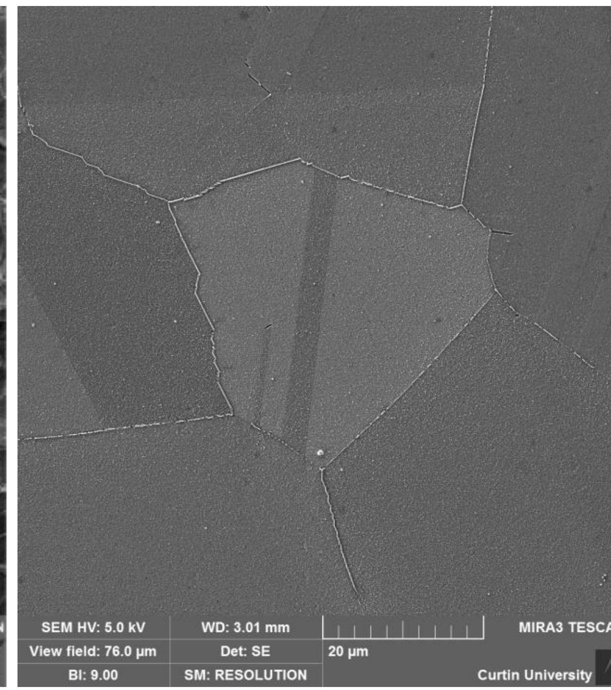
Effect of Thermomechanical Processing.

Age-hardened nickel alloys, such as UNS N07725 (NA725), have suffered intergranular cleavage failures in service.

Cracking was associated with the presence of grain boundary precipitates, initially characterized as σ-phase. Thermomechanical Processing could have played a decisive role on precipitation kinetics.



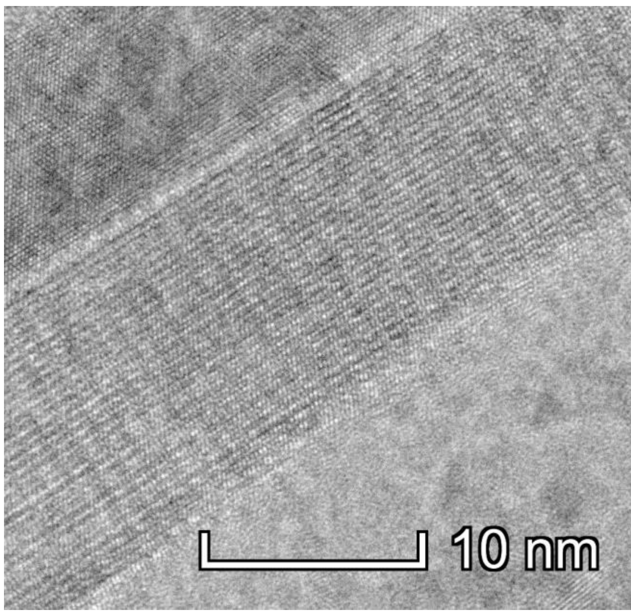




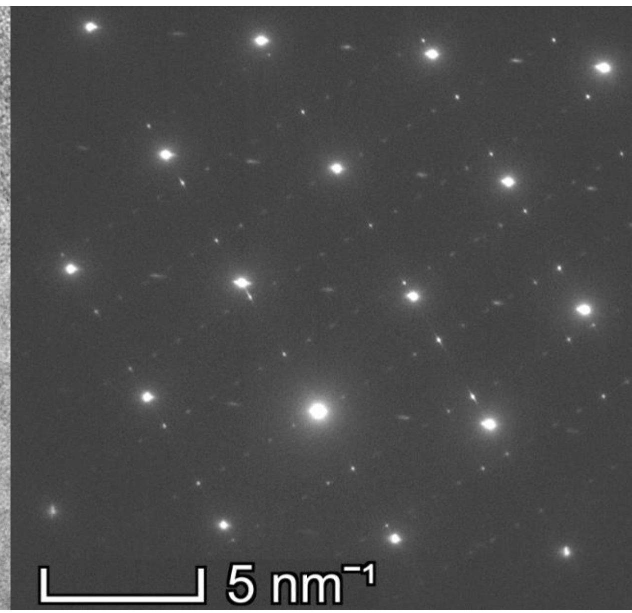
Intergranular Cleavage Failure of NA725 → Full GB Decoration

Using HR-TEM, we determined that GB precipitates are not σ–phase, but a combination of $M_{23}C_6$ carbides & an un-indexed crystal structure, must likely M_6C.

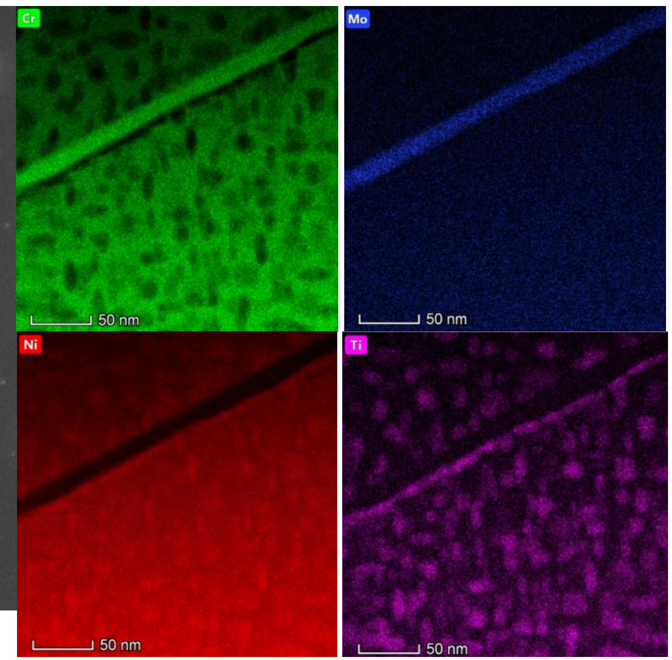
In all cases, GB precipitates were enriched in Cr and Mo.



High Resolution TEM



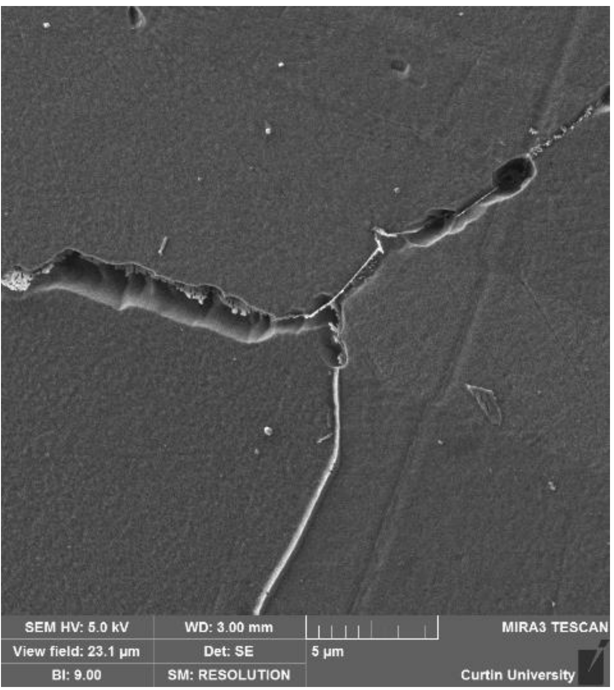
Diffraction Pattern



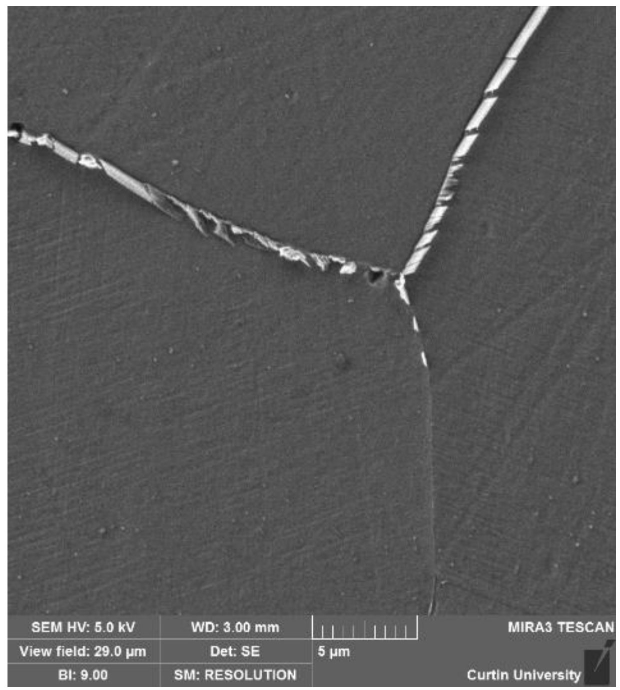
Cr Mo Ni Ti

We are working on a simple electrochemical Quality Assurance test to detect the presence of deleterious phases.

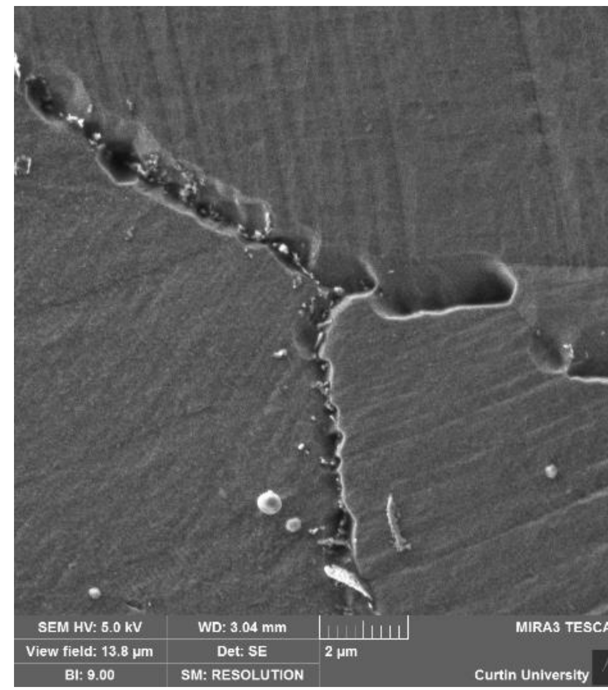
The methodology takes advantage of the observed Cr and Mo gradient across the matrix/precipitate interface.



Failed Component



Proper Heat Treat.

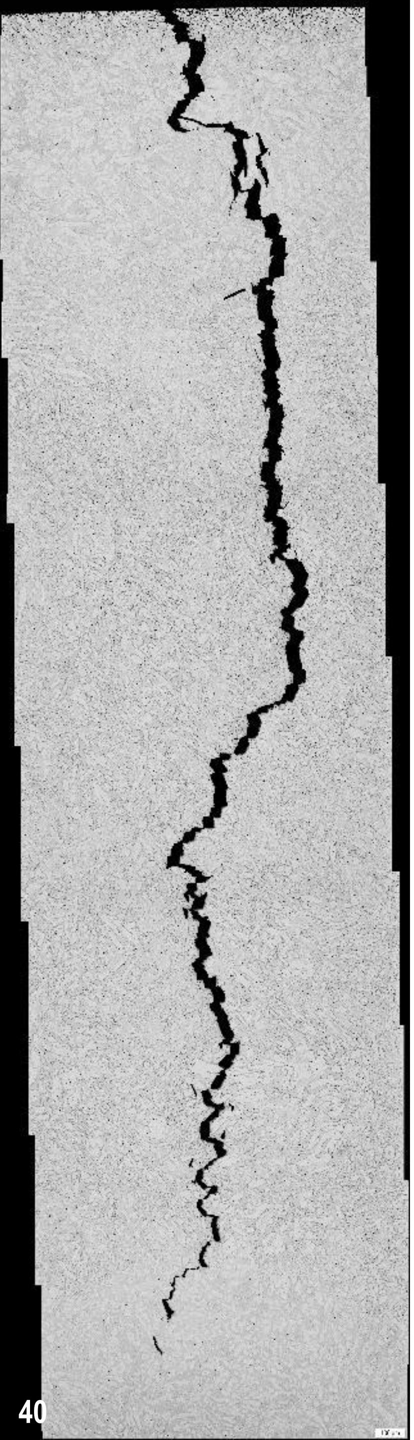


As Forged.

Electrolyte: 200 g KCl, 50 g citric acid, 200ml HCl, and 1000 ml H_2O solution.

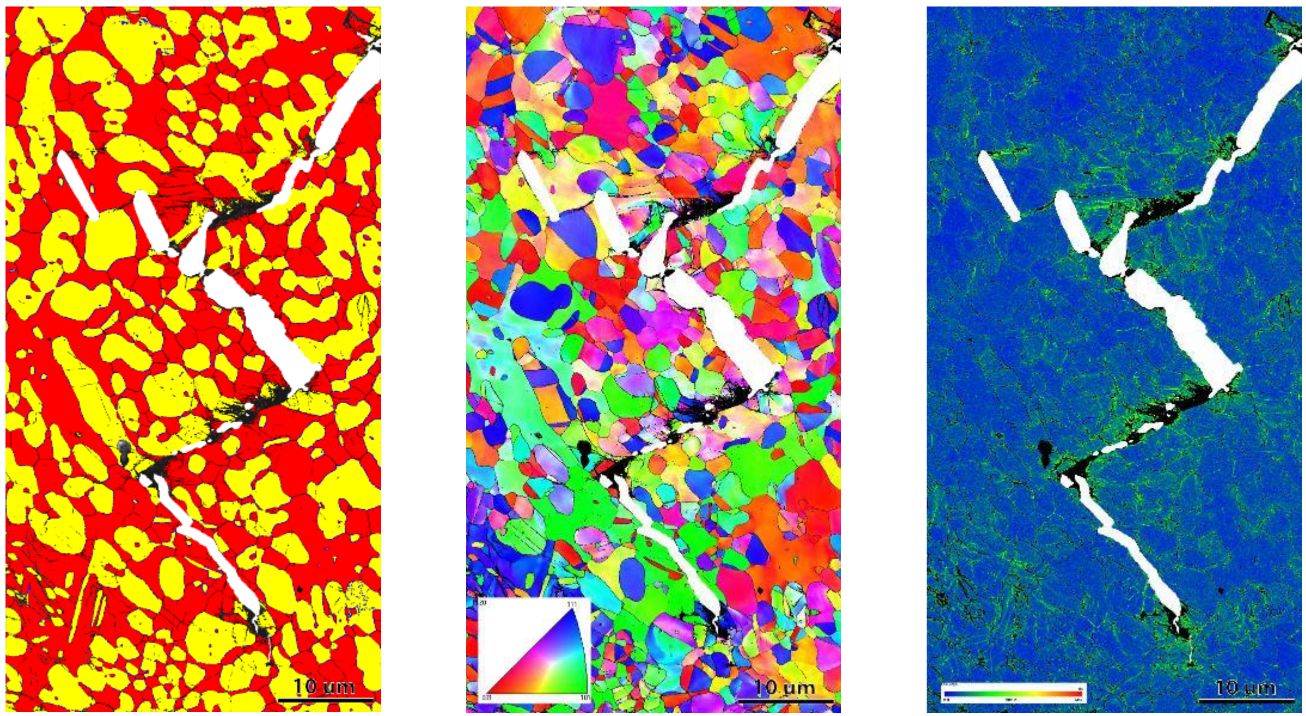
HISC of 25Cr SDSS

Effect of cold work.



A recent subsea failure of 25Cr Super Duplex Stainless Steel components was attributed to Hydrogen Induced Stress Cracking (HISC), where cold work exacerbated the issue.

Advanced characterization tools, such as EBSD, allowed us to gained a better understanding of the HISC mechanism.



Phase map | Z-IPF map | KAM map

☐ Crack shape as in the SEM image.

■ Zero results: highly deformed areas and grain boundaries

Austenite

Ferrite

Industry/Academia Collaborations

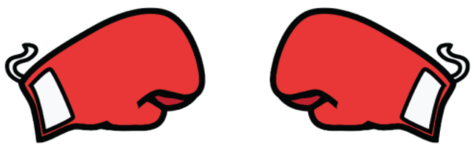
The Bad and the Ugly.

The most frequent and difficult struggle is

Time.

Time is the most valuable contribution to a successful partnership.

There are clear inherent contradictions between the success metrics of industry and academia.



Short-term focused.

Long-term outputs.

Preconceptions

Confidentiality.

Publications.

Conclusions

Conclusions

Industry/academia collaboration creates a virtuous innovation cycle that trickles down to different layers of society.

Open and collegial interpersonal relationships are the foundation of successful collaborations.

Openly sharing information through publications, conferences, procedures, etc. is paramount to maintain a high-level of engagement with academia.

Intellectual property rights and royalty models shall be addressed upfront.

The Chevron and Woodside Chair in Corrosion alliance is an example of a successful long-term commitment to strategic research aimed at solving pervasive, recurrent corrosion problems.

CURTIN CORROSION CENTRE

Tel: +61 8 9266 2136
Email: corrosion@curtin.edu.au

corrosion.curtin.edu.au