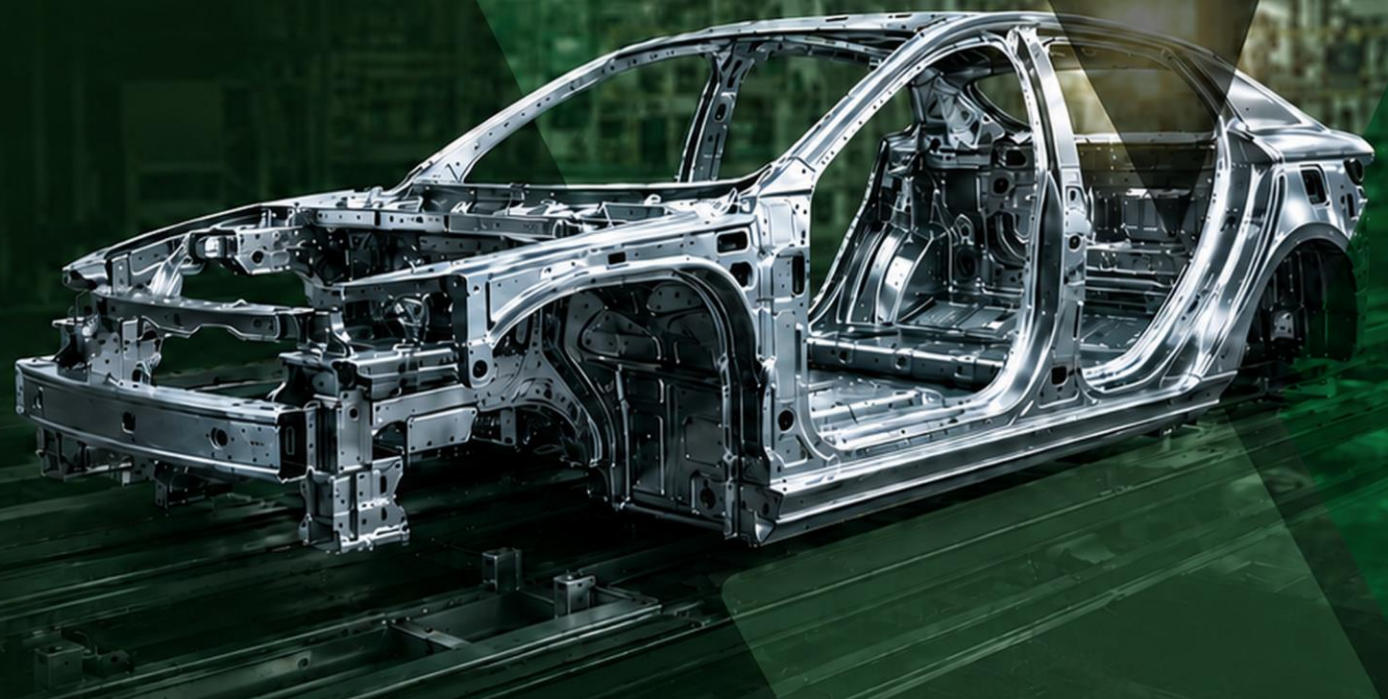
HIGH-STRENGTH STEELS

Beneficial Effects of Vanadium on Hydrogen Embrittlement Resistance in High-Strength Steels



David Crowther • Yu Li

Vanitec Ltd

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TRANSFORMING POSSIBILITIES

Strength Amplifies the Risk from Diffusible Hydrogen

Higher local stresses and lower damage tolerance make stronger steels more susceptible; risk is governed mainly by diffusible, not total, hydrogen.

1 HYDROGEN ENTRY

Pickling, welding, electroplating; corrosion, cathodic protection and H_2 gas

2 TRANSPORT + TRAPS

Diffusible H interacts with defects, boundaries, precipitates and interfaces

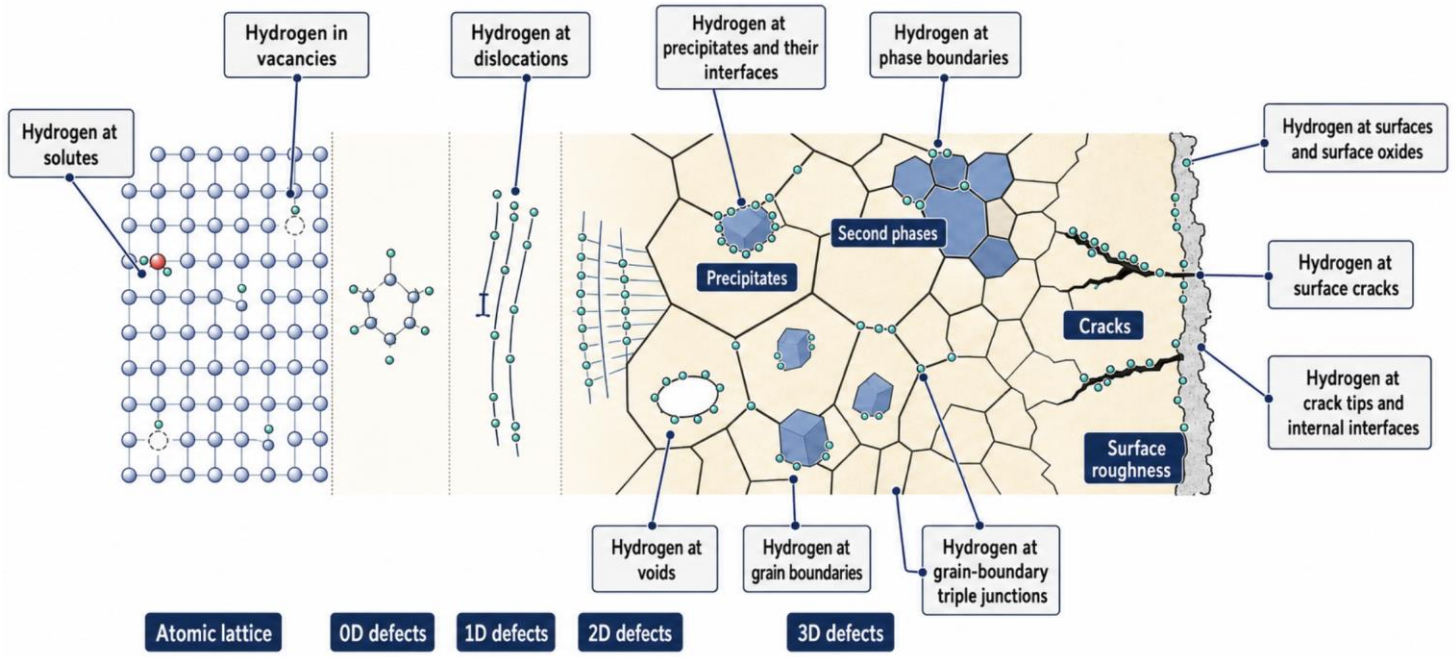
3 STRESS LOCALISATION

Hydrostatic stress concentrates H near notches and crack tips

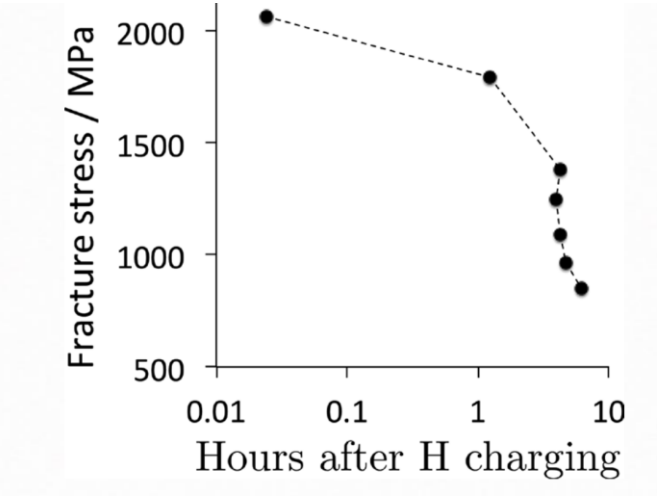
4 HYDROGEN-ASSISTED DAMAGE

Reduced cohesion or highly localised plasticity drives crack initiation and growth

WHERE HYDROGEN RESIDES



TIME-DEPENDENT DAMAGE



In a 1516 MPa steel, fracture stress falls rapidly after charging; short-time fracture remained above ~600 MPa.

Bhadeshia (2016)

Fine VC Precipitates Trap Diffusible Hydrogen

By lowering hydrogen mobility, vanadium delays crack initiation and helps retain ductility.

PERFORMANCE IMPACT

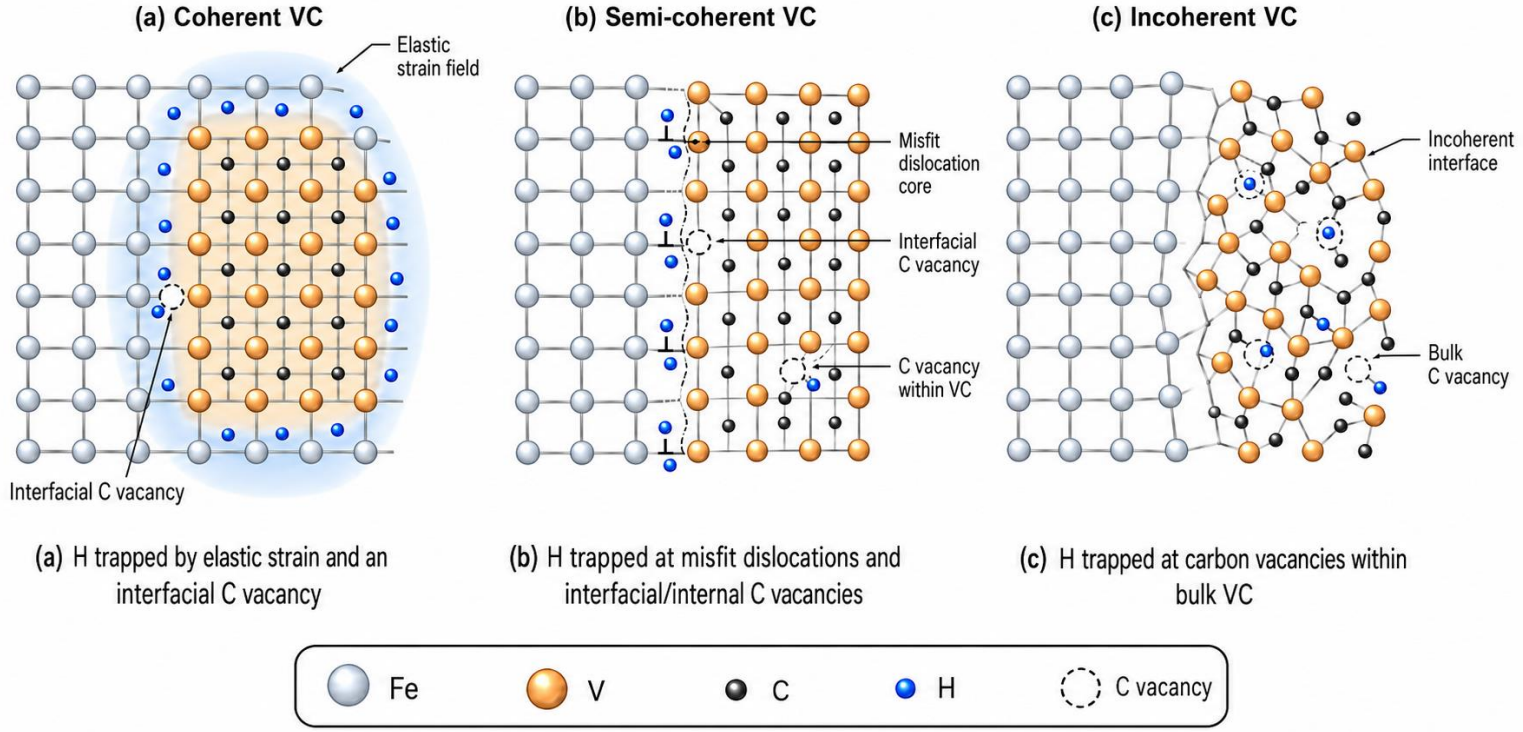
Lower H diffusivity • Less diffusible H • Improved delayed-fracture resistance • Retained ductility

PRECIPITATE DESIGN CONDITIONS

Nanoscale • Coherent or semi-coherent • High density • Optimized processing

How VC interface character changes hydrogen trapping

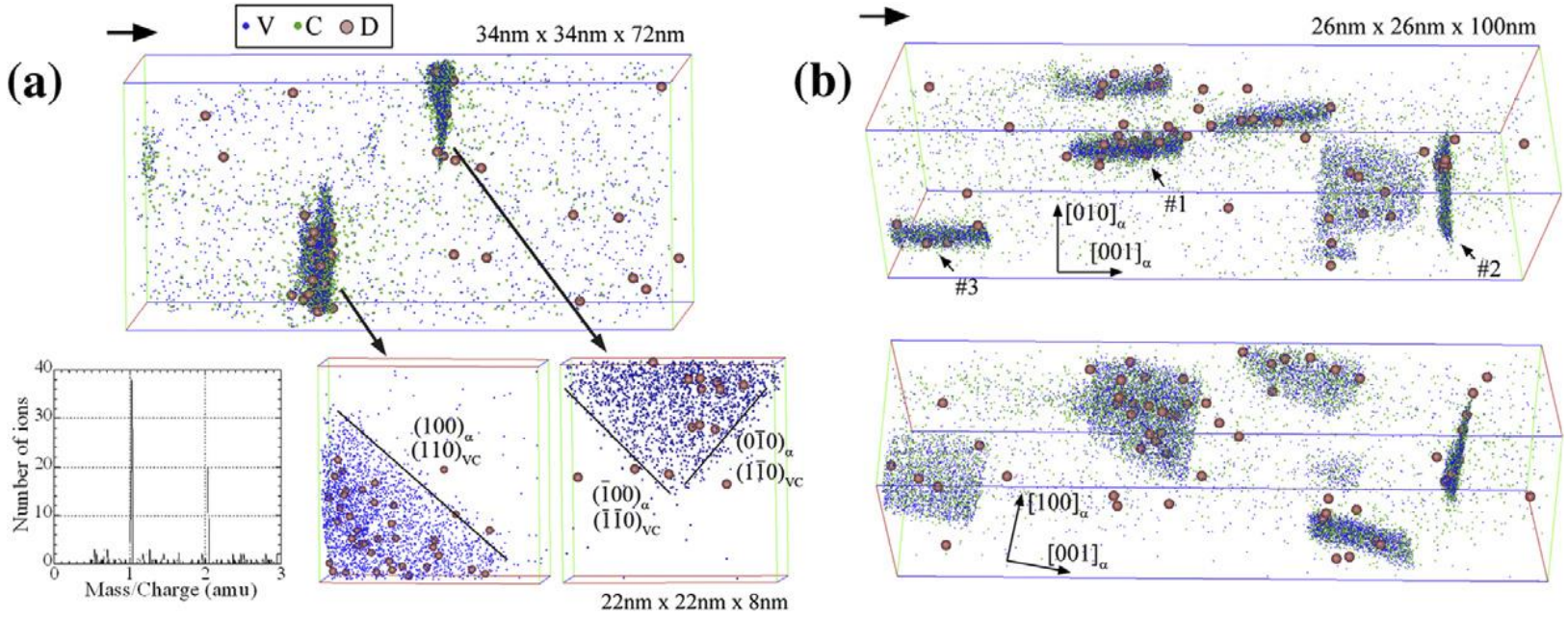
Blue = H • Orange = V • Black = C • Dashed circle = C vacancy



Atomic-scale Evidence of H Trapping at VC Precipitates

The experiment charged deuterium (D) - a hydrogen-isotope tracer that can be distinguished from background H by atom-probe mass spectrometry.

OBSERVED TRACER DISTRIBUTION: Three-dimensional atom probe tomography (3DAP) MAPS OF DEUTERIUM AROUND VC



Blue = V • Green = C • Brown = D tracer

HOW D REVEALS H TRAPPING

1 ISOTOPE PROXY

D has almost the same chemical behaviour as H and occupies the same types of trapping sites. Its diffusion is slightly slower because of the isotope effect.

2 MASS-RESOLVED TRACER

APT detects D^+ at mass 2, separating charged D from residual background H^+ at mass 1.

3 TRAP-SITE EVIDENCE

D enrichment at larger, semi-coherent V_4C_3 platelets reveals where H is trapped; misfit-dislocation cores are identified as deep traps.

Charging: 99.9998% D_2, ~0.8 atm, 200–300 °C, 5 min; rapid cryogenic transfer.

Takahashi, J., Kawakami, K. & Tarui, T. Direct observation of hydrogen-trapping sites in vanadium carbide precipitation steel by atom probe tomography. Scripta Materialia 67 (2012) 213–216. doi:10.1016/j.scriptamat.2012.04.022

HYDROGEN EMBRITTLEMENT • PRESS-HARDENED STEEL

Vanadium in Ultra-High-Strength Press-Hardened Automotive Steel

Fine VC precipitation improves resistance to hydrogen-assisted fracture in hot-formed martensitic components.

REFINED MICROSTRUCTURE

HYDROGEN TRAPPING

DUCTILE FRACTURE

Refined grains → trapped hydrogen → ductile fracture

Ref: Cho, L., Seo, E. J., Sulistiyo, D. H., et al. (2018). Influence of vanadium on the hydrogen embrittlement of aluminized ultra-high strength press hardening steel. Materials Science and Engineering A, 735, 448–455.

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TRANSFORMING POSSIBILITIES

Vanadium in Aluminized 1800–2000 MPa PHS

30MnB5 ≈1800 MPa • 35MnB5 ≈2000 MPa | each grade: V-free vs +0.2 wt.% V

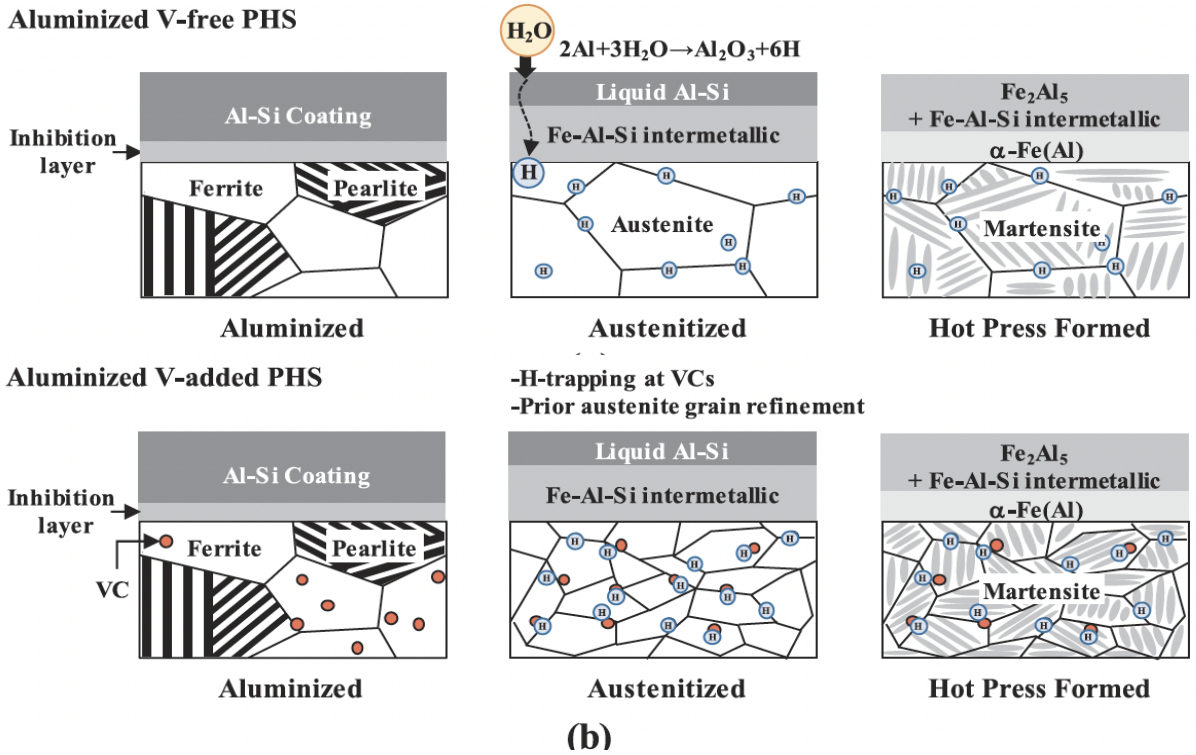
1 AL–10%Si COATING
~30 µm industrial coating

→ **2 AUSTENITIZE**
900 °C for 5 min in moist air

→ **3 DIE-QUENCH**
Fully martensitic structure

→ **4 EVALUATE**
TDA, tensile testing, SEM/EBSD/TEM

HYDROGEN ENTRY AND VANADIUM RESPONSE THROUGH PROCESSING



WHY HYDROGEN ENTERS

1 During austenitization, aluminium in the coating reacts with furnace water vapour and generates hydrogen.

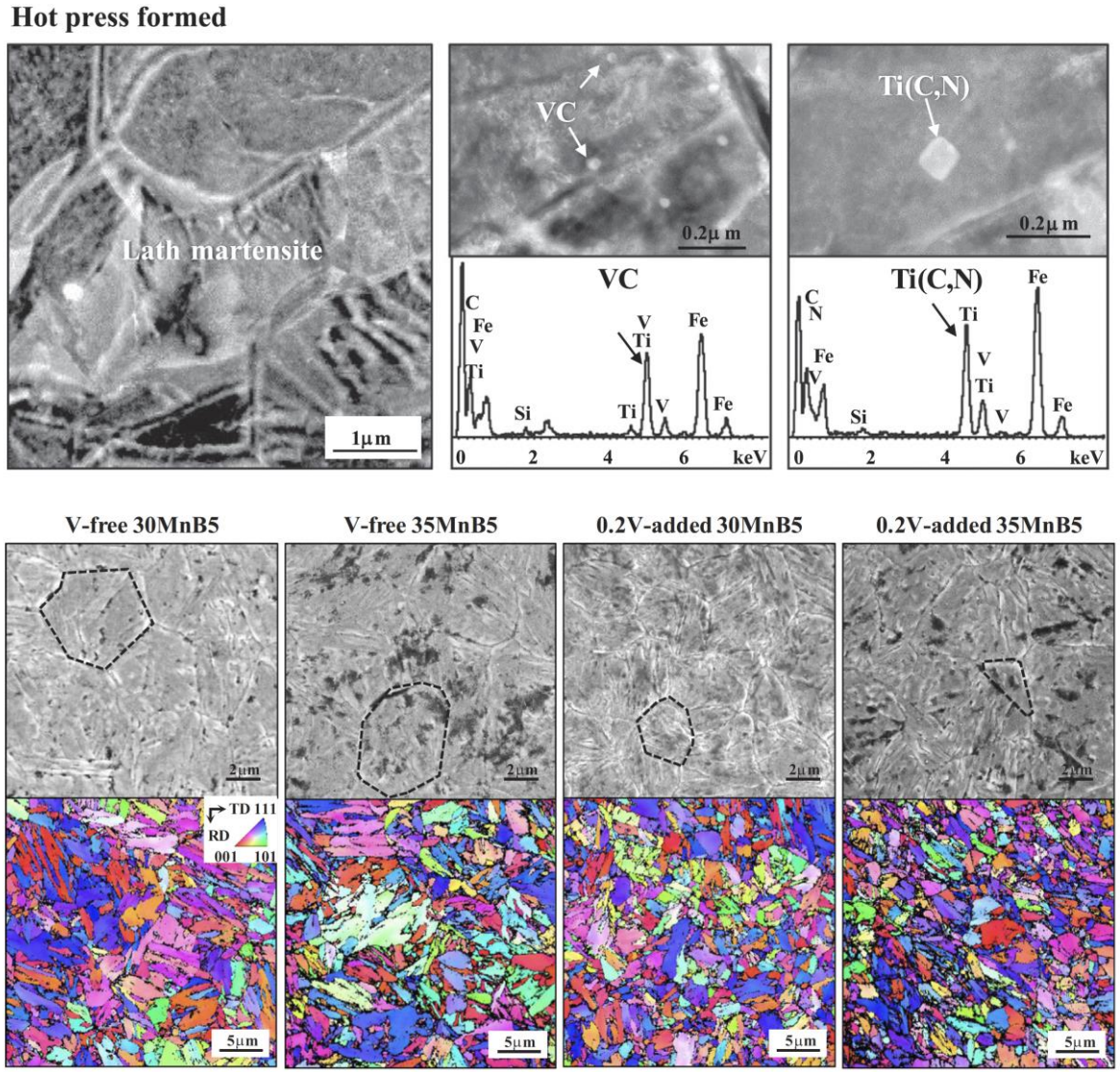
2 Hydrogen enters austenite; after die-quenching, the reacted coating slows its escape from martensite.

V RESPONSE

VC precipitates trap H and refine prior-austenite grains.

≈2000 MPa grade: greater brittle-fracture risk.

Vanadium Blocks Hydrogen and Refines Martensite



TWO COMPLEMENTARY BARRIERS

1

Fine VC traps mobile hydrogen

Nanometre-scale VC precipitates reduce hydrogen transport to vulnerable interfaces.

2

Refinement interrupts crack paths

Smaller prior-austenite grains and martensitic units make crack propagation more difficult.

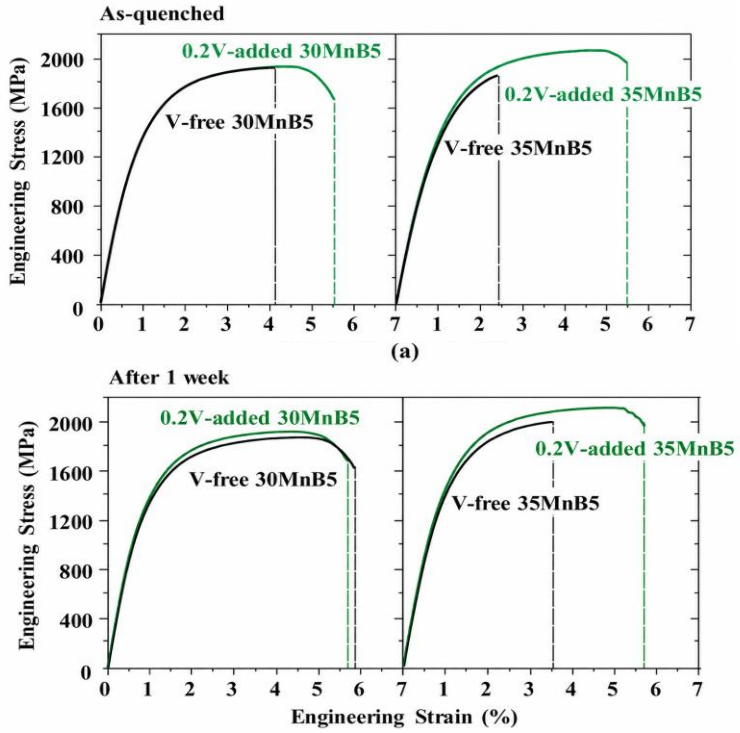
COMBINED EFFECT

Less mobile hydrogen—and a harder path for cracks.

Vanadium Carbides Trap Hydrogen - Preserving Ductility After Ageing

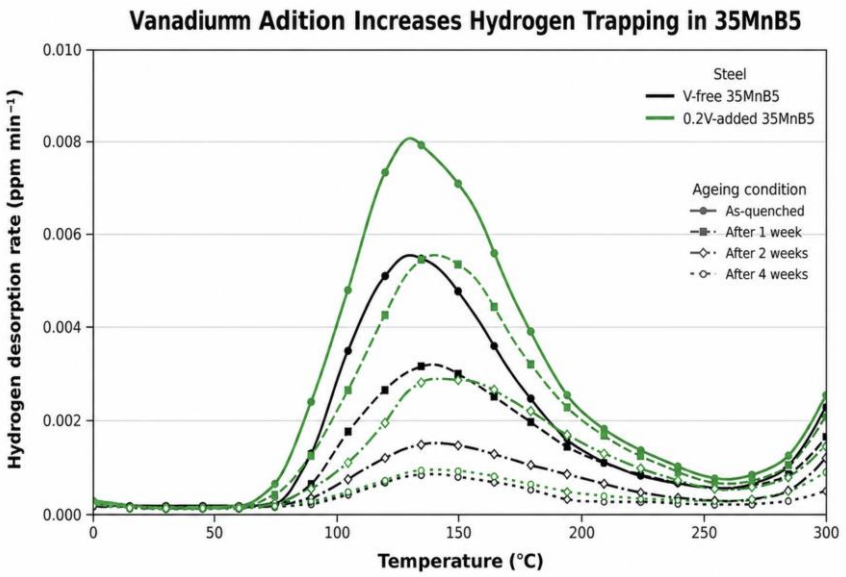
0.2 wt.% V adds strong hydrogen-trapping sites while sustaining strength and elongation in 30MnB5 and 35MnB5.

MECHANICAL RESPONSE



V-added steels retain the longer strain-to-fracture response after one week.

HYDROGEN TRAPPING



Fine VC precipitates → More H trapped → Less mobile H

Higher TDA intensity indicates greater trapping capacity - not greater embrittlement risk.

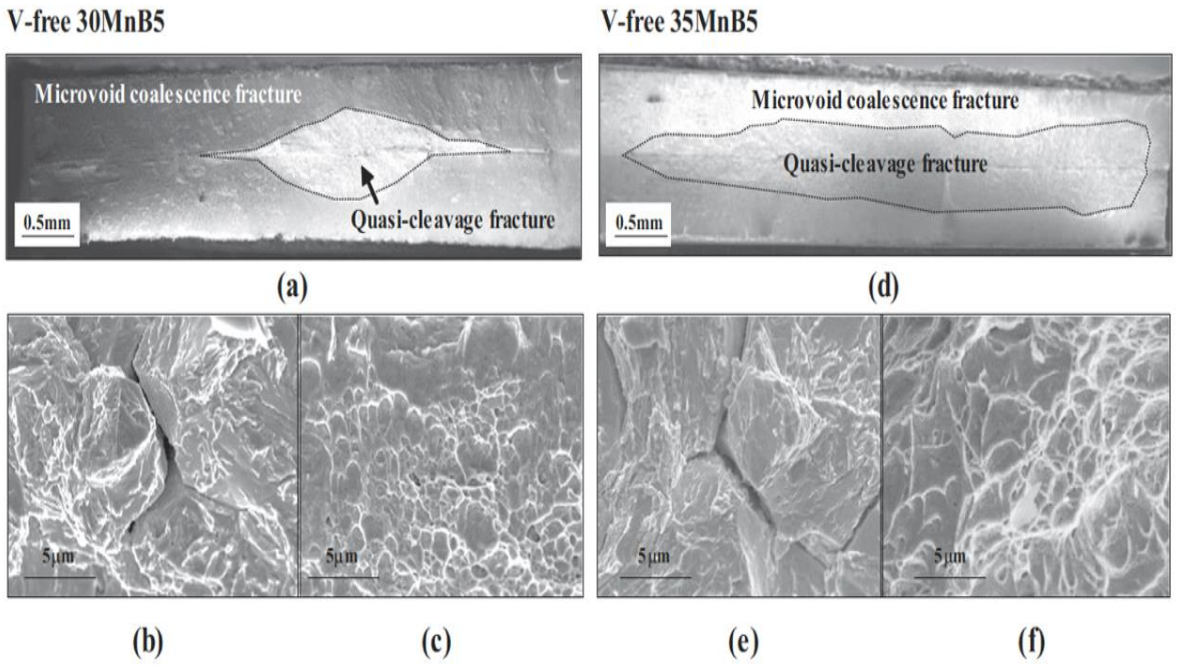
AFTER 1 WEEK **≈5.5%** **elongation in both grades** + **up to 40 MPa** higher strength

0.2 wt.% V Eliminates the Brittle Fracture Zone

Fractography of 30MnB5 and 35MnB5 after hot press forming and ageing

V-free steels

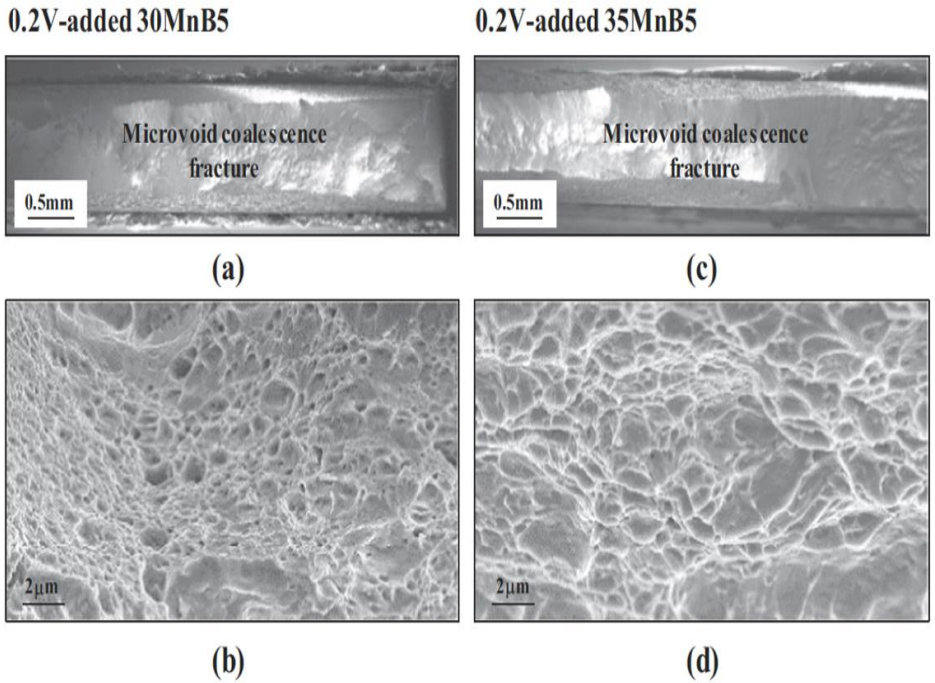
Mixed fracture response



! **Premature quasi-cleavage and intergranular cracking**

0.2 wt.% V-added steels

Uniform ductile fracture



✓ **Dimpled microvoid coalescence**
No brittle zone observed

V addition preserves local plasticity and delays brittle crack initiation.

HYDROGEN EMBRITTLEMENT • FERRITIC STEELS

Vanadium Improves Hydrogen-Embrittlement Resistance in Ferritic Steel

Fine vanadium carbides provide more effective protection against hydrogen-assisted damage than titanium carbides.

FINE PRECIPITATES	HYDROGEN TRAPPING	FRACTURE RESISTANCE

More effective traps → less mobile hydrogen → improved ductility

Ref: Boot, T. et al. “Effect of titanium and vanadium nano-carbide size on hydrogen embrittlement of ferritic steels.” npj Materials Degradation, 2025.

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TRANSFORMING POSSIBILITIES

VC Traps Hydrogen More Effectively Than TiC

TiC steel

0.07 C | 0.30 Ti (wt.%)

VC steel

0.07 C | 0.31 V (wt.%)

Both model alloys: fully ferritic

Each alloy compared

Short ageing (SN) vs **Long ageing (LN)**

2 h

1 Heat treat

TiC: 700 °C
VC: 650 °C
5 °C/min in N_2

2 Vary carbide size

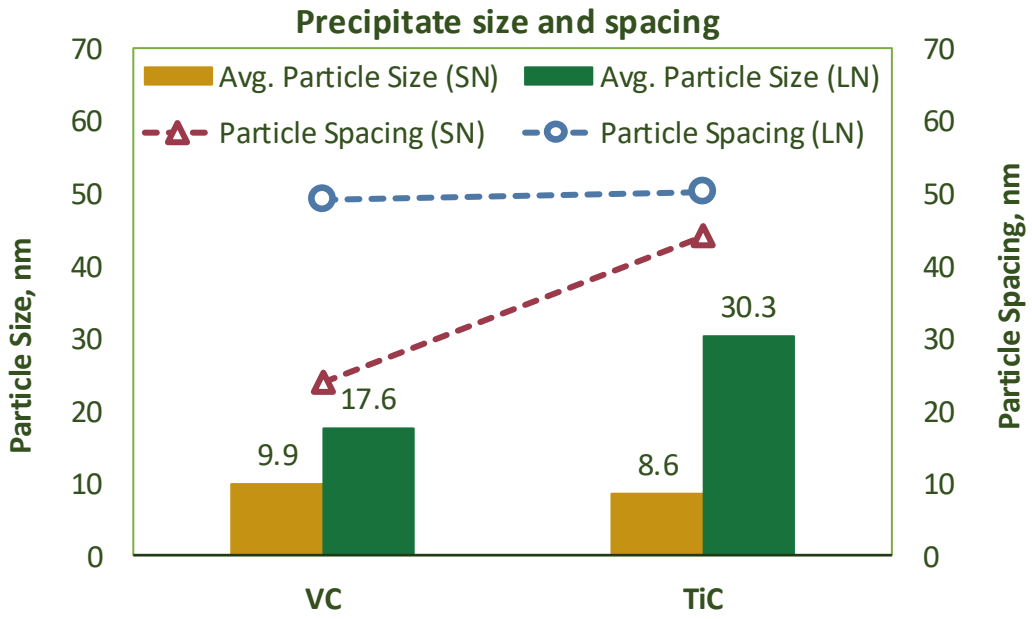
SN: 2 h isotherm
LN: 20 h isotherm
≈1 °C/min cooling

3 Charge + SSRT

3.5% NaCl + 3 g/L NH_4SCN
1 mA/cm²; 2 h pre-charge
Charging continued during test

4 Evaluate

TDS + HE index
SEM / EDS / EBSD / TEM
Fracture mechanisms



VC OUTPERFORMS TiC

Finer after long ageing

Average size: 17.6 nm for VC vs 30.3 nm for TiC - VC remains about 42% finer after 20 h ageing.

Tighter short-aged spacing

Particle spacing is approximately 24 nm for VC vs 44 nm for TiC, creating a denser population of trapping interfaces.

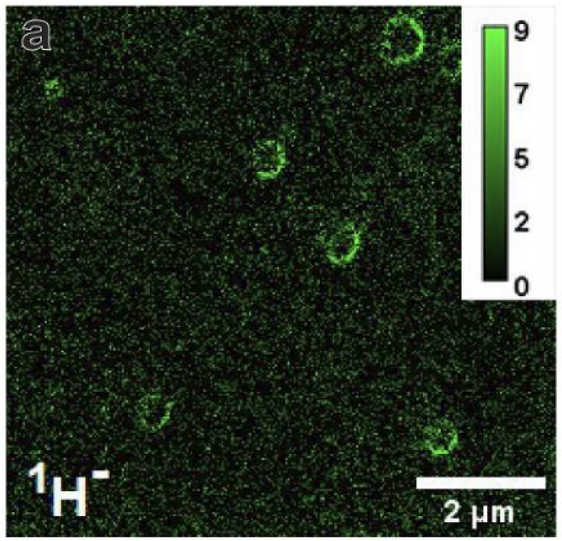
More effective hydrogen traps

More VC interfaces trap hydrogen and restrict its transport to grain boundaries, dislocations and crack-tip regions.

- **In fully ferritic steel, VC provides more hydrogen-trapping interfaces and greater resistance to hydrogen embrittlement than TiC.**

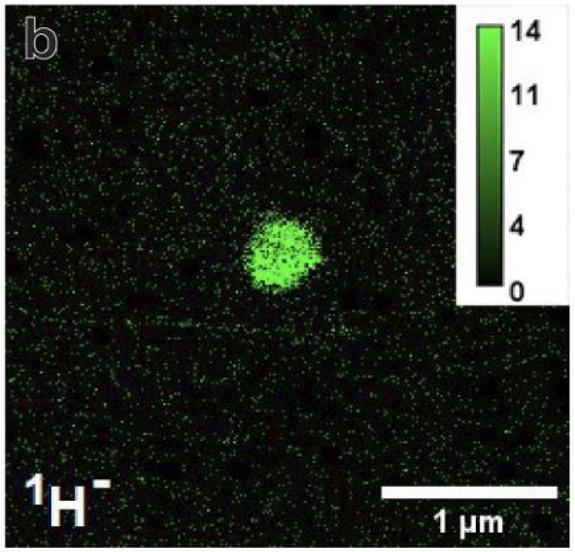
SIMS Shows VC Traps Hydrogen More Extensively than TiC

Hydrogen distribution around carbide precipitates measured by secondary ion mass spectrometry



TiC

Hydrogen concentrated mainly around the interface



VC

Stronger signal extends through the precipitate

THE SIMS MAPS SHOW

TiC: mainly interfacial trapping

Ring-like hydrogen enrichment indicates trapping predominantly at the TiC-matrix interface.

VC: interfacial + internal trapping

Hydrogen is detected at the interface and inside VC, consistent with trapping at carbon-vacancy sites.

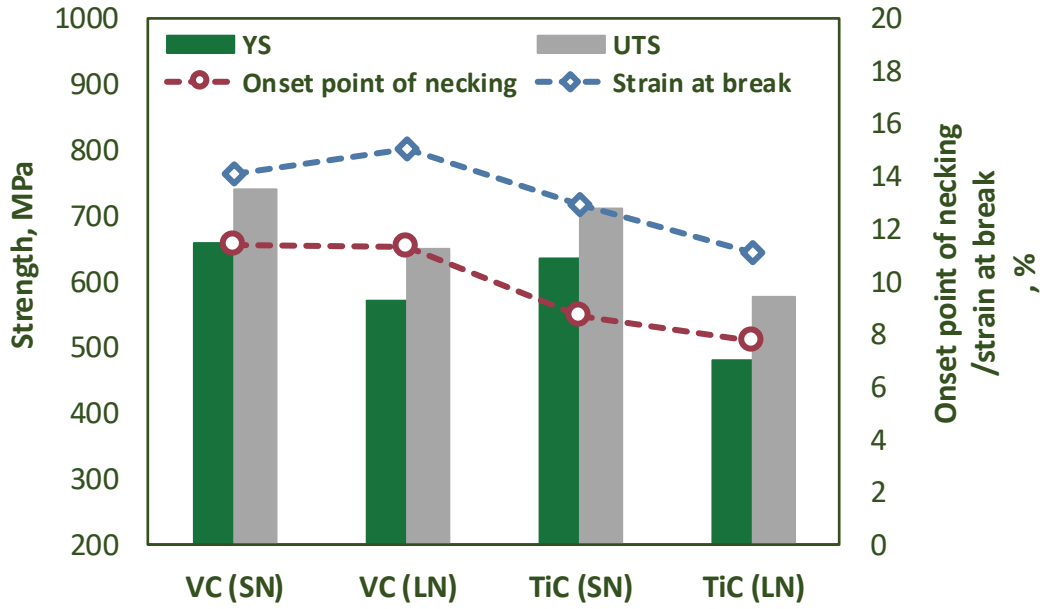
Higher trapping capacity

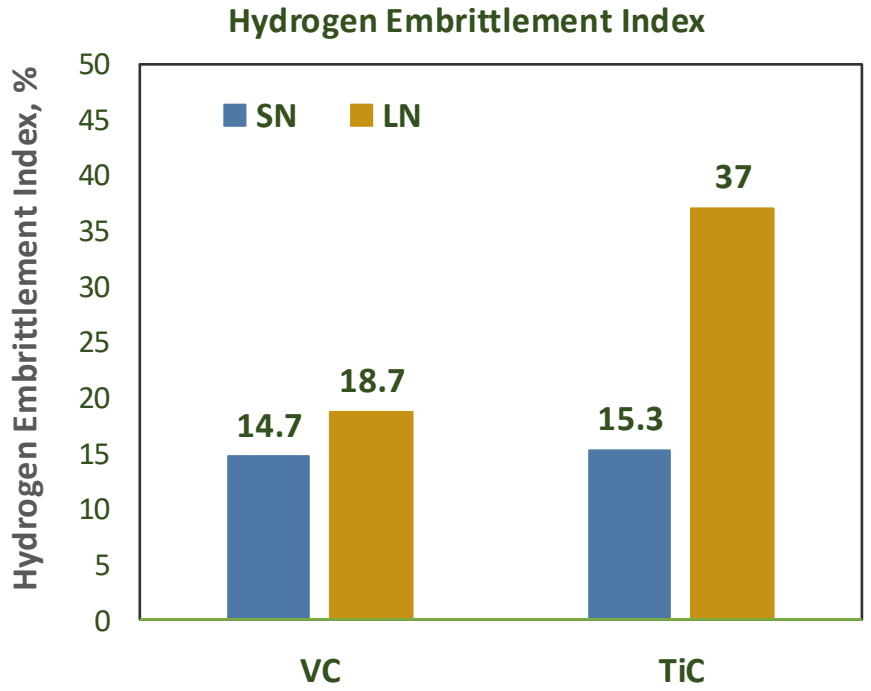
Additional internal sites allow VC to immobilize more hydrogen and reduce the mobile hydrogen available for damage.

- **VC traps hydrogen both around and within the precipitate, giving it a higher trapping capacity than TiC.**

VC Steel Delivers the Best Strength-HE Resistance Balance

In-situ slow strain-rate tensile testing under continuous electrochemical hydrogen charging





VC-SN: strongest + low HEI

Highest strength with good ductility and the lowest HEI: 14.7%.

VC-LN: highest ductility

Strain at break reaches 15.0%, while HEI remains comparatively low at 18.7%.

TiC-LN: poorest performance

Early necking, lower strength and the highest HEI: 37.0% - nearly double VC-LN.

- **Fine VC precipitates provide the best combination of strength, ductility and hydrogen-embrittlement resistance.**

HYDROGEN EMBRITTLEMENT • PRESSURE-VESSEL STEELS

Vanadium Mitigates Hydrogen Damage in Cr-Mo(V) Steels

Fine VC/(Mo,V)C precipitates improve hydrogen resistance in high-pressure vessels and pipeline components.

STRONG TRAPS

SLOWER TRANSPORT

TOUGHER CRACK RESPONSE

Strong carbide traps → less mobile H → tougher crack response

2.25Cr-1MoV • tempered martensite • hydrogen-service components

VANITEC
TRANSFORMING POSSIBILITIES

Ref: 3Peral, L. B., Fernández-Pariente, I., Colombo, C., Rodríguez, C. and Belzunce, J. "The Positive Role of Nanometric Molybdenum–Vanadium Carbides in Mitigating Hydrogen Embrittlement in Structural Steels." Materials 14 (2021): 7269.

Nano - (Mo,V)C Carbides Strongly Immobilize Hydrogen

2.25Cr–1Mo
V-free • $\sigma_y \approx 430$ MPa

2.25Cr–1MoV
+0.31 wt.% V • $\sigma_y \approx 567$ MPa

Steel grades compared
V-free vs **+0.31 wt.% V**

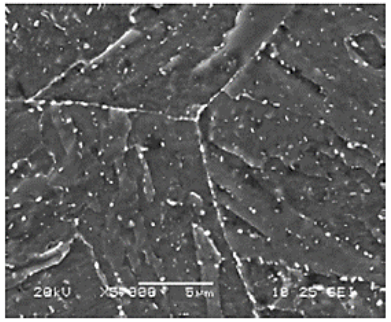
1 Heat treat
Water quench + temper
690 °C (V-free) / 720 °C (V-added)

2 Precharge with H_2
19.5 MPa, 450 °C, 21 h
Store in liquid N_2 before testing

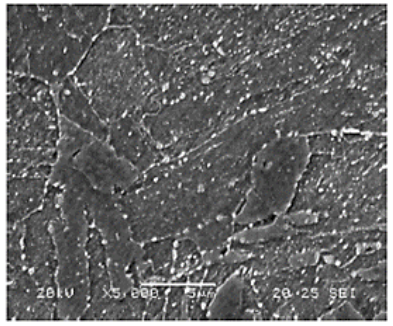
3 Mechanical testing
Smooth/notched tensile; J–R fracture toughness; fatigue-crack growth

4 Evaluate
TDA/egression, permeation, SEM/TEM, fractography + embrittlement index

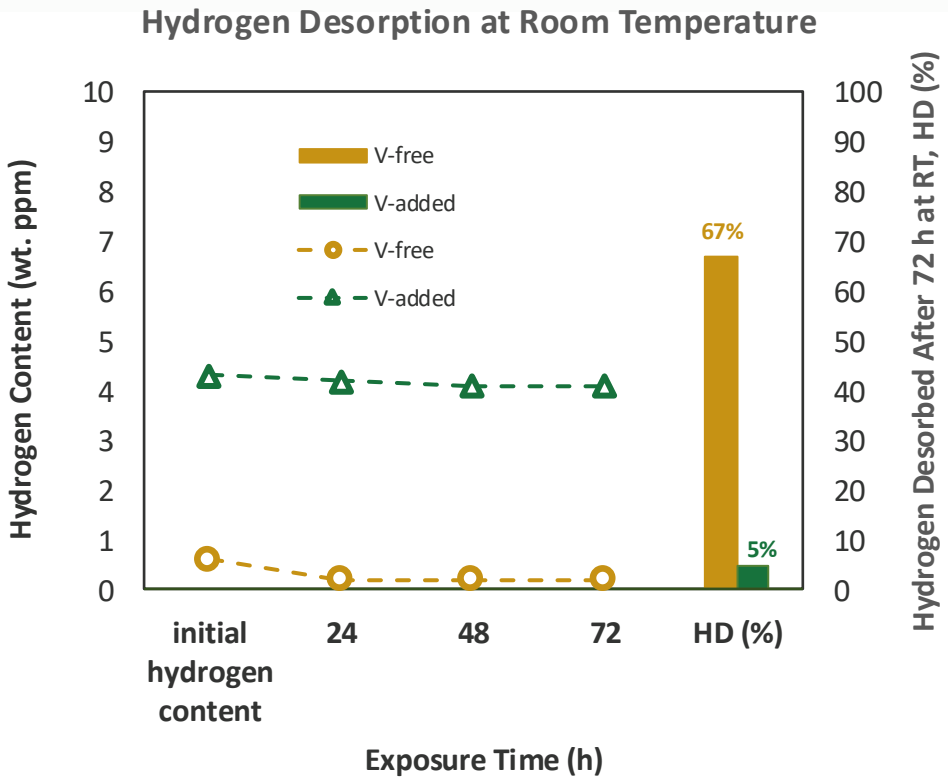
Tempered Martensite



V-free (M_3C, $M_{23}C6$ and M_7C_3)



V-added ((Mo,V)C, 10-30 nm and M_7C_3)



V-free: hydrogen remains mobile

67% desorbs within 72 h at room temperature, indicating relatively weak trapping.

V-added: 95% remains trapped

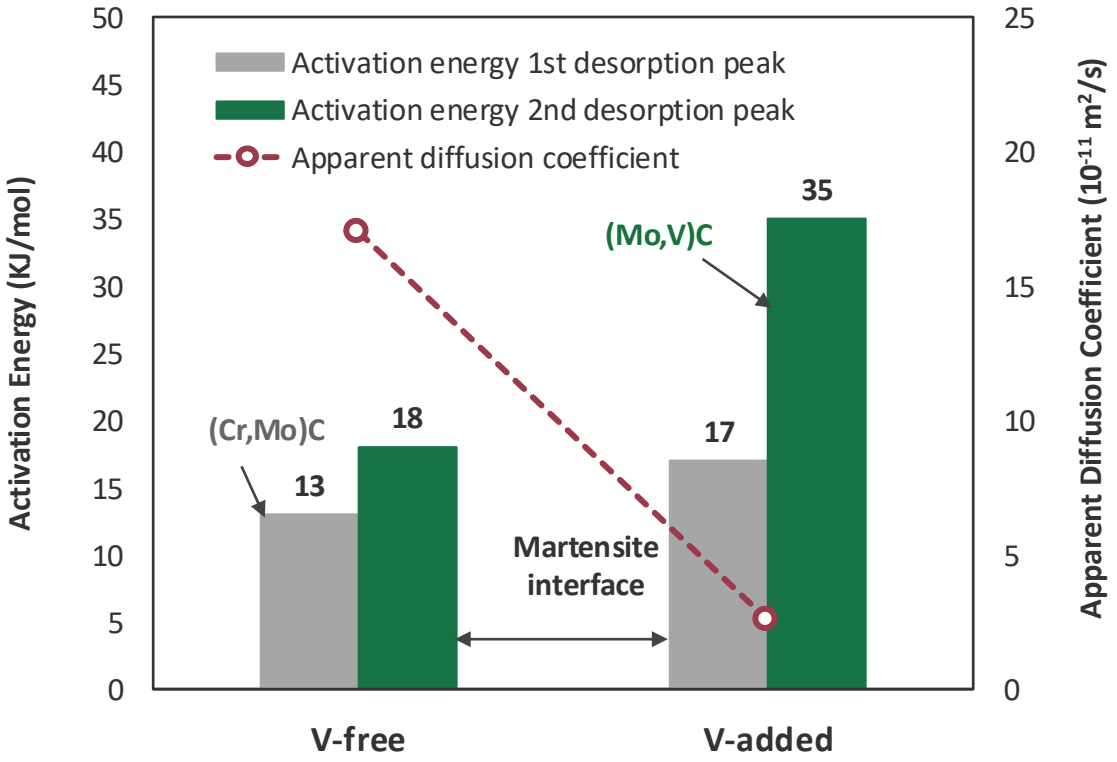
Only 5% desorbs, even though the initial hydrogen content is about seven times higher.

Strong traps from nano-carbides

A high density of 10-30 nm (Mo,V)C precipitates immobilizes hydrogen and restricts its transport.

Vanadium Carbides Reduce Hydrogen Diffusivity by ~85%

A new 35 kJ·mol^{-1} desorption peak identifies strong hydrogen trapping by fine (Mo,V)C precipitates



WHAT VANADIUM CHANGES

35 kJ·mol^{-1}

A new high-temperature desorption peak appears, indicating strong hydrogen trapping by fine (Mo,V)C carbides.

1.7×10^{-10} → 2.6×10^{-11} m^2·s^{-1}

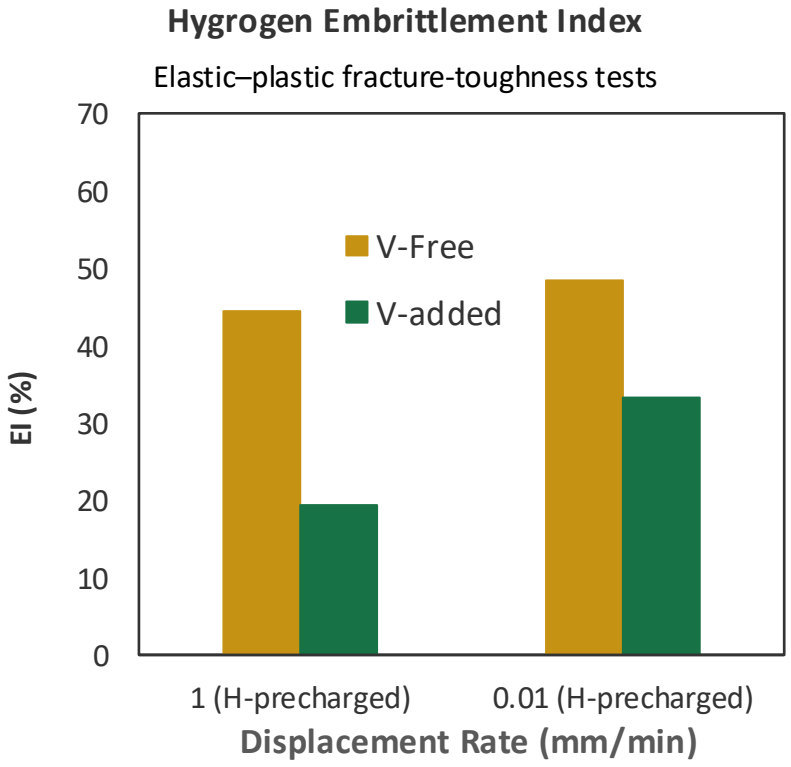
The apparent diffusion coefficient falls by approximately 85%, restricting hydrogen transport through the steel.

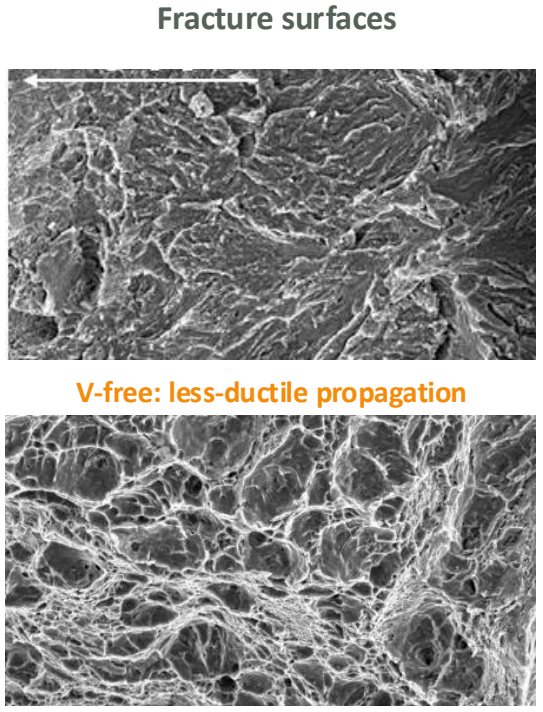
≈85% LOWER APPARENT DIFFUSIVITY

- **Fine (Mo,V)C precipitates strongly trap hydrogen and restrict its transport toward crack-sensitive regions.**

Vanadium Preserves Toughness and Ductile Fracture

Elastic-plastic fracture-toughness tests on hydrogen-precharged V-free and V-added steels





VANADIUM PRESERVES

57% lower EI at 1 mm/min

The embrittlement index falls from 44.5% to 19.3% with vanadium.

31% lower EI at 0.01 mm/min

Even at the slower rate, EI decreases from 48.6% to 33.3%.

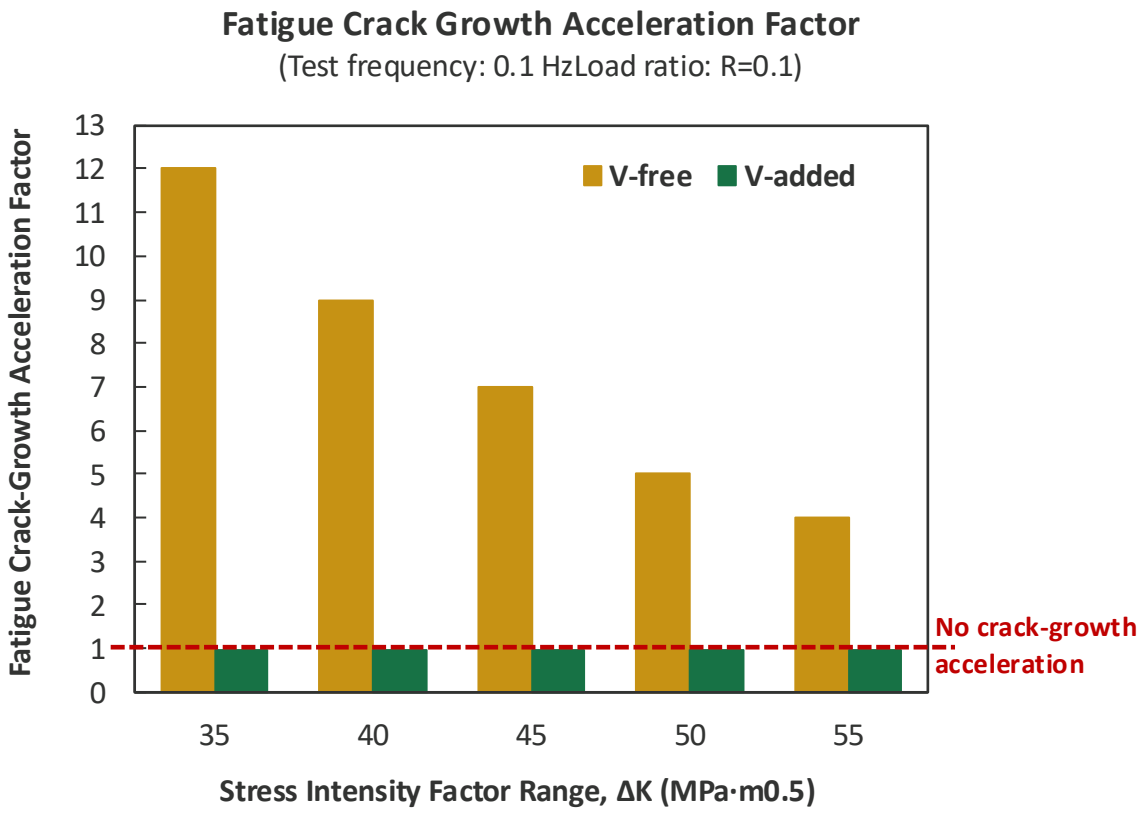
Ductile fracture is retained

The V-added surface remains dimpled, indicating greater plasticity and microvoid coalescence.

- **Vanadium reduces toughness loss and preserves ductile fracture by trapping mobile hydrogen at fine VC/(Mo,V)C precipitates.**

Vanadium Suppresses Hydrogen-Accelerated Fatigue Cracking

Fatigue-crack growth at 0.1 Hz and load ratio R = 0.1 under hydrogen charging



Acceleration factor ≈1: hydrogen caused no measurable increase in fatigue-crack growth.

HYDROGEN EFFECT ON CRACK GROWTH

V-free: 4-12× acceleration

Hydrogen markedly accelerates fatigue-crack propagation throughout the tested ΔK range.

V-added: remains near 1×

No clear hydrogen-induced increase in crack-growth rate is observed at 0.1 Hz.

Hydrogen delivery is restricted

Fine VC/(Mo,V)C traps reduce the mobile hydrogen reaching the fatigue-crack tip.

- **VC/(Mo,V)C precipitates suppress hydrogen-accelerated fatigue cracking by limiting hydrogen delivery to the crack tip.**

Vanadium Strengthens Hydrogen Resistance in 1300 MPa Bolt Steels

Fine VC precipitates provide stronger hydrogen trapping while retaining the strength required for demanding fastener applications.

V-free bolt steel → **0.14 wt.% V bolt steel**

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TRANSFORMING POSSIBILITIES

Ref. Zhao, H., Li, W., Hu, P., Fu, H. and Li, J. “Comprehensive Analysis of Microalloying Element V Improving Hydrogen Embrittlement Resistance of 1300 MPa Bolt Steel.” Metallurgical and Materials Transactions A 53 (2022): 861–872.

0.14 wt.% V Produces an Abundant Population of Nanoscale VC Traps

TEM evidence and particle-size distributions after tempering in 1300 MPa bolt steels

V-Free Steel

V-free • σy ≈ 1226 MPa

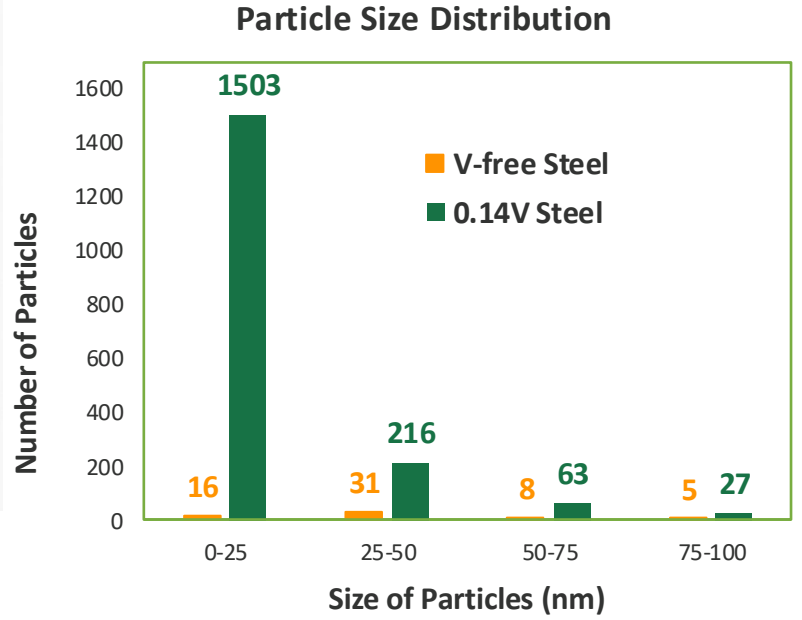
0.14V-steel

+0.14 wt.% V • σy ≈ 1293 MPa

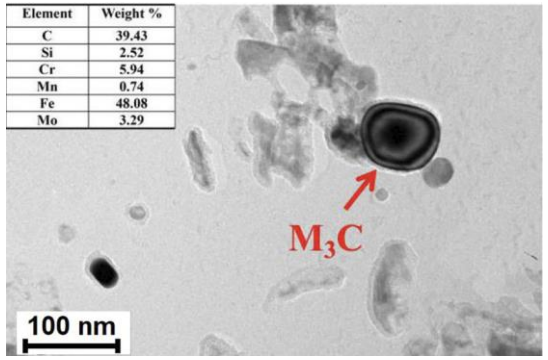
1300 MPa bolt steels compared

V-free vs **+0.14 wt.% V**

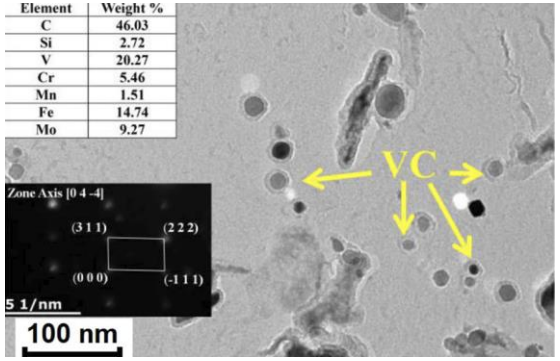
1 Heat treat	2 Expose to H_2	3 Test performance	4 Evaluate
Oil quench after 70 min:	3% NaCl + 0.3% NH_4SCN	Slow strain-rate tensile test	SEM / EBSD / TEM + XRD
850 °C (V-free) / 900 °C (V-added)	SSRT: 0.1–6 mA·cm^{-2}	Strain rate: 1 × 10^{-6} s^{-1}	Grain size, VC + dislocations
Temper 120 min: 470 °C / 600 °C	TDS: 1 mA·cm^{-2} for 72 h	Hydrogen permeation + TDS	H diffusion + trap density
then air cool	HMT / permeation: 5 mA·cm^{-2}	Hydrogen microprint technique	Fractography + HE sensitivity



TEM Micrographs Showing Precipitates in the Steels after Tempering



V-free Steel



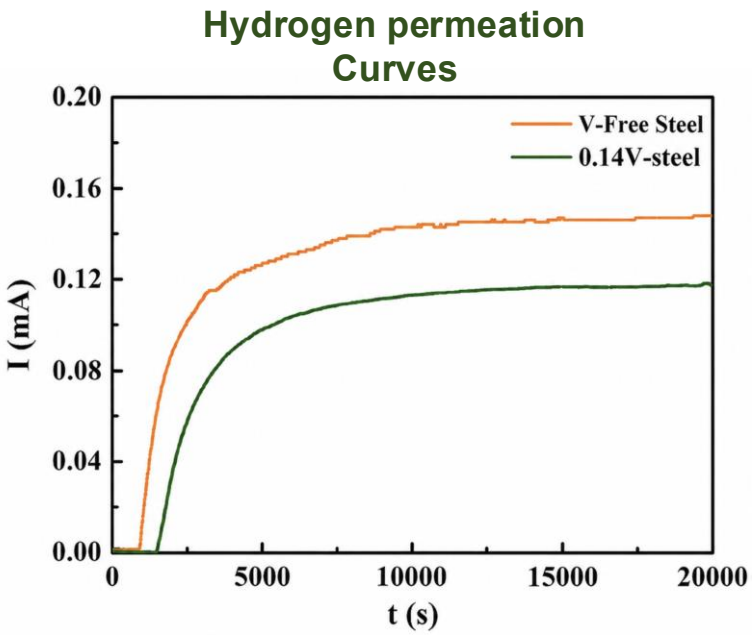
0.14V Steel

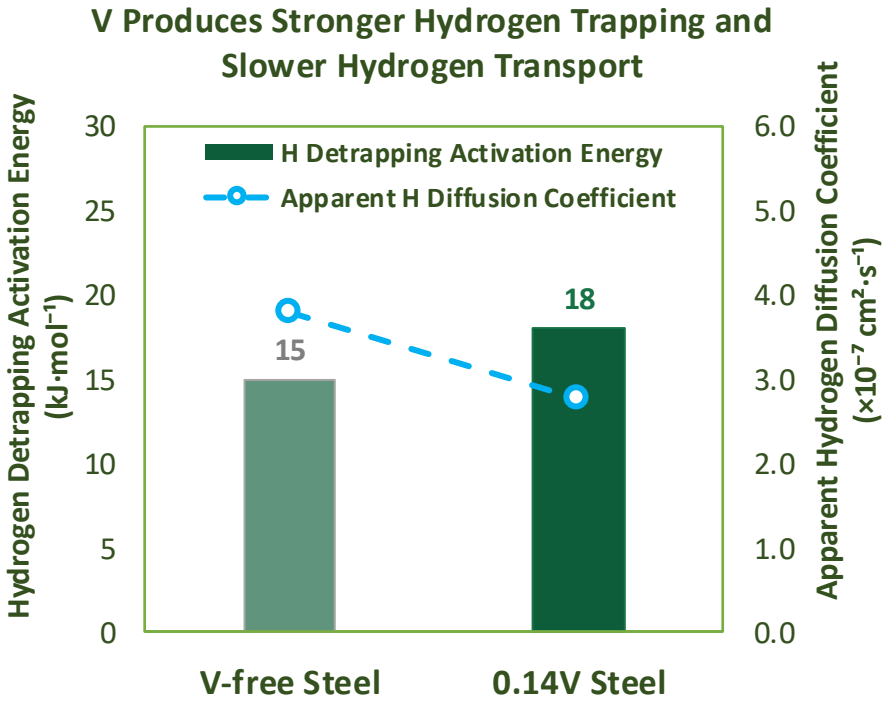
83% of V-steel particles are <25 nm

The V-added steel contains 1,809 particles across the measured size range versus only 60 in the V-free steel - creating a far greater density of potential hydrogen traps.

Vanadium Strengthens Hydrogen Trapping and Slows Hydrogen Transport

Electrochemical hydrogen permeation and trapping response of V-free and 0.14 wt.% V bolt steels





The 0.14V steel shows a delayed rise and lower steady permeation current, indicating slower hydrogen transport and increased trapping.

EFFECT OF 0.14 wt.% V

+20%

Higher detrapping activation energy

15 → 18 kJ·mol^{-1}

−27%

Lower apparent hydrogen diffusivity

3.78 → 2.76 ×10^{-7} cm^2·s^{-1}

+50%

Higher hydrogen-trap density

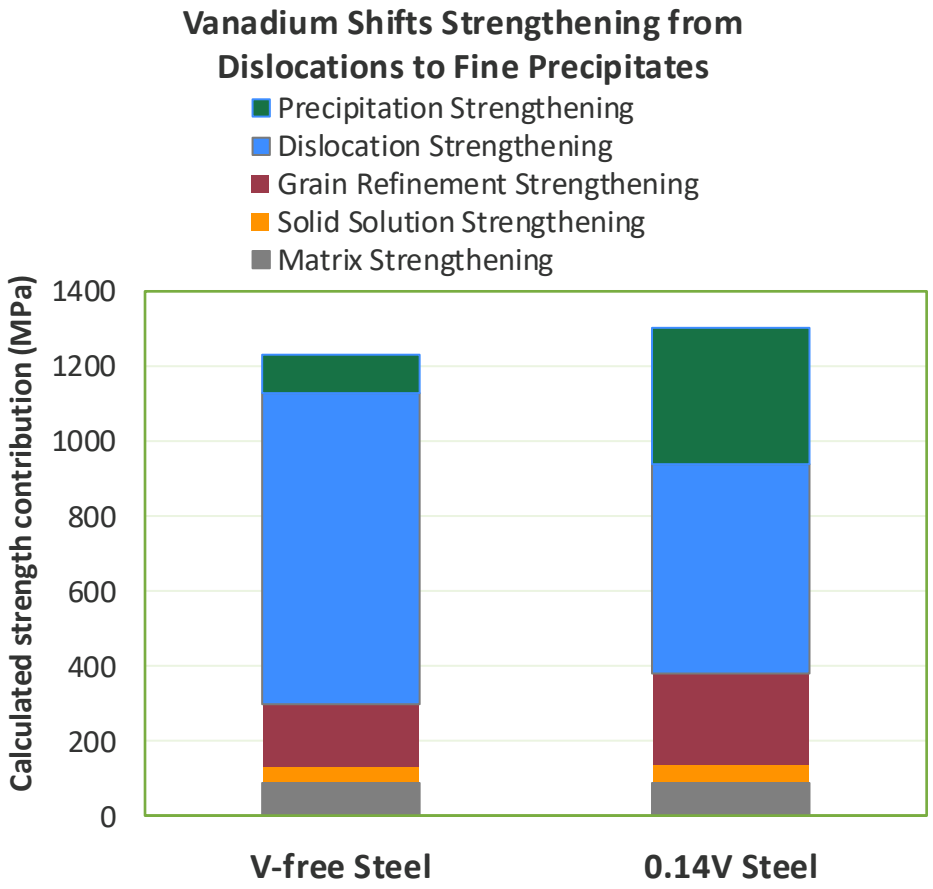
V-free steel: 5.57×10^{20} cm^{-3}

0.14V steel: 8.36×10^{20} cm^{-3}

Fine VC precipitates add hydrogen traps, reducing mobile hydrogen and slowing transport to crack-sensitive regions.

Vanadium Enables Higher-Temperature Tempering for Better HE Resistance

Higher-temperature tempering replaces dislocation-dominated strength with fine precipitation and grain refinement



THE V-ADDED MICROSTRUCTURE IS MORE H-RESILIENT

3.5× precipitation strengthening

104 → 361 MPa. Fine VC particles strengthen the steel while adding effective hydrogen traps.

+80 MPa grain refinement

165 → 245 MPa. Finer grains distribute strain and hydrogen across more boundaries.

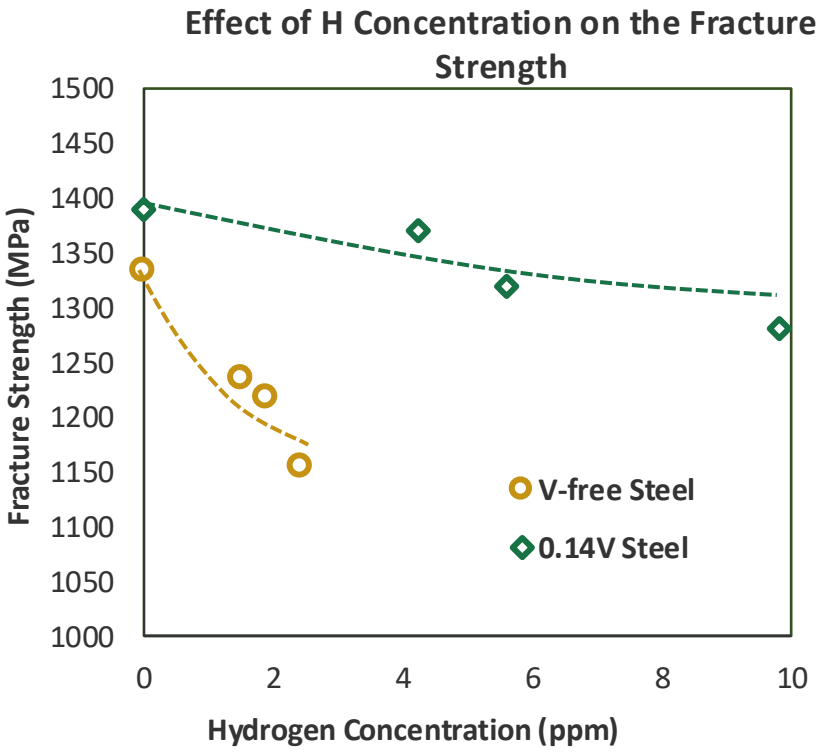
55% lower dislocation density

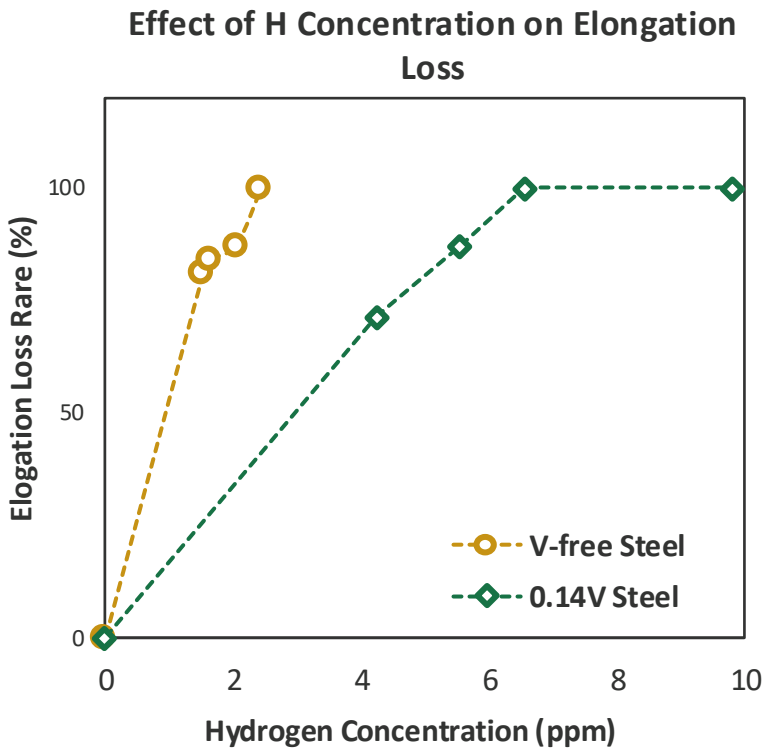
9.59 → 4.33 $\times 10^{11}$ cm^{-2}, reducing hydrogen-dislocation interactions and localized plasticity.

Vanadium retains high strength through VC precipitation and grain refinement - while reducing the dislocation structure that promotes localized hydrogen damage.

Vanadium Delays Hydrogen-Induced Strength and Ductility Loss

Slow strain-rate tensile response response of V-free and 0.14 wt.% V 1300 MPa bolt steels under hydrogen charging





EFFECT OF 0.14 wt.% V

≈2.7×

More H required for complete elongation loss

2.43 → ≈6.55 ppm H

1.28

GPa fracture strength retained

at ≈9.8 ppm H

ppm H = µg hydrogen per g of steel after fracture

SSRT: 3% NaCl + 0.3% NH_4SCN • strain rate 1×10^{-6} s^{-1} • charging current 0.1-6 $mA\cdot cm^{-2}$

Vanadium substantially increases the hydrogen tolerance of 1300 MPa bolt steel.

Vanadium Protects Spot-Welded Automotive AHSS

0.30 wt.% V helps retain hydrogen-embrittlement resistance in 1600-1750 MPa cold-formed steels after spot welding.

V-free steel → **0.30 wt.% V steel**

Ref. Swerim / SSAB project reports • 1600–1750 MPa cold-formed steels

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Does 0.30 wt.% V Preserve HE Resistance After Spot Welding?

Uncoated 1600-1750 MPa martensitic AHSS compared under baseline and weld-affected conditions

TWO MARTENSITIC AHSS CONCEPTS

V-FREE

REF / 1700M

0 wt.% V • 1600–1750 MPa

0.30% V

1700M + V

0.30 wt.% V • 1600–1750 MPa

PROCESSING CONDITIONS

SURFACE CONDITION

Uncoated / pickled

NON-WELDED

Baseline material response

SPOT-WELDED

Weld-affected performance

TWO COMPLEMENTARY MEASUREMENTS

1 MECHANICAL FRACTURE RESPONSE

Electrochemical charging: 0.5 M Na_2SO_4, $-0.2\ mA \cdot cm^{-2}$
Sustained load: 50% R_m for up to 24 h
Load increased at 5% $R_m \cdot h^{-1}$

2 HYDROGEN-TRAPPING RESPONSE

Precharge before TDMS: 3 wt.% NaCl + 1 $g \cdot L^{-1}$ thiourea
Current density: 1 $mA \cdot cm^{-2}$ for 48 h
Trap response compared before and after welding

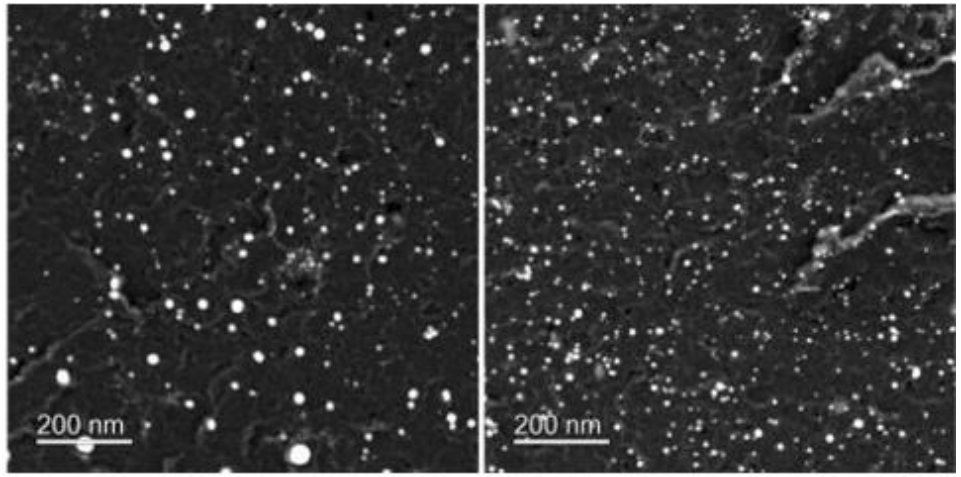
0.30% V is evaluated for its ability to retain hydrogen-trapping capacity and extend fracture life after spot welding.

V-Rich Precipitates Survive the Spot-Welding Thermal Cycle

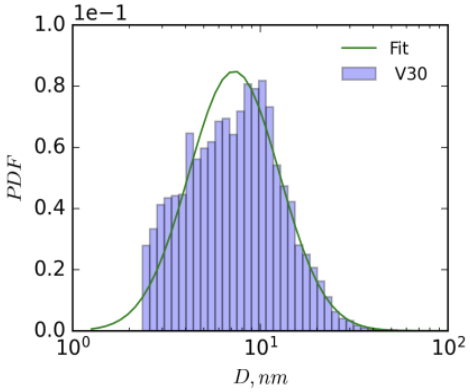
TEM/STEM evidence from 0.30 wt.% V automotive AHSS shows retained precipitates within the welded region

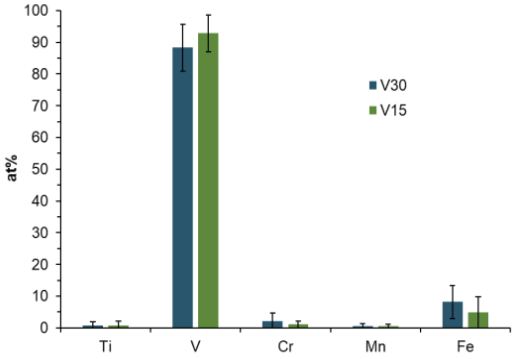
BEFORE WELDING

Dense nanoscale precipitate population



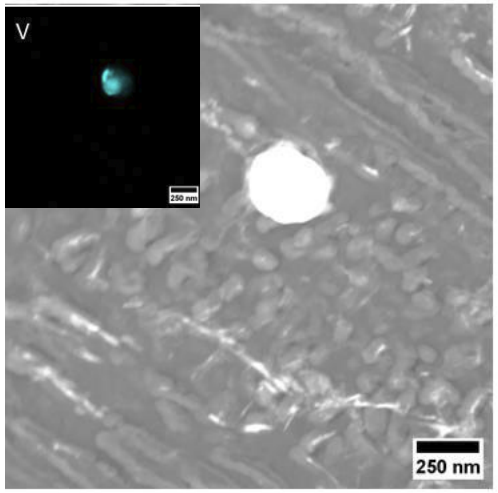
Bright particles are distributed throughout the V30 microstructure





AFTER SPOT WELDING

V remains inside a weld-region precipitate



EVIDENCE SHOWS

Dense V-rich precipitates exist before welding.

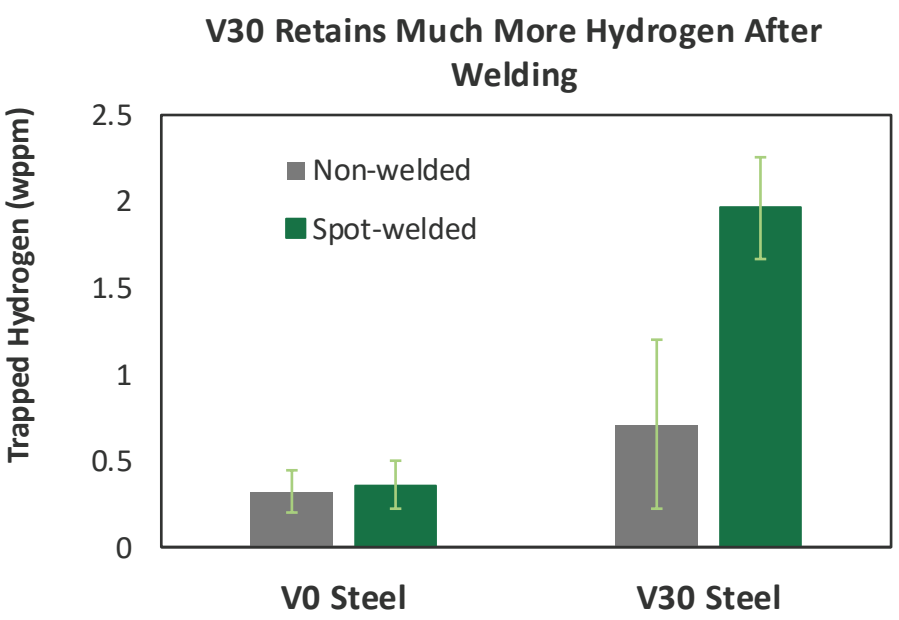
Vanadium is directly detected in a weld-region precipitate.

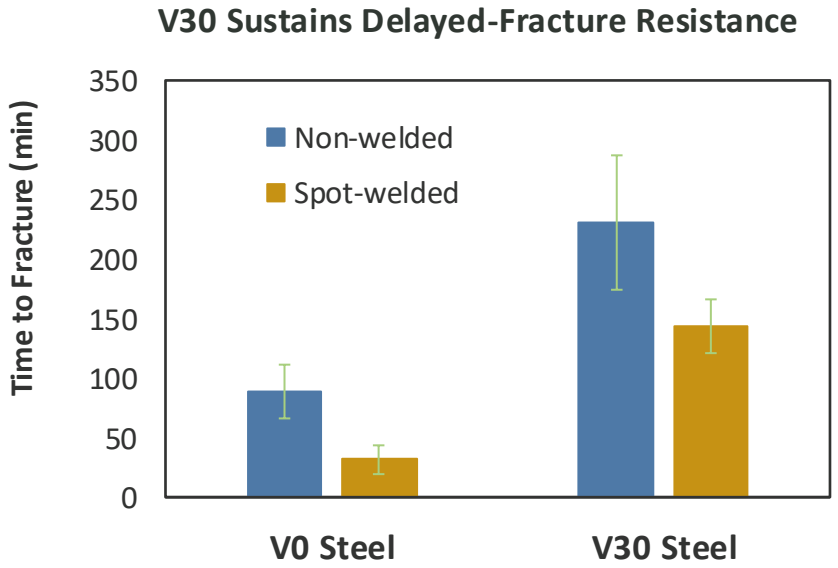
A substantial population survives welding.

Retained V-rich precipitates can preserve hydrogen-trapping capacity within the weld and heat-affected region.

Vanadium Preserves Trapping and Delays Fracture After Spot Welding

V-free (V0) and 0.30 wt.% V (V30) automotive AHSS compared before and after welding





VANADIUM TRAPS HYDROGEN

≈5.6× more trapped hydrogen after spot welding

VANADIUM DELAYS FRACTURE

≈4.8× longer fracture time after spot welding

Retained V-rich precipitates immobilize hydrogen and preserve delayed-fracture resistance through spot welding.

Vanadium Enables Safer High-Strength Steel Applications

CONCLUSIONS

- Fine VC precipitates trap diffusible hydrogen, reducing hydrogen mobility and accumulation at crack-sensitive regions.
- Press-hardened automotive steels retain greater ductility and resist brittle fracture, supporting safer ultra-high-strength vehicle structures.
- Cr–Mo–V steels show improved fracture toughness and fatigue-crack resistance, benefiting hydrogen vessels, pipelines and other pressure components.
- High-strength bolt steels gain slower hydrogen transport and better delayed-fracture resistance, increasing fastener reliability.
- Spot-welded automotive steels retain hydrogen-trapping capacity after welding, extending fracture life in both the base metal and heat-affected zone.
- The greatest benefit comes from a fine, dense and thermally stable VC precipitate population, achieved through appropriate vanadium addition and processing.

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Thank You

Questions & Discussion

Vanadium enables stronger, safer and more durable steels for hydrogen-exposed applications.

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