Hydrogen embrittlement in AHSS containing metastable austenite

X.J. Jin[1],W. Li[1], X. Zhu[1], Y.H. Rong[1], L. Wang[2], H. Jiao[3]

[1] School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
[2] Baosteel Research Institute, Shanghai 201900, China
[3] Oxford Instruments, Shanghai, 201102, China

August 2014 @ Northeast University, Shenyang, China

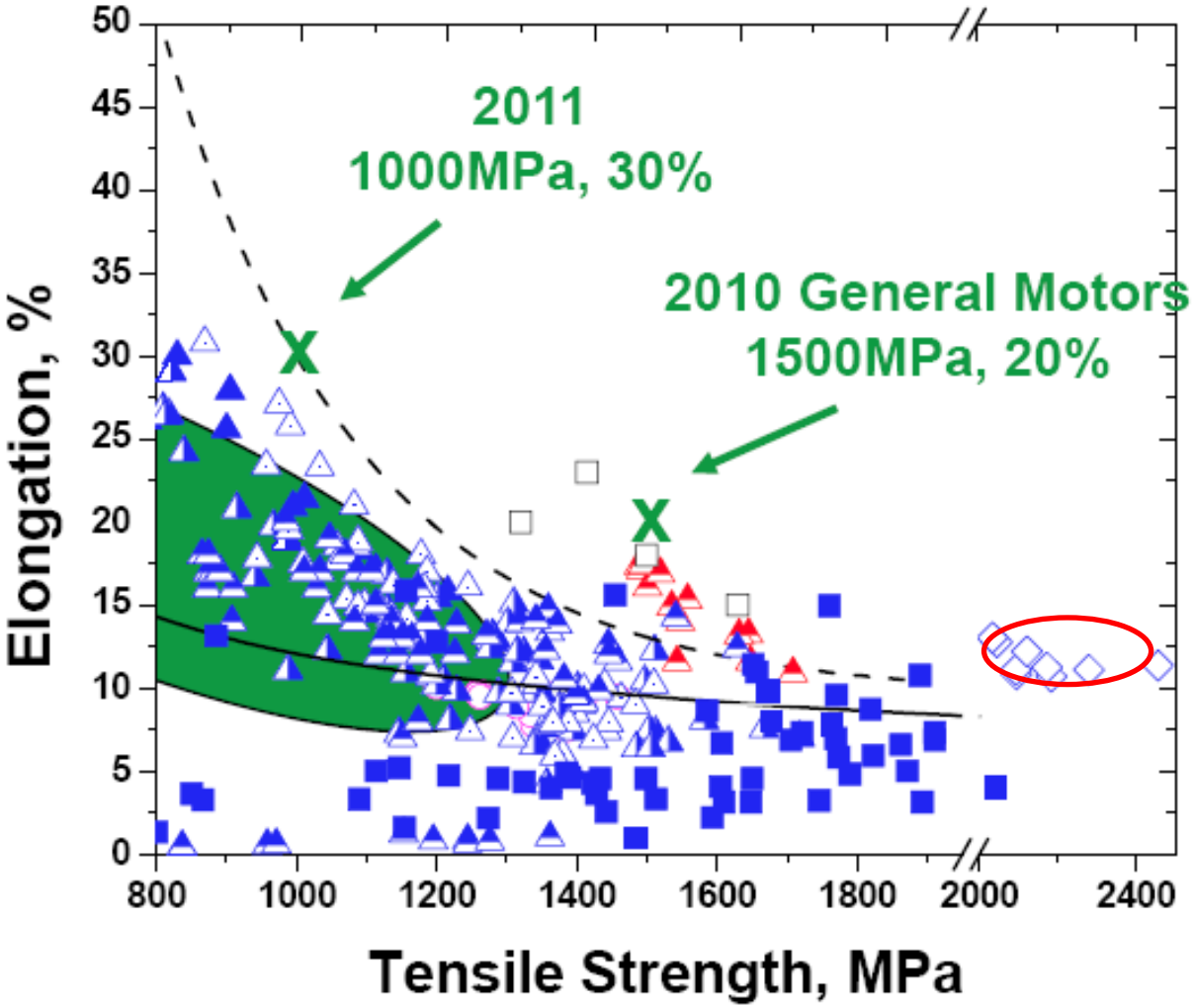
jin@sjtu.edu.cn

OUTLINE

- Introduction
- Hydrogen embrittlement of QP980 steel
- Improved HE of TRIP780 by tempering
- Improved HE of QP980 by tempering
- Conclusion remarks

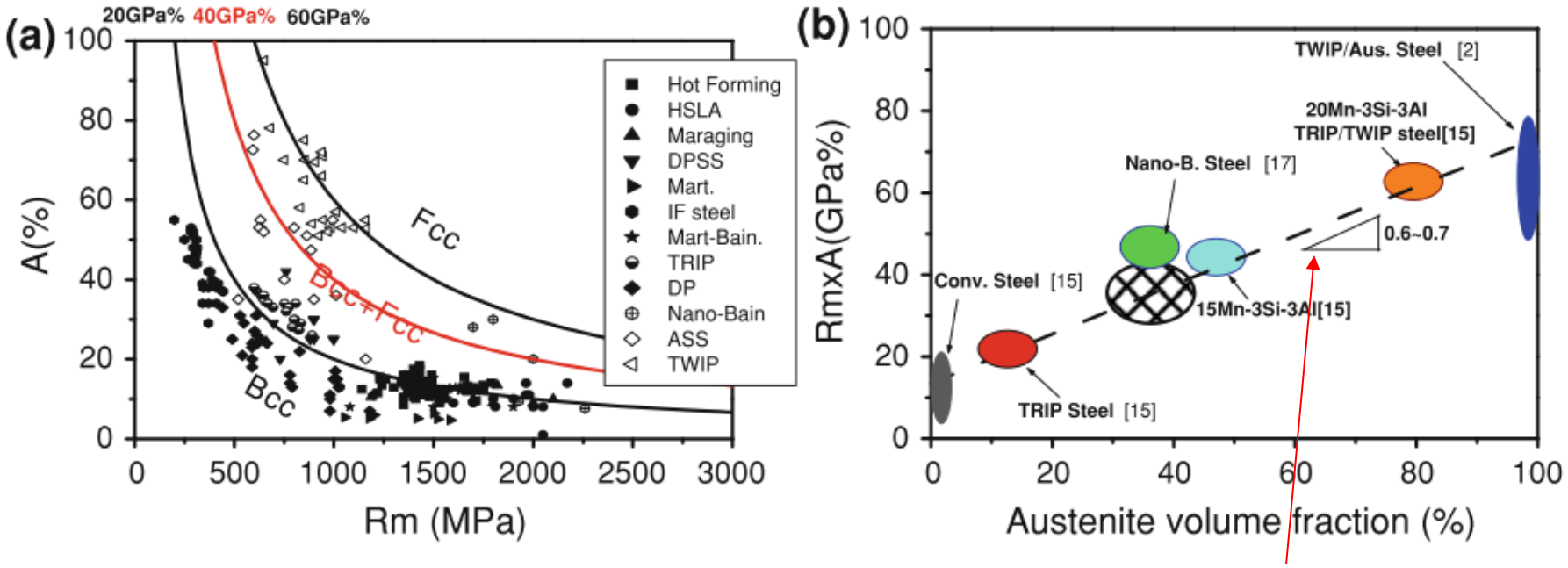
Third Generation AHSS property band

US – DOE Targets in 2012 Integrated Computational Materials Engineering（ICME）Program are even greater (30%/1200MPa and 25%/1500MPa)



E. De Moor, P.J. Gibbs, J.G. Speer, D.K. Matlock, and J.G. Schroth: AIST Trans., 2010, vol. 7 (3), pp. 133–44.
J.G. Speer, D.K. Matlock , et al, METALLURGICAL AND MATERIALS TRANSACTIONS A, September 2011

How to develop Third Generation AHSS

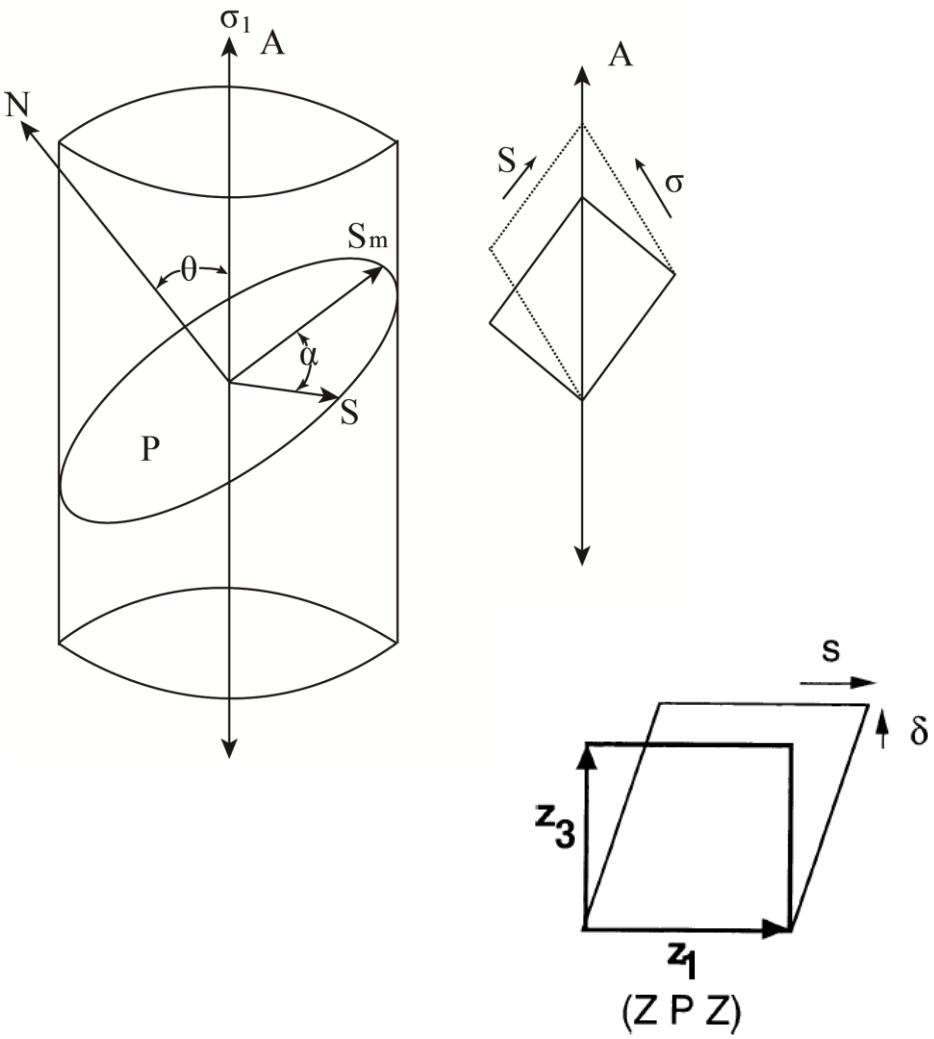


Function of austenite volume fraction

Dependence of elongation to failure on tensile strength and residue austenite fraction of different steel (a) total elongation and ultimate tensile strength and (b) product of ultimate tensile strength to total elongation and austenite volume fraction

Dong H., Sun XJ., Cao WQ., Liu ZD., et al., On the performance improvement of steels through M 3 structure control, Advanced Steels, 2011, 35-57.

From TRIP effect to TRIP-assisted



$s=0.26$ and $\delta=0.03$, $\theta=42°$; it follows that
xis, represented as a unit vector with respec
Z, is given by

$$[Z;\mathbf{u}]=[\sin\theta\ 0\ \cos\theta]$$

$$[Z;\mathbf{v}]=(Z\ P\ Z)[Z;\mathbf{u}]$$

t

$$[Z;\mathbf{v}]=[(\sin\theta+s\cos\theta)\ 0\ (1+\delta)\cos\theta]$$

$$1-|\mathbf{v}|/|\mathbf{u}|=0.15$$

0.15*15%=2.25%

Composite deformation behavior.

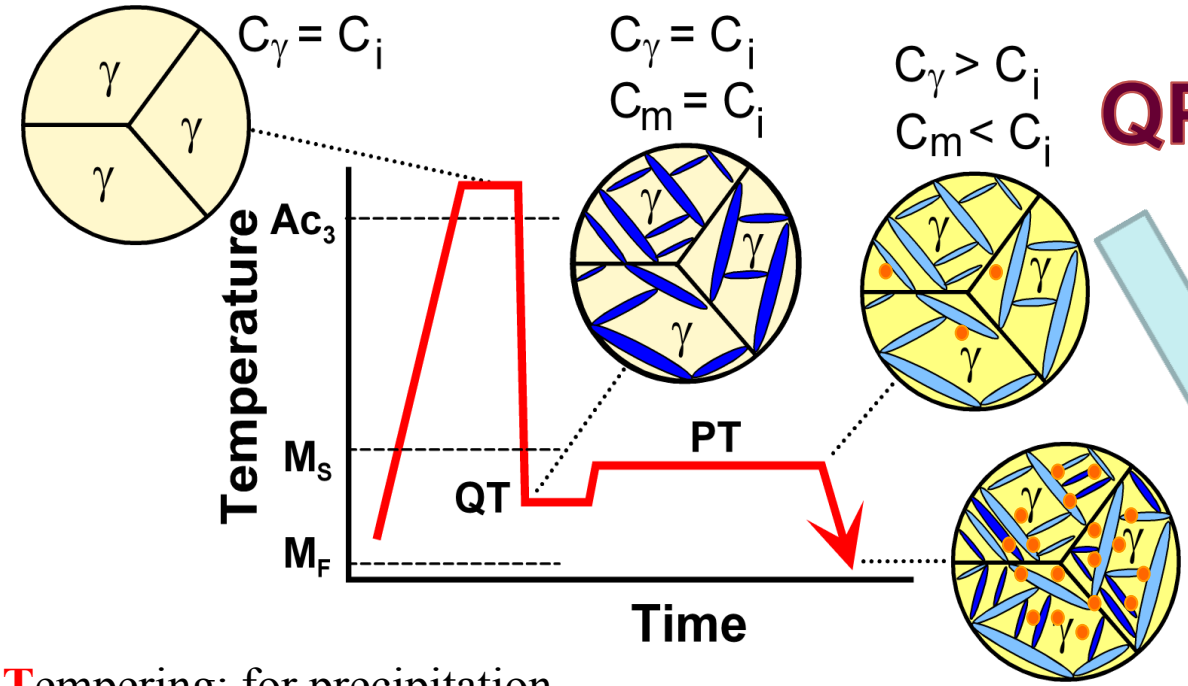
H.K.D.H. Bhadeshia, “TRIP-assisted steels?”, ISIJ International, Vol. 42 (2002), No. 9, pp. 1059–1060

* Schematic Process for QP & QPT

Quenching: Fraction of Martensite
Partioning: Carbon diffuse into residual austenite

C-Si-Mn

15000MPa·%



Lath martensite
＋retained austenite in thin film

QPT

Tempering: for precipitation

Speer&Edmonds, 2003, QP
T. Y. Hsu, 2007, QPT

Microalloying + tempering = strengthening by precipitatoin

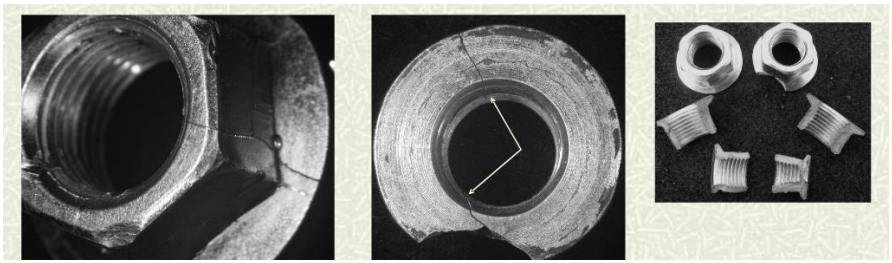
> 15000MPa·%

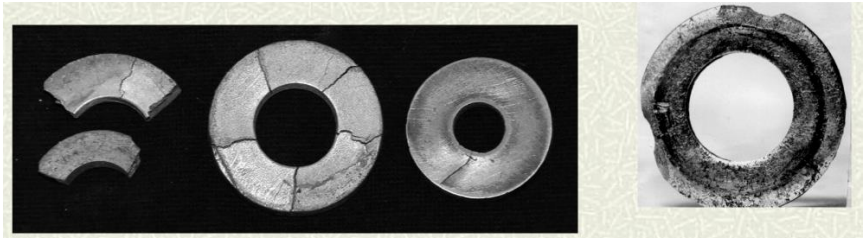
Introduction

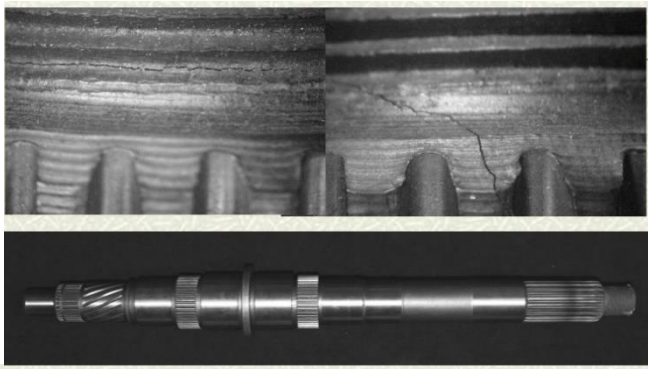
Hydrogen-induced cracking (HIC) is a failure by the generation and propagation of the cracks due to **hydrogen** atoms concentrating at highly stressed regions, i.e. the degradation of mechanical properties (mainly ductility) in the presence of hydrogen.

When the tensile strength of over about **1.2 GPa**, the HIC increase dramatically.

HIC cases in automotive industry

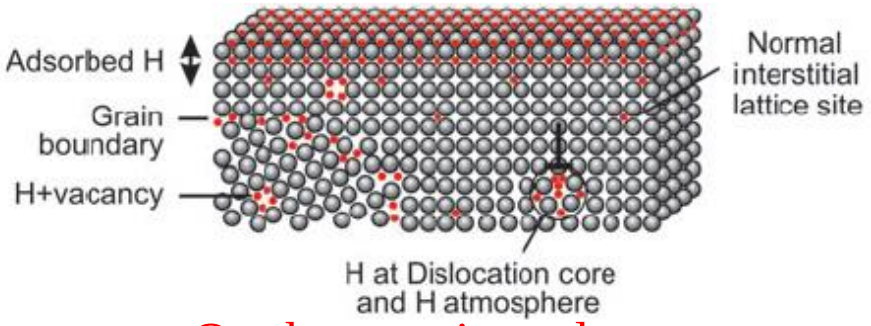




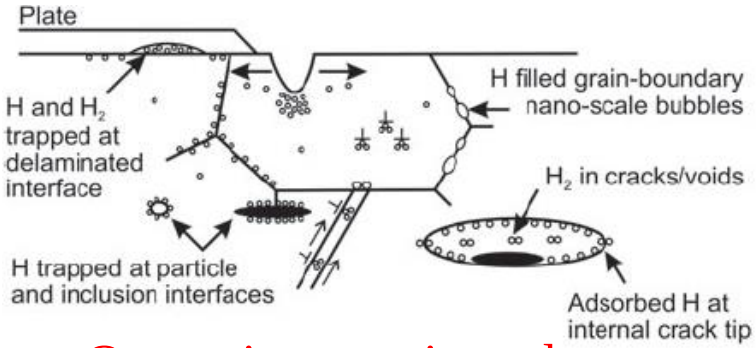


Hydrogen trapping sites in steel

Schematic illustrations of sites and traps for hydrogen in materials



On the atomic scale



On a microscopic scale

Type of Trap	Peak Temperature (K)	Activation Energy (kJ/mol)	Heating Rate (K/min)	Material
Reversible hydrogen traps				
Grain Boundaries	385.15	17.2	3	pure iron
Dislocations	488.15	26.8	3	pure iron
Microvoids	578.15	35.2	3	pure iron
Retained Austenite	~493.15	—	2.6	high carbon steel
TiC (Semi-Coherent)	~503.15	—	1.7	low carbon steel
Ferrite/Fe_3C Interface	~393.15	18.4	2.6	medium carbon steel
Dislocations	478.15	—	2.6	medium carbon steel
V_4C_3 (Coherent)	~493.15	30	2.6, 1.7	high and low carbon steel
Irreversible Hydrogen Traps				
TiC (Incoherent)	~983.15	86.9	3	medium carbon steel
MnS	~768.15	72.3	3	low alloy steel
Fe_3C (Incoherent)	—	84	4	medium carbon steel
Retained Austenite	~873.15	55	4	dual phase steel

Szost B et al. Metall Mater Trans A 2013;44:4542-50

Stan Lynch, Hydrogen embrittlement phenomena and mechanisms. *Corros Rev*, 2012, 105-123

H solubility in multiphase microstructure

- Hydrogen is 10 times more soluble in austenite than in ferrite
- The martensitic structure contained the highest amount of hydrogen and possessed the highest hydeogen solubility compared with lower bainite, upper bainite, banded ferrite/pearlite structures and random ferrite/pearlite.
- Stress-induced transformation changed the hydrogen transport behavior due to the high diffusion rate and low solubility in the resulting martensite phase.

Bhadeshia, Effect of deformation on hydrogen trapping and effusion in TRIP-assisted steel. *Acta materalia* , 2012, 4085-4092
D. Perez Escobar, Hydrogen trapping in cold deformed TRIP steel. *Acta materalia* , 2012, 2593-2605
Park et al, Retained austemite as a hydrogen trap in steel welds. *Welding journal*, 2002, 27-35

H diffusivity in multiphase microstructure

- The diffusivity of hydrogen at 323K in **ferrite** is 3-4 orders of magnitude greater than in **austenite**.
- Compared 304 prestrained at 29℃ with 304 prestrained at -70℃, the diffusivity of hydrogen in **martensite** is much greater than in **austenite**.
- Martensite is also known to have a hydrogen diffusion coefficient which is about 10^2–10^3 times lower than the diffusion coefficient in ferrite

Table I. Hydrogen Diffusion Coefficients in Specimens: (a) Hydrogen Diffusion Coefficient at 323 K in Solution-Treated Austenitic Stainless Steels and an Annealed Ferritic Stainless Steel (Type 405) and (b) Hydrogen Diffusion Coefficient at 353 K in Prestrained Specimens of Types 304 and 316L and a Solution-Treated Specimen of Type 304

(a)

Type	Hydrogen diffusion coefficient at 323 K (m^2/s)
304	1.1×10^{-15}
316	2.0×10^{-15}
316L	2.4×10^{-16}
405	2.8×10^{-12}

FCC

BCC

(b)

Type	Hydrogen diffusion coefficient at 353 K (m^2/s)
Solution-treated 304 (α': to approximately 3 pct)	5.5×10^{-15}
304 prestrained at 29 °C (ε_p = 0.29, α': 1 to approximately 3 pct)	5.5×10^{-15}
304 prestrained at –70 °C (ε_p = 0.28, α': 65 to approximately 69 pct)	2.4×10^{-13}
316L prestrained at –70 °C (ε_p = 0.30, α': 26 to approximately 28 pct)	5.4×10^{-14}

ε_p: plastic prestrain, and α': martensite content.

Hanada et al, Profiling of hydrogen accumulation in a tempered martensite microstructure. *Scripta Mat* 2005, vol.53, p. 1279

Yukitaka et al, Hydrogen embrittlement mechanism in fatigue of austenitic stainless steels. *Met. Trans. A*, 2008, vol.39A, p. 1327

Mechanism of hydrogen embrittlement

1.*Hydride formation and fracture*

Repeated sequence:

- ☑ hydrogen diffusion to regions of high hydrostatic stress ahead of cracks
- ☑ nucleation and growth of a hydride phase
- ☑ cleavage of the hydride when it reaches a critical size
- ☑ crack-arrest at the hydride-matrix interface

Only occurs:

- ◆ Hydrogen has time to diffuse to regions ahead of crack tips
- ◆ Hydride phase is stable and brittle

Stan Lynch, Hydrogen embrittlement phenomena and mechanisms. *Corros Rev,* 2012, 105-123

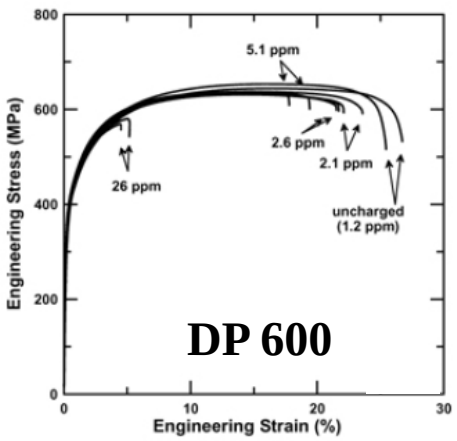
Mechanism of hydrogen embrittlement

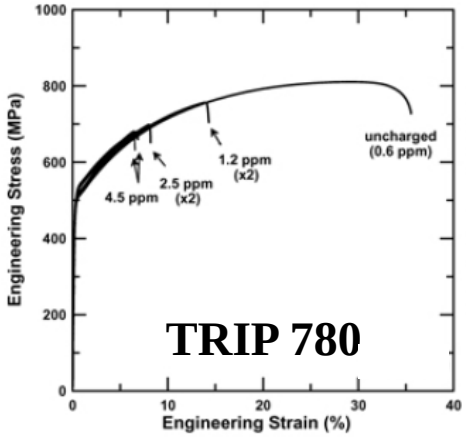
In non-hydride formation system, two mechanisms for hydrogen embrittlement appear to be viable at room temperature:

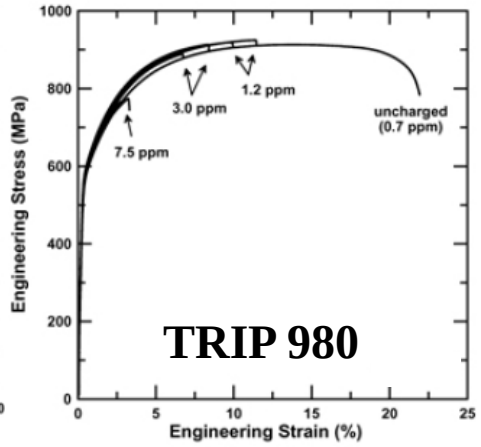
1. Hydrogen-induced decohesion (HID)
2. Hydrogen-enhanced localized plasticity (HELP)
3. Nano-void coalescence mechanism

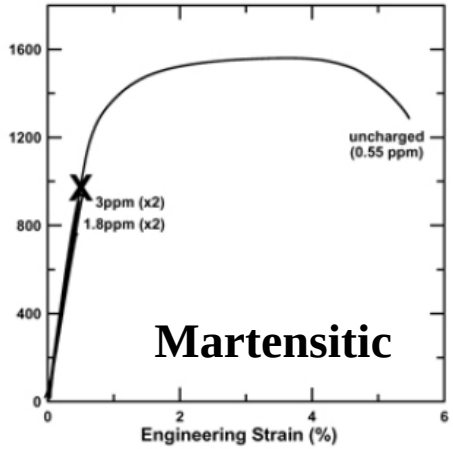
HE in modern AHSS

AHSS is sensitive to HE

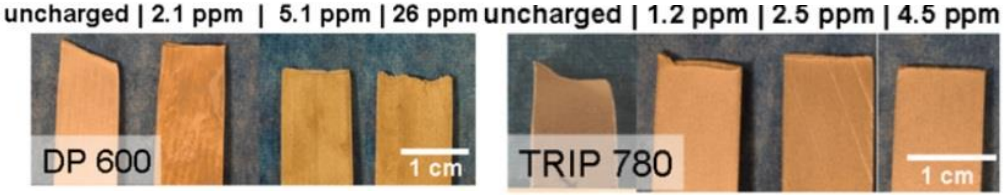


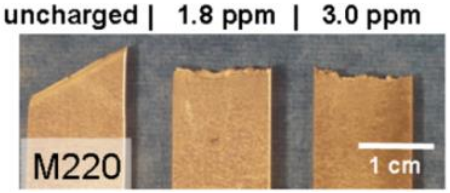




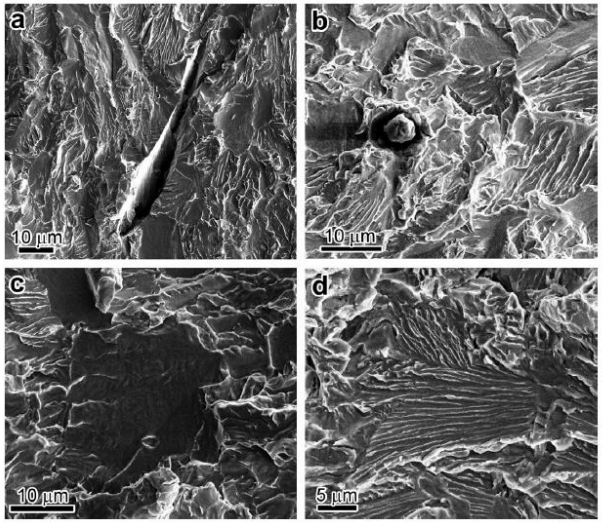


Hydrogen embrittlement susceptibility increases with increasing steel strength levels





Characteristic macroscopy of hydrogen induced fracture



Ronevich JA, Speer JG, Matlock DK. SAE Int J Mater Manuf 2010;3:255-67

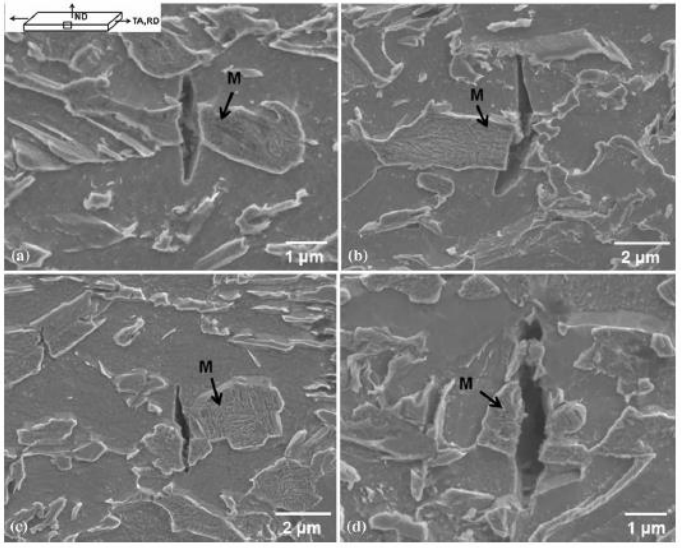
HE in modern AHSS

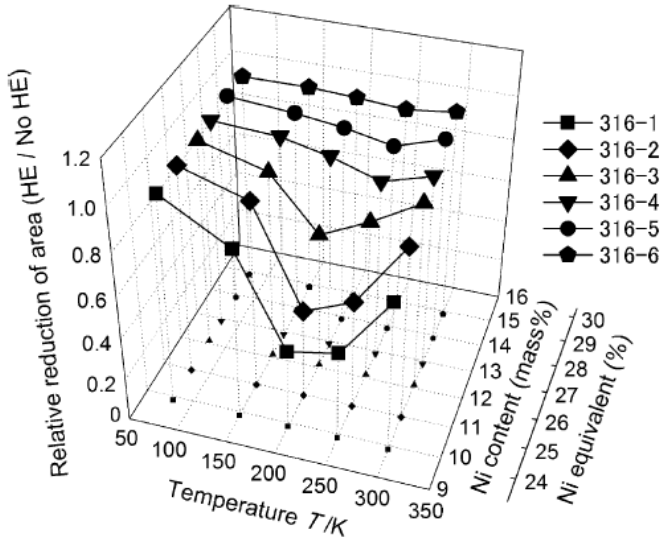
1. Transformation induce plasticity effect may deteriorate HE

TRIP

- Hydrogen solubility in austenite is higher than that in martensite--microstructure
- Hydrogen diffusivity in martensite is high than that in austenite
- A large number of misfit dislocations
- High internal stress caused by volume expansion

→ inhomogeneous hydrogen distribution





- Hydrogen induced cracking in martensite area
- HE susceptibility reduces with the increased austenite stability

Ronevich et al. SAE International Journal of Materials & Manufacturing 2010;3:255-67.

Lin ZHANG et al. ISIJ international 2012: 240-46

HE in modern AHSS

2. Introducing irreversible trapping sites may alleviate HE

Trap sites → decrease H diffusivity / immobilize hydrogen → prevents H from segregating to the dilated region under triaxial tensile stress ahead of the crack tip

ε carbides
NbC

on the one hand increase the strength level

on the other hand introduce a high density of strong trapping sites

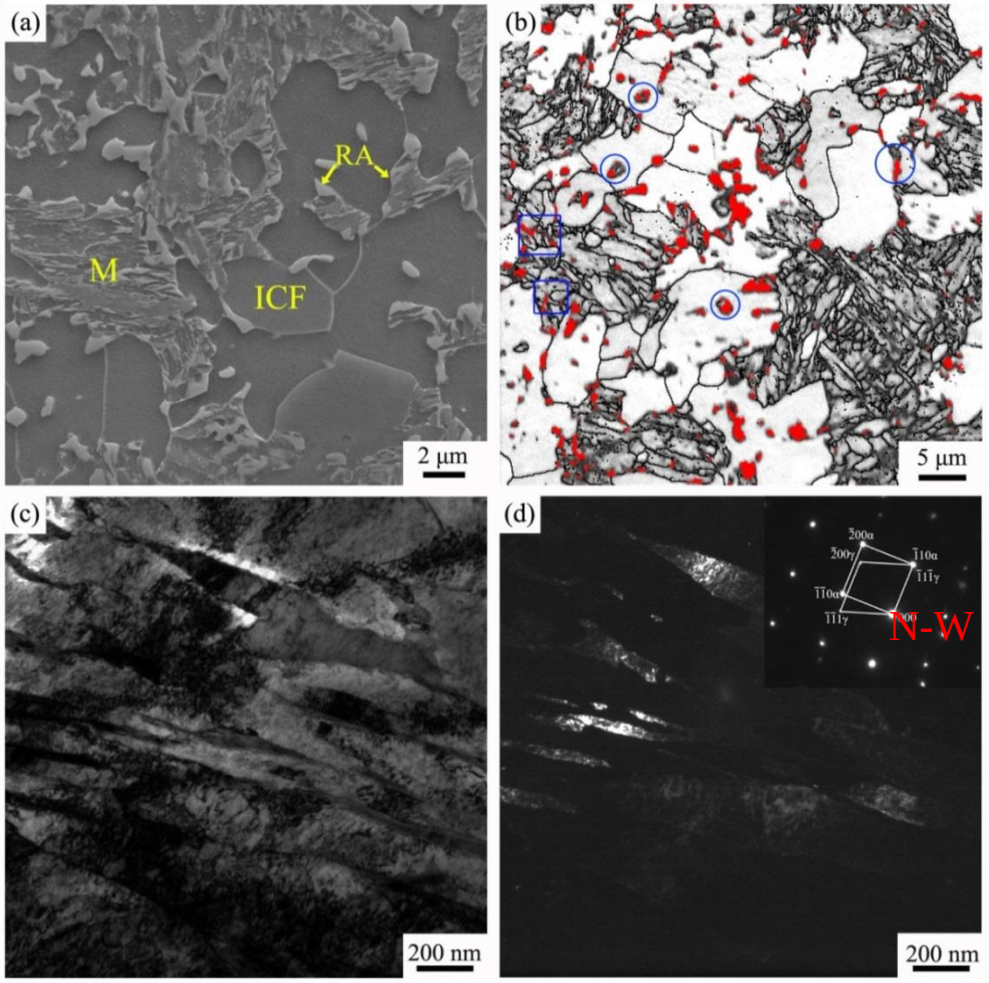
Type of Trap	Peak Temperature (K)	Activation Energy (kJ/mol)	Heating Rate (K/min)	Material
Reversible hydrogen traps				
Grain Boundaries	385.15	17.2	3	pure iron
Dislocations	488.15	26.8	3	pure iron
Microvoids	578.15	35.2	3	pure iron
Retained Austenite	~493.15	—	2.6	high carbon steel
TiC (Semi-Coherent)	~503.15	—	1.7	low carbon steel
Ferrite/Fe_3C Interface	~393.15	18.4	2.6	medium carbon steel
Dislocations	478.15	—	2.6	medium carbon steel
V_4C_3 (Coherent)	~493.15	30	2.6, 1.7	high and low carbon steel
Irreversible Hydrogen Traps				
TiC (Incoherent)	~983.15	86.9	3	medium carbon steel
MnS	~768.15	72.3	3	low alloy steel
Fe_3C (Incoherent)	—	84	4	medium carbon steel
Retained Austenite	~873.15	55	4	dual phase steel

T.Y. Hsu, Mater. Sci. Forum 561 (2007) 2283
J. Takahashi, K. Kawakami, Y. Kobayashi, T. Tarui, Scr. Mater. 63 (2010) 261
Szost B et al. Metall Mater Trans A 2013;44:4542-50
B. Szost, R. Vegter, P.E.J. Rivera-D áz-del-Castillo, Mater. Des. 43 (2013) 499

OUTLINE

- Introduction
- Hydrogen embrittlement of QP980 steel
- Improved HE of TRIP780 by tempering
- Improved HE of QP980 by tempering
- Conclusion remarks

QP980 Steel Commercially Manufactured



ferrite

lath martensite

austenite

Processing

Austenization

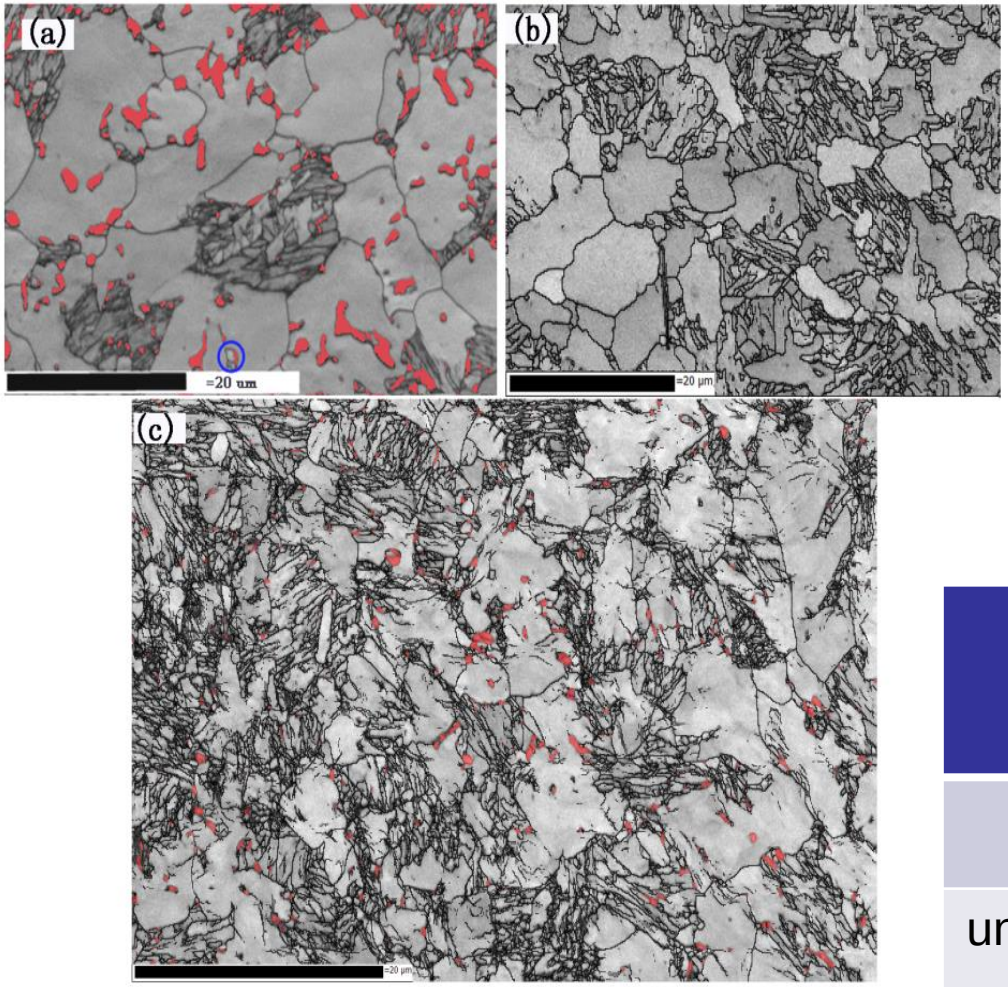
↓

Intercritical annealing

↓

Quenching & Partitioning

Quantitative Phase Evaluation for QP980 by EBSD



ferrite

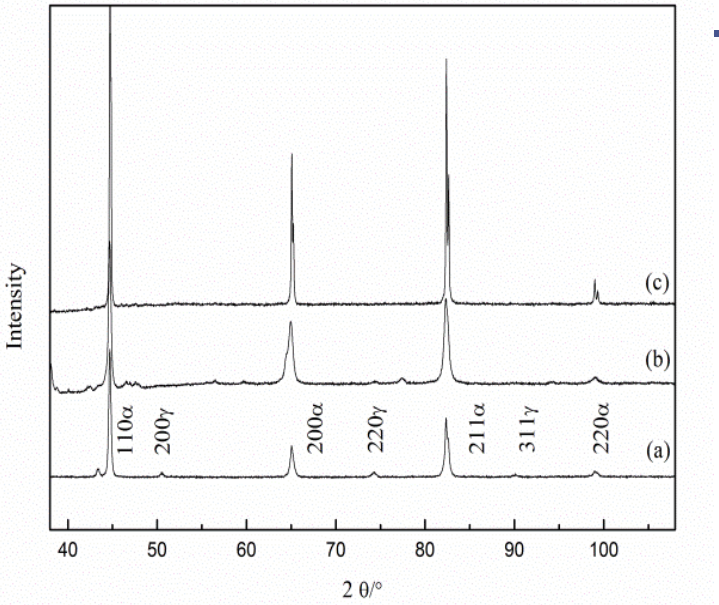
lath martensite

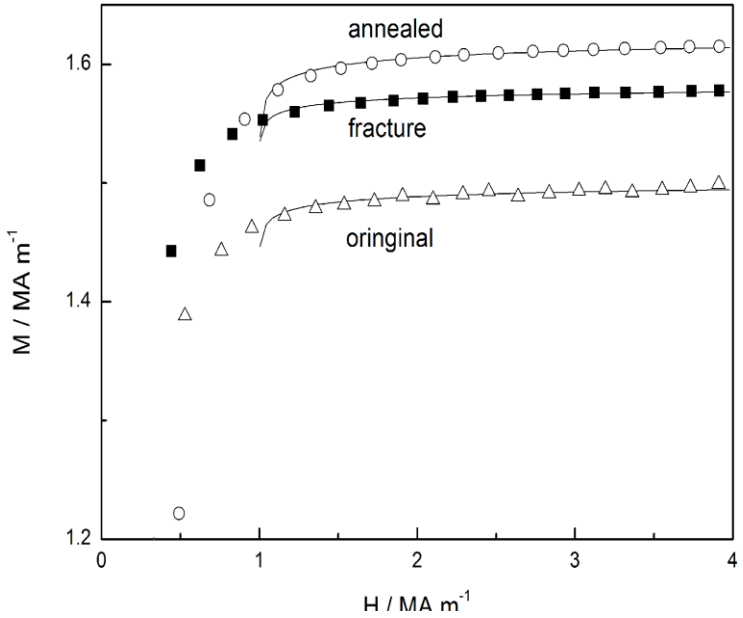
austenite

EBSD	As received	After tensile fracture
RA%	6.2%	1.46
unidentified	4.46%	9.2%

a) as-received sample;
b) annealed sample of as received;
c) after-tensile test sample;

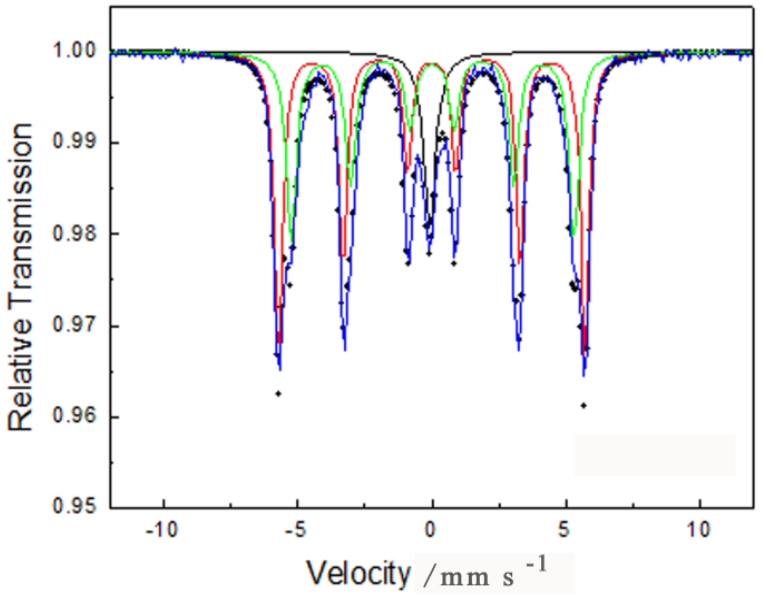
XRD, Magnetization and Mössbauer





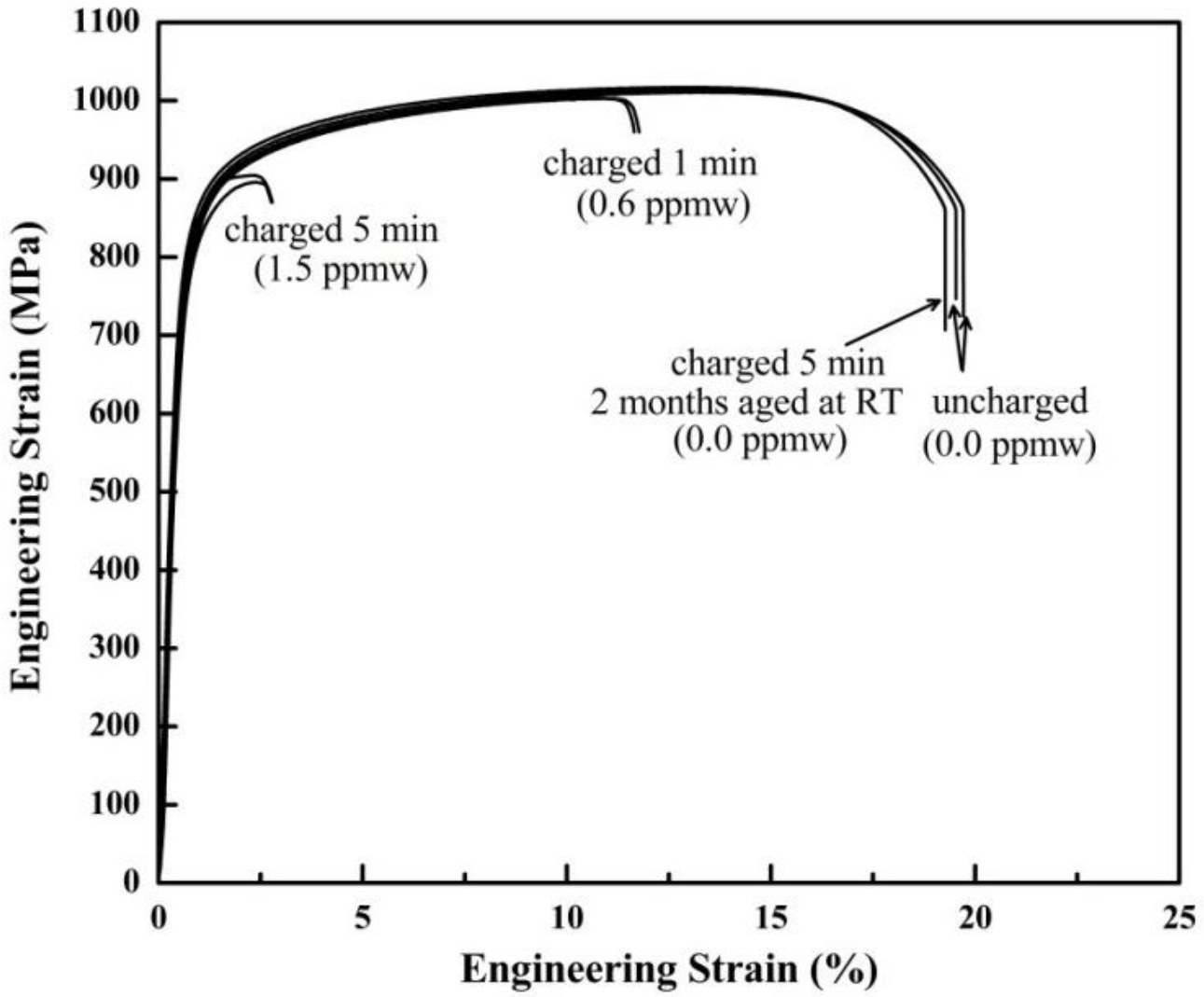
XRD	Magnetization
	Mössbauer

	As received	After tensile fracture
XRD	**8.3%**	——
magnetization	**9.0%**	4.0%
Mössbauer	**10.4%**	——



H. S. Zhao, X. Zhu, W. Li*, X. J. Jin*, L. Wang, H. Jiao and D. M. Jiang, *Austenite stability for quenching and partitioning treated steel revealed by colour tint-etching method*, **Materials Science and Technology 2014. 30**: p.1008-1013.

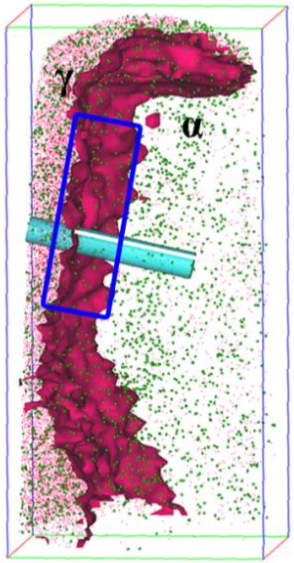
Part I: Hydrogen Embrittlement

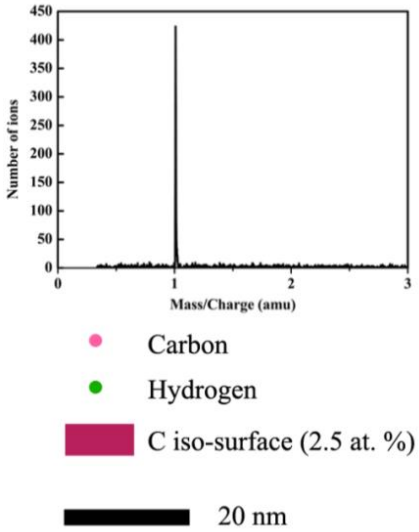


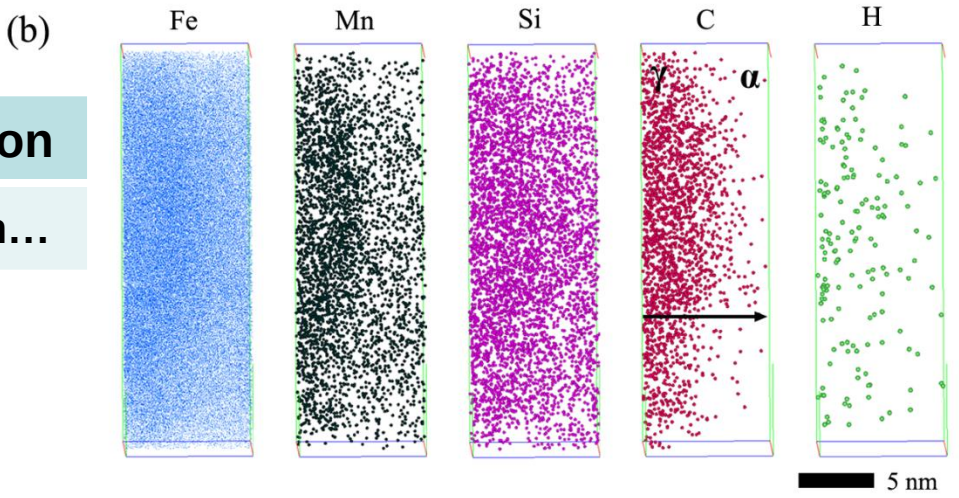
- QP980 was observed hydrogen susceptible.
- Mechanical property was resumed after hydrogen desorption.

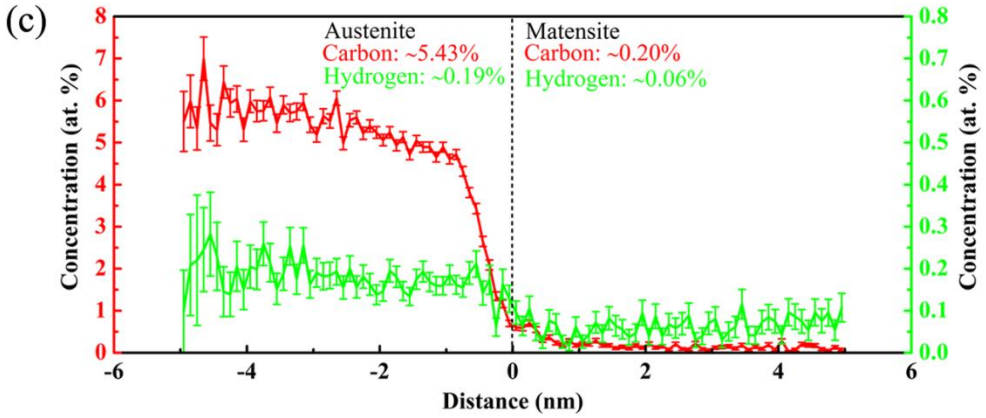
Part I: Hydrogen Embrittlement

Iso-concentration surface	Elements distribution
	Carbon and hydrogen…



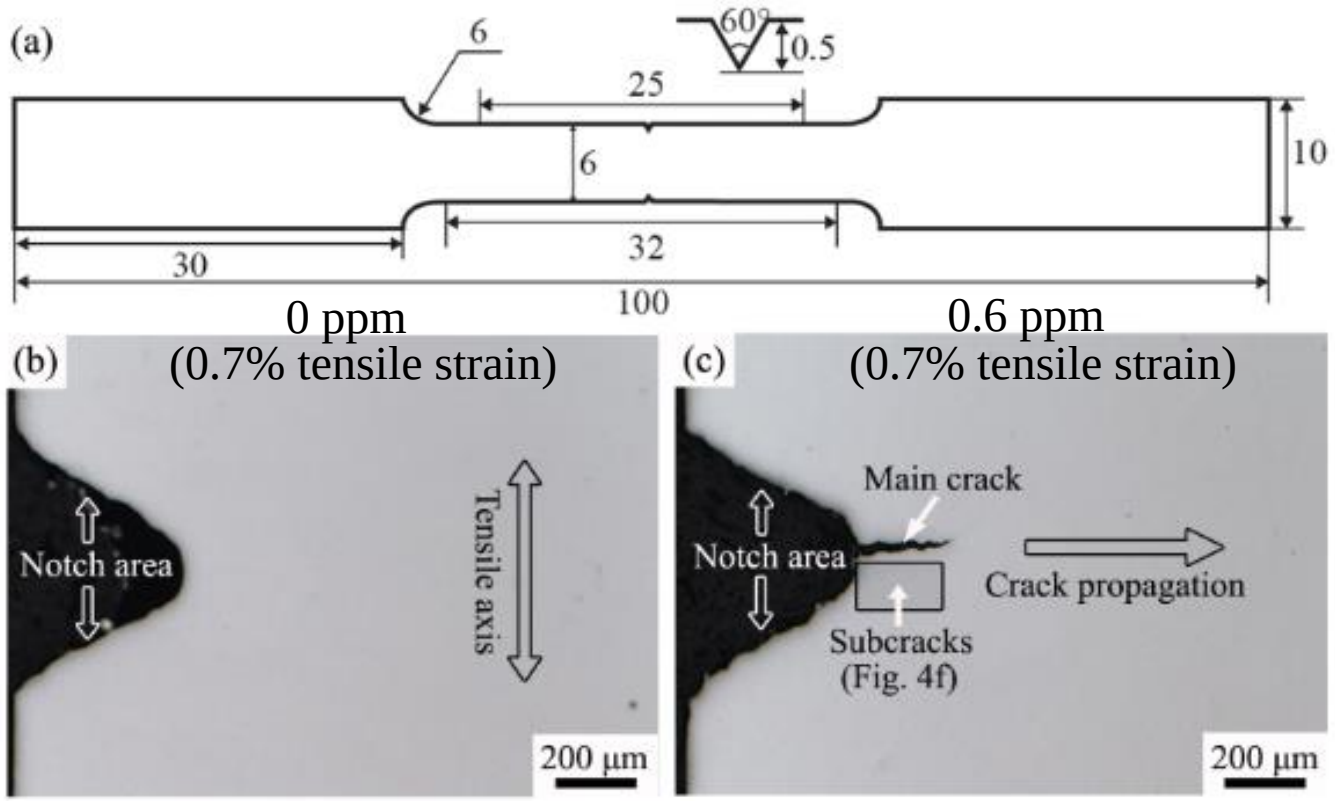






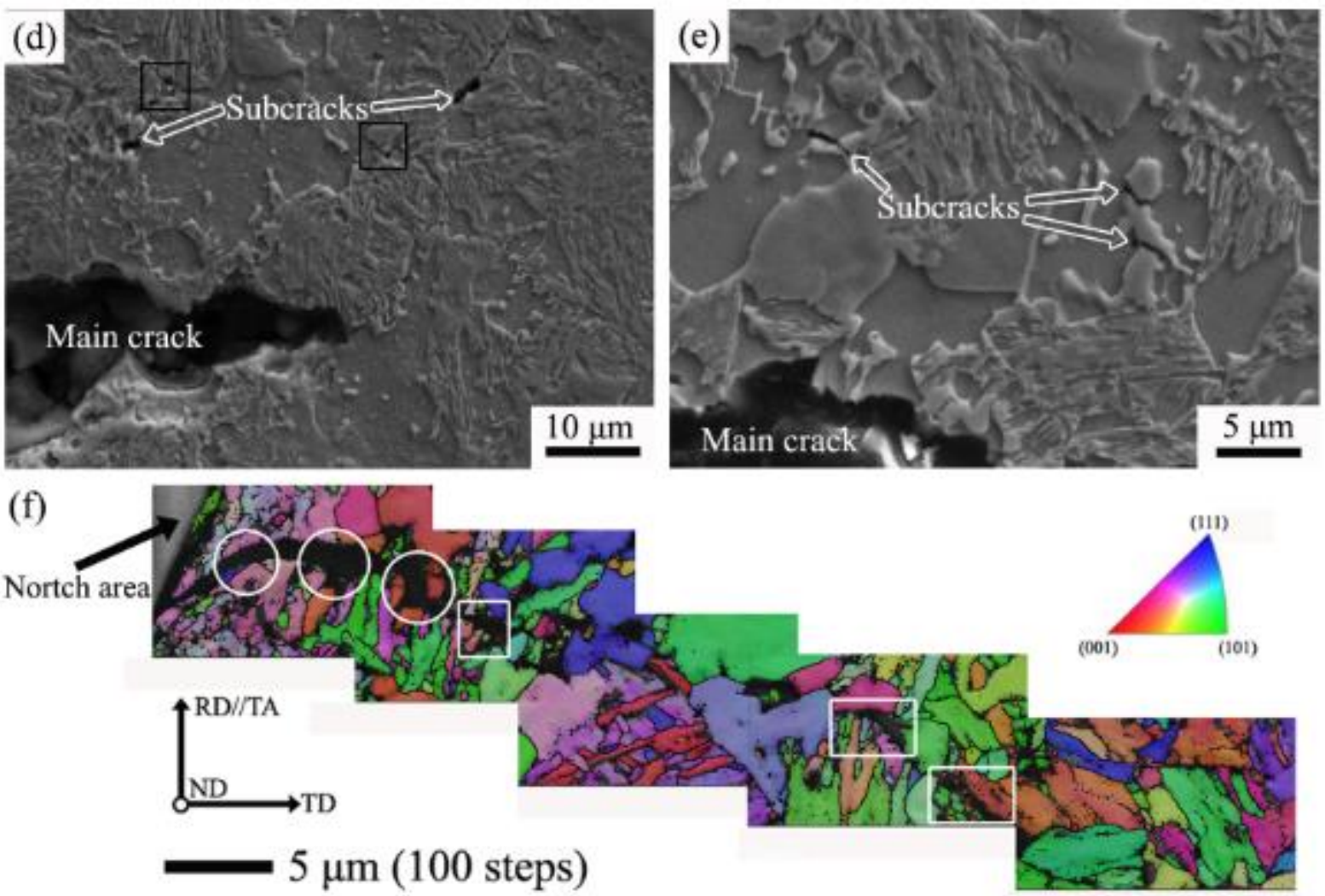
- Hydrogen trapping sites are directly observed by atom probe tomography.
- Hydrogen is three times more soluble in austenite than that in martensite

hydrogen induced cracking (HIC)



- No crack is found in the uncharged specimen.
- An obvious crack is observed perpendicular to the tensile axis.
- Main crack is initiated at the corner of the notch area and propagates into the center.

EBSD observation of HIC



- Stepwise HIC cracks are observed and the cracks are both intergranular (as indicated by white square) and transgranular (as indicated by white circle).
- It is worth mentioning that no crack is found in intercritical ferrite.

Hydrogen Embrittlement of QP980 Sheet Steels

- Hydrogen dramatically causes degradation in the Q&P treated steels.
- Hydrogen trapping sites are directly observed by atom probe tomography technology, which shows that hydrogen in austenite (33.9 ppmw) is 3 times more soluble than that in martensite (10.7 ppmw) in these Q&P treated steels.
- By using DENT specimen, hydrogen-induced cracks were observed.

X. Zhu, X. Jin, et al, International Journal of Hydrogen Energy (2014), http://dx.doi.org/10.1016/j.ijhydene.2014.06.079

OUTLINE

- Introduction
- Hydrogen embrittlement of QP980 steel
- Improved HE of TRIP780 by tempering
- Improved HE of QP980 by tempering
- Conclusion remarks

Background

- The sensitivity to HE increases with increasing steel strength levels. However, TRIP 780 steels are more susceptible to hydrogen than the TRIP 980 steels. (Why? ——Retained austenite stability)
- How to verify?
- Part of the initial metastable retained austenite in the TRIP steels can transform to martensite via cryogenic treatment. The carbon partitioning from the transformed martensite to Ar during tempering makes remained austenite more stable.

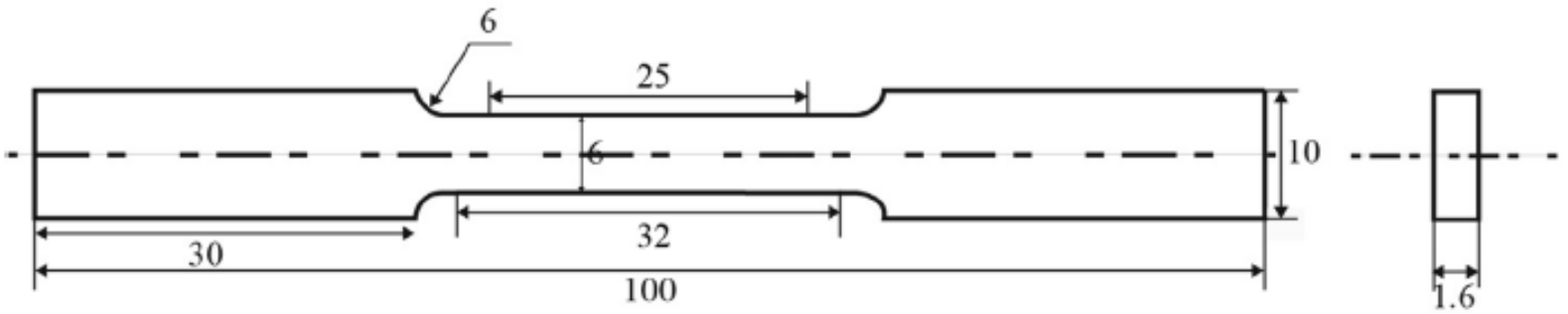
Therefore, CT treatments were applied to adjust the phase fraction, to stabilize the RA and to look into the effect of RA stability on HE in TRIP 780 steels.

Materials

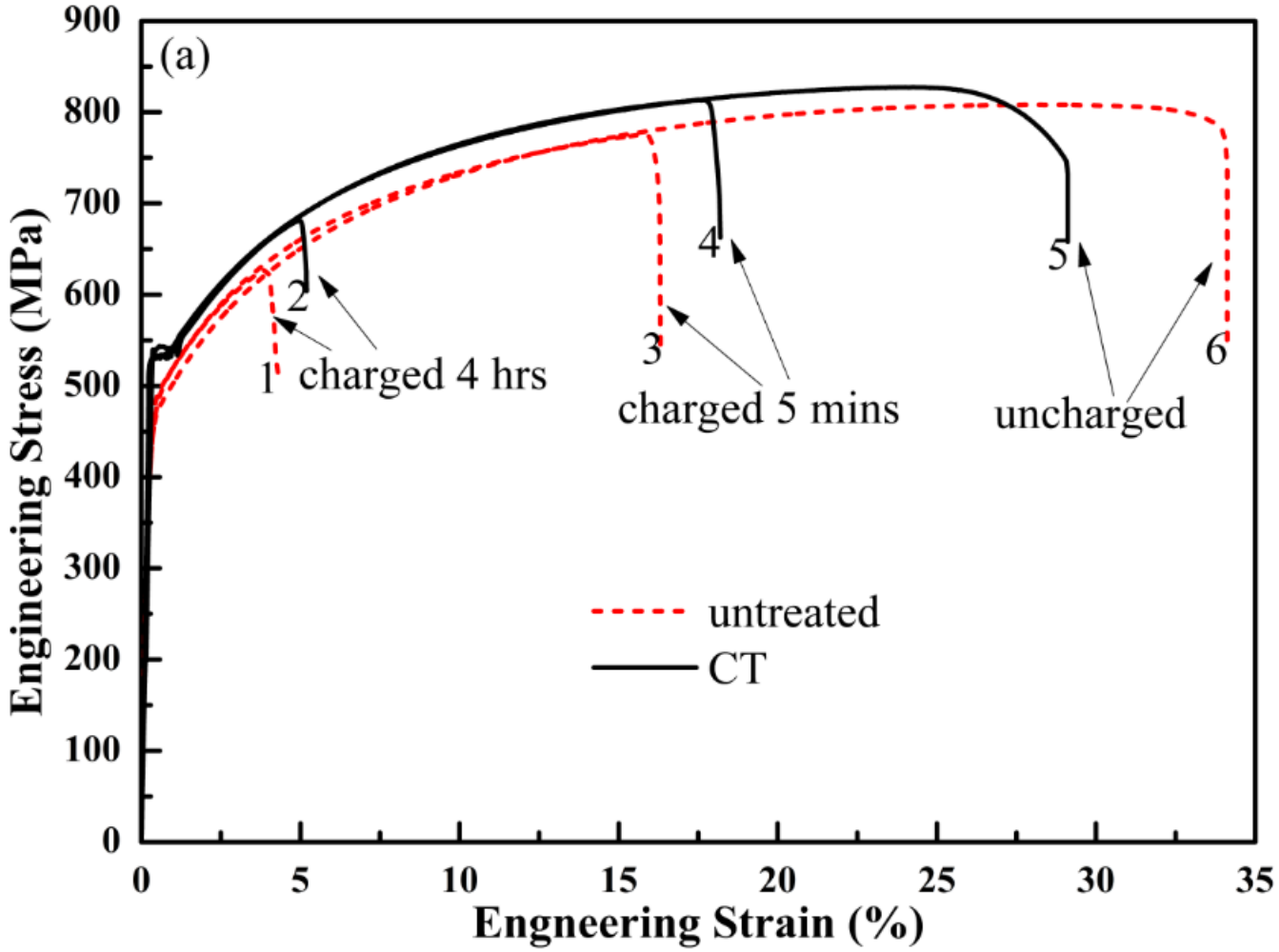
A commercial TRIP 780 steel sheet with a dimension shown in the Fig is first cryogenic treated in liquid nitrogen (-196℃) for 100 minutes and then tempered at 200℃ for 2 hours.

Chemical composition(wt.%)

C	Mn	Al	Si	P	N	Fe
0.20	1.87	0.04	1.42	0.012	0.004	Bal.

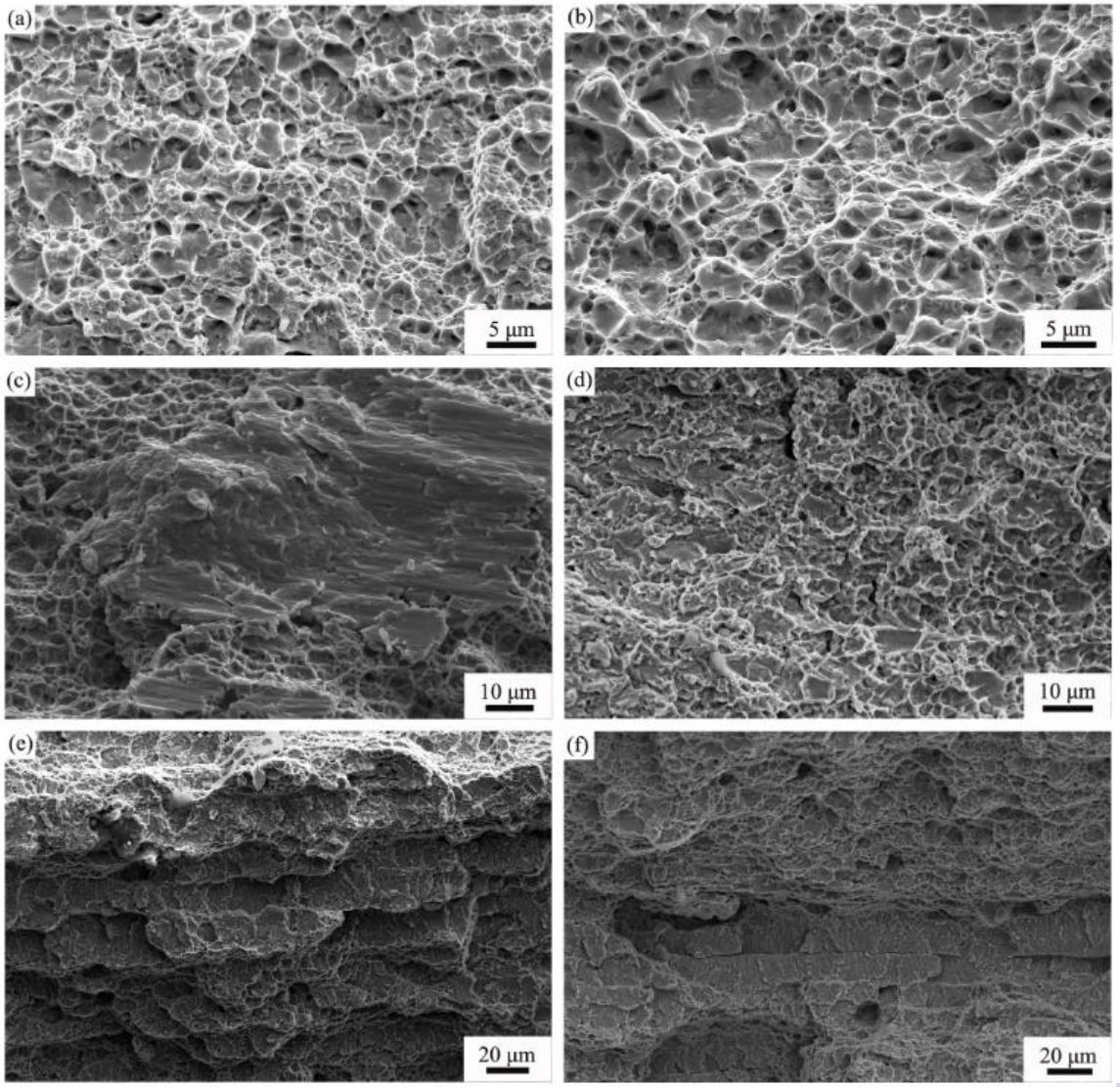


Mechanical properties



CT treatment mitigates the extent of hydrogen effect on the deterioration in mechanical properties

Fracture surface

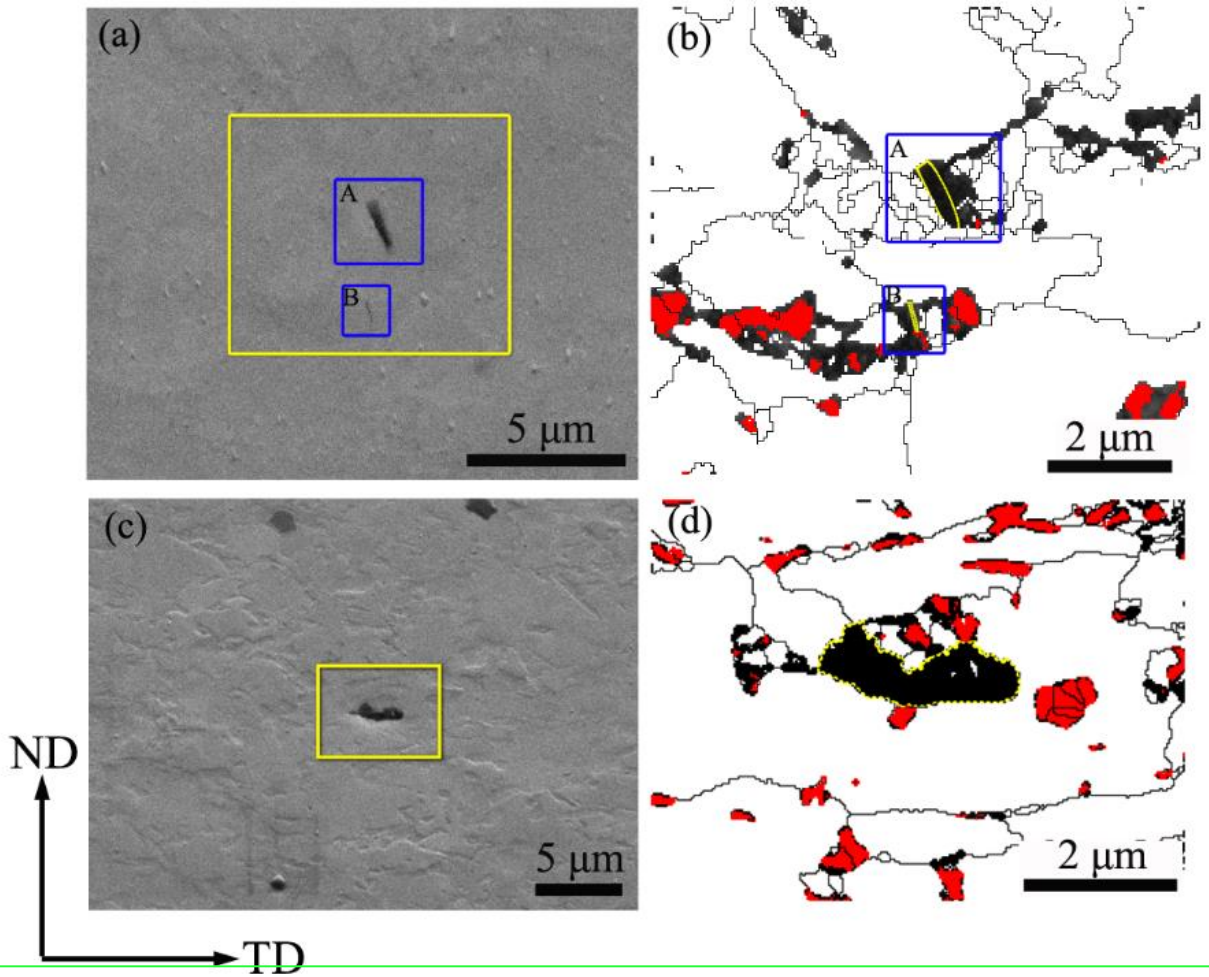


Typical ductile microvoid coalescence

Microvoid mixed with flat feature regions and cracks

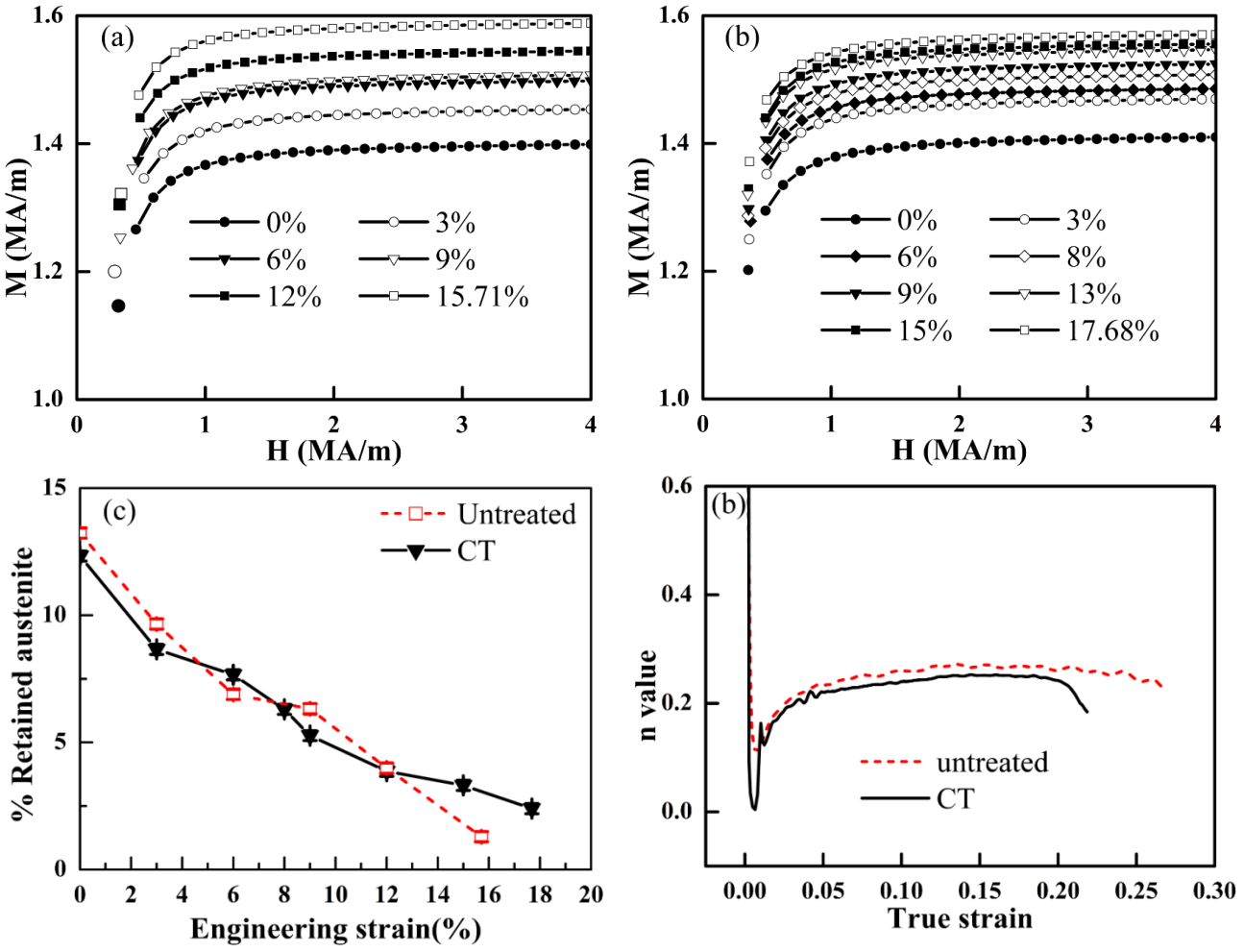
A mixture of microvoid with quasi-cleavage regions

EBSD characterization of HIC



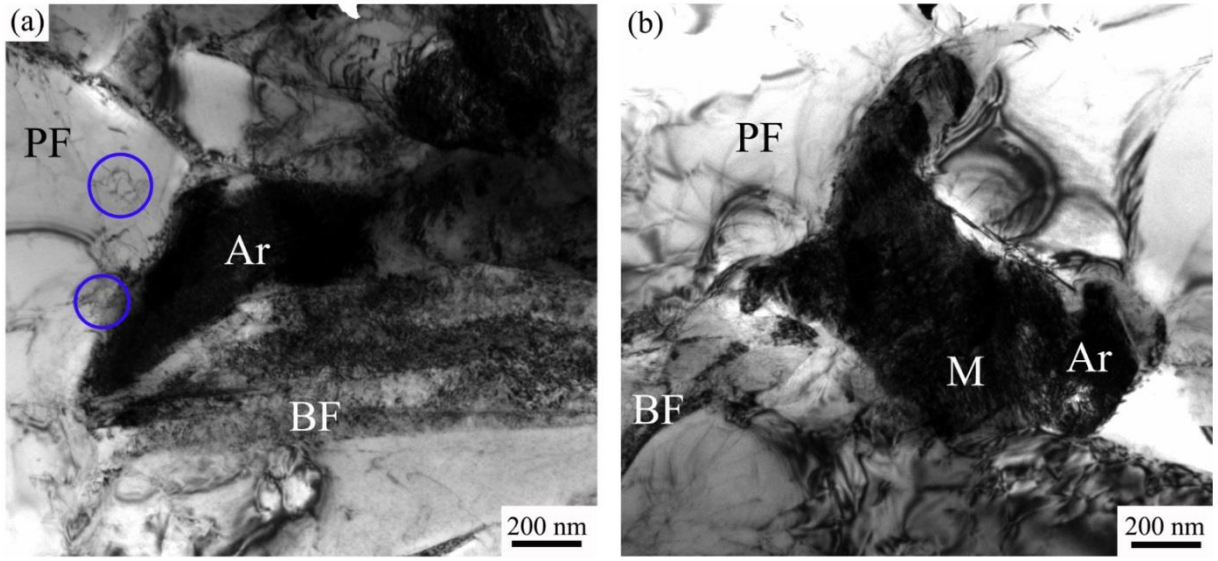
- HIC cracks are initiated and constrained in martersite-austenite islands and propagate into the adjacent ferrite.
- No crack is found in the ferrite area and fully austenite area

RA stability



CT treatment enhances the stability of retained austenite

Dislocation distribution



- Clusters of dislocations (identified by blue circles) are observed in the polygonal ferrite (PF) adjacent to RA.
- Differently, CT treated samples show no obvious dislocations in PF adjacent to RA.
- This dislocation distribution in CT treated samples may lower the local concentration of hydrogen near RA.

Summary II

1. Relative reduced susceptibility to HE is obtained by CT treatment.
2. About 1% Ar transforms to martensite during the CT treatment. Particularly, the stability of remaining Ar is enhanced by CT treatment.
3. Micro-cracks initiate from the fresh untempered martensite which is generated from the unstable austenite and propagate into the adjacent ferrite.
4. The reduced susceptibility to HE for CT treated specimens is attributed to the enhanced stability of RA and the dispersion effort of dislocations.

OUTLINE

- Introduction
- Hydrogen embrittlement of QP980 steel
- Improved HE of TRIP780 by tempering
- Improved HE of QP980 by tempering
- Conclusion remarks

Background

- Any promising ways to alleviate HE susceptibility? exploitation of carbides?

  1. Carbides increase the strength based on the precipitation strengthening

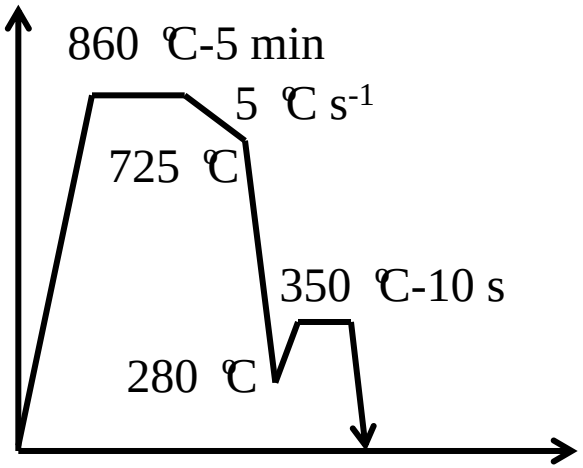
  2. Simultaneously introduce strong trapping sites that immobilize hydrogen

- The presence of ε-carbide, which is obtained by prolonged partitioning time, can markedly increase the strength level in Q&P treated steel.
- How to verify the alleviation effect of ε-carbide on HE susceptibility?

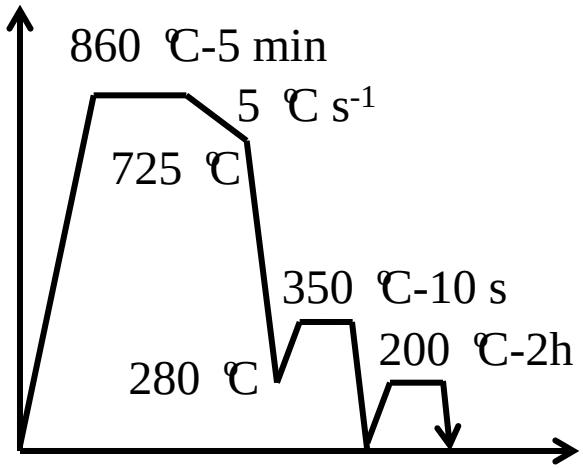
  (TDS and 3DAPT)

Materials

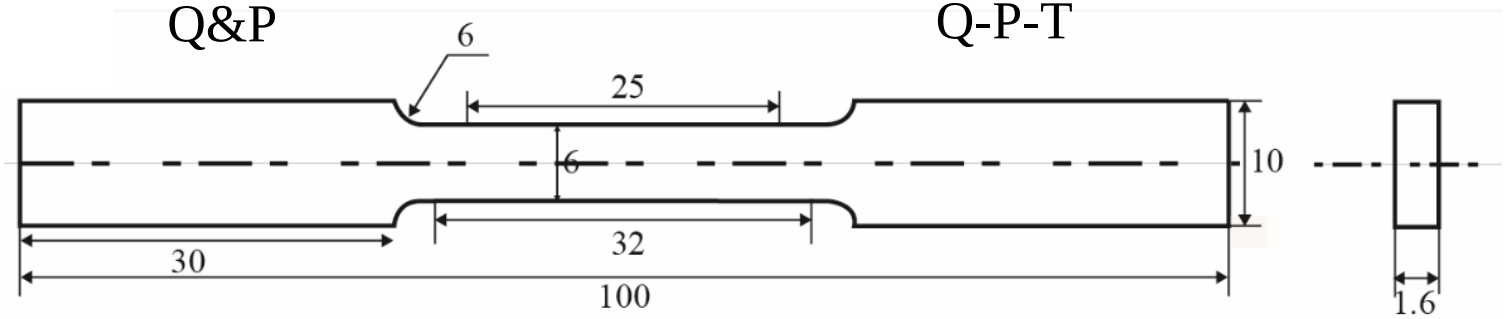
Heat treatment:



Q&P

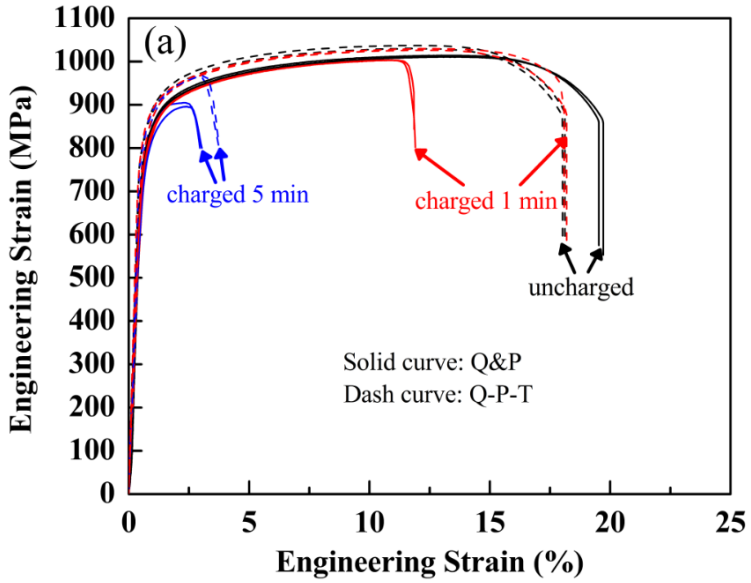


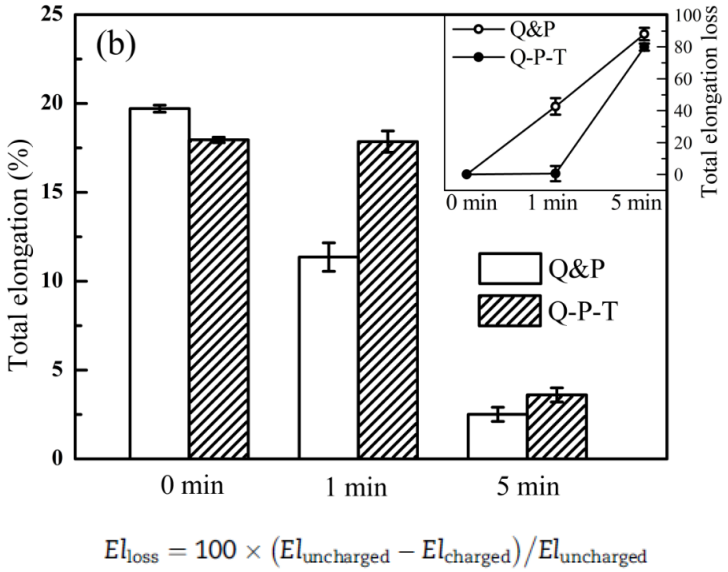
Q-P-T



Geometry of SSRT

Tensile properties

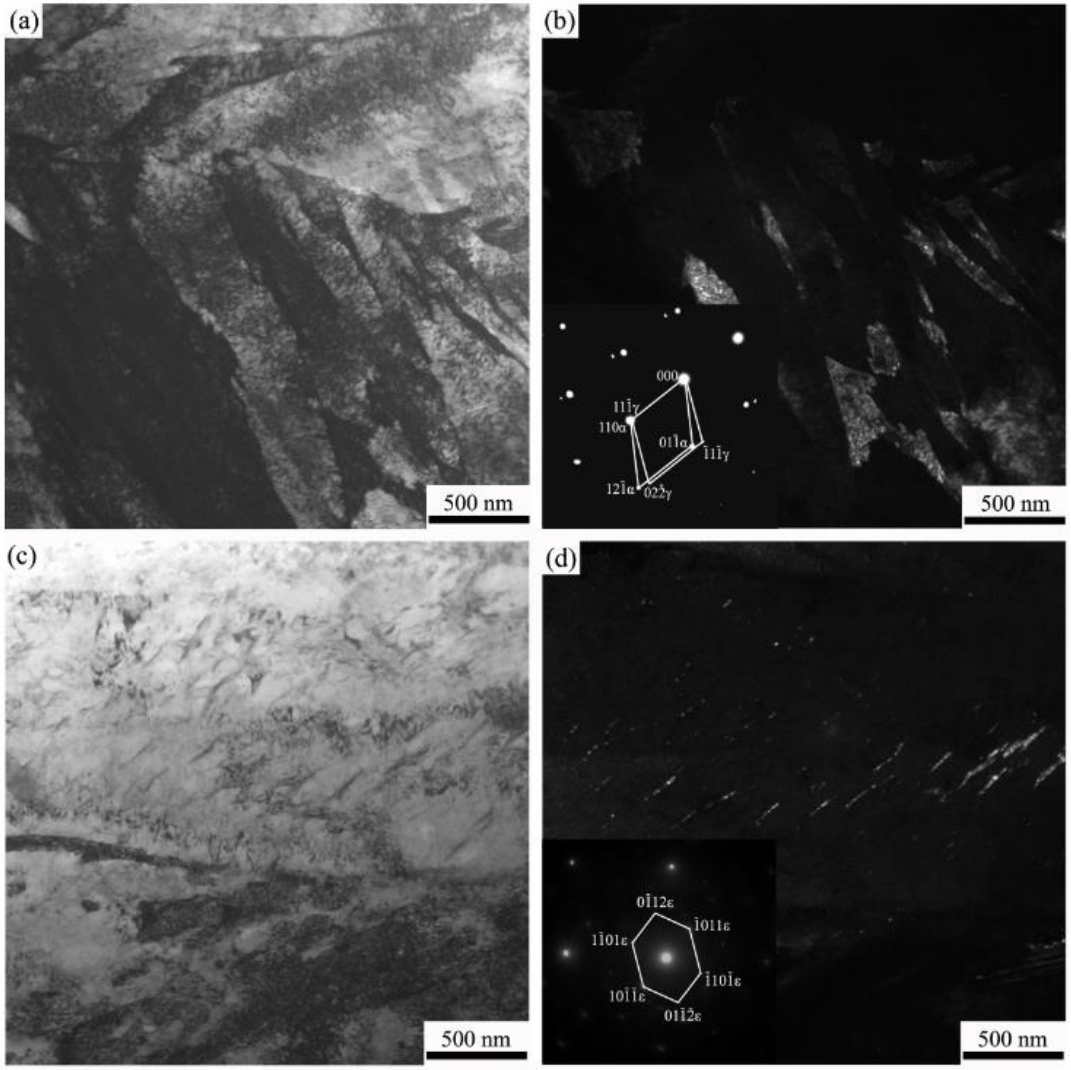




$$El_{loss} = 100 \times (El_{uncharged} - El_{charged})/El_{uncharged}$$

1. Tempering treatment increases the ultimate tensile strength (~ 30 MPa) but decreases the total elongation (from 19.5 pct to 17.9 pct).
2. Tempering treatment mitigates the extent of hydrogen effect on the deterioration in mechanical properties.
3. ε carbides play a limited role in the alleviation of HE, given that the susceptibility to HE is returned with the saturation of hydrogen trapped at ε carbides.

TEM characterization



Typical TEM micrographs of Q&P and Q-P-T steels

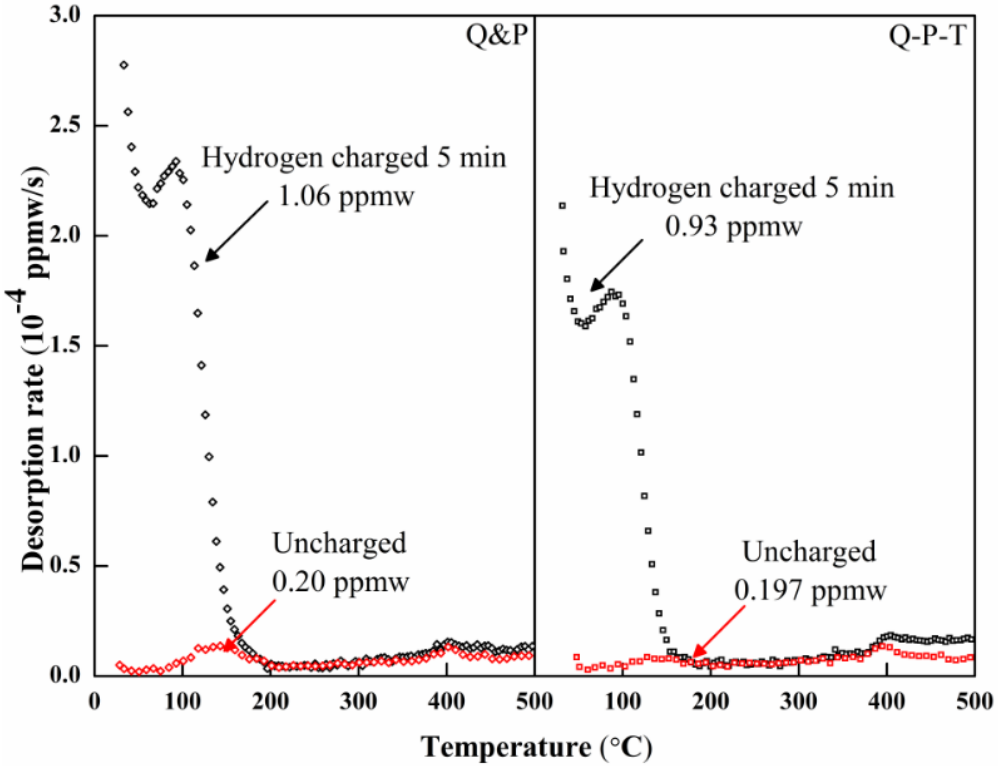
Q&P steel

- Typical lath-type martensite structure with a thickness of ~ 200 - 300 nm.
- Retained austenite is presented at the interlath boundaries.
- No visible carbide is revealed in the martensite matrix.

Q-P-T steel

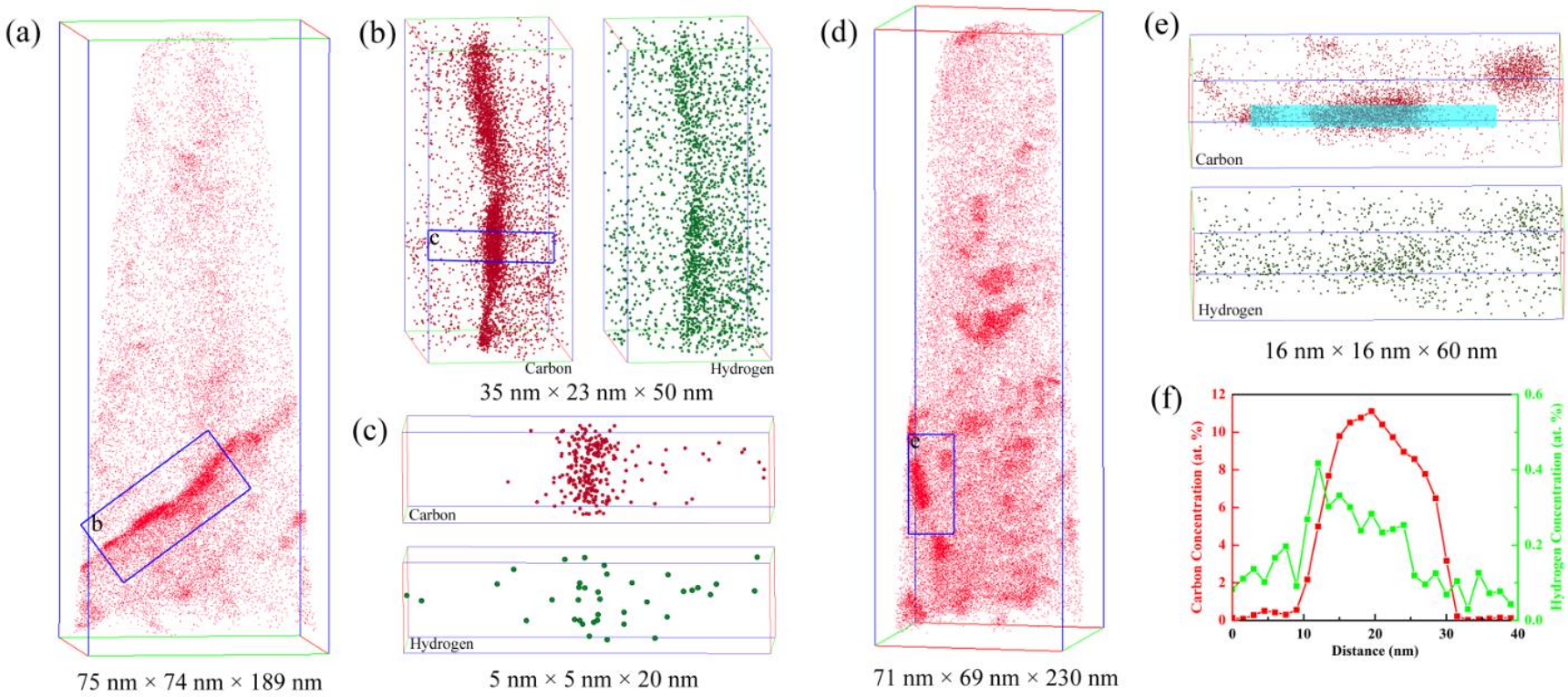
- Similar microstructures to that of Q&P steel with the exception of carbides.
- An array of needle-shaped carbides are observed within the plate martensite matrix (ε carbides).

TDS analysis



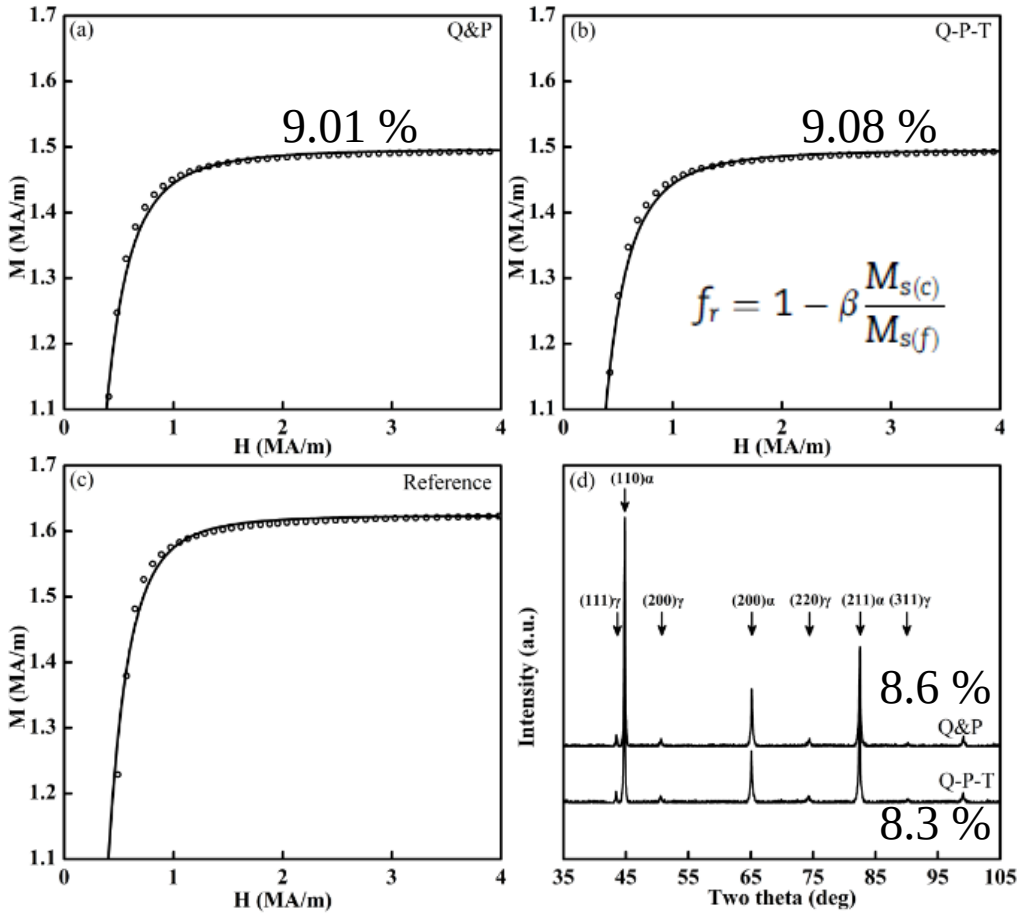
- The diffusible H concentration relevant to peak (90 ℃) was evaluated to be 0.86 and 0.62 ppmw in Q&P and Q-P-T steels, respectively.
- A relative higher peak around 400 ℃ is found in Q-P-T steel, which is due to ε carbides.
- The nondiffusible H concentration was evaluated to be 0.20 and 0.31 ppmw in Q&P and Q-P-T steels.
- H is prior to be trapped at ε carbides, giving rise to a lower content of diffusible H.

Hydrogen trapping ——3DAPT



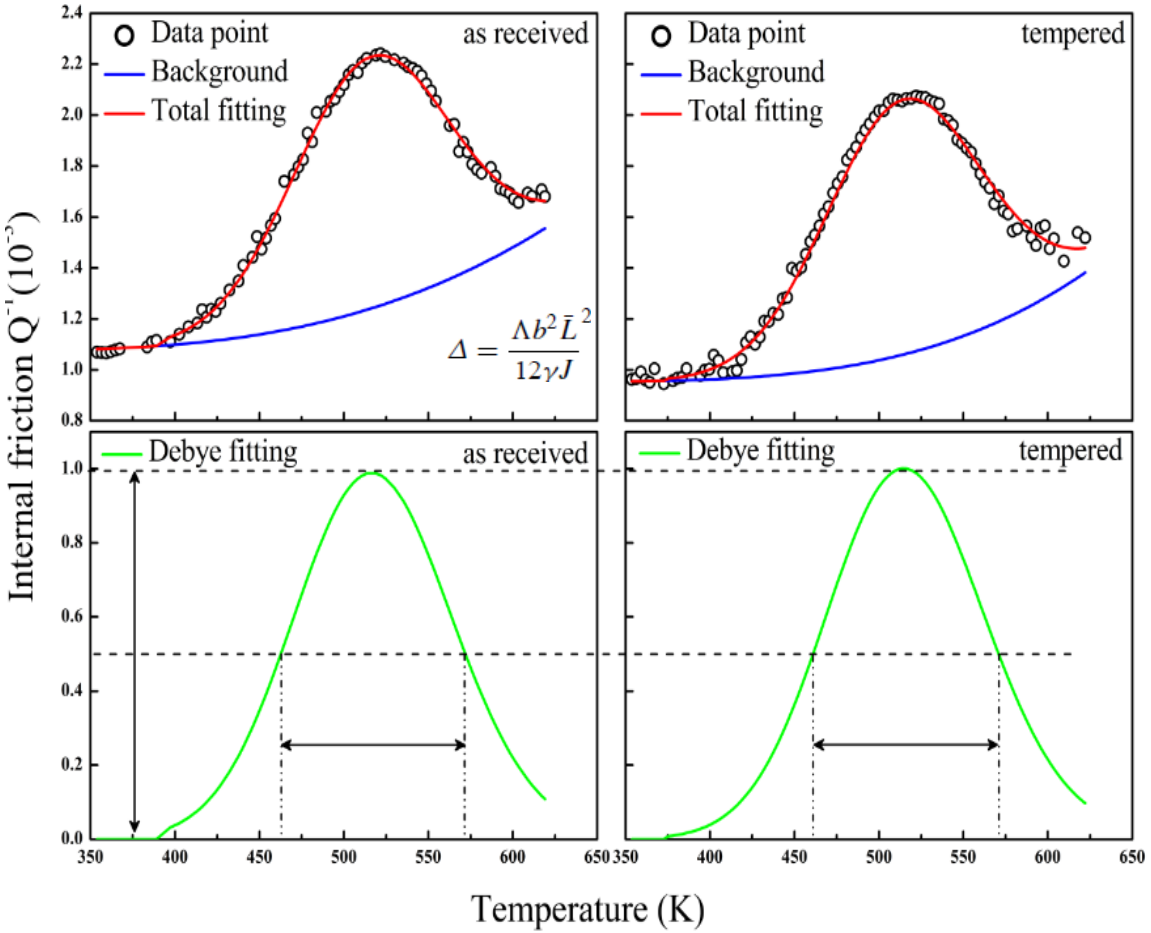
- Verifies the hydrogen trapping effect of ε carbides
- Hydrogen concentration in ε carbides (60.4 ppmw) is 5 times more soluble than that (11.3 ppmw) in the matrix, most probably martensite.

Volume fraction of RA



Calculated volume fraction of retained austenite by PPMS in Q&P and Q-P-T steel is 9.01 % and 9.08 %, indicating no austenite transformation during tempering treatment, which is in accordance with XRD results.

Dislocation density



Snoek-Koster (SK) peak for Q&P and Q-P-T steels shows negligible distinction of the amplitude and full width at half maximum, indicating that this tempering treatment has little effect on dislocation density in BCC phases.

Summary III

1. An improved resistance to HE of a Q&P steel is obtained by introducing transition ε carbides in the martensite matrix that effectively trap hydrogen.
2. With ε carbides precipitation, nondiffusible hydrogen concentrations in Q-P-T steel and Q&P steel are 0.20 and 0.31 ppmw respectively, giving rise to a reduced diffusible hydrogen content.
3. Direct atomic-scale observation by 3DAPT verifies that hydrogen in ε carbides is 5 times more soluble than that in the matrix due to the abundant carbon vacancies.

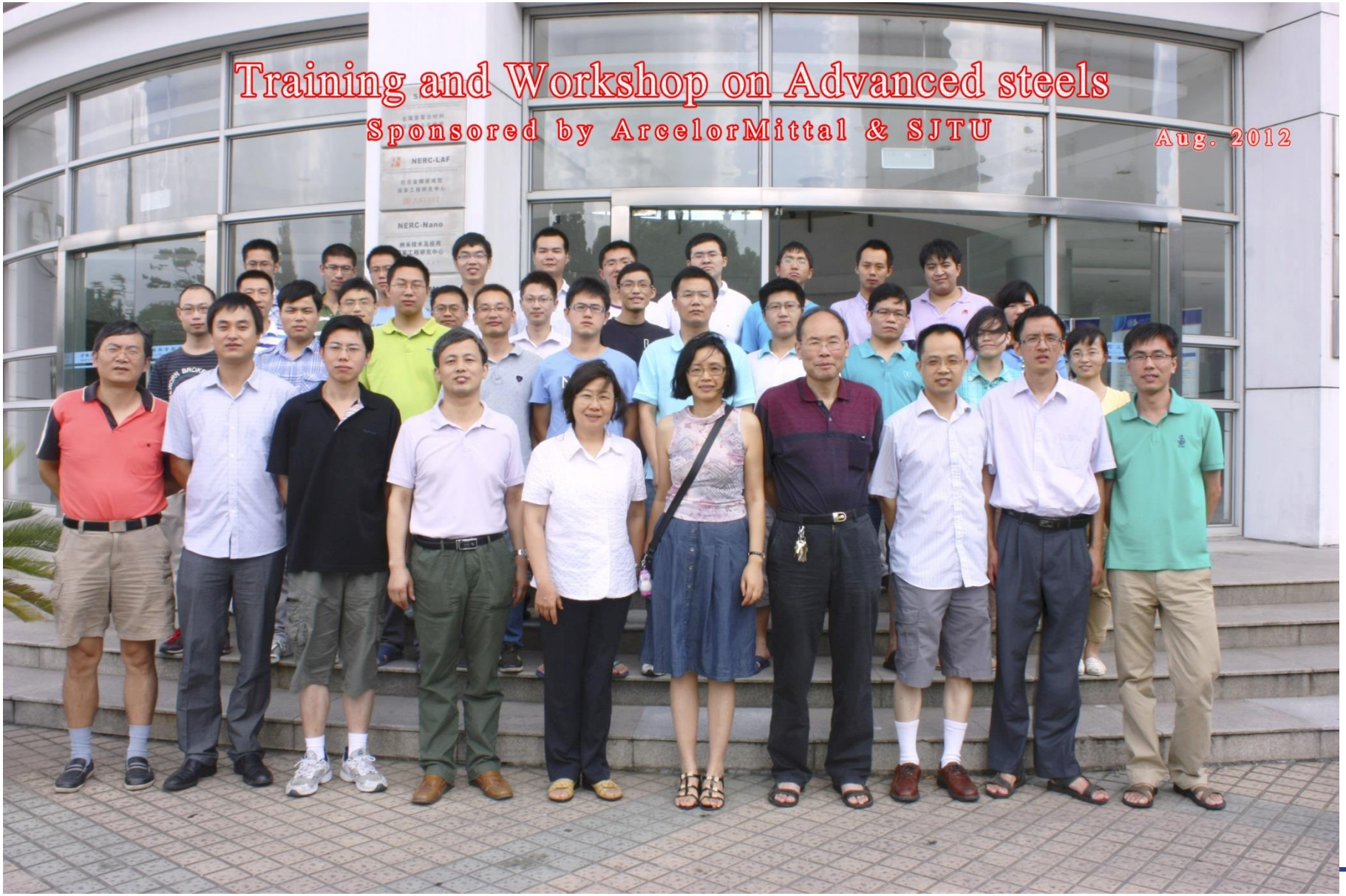
OUTLINE

- Introduction
- Hydrogen embrittlement of QP980 steel
- Improved HE of TRIP780 by tempering
- Improved HE of QP980 by tempering
- Conclusion remarks

Conclusion remarks

- Hydrogen causes degradation in the Q&P treated steels. Hydrogen trapping sites are directly observed by atom probe tomography technology, which shows that hydrogen in austenite (33.9 ppmw) is 3 times more soluble than that in martensite (10.7 ppmw) in these Q&P treated steels.
- An improved resistance to HE of a Q&P steel is obtained by introducing transition ε carbides in the martensite matrix that effectively trap hydrogen.
- QPT treatment may be beneficial to improve the HE performance in addition to the enhancement of mechanical properties

Thanks !


Training and Workshop on Advanced steels
Sponsored by ArcelorMittal & SJTU
Aug. 2012
NERC-LAF
NERC-Nano