Hydrogen Embrittlement in Fe-Mn-C High Strength Austenitic Steels

K. Tsuzaki

Department of Mechanical Engineering
Kyushu University, Fukuoka
JAPAN

I had moved from NIMS to Kyushu University on April 1st 2013, but keep a position at NIMS and work for three-four days a month in Tsukuba.
Both e-mail addresses are available.

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Kaneaki TSUZAKI
Dr of Engineering, Professor

Department of Mechanical Engineering
Kyushu University
744 Motooka, Nishi-ku, Fukuoka 819-0397, Japan
e-mail: <ktsuzaki@mech.kyushu-u.ac.jp>

Senior Special Mission Scientist
Research Center of Strategic Materials
National Institute for Materials Science
1-2-1, Sengen, Tsukuba 305-0047, Japan
e-mail: <tsuzaki.kaneaki@nims.go.jp>

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Outline and Abstract

- High Mn Steels *(Background and Motivation)*
  - Many kinds since Hadfield steel in 1882
- Tensile Testing during H-charging
  - Reduced ductility in Fe-high Mn-C steels
- Fractography
  - Crack path along grain & twin boundaries
- HE in Single Crystalline 316 Steel
  - Orientation dependence of reduced ductility

Co Workers

Dr. Motomichi **KOYAMA** (NIMS, MPIE)
Dr. Eiji **AKIYAMA** (NIMS)
Dr. Takahiro **SAWAGUCHI** (NIMS)
Prof. Dierk **RAABE** (MPIE)

High Mn Steels

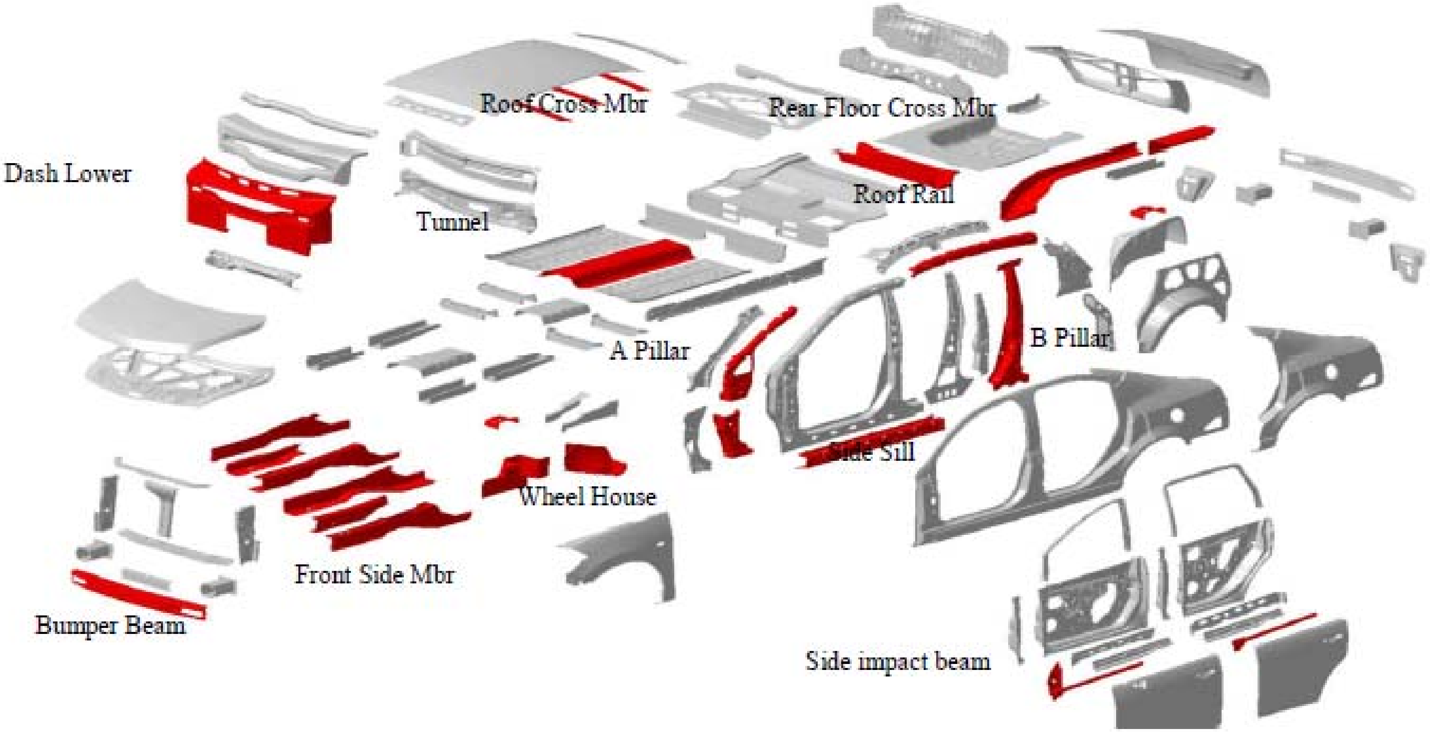
High Mn austenitic steels are used as Hadfield (1882) [1-3], shape memory [4,5], damping [6], seismic-resistant [7], transformation induced plasticity (TRIP) [8-10], and twinning induced plasticity (TWIP) steels [9-13].

[1] R.A. Hadfield, J. Forrest, Manganese steel: Manganese In Its Application To Metallurgy, Some Newly-Discovered Properties Of Iron And Manganese, Kessinger Publishing, United states (1888). [2] Y.N. Dastur, W.C. Leslie, Metall. Trans. A 12A (1981) 749. [3] P.H. Adler, G.B. Olson, W.S. Owen, Metall. Trans. A 17A (1986) 1725. [4] A. Sato, E. Chishima, K. Soma, T. Mori, Acta Metal. 30 (1982) 1177. [5] M. Murakami, H. Otsuka, H.G. Suzuki, S. Matsuda, Proc. ICOMAT (1986) 985. [6] S.-H. Baik, J.-C. Kim, K.-K. Jee, M.-C. Shin, C.-S. Choi, ISIJ Int. 37 (1997) 519. [7] T. Sawaguchi, L.-G. Bujoreanu, T. Kikuchi, K. Ogawa, M. Koyama, M. Murakami, Scr. Mater. 59 (2008) 826. [8] I. Tamura, Metal Sci. 16 (1982) 245. [9] O. Grässel, G. Frommeyer, Mater. Sci. Technol. 14 (1998) 1213. [10] L. Remy, A. Pineau, Mater. Sci. Eng. 28 (1977) 99. [11] O. Bouaziz, S. Allain, C. Scott, Scr. Mater. 58 (2008) 484. [12] I. Gutierrez-Urrutia, D. Raabe, Acta Mater. 59 (2011) 6449. [13] C. Curtze, V.-K. Kuokkala, Acta Mater. 58 (2010) 5129.

TWIP Steels

Twinning Induced Plasticity Steels

which are expected to be used for automobile materials.

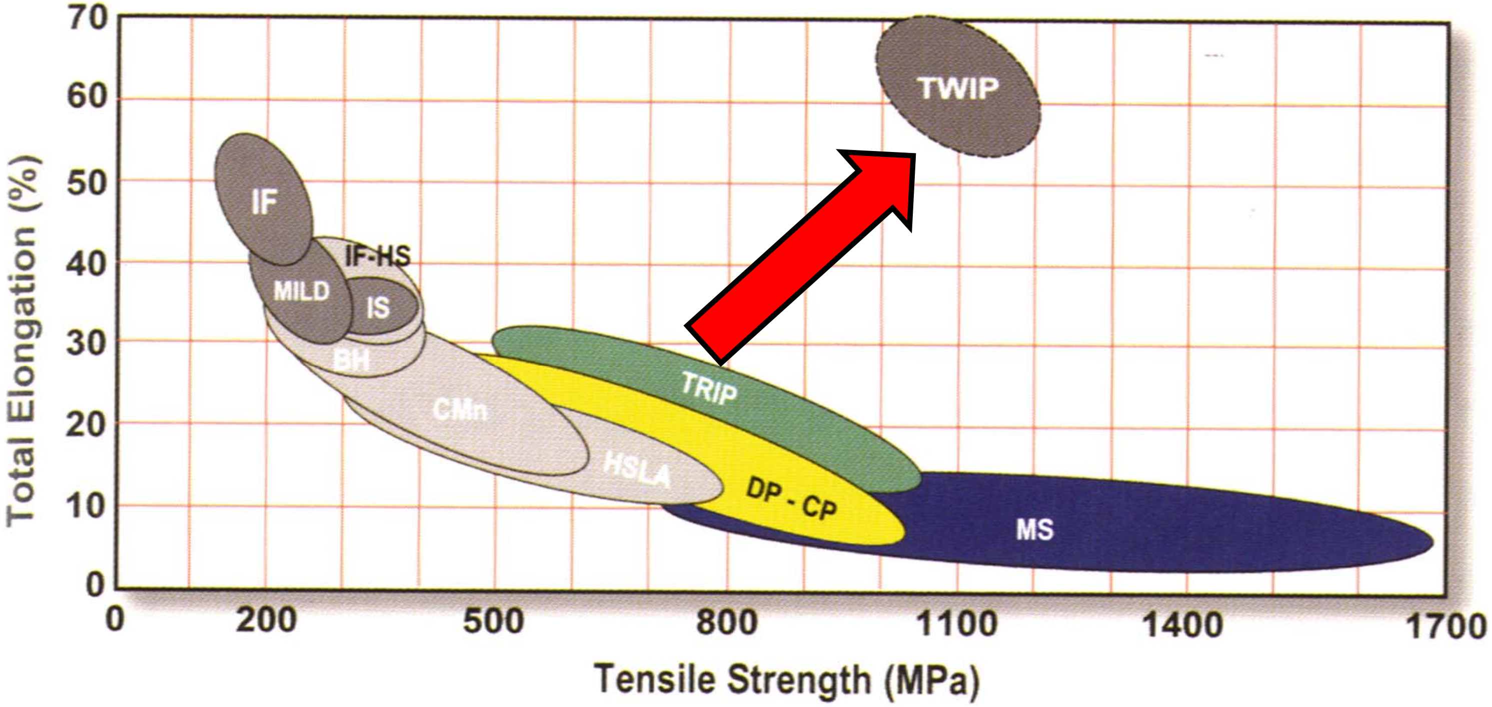


O. Kwon, Proc. International Conference on High Manganese Steels (2011) P-4.

TWIP Steels

Twinning Induced Plasticity Steels

which show high strength and high ductility

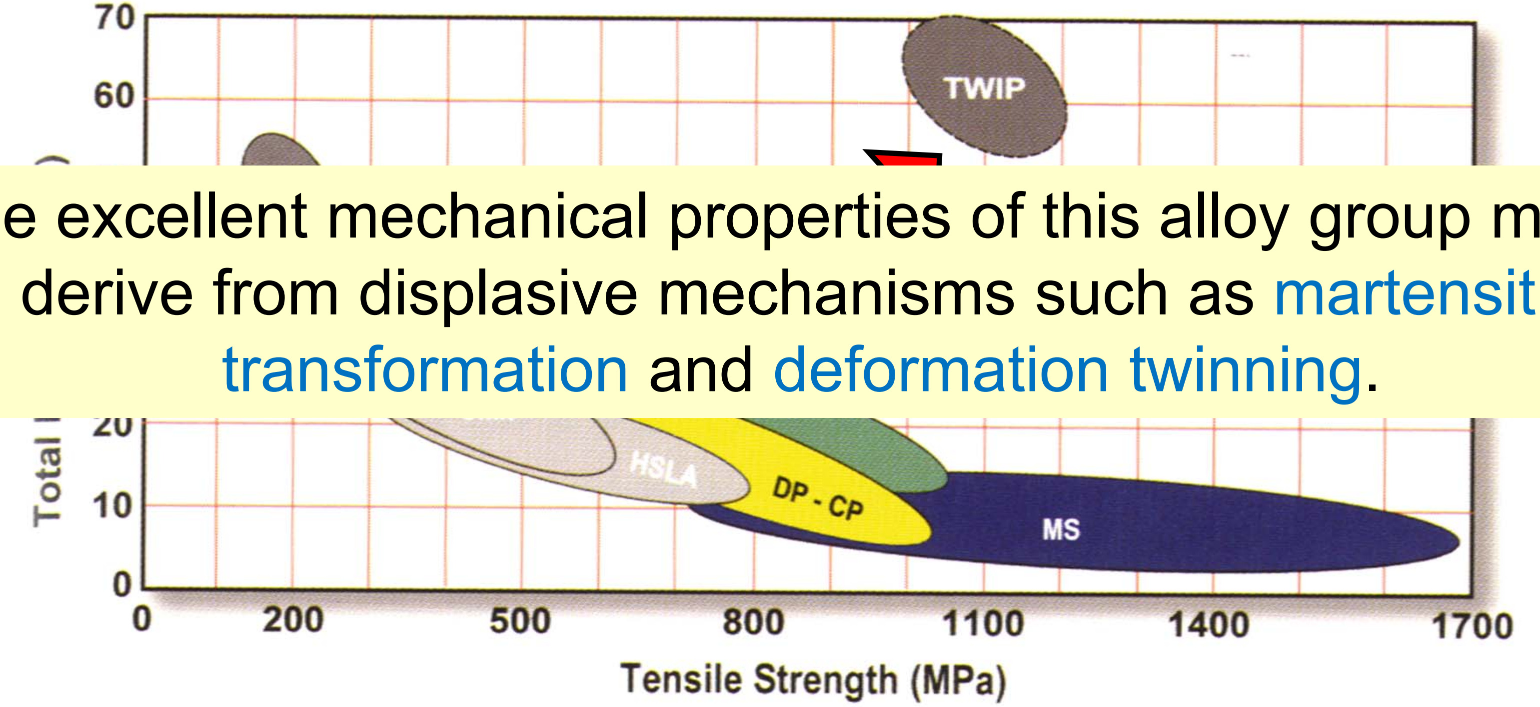


Ref) World Auto Steel of World Steel Association: スーパー鉄鋼｢先進ハイテン｣(2009) p.15.

TWIP Steels

Twinning Induced Plasticity Steels

which show high strength and high ductility



The excellent mechanical properties of this alloy group mainly derive from displasive mechanisms such as martensitic transformation and deformation twinning.

Ref) World Auto Steel of World Steel Association: スーパー鉄鋼「先進ハイテン」(2009) p.15.

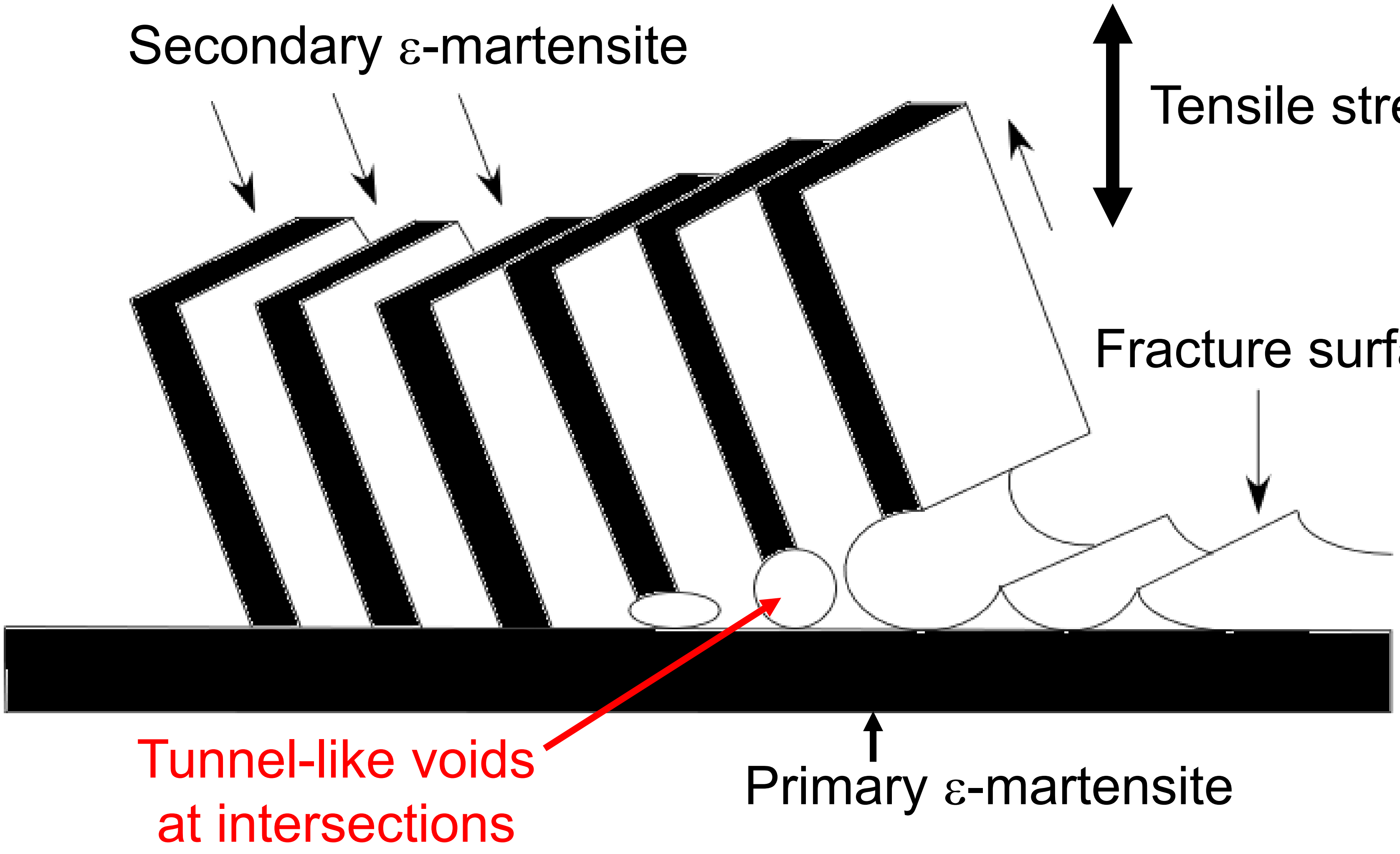
Drawbacks, High Mn (TWIP) Steels

However, high Mn steels undergo premature fracture under a variety of microstructural conditions such as stress concentrations at tips of ε-martensite plates (HCP phase) [14] or FCC deformation twins [15] interacting with grain and phase boundaries; at cementite particles [16]; in Mn-enriched segregation zones at grain boundaries [17]; and in interaction zones between annealing twin boundaries and ε-martensite [18].

[14] K. Sipos, L. Remy, A. Pineau, Metal. Trans. A 7A (1976) 857.
[15] H. Suto, B.S. Chun, Tech. Report, Tohoku University 44 (1979) 317.
[16] A. Goldberg, O.A. Ruano, O.D. Sherby, Mater. Sci. Eng. A 150 (1992) 187.
[17] Y. Tomota, M. Strum, J.W. Morris, Jr, Metal. Trans. A 18A (1987) 1073.
[18] M. Koyama, T. Sawaguchi, K. Tsuzaki, ISIJ Int. 52 (2012) 161.

A model of premature fracture due to ε-martensite

[Ref] S. Takaki et al, ISIJ Int. 30 (1990) 632.



Drawbacks, High Mn (TWIP) Steels

Moreover, stress corrosion cracking [19] and hydrogen embrittlement [20-24] are observed. In particular, hydrogen embrittlement, HE, has recently become a point of major interest due to the use of TWIP steels in automotive and safety-relevant parts for carbon-reduced industry infrastructure [20,25].

[19] H.C. Lin, K.M. Lin, C.S. Lin, T.M. Ouyang, Corr. Sci. 44 (2002) 2013.
[20] O. Kwon, Proceedings of HMnS (2011) CD-ROM.
[21] K-G. Chin, C-Y. Kang, S.Y. Sin, S. Hong, S. Lee, H-S. Kim, K-H. Kim, N.J. Kim, Mater. Sci. Eng. A 528 (2011) 2922.
[22] B.C. De Cooman, K-G Chin, J. Kim, Marcello Chiaberge (Ed.), 2011; ISBN: 978-953-307-517-4, InTech.
[23] R.T. van Tol, L. Zhao, J. Sietsma, Proceedings of HMnS (2011) CD-ROM.
[24] M. Koyama, E. Akiyama, K. Tsuzaki, Corr. Sci. 54 (2012) 1.
[25] C. Scott, S. Allain, M. Faral, N. Guelton, Rev. Metal. Cah. D'inf. Tech. 103 (2006) 293.

The hydrogen embrittlement, HE, was caused by cup-forming tests and subsequent exposure in air in *Fe-15Mn-0.6C* [1,9], *Fe-16Mn-0.6C* [1,9], *Fe-15Mn-0.7C-3Al* [10], *Fe-17Mn-0.6C* [1,9], and *Fe-22Mn-0.6C* [1,8,9] TWIP steels. Tensile tests after electrochemical hydrogen charging also demonstrated the hydrogen embrittlement in *Fe-17Mn-0.4C-2.7Al* austenitic steels [6]. The fracture mode shown in the literatures [6,8] was intergranular fracture.

[1] O. Kwon, Proceedings of HMnS (2011) CD-ROM.
[6] S.C. Mittal, R.C. Prasad and M.B. Deshmukh, ISIJ int. 34 (1994) 211-216.
[8] K-G. Chin, C-Y. Kang, S.Y. Sin, S. Hong, S. Lee, H-S. Kim, K-H. Kim and N.J. Kim, Mater. Sci. Eng. A 528 (2011) 2922-2928.
[9] B.C. De Cooman, K-G Chin and J. Kim, New Trends and Developments in Automotive System Engineering, Marcello Chiaberge (Ed.), (2011) ISBN: 978-953-307-517-4, InTech.
[10] R.T. Van Tol, L. Zhao, J. Sietsma, Proceedings of HMnS (2011) CD-ROM

Open Questions @ 2011

About feature of tensile behavior of High Mn austenitic steels containing hydrogen.

Effect of H on stress-strain response?
(yield stress, work hardening)

Effect of H on fracture stress, fracture strain?
(fracture stress vs. H content)

Effect of H on fracture mode?
(crack propagation path)

Open Questions @ 2011

About feature of tensile behavior of High Mn austenitic steels containing hydrogen.

Effect of H on stress-strain response?

(yield stress, work hardening)

Our recent work with the aim of getting more experimental evidence.

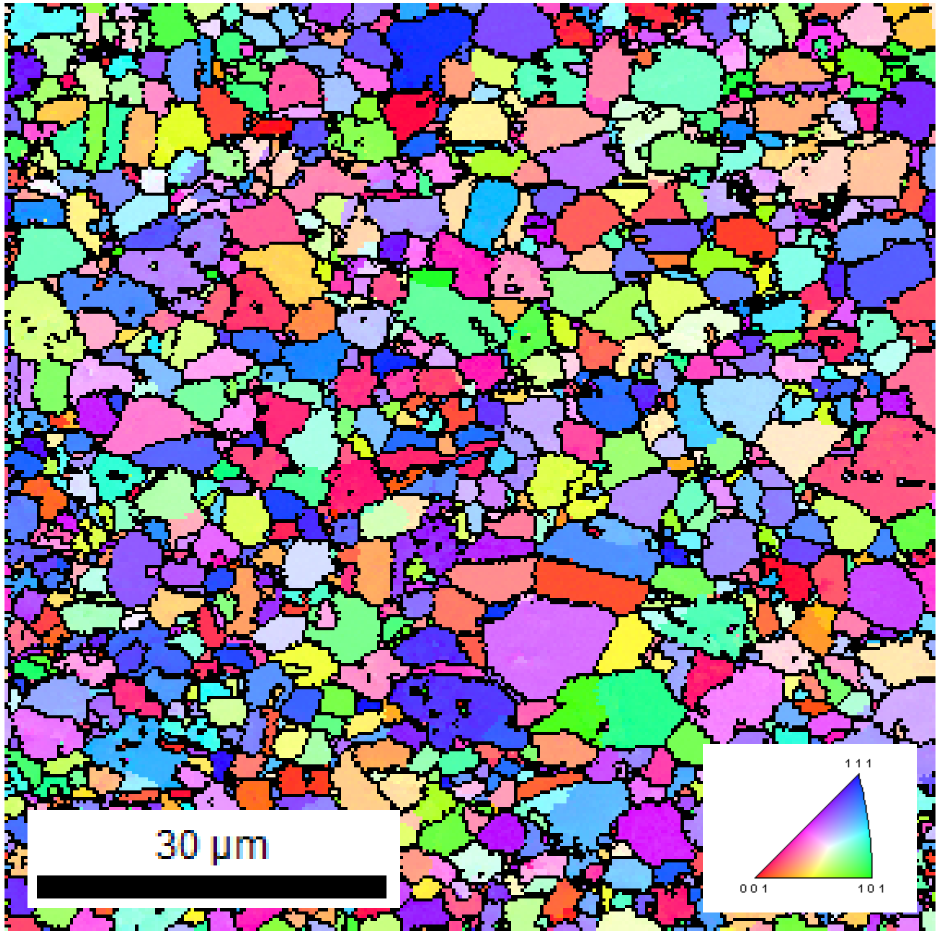
(fracture stress vs. H content)

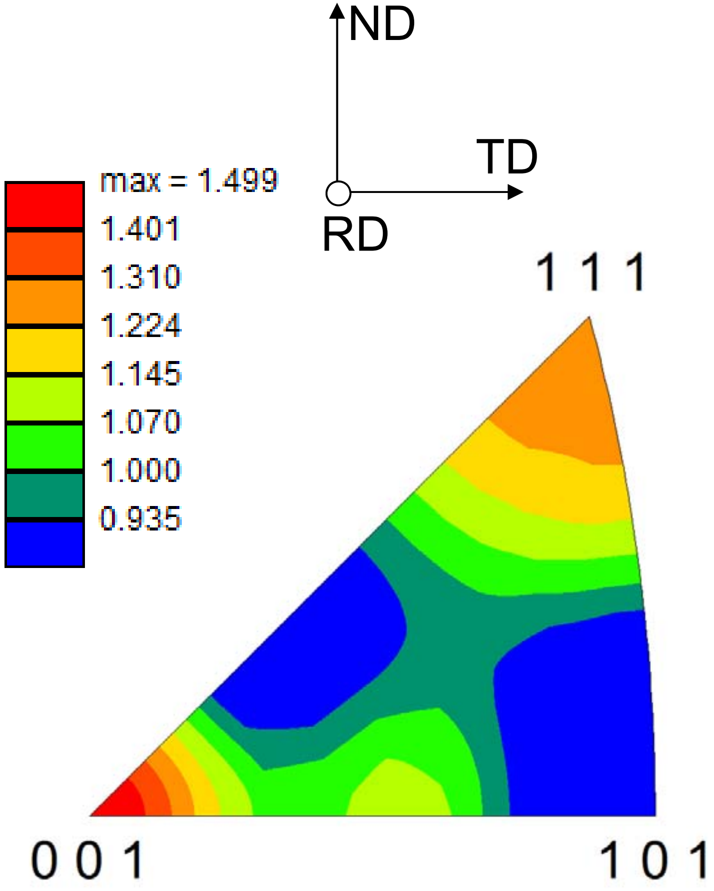
Effect of H on fracture mode?

(crack propagation path)

Fe-18Mn-0.6C, a typical TWIP steel

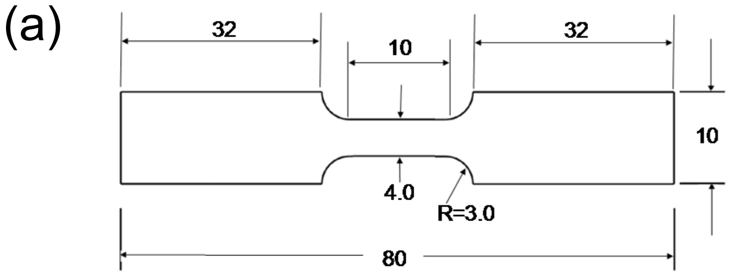
60% cold rolled, 1073 K for 1 h

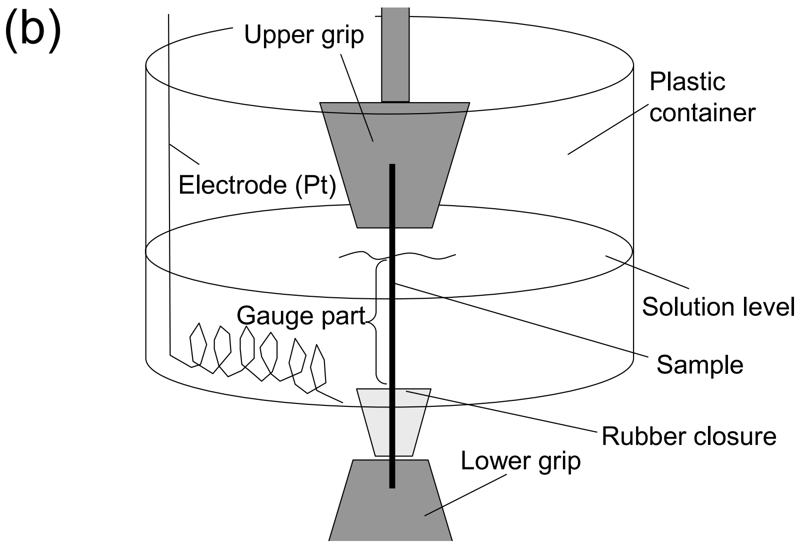


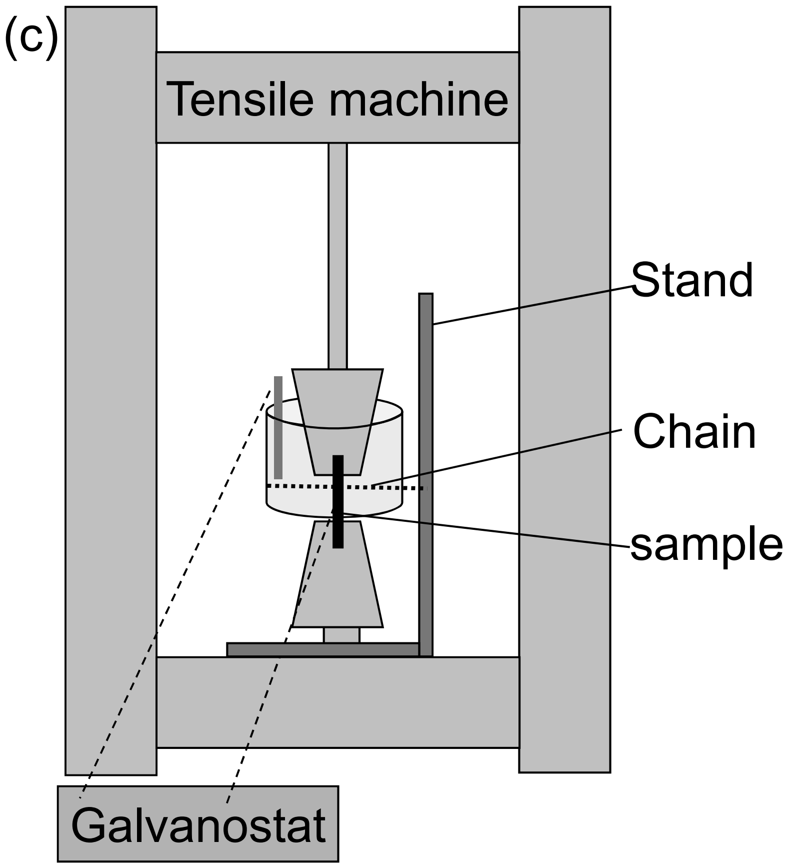


M. Koyama, E. Akiyama, K. Tsuzaki, Corrosion Science, 54 (2012) 1-4.

t = 0.3 mm





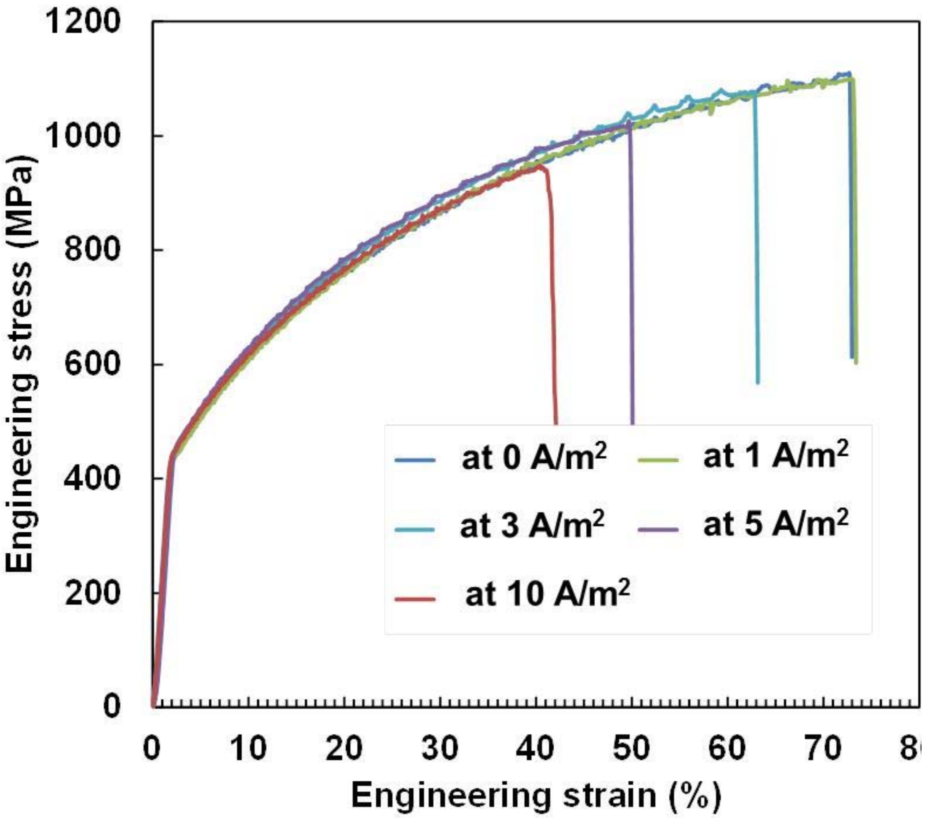


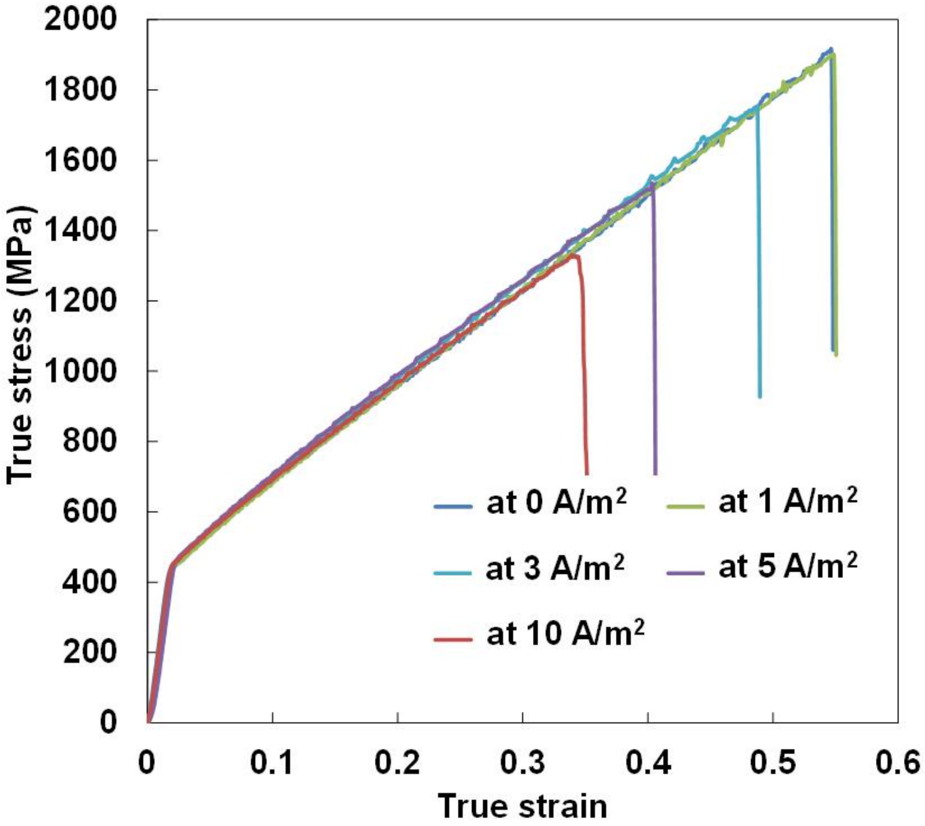
3% NaCl solution with 3 g/L NH_4SCN
Current density = 0, 1, 3, 5, 10 A/m^2

Strain Rate = 5 x 10^{-5} /s

M. Koyama, E. Akiyama, K. Tsuzaki, Corrosion Science, 54 (2012) 1-4.

Strain Rate = 5 x 10^{-5} /s @ RT

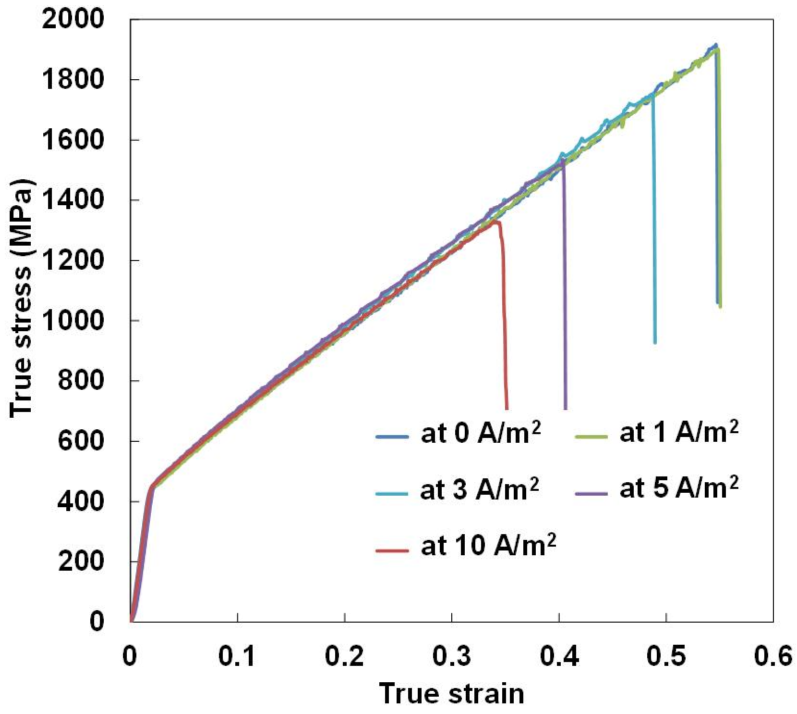




YS and work hardening behavior: No change.
But elongation is decreased.

M. Koyama, E. Akiyama, K. Tsuzaki, Corrosion Science, 54 (2012) 277-281.

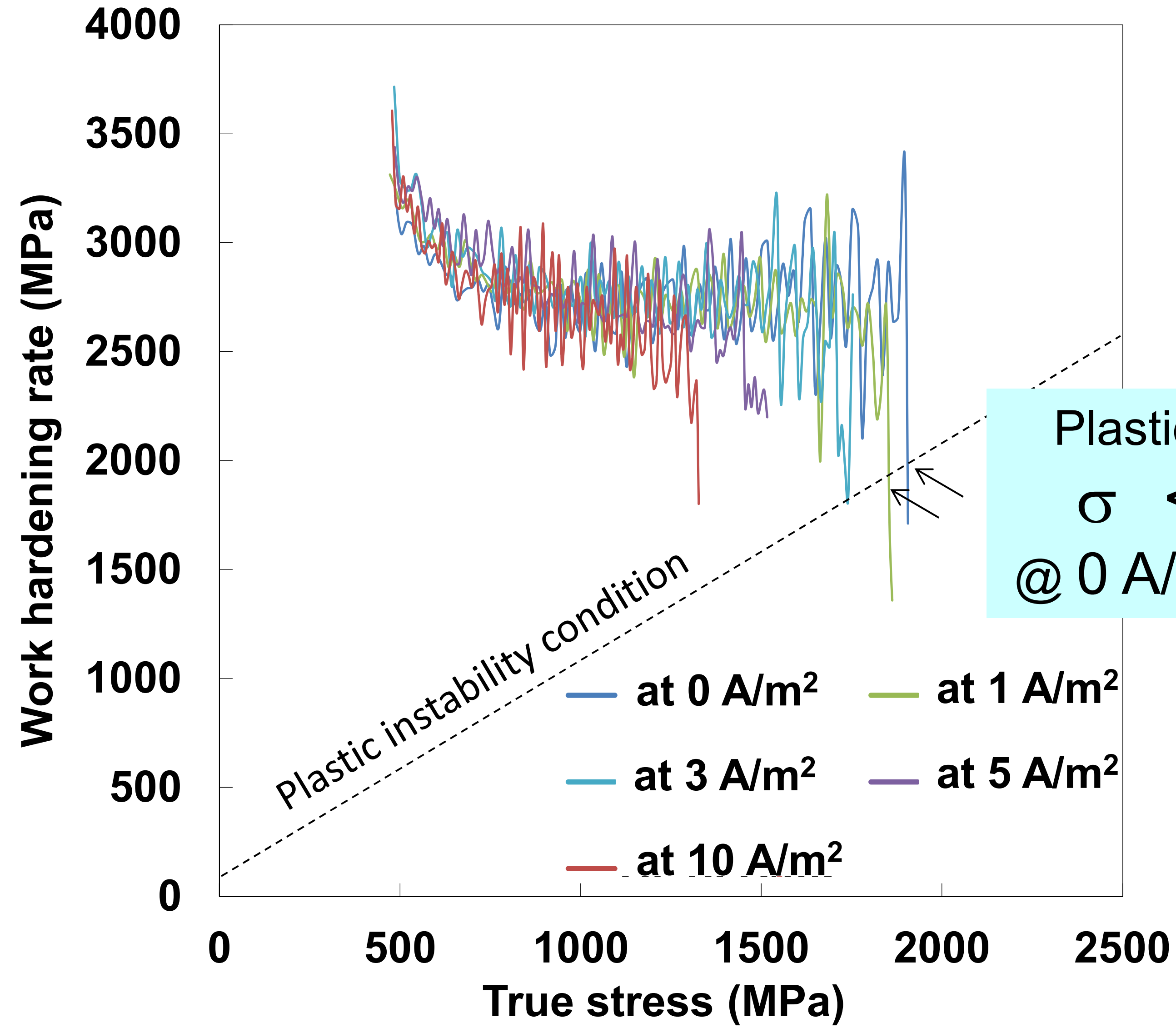
Same YS & work hardening



Hydrogen can have multiple effects in this context. It was reported that hydrogen entry into austenitic steels reduces their stacking fault energy [32,33]. This effect promotes ε-martensitic transformation [34,35] and deformation twinning [36,37], resulting in a marked change in stress-stress response.

[32] M.B. Whiteman, A.R. Troiano, Phys. Stat. Sol. 7 (1964) K109.
[33] A.E. Pontini, J.D. Hermida, Scr. Mater. 37 (1997) 1831.
[34] P. Rozenak, D. Eliezer, Acta Metal. 35 (1987) 2329.
[35] N. Narita, C.J. Altstetter, H.K. Birnbaum, Metal. Trans. A 13A (1982) 1355.
[36] J.M. Rigsbee, J. Mater. Sci. 12 (1977) 406.
[37] E.G. Astafurova, G.G. Zakharova, H.J. Maier, Scr. Mater. 63 (2010) 1189.

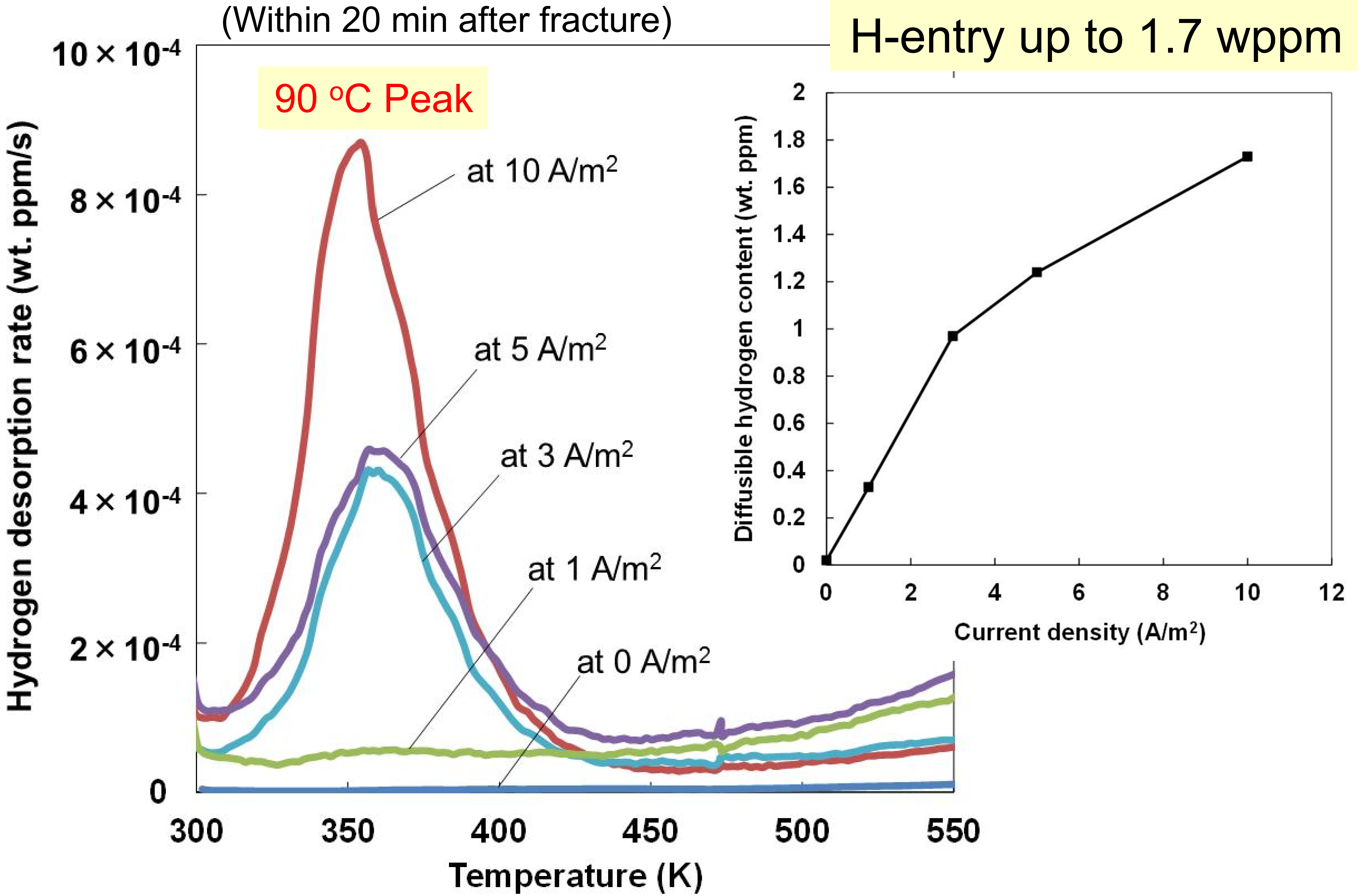
Premature fracture @ 3, 5, and 10 A/m^2.



Plastic instability

$\sigma < d\sigma/d\varepsilon$

@ 0 A/m^2, 1 A/m^2



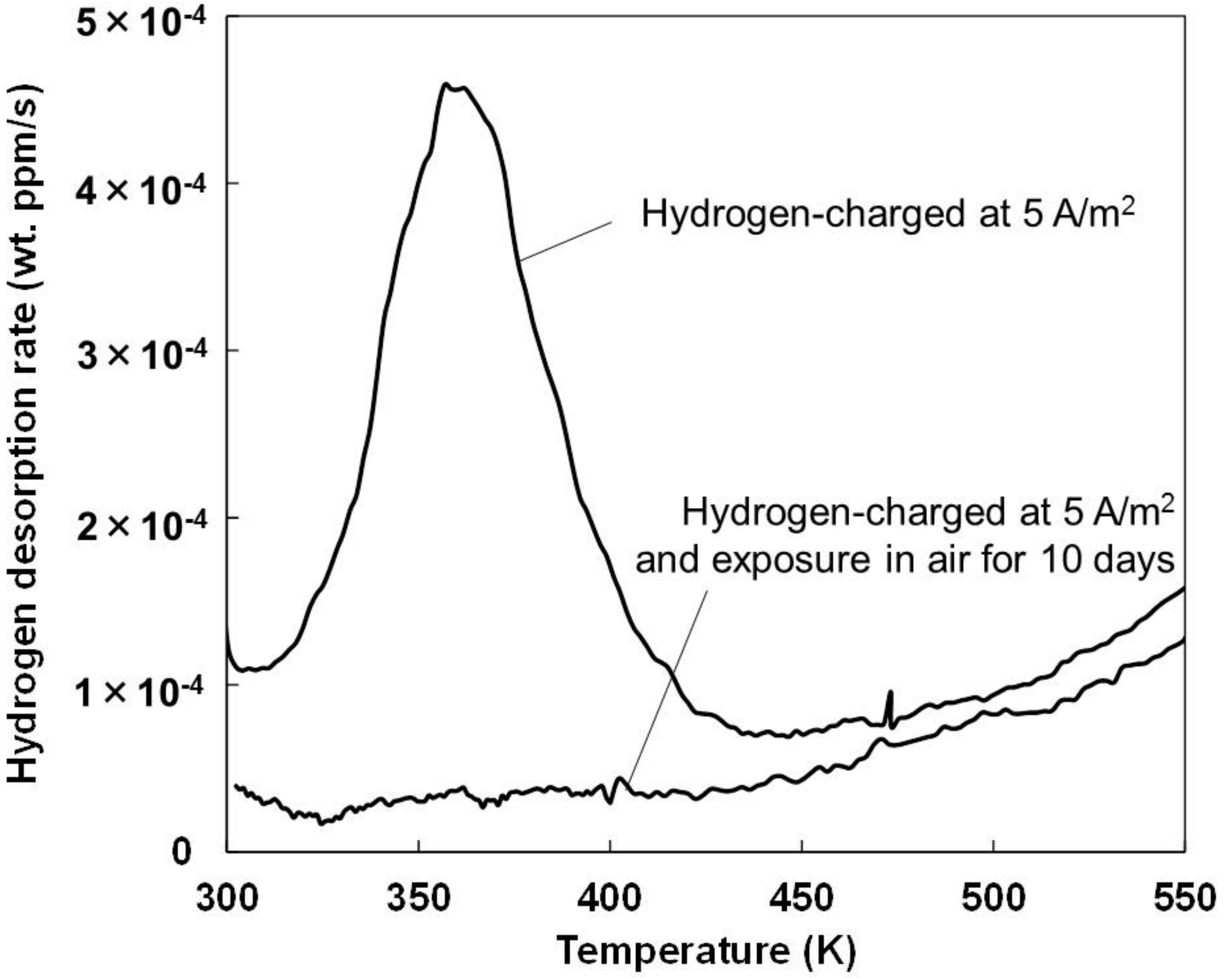
(Within 20 min after fracture)

H-entry up to 1.7 wppm

90 ^{o}C Peak

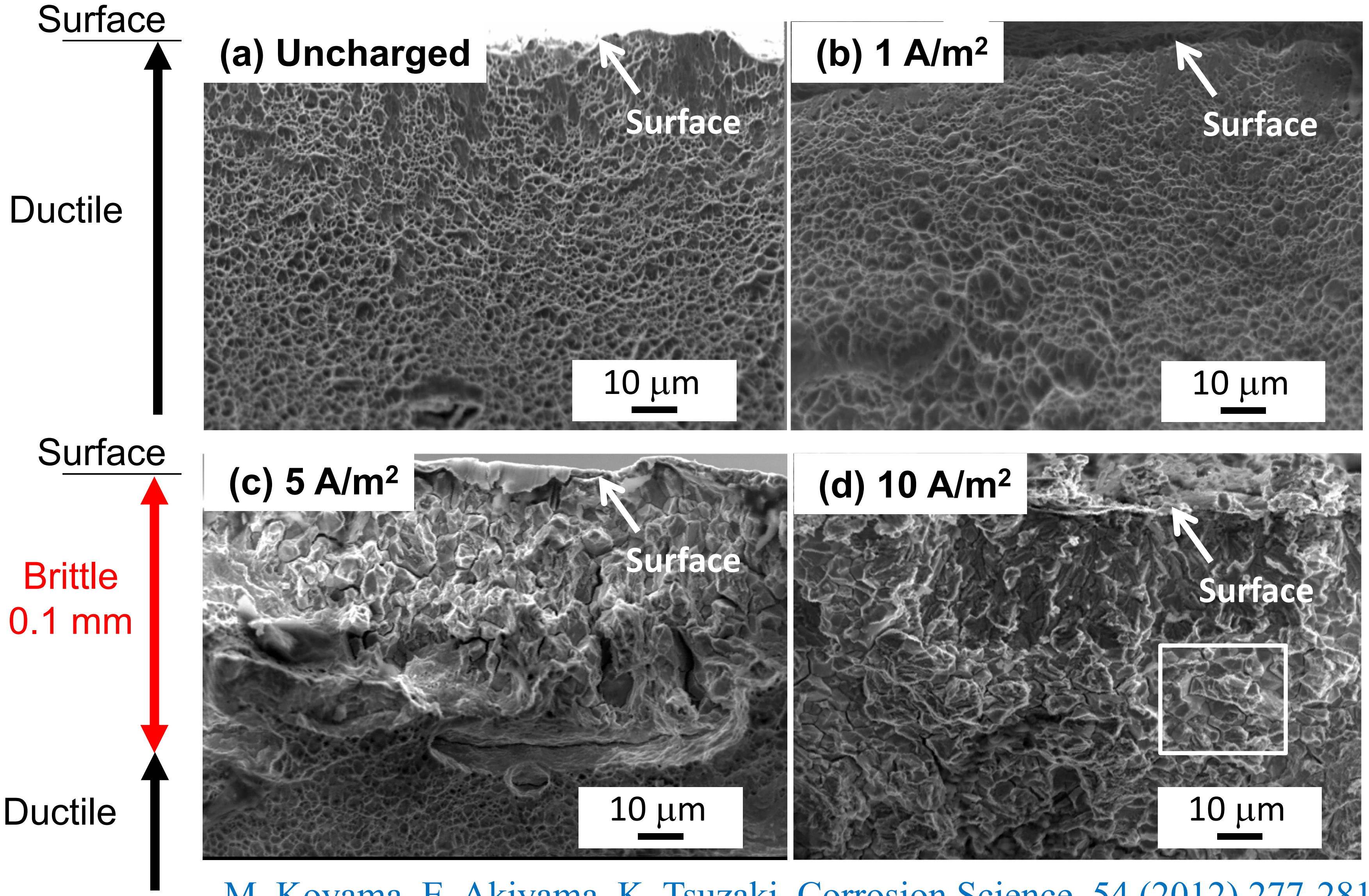
M. Koyama, E. Akiyama, K. Tsuzaki, Corrosion Science, 54 (2012) 277-281.

Hydrogen of 90 °C peak is diffusible.



M. Koyama, E. Akiyama, K. Tsuzaki, Corrosion Science, 54 (2012) 277-281.

Fe-18Mn-0.6C, Strain Rate = 5 x 10^{-5} /s @ RT

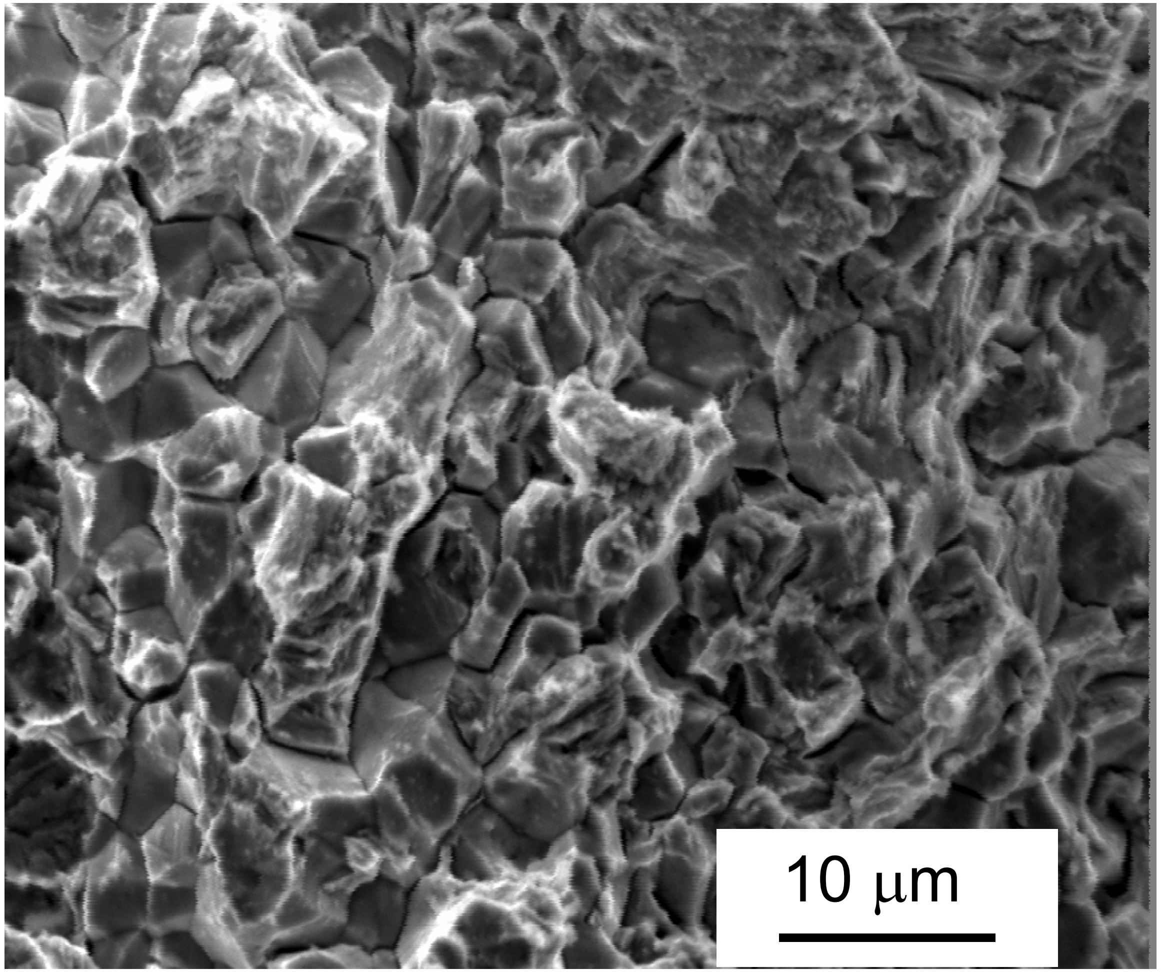


M. Koyama, E. Akiyama, K. Tsuzaki, Corrosion Science, 54 (2012) 277-281.

Fe-18Mn-0.6C, t = 0.3 mm

@ 10 A/m^2 , 1.7 wppm H

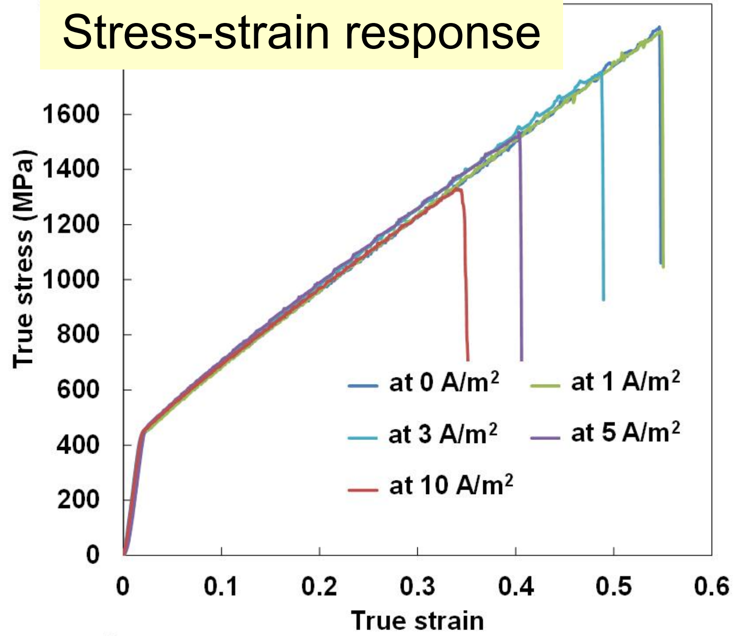
IG Fracture



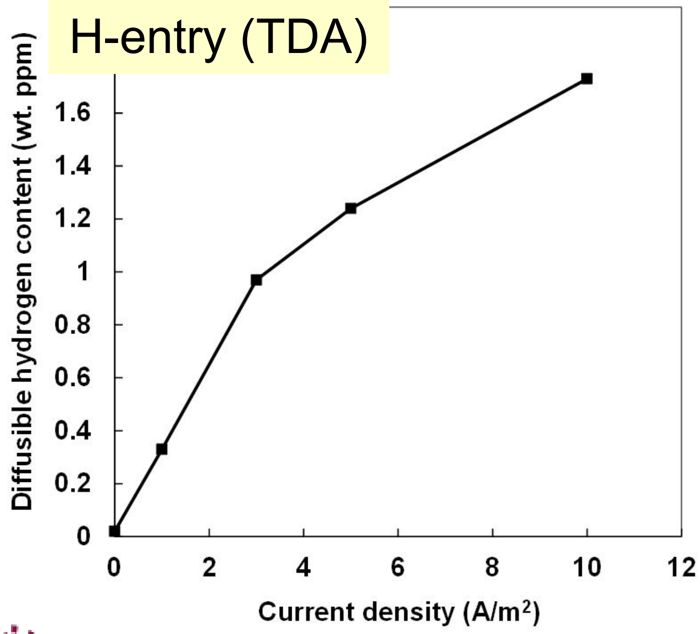
M. Koyama, E. Akiyama, K. Tsuzaki, Corrosion Science, 54 (2012) 277-281.

Conclusion for 1st Part

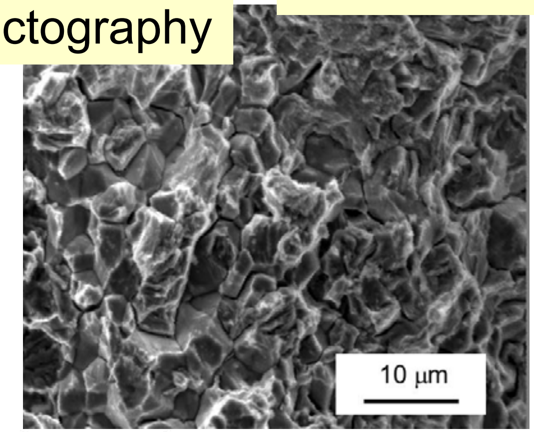
Stress-strain response

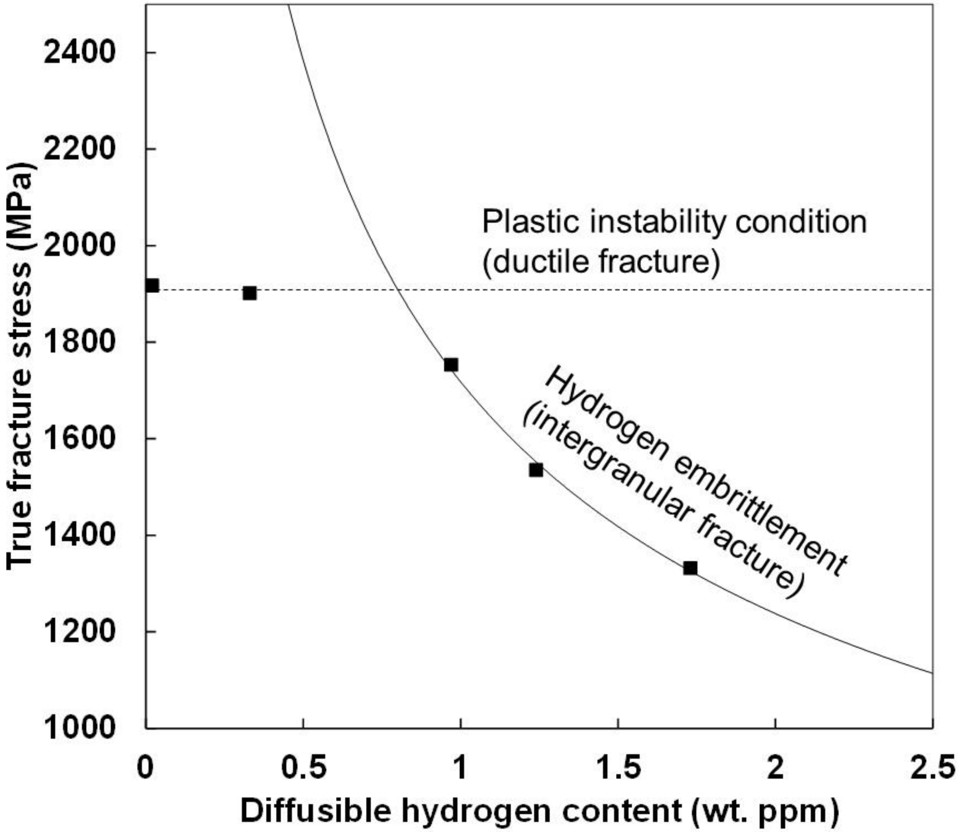


H-entry (TDA)



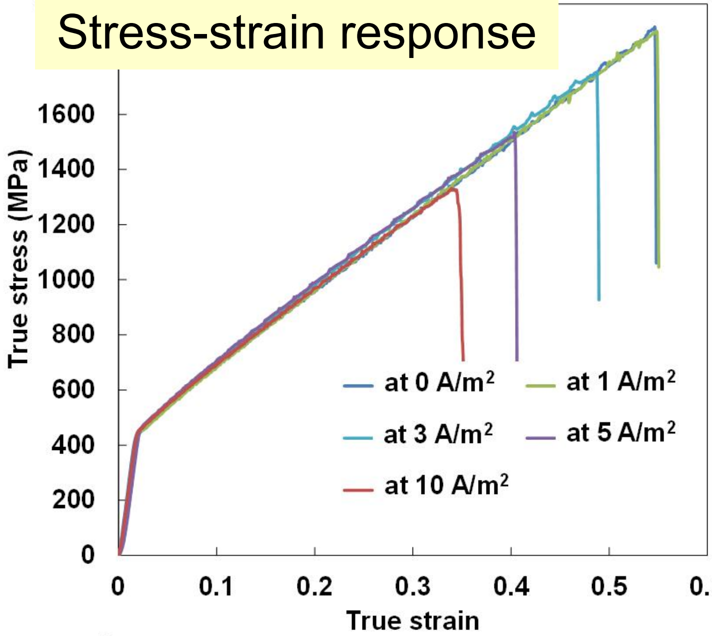
Fractography



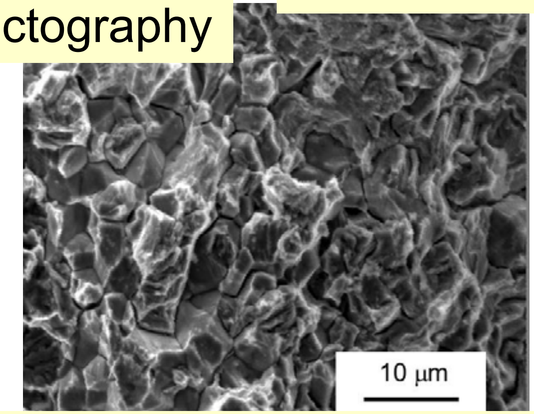


Conclusion for 1st Part

Stress-strain response

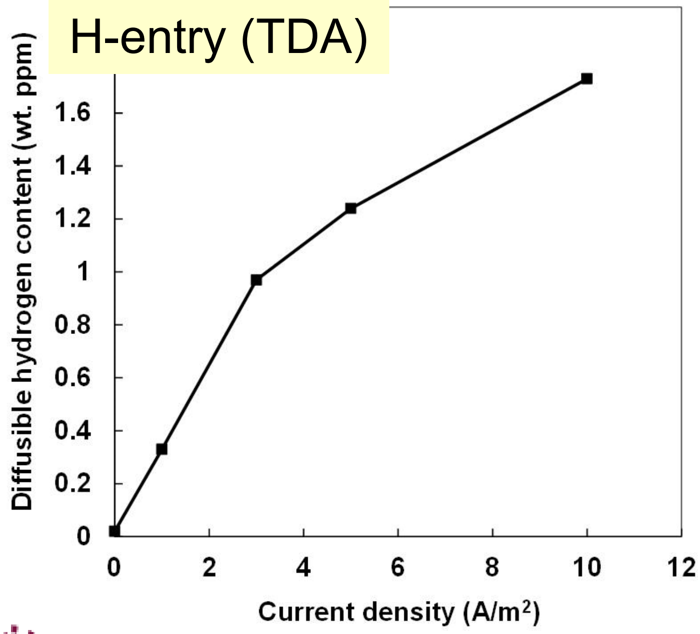


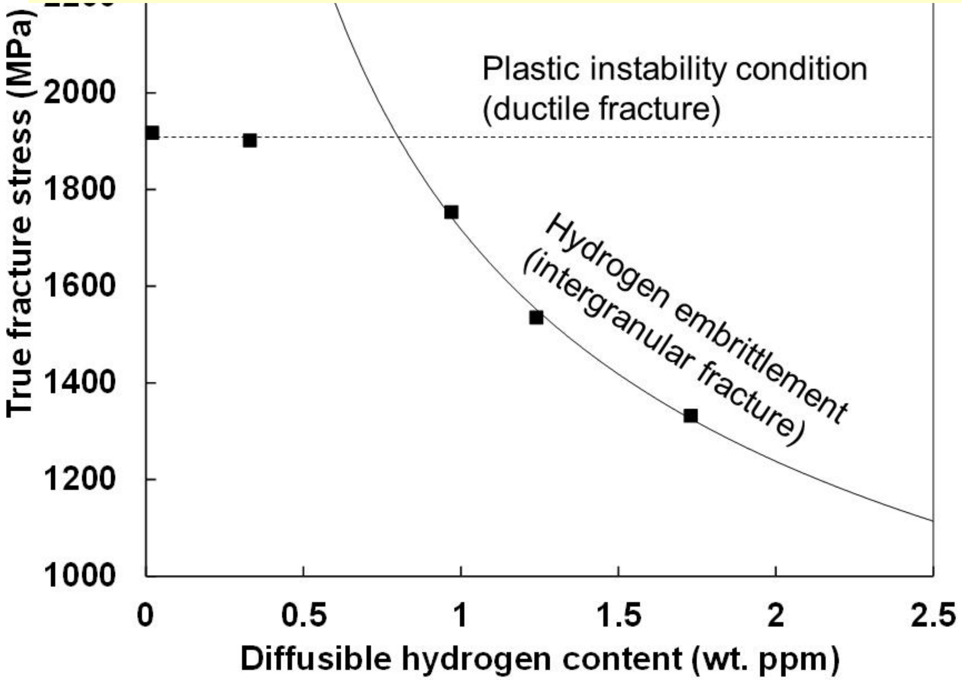
Fractography



Premature fracture due to H-entry is associated with IG fracture.

H-entry (TDA)





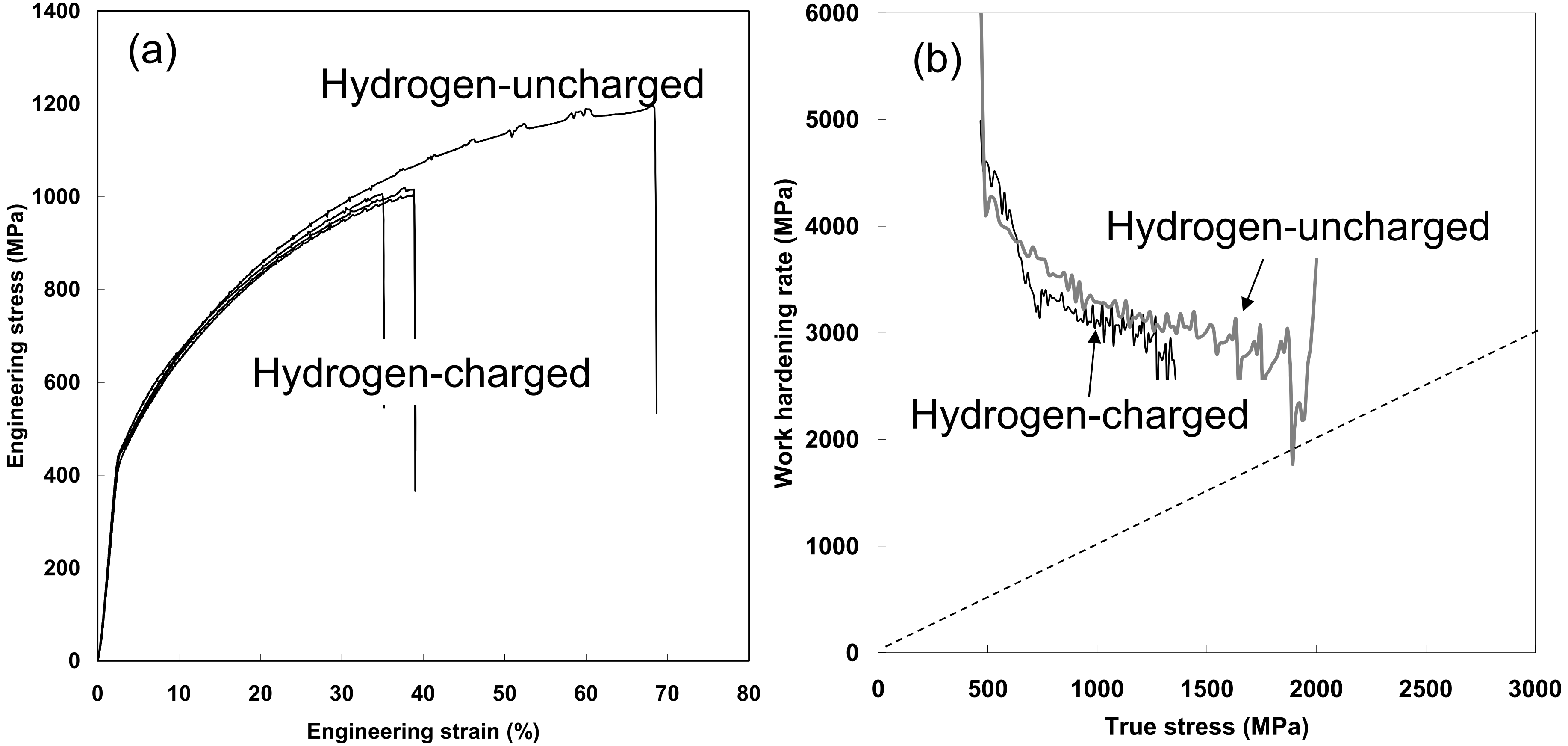
Further Questions for HE

Effect of sample shape?
(especially thickness)

Effect of phase stability of alloy?
(especially hcp martenisite)

Effect of deformation twins?
(especially twin-twin intersection)

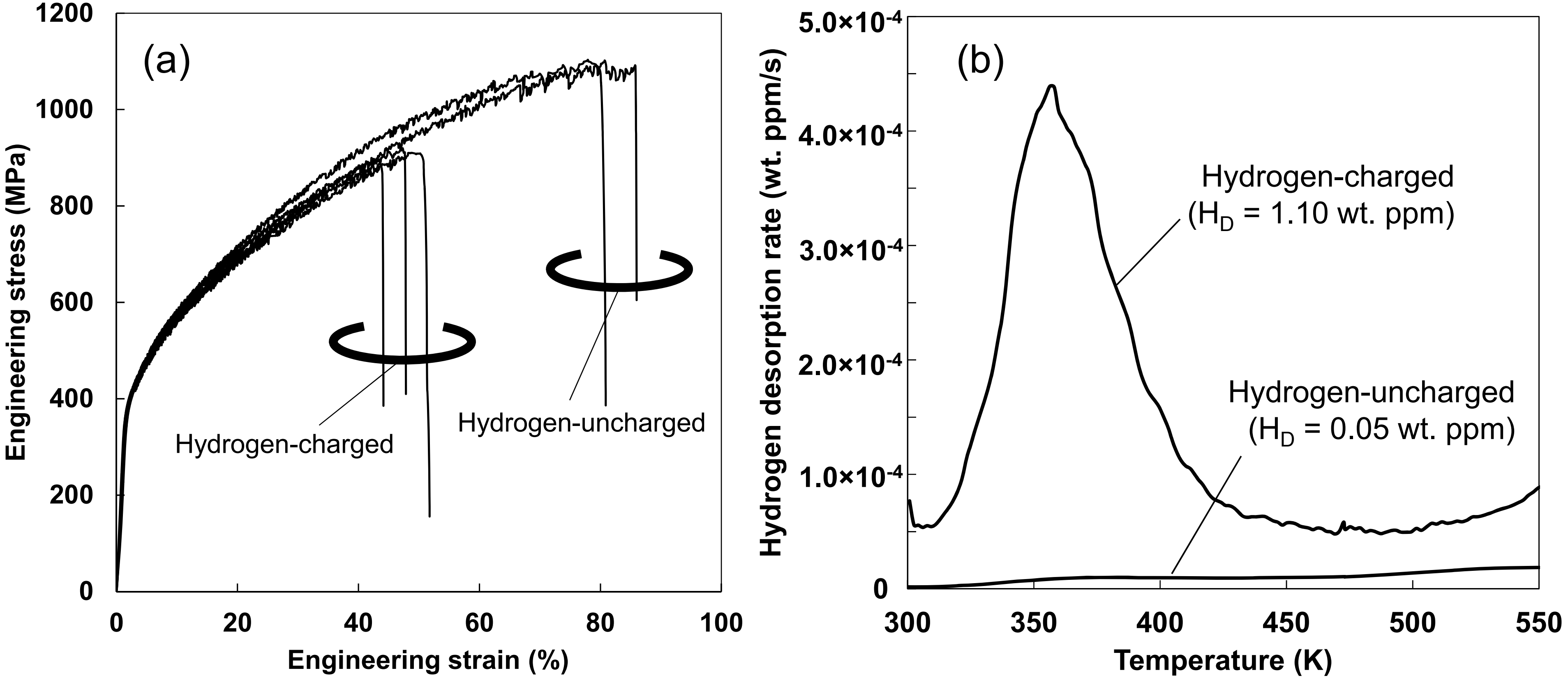
Fe-18Mn-0.6C, t = 1.2 mm @ 10 A/m^2



Reduced ductility is observed in a thicker specimen with 1.2 mm t.

M. Koyama, E. Akiyama, K. Tsuzaki, Corrosion Science, 54 (2012) 1-4.

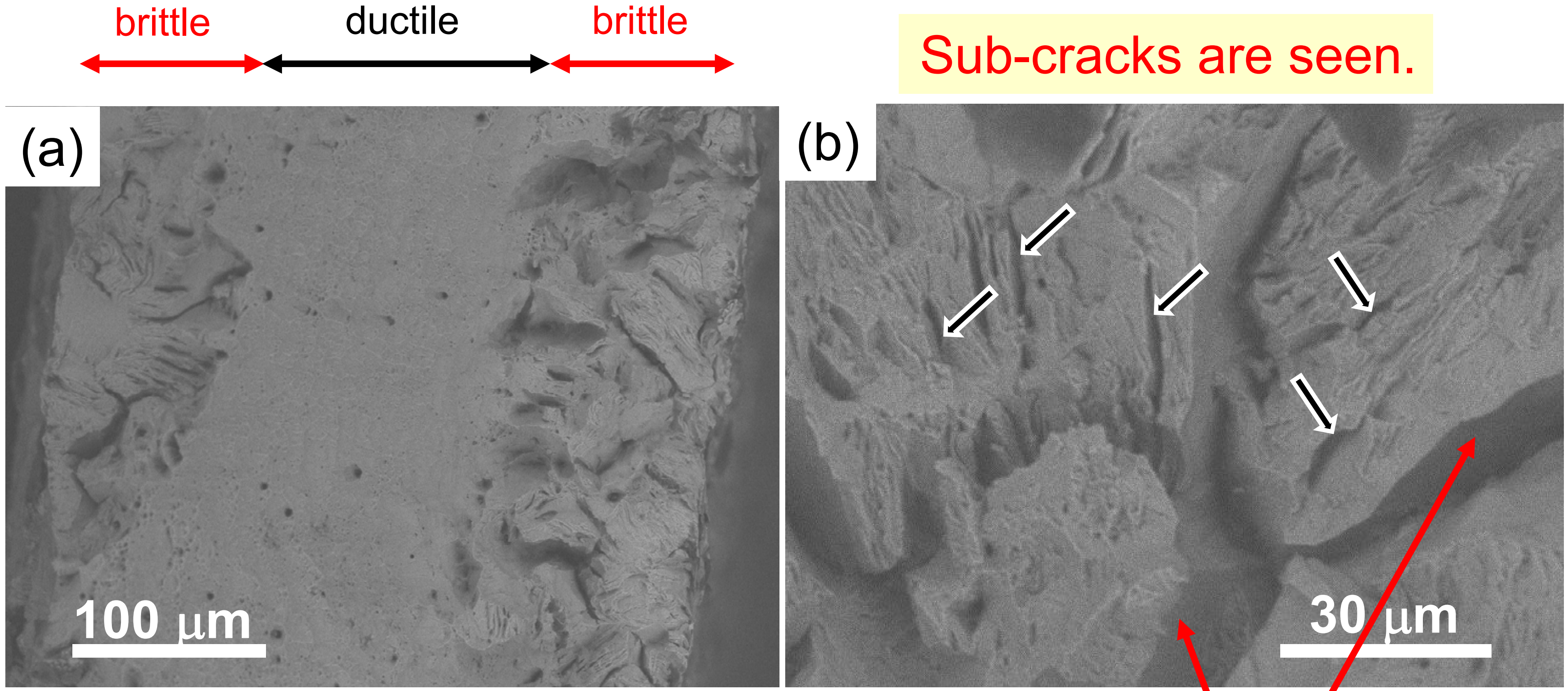
Fe-18Mn-1.2C, t = 0.5 mm @ 10 A/m^2 (more stable against HCP martensite)



Reduced ductility is observed in a more stable Fe-Mn-C alloy.

M. Koyama, E. Akiyama,T. Sawaguchi, D. Raabe, K. Tsuzaki, Scr. Mater., 66 (2012) 459-462.

Fe-18Mn-1.2C, t = 0.5 mm @ 10 A/m^2



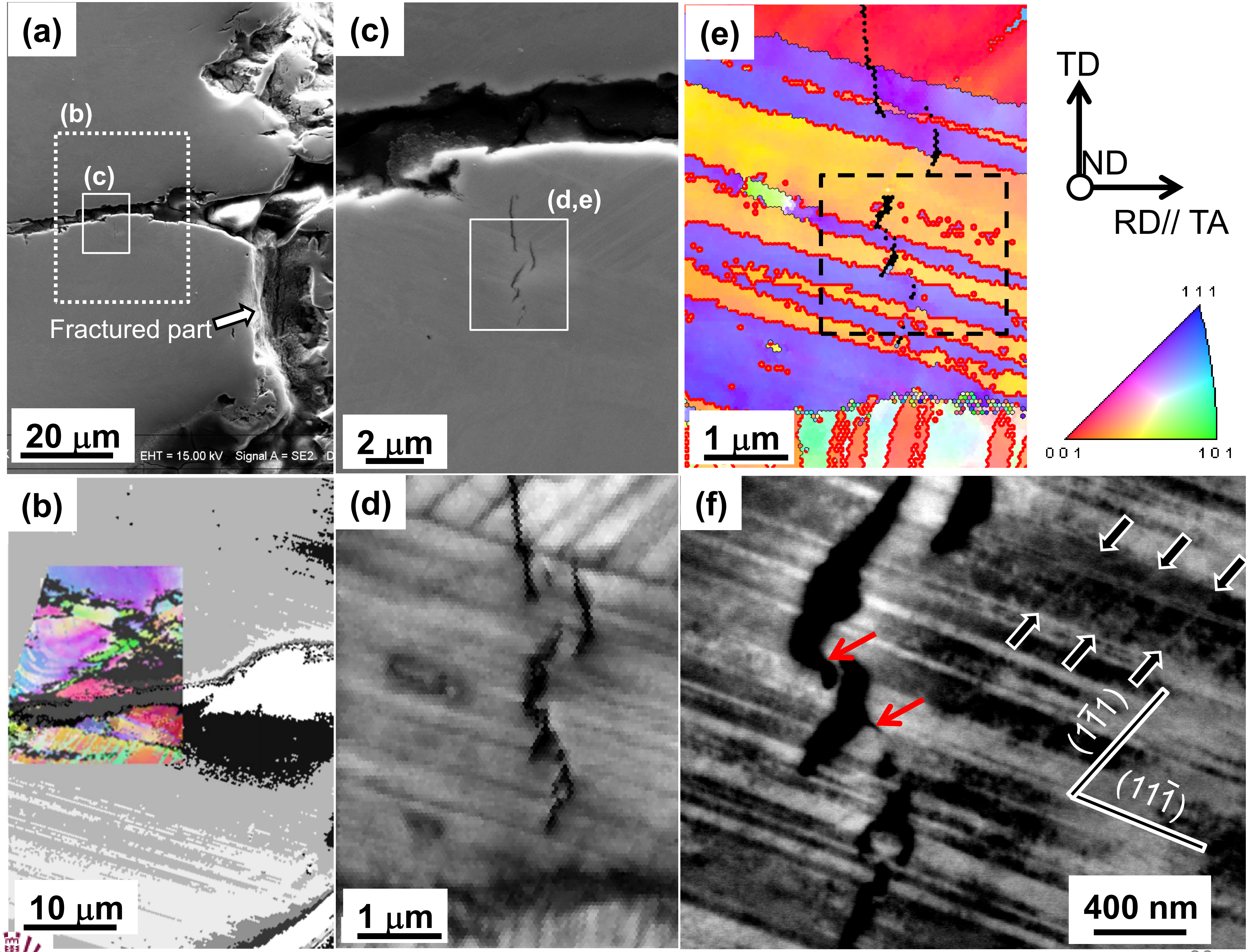
Sub-cracks are seen.

Low Mag.

High Mag.

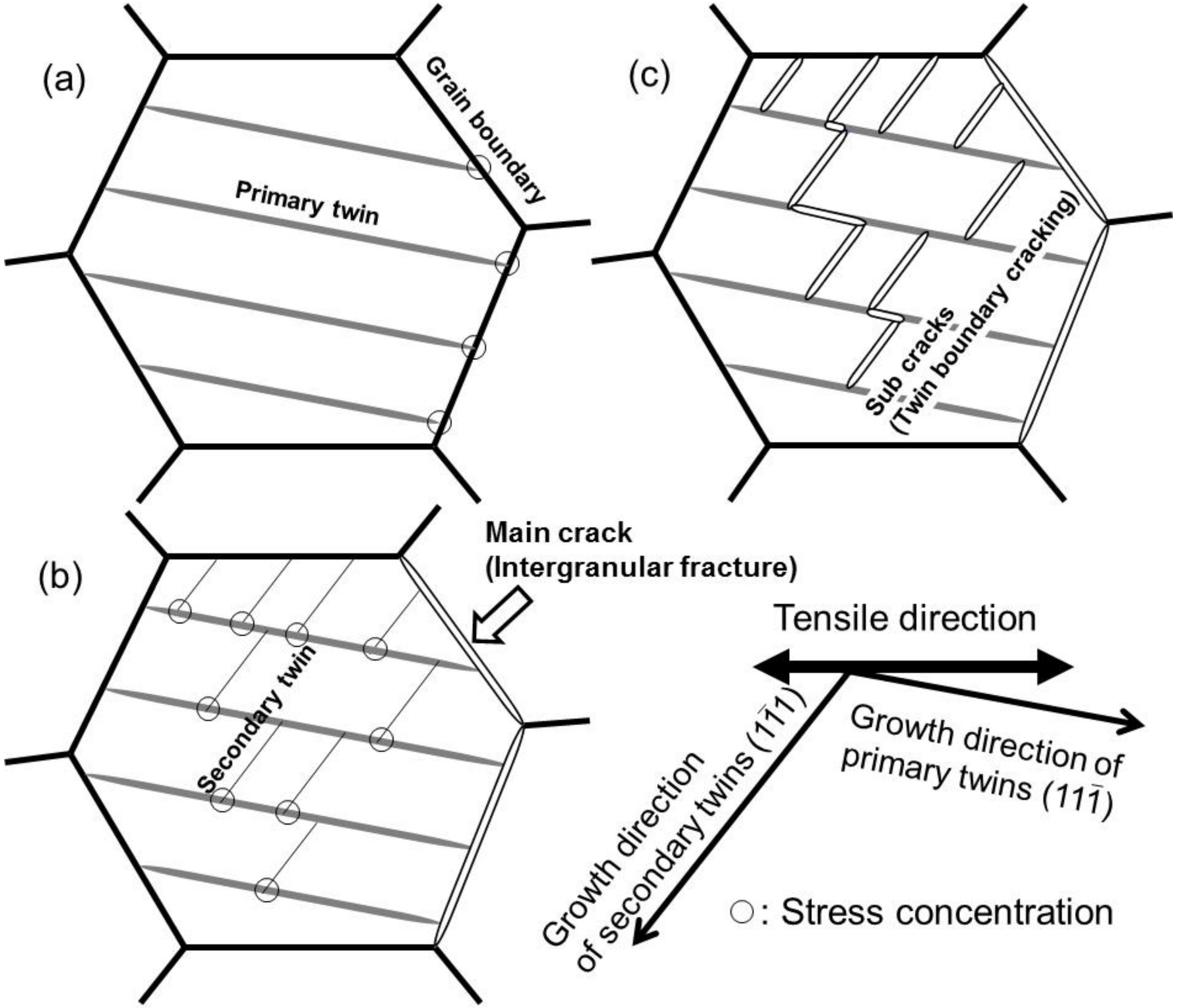
Intergranular cracking

M. Koyama, E. Akiyama,T. Sawaguchi, D. Raabe, K. Tsuzaki, Scr. Mater., 66 (2012) 459-462.



Koyama, E. Akiyama,T. Sawaguchi, D. Raabe, K. Tsuzaki, Scr. Mater., 66 (2012) 459-462.

Cracks propagate along *grain boundaries* and *twin boundaries*.



M. Koyama, E. Akiyama,T. Sawaguchi, D. Raabe, K. Tsuzaki, Scr. Mater., 66 (2012) 459-462.

Next Question

Is reduced ductility observed in a single crystalline sample with deformation twinning?

316 steel (Fe-16.8Cr-10.4Ni-2.1Mo-1.4Mn-0.20C)
Single crystals by Bridgmen method, t = 0.5 mm

(After I. V. Kireeva and Yu. I. Chumlyakov, Tomsk State Univ., Russia)

<111> tensile direction; twinning is major
<100> tensile direction; twinning is minor

[Ref] I. Karaman, H. Sehitoglu, H.J. Maier, Y.I. Chumlyakov, Acta Mater. 49 (2001) 3919.

Conclusions

The tensile tests during in-situ H charging were conducted in Fe-high Mn-C steels which are stable against bcc and hcp martensites.

1) H-entry up to 1.7 wppm was obtained.
2) YS and work-hardening behavior did not change.
3) Elongation was markedly decreased.
4) Cracks propagated along grain boundaries and twin boundaries in near surface regions.
5) Reduced elongation was observed in the <111> oriented single crystal with twinning.

Conclusions

The tensile tests during in-situ H charging were conducted in Fe-high Mn-C steels which are stable against bcc and hcp martensites.

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nd
twin boundaries in near surface regions.

5) Reduced elongation was observed in the <111> oriented single crystal with twinning.

Further study is necessary for “hydrogen - deformation twin” interaction, especially H - interfacial nano-structure.

Acknowledgements

Most of the TWIP steels used in the present study were provided by POSCO.

M.Koyama thanks a Research Fellowship of NIMS Junior Researcher (2009-2010) and the Japan Society for the Promotion of Science for Young Scientists (2011-2013) .

THANK YOU
FOR YOUR KIND ATTENSION