

Colloque National Aussois 2024

Simulation & instrumentation des Procédés de Fabrication

Fonctionnalisation des surfaces et hyperdéformation

Application aux secteurs de l'hydrogène et du biomédical

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International Partnerships



Université du Québec à Trois-Rivières

J. HUOT

Activation by plastic deformation (rolling) of light-weight alloys for solid-state H storage



Kyushu university

K. EDALATI

Activation by severe plastic deformation for solid-state H-storage



Ecole de Technologie Supérieure

P. BOCHER

Fatigue of Ti and Al alloys after SMAT
(PhD P. MAUREL)



Technische Universität Dresden

W. SKROTZKI

Deformation gradient in high entropy alloys



Université de Rouen

X. SAUVAGE

Hydride formation characterization through in-situ TEM observations

LEM3



Institut Néel

P. de RANGO

Solid-state H-storage of Mg alloys activated by SPD

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Institut P'

M. ARZAGHI, Y. NADOT

(PhD C. DUREAU)

Fatigue life of stainless steels after severe SMAT

Summary

Introduction to Severe Plastic Deformation

1. Bulk SPD processes
2. Surface SPD processes
3. Surface Mechanical Attrition Treatment / Ultrasonic shot peening

Surface SPD : microstructure and mechanical properties

1. Effect of processing parameters on microstructure
2. Effect of temperature on microstructure
3. Temperature as a processing parameters
4. Importance of restitution coefficient

Duplex treatments

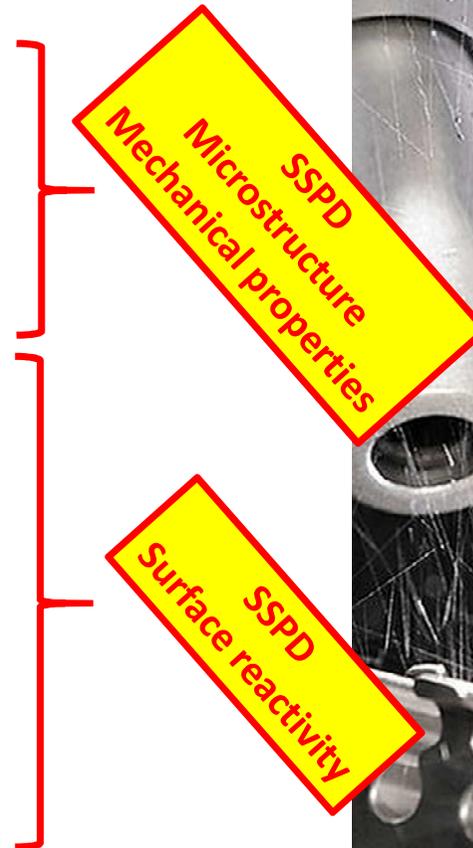
1. Example of cold plasma nitriding + SMAT

SPD and SSPD for hydrogen application

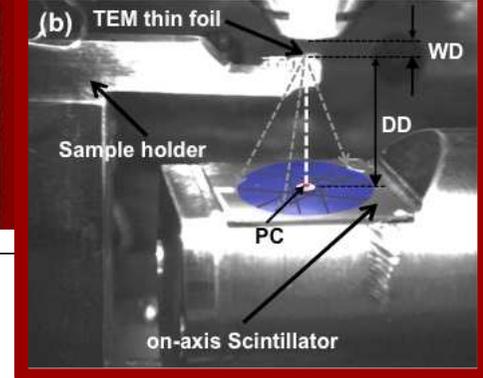
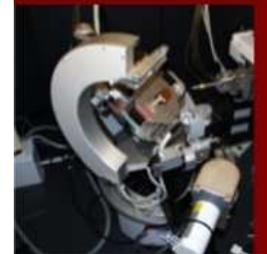
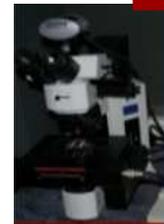
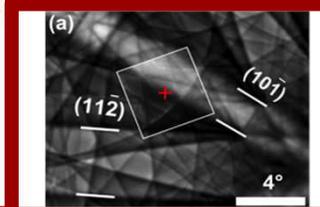
1. Hydrogen embrittlement
2. Solid-state hydrogen storage

Surface SPD and biocompatibility

1. Use of functionally graded material



Ingénierie Des Microstructures Procédés, Anisotropie, Comportement



Crystallographic textures of materials

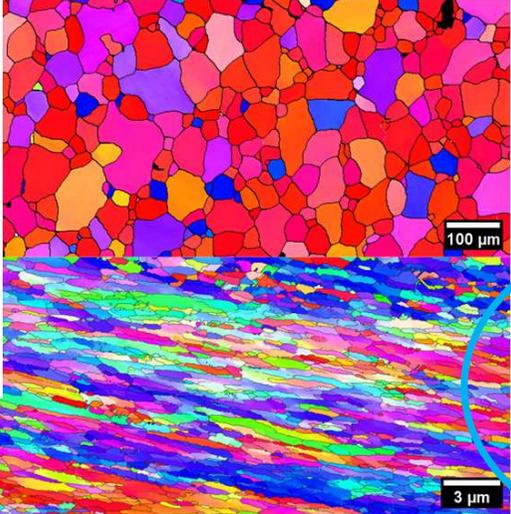
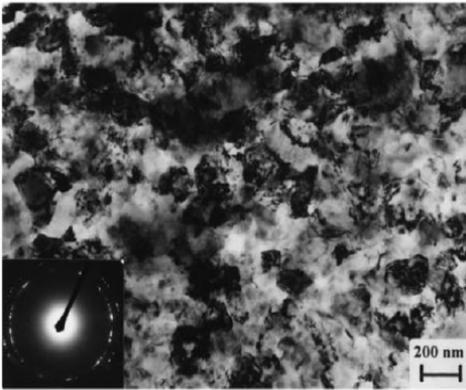
- Anisotropic Properties (elasticity, plasticity)
- Evolution of microstructure and texture during material processing
 - Development or improvement of thermo-mechanical treatment and processing that modify texture
 - Development and improvement of Characterization Techniques (XRD, EBSD, TKD, TEM ...)



Severe Plastic Deformation (SPD)

Microstructure refinement

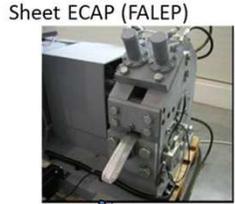
LEM3 Hyperdeformation platform



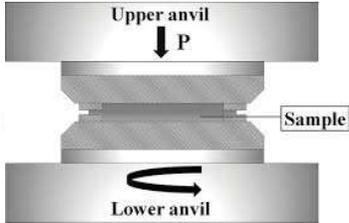
Valiev et al., Progress in Materials Science 45 (2000) 103-189



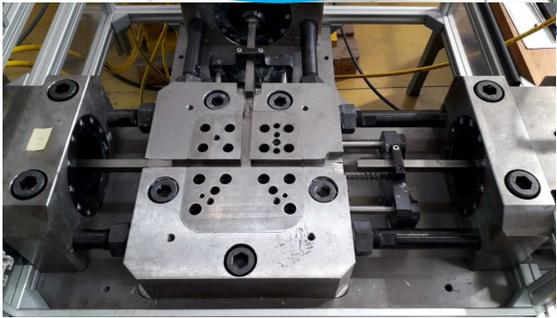
Surface SPD



Sheet ECAP (FALEP)

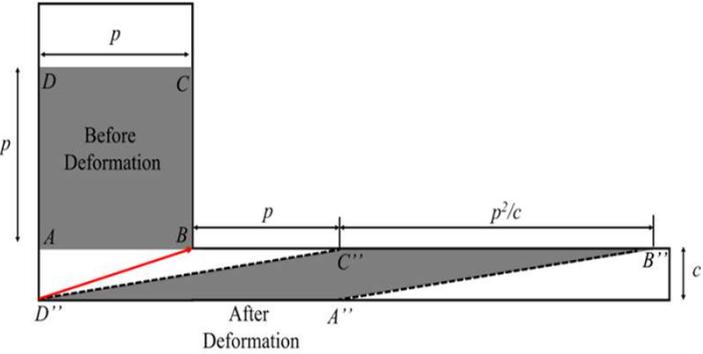


High Pressure Torsion (HPT)



(+Powder SPD)

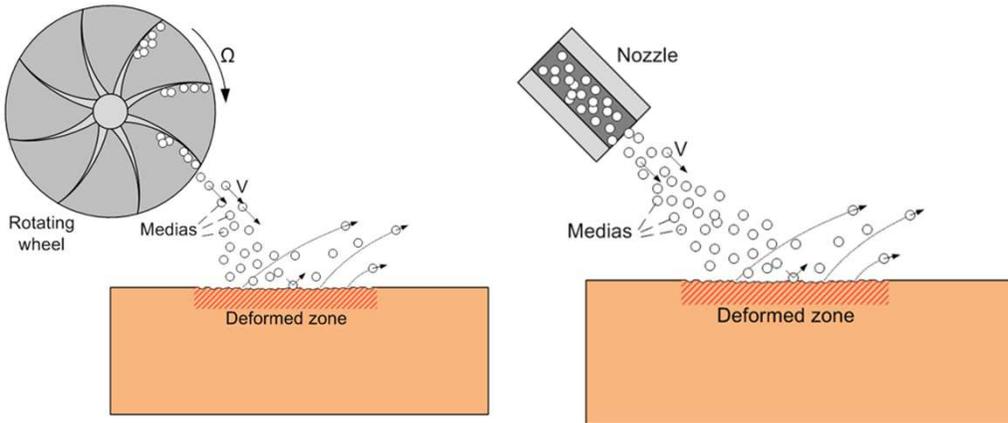
(+Large strain torsion)



contact : marc.novelli@univ-lorraine.fr

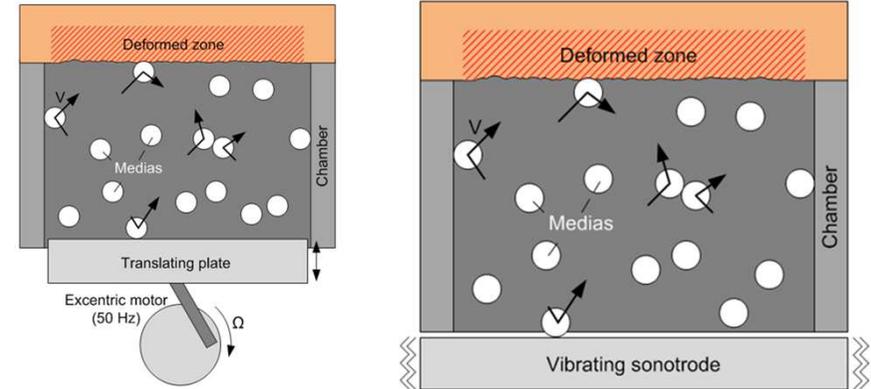
Surface Severe Plastic Deformation (SSPD)

Unidirectional impact



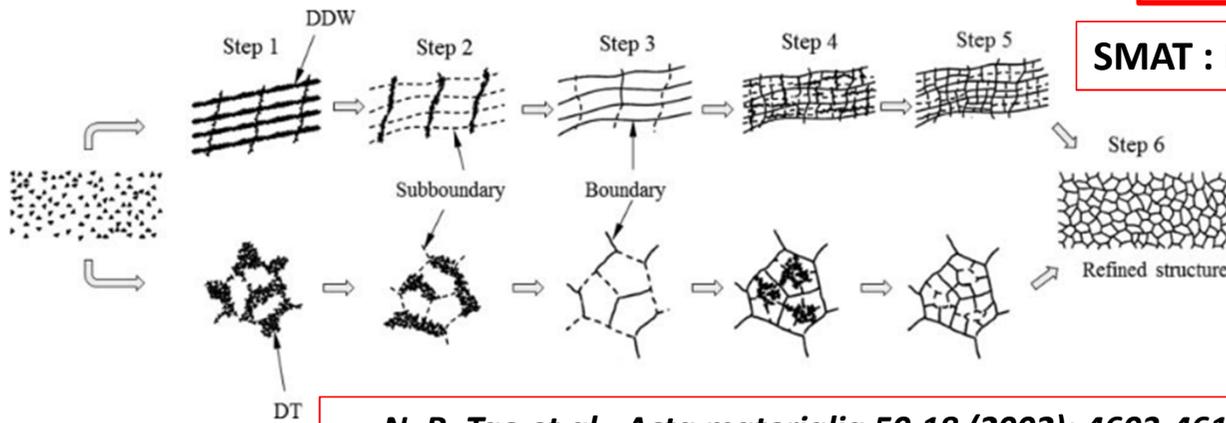
T. Grosdidier et al., MATERIALS TRANSACTIONS (2023): MT-MF2022040.

Multidirectional impact

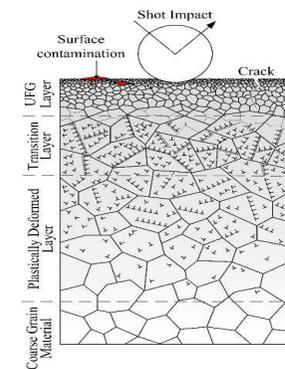


SMAT: Surface Mechanical Attrition Treatment
USP : Ultrasonic Shot Peening

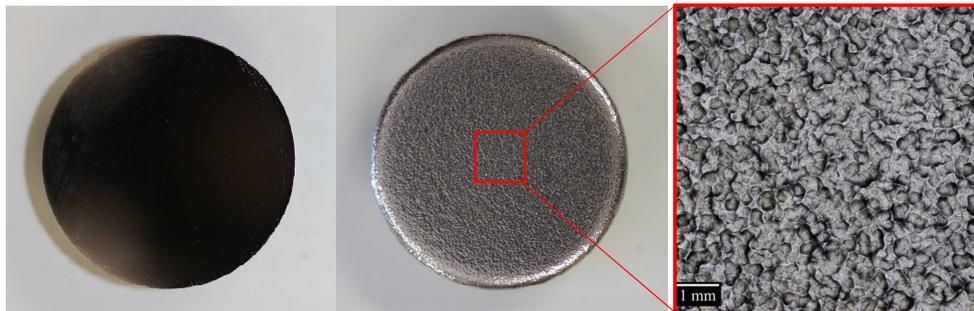
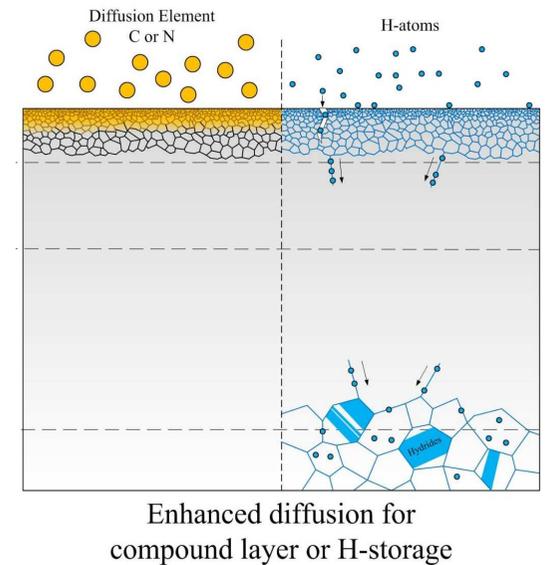
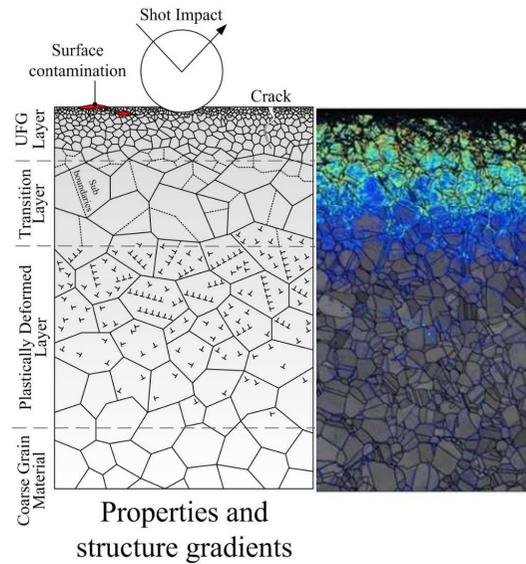
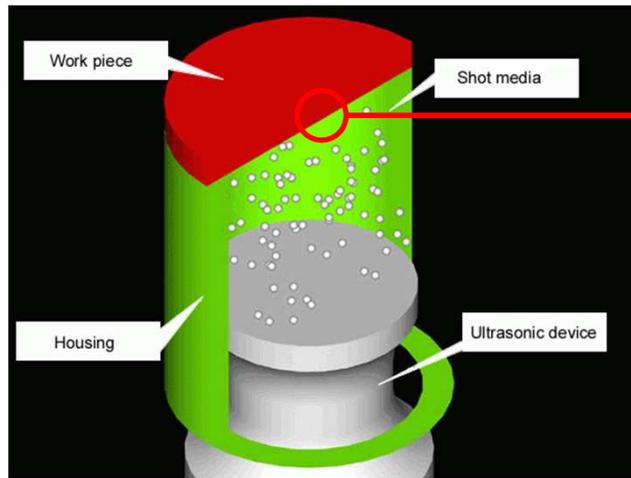
SMAT : Lu K. and Lu J., Mater. Sci. Eng., 2002 , 38, p. 375



N. R. Tao et al., Acta materialia 50.18 (2002): 4603-4616..



Surface Severe Plastic Deformation (USP / SMAT)



Derived from Shot Peening

- + Compressive stresses
- Surface defects (Notch sensitivity)
- **SSPD** => Gradient microstructure
- + Surface ultrafine / Nanograins and gradient microstructure

Used for :

- Fatigue
- Surface reactivity

Gradient microstructures : their natures and modifications

Effect of processing parameters

Numerous processing parameters

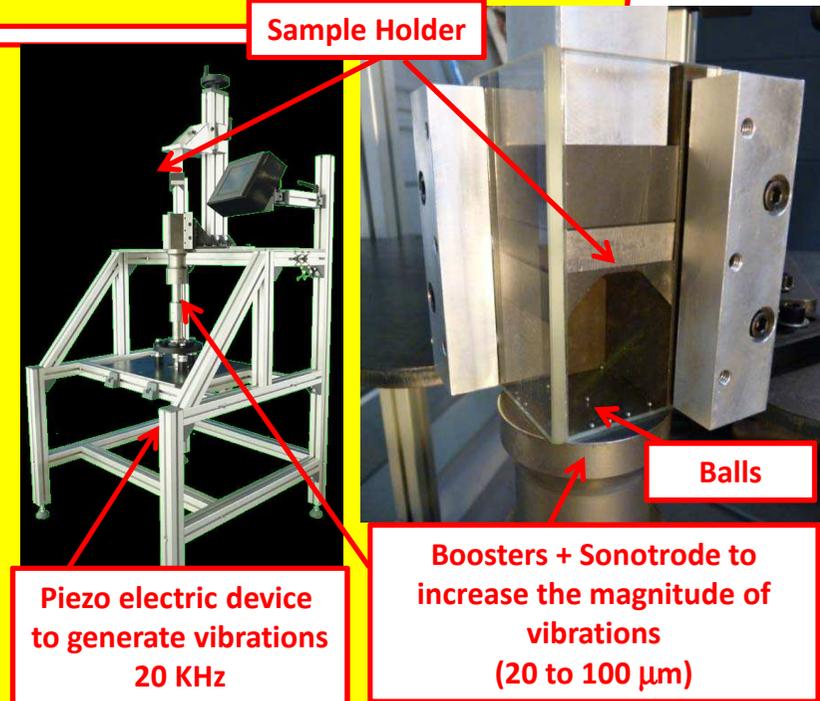
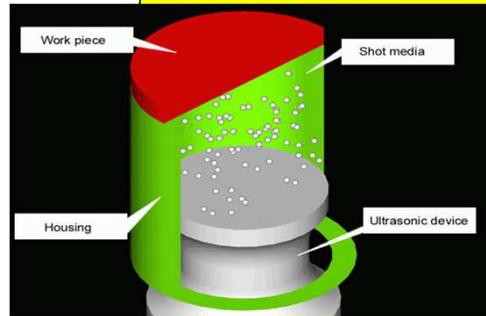
Vibrating frequency of the sonotrode (Hz)

Nature of the ball material

Diameter of ball (mm) and weight (g)

Surface coverage (number of balls)

Treatment time (min)



1. Example of the effect of the processing parameters

2. Process control (high speed camera for velocity and incidence angle) and their effect on the microstructure by automated EBSD

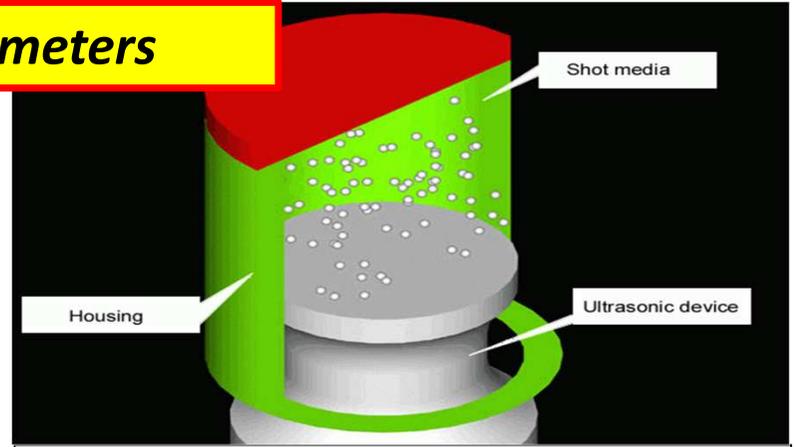
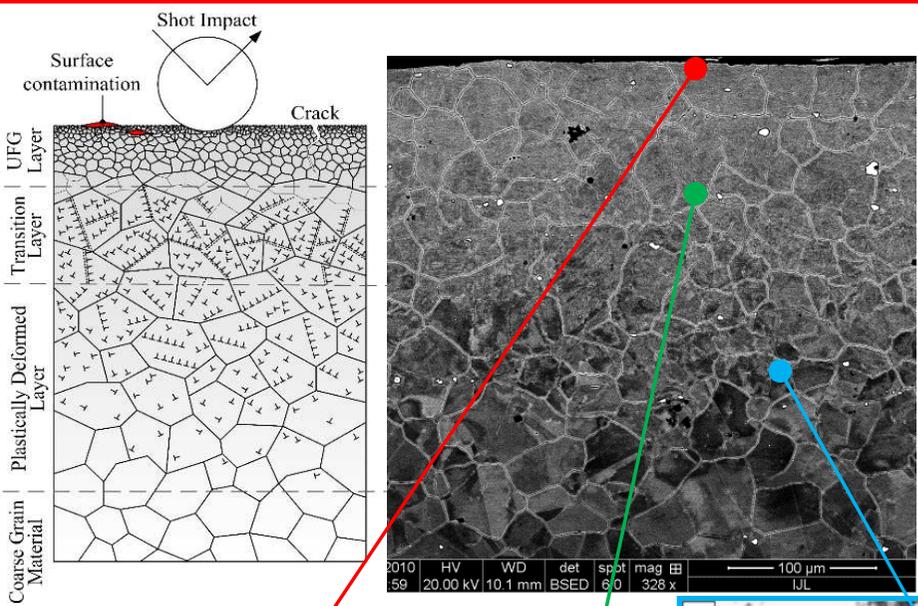
3. Temperature is a very versatile parameter

3.A Cryogenic treatments

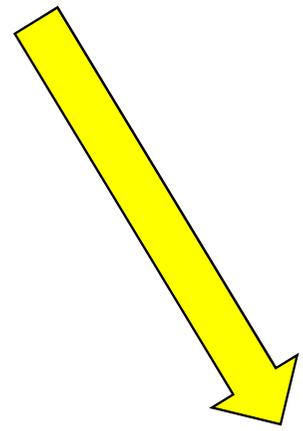
3.B Warm treatments (up to about 800K)

4. Importance of restitution coefficients

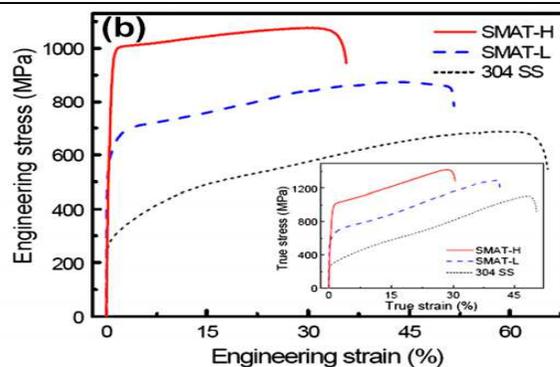
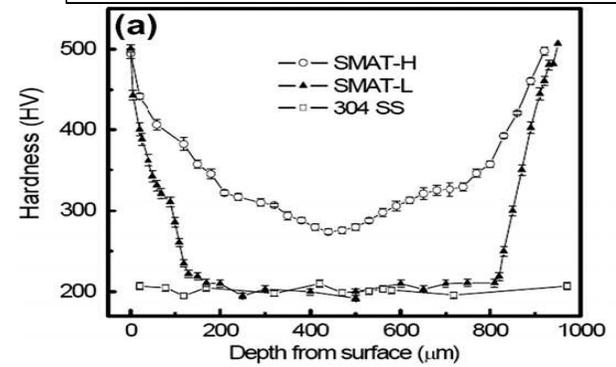
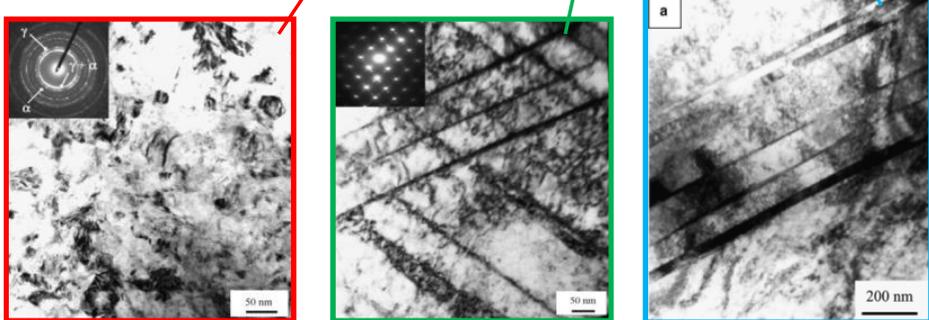
1. Example : SS after very different SMAT processing parameters



Numerous processing parameters
 Vibrating frequency : (Hz) 20000 (H) / 50 (L)
 Impact velocity (m /s): 10 (H) / 0.5 (L)
 Ball material Diameter of ball (mm) : 2 (H) / 8 (L)
 Treatment time (min) : 15 (H) / 40 (L)



Change in hardness profile and tensile properties



Roland T., Reirant D., Lu K. Lu J., Scripta Mater., 2006 , 54, p 1949
 Roland T., Reirant D., Lu K. Lu J., Mater. Sci. Eng.A, 2007, 445, p 281

Chen A.Y. Ruan H.H., ... Lu J. , Acta Mater., 59 (2011), 3697-3709

Process improvement : What is the comparative effect of the different processing parameters ?

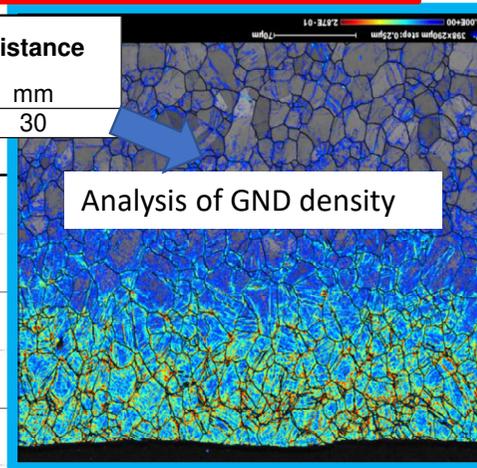
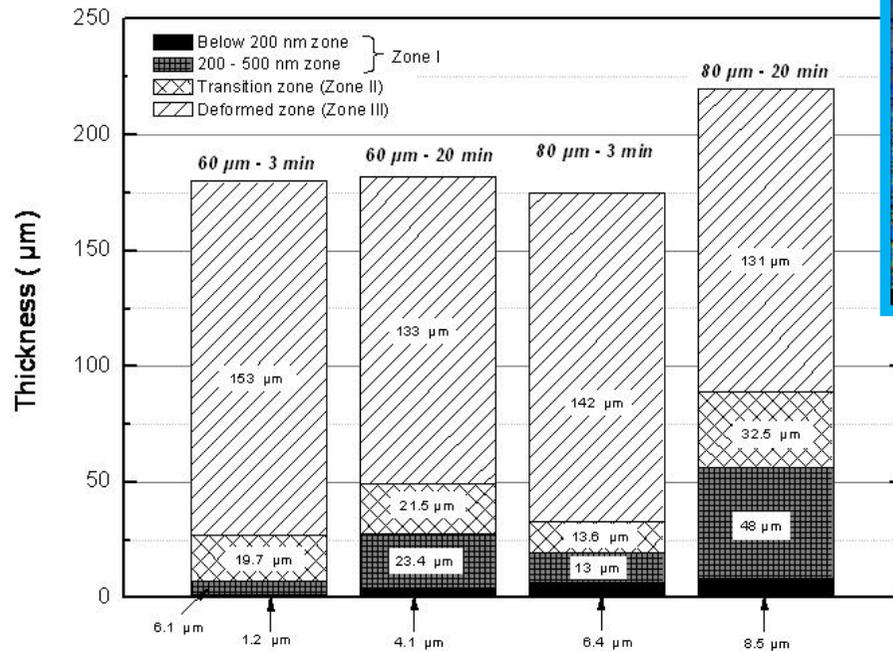
2. Improve reproducibility of the SMAT

Quantitative and automated EBSD analysis of the microstructure

Process improvement : How to quantify more “efficiently” (rapidity) ?
 - What is the comparative effect of the different processing parameters ?



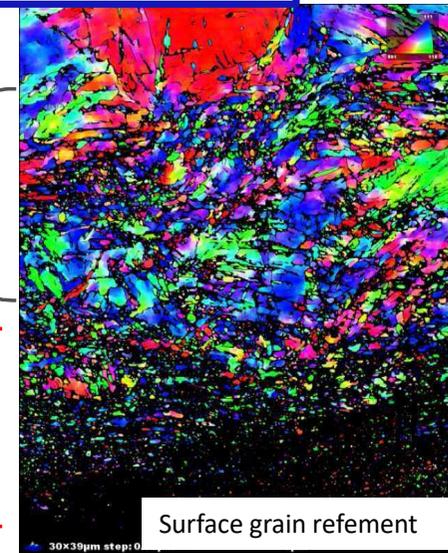
Nature	Diameter	Weigth	Nbr of balls	Magnitude	Frequency	Distance
	mm	g		μm	kHz	mm
100Cr6	1	7,60	1859	60	20	30



Deformed zone

Transition zone

Zone 1 :
UFG and Nano-grains



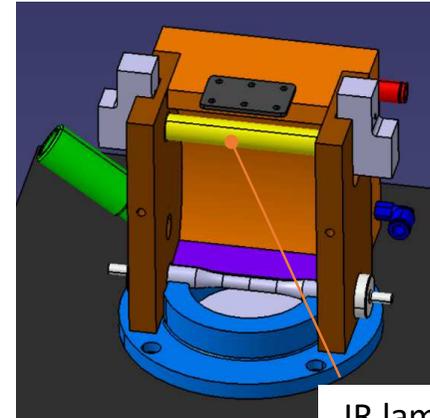
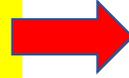
Effect of two processing parameters : Magnitude of the sonotrode / Treatment time

Y. Samih, B. Beausir, B. Bolle, T. Grosdidier, *In-depth quantitative analysis of the microstructures produced by Surface Mechanical Attrition Treatment (SMAT)*, Materials Characterization, 83 (2013) 129 – 138.

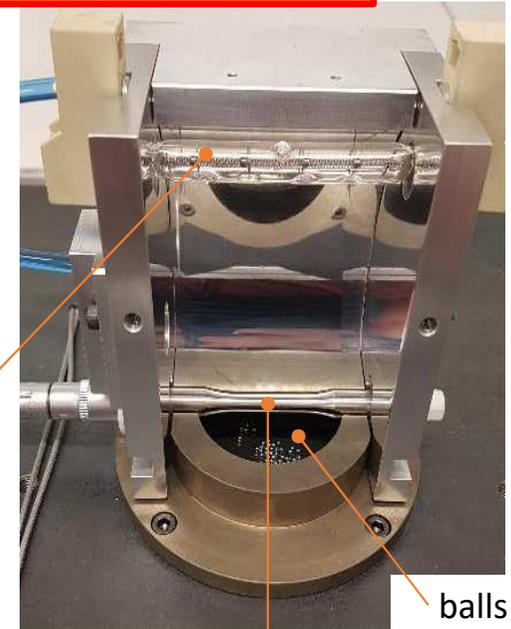
3. Temperature as a versatile processing parameter

Modification of the sample holder

- Heating device
(up to about 500°C).

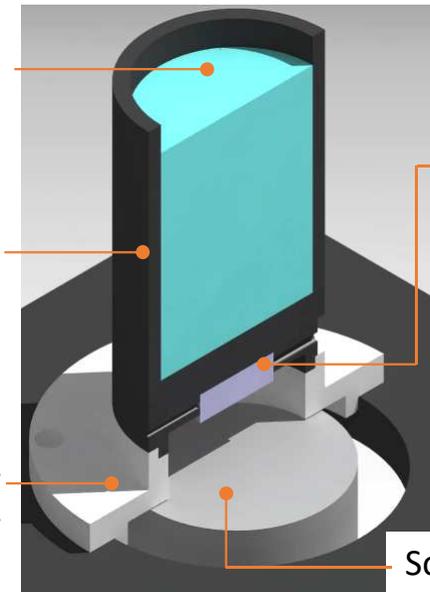


IR lamp
500W



balls

- Cooling device
(-80°C or -130°C)

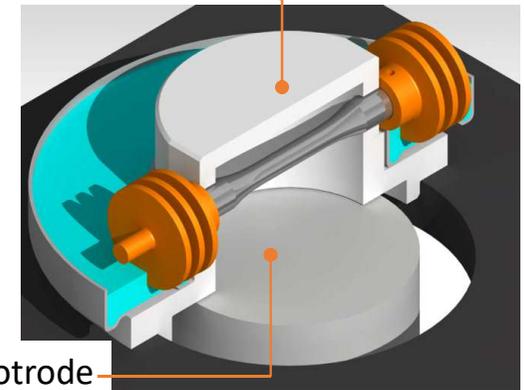


Liquid Nitrogen

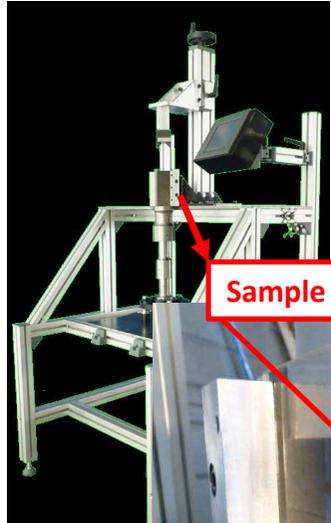
Upper Chamber

Lower Chamber

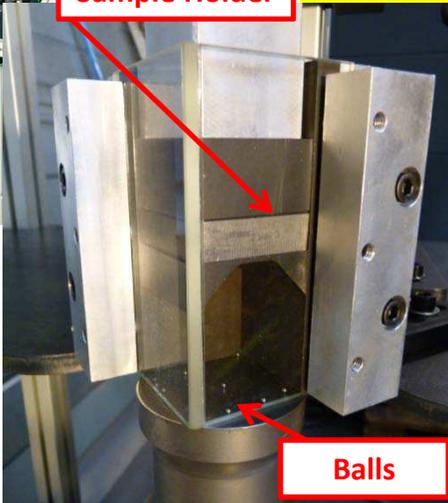
Samples



Sonotrode



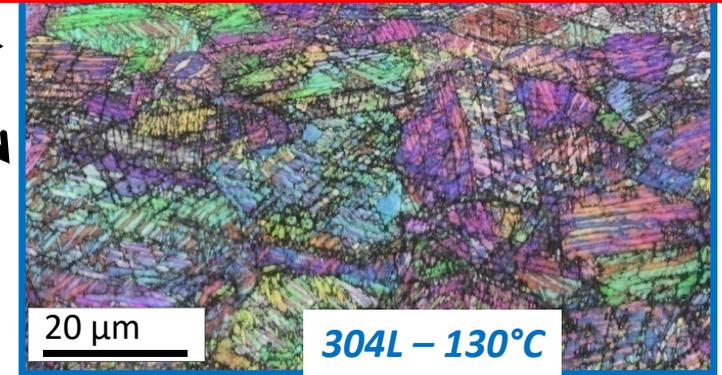
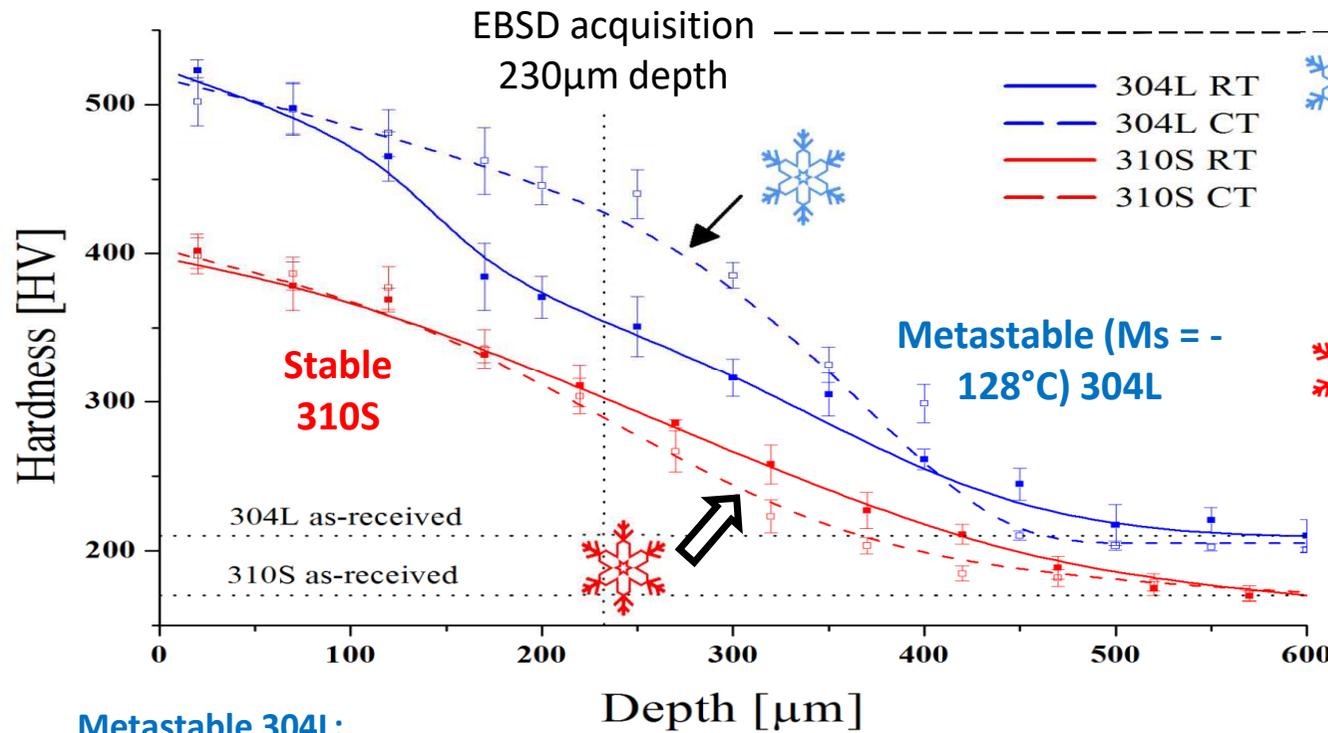
Sample Holder



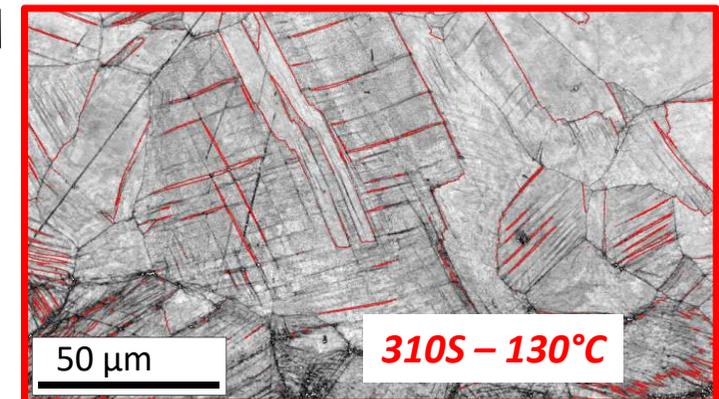
Balls

3. A Cryogenic treatment to modify the surface gradients

(different steels : different deformation mechanisms at the sub-surface)



Martensite , austenite in pattern quality



Austenite in pattern quality
<111> 60° twins in red lines

Metastable 304L:

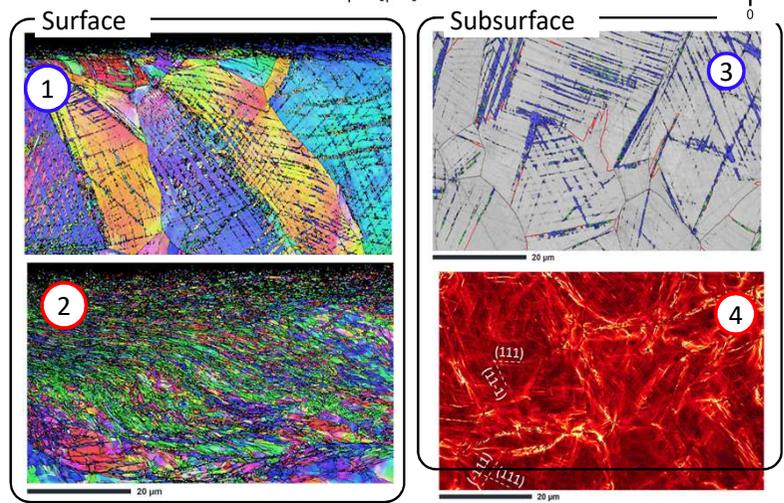
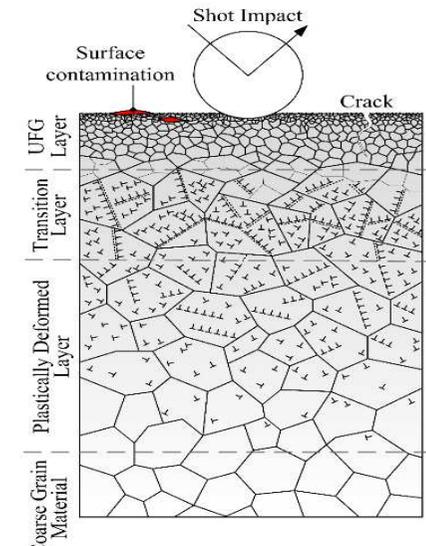
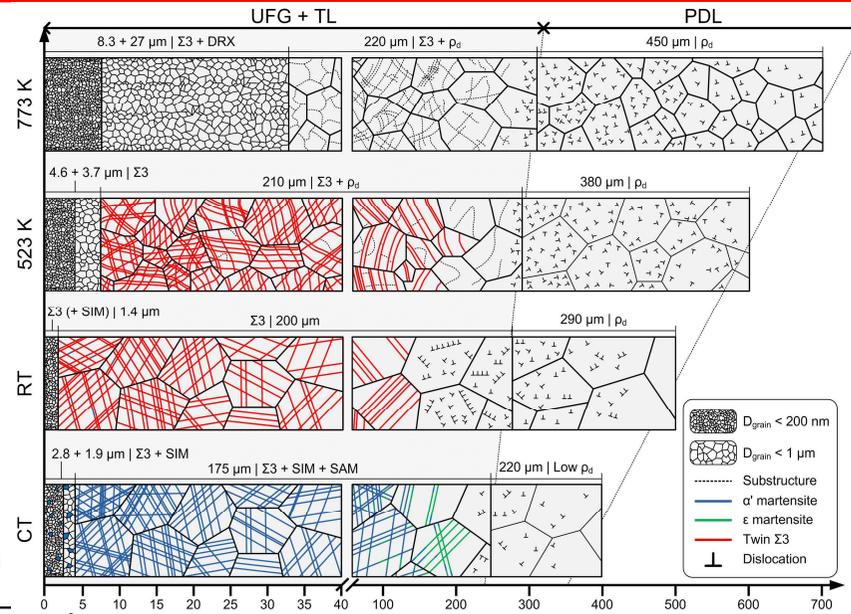
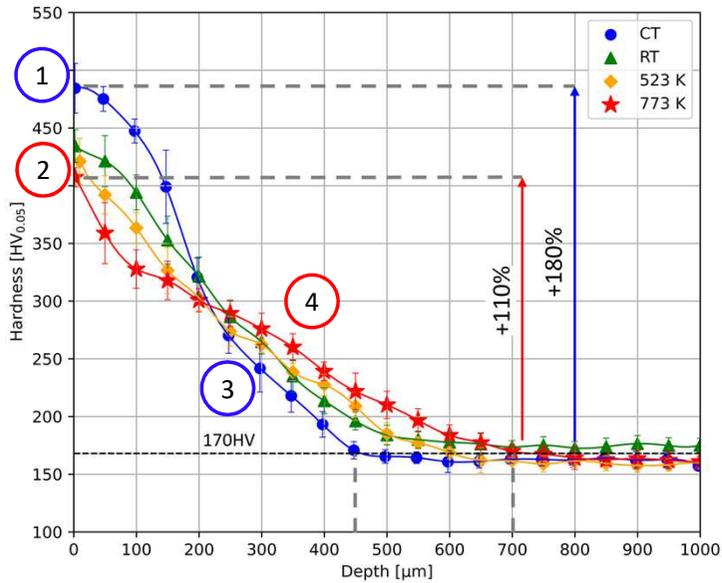
- Increase of the subsurface hardness
- Martensitic transformation is promoted at CryoT

Stable 310S:

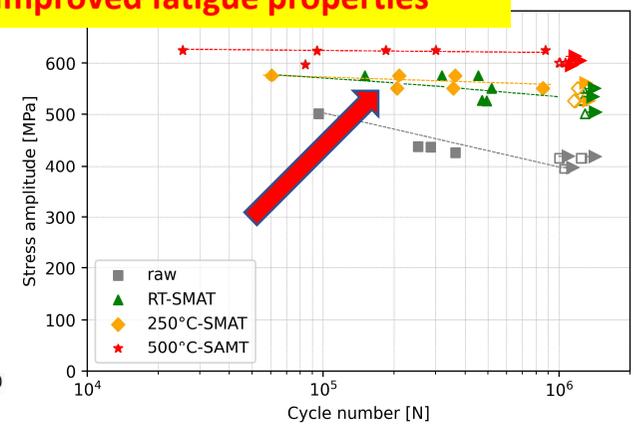
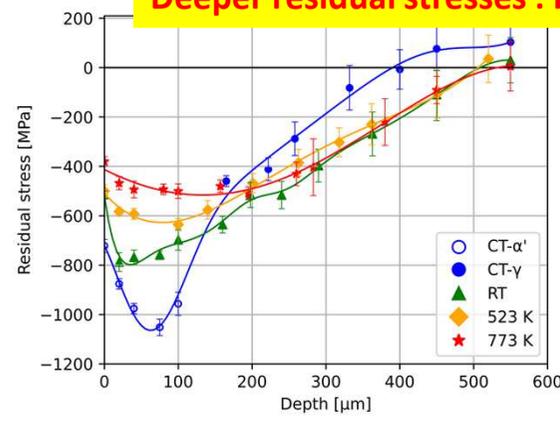
- Decrease of the subsurface hardness under CryoT because material is more resistant

M. Novelli, J.-J. Fundenberger, P. Bocher, T. Grosdidier, "On the effectiveness of surface severe plastic deformation by shot peening at cryogenic temperature", Appl. Surf. Sci. 389 (2016) 1169–1174.

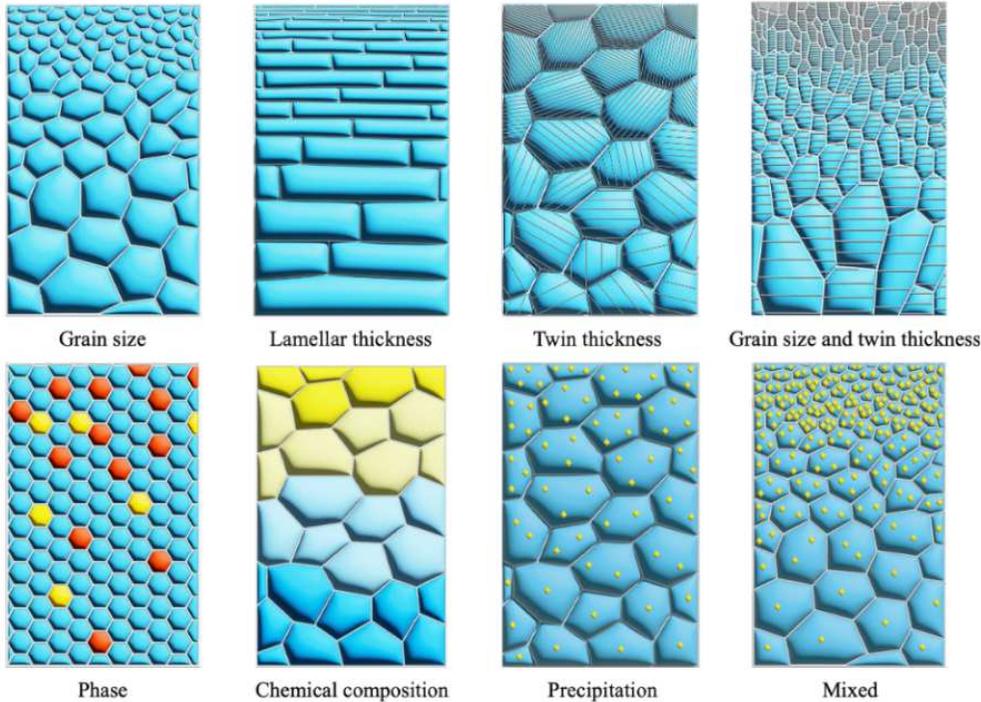
3.B Warm treatments to modify the surface gradients (same steel - 316L : different deformation mechanisms at the surface and sub-surface)



Deeper residual stresses : Improved fatigue properties

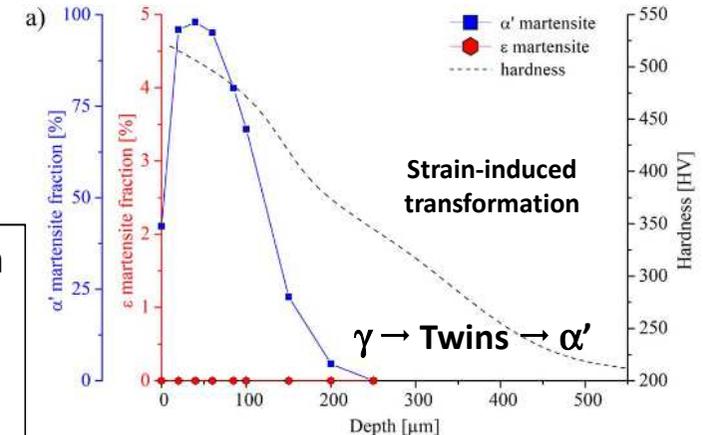


Nature of the gradients (different deformation mechanisms)

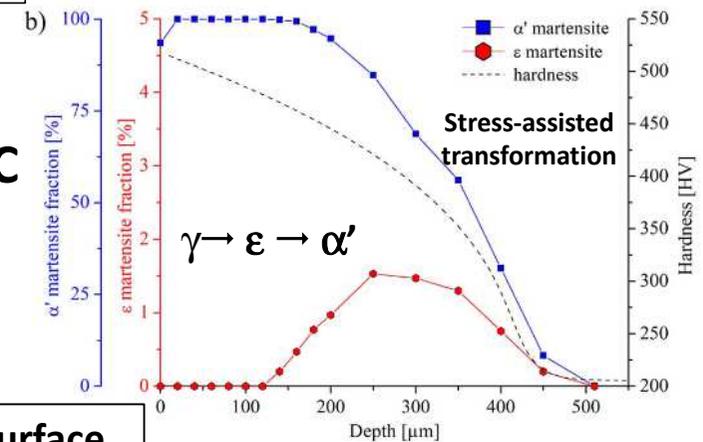


304L RT

Gradient structures can superimposes:
(i) grain size
(ii) Phase distributions.



304L -130 °C

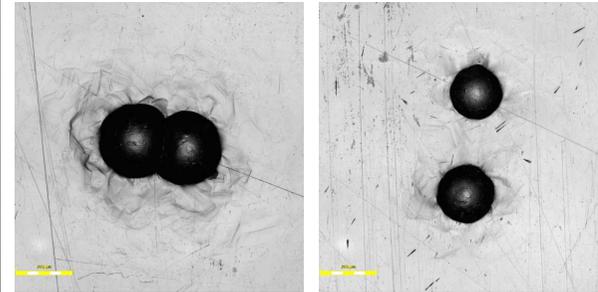
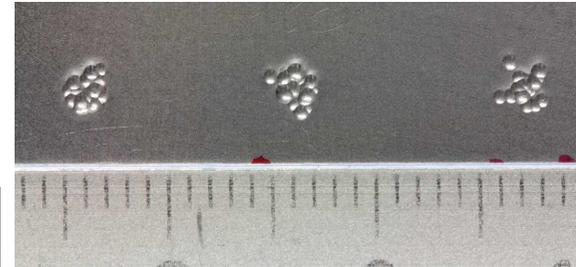
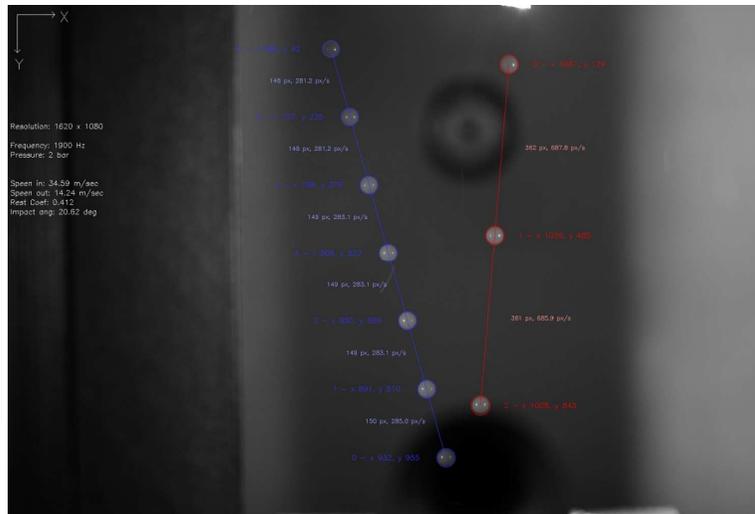
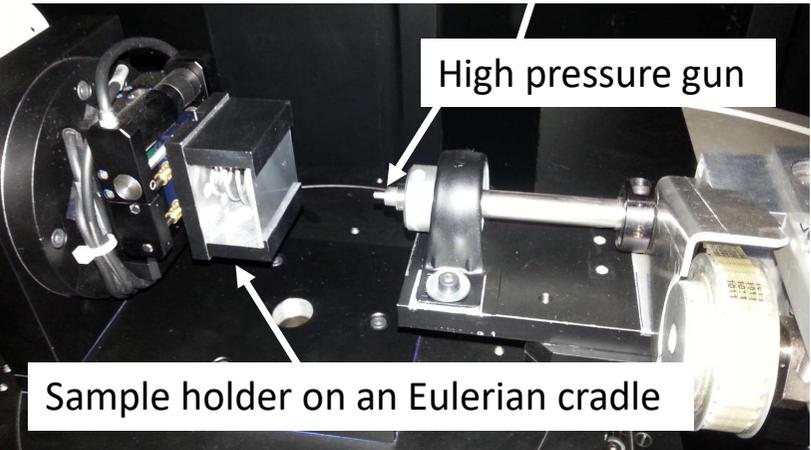
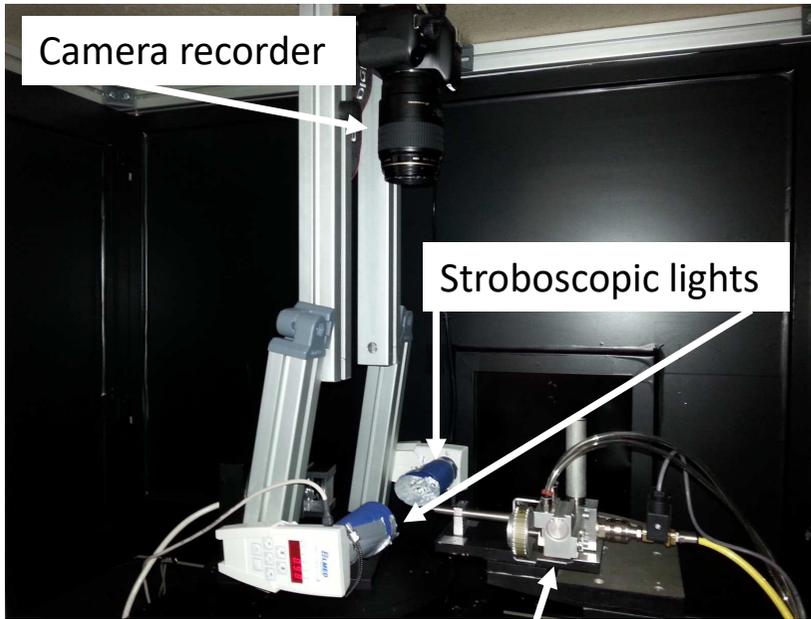


W.M. Ji , R.H. Zhou , P. Vivegananthan , M.S. Wu , H.J. Gao, K. Zhou,
Progress in Materials Science 140 (2023) 101194

The max of martensite is not at the top surface but within the sub-surface.

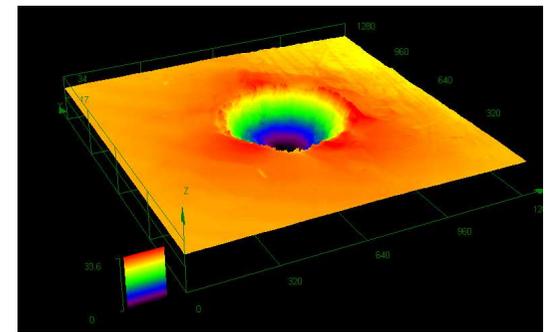
M. Novelli, P. Bocher, T. Grosdidier, "Effect of cryogenic temperatures and processing parameters on gradient-structure of a stainless steel treated by ultrasonic surface mechanical attrition treatment", Mater. Charact. 139 (2018) 197–207

4. Importance of restitution coefficient : single impact analysis

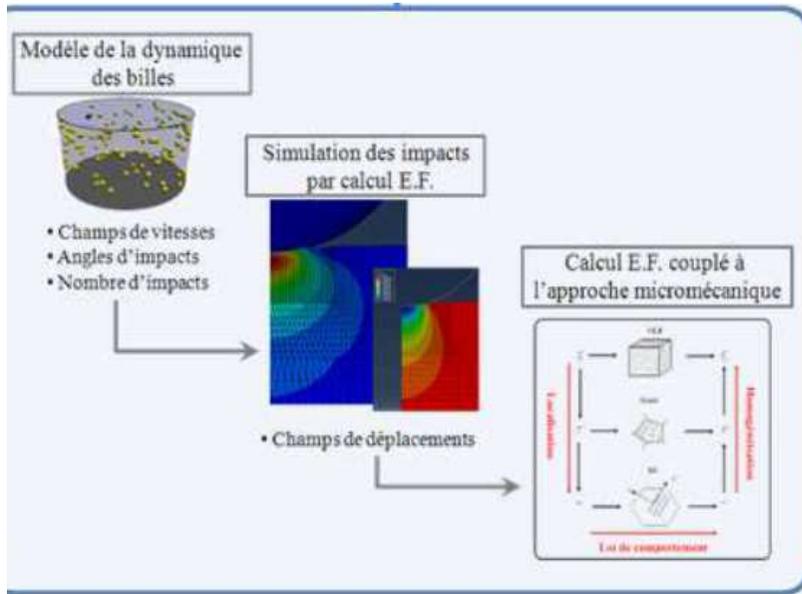


SAMPLES of Different materials and hardnesses

Cr = 1 Elastic contact
 Cr < 1 Energy imparted to the material



Restitution coefficient is a key parameter for modelling

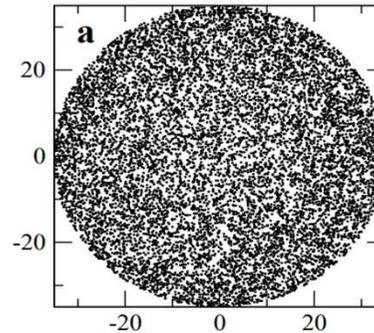


Démarche globale

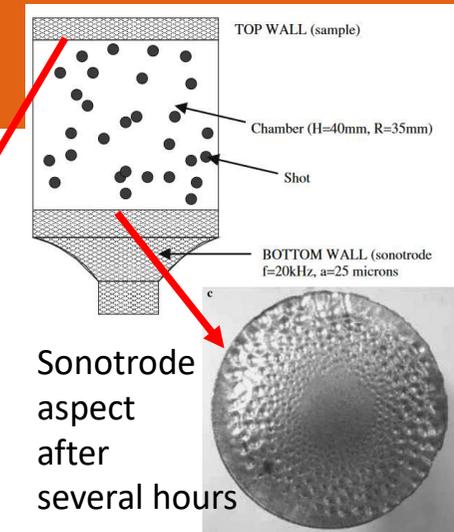
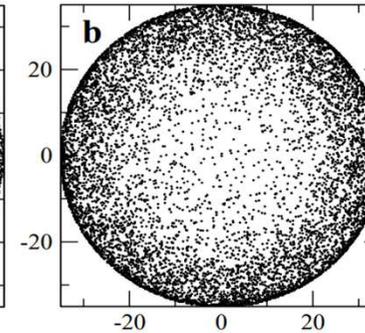
S. Ben Afia, D. Reintant, B. Panicaud, E. Rouhaud ...
 « Modélisation par transition d'échelles de la nanostructuration d'un acier 316L par le procédé SMAT. »

11e colloque national en calcul des structures, CSMA, May 2013, Giens, France.

$C_{wall} = 0.91 / 1 \text{ second}$



$C_{wall} = 0.20 / 1 \text{ second}$

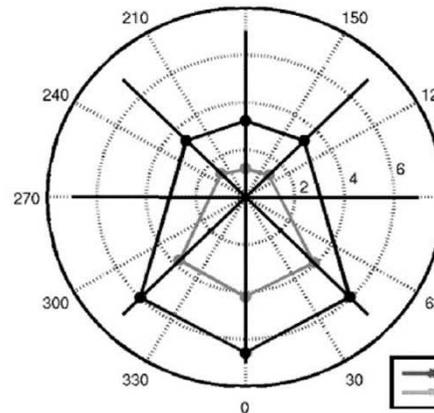


M. Micoulaut et col., *Granular Matter* 9 (2007): 25-33

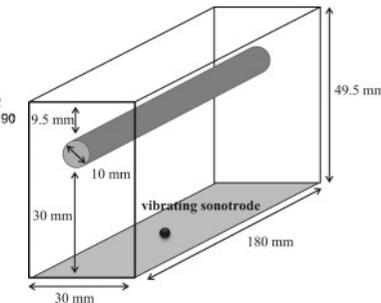
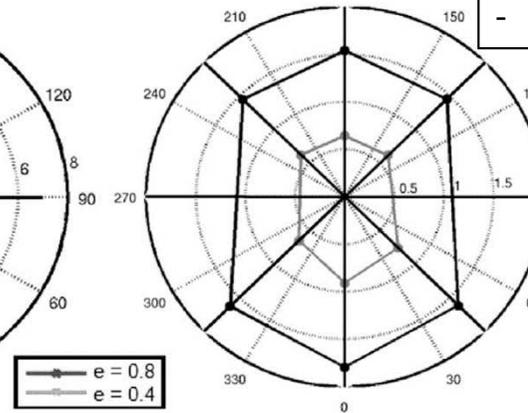
Effect of chamber restitution (POM vs Tool steel) on

- The impact distribution
- The impact velocity

Impact speed



Impact / mm²



C. Nouguier-Lehon et col., *Wear* 302.1-2 (2013): 1058-1063.

Gradient microstructure and mechanical properties

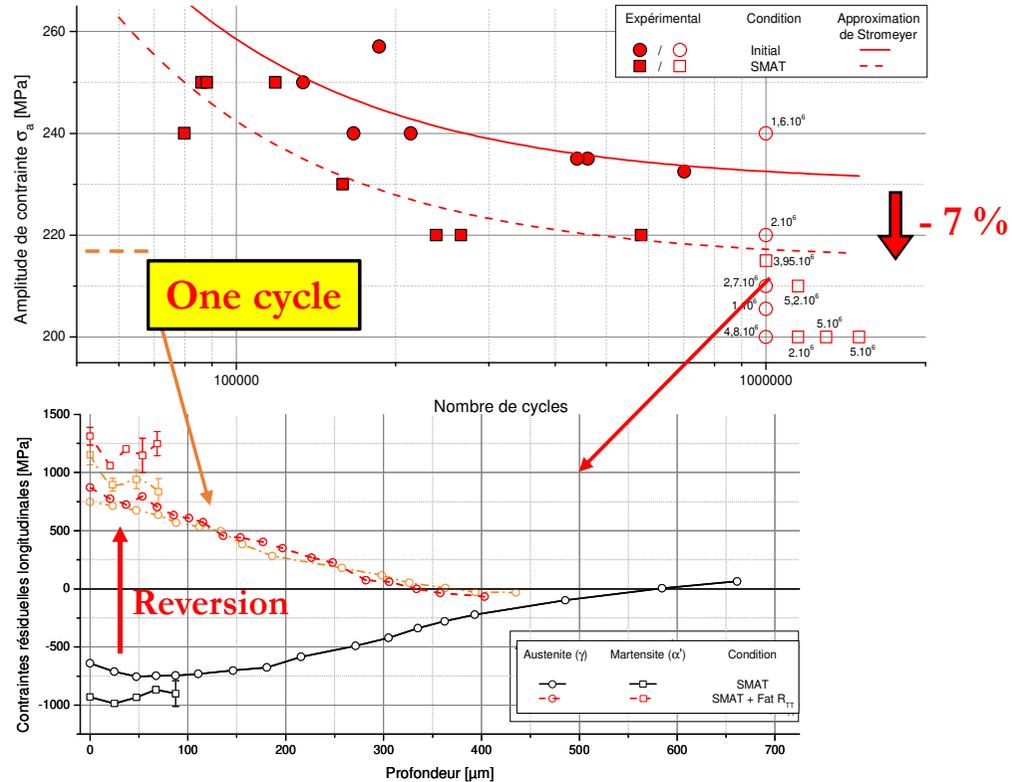
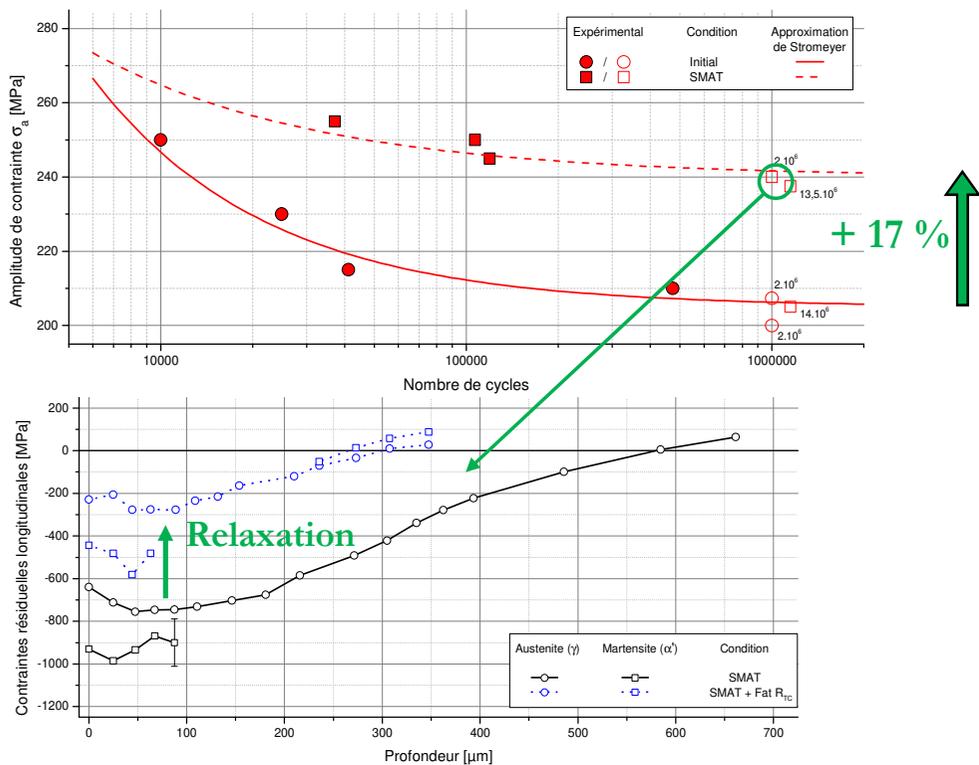
A short instructive focus on Fatigue properties

1. **Effect of loading and stress relaxation / redistribution** (austenitic stainless steel)
2. **Effect of the processing route / notch and surface defects** (two different Al alloys)

SMAT with gradient microstructure Austenitic Stainless Steel Effect of loading ratio / residual stress redistribution

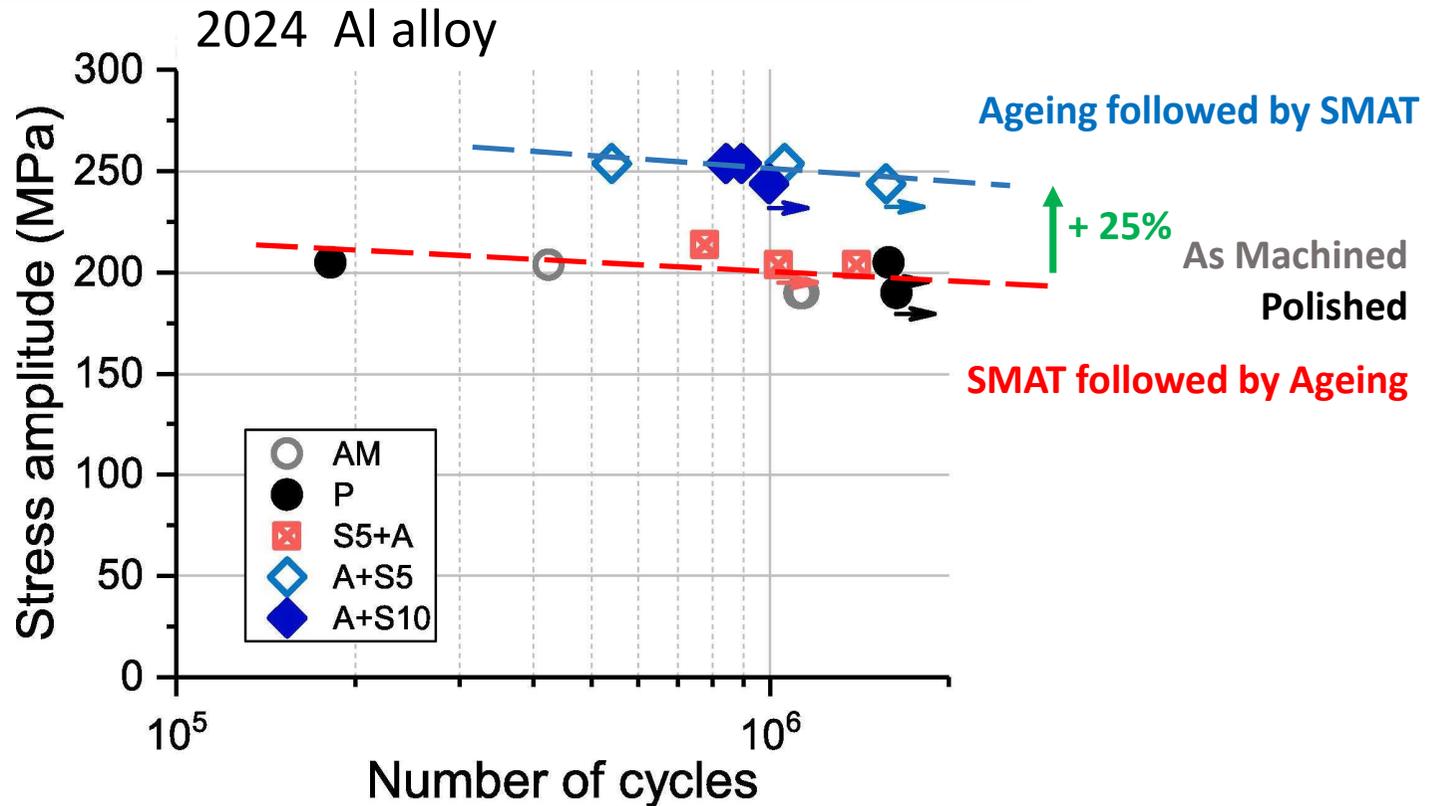
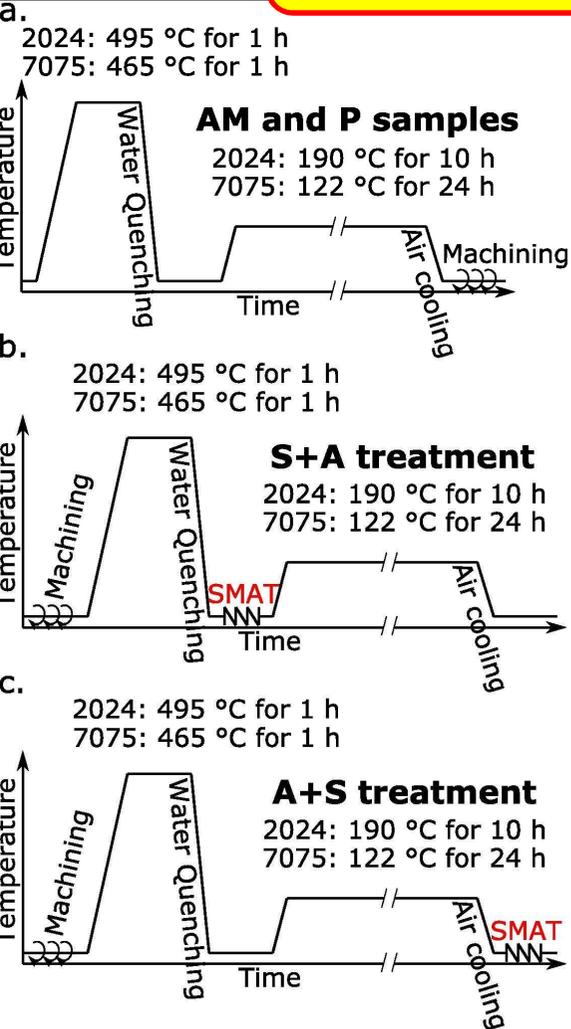
Tension-Compression $R_{TC} = -1$

Tension-Tension $R_{TT} = 0,1$

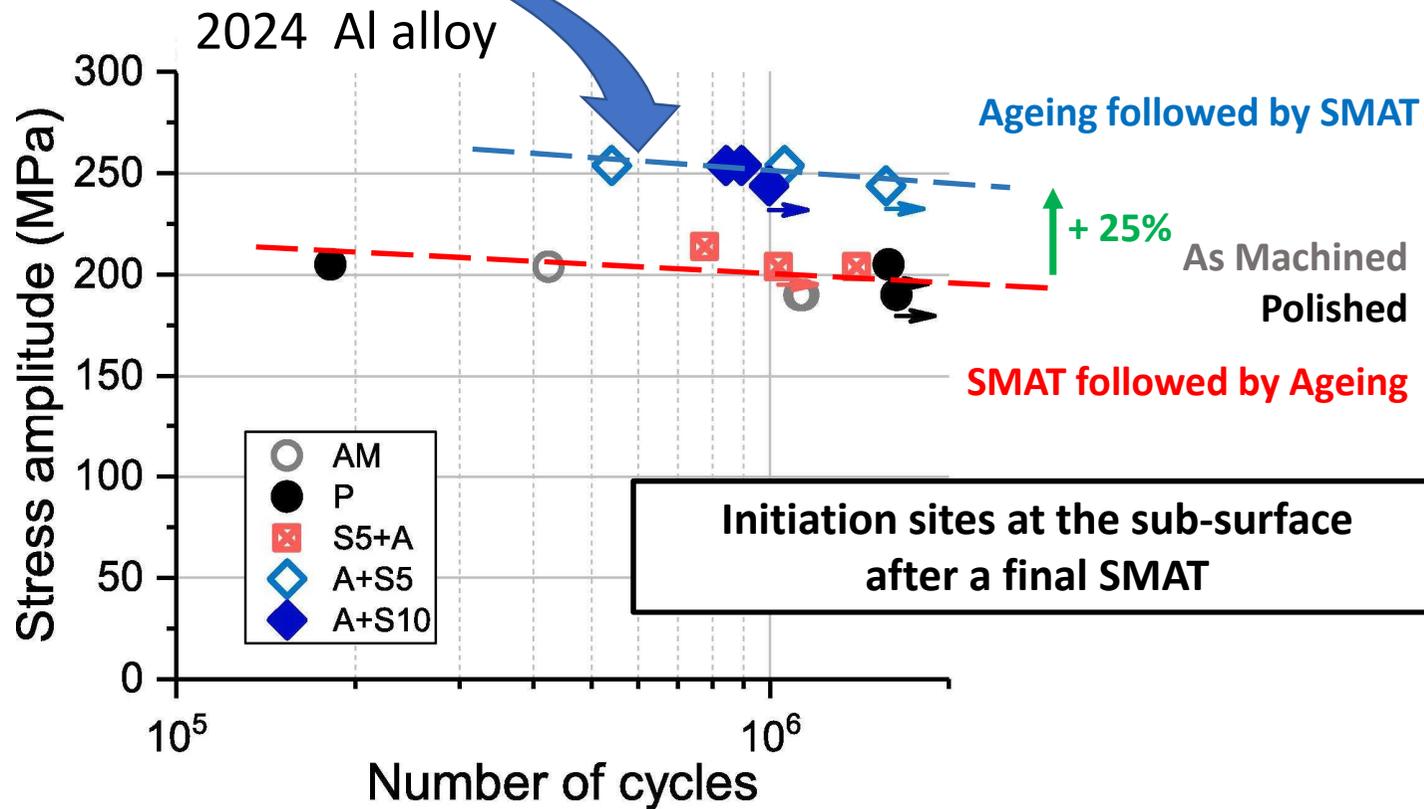
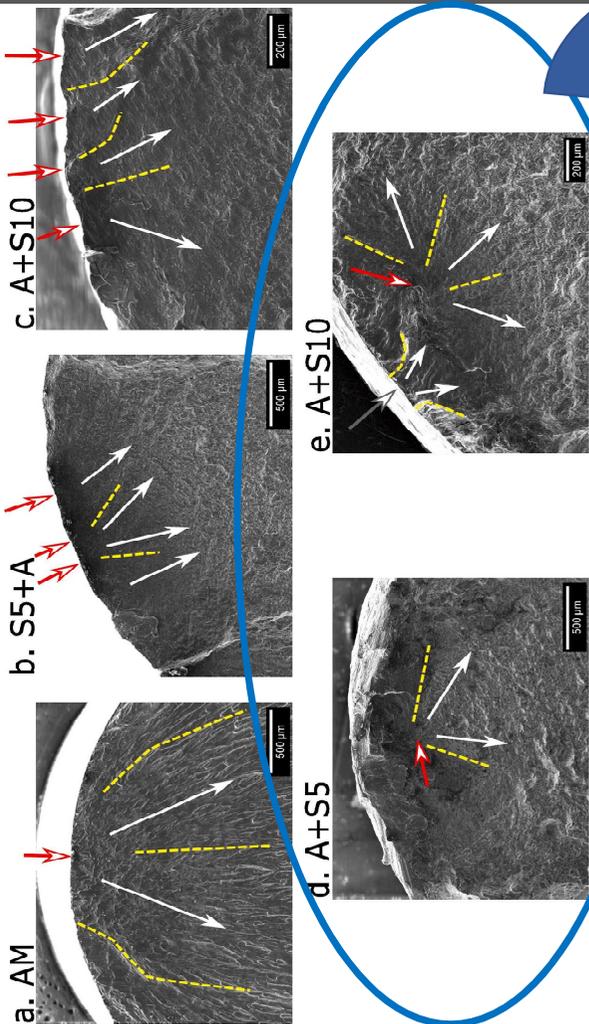


C Dureau, M Arzaghi, R Massion, Y Nadot, T Grosdidier, *On the high cycle fatigue resistance of austenitic stainless steels with surface gradient microstructures: Effect of load ratio and associated residual stress modification*, Materials Science and Engineering: A 840 (2022)142916.

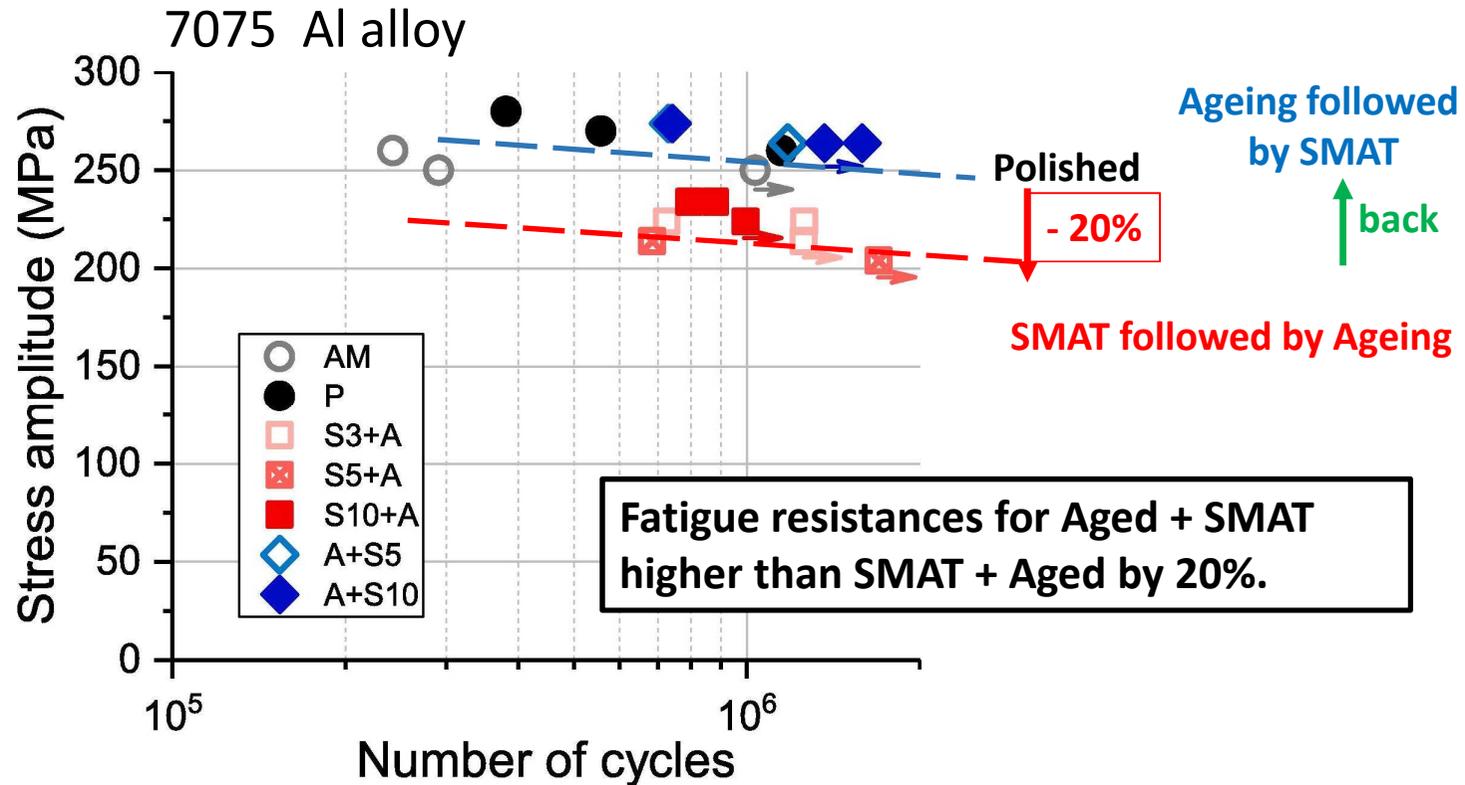
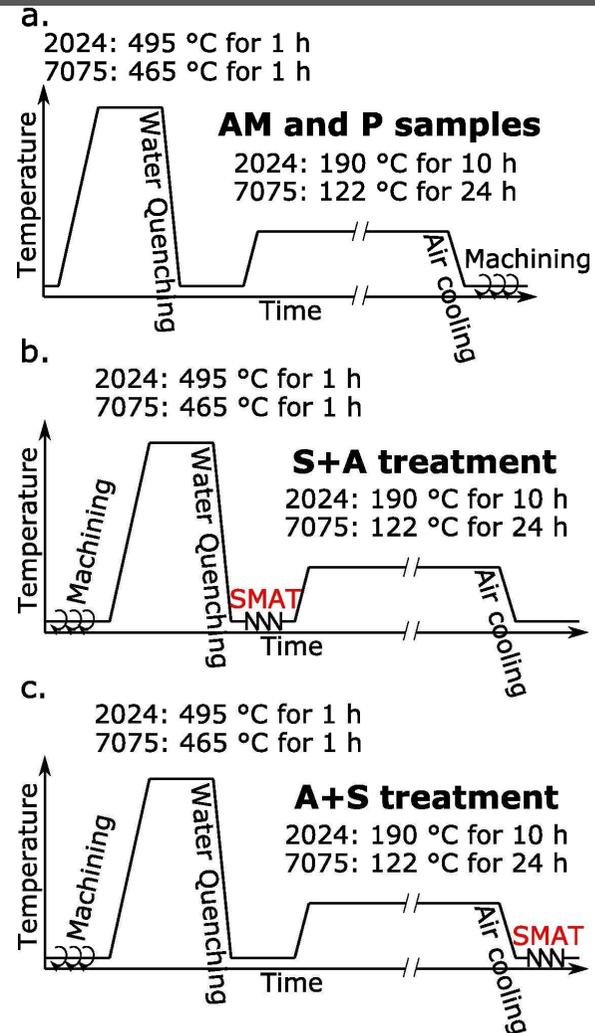
SMAT with gradient microstructure Aluminium alloys Effect of the processing route



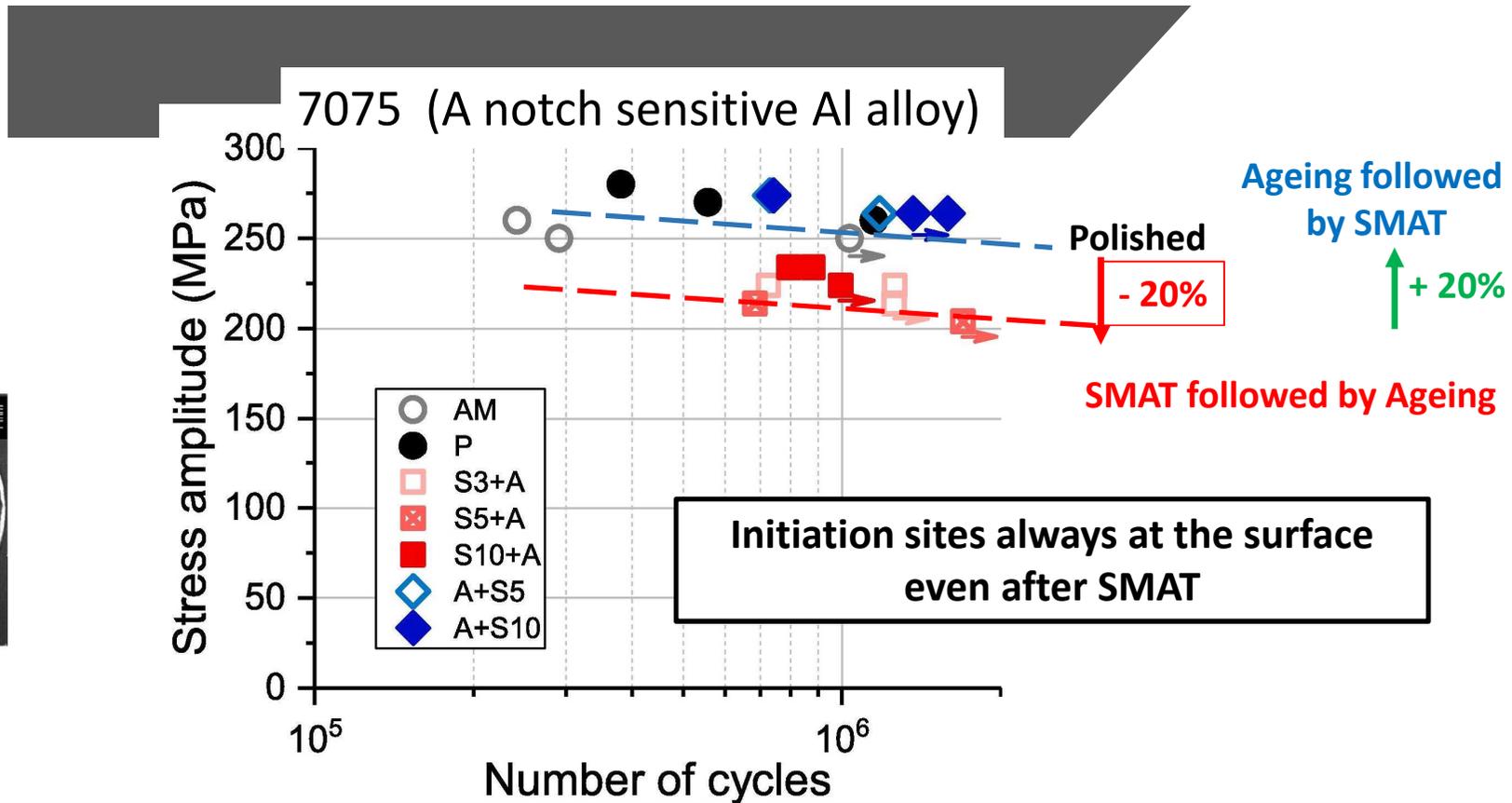
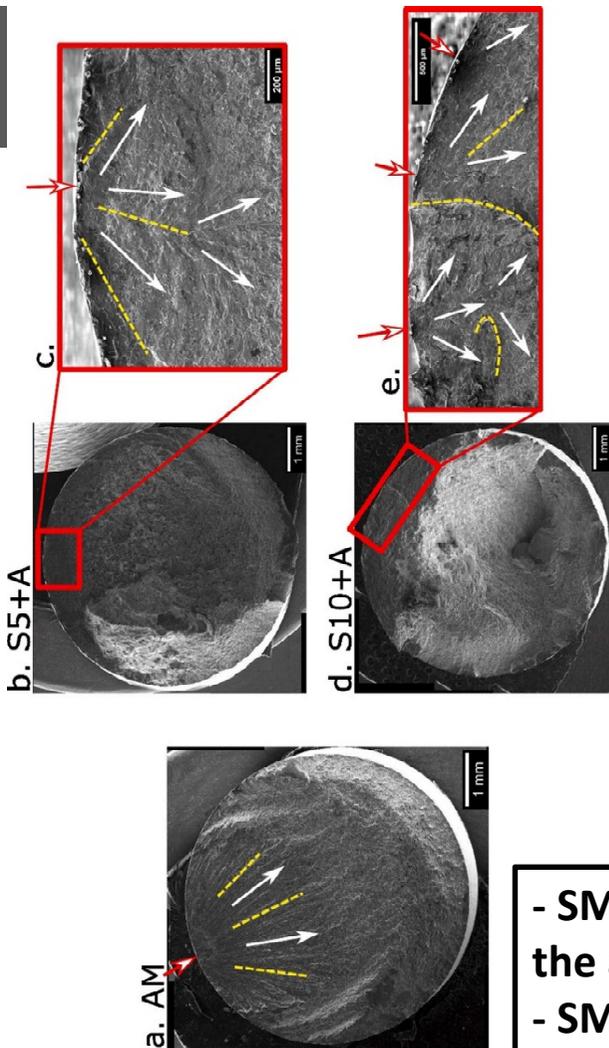
- Fatigue resistances for Aged + SMAT higher than SMAT + Aged by 25%.



- Fatigue resistances for Aged + SMAT higher than SMAT + Aged by 25%.



- Drop in fatigue resistance for SMAT + Aged compared to Machined or Polished
 - Aged + SMAT is barely better than Polished for the 7075.



- SMAT induced surface defects are detrimental for the 7075 fatigue resistance (due to the alloy high notch sensitivity).
- SMAT must be avoided on aluminium alloys with high notch sensitivity.
- Ageing followed by SMAT is always preferable (for both 2024 and 7075)

P Maurel, L Weiss, T Grosdidier, P Bocher, *How does surface integrity of nanostructured surfaces induced by severe plastic deformation influence fatigue behaviors of Al alloys with enhanced precipitation?*, Inter. J. of Fatigue 140 (2020) 105792

Gradient microstructure and enhanced surface reactivity

SSPD to improve several chemically assisted industrial processes

1. Duplex treatments

SSPD : Nitriding of a stainless steel

- Nitriding : W.P. Tong, N.R. Tao, Z.B. Wang, J. Lu and K. Lu: Science 299 (2003) 686 688
- Pack boronizing : T. Balusamy, T.S.N. Sankara Narayanan, K. Ravichandran: Surf. Coat. Technol. 213 (2012) 221 228.
- Aluminizing : X. Si, B. Lu and Z. Wang: J. Mater. Sci. Technol. 25 (2009) 433 436
- Chromizing : S.D. Lu, Z.B. Wang and K. Lu: Mater. Sci. Eng. A 527 (2010) 995 1002.
- Plasma electrolytic oxidation : L. Wen, Y. Wang, Y. Zhou, L. Guo and J.H. Ouyang: Corros. Sci. 53(2011) 473 480.

2. Applications for the Hydrogen sector

2.A. Hydrogen embrittlement

- High Entropy Alloys :

Tensile behaviour of a **CrMnFeCoNi** alloy after H-charging

2.B Hydrogen storage

Ti₁₀V₇₅Cr₁₅ Alloy

Reversible phase transformation

Metal ↔ Hydride

Activation to by-pass the surface oxide layer

3. Applications to the Biomedical sector

1. Surface reactivity (316L Stainless steel): Interest of the SMAT + Nitriding duplex treatment

❖ Improved tribological properties

- Hardness improvement (factor 5)
- Wear volume decreased by a factor 2

❖ Discovered by two teams in the mid 1980

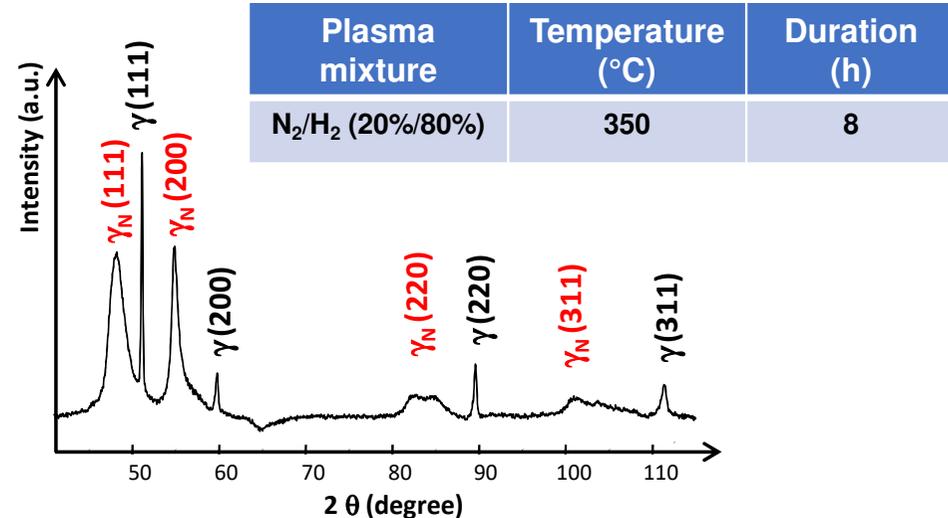
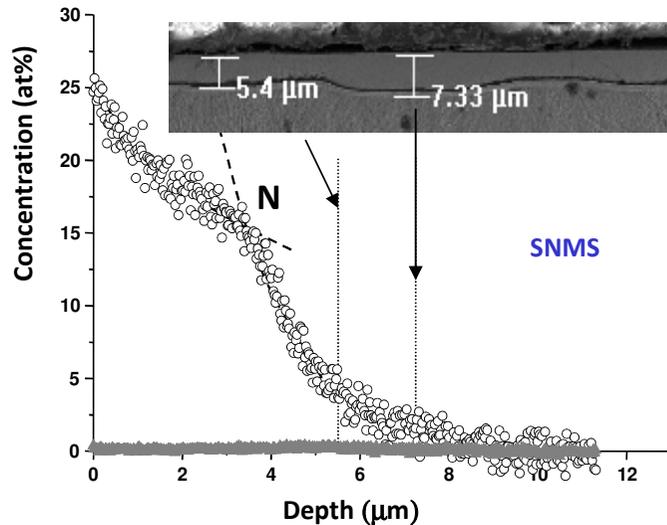
- Z.L. Zhang, T. Bell, Surf. Eng., 1 (1985) 131.
- K. Ichii, K. Fujimara, T. Takase, Technol. Rep. Kansai Univ. 27 (1986) 135.

❖ Good corrosion resistance if nitriding is done at “low temperature” (below 400°C)

(single phase - no precipitation of CrN)

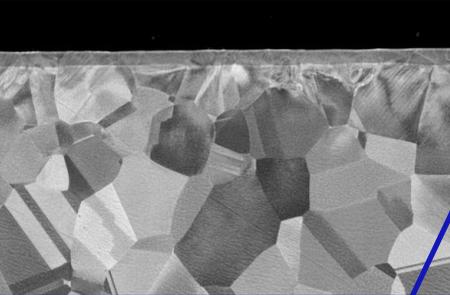
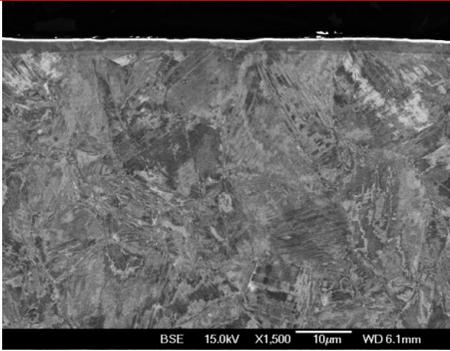
Nitriding : Expanded austenite by nitrogen

Low Temperature Plasma Nitriding (LTPN) of an Austenitic 316L Stainless Steel
formation of a **metastable supersaturated solid solution**



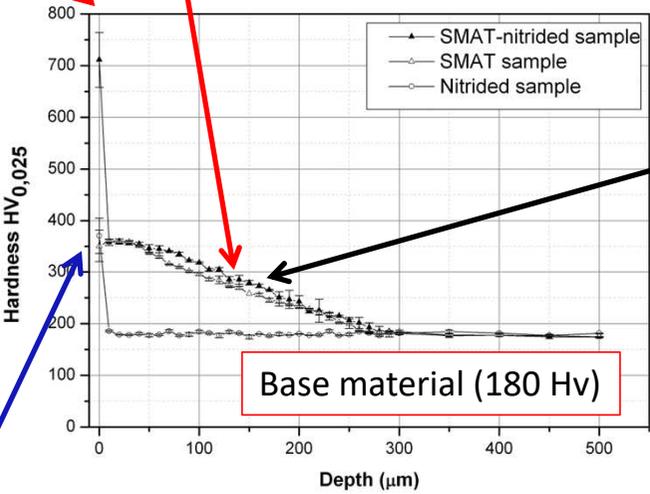
1. Surface reactivity (316L Stainless steel): Interest of the SMAT + Nitriding duplex treatment

SMAT+nitriding : 720Hv
(Strain hardening + Solid solution hardening)



Nitriding (only): 380 Hv

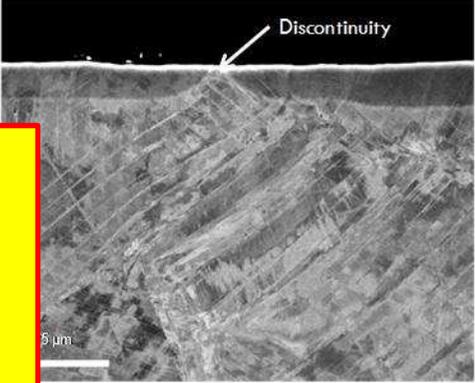
**SMAT+nitriding :
sub-surface still hard**



After SMAT (only):
Hard sub-surface

Strain gradients
⇒ microstructure gradients
⇒ property gradients.

Base material (180 Hv)

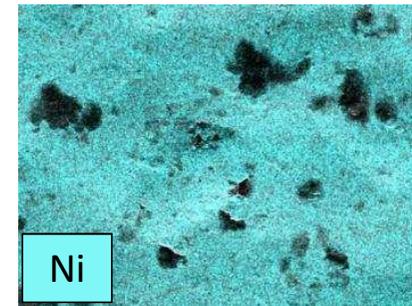
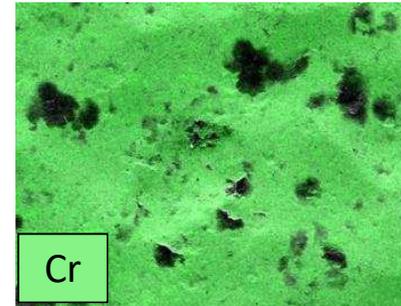
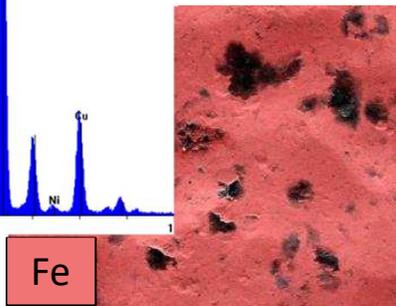
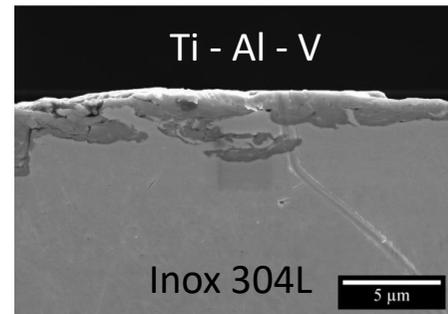
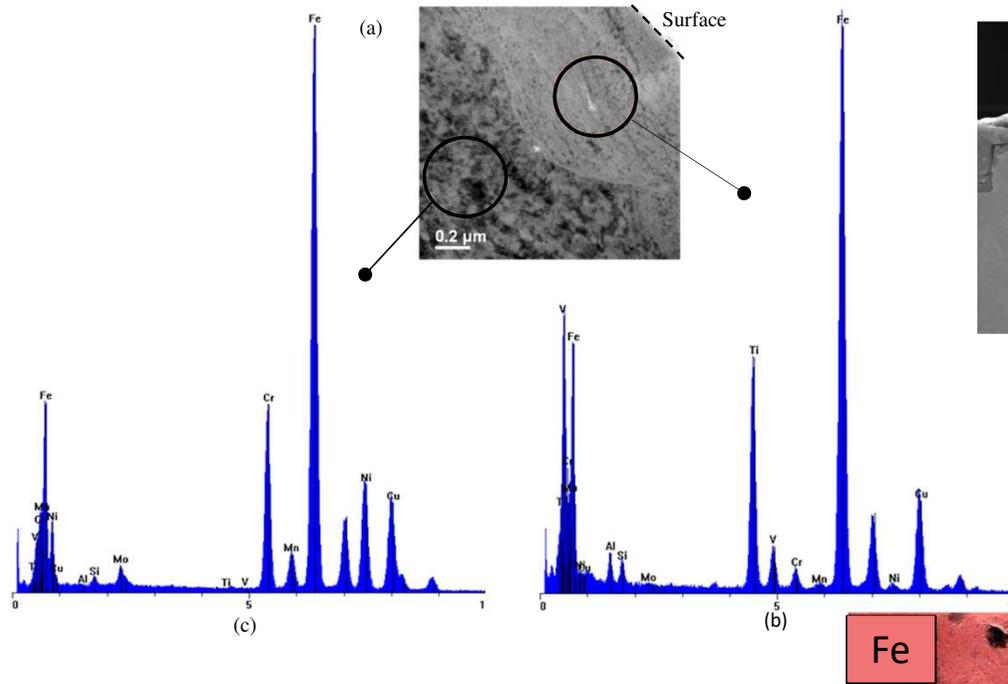


- ☺ Surface and sub-surface hardening
 - Top surface (X 1.8)
 - Sub-surface remains hard even after 350°C for 8 hrs
- ☹ Discontinuity of the nitrided layer (Contamination)
 - => Galvanic corrosion

Nature of the contamination under SMAT / USP

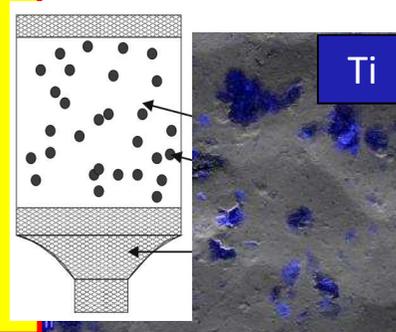
TEM analyses of the contaminated domains and sub-surface

Sample SMAT treated for 20 min with steel balls

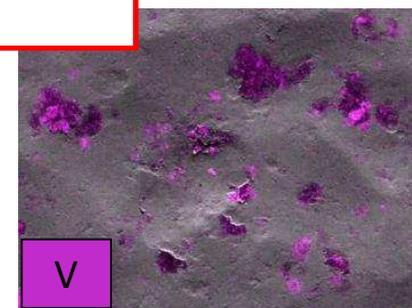
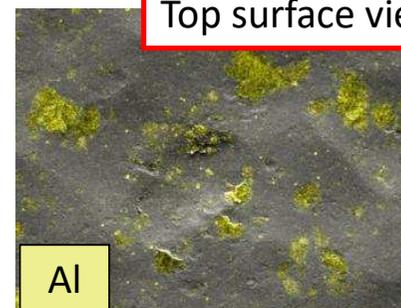


Some nanostructures at the surface are :

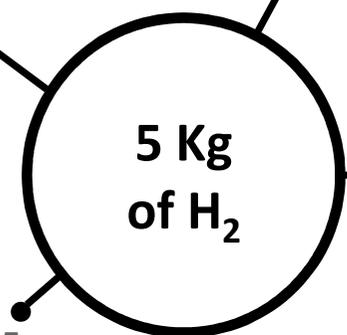
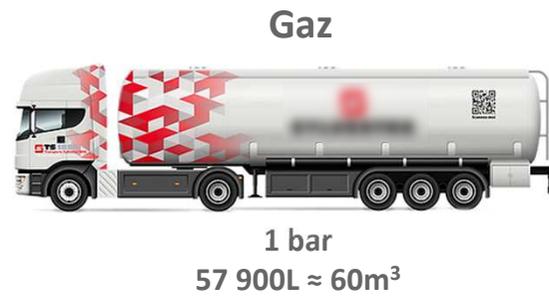
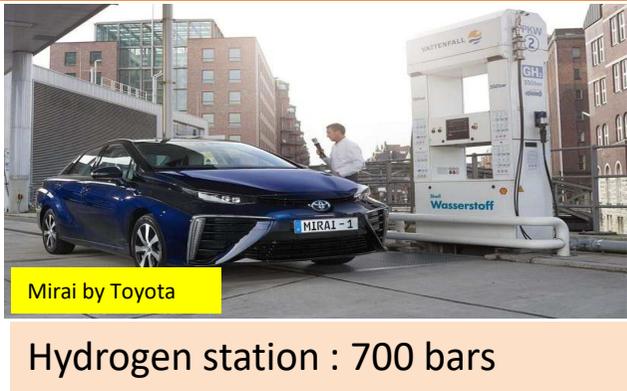
- Contaminations in Ti, Al and V
... coming from the sonotrode
- Contaminations in Fe, C
... coming from the Steel balls and chamber
or
- Contaminations in Zr, O, Y from the Zirshot balls



Top surface view



2. H-storage : the context



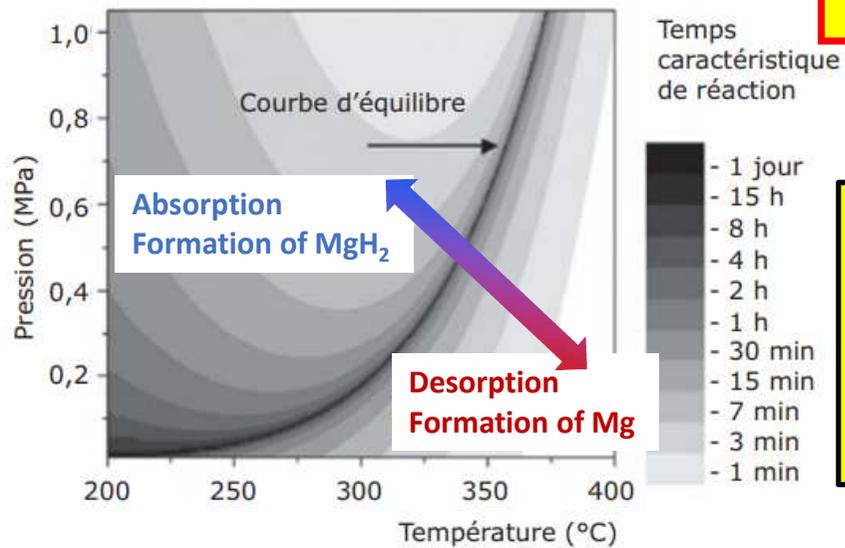
100kg MgH₂
contains 7,6 kg H₂
and occupies 60L
(2x more compact than at 700bars)



Reversible phase transformation
Metal ↔ Hydride
Activation to by-pass the surface oxide layer

Stored as a gas : 2 tanks : 5 Kg H₂ under 700 bars
- Security issues // volume (160 litres) ! //Cost !!!

Metal hydrides are compacts, stables ... and safe !



Solid state H storage is required

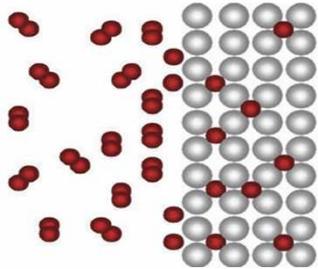


Could we fill-up with a phase transformation ?

Reversible phase transformation

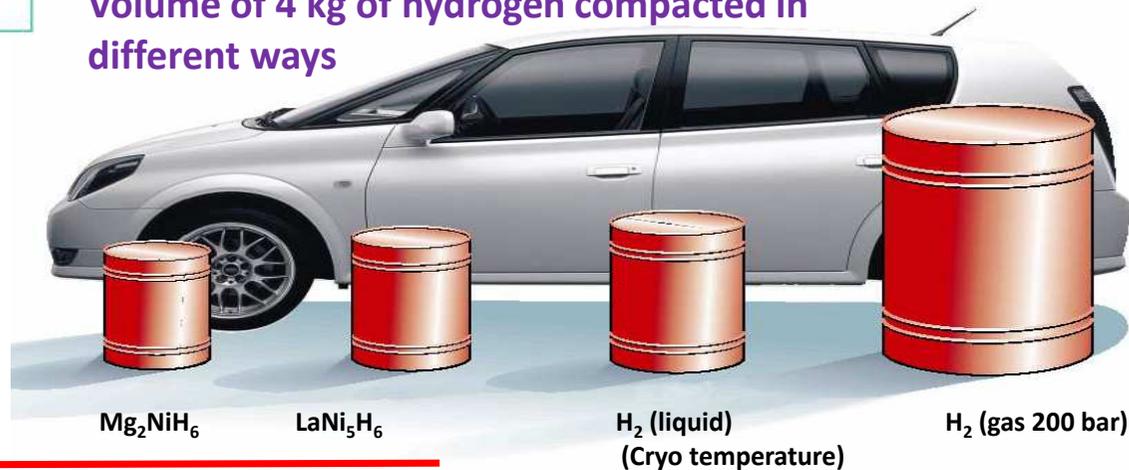
Metal \leftrightarrow Hydride

Activation to by-pass the surface oxide layer



**Storage of H atoms
in Solids :
Metallic Hydrides**

Volume of 4 kg of hydrogen compacted in
different ways



***Adsorption problem : high temperature + high pressure to force H inside
activation is required to enhance kinetics and lower T and P***

Severe plastic deformation techniques for improving H-storage activation and kinetics

Use of chemical catalysts :

- Alloying with transition metals (Ni, Ti, Fe ... For Mg)
- Introduction of fine oxides

- Powder metallurgy (High Energy Ball Milling)

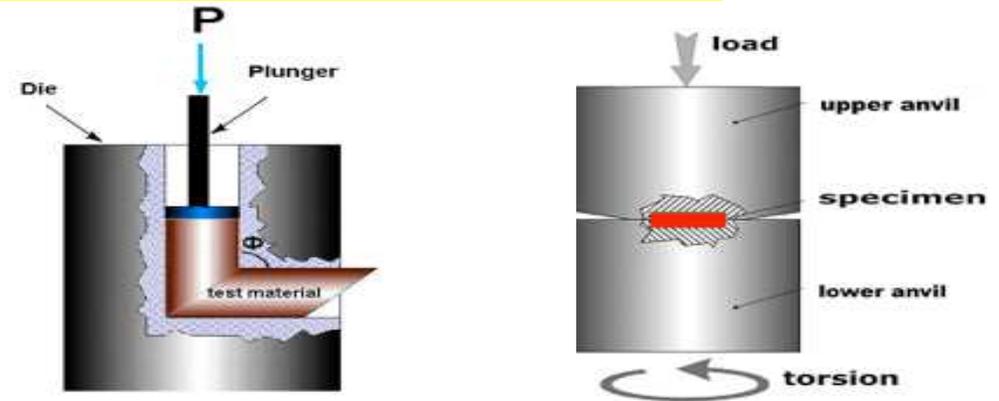


Huot J, Liang G, Boily S, Van Neste A, Schulz R,
J Alloys Comp 288 (1999) 217

Drawbacks : - Contamination / Safety for Mg or reactive metals

Refine the microstructure : UFG (amount of grain boundaries)
Introduce structural defects (dislocations, vacancies ...)

- Severe plastic deformation of bulk samples (ECAE, HPT, ...)



Skripnyuk VM, Rabkin E, Estrin Y, Lapovok R,
Acta Mater 52 (2004) 405-414

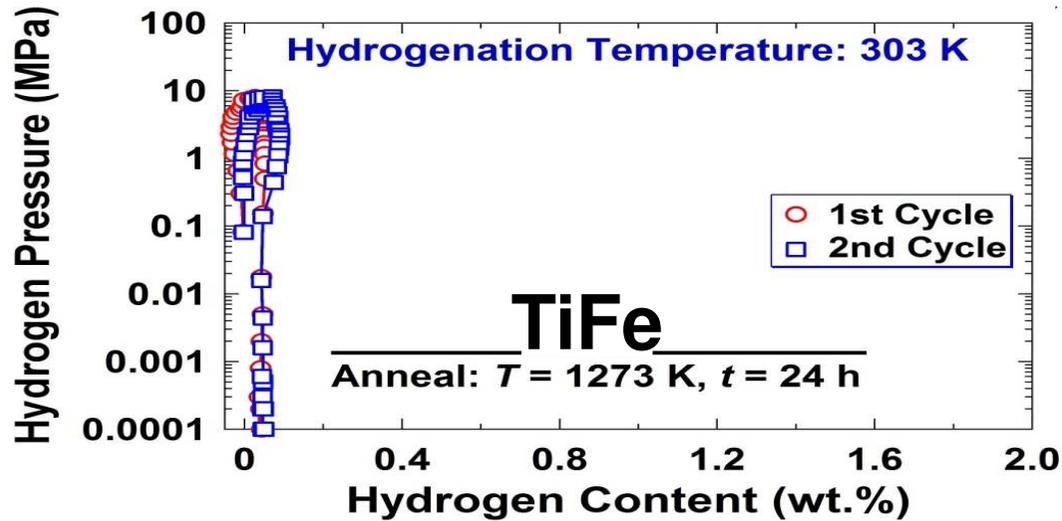
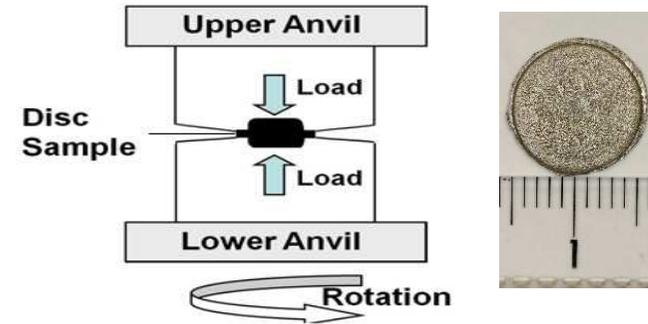
Drawbacks : - Small samples / quantities

Difficulty to scale-up for industry

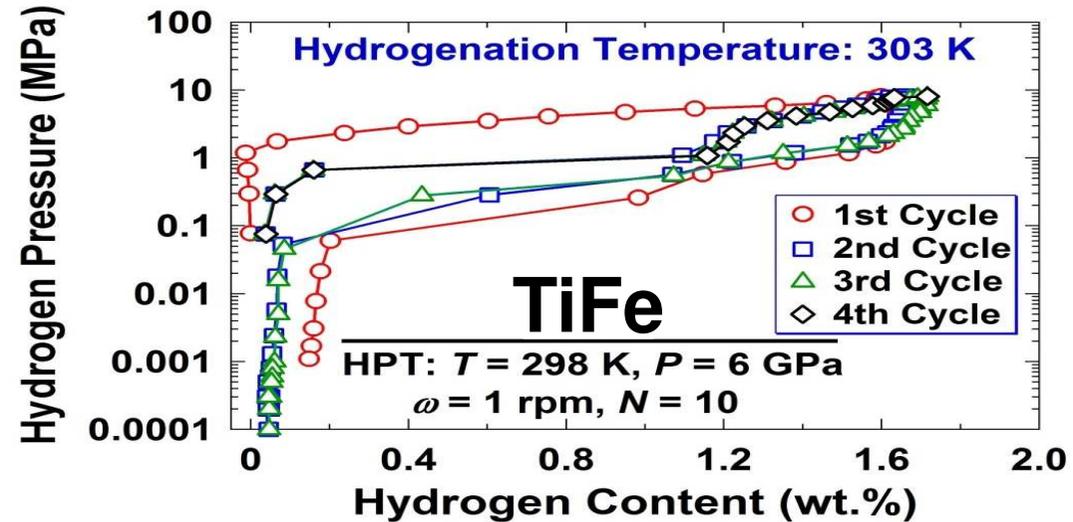
Example of severe plastic deformation techniques for improving H-storage activation

Activation by Severe Plastic Deformation

Here : High-Pressure Torsion (HPT)



No absorption in TiFe sample due to difficult activation.



Full activation after HPT even after 400 days air storage.

Edalati, Matsuda, Iwaoka, Toth, Akiba, Horita, Int. J. Hydrogen Energy 38 (2013) 4622.

BCC Ti-V-Cr alloys for Hydrogen Storage

- Current activation :
- Heat treatment at high temperatures ($T > 400$ °C)
 - vacuum and/or high hydrogen pressures (several MPa).

Akiba, Iba, Intermetallics 6 (1998) 461-470.

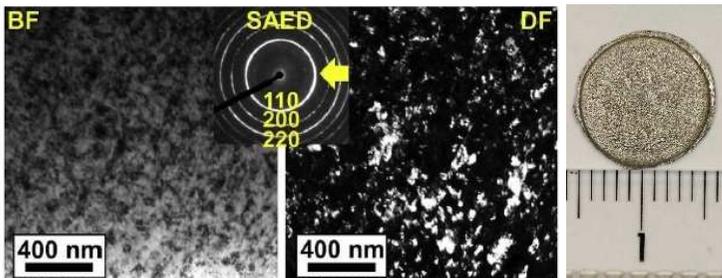
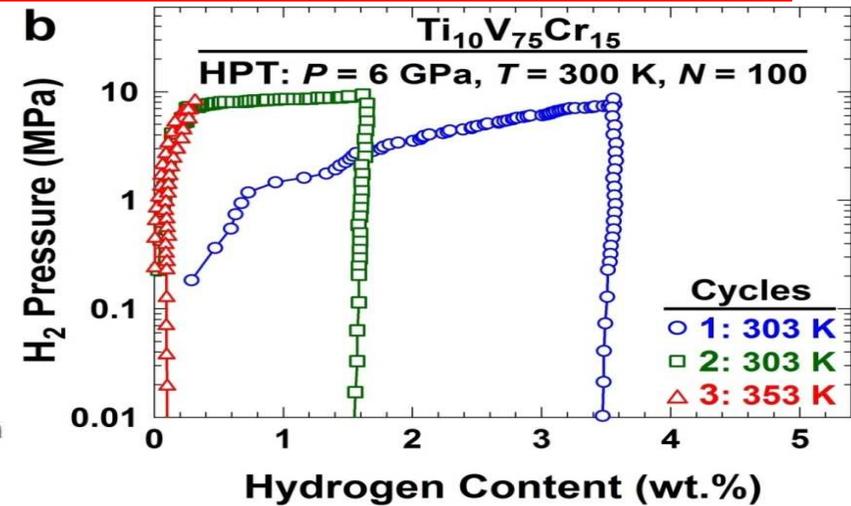
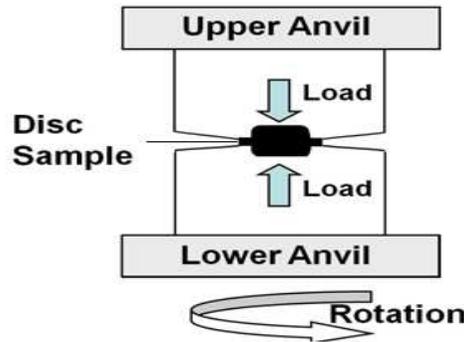
Makes Storage System Expensive

(system should be designed based on activation condition)

TOYOTA



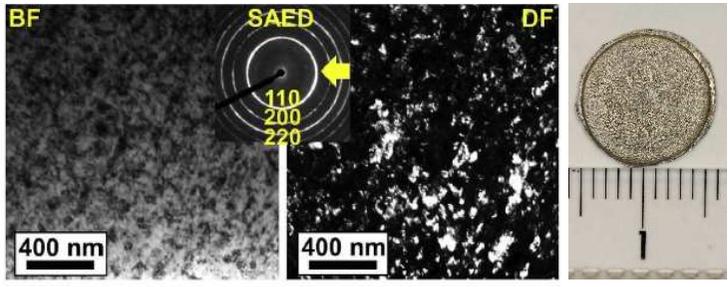
FCHV-3 March 2001



Bulk
(HPT)

Drawback for Ti-V-Cr alloys
Uniform Nanstructure by HPT
Active at 303 K - No Reversibility

2.B Surface reactivity : Application of SSPD for H-storage

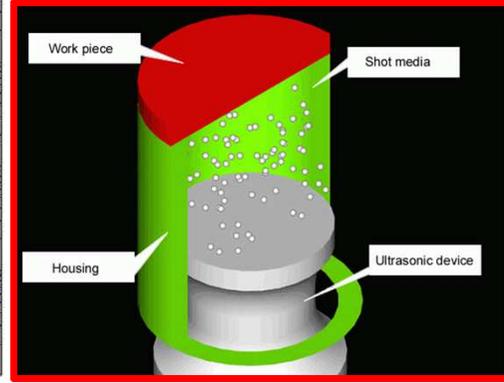
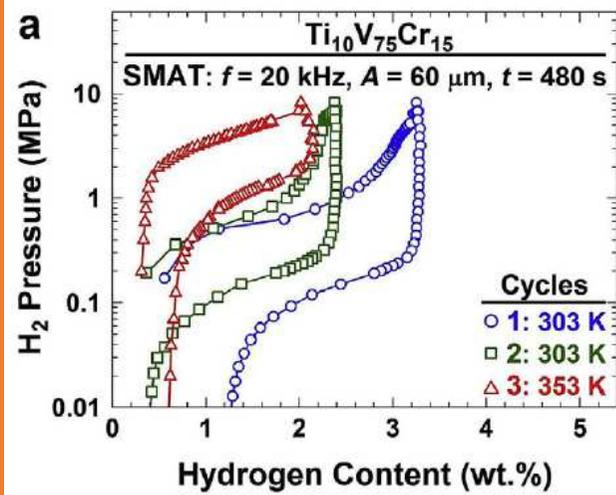
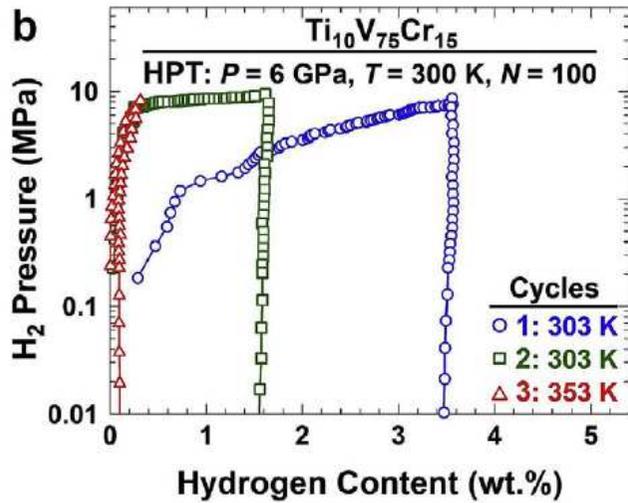
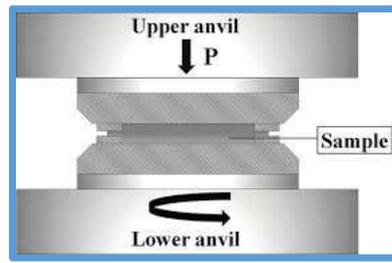
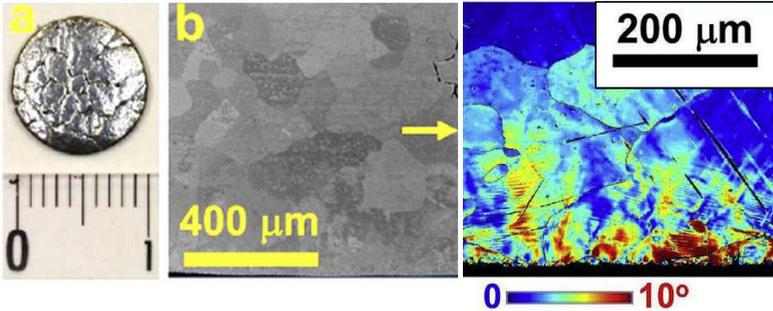


Ti₁₀V₇₅Cr₁₅ Alloy

Bulk
(HPT)

vs

Surface
(SMAT)



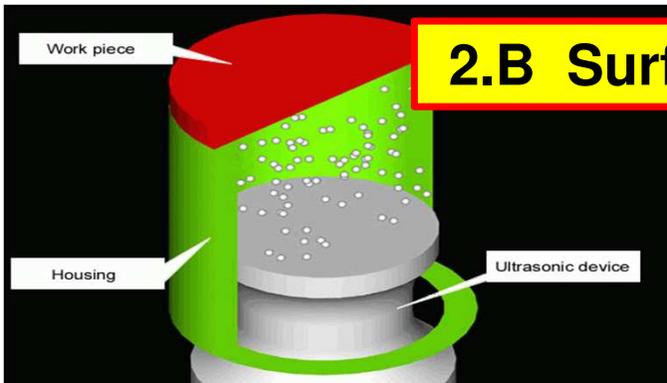
Uniform Nanostructure by HPT
Active at 303 K - No Reversibility

Gradient Structure by SMAT
Active at 303 K + **Reversibility**

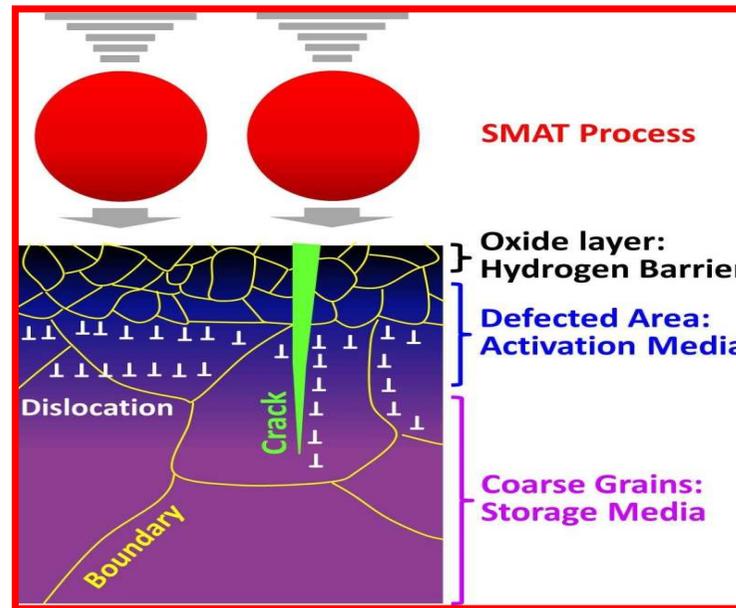
- at least 1 month storage in air after SMAT

- 2 hours evacuation at 303 K between cycles

2.B Surface reactivity : Application of SSPD for H-storage



Another application of SSPD treatment due to the formation of a gradient structure.

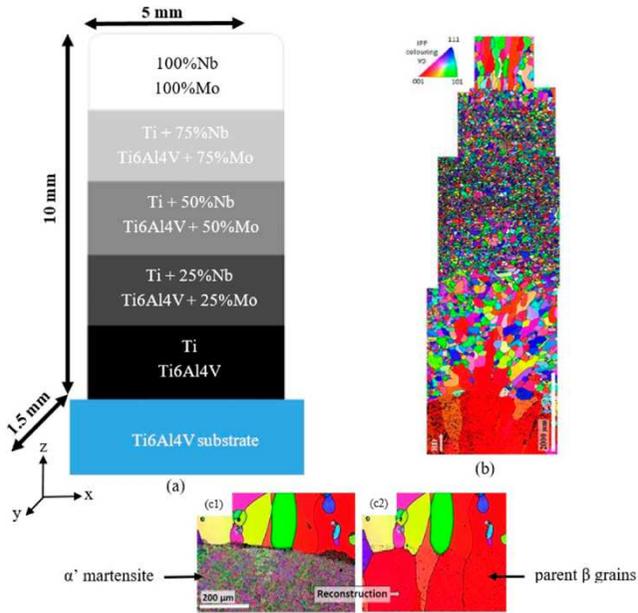


K. Edalati, M. Novelli, S. Itano, H-W. Li, E. Akiba, Z. Horita, T. Grosdidier, "Effect of gradient-structure versus uniform nanostructure on hydrogen storage of Ti-V-Cr alloys: Investigation using ultrasonic SMAT and HPT processes", J. Alloys Compd. 737 (2018) 337-346

M. Novelli, K. Edalati, S. Itano, H-W. Li, E. Akiba, Z. Horita, T. Grosdidier, "Microstructural Details of Hydrogen Diffusion and Storage in Ti-V-Cr Alloys Activated Through Surface and Bulk Severe Plastic Deformation", Int. J. of Hydrogen Energy, 45 (2019) 5326-5336

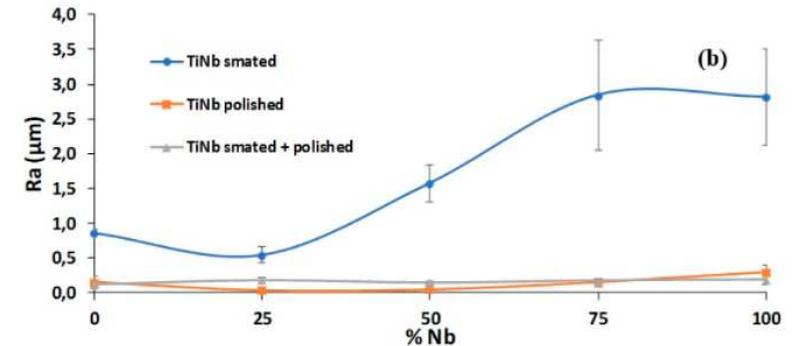
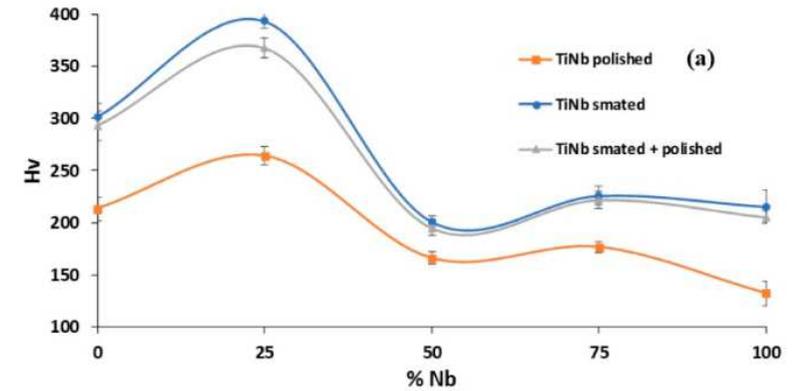
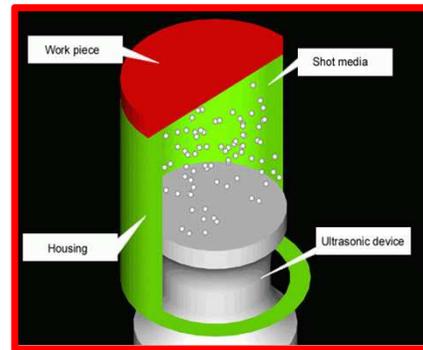
3. Surface reactivity : Interest of SSPD for bio-medical applications

Effect of roughness, chemistry and microstructure modification on biocompatibility?

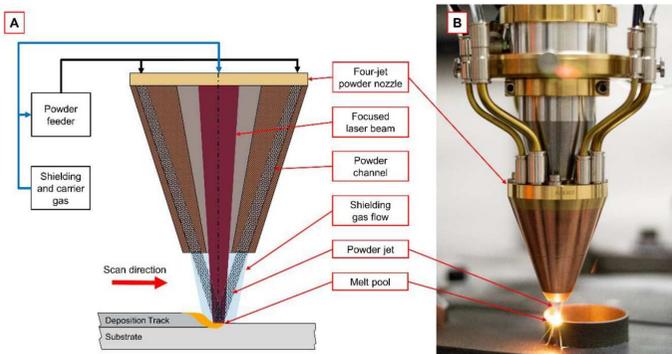


Different surface conditions : **Polished** / SMAT + polished / **SMAT**

Different modifications of surface hardness, microstructure and roughness.



Weiss, Laurent, et al., Metals 9.12 (2019): 1344.



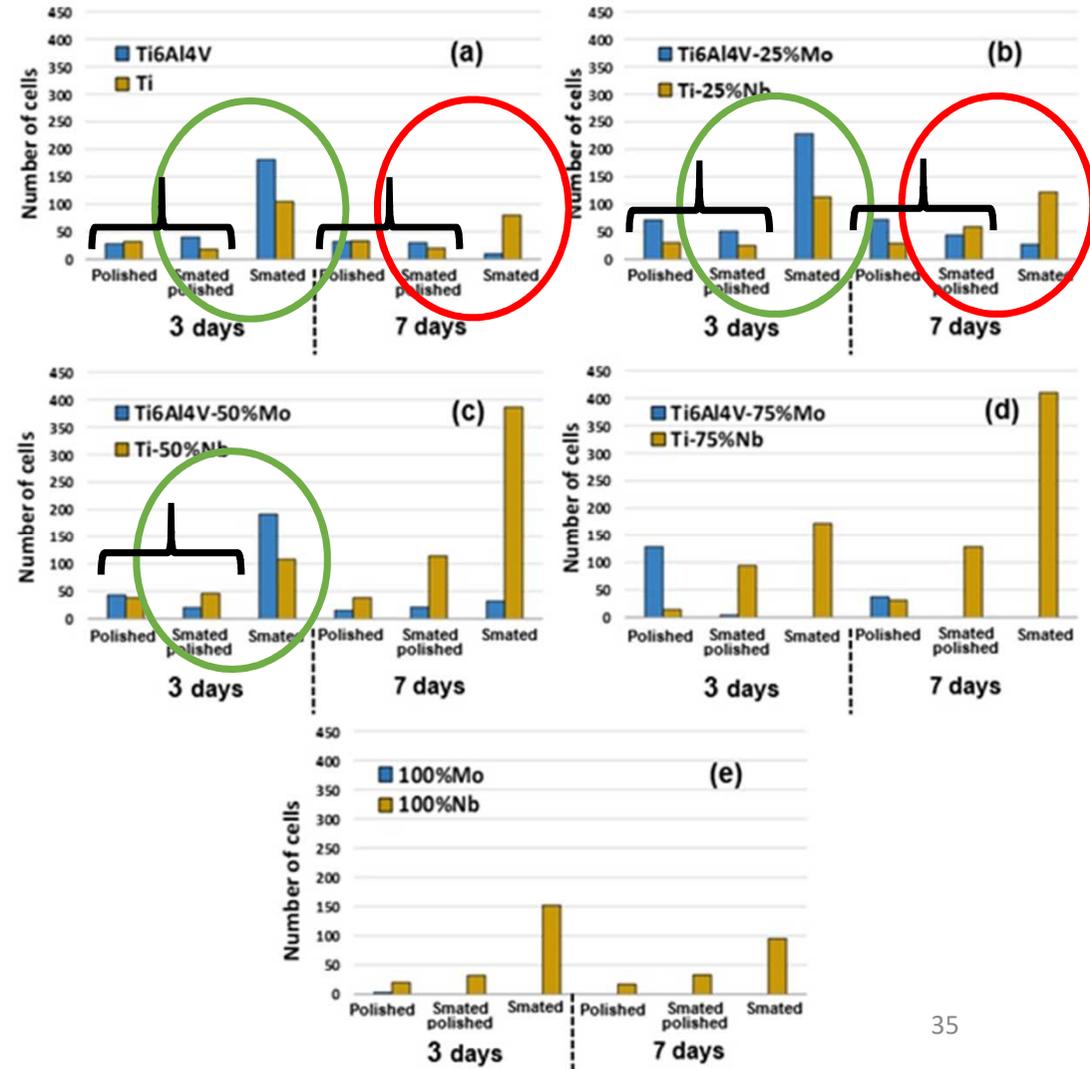
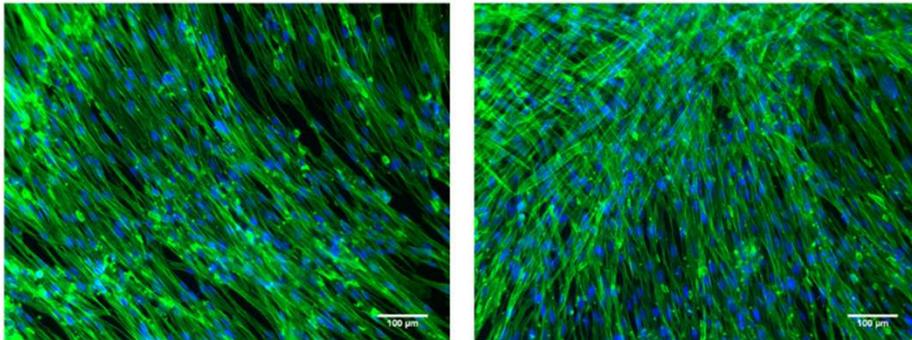
- The use of FGMs reduces the number of samples needed in biocompatibility studies by ensuring at the same time that all tests are done under the same conditions.

Biocompatibility

Biocompatibility :

cell adhesion followed by **cell proliferation**
(human mesenchymal stem cells culture)

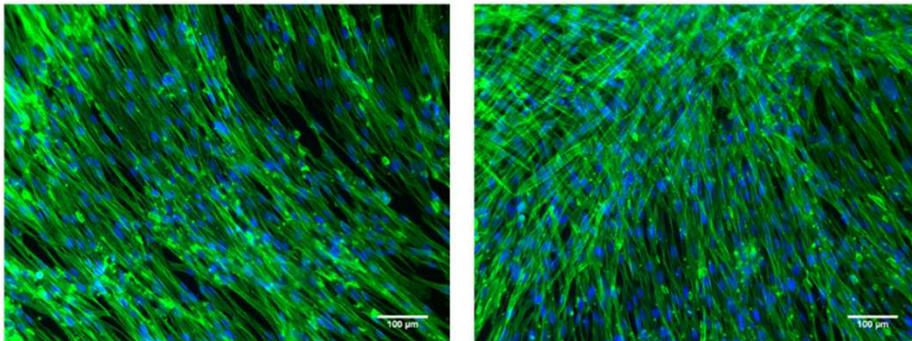
- Higher roughness (by SMAT)
 - improves the cellular adhesion.
 - did not modify the proliferation capability.
- (Limited effect of structural defects and grain size)



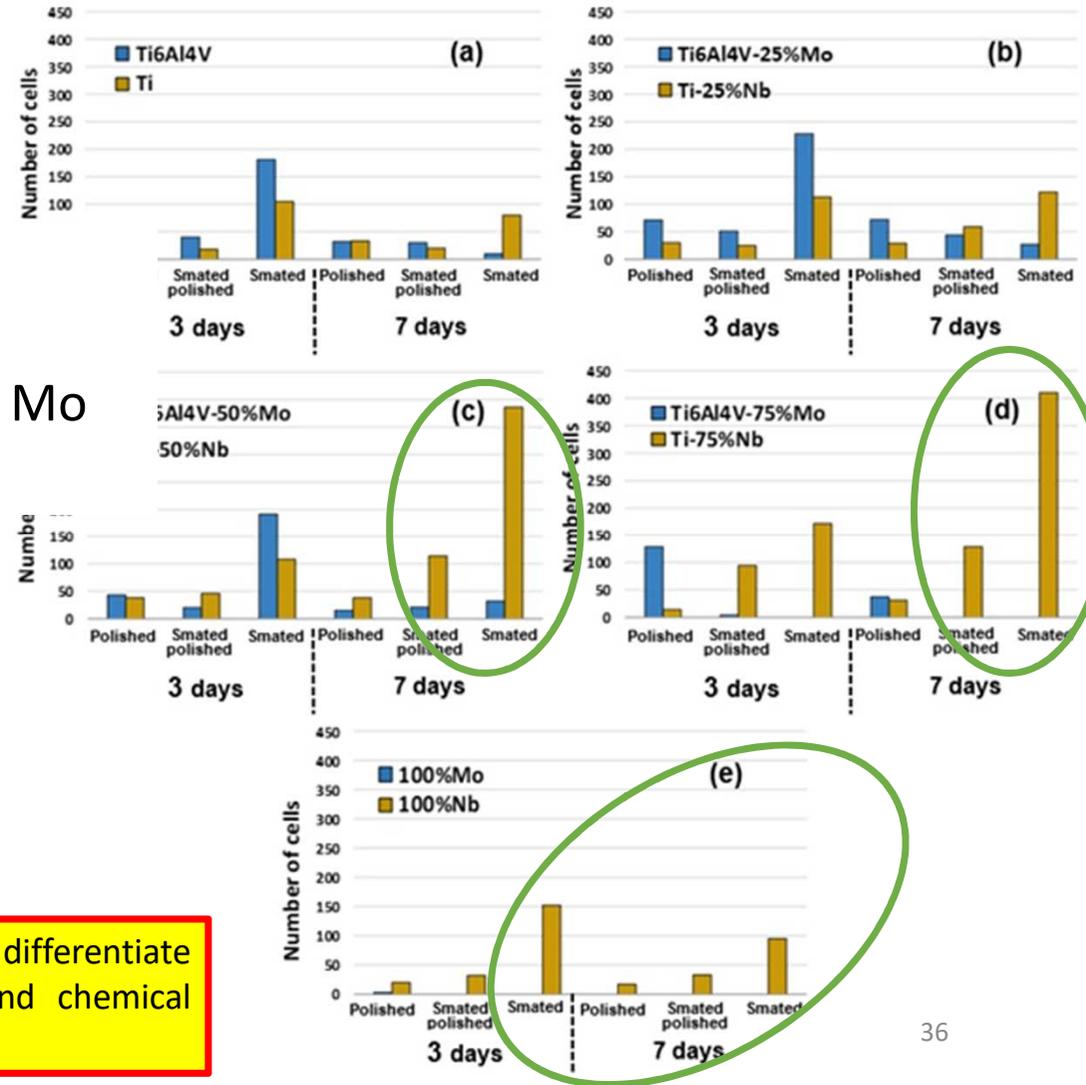
Biocompatibility

Biocompatibility :
cell adhesion followed by cell proliferation

- Chemistry :
 - major factor for **long-term cell proliferation**.
 - Nb has better **long-term biocompatibility** than Mo (pure or when alloyed with titanium).



Weiss, Laurent, et al. "On the use of functionally graded materials to differentiate the effects of surface severe plastic deformation, roughness and chemical composition on cell proliferation." *Metals* 9.12 (2019): 1344.





thierry.grosdidier@univ-lorraine.fr

Merci pour votre attention

**A Mohammadi, M Novelli, M Arita, JW Bae, HS Kim, T Grosdidier, K. Edalati
Gradient-structured high-entropy alloy with improved combination of strength and
hydrogen embrittlement resistance
Corrosion Science 200, 110253, 2022**

**K Edalati, E Akiba, WJ Botta, Y Estrin, R Floriano, D Fruchart, T Grosdidier, Z Horita, J Huot,
H-W Li, H-J Lin, Á Révész, MJ Zehetbauer.
Impact of severe plastic deformation on kinetics and thermodynamics of hydrogen storage
in magnesium and its alloys
Journal of Materials Science & Technology, Vol. 146, pp. 221-239, 2023**

**T Grosdidier, M Novelli, L Weiss, Surface Severe Plastic Deformation for Improved
Mechanical/Corrosion Properties and Further Applications in the Bio-Medical and Hydrogen Sectors
MATERIALS TRANSACTIONS, MT-MF2022040, 2023**

***Some papers
on Surface SPD for
H-applications***