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Arts et Métiers Institute of Technology

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

Speaker: Sébastien Jégou, Associate Professor
Arts et Métiers ParisTech, MSMP Laboratory
France

L.Barrallier, Professor, Arts et Métiers ParisTech, MSMP Laboratory
B.Guillot, PhD, Arts et Métiers ParisTech, MSMP Laboratory

ABOUT THE SPEAKER

2009 – PhD – Arts et Métiers ParisTech, Aubert & Duval, France
- → Gaseous Nitriding
- → Residual Stresses

2010 – PostDoc – DTU, Denmark
- → Expanded Austenite
- → Nitriding / Carburizing
- → Residual Stresses

2011-… - Associate Professor – Arts et Métiers ParisTech, France
- → Materials Science
- → Surface Engineering

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

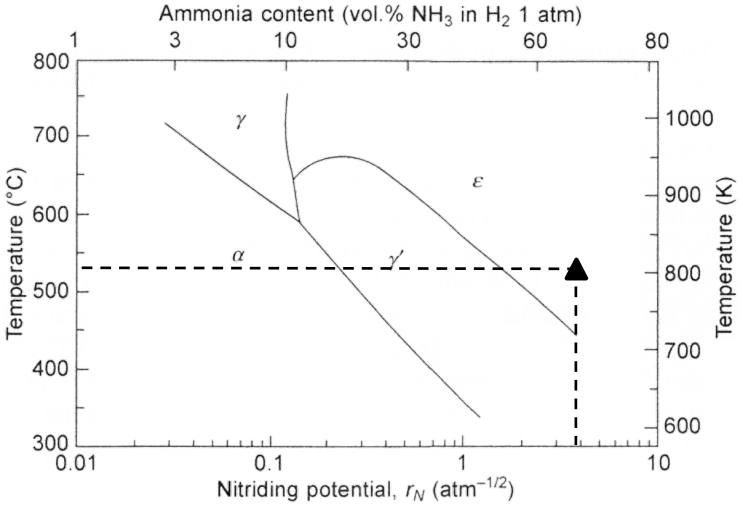
AGENDA

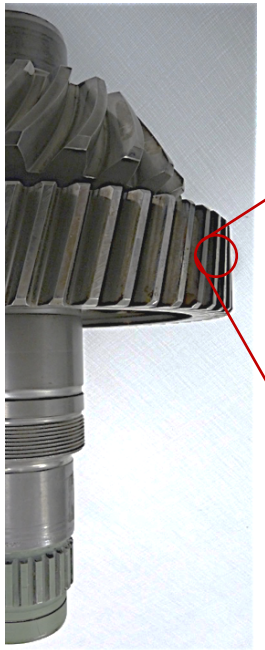
1. Introduction
2. Experiments
3. Results
4. Conclusion

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

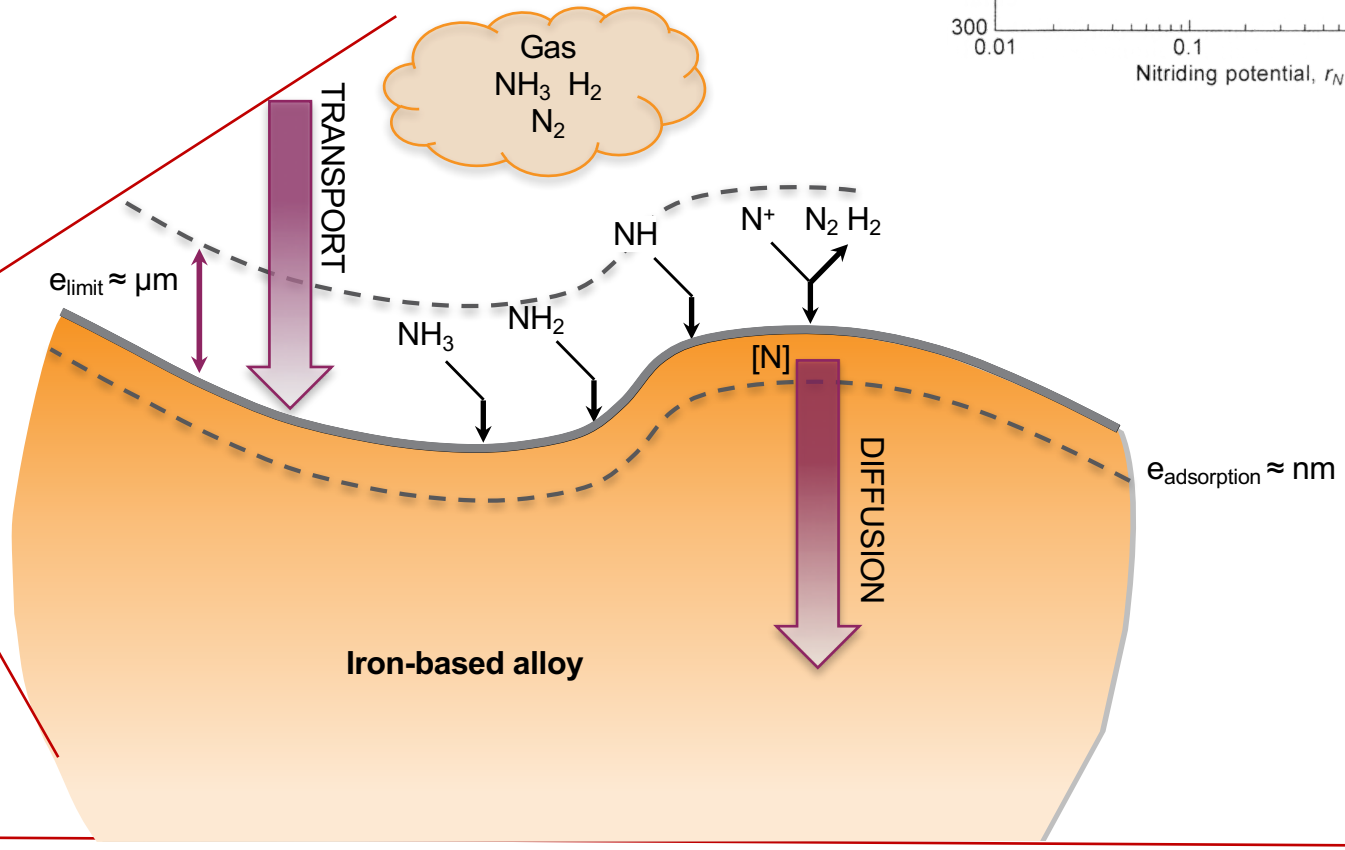
1. Introduction - Context

$$NH_3(s) \rightleftarrows [N] + \frac{3}{2}H_2(g) \qquad K_N = \frac{p_{NH_3}}{p_{H_2}^{3/2}}$$





courtesy of Airbus Helicopters



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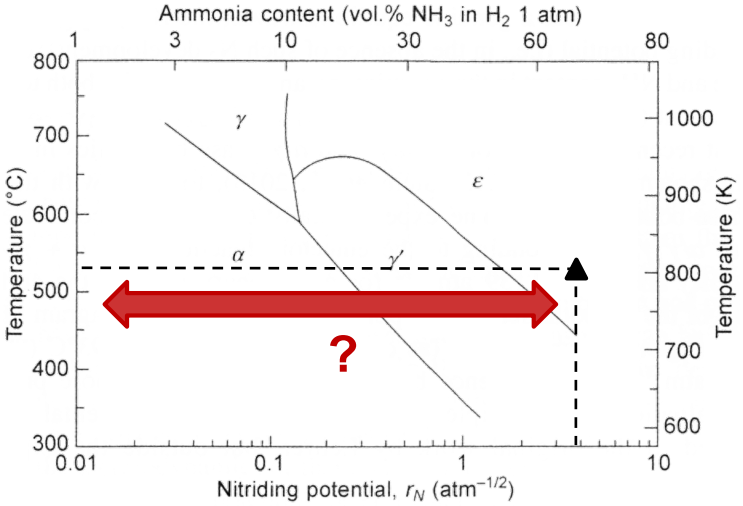

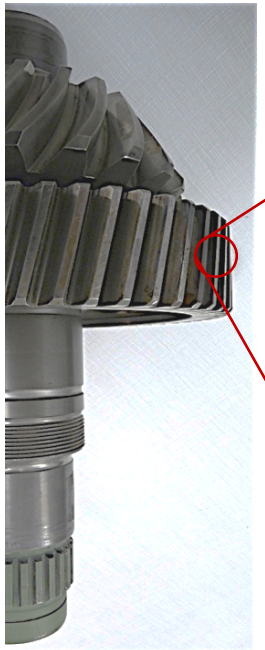

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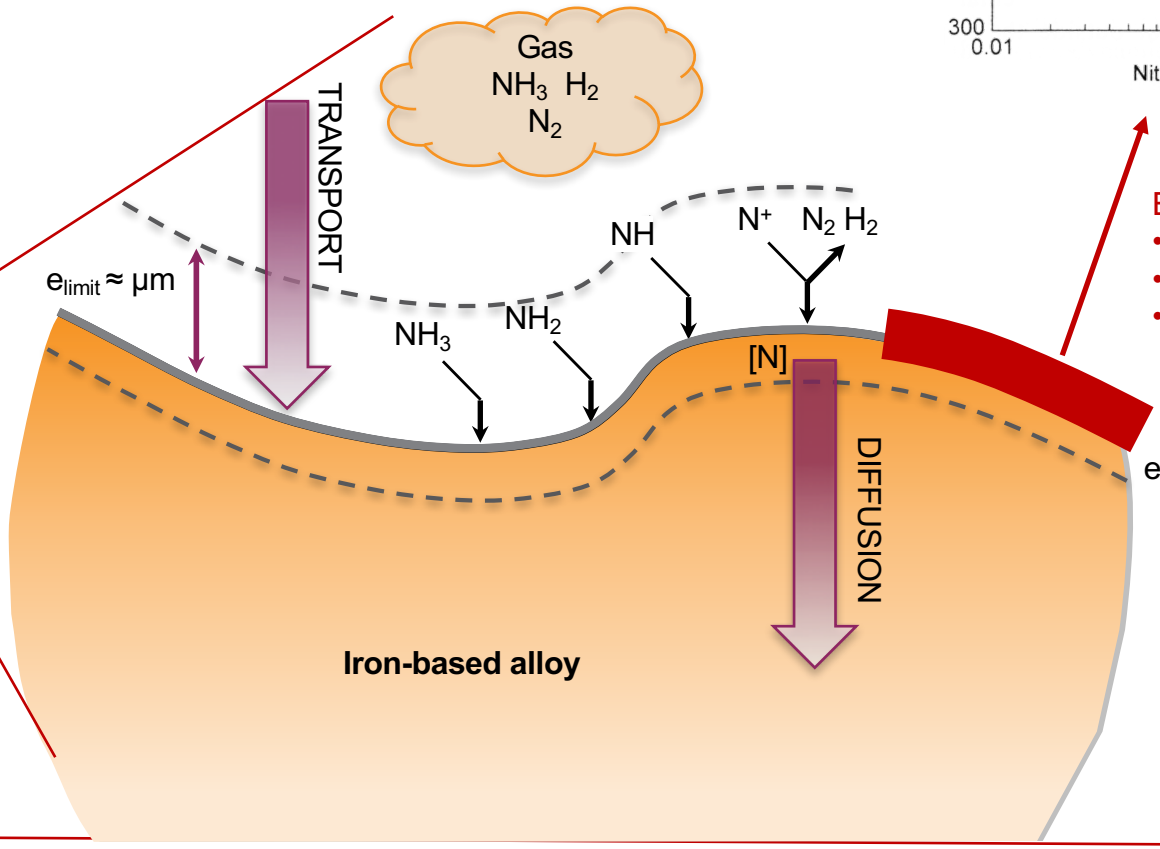


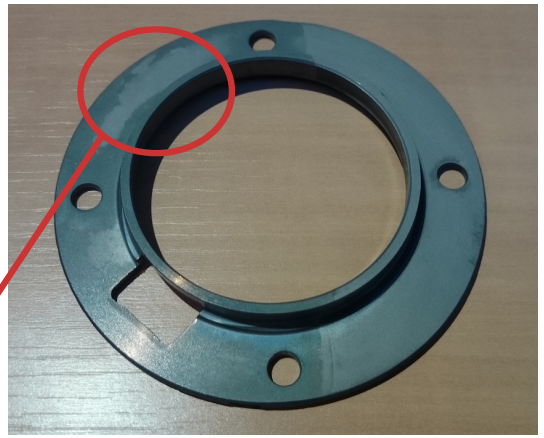
Ex.:
- Contamination layer
- Reaction layer
- Deformed layer

MSMP Mechanics, Surfaces and Materials Processing

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

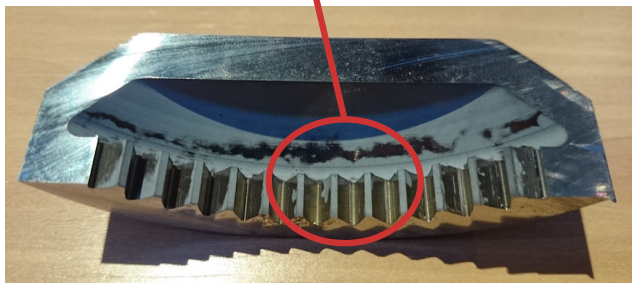
1. Introduction - Context

courtesy of Airbus Helicopters



courtesy of Bodycote

- Soft spot
- Lack of nitriding
- Heterogeneous nitriding



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MSMP Mechanics, Surfaces and Materials Processing

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

1. Introduction - Context

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

1. Introduction - Context

Casting / Forging

Heat Treatments

Machining

- Surface hardening
- Surface softening
- Residual stresses

⇒ Microstructure transformations

- Surface residues

risks of LOW

Gaseous Nitriding

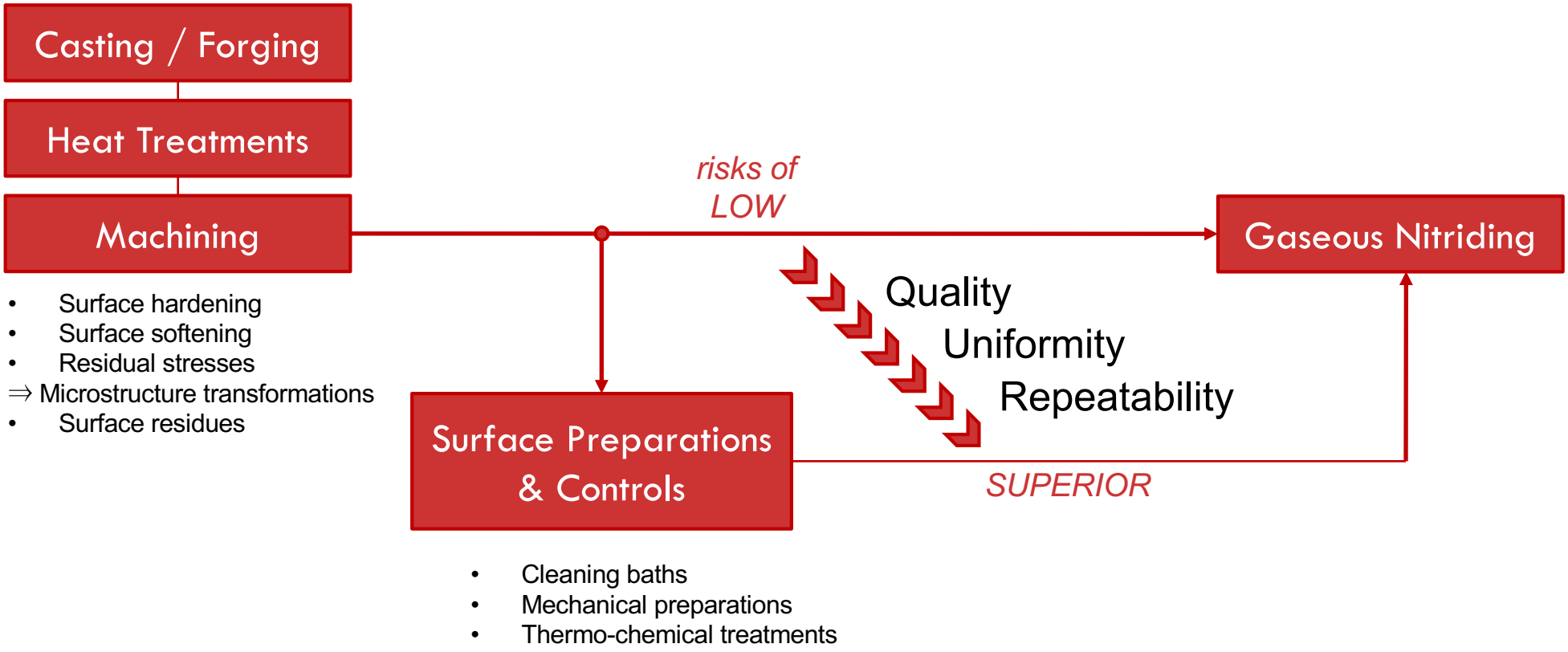
Quality

Uniformity

Repeatability

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

1. Introduction - Context



Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

1. Introduction - Context

Surface Preparations & Controls

- Cleaning baths: residues from
  - Machining oil (sulphate, phosphate, silicon, …)
  - Cleaning baths (anionic surfactant (sulphonates, sulphates…))

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

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Surface Preparations & Controls

- Cleaning baths: residues from
  - Machining oil (sulphate, phosphate, silicon, …)
  - Cleaning baths (anionic surfactant (sulphonates, sulphates…))

- Mechanical preparations: Sandblasting (sanding)
  - Passivation/corrosion layer
  - Heterogeneous metallurgy/microstructure

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

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- Cleaning baths: residues from
  - Machining oil (sulphate, phosphate, silicon, …)
  - Cleaning baths (anionic surfactant (sulphonates, sulphates…))
- Mechanical preparations: Sandblasting (sanding)
  - Passivation/corrosion layer
  - Heterogeneous metallurgy/microstructure
- Thermo-chemical treatments: **controlled** layer (nature, thickness)
  - Oxidization
  - Phosphating (Zn, Mn)
  - …

⇒ Surface homogeneity visual control

⇒ Protection from (heterogeneous) surface reactions
⇒ Activation of the NH_3 decomposition

MSMP Mechanics, Surfaces and Materials Processing

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

1. Introduction - Context

Surface Preparations & Controls

- Thermo-chemical treatments: **controlled** layer (nature, thickness)
  - ⇒ Surface homogeneity **visual control**
  - ⇒ **Protection** from (heterogeneous) surface reactions
  - ⇒ **Activation** of the NH_3 decomposition
    - Oxidization (NH_3 decomposition catalyst)
    - Phosphating (Zn, Mn)

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

1. Introduction - Context

Surface Preparations & Controls

- Thermo-chemical treatments: **controlled** layer (nature, thickness)

  ⇒ Surface homogeneity **visual control**
  ⇒ **Protection** from (heterogeneous) surface reactions
  ⇒ **Activation** of the NH_3 decomposition

  - Oxidization (NH_3 decomposition catalyst)
  - Phosphating (Zn, Mn)

  ⇒ Better Process Flexibility: **In-situ pre-treatments**
  - cleaning
  - activation

  - Oxidization : oxygen reactivity with contaminants
  - Urea

$$NH_2 - CO - NH_2(aq,s) \rightarrow HNCO(g) + NH_3(g) \rightarrow CO_2(g) + NH_3(g)$$

  - NH_4Cl

$$NH_4Cl(aq,s) \rightarrow HCl(g) + NH_3(g)$$

⇒ Heating stage: atmosphere of Acids + N-adsorption

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Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

2. Experiments

- **Material: 33CrMoV12-9**
  - 17 x 13 x 5 mm^3
  - Austenitized @ 920 °C, 90 min
  - Oil quenched
  - Tempered @ 640 °C, 1 h

Composition (wt.%)					
C	Cr	Mo	V	Mn	Fe
0.32	2.97	0.84	0.28	0.55	bal.

- Sample preparation:
  - Degreased
  - Rinsed in water
  - Dried in alcohol

- **Surface contamination:**
  - **Water-dissolved machining oil**
    - 1 to 100 vol.%
    - 1 min dipping
    - Droplets removed

- **In-situ treatments**: 350-400 °C, 1 h
  - Vacuum Stages
  - Oxidization (O_2)
  - Urea / NH_4Cl
    - 200 mg
    - Neutral atmosphere

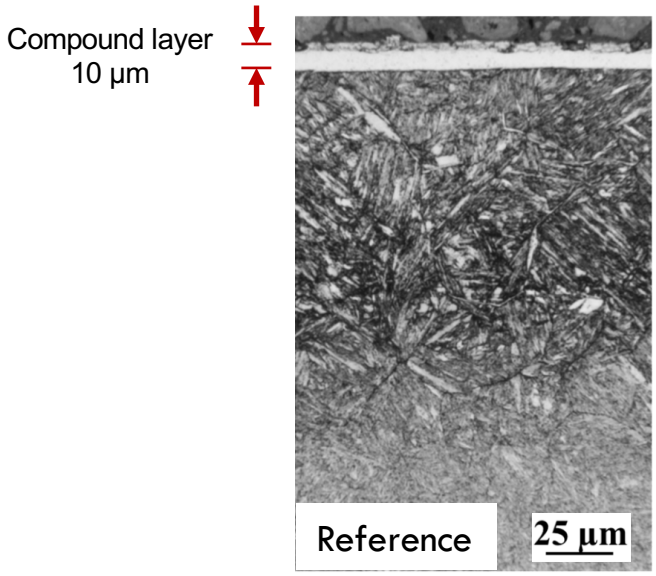
- **Gaseous Nitriding:**
  - Thermogravimetric analyser (Setsys Evo.)
  - Vacuum Stages
  - Heating/Cooling @ 10 °C.min^{-1} under N_2
  - **520 °C, 5 h, K_N 3.7 $atm^{-1/2}$**
  - NH_3-N_2-H_2 (200 mL.min^{-1})

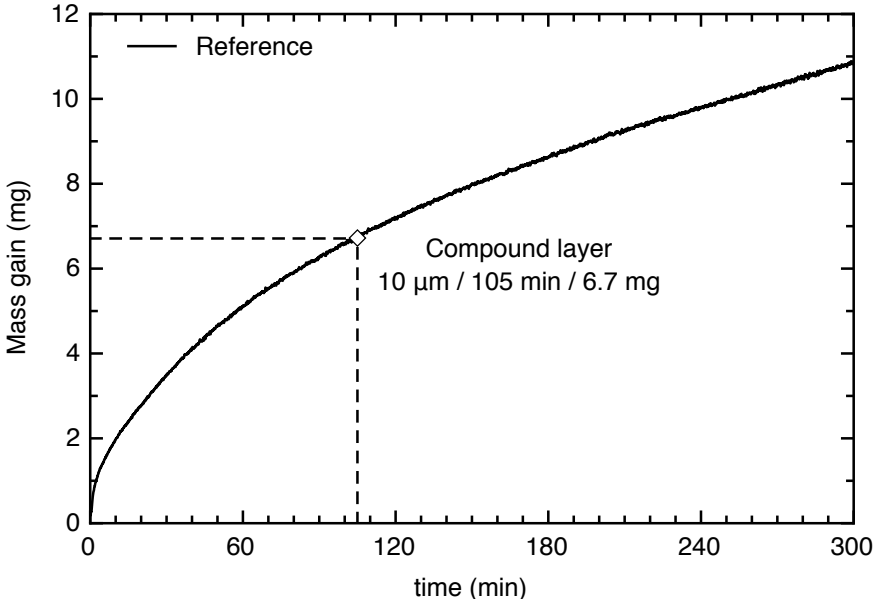
MSMP Mechanics, Surfaces and Materials Processing

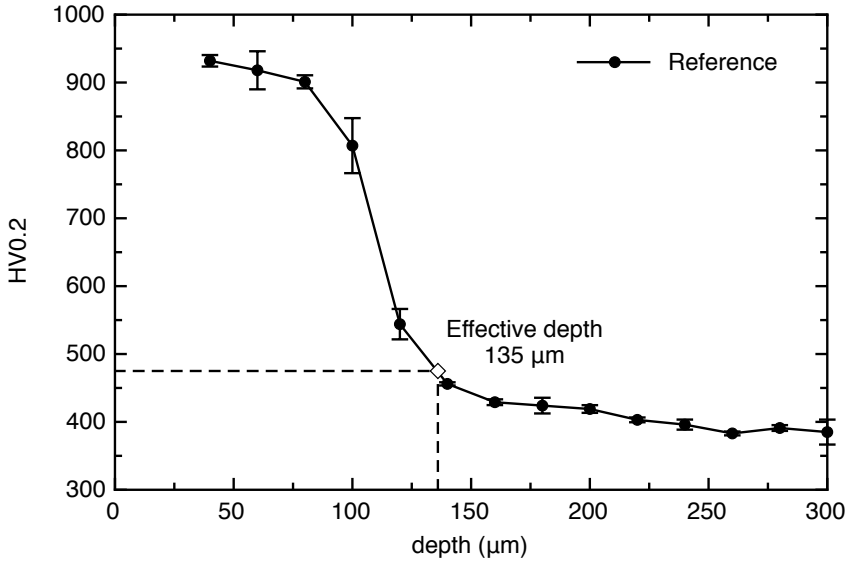
Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

3. Results

0. The reference





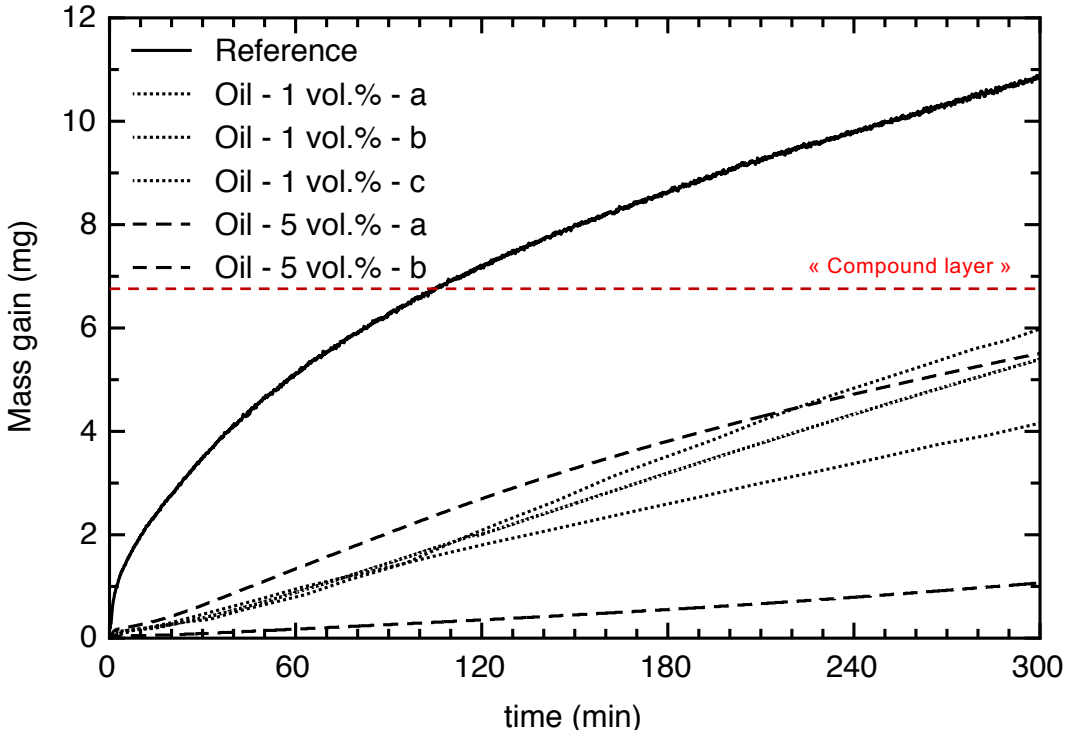


MSMP Mechanics, Surfaces and Materials Processing

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

3. Results

a. Influence of water-dissolved oil contaminations



Sample	Mass gain after nitriding (mg)
Reference	10.89 ± 0.33
Oil 1 vol.% - a	5.39 (49.5 %)
Oil 1 vol.% - b	5.98 (54.9 %)
Oil 1 vol.% - c	4.16 (38.2 %)
Oil 5 vol.% - a	1.07 (9.8 %)
Oil 5 vol.% - b	5.51 (50.6 %)

MSMP Mechanics, Surfaces and Materials Processing

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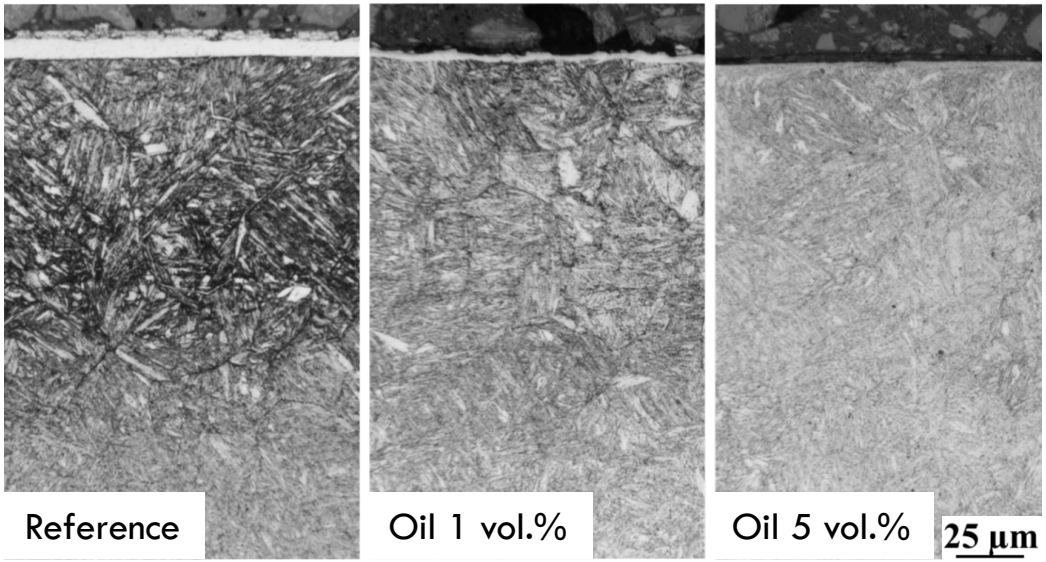


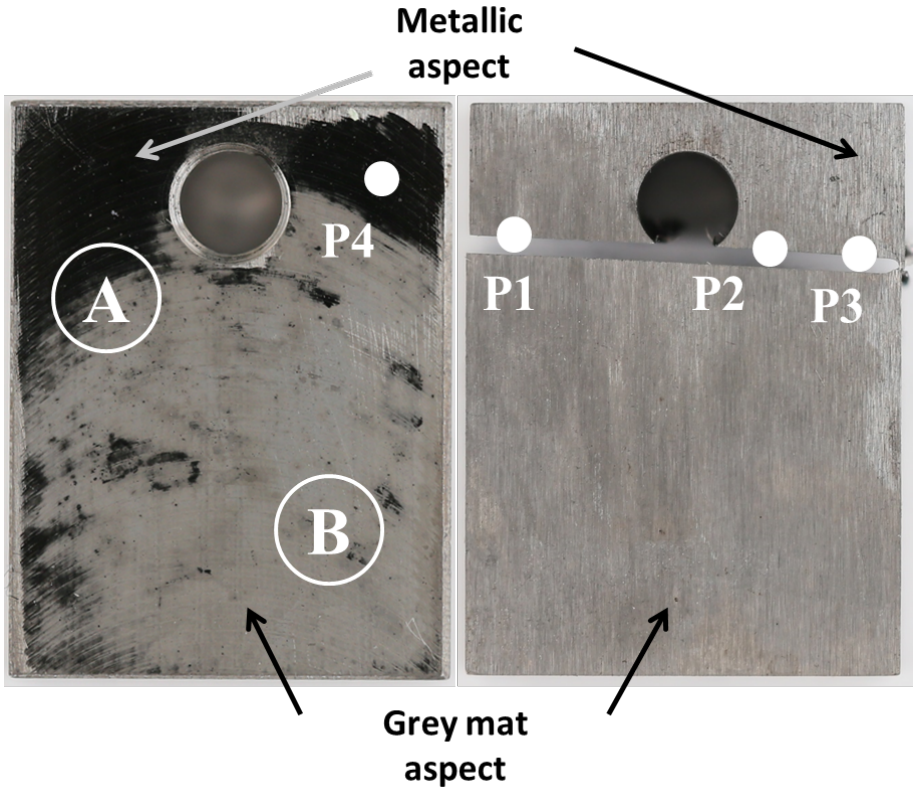
Sample	Mass gain after nitriding (mg)
Reference	10.89 ± 0.33
Oil 1 vol.% - a	5.39 (49.5 %)
Oil 5 vol.% - a	1.07 (9.8 %)

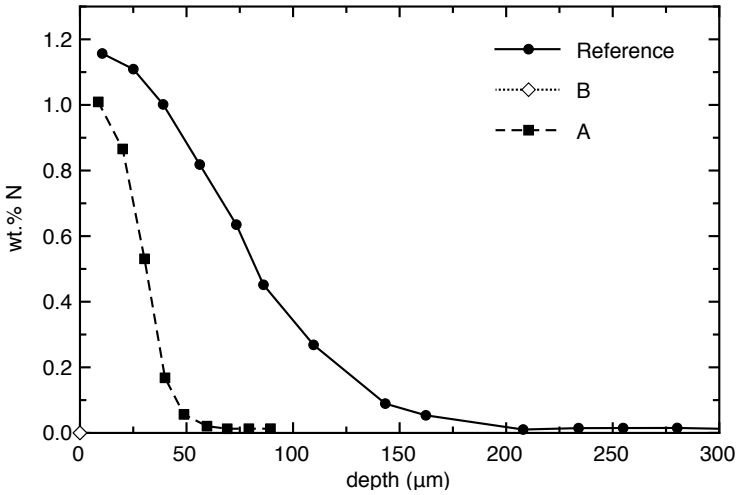
Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

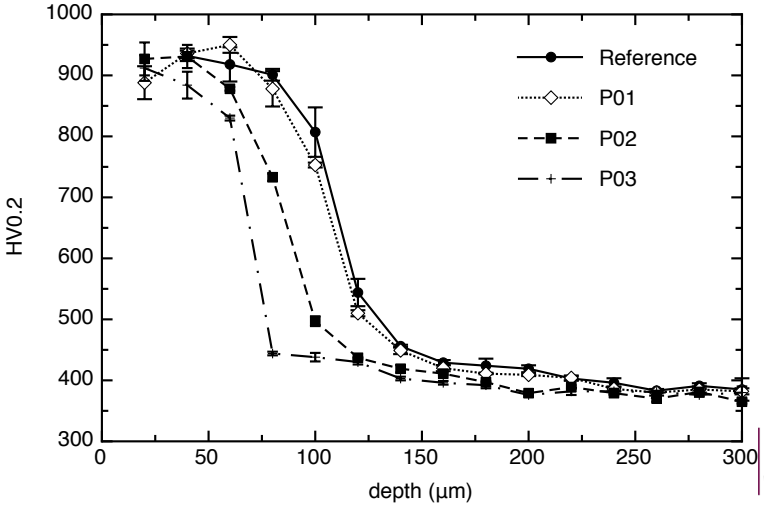
3. Results

a. Influence of water-dissolved oil contaminations

i. Oil 1 vol.%







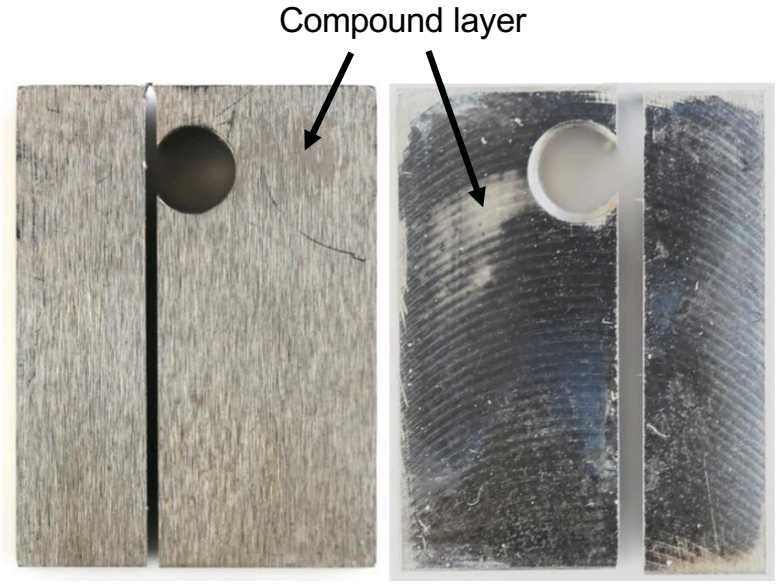
SMP Mechanics, Surfaces and Materials Processing

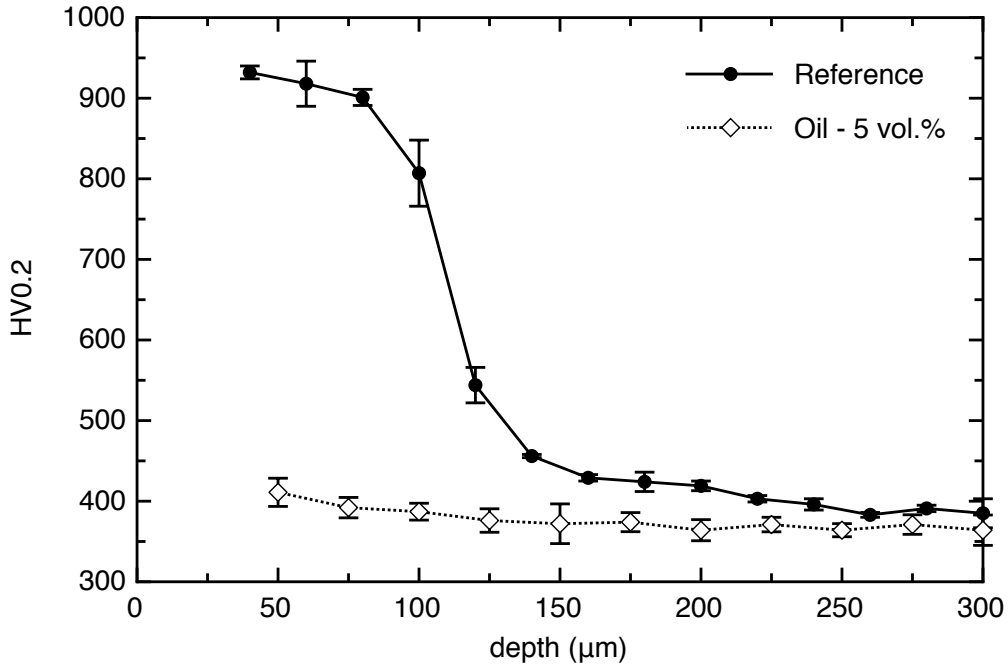
Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

3. Results

a. Influence of water-dissolved oil contaminations

ii. Oil 5 vol.%

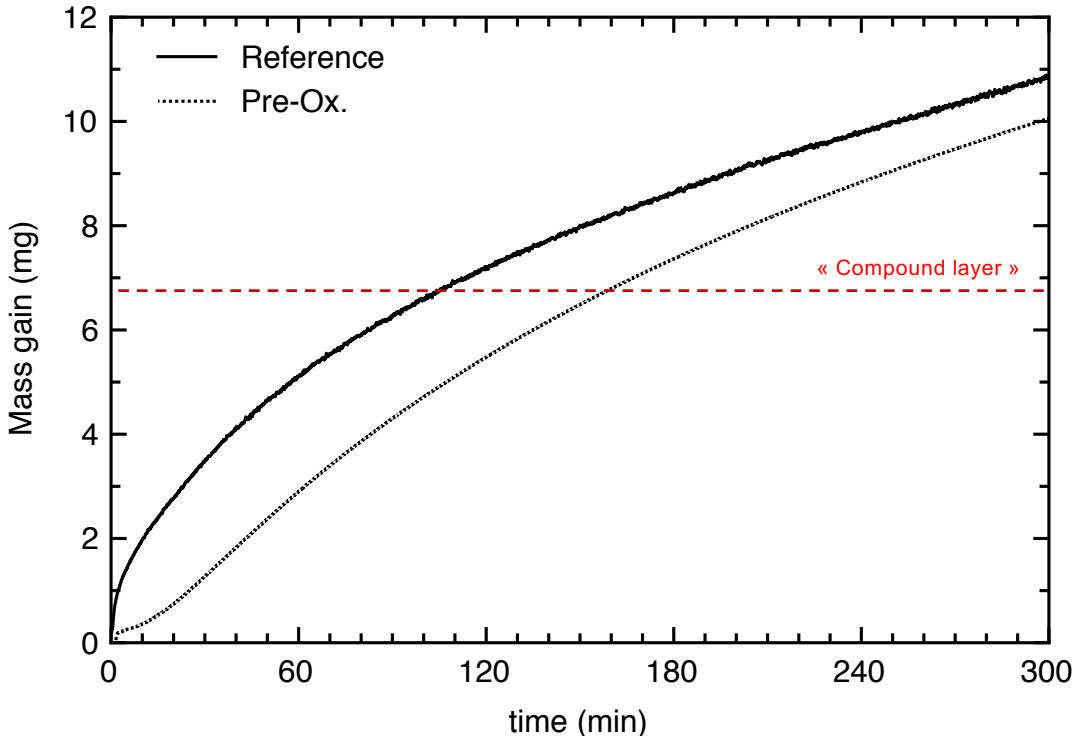




Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

3. Results

b. Influence of pre-oxidization (O_2, 350 °C, 1h)



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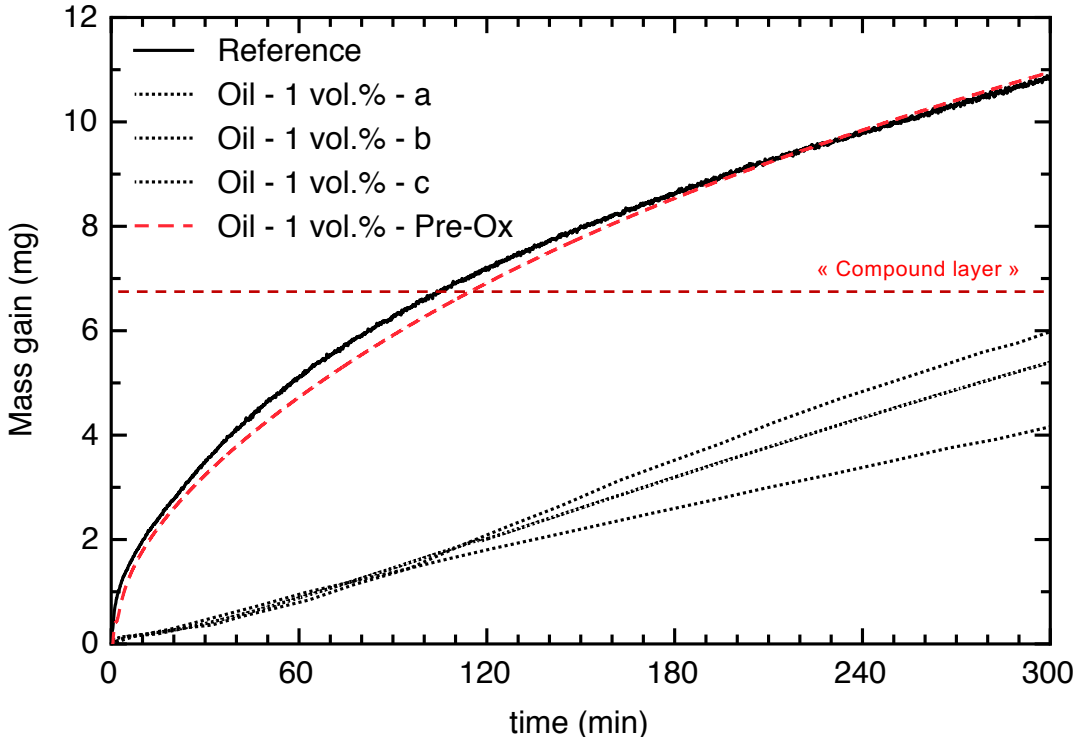

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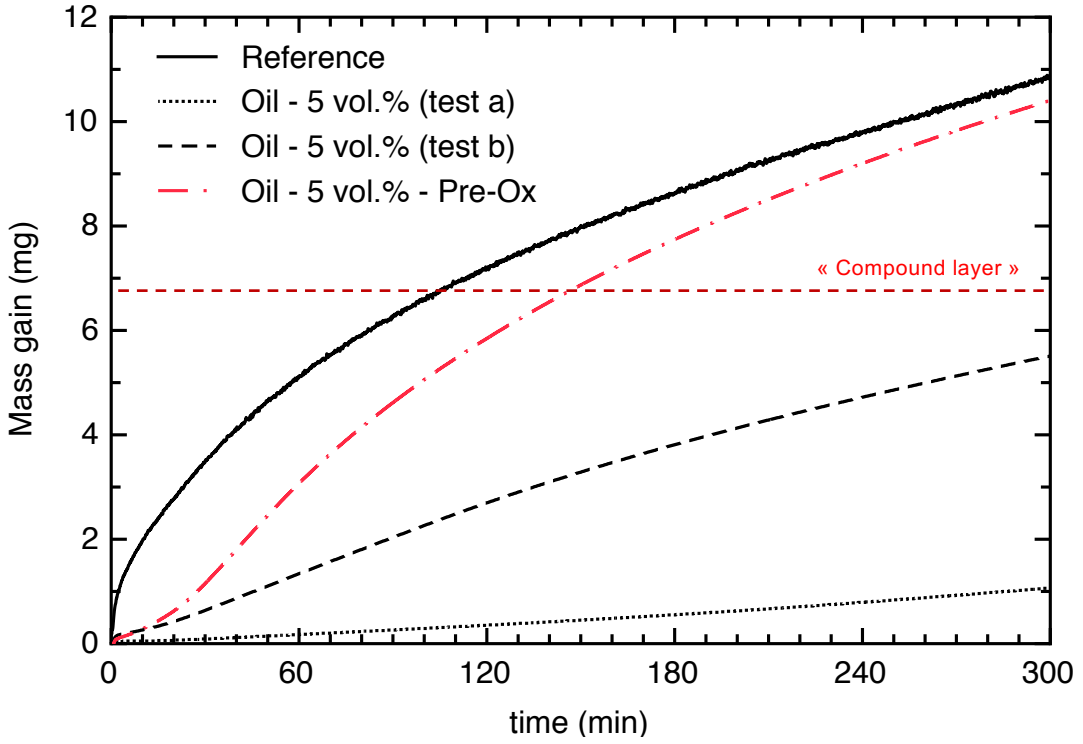

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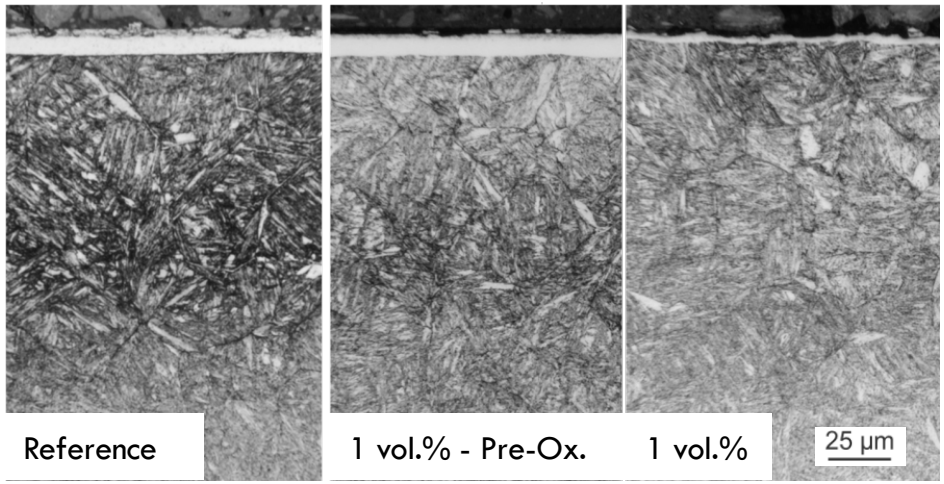

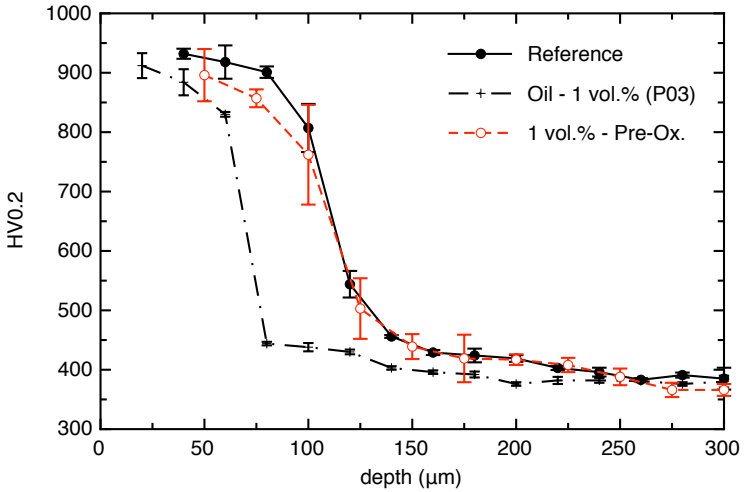

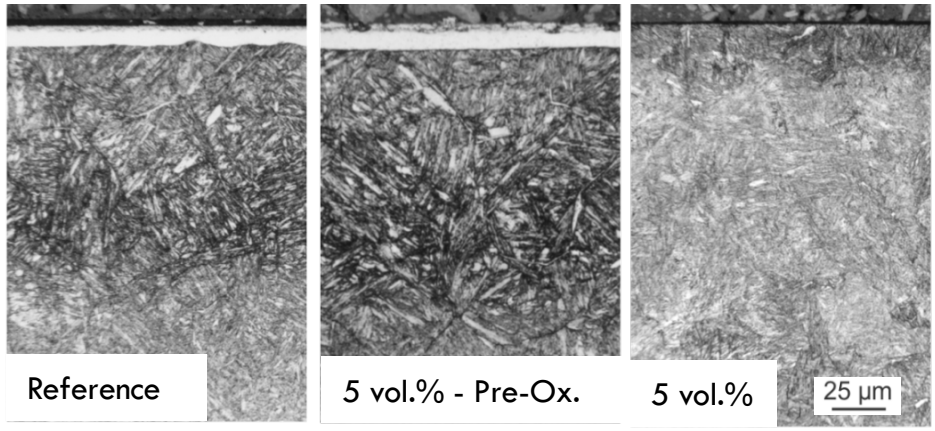

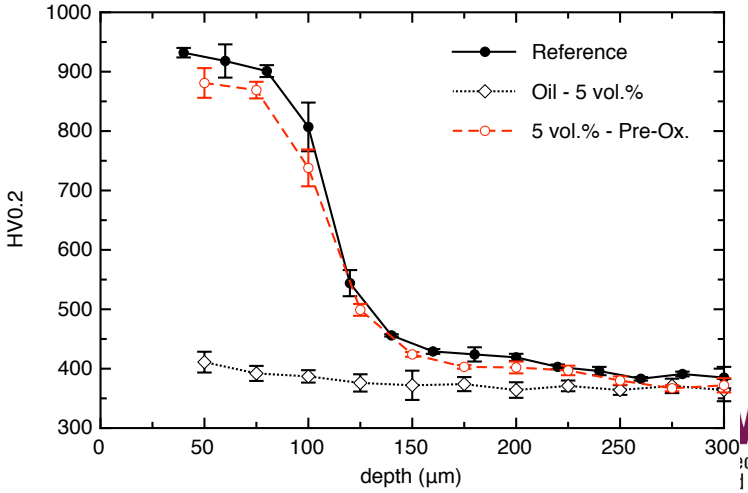

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Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

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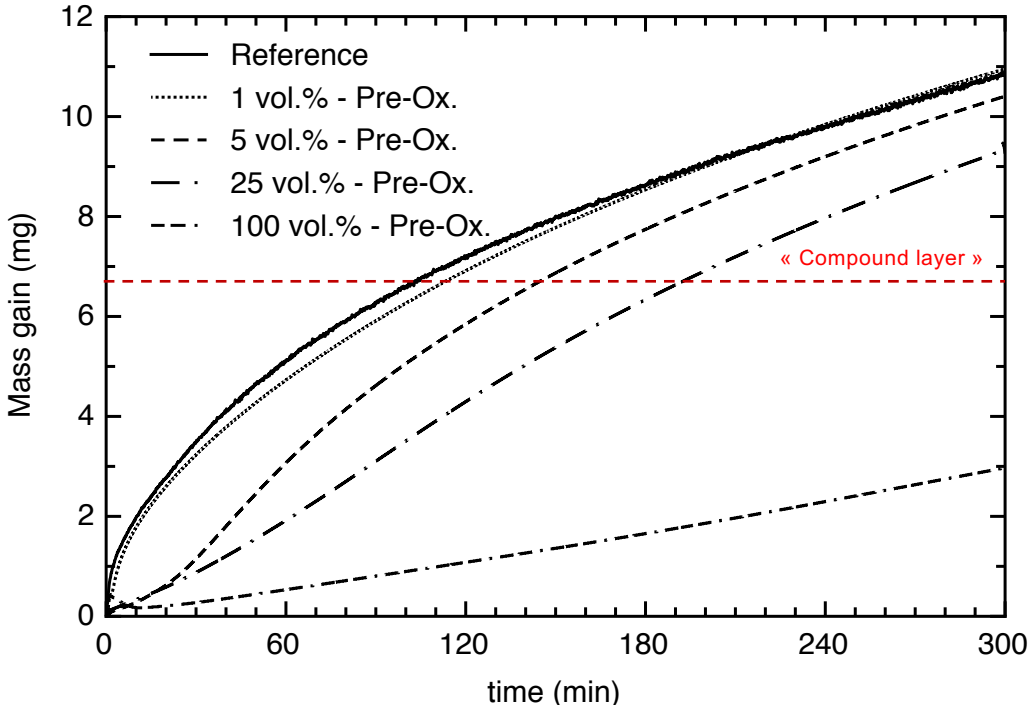
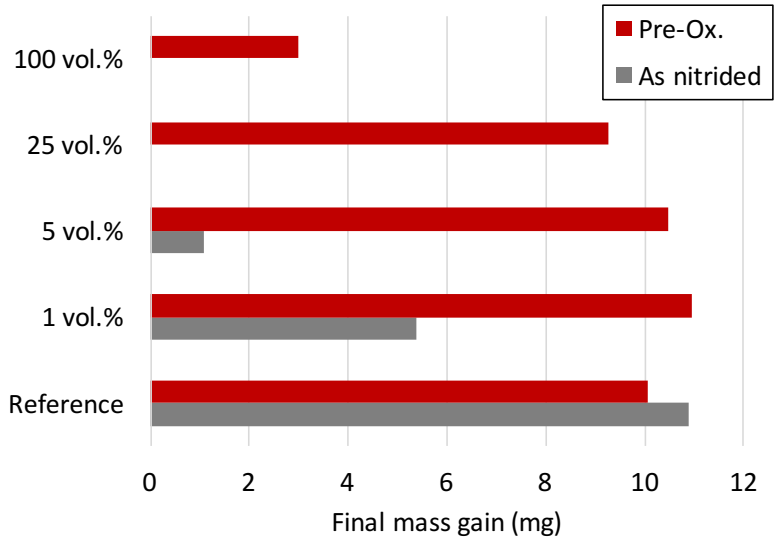


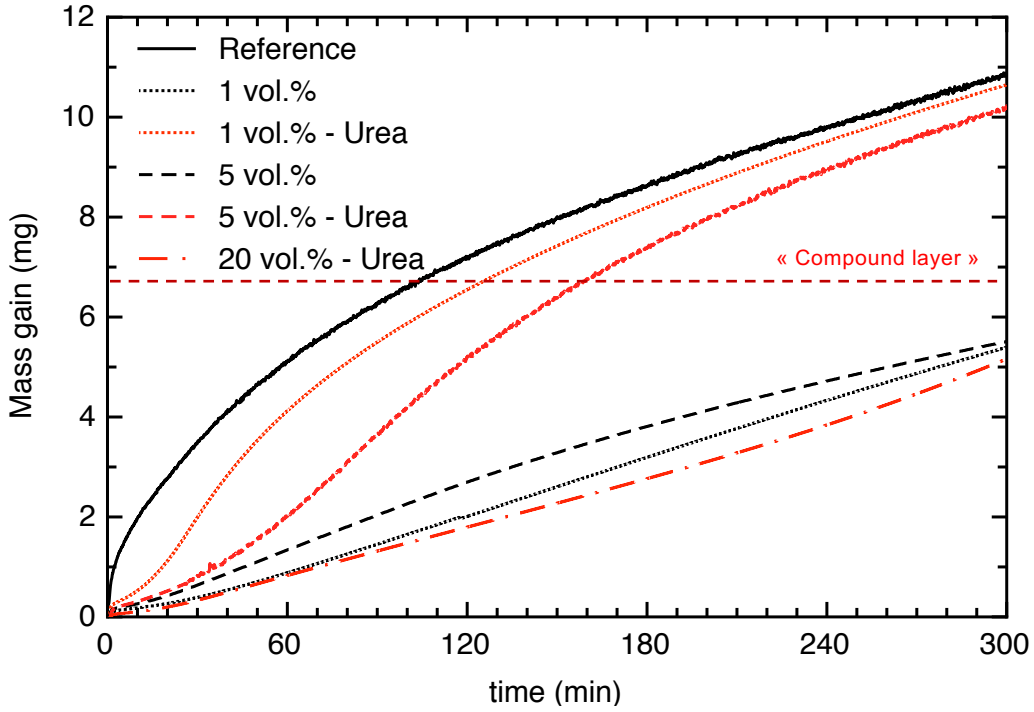


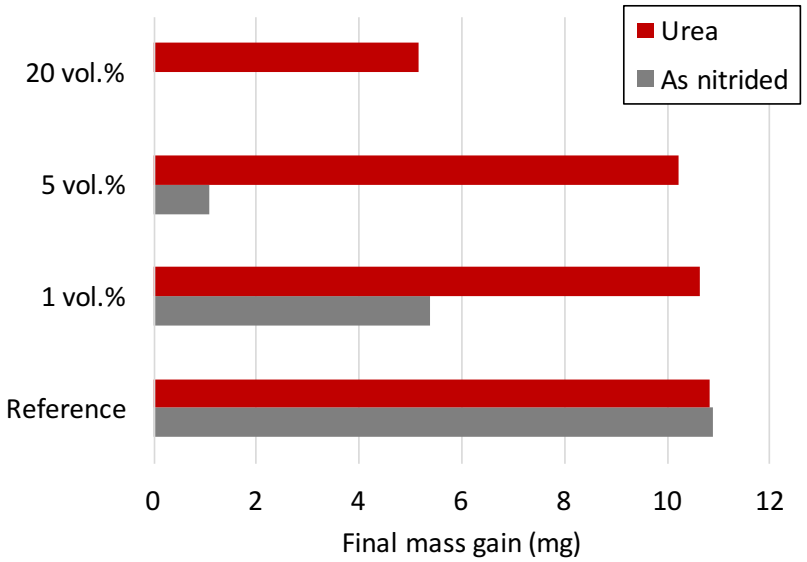
MSMP Mechanics, Surfaces and Materials Processing

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

3. Results

c. Influence of urea





MSMP Mechanics, Surfaces and Materials Processing

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

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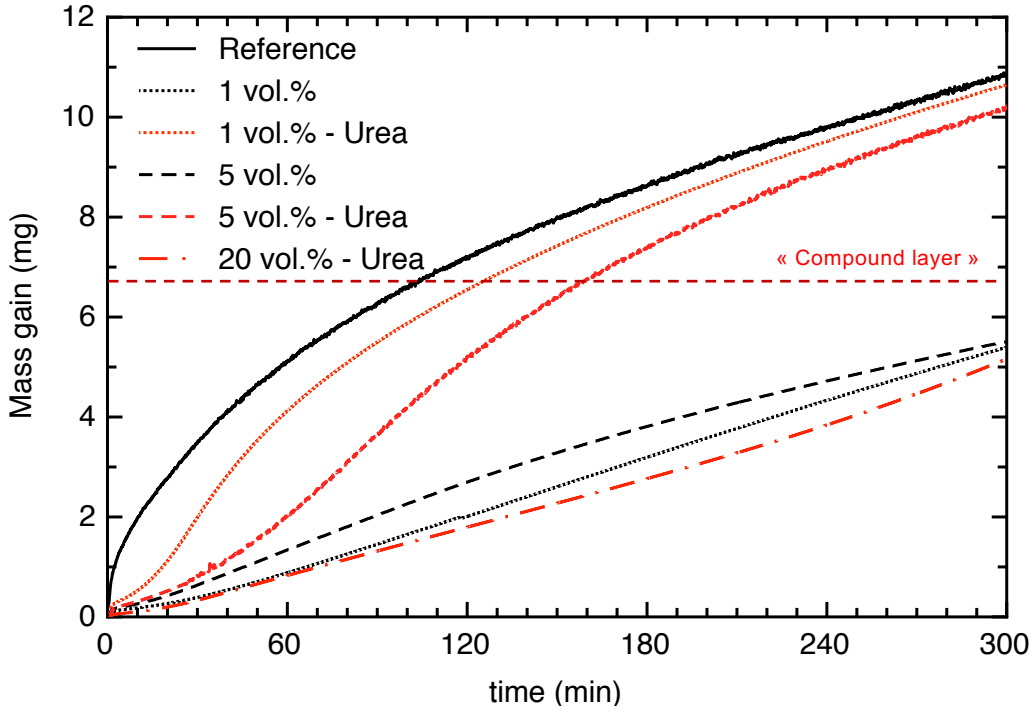
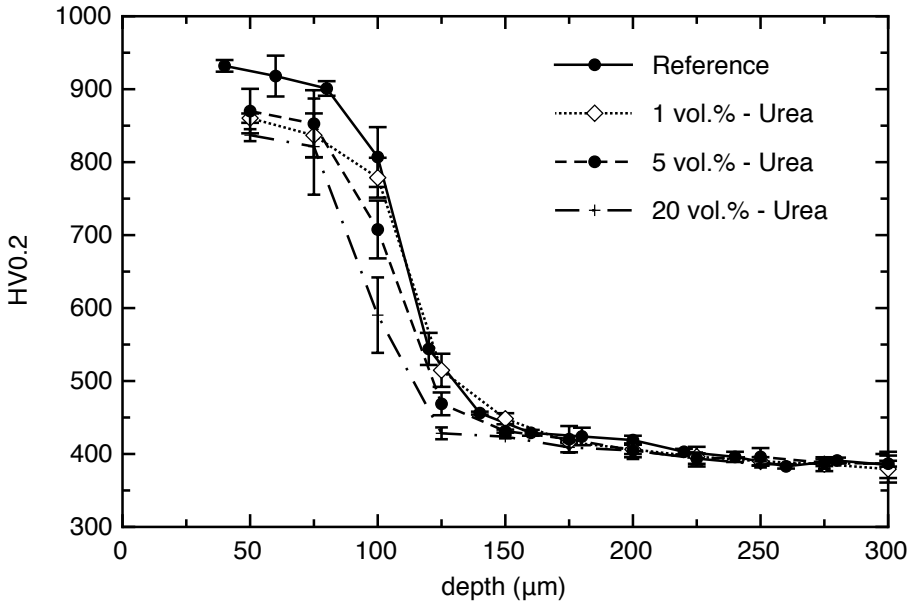
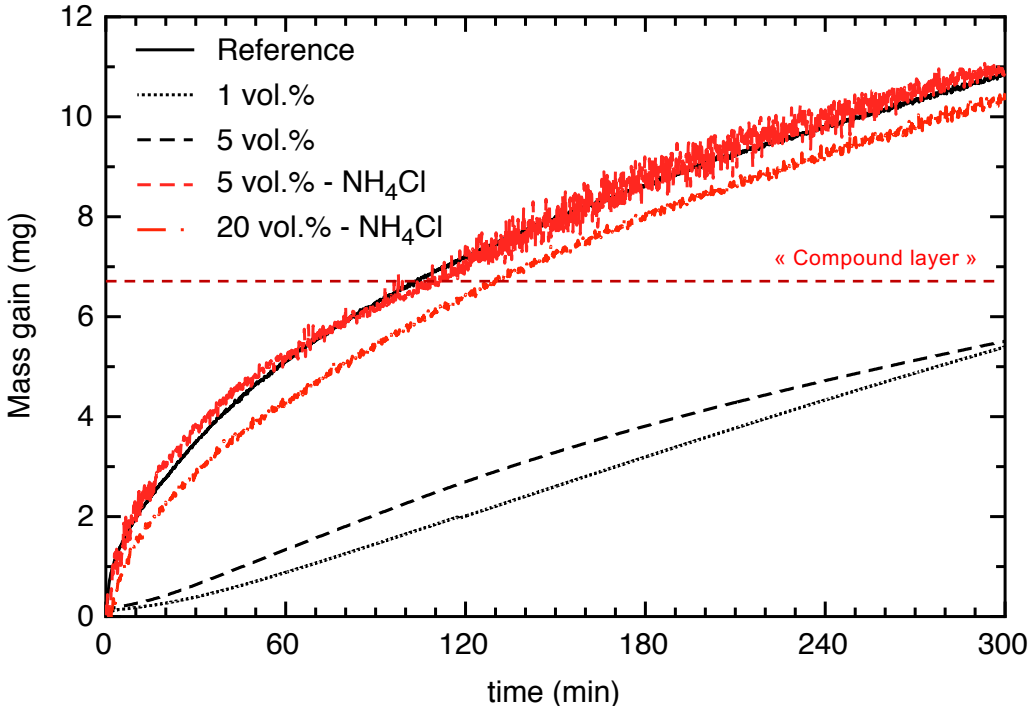


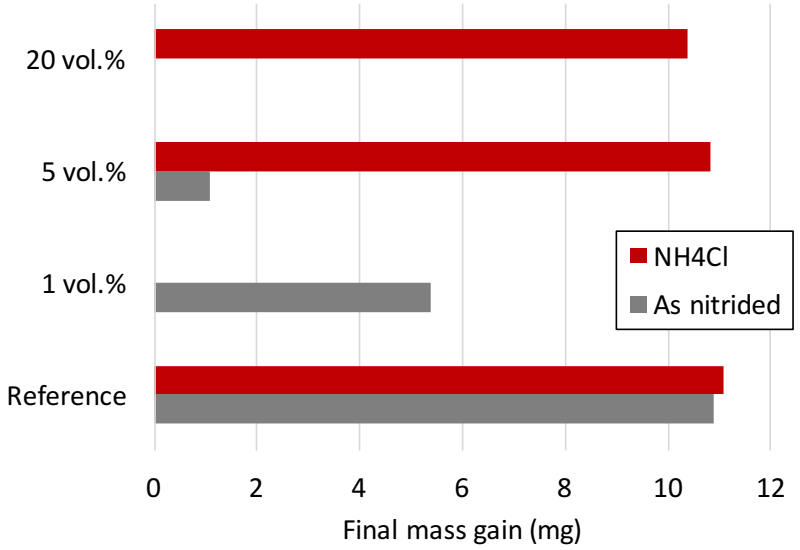


Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

3. Results

d. Influence of NH_4Cl





Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

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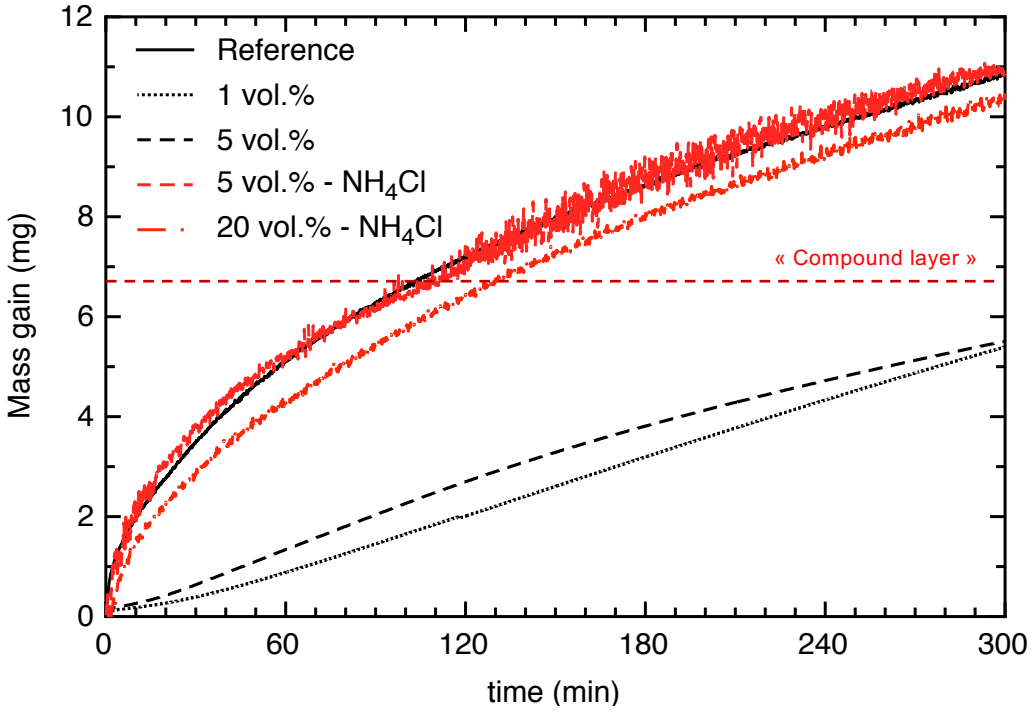

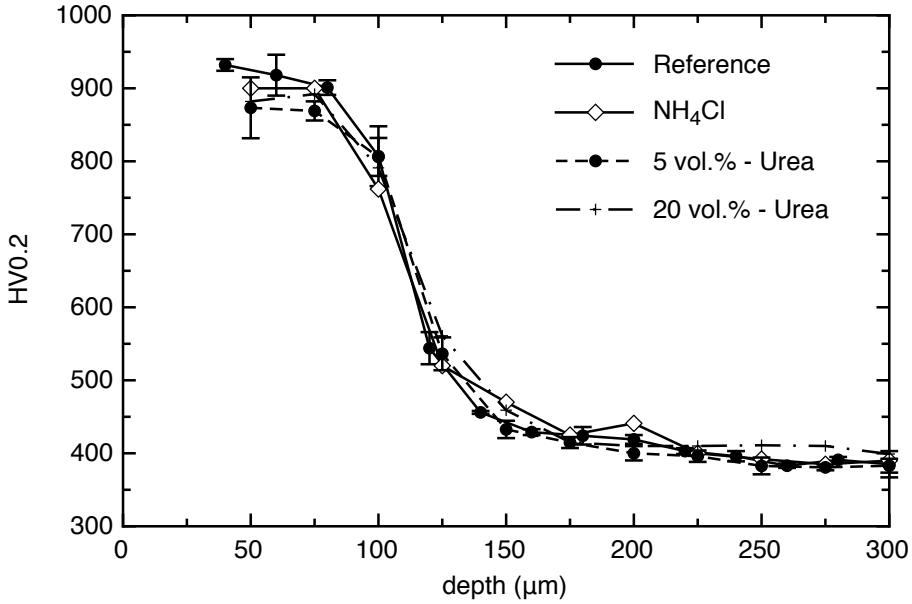

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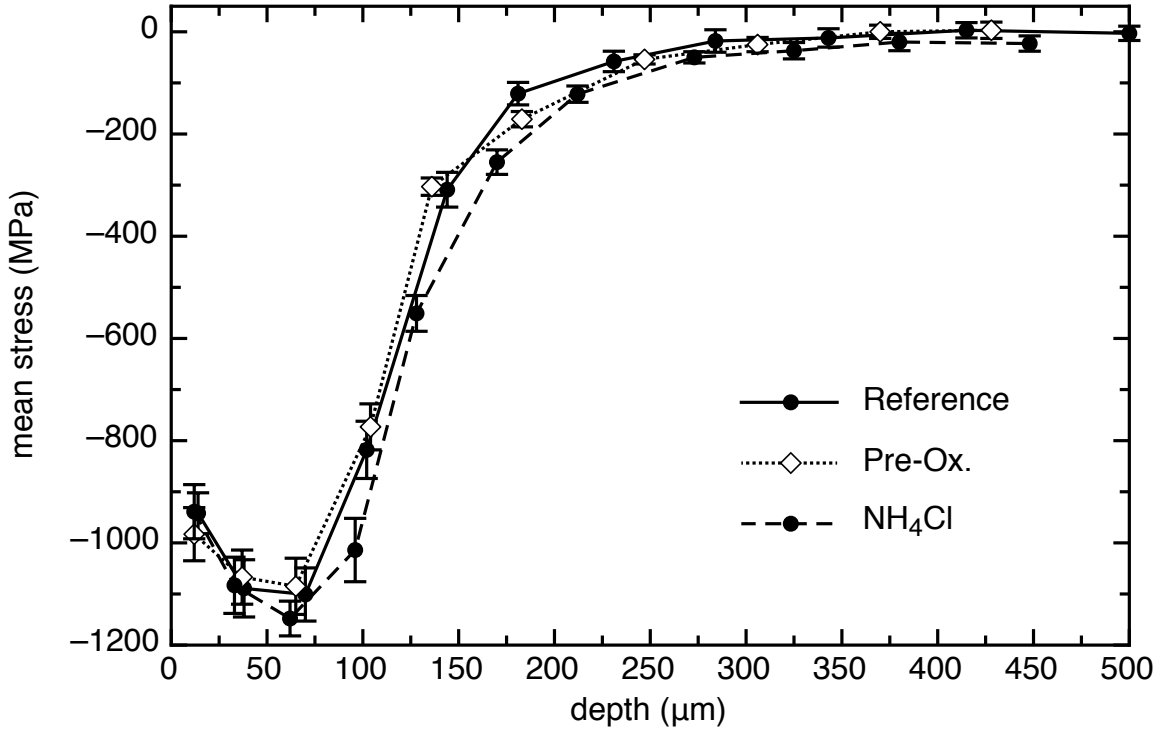
Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

3. Results

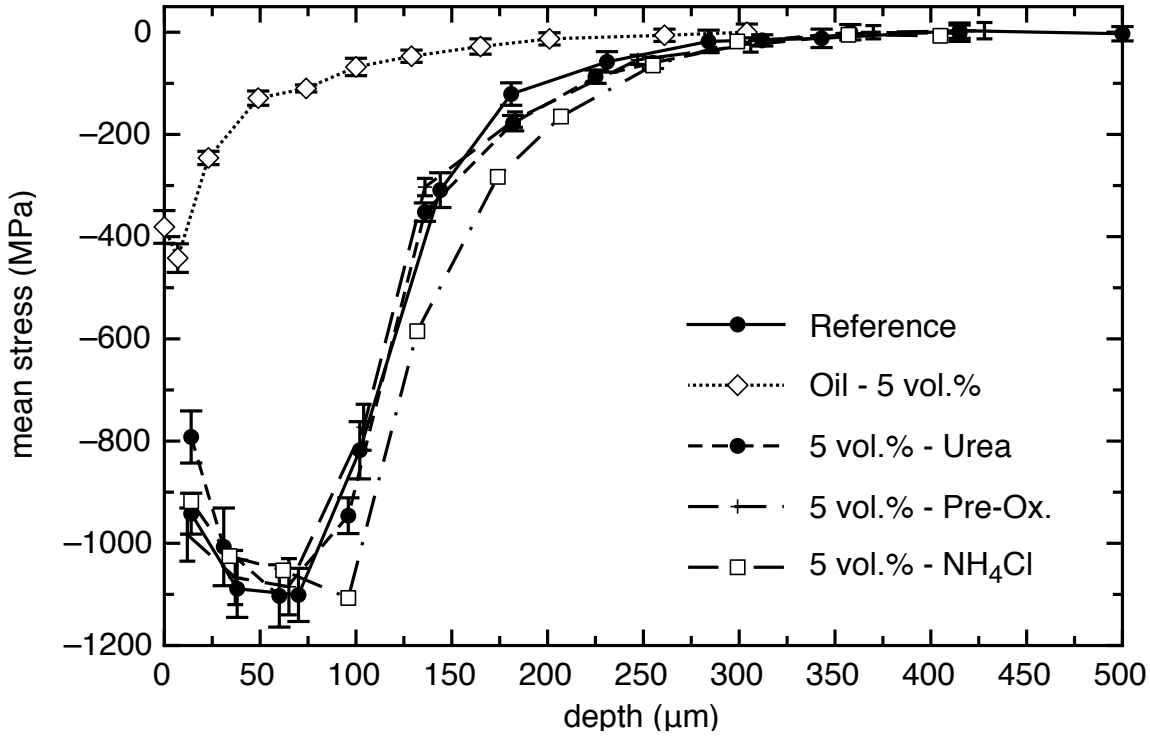
e. Pre-treatments & residual stresses



Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

3. Results

e. Pre-treatments & residual stresses



MSMP Mechanics, Surfaces and Materials Processing

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

3. Results

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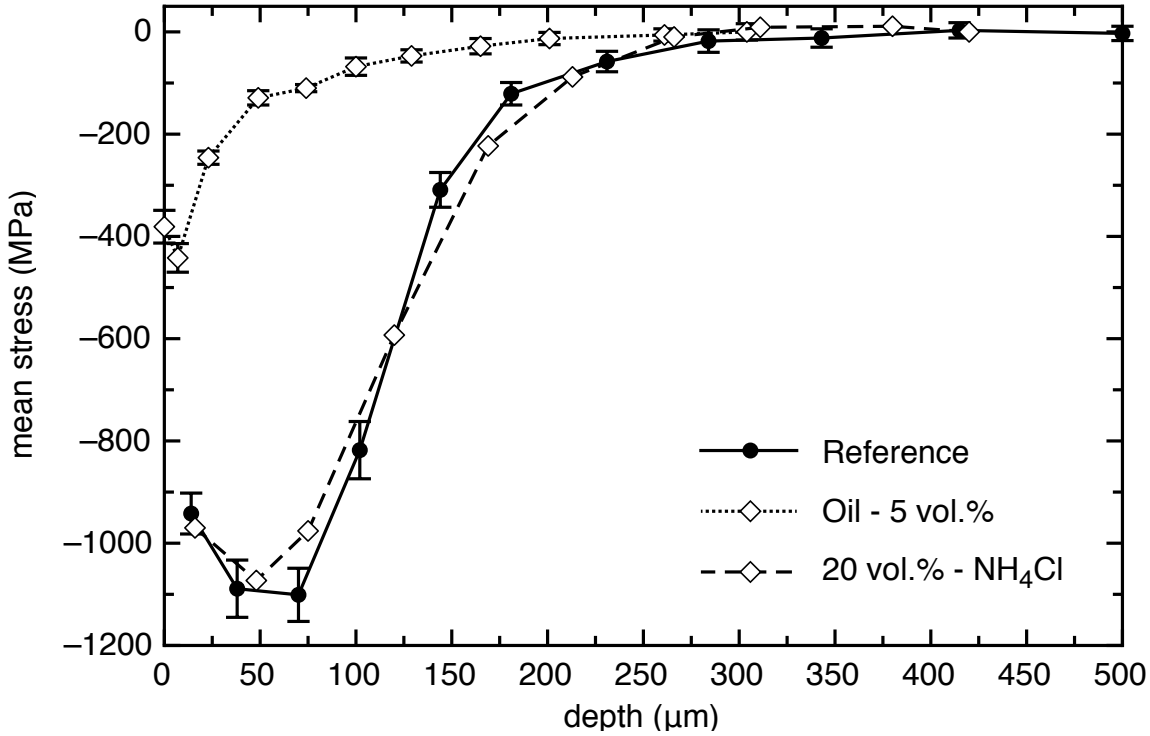
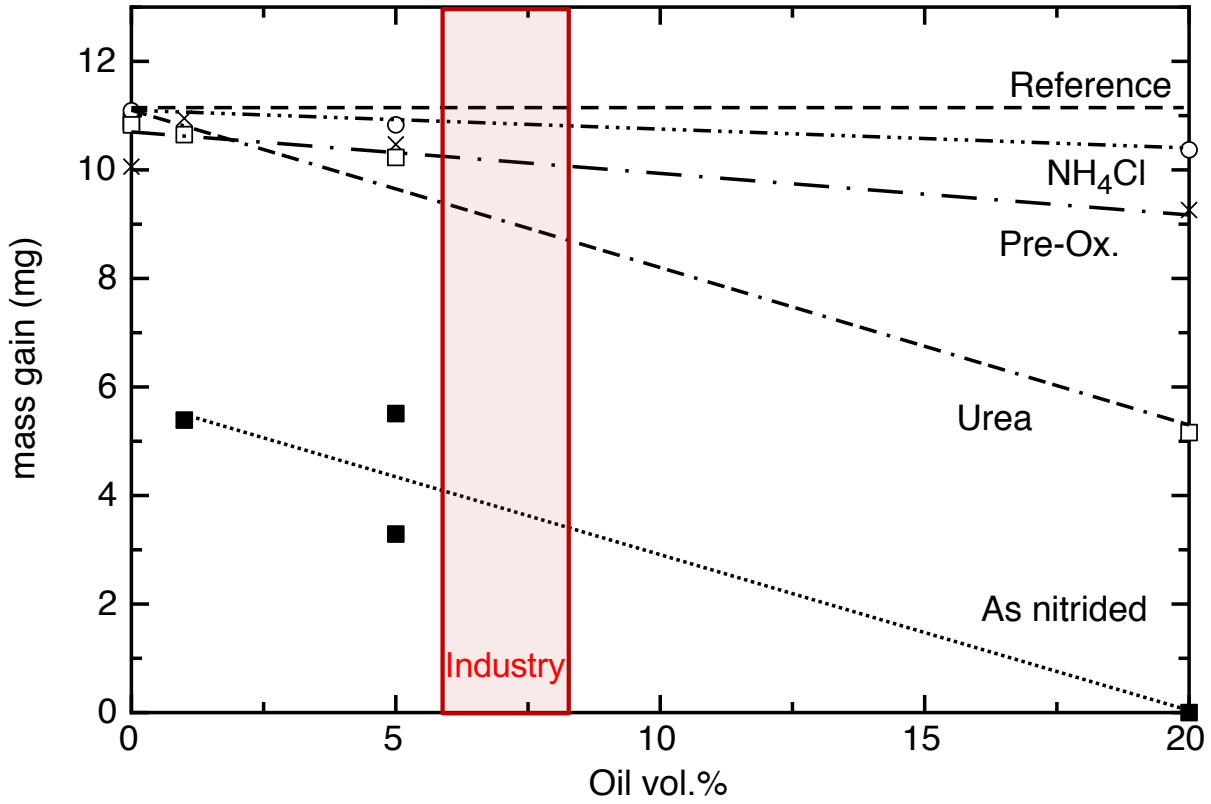


MSMP Mechanics, Surfaces and Materials Processing

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

4. Conclusion (nitriding 520 °C, 5 h, K_N 3,7 $atm^{-1/2}$)



Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

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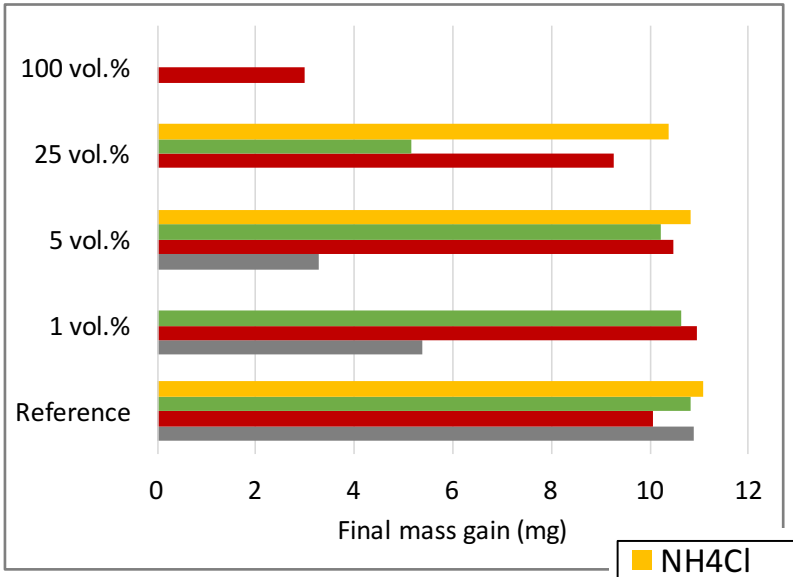
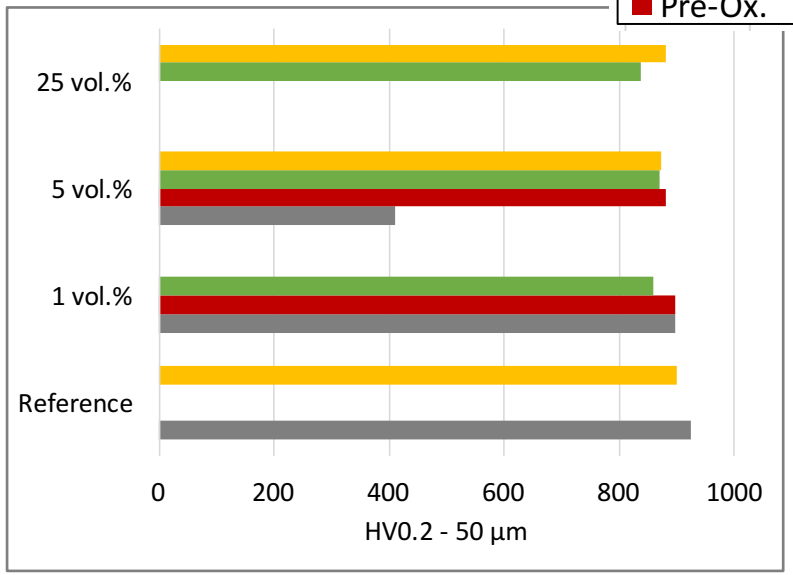
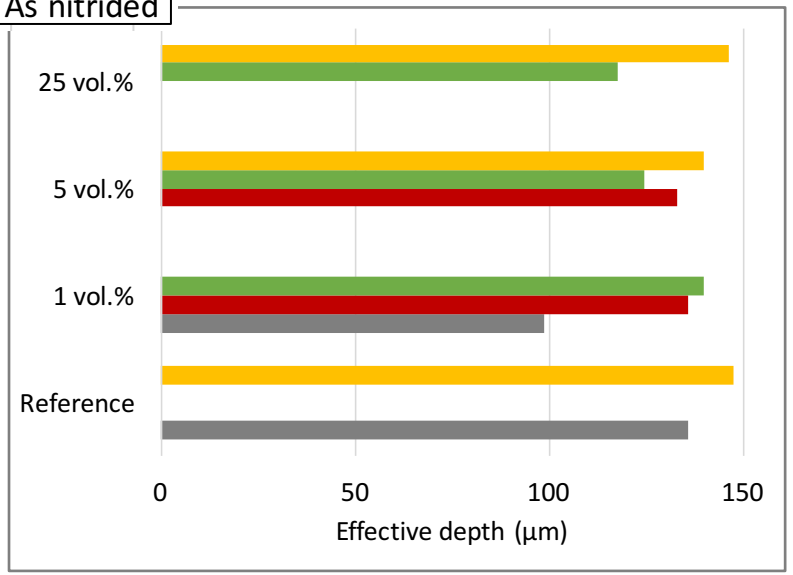


efficiency ↓

- In-situ pre-treatment:
  - Urea
  - Oxidization (thickness layer dependence)
  - NH_4Cl
- Advantage:
  - In-situ (during the heating stage)
  - NH_4Cl
    - Decomposition into NH3
    - Acidic cleaning/sanding





MSMP Mechanics, Surfaces and Materials Processing

Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

Thank you for your attention !

B.Guillot, S.Jégou, L.Barrallier, *Degradation of gaseous nitriding of steel by lubricant contamination - Effect of in-situ pre-treatments*, submitted to Surface & Coating Technology (2016)