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

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

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  → 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
1. Introduction - Context

\[ \text{NH}_3(s) \rightleftharpoons [N] + \frac{3}{2} \text{H}_2(g) \]

\[ K_N = \frac{P_{\text{NH}_3}^{3/2}}{P_{\text{H}_2}} \]

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1. Introduction - Context

\[ NH_3(s) \rightleftharpoons [N] + \frac{3}{2}H_2(g) \]

\[ K_N = \frac{p_{NH_3}^{3/2}}{p_{H_2}^3} \]

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

Iron-based alloy

\( e_{\text{limit}} \approx \mu\text{m} \)

\( e_{\text{adsorption}} \approx \text{nm} \)

courtesy of Airbus Helicopters
1. Introduction - Context

- Soft spot
- Lack of nitriding
- Heterogeneous nitriding

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

Casting / Forging
Heat Treatments
Machining

Gaseous Nitriding
1. Introduction - Context

- Casting / Forging
- Heat Treatments
- Machining

  - Surface hardening
  - Surface softening
  - Residual stresses
  - Microstructure transformations
  - Surface residues

Quality
  - Uniformity
  - Repeatability

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

Surface Preparations & Controls
• Cleaning baths
• Mechanical preparations
• Thermo-chemical treatments

Gaseous Nitriding

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

Quality
Uniformity
Repeatability

SUPERIOR

risks of LOW
1. Introduction - Context

Surface Preparations & Controls

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

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
1. Introduction - Context

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

- Thermo-chemical treatments: controlled layer (nature, thickness)
  - Oxidization
  - Phosphating (Zn, Mn)
  - …

⇒ Surface homogeneity visual control

⇒ Protection from (heterogeneous) surface reactions
⇒ Activation of the NH₃ decomposition
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$_4$Cl
  \[ NH_4Cl(aq, s) \rightarrow HCl(g) + NH_3(g) \]

⇒ Heating stage: atmosphere of Acids + N-adsorption
2. Experiments

- **Material**: 33CrMoV12-9
  - 17 x 13 x 5 mm³
  - Austenitized @ 920 °C, 90 min
  - Oil quenched
  - Tempered @ 640 °C, 1 h

- **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 (O₂)
  - Urea / NH₄Cl
    - 200 mg
    - Neutral atmosphere

- **Gaseous Nitriding**:
  - Thermogravimetric analyser (Setsys Evo.)
  - Vacuum Stages
  - Heating/Cooling @ 10 °C.min⁻¹ under N₂
  - 520 °C, 5 h, K_N 3.7 atm⁻¹/²
  - NH₃-N₂-H₂ (200 mL.min⁻¹)

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.32</td>
<td>2.97</td>
<td>0.84</td>
<td>0.28</td>
<td>0.55</td>
<td>bal.</td>
</tr>
</tbody>
</table>

- **Sample preparation**:
  - Degreased
  - Rinised in water
  - Dried in alcohol
3. Results

0. The reference

- Compound layer: 10 µm

Reference

- Compound layer: 10 µm / 105 min / 6.7 mg

- Effective depth: 135 µm

- HV0.2
3. Results

a. Influence of water-dissolved oil contaminations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass gain after nitriding (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>10.89 ± 0.33</td>
</tr>
<tr>
<td>Oil 1 vol.% - a</td>
<td>5.39 (49.5 %)</td>
</tr>
<tr>
<td>Oil 1 vol.% - b</td>
<td>5.98 (54.9 %)</td>
</tr>
<tr>
<td>Oil 1 vol.% - c</td>
<td>4.16 (38.2 %)</td>
</tr>
<tr>
<td>Oil 5 vol.% - a</td>
<td>1.07 (9.8 %)</td>
</tr>
<tr>
<td>Oil 5 vol.% - b</td>
<td>5.51 (50.6 %)</td>
</tr>
</tbody>
</table>
3. Results
   a. Influence of water-dissolved oil contaminations

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3. Results

a. Influence of water-dissolved oil contaminations

i. Oil 1 vol.%

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

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**Graph 1:**
- Reference
- B
- A

**Graph 2:**
- Reference
- P01
- P02
- P03

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**Images:**
- Metallic aspect
- Grey mat aspect
3. Results

a. Influence of water-dissolved oil contaminations

ii. Oil 5 vol.%

![Compound layer](image)

![Graph](image)
3. Results

b. Influence of pre-oxidization (O$_2$, 350 °C, 1h)

![Graph showing influence of pre-oxidization on mass gain](image)
3. Results

b. Influence of pre-oxidization (O$_2$, 350 °C, 1h)
3. Results

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

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

b. Influence of pre-oxidization (O₂, 350 °C, 1h)

![Graph showing the influence of pre-oxidization on mass gain over time.](image)

- Reference
- 1 vol.% - Pre-Ox.
- 5 vol.% - Pre-Ox.
- 25 vol.% - Pre-Ox.
- 100 vol.% - Pre-Ox.

« Compound layer »
3. Results

c. Influence of urea

![Graph showing the influence of urea on the activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy.](image)

- **Reference**
- 1 vol.%
- 5 vol.%
- 20 vol.%

![Bar chart comparing final mass gain for different urea concentrations.](chart)

- **As nitrided**
- **Urea**

0 2 4 6 8 10 12 0 60 120 180 240 300

**Mass gain (mg)**

**time (min)**

« Compound layer »
3. Results

c. Influence of urea

![Graph showing the influence of urea on mass gain and hardness versus time and depth. The graphs depict the mass gain over time for different urea concentrations (1 vol.%, 5 vol.%, 20 vol.%) and the hardness distribution over depth for the reference and urea-treated samples. The graph indicates a decrease in mass gain with increasing urea concentration and a corresponding increase in hardness depth, suggesting an improvement in the nitriding process.]
3. Results

d. Influence of NH$_4$Cl

![Graph showing the mass gain versus time for different concentrations of NH$_4$Cl activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy.](image)

- Reference
- 1 vol.%
- 5 vol.%
- 5 vol.% - NH$_4$Cl
- 20 vol.% - NH$_4$Cl

«Compound layer»

![Bar chart showing the final mass gain (mg) for different NH$_4$Cl concentrations.](image)
3. Results

d. Influence of NH$_4$Cl
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

![Graph showing mean stress (MPa) vs. depth (μm) for different treatments: Reference, Oil - 5 vol.%, 5 vol.% - Urea, 5 vol.% - Pre-Ox., and 5 vol.% - NH₄Cl.](image)
3. Results

e. Pre-treatments & residual stresses

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$^{-1/2}$)

![Graph showing the relationship between oil volume percentage and mass gain (mg). The graph includes lines for Reference, NH$_4$Cl, Pre-Ox., Urea, As nitrided, and a shaded area representing an industry range.]
4. Conclusion (nitriding 520 °C, 5 h, K\textsubscript{N} 3,7 atm\textsuperscript{-1/2})

- In-situ pre-treatment:
  - Urea
  - Oxidization (thickness layer dependence)
  - NH\textsubscript{4}Cl

- Advantage:
  - In-situ (during the heating stage)
  - NH\textsubscript{4}Cl
    - Decomposition into NH3
    - Acidic cleaning/sanding

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**Reference**

- vol.%
- 1-vol.%
- 5-vol.%
- 25-vol.%
- 100-vol.%

**Final mass gain (mg)**

- NH\textsubscript{4}Cl
- Urea
- Pre-Ox.
- As nitrided

**Effective depth (µm)**

- 0
- 100
- 150

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Thank you for your attention!