On the Performance of Coated Type 304 Stainless Steel to Combat Metal Dusting Corrosion in the Petrochemical Environment

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Background

- SA enjoyed an insignificant share of the recent commodity booms
- Worldwide recession, slump in demand for commodities and falling prices calls for change
- Strategic investment in assets to maximise long term growth
- Beneficiation projects – enhance value of exports, localise imports & create sustainable jobs
- R&D, Innovation & High-level engineering and scientific competence needed
- The plan is to transform SA from a resource to knowledge economy
To lead a global revolution in advanced metals generating significant export income and new industries for South Africa while reducing environmental impact.

**Enabling Platform of Projects and Partnerships**

**LMDN**
- Lighter, functional alloy materials for the automotive and aerospace industries
  - Titanium, Aluminium

**PMDN**
- Value-added PGM products (autocatalysts, PGM coatings, etc.)
  - PGM’s and Gold

**NMDN**
- Beneficiation of nuclear materials used in nuclear reactors
  - Zirconium, Hafnium, Tantalum, Niobium

**FMDN**
- High-performance materials for energy, petrochemical and transport sectors
  - Iron, Nickel, Chromium

**Additional Resources**
- CSIR: See our future through science
- MINTEK: Specialists in mineral and metallurgical technology
- NECSA: We’re in your world
Key Objectives - FMDN

- Improve the competitiveness of existing industries with growth potential in aerospace, advanced manufacturing, chemicals, advanced metals, mining
- Facilitate the development of R&D-led new targeted industries
- To research, develop and produce advanced ferrous alloys for application in the critical sectors (such as mining, energy, construction, transportation, etc.) of the South African economy
Research Focus Areas

• **Thermomechanical processing** of carbon/alloy steels, stainless steels and Ti-alloys with the primary aim of:
  - Optimizing process (casting, hot rolling, heat treatments, cold rolling)
  - Improving product quality (bainite in steels, texture in SS, Al and Ti Alloys)
  - Developing new products (advanced steels, new Ti-alloys)

• **Focus areas**
  - Texture development and optimisation (XRD, SEM-EBSD)
  - Grain size and microstructure control (SEM, TEM etc.)
R&D Projects – Ferrous Metals

Conducts Materials-related R&D in Support of the Mining and Metals-related Industries in South Africa

End Users

Product Development

Advanced Alloy Development

Advanced Processing Techniques

Ferrous Metals (Fe (Iron), Mn, Ni, Cr, Si)

Foundry Technology
R&D Projects – Ferrous Metals

**Lightweight Steels - Transportation**
- Development of a Lightweight Alloy – Bainitic Steels
- Comparative Tribological Behaviour of Pearlitic Alloys for Railway Wheel

**Materials for Energy and Extreme Environments**
- Modelling of Metal Dusting Corrosion to Enable Early Detection and Continuous Monitoring
- Development of Functionally-graded Coating for Prevention of Metal Dusting Corrosion

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**Diagram Description**
- **Mechanisms**
  - Thermodynamics
  - Kinetics
  - Catalysis
- **Examination tools**
  - FEG SEM
  - TEM
  - XRD
- **Exposure conditions**
  - Laboratory Plant

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**Questions and Answers**

Lightweight Steels - Transportation

- Development of a Lightweight Alloy – Bainitic Steels
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Materials for Energy and Extreme Environments

- Modelling of Metal Dusting Corrosion to Enable Early Detection and Continuous Monitoring
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**Image Description**

- Rim
- Plate
- Hub
- Flange
- Thread

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**Technical Details**

- **Mechanisms**
  - Thermodynamics
  - Kinetics
  - Catalysis
- **Examination tools**
  - FEG SEM
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**Data and Analysis**

- **Mechanisms**
- **Examination tools**
- **Exposure conditions**
Caused by the tendency to form graphite, and the Gibbs free energy for the process is:

$$\Delta G = -RT \ln a_C$$

It often occurs in synthesis gas mixtures of CO-H$_2$ through the following reaction:

$$CO + H_2 \leftrightarrow H_2O + C$$

$$(a_C)_1 = K_1 \frac{pCO \cdot pH_2}{pH_2O}$$

$$\log K_1 = \frac{7100}{T} - 7.496$$

- **Environment:** Gas phase, carburising and reducing
- **Temperature:** Usually 400 - 800°C
- **Form:** Localised or general pitting
- **Product:** Graphite mixed with metal, carbides and oxides
Schematic outline of the secondary reformer train at PetroSA GTL Refinery showing in red dotted circles where metal dusting mostly occurs.
Metal Dusting Examples – Industry

- Ferrules (alloy 800) exposed in a metal dusting environment (PetroSA)
- Disintegration of metals and alloys into a dust of graphite and metal particles after carbon ingress and over-saturation

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Al</th>
<th>C</th>
<th>Ti</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>19-23</td>
<td>0.15-0.6</td>
<td>0.06-0.1</td>
<td>0.15-0.6</td>
<td>30-35</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
Metal Dusting Examples – Industry

Metal dusting in a heater tube (HK 40) by reduction gas at 600°C

Alloy 800 parts in a reduction furnace

Alloy 800 in synthesis gas at about 600°C
Two types of metal dusting corrosion:

**Fe-based Alloy**

**Ni-based Alloy**
The main steps of the MD on pure iron and Fe-based alloys
The effect of carbide-forming elements on the metal dusting rate of similar stainless steel alloys was investigated.

Austenitic: Type 304 vs 321 (Type 304 + Ti
Type 316 vs 316Ti (Type 316 + Ti)
Ferritic: Type 430 vs 441 (Type 430 + Ti and Nb)

The degree of metal dusting attack was characterised by weight loss, optical microscopy, scanning electron microscopy, transmission electron microscopy, x-ray diffraction and Raman spectroscopy.

Materials Exposed to Metal Dusting Environment

7 day exposure

30 day exposure

Coking associated with the 30 day exposure
Fe and Ni Based Alloys Tested

Parameters: 25CO-70H₂-5H₂O (vol.%), \( a_C = 5.50 \) and \( p_{O_2} = 3.47 \times 10^{-25} \) atm

Alloy 600

Alloy 601

Alloy 800

Before

After 24 h

After 168 h

After 336 h

336 h (Coke removed)
Alloy 800 after 336 h exposure

**XRD Analysis:**
Alloy–γ, α-CrFe and Cr$_{23}$C$_6$
Coke –Fe$_3$O$_4$ and graphite; C

Cr$_{23}$C$_6$ precipitation results in the depletion of Cr to extent that the protective chromia scale is not maintained, and therefore Metal Dusting occurs (Röhnert et al.).
Current Project

- **Fe-based alloy: Alloy 800** is an austenitic alloy of Fe containing 32Ni, 21Cr and about 0.1C.

- **Ni-based alloys:** Alloys 600, 601, 602CA, 693, and HR 160 strengthened by carbides, with oxidation resistance provided by oxides of chromium (Cr) and aluminium (Al)

- Fe-based alloy was found to be less resistant to **Metal Dusting Corrosion (MD)**,
  - and was therefore used as one of the materials to mitigate metal dusting by being coated on lesser MD resistant material/s
Powder Production

- Water atomisation
- Gas atomisation
- Mechanical alloying

Gas atomiser

Retsch PM 100 milling machine
Coating Process and Metal Dusting Test Rig

- **Fe-based alloy:** 304 Stainless steel coated with 50Ni/50Cr material
  - Surface preparation: Degrease and grit blast
  - Coating thickness: 200µm
  - Coating method: High Velocity Thermal Spray System (HVOF)

**Parameters:** 25CO-70H₂-5H₂O (vol.%) @ 650°C

\[ a_C = 5.50 \text{ and } p_{O_2} = 3.47 \times 10^{-25} \text{ atm} \]
Coke Deposits Analyses

SEM – SE image

EDX spectrum

XRD Pattern of Coke deposits
Coke Deposits Analyses

TEM image

EDX spectrum

Fe, Ni, Cr Particles
Raman spectroscopy confirmed the existence of nano-crystalline graphite showing D- and G-peaks.
Concluding Remarks

- Develop a coating material resistant to the metal dusting extreme environments
- Type 304 performed significantly better probably due to a higher chromium content.
- The effect of Mo is unknown, but is under investigation
- Die filaments in the coke in austenitic alloys contained predominantly Multiple Wall Carbon Nanotubes (MWCNT), whereas the coke in ferritic alloys contained more solid filaments
- A better mitigating approach is needed to reduce /eliminate this attack on plant components
- Type 304 stainless steel coated with 50Cr/50Ni coating showed resistance to metal dusting at 650°C.
Future Work

- Develop a coating material more resistant to the metal dusting extreme environments
- Modelling of Metal Dusting Corrosion to Enable Early Detection and Continuous Monitoring
- Further characterisation of coated Type 304 stainless steel (effect of coating thickness, etc.)
- Using the Mintek-designed Metal Dusting Simulation Rig
- Thermodynamic Stability of the Coatings used under Extreme Thermomechanical Conditions
- Development of Functionally-graded Coating for Prevention of Metal Dusting Corrosion
Possible Collaborative Areas

- Research partner into materials for energy, extreme environment and transport
- Quantification of Microstructure of Steel, Aluminium and High Chromium Cast Iron via Modelling (Modeling and Simulation)
- Development of corrosion resistance materials and coatings
- Skills development - Possible student exchange (Visit to US)
- Visit to South Africa – Special lecture/workshop/seminar
- Participate on AMI-FMDN 2016 Conference (Key Note Speakers)
- Part of the Advisory Committee (Powder, Energy and Transportation)
- Thermodynamic Stability of the Coatings used under Extreme Thermomechanical Conditions
Thank You
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