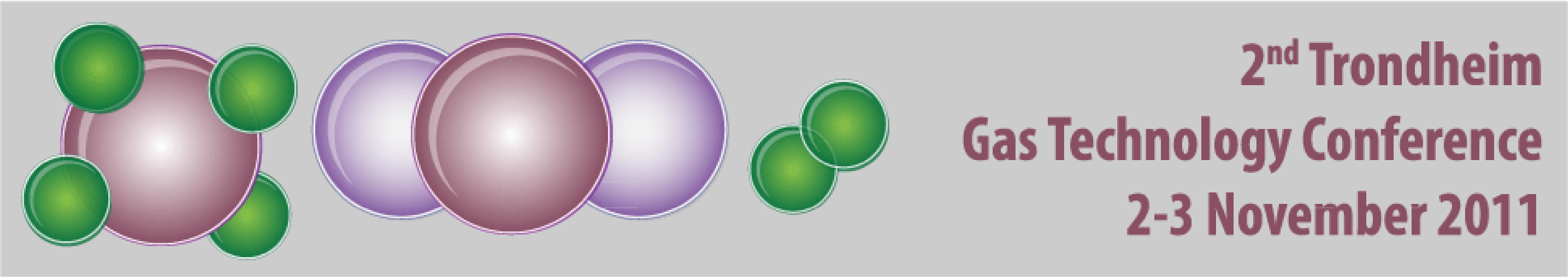
Metal dusting corrosion initiation in conversion of natural gas to synthesis gas



Professor Hilde Venvik
Department of Chemical Engineering, NTNU
2011-11-03

- inGAP is a National Centre of Research-based Innovation (SFI), appointed by the Norwegian Research Council.
- inGAP's vision is value creation in natural-gas processes through rational design of processes and products based on atomistic and mechanistic insight in catalyst and reactor parameters under operative conditions
- “inGAP has very successfully developed research on natural gas processing in the international frontline and maintains excellent contacts and technology transfer with partner industries”;
  - 2010 mid-term evaluation of all CRI (SFI) centres.
- inGAP’s partners include UiO, SINTEF, Statoil, Borealis, Ineos and Halldor Topsøe AS (Denmark).

Acknowledgement

- **PhD student P.V.D.S. (Daham) Gunawardana**, Professor Anders Holmen, Professor De Chen, Department of Chemical Engineering
- **Senior scientist John Walmsley**, Ingvar Kvande, SINTEF Materials and Chemistry, Trondheim, Norway
- Thoa Thi Minh Nguyen, Halldor Topsøe AS, Kgs. Lyngby, Denmark.
- Jorun Zahl Albertsen, Bente Krogh, Emil Edwin, Iver Espen Pedersen, Statoil Research Centre, Trondheim, Norway 4, Arkitekt Ebbells vei 10, 7005.
- Professor Unni Olsbye, University of Oslo, Norway

Outline

- What is metal dusting?
- Important existing knowledge
- Our approach to *metal dusting*
- Recent results in *metal dusting*
- Conclusions and outlook

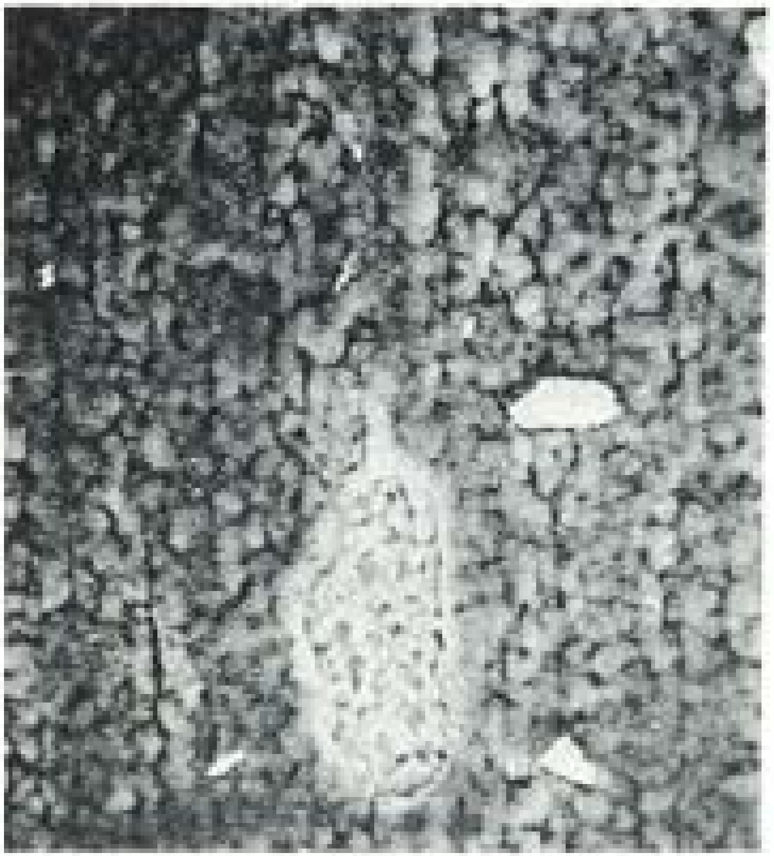


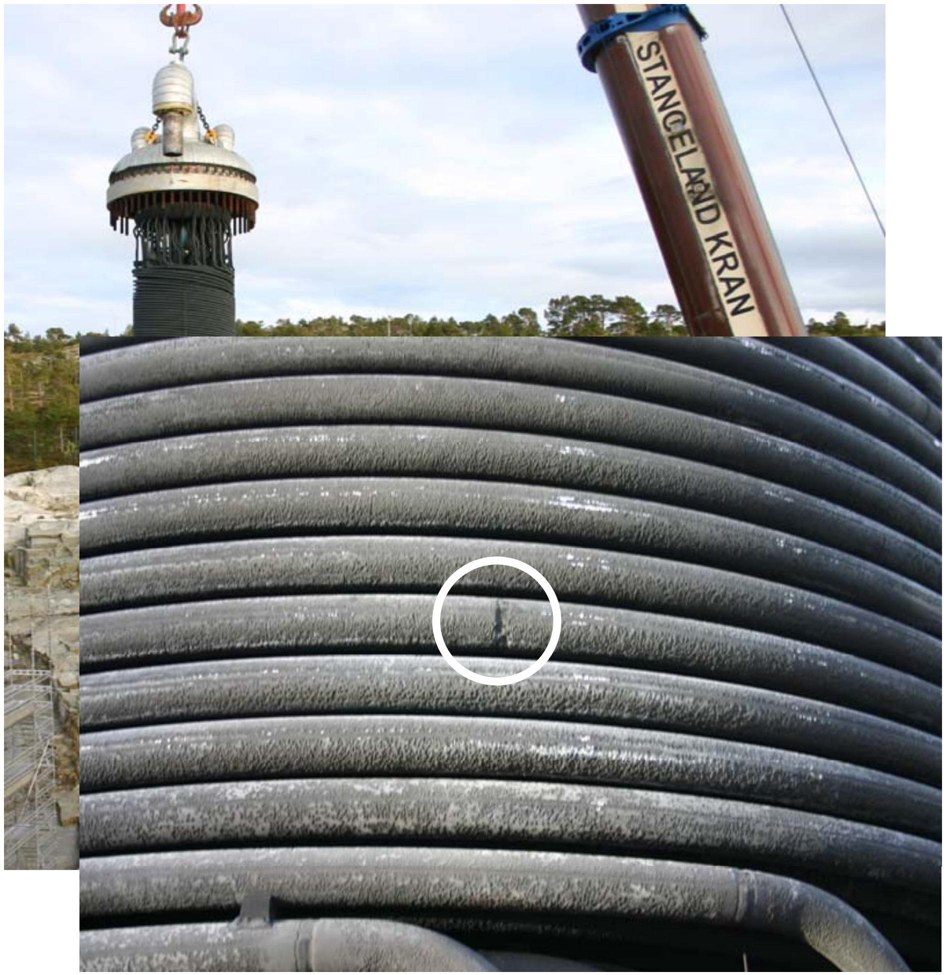
Figure 5. Micrograph of an oxidised foil (×500).

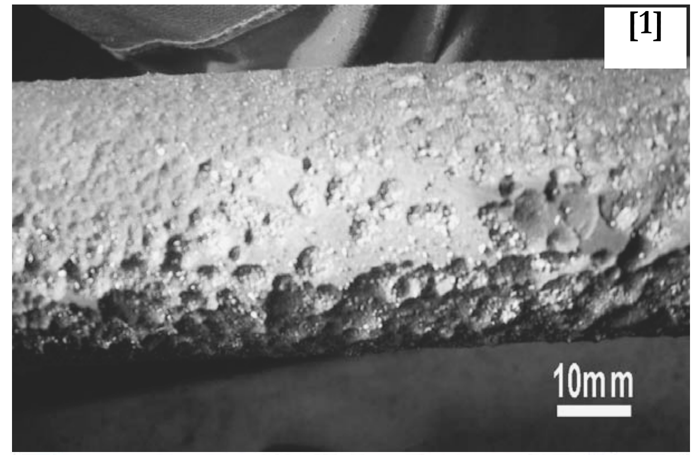
Koksdannelse ved cracking,
A. Holmen, O. A. Lindvåg,
SINTEF Kjemi, 1980

Metal dusting corrosion:

- ✓ A potentially catastrophic materials degradation phenomenon
- ✓ Affects process equipment applied in natural gas conversion at elevated temperature
- ✓ Occurs due to the decomposition of carbon containing molecules to form carbon on the inner surfaces of the equipment
- ✓ Proceeds by dissolution of carbon in the alloy, carbide formation and carbide decomposition
- ✓ Eventually turns the alloy into fine particles

Metal dusting @ Statoil Tjeldbergodden methanol plant

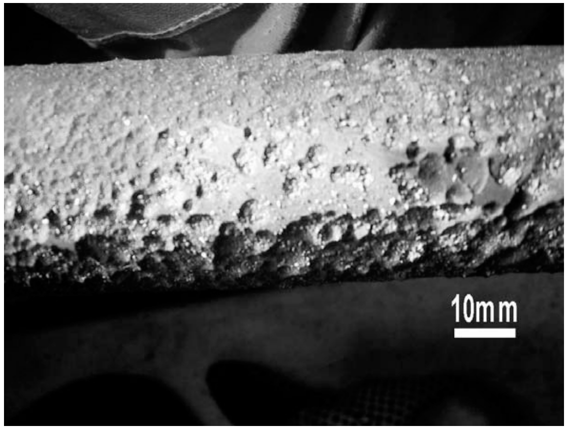




1. Experimental and theoretical investigations of metal dusting corrosion in plant exposed nickel-based alloys. J.Z. Albertsen; PhD thesis at NTNU, 2007:05.
2. Corrosion by carbon and nitrogen - Metal dusting, carburization and nitridation; Woodhead Publishing Limited, Cambridge.

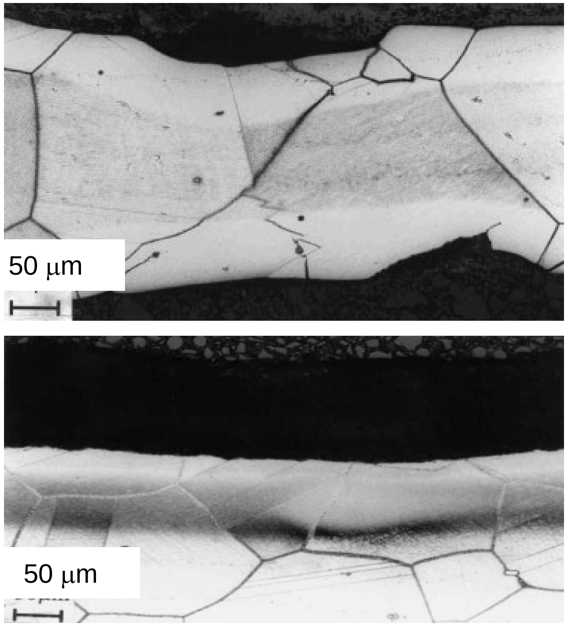
What is metal dusting?

1. **Carbon formation on inner surfaces**
2. **Carbide phase formation and decomposition cycles within the material**
   - hemispherical pits
   - uniform attack
3. **Material is gradually turned into a dustlike corrosion product**
   - also contains carbides and oxides



Metal dusting in a drain line of a Ni based alloy located in a steam superheater

Example of pit formation



Metal dusting in a heat exchanger for synthesis gas made by a large grained alloy 800

Top: wall segment

Bottom: Uniformly attacked surface with coke and carburized zones

Which processes and units can be affected by metal dusting?

- Syngas production for ammonia, methanol/DME, GTL, steam crackers, high-temperature fuel cells
- Could save $500 million to $1.3 billion per year in the hydrogen industry if prevented
  – "Increased industrial productivity by enabling machinery to function with fewer maintenance shutdowns. Such savings will become increasingly important as hydrogen is used more as a source of energy " (Argonne national laboratory, US)
- Plant conditions natural gas reforming:
  – Reduction of costs is a natural target
  – Decrease the steam content in the process gas while increasing the overall reformer capacity
  – Steam/carbon ratio decreased $\Rightarrow$ Risk for metal dusting in heat recovery units will be higher

The thermodynamic driving force

- Carburizing atmosphere
- High carbon activity (a_c>1)
- Critical T-range: 400-1000 ˚C

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

$$a_{C,1} = K_1(T)\cdot\frac{p_{H_2}p_{CO}}{p_{H_2O}}$$

$$2CO \leftrightarrow C + CO_2$$

$$a_{C,2} = K_2(T)\cdot\frac{(p_{CO})^2}{p_{CO_2}}$$

$$CH_4 \leftrightarrow C + 2H_2$$

$$a_{C,3} = K_3(T)\cdot\frac{p_{CH_4}}{(p_{H_2})^2}$$

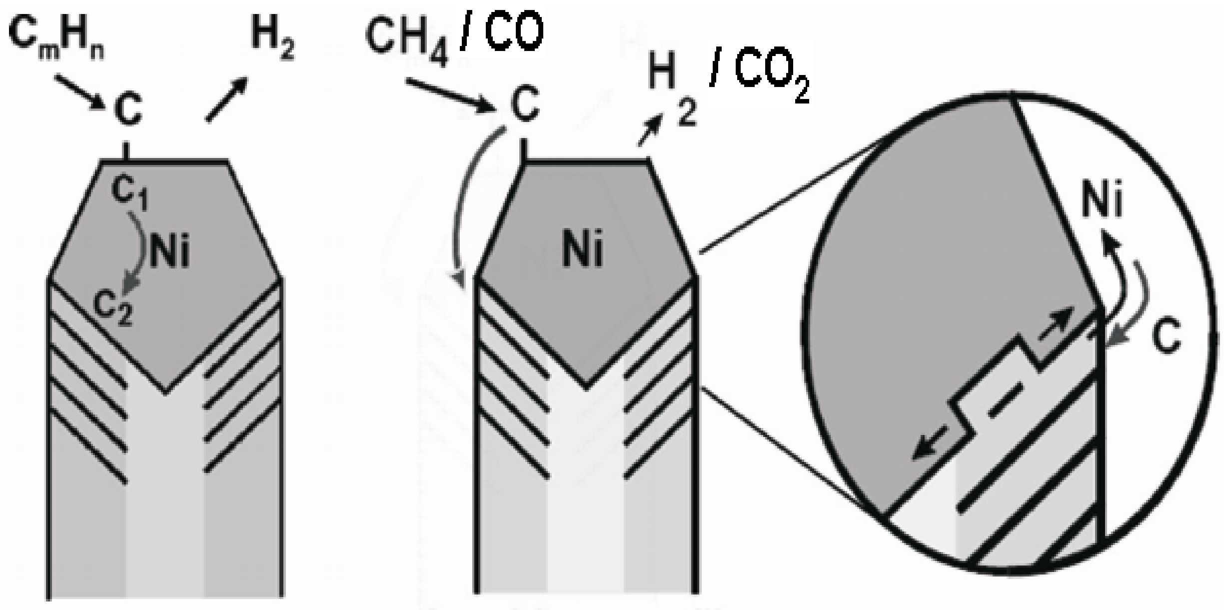
$$CO + H_2O \leftrightarrow CO_2 + H_2$$

$$M_3C \leftrightarrow 3M + C$$

$$M \in \{Ni, Fe, Cr\}$$

The kinetic control of carbon formation

- The extent of carbon formation is determined by the surface on which the carbon forms; i.e. unwanted catalytic reactions
- Metallic phases (particles) known to activate CO (CH_4) and to form carbides; i.e. Ni, Fe, Co, …
- The metals are important in steel/HT-alloys
- Carbon formation analogous to on Ni(Fe)-based catalysts



Carbon formation on Ni observed in situ at Halldor Topsoe AS

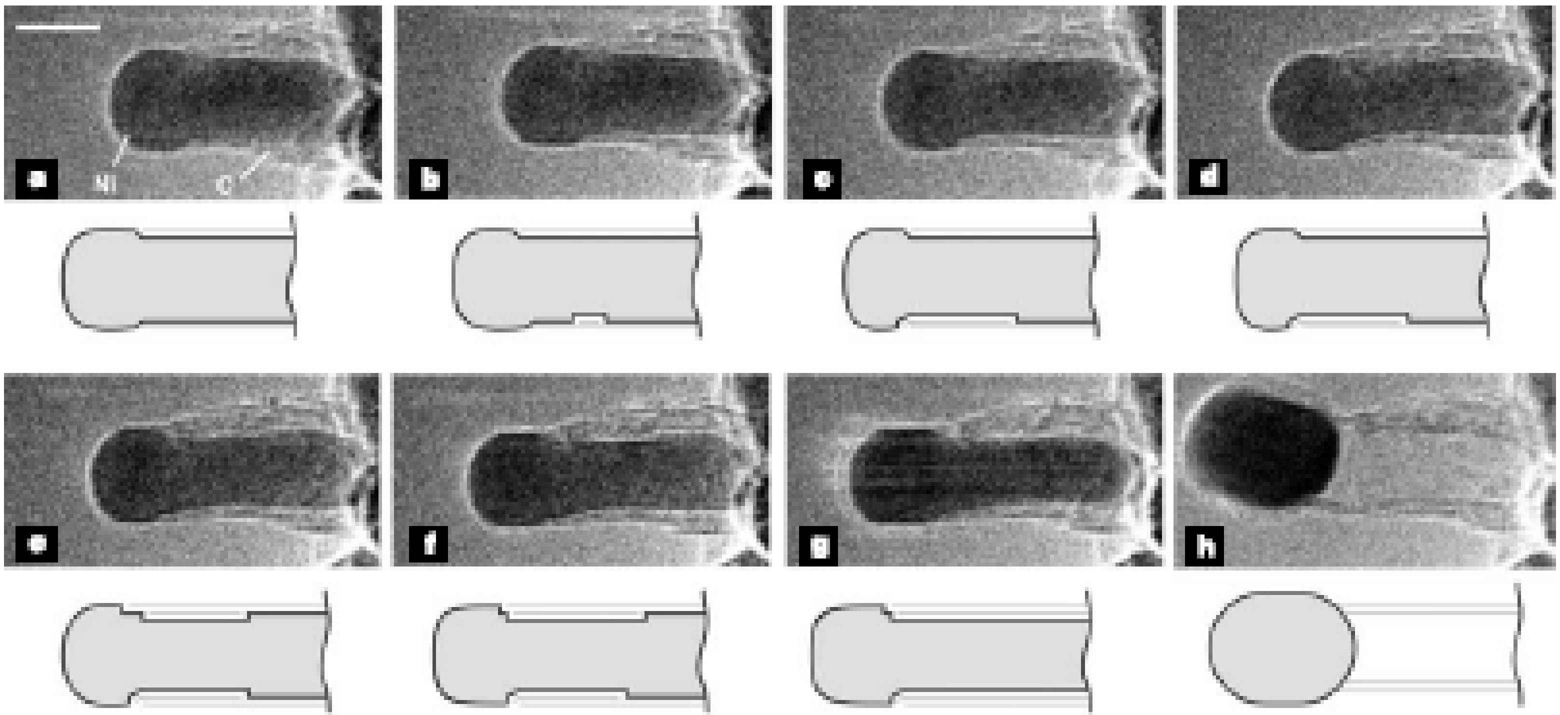
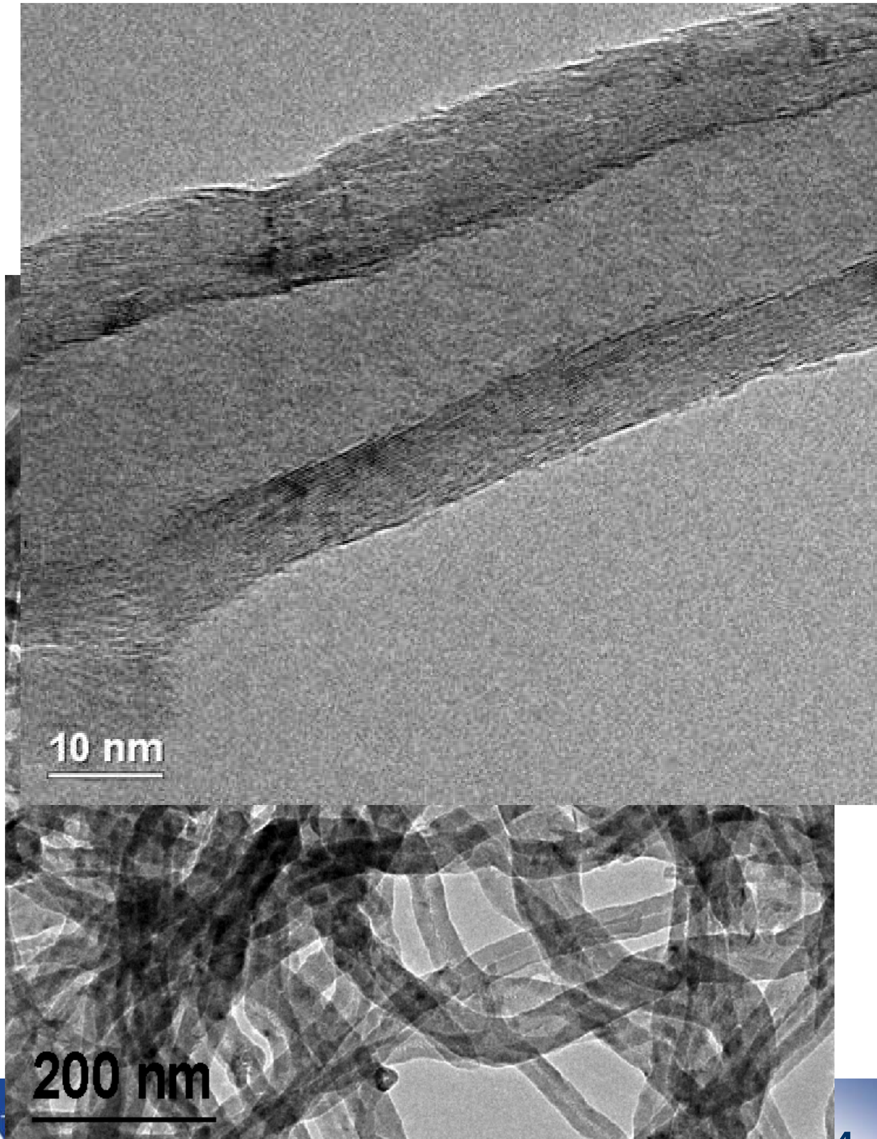
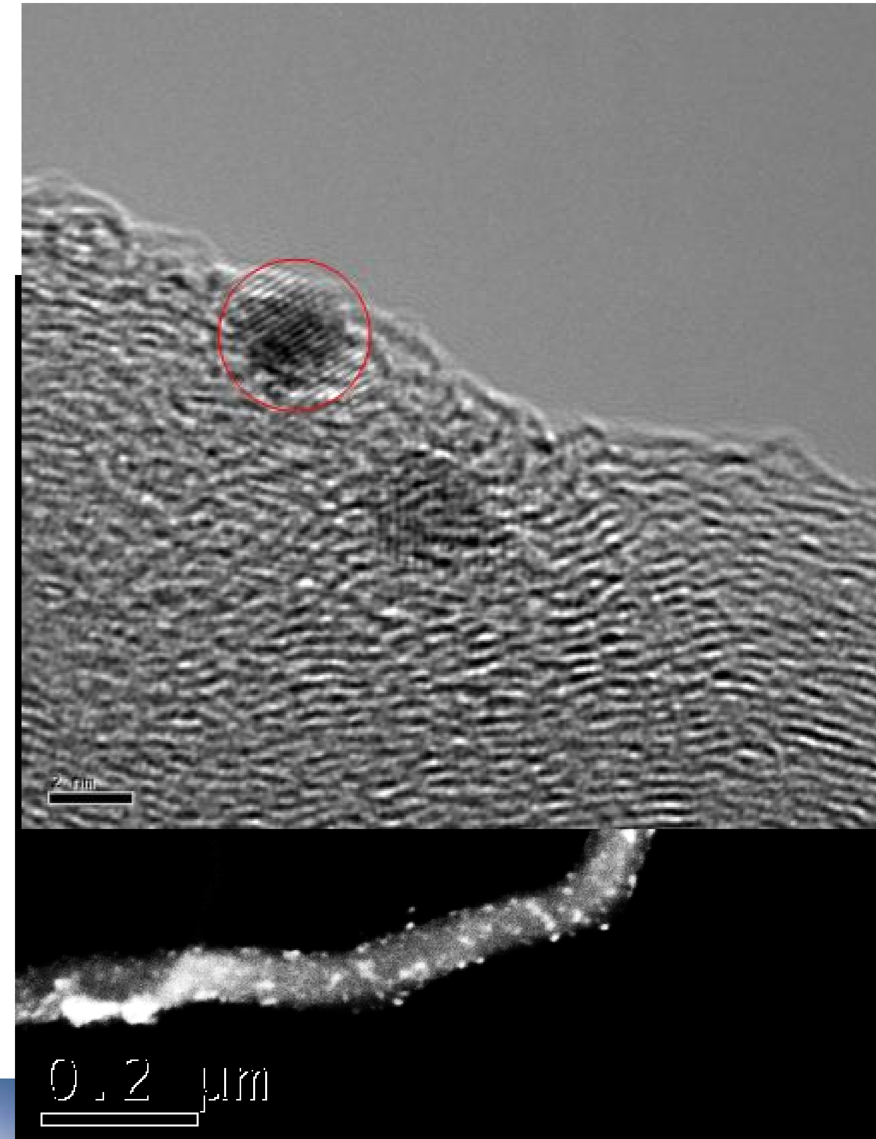


Figure 2 Image sequence of a growing carbon nanofibre extracted from movie N1. Images a–h illustrate the elongation/contraction process. Drawings are included to guide the eye in locating the positions of mono-atomic Ni step edges at the C–Ni interface. The images are acquired *in situ* with CH_4:H_2 = 1:1 at a total pressure of 2.1 mbar with the sample heated to 536 °C. All images are obtained with a rate of 2 frames s^{-1}. Scale bar, 5 nm.

Selective synthesis of CNF/CNT



CNT/CNF as catalyst supports



Metal dusting prevention

- Adjustment or careful selection of process parameters (T, P, C)
- Development of new, metal dusting resistant, alloys
- Application of coatings to protect the underlying metal/alloy matrix
  $\Rightarrow$ (Cr-, Al- surface oxide layer)
- Mixing process gas with low concentration of sulfur compounds (H2S, CS2, (CH3)2S2, etc.)

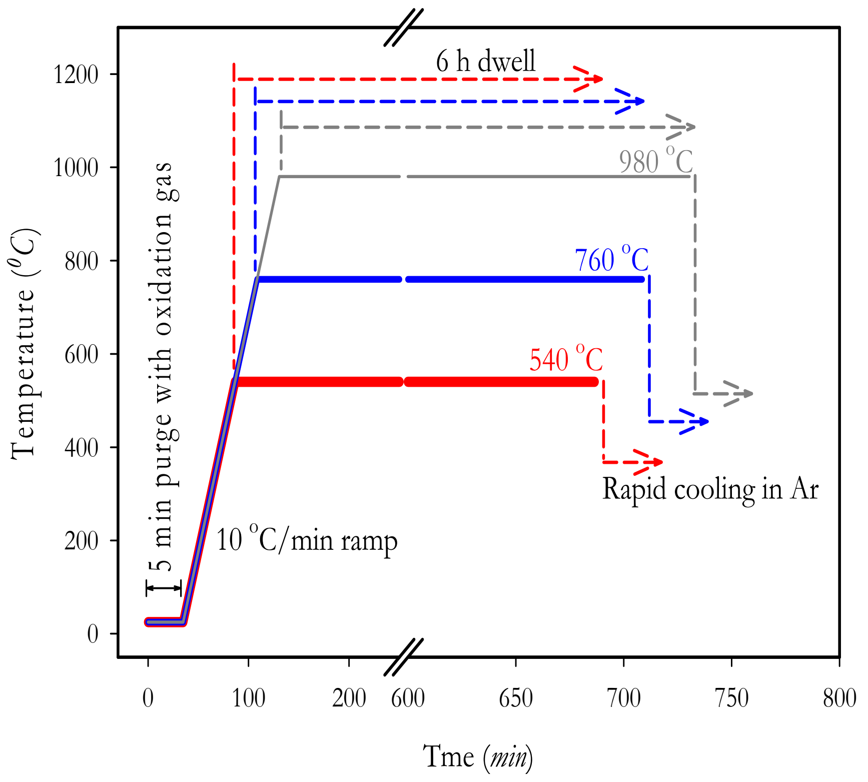
Our (non-metallurgical) approach

Any better predictive tools for the carbon formation is an immediate cash saver, therefore

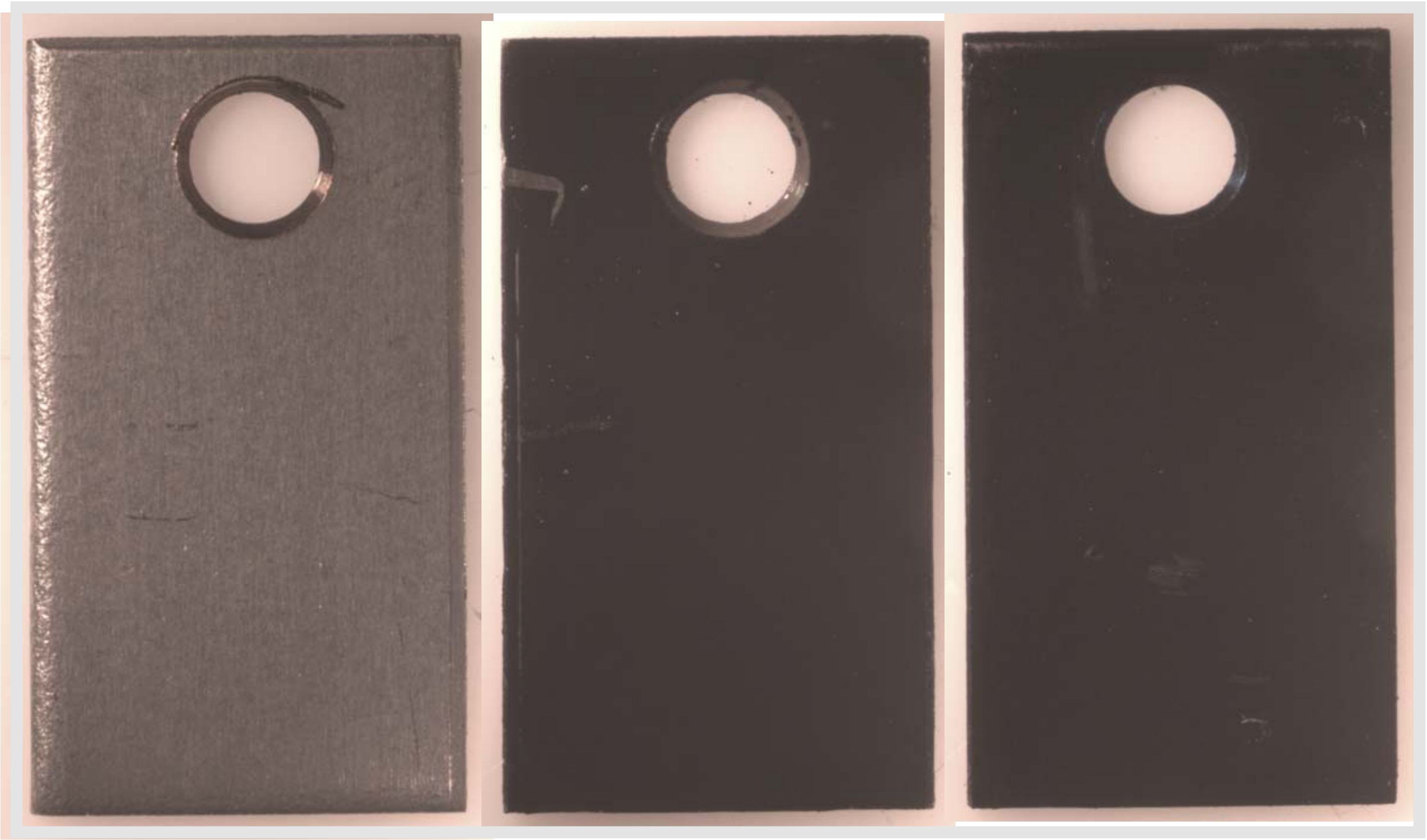
- Understand the initiation of the carbon formation
  - Where does the first carbon form and what is the structure and composition of these “sites”?
  - Can these sites be manipulated_
- Develop experimental procedures that are informative yet representative
  - “Shorten” the phenomenological time scale from months/years to hours/days
  - Control the alloy composition and pretreatment
  - Apply advanced characterization tools

Effect of oxidation pretreatment conditions on a commercial alloy

- Inconel alloy 601:
  (58–63%Ni, 21–25%Cr, balance-Fe with Al, C, Mn, S, Si, Cu)
- As-received and polished samples
- 3 oxidation atmospheres:
  - 100% O_2
  - 0.5% O_2 in Ar
  - 10 % steam – 90% Ar
- Oxidation temperatures:
  - 540 °C - 980 °C
- Initial test in different carburization activity at 550 °C for 20h :
  - 10% CO in Ar (infinite a_c)
  - 10% CO-10%Steam–Ar (finite a_c)



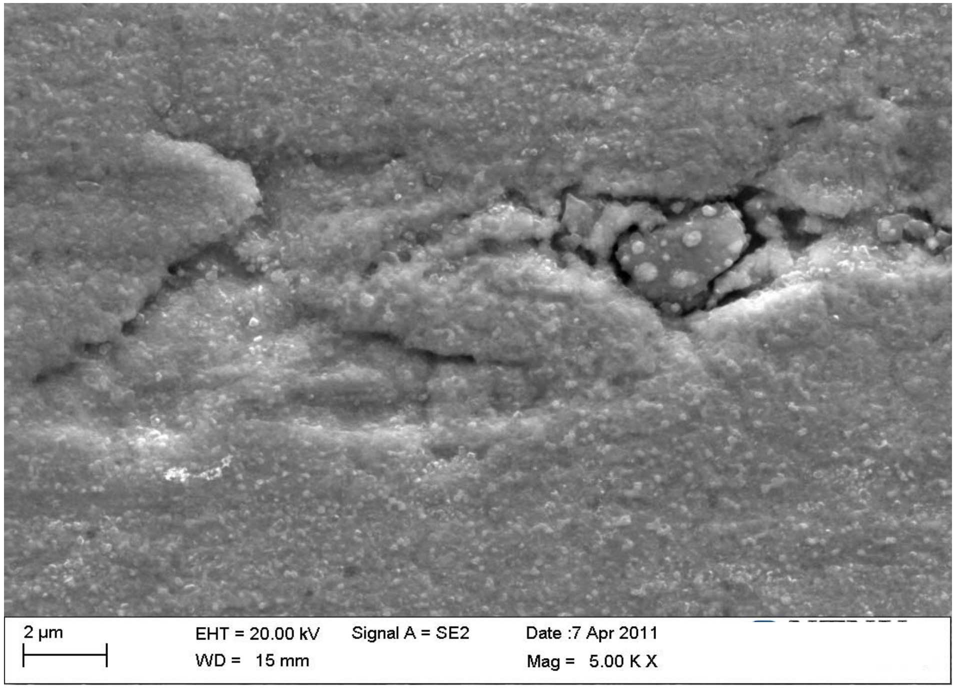
Results

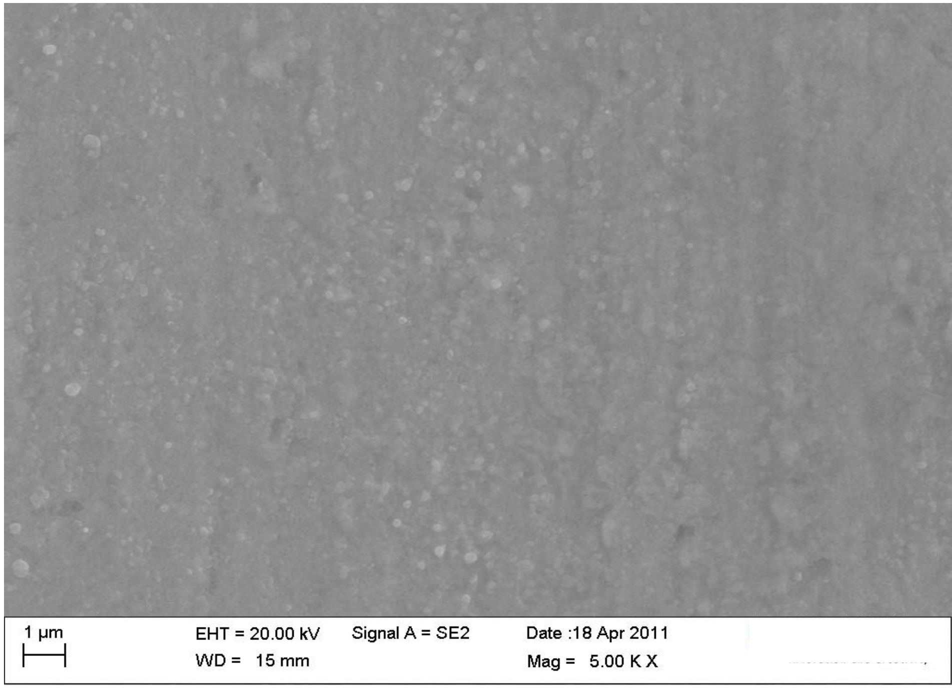


As-received 100% O_2 0.5% O_2 – Ar

All samples subjected to 10% CO in Ar (infinite a_c)

✓ The “harsher” the oxidation conditions the higher the carbon formation





100% O_2 0.5% O_2 – Ar

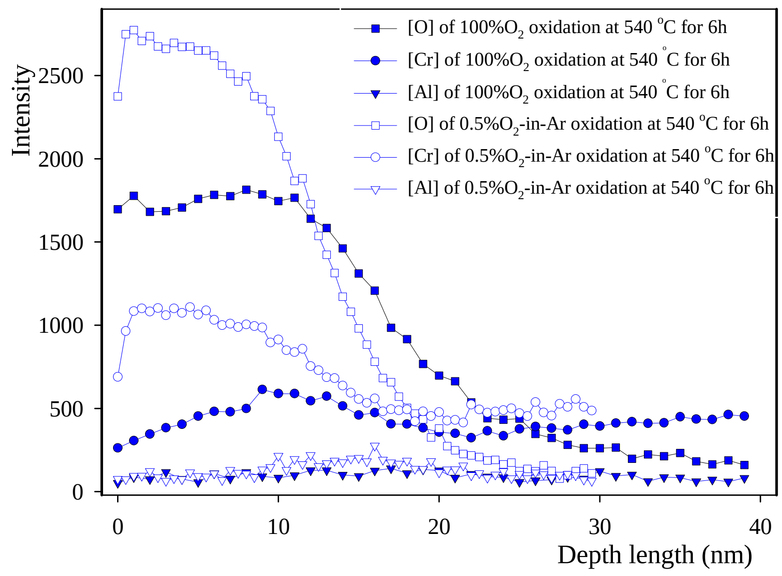
Characterization by scanning electron microscopy (SEM)

- ✓ Oxide surface formed under “harsh” conditions (p-O_2, T) is less dense and with more defects

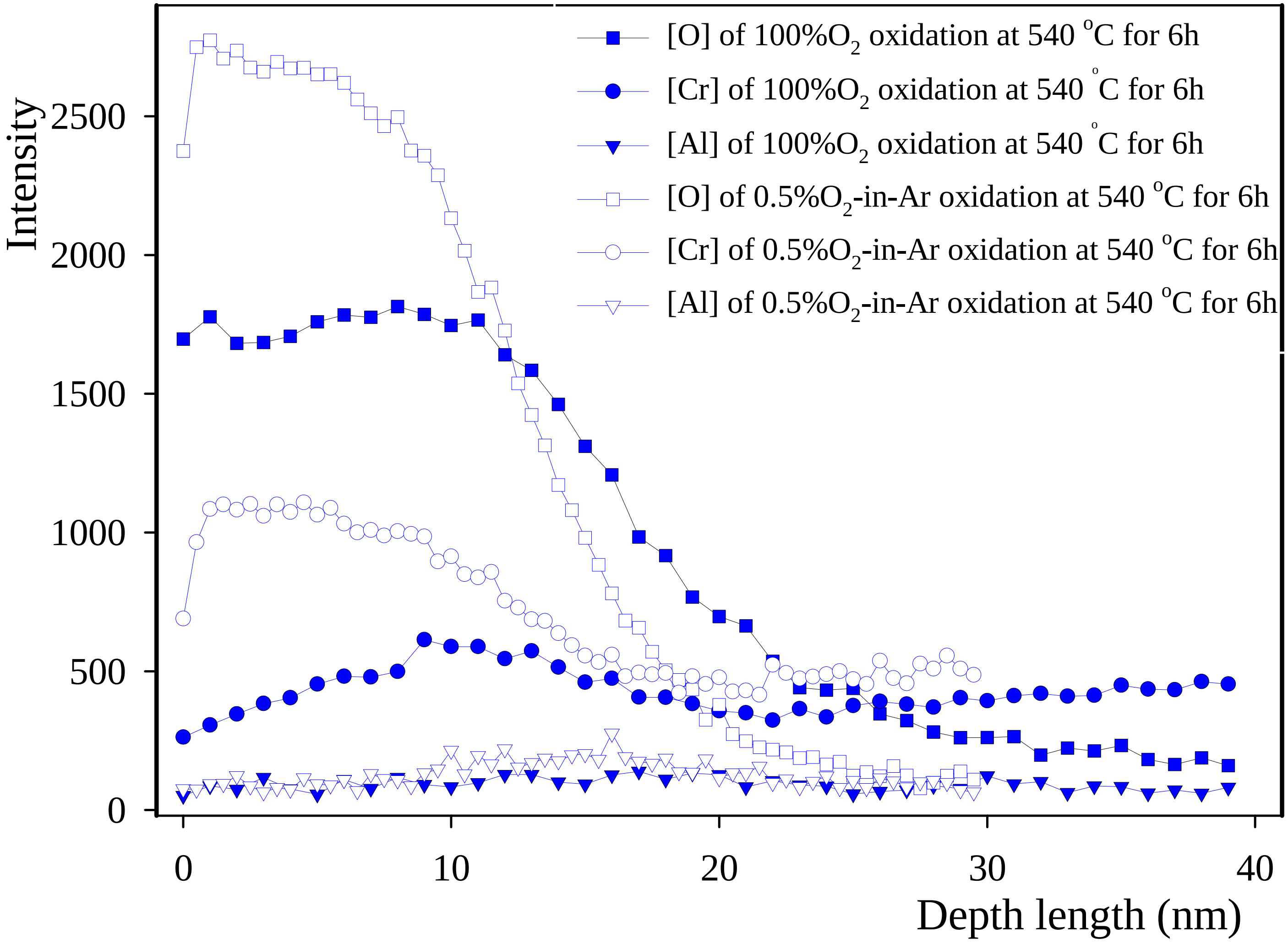
Advanced characterization

- <u>Depth profiling</u> of oxide layer composition and structure by combined Ar sputtering, Auger spectroscopy and SEM

Behavior of polished (1um) surfaces in different oxidation conditions
(Inconel 601)



Behavior of polished (1um) surfaces in different oxidation conditions (Inconel 601)



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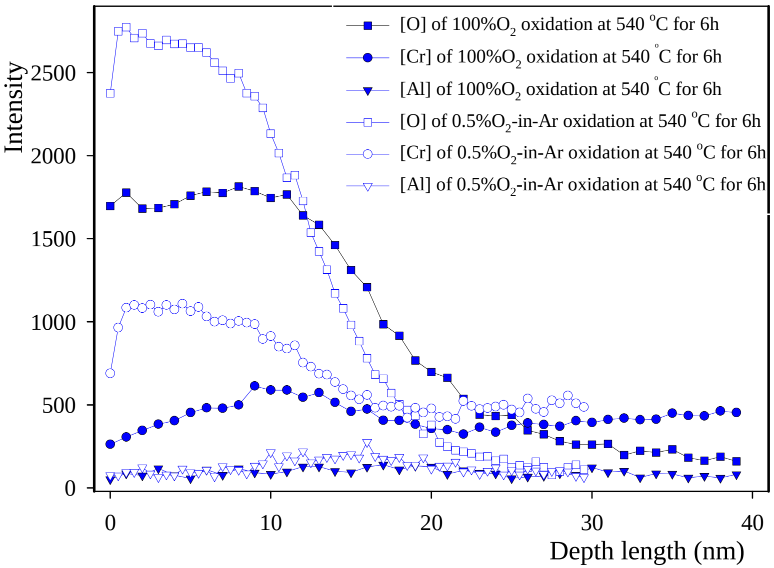
Advanced characterization

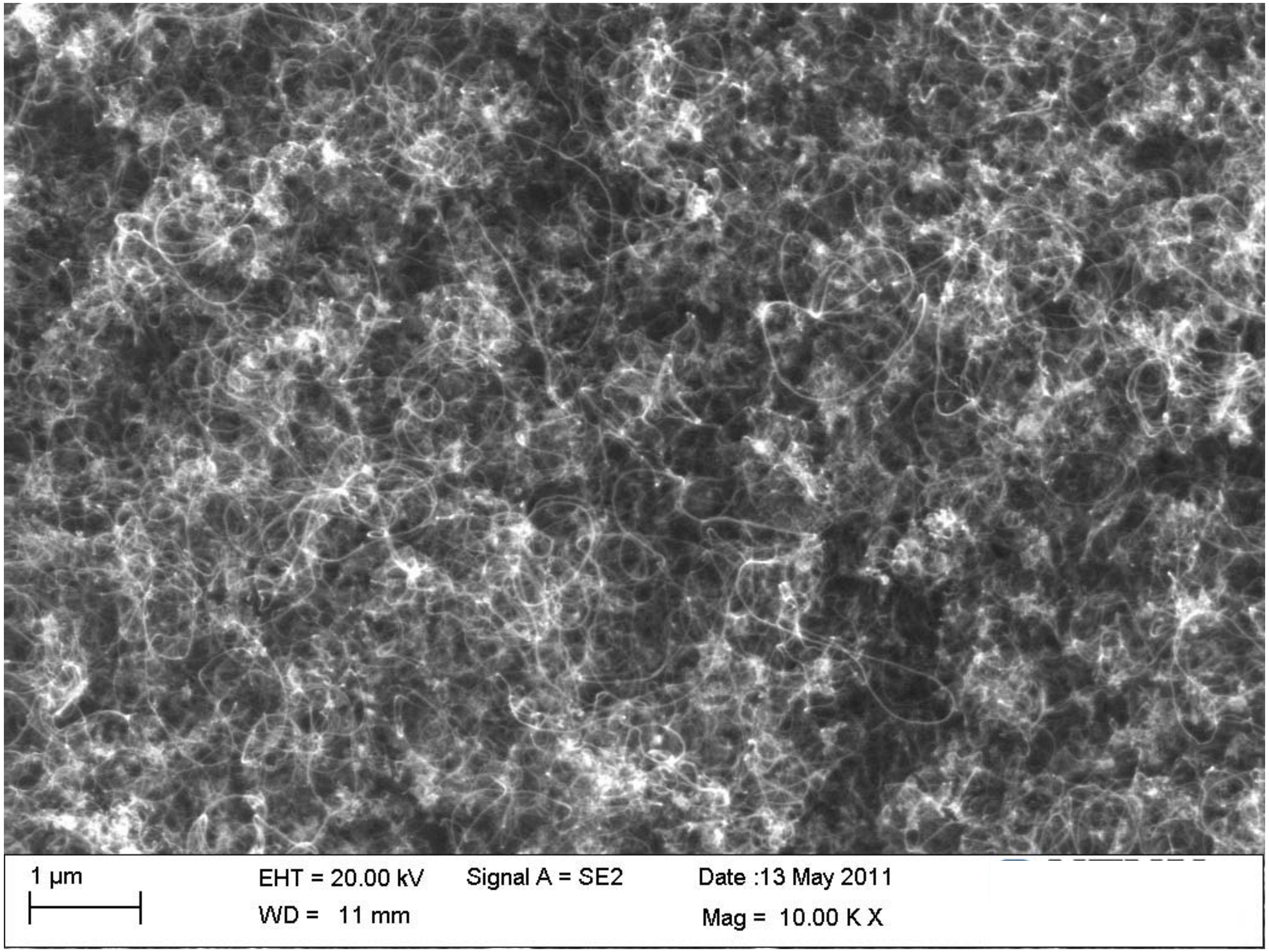
- Depth profiling of oxide layer composition and structure by combined Ar sputtering, Auger spectroscopy and SEM

- Resistance to carbon formati[...] appears correlated with high O and Cr in outer layer

- Results so far inconsistent with respect to Al

Behavior of polished (1um) surfaces in different oxidation conditions (Inconel 601)





- ✓ Carbon formation observed under conditions applied extends from little/no observable carbon to thick deposits of filamentous carbon

Some conclusions

- Preparation/pretreatment protocols are very important
  - Polishing
  - Oxidation conditions
- Dense Cr-containing oxide is more protective
  - Pre-polished samples treated in H_2O/Ar at the lowest temperature appear to have the best resistance
- Actual “catalyst” remains to be identified

Thank you for your attention!