Catalytic phenomena critical to the initiation of metal dusting corrosion

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Catalysis Group – SINTEF – NTNU

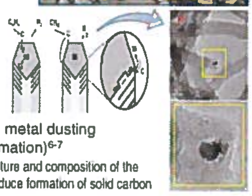
P.V. Daham S. Gunawardana[1], Jihye Hwang[1], John C. Walmsley[2], Hilde J. Venvik[1]

1. Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Sem Sælands vei 4, NO–7491, Trondheim, Norway
2. SINTEF Materials and Chemistry, Sem Selands vei 2A, N-7465 Trondheim, Norway

Introduction

Metal dusting corrosion

- Corrosive degradation process
- A critical issue in the natural gas conversion, resulting from unwanted carbon formation on the inner surface of process equipment[1-3]
  - Carburizing atmosphere (*i.e* a_C>1)
  - Elevated temperature (T > 400 °C)
  - *HT-alloys* containing Fe, Ni, Al, Cr, *etc.*
- The initial stage is analogous to carbon formation on catalysts,[4-5] but less described in the research literature



Objective

- Understanding of the initial stages in metal dusting corrosion (*i.e.* initiation of carbon formation)[6-7]
  - Find possible correlations between the structure and composition of the surface layer (oxide) and its propensity to induce formation of solid carbon

Carbon activity

Carbon formation potential (a_C)

- Under 10%CO in Ar; 100 ml/min (6 L/h)
  - 550 °C at 1 bar for 20 h
  - Reaction: $2CO_{(g)} = C_{(s)} + CO_{2(g)}$ Boudouard (1)
  - Carbon activity: $a_{C_1} \rightarrow$ << *infinite* >>

$$a_{C_1} = K_1(T)\cdot\left[\frac{P_{CO}^2}{P_{CO_2}}\right]$$

- Under 20%CO and 50%CO containing gas mixtures (in H_2, CO_2, H_2O and Ar); 100 L/h
  - 550 °C, 650 °C and 750 °C at 20 bar for 20 h
  - Reactions: $2CO_{(g)} = C_{(s)} + CO_{2(g)}$ Boudouard (1)
    $CO_{(g)} + H_{2(g)} = C_{(s)} + H_2O_{(g)}$ CO reduction (2)
  - Carbon activities: a_{C_1} and $a_{C_2} \rightarrow$ << *finite* >>

$$a_{C_1} = K_1(T)\cdot\left[\frac{P_{CO}^2}{P_{CO_2}}\right] \qquad a_{C_2} = K_2(T)\cdot\left[\frac{P_{CO}P_{H_2}}{P_{H_2O}}\right]$$

Experiments

Samples

- Ni-based industrial alloy (Inconel 601)
  - Bulk composition confirmed by EPMA (Table-1)

As-received / polished
Size: 15 × 8 × 0.5 mm³

Table 1: Inconel alloy 601 Composition basis

Composition basis	Ni	Cr	Fe	Al	Mn	O	Ti
Mass % (average)	60.85	22.71	13.38	1.29	0.80	0.14	0.21

CO / syngas exposures

	Reaction step	Time (h)	Temperature (°C)	P (bar)	CO	H_2	CO_2	H_2O	Ar	N_2	Flow rate (L/h)
1.4	Oxidative pretreatment: in steam-N_2 (Ar)	6	540	1	-	-	-	10	-	90	18 (6)
2.2	Cooling: in N_2 (or Ar)	-	Up to room temp.	1	-	-	-	-	-	100	18 (6)
3.1	CO exposure: in 10%CO-Ar	1–20	550, 650	1	10	-	-	-	90	-	6
3.2	Syngas exposure: With 20%CO	20	550, 650, 750	20	20	25	15	10	30	-	100
3.3	Syngas exposure: With 50%CO	20	550, 650, 750	[illegible]	50	25	15	10	-	-	100

Results and discussion

Figure 1: Effect of water gas shift (WGS) reaction on carbon activity a_C

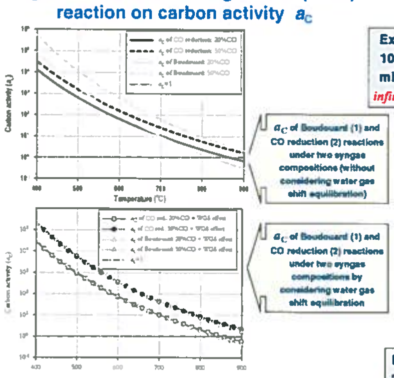


Figure 2: Carbon formation under *infinite* a_C conditions at different time scales

Electron micrographs of CO exposed sample

Polished, oxidized in 10%steam-Ar (@540 °C) and exposed to 10%CO-Ar gas mixture @550 °C and 1 bar (a) 1 h, (b) 2 h, (c) 5 h, (d) 20 h

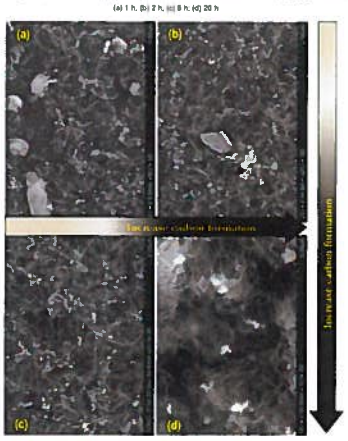


Figure 3: Carbon formation under *infinite* a_C conditions (a_C>>1).

Optical and electron micrographs of CO exposed sample and Auger depth profile of oxidized sample

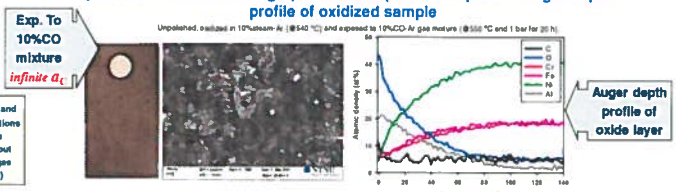


Figure 4: Carbon formation under *finite* a_C conditions (a_C>1).

Optical images and SEM images

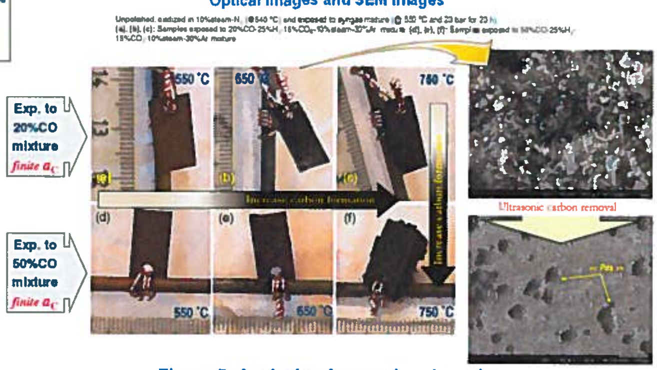


Figure 5: Analysis of corrosion deposits.

TEM and EDS of filamentous carbon formed

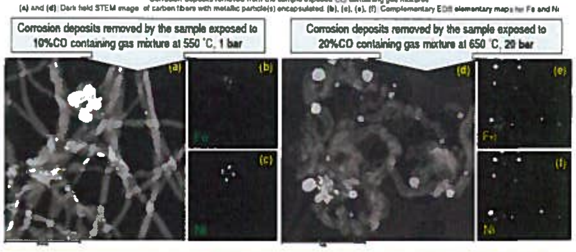
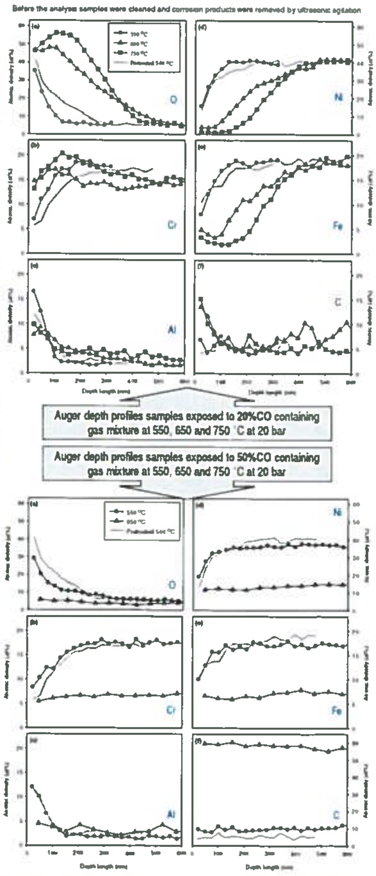


Figure 6: Characteristics of oxide/alloy surface.

Auger depth profiles of surfaces after removing corrosion products



Conclusions

- Increased exposure temperature under syngas ⇒ Higher C-formation (largest difference between 550 °C and 650 °C)
- <<*Pitting*>> or loss of material due to *spallation* was observed under pressurized syngas exposure for 20 h
- Higher P_{CO} (50% vs. 20%) in syngas ⇒ Higher C-formation
- Carbon formation and metal oxidation occurs in parallel under syngas (20%CO containing) mixture: Oxidation by H_2O increases with increasing temperature
- Carbon formation is kinetically controlled and appears to be associated with inclusion of Ni and/or Fe species in the surface oxide layer

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