MECHANISMS OF METAL DUSTING

Peter Szakálos

Doctoral Thesis

(KTH logga infogas)

Department of Material Science and Engineering
Division of Corrosion Science,
Royal Institute of Technology,
SE-100 44 Stockholm, Sweden
and
Swedish Institute for Metals Research
Drottning Kristinas väg 48
SE-114 28 Stockholm, Sweden

ISRN KTH/MSE--04/13--SE+CORR/AVH
Akademisk avhandling som med tillstånd av Kungliga Tekniska Högskolan i Stockholm framlägges till offentlig granskning för avläggande av teknologidoktorsexamen fredagen den 2:a april kl. 13:00 i Kollegiesalen, Administrationsbyggnaden, Kungliga Tekniska Högskolan, Valhallavägen 79, Stockholm. Avhandlingen försvaras på engelska. Fakultetsopponenten är Prof. F. H. Stott, University of Manchester Institute of Science and Technology (UMIST).

© Peter Szakálos 2004
Mechanisms of Metal Dusting

Peter Szakálos, 2004
Department of Material Science and Engineering
Division of Corrosion Science,
Royal Institute of Technology,
SE-100 44 Stockholm, Sweden
and
Swedish Institute for Metals Research
Drottning Kristinas väg 48
SE-114 28 Stockholm, Sweden

Abstract

The primary intention with this Doctoral thesis is to fill in the knowledge gaps and raise the level of understanding regarding the different metal dusting mechanisms in general and explain the process in detail for high alloyed materials. Considerable effort is put into identifying the driving forces and elucidating the diffusional processes in metal dusting.

The results are based on a series of long-term laboratory exposures of stainless steels and high-performance commercial alumina-forming Fe- and Ni-base alloys in synthesis gas mixtures, plus a separate shorter study on ultra pure iron. A Ni-base alloy was also investigated after a two years field exposure in a methanol plant.

Post exposure metallographic examinations and analysis as well as thermodynamic calculations were made in order to identify and describe the operating metal dusting mechanisms.

Two main mechanisms were previously used to explain metal dusting, one on the basis of decomposition of metastable carbides (Type I) the other on graphite formation (Type II).

A new metal dusting mechanism has been identified in this Thesis which appears on high alloyed steels and Ni-base alloys, an active corrosion induced by carbon and oxygen, denoted Type III. Both the mechanisms and the type of corrosion products were consistent with the thermodynamic conditions of the material under the influence of a carbon and oxygen gradient. It was shown that this mechanism not only accelerates the metal dusting process, in fact, it determines the overall metal dusting kinetics on stainless steels and Ni-base alloys.

Another feature, which may occur at temperatures where metal bulk and even static grain boundary diffusion is too slow for explaining the metal dusting corrosion process, was identified on a Ni-base alloy. It involves a fast growing cellular structure with discontinuous precipitated carbides which provides fast metal dusting kinetics by the Type III mechanism.

A Type IV metal dusting mechanism, continued fragmentation by graphitization until nano-sized particles are formed and catalyse carbon nanotube formation is also described.

The steady state process and the driving force for metal dusting on pure iron was identified and described.

With these additional processes it is now possible to extend our understanding of the metal dusting processes to a wide range of engineering alloys.

Keywords: metal dusting, mechanism, driving force, kinetics, high temperature corrosion, carburization, stainless steel, Ni-base alloys, iron, alumina formers, FeCrAl, oxidation, carbon nanotubes, discontinuous precipitation.
Preface

This thesis is based on research carried out at the Swedish Institute for Metals Research (SIMR) and includes the following papers, which will be referred to by the following numbers:


The following papers are omitted in this thesis; Paper 8 due to overlap and Paper 9 is outside the scope of the thesis:


CONTENTS

1 INTRODUCTION 1
1.1 Historic background 1
1.2 A general description of the corrosion phenomenon 2
1.3 Metal dusting—an important problem to solve for the future energy production 3
1.4 Aim of this work 4

2 EXPERIMENTAL 5
2.1 Material and laboratory exposures 5
2.2 Tube furnace exposure 5
2.3 Low cycle fatigue testing (LCF) 6
2.4 Microscopy and analysis 7
2.5 ThermoCalc 7

3 GAS ATMOSPHERES; EFFECT OF TEMPERATURE AND PRESSURE ON THE CARBON ACTIVITY 8
3.1 Synthesis gas mixture 25%CO+72%H₂+3%H₂O 10
3.2 Synthesis gas mixture 14%CO + 6%CO₂ + 32%H₂O + 48%H₂ 11
3.3 Measurements of H₂O and CO₂ content in the exhaust gas 12

4 MECHANISMS AND DRIVING FORCES OF METAL DUSTING 14
4.1 Metal dusting on non protective oxide formers 15
4.1.1 Metal dusting on iron 16
4.1.2 Metal dusting on nickel and cobalt 22
4.2 Metal dusting on chromia-forming austenitic alloys 22
4.2.1 Mechanisms proposed by other researchers 23
4.2.2 Type III mechanism: Active corrosion by carbon and oxygen 26
4.2.2.1 Principal reactions of the Type III mechanism 29
4.2.2.2 Diffusion processes in the Type III mechanism 31
1 INTRODUCTION

1.1 Historic background

Metal dusting or catastrophic carburization is a disintegration of metals and alloys into a dust of metal particles, oxides and graphite under formation of hemispherical pits or general attack. This occurs at high temperatures in carburizing atmospheres or, more commonly, in carburizing and selectively oxidizing atmospheres. The phenomenon is not new, in 1876 Pattinson [1] observed a deterioration of pig iron in CO-containing waste gases from a blast furnace;

“It is marvellous to consider how this action (MD) has succeeded in disintegrating, probably large pieces of metal (Cleveland pig iron), gradually lifting the particles of iron farther and farther away from their original position, and distributing them amongst the large masses of accumulated carbon.”

This description CO-initiated metal dusting on iron is far-sighted and could easily have been published at least 100 years later.

Metal dusting deterioration as a concept was first reported by E. Camp and co-workers [2] in 1945. The corrosion problem was initially detected in a superheater for reforming naptha. Several laboratory exposures were performed on 18-8 stainless steel in order to minimise the newly detected corrosion phenomenon and it was concluded that different forms of sulphur additions eliminate the corrosion.

More focused studies on the mechanisms of metal dusting were initiated by Prange [3] during the 1950’s with studies on the effects of carbon-bearing gases on alloys in petrochemical applications and were a major feature at the 1959 NACE conference. Several excellent papers from the conference on the subject were published by Prange [3], Eberle and Wylie [4], Hoyt and Caughey [5], Hopkins and Copson [6]. A statement by Prange summarises the state of the art of metal dusting research on high alloyed materials during the time period: ”While a few aspects are discernible (regarding MD), the picture as a whole is hazy. At first glance it might seem that oxidation phenomena govern the entire problem…” This seems to anticipate, 40 years later, the lively debate on effect and role of oxygen in metal dusting of high alloyed materials, which is thoroughly described in this thesis.

Pure carbon-induced MD on binary Fe-Ni alloys was described during the 1950’s by Hultgren and Hillert [7]. Today, this disintegration by graphitisation is considered to be one of the major degradation mechanisms of metal dusting. This paper has not been referred to until recently, perhaps because, in the words of one of the authors, (Hillert); “At that time we did not know that the phenomenon was denoted metal dusting.”
In the 1960’s, Hochman et al. identified an additional mechanism that operates on iron and low alloyed steels which includes decomposition of metastable cementite [8]. However, the steady state situation and driving force of this mechanism were never elucidated.

A statement by Zeng et al. (2002) may summarise the situation of MD research a few years ago; “Metal dusting has been studied for more than 50 years, but the mechanisms are not fully understood” [9]. Obviously, there are still several gaps in the understanding of MD mechanisms, especially concerning high alloyed materials.

1.2 **A general description of the corrosion phenomenon**

A definition of metal dusting and the various factors involved in MD were presented at the annual NACE conference in 1963 [10]:

1. **Environment**: Gas phase, potentially carburizing and reducing with or without oxygen.
2. **Temperature**: Usually 450°-800°C.
3. **Form**: Localized or general pitting and/or general overall surface wastage; surface usually carburized.
4. **Product**: Dust or powder composed of graphite mixed with metal, metal carbides and metal oxides.

This type of high temperature corrosion is treacherous since when initiated, the MD pit growth rate may reach at least a millimetre per month on stainless steels and an order of magnitude higher on low alloyed steels. It is a widespread problem in the petrochemical industry, particular in cracker furnaces and reforming units, i.e. in hydrocarbon synthesis gas containing predominantly CO and H₂ with some water vapour. This means that basically all production of monomers, which are the raw materials for polymer production like polyethylene may be subjected to metal dusting. Other chemical processes where organic compounds are reacting, such as in butane dehydrogenation, hydrodealkalation, acetic acid cracking and pyridine production are also subjected to metal dusting [11]. Industrial processes within the heat-treating industry, energy production (coal gasification plants) and ammonia plants are other examples. During the recent years MD has attracted considerable attention due to development of new processes in the petrochemical industry as well as in electric power generation.
1.3 Metal dusting – an important problem to solve for the future energy production

It is fairly safe to say that humankind will not stop the usage of fossil fuel until all of the earth’s reservoirs of oil, gas and coal have been emptied. However, their exploitation via today’s technology at the current rate is also associated with negative ecological and climatic consequences. The solution of these problems is believed to be in new technology, where only the hydrogen part of the fossil fuels is used for energy production or by using CO₂ sequestration techniques.

A more immediate problem is that the global production of conventional oil is predicted to peak toward the end of this decade. However, it is possible to compensate the forthcoming decrease in oil production with natural gas, but it requires more efficient conversion techniques.

The prevailing circumstances have recently increased the interest in Fisher-Tropsch gas-to-liquid (GTL) hydrocarbon processing technologies and the pursuit of maximum efficiency in steam-reforming technologies. Another important future technique for energy production is represented by the solid oxide- (SOFC) and molten carbonate- (MCFC) fuel cell technologies. Significant progress on reducing the operating temperatures of an SOFC has been achieved recently, from ~1000°C down to 550°C-800°C (ITSOFC). However, the Achilles' heel in all these techniques is the development of equipment, i.e. metallic materials capable of operating at increased carbon activities across the temperature range 450°C-850°C, where metal dusting can cause severe damage to alloy components.

Even today’s technology suffers significant problems with metal dusting. The US Department of Energy (DOE) has calculated that savings of $ 220-290 million could be made annually in hydrogen production alone if the limitations caused by the metal dusting phenomenon could be circumvented.

A solution to the metal dusting problem without lowering the carbon activity or introducing inhibitors, i.e by development of a new generation of engineering alloys immune to metal dusting corrosion, would represent an important contribution towards a more durable and environmentally non destructive society- The hydrogen society.
1.4 Aim of this work

The primarily intention with this work is to fill in the knowledge gaps and raise the level of understanding regarding the different metal dusting mechanisms in general and explain the process in detail for high alloyed materials. Considerable effort is put in to identifying the driving forces and elucidating the diffusional processes in metal dusting.

The overall aim is to understand how to avoid metal dusting, i.e. what kind of alloy system, if any, can be used in for instance a petrochemical plant operating with high carbon activity without suffering from metal dusting and extensive coke formation.
2 EXPERIMENTAL

2.1 Material and laboratory exposures

The chemical compositions of the steels investigated are given in Table 1 and the reference to the Papers in this thesis is shown in Chapter 4 (Table 4).

Table 1. Chemical composition of the steels investigated [wt%].

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>REM</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>0.013</td>
<td>18.35</td>
<td>10.1</td>
<td>0.39</td>
<td>0.043</td>
<td>0.42</td>
<td>1.26</td>
<td>0.004</td>
<td>-</td>
<td>-</td>
<td>Bal.</td>
<td>-</td>
</tr>
<tr>
<td>253MA</td>
<td>0.090</td>
<td>21.3</td>
<td>10.8</td>
<td>0.1</td>
<td>0.154</td>
<td>1.60</td>
<td>0.55</td>
<td>0.001</td>
<td>-</td>
<td>-</td>
<td>Bal.</td>
<td>0.04</td>
</tr>
<tr>
<td>TP446</td>
<td>0.16</td>
<td>25.9</td>
<td>0.61</td>
<td>0.05</td>
<td>0.054</td>
<td>0.42</td>
<td>0.85</td>
<td>0.004</td>
<td>-</td>
<td>-</td>
<td>Bal.</td>
<td>-</td>
</tr>
<tr>
<td>APM</td>
<td>0.03</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>0.08</td>
<td>0.001</td>
<td>5.5</td>
<td>0.03</td>
<td>Bal.</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>OC404</td>
<td>0.01</td>
<td>20.37</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
<td>0.14</td>
<td>0.18</td>
<td>-</td>
<td>5.5</td>
<td>-</td>
<td>Bal.</td>
<td>-</td>
</tr>
<tr>
<td>602CA</td>
<td>0.17</td>
<td>24.5</td>
<td>Bal.</td>
<td>0.04</td>
<td>-</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>2.1</td>
<td>0.2</td>
<td>9.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Iron</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(Ultra pure iron, less than 10 ppm impurities)</td>
</tr>
</tbody>
</table>

-Not analysed

2.2 Tube furnace exposure

The laboratory exposures were conducted at 600°-750°C at atmospheric pressure in a quartz tube furnace with a diameter of 25mm, see Figure 1. The test samples with typical dimensions of (10-20)×(7-15)×(2-4) mm were prepared by grinding to 600 mesh and cleaned in acetone prior to testing and placed in the cold furnace. To reach a low oxygen partial pressure, pure hydrogen was flushed through the furnace for three hours before heating to exposure temperature. The input compositions of the reaction gases, which were introduced during heating, were in the range 20-50%CO +0-3%H2O +47-80%H2, with a calculated equilibrium oxygen partial pressure in the range \( pO_2 = 10^{-23} \) to \( 10^{-26} \) at 650°C. The flow rate was 200-250 ml/min, which corresponds to a gas velocity over the specimen of 7-9 mm/s. The intermittent exposure times varied from 48-5000h, with typical intervals of 500h or 1000h.
2.3 Low cycle fatigue testing (LCF)

The LCF testing described in Paper 1 was performed in a 30 kN Instron electro-mechanical Creep Fatigue Machine equipped with a three-zone split furnace for high temperature testing. All tests were conducted in direct axial displacement control. The tests were run under symmetrical ($R_e = -1$) total displacement control with a triangular waveform and a constant strain rate of $10^{-4}$ s$^{-1}$.

During heating from room to testing temperature, the sealed chamber formed by the outer quartz cylinder was subjected to a constant flow of argon. Once a stable test temperature was reached, a constant flow of the desired gas mixture was conducted directly into the inner cylinder and applied to the specimen. Thus, the inner cylinder provided the desired controlled environment during testing and the outer hermetically sealed cylinder prevented any gaseous exchange with the external atmosphere. A drawing of the equipment design is given in Figure 2.

All tests were started from zero stress and began with the compressive part of the cycle.

Data recording for all LCF tests were carried out by means of a PC-based data acquisition system. This system performs a real-time recording and processing of test data, making the information available instantly.

Figure 1. The experimental set-up for the static tube furnace exposures.
2.4 Microscopy and analysis

The post exposure metallographic examination was made with a JEOL JSM-6400 Scanning Electron Microscope (SEM) and the analyses with a Link-Inca Energy Dispersive Spectrometer (EDS) with an ultra thin mylar window for analysis of light elements. Higher resolution micrographs were taken with a Field Emission Gun-SEM Leo-1530 (FEG-SEM). Macrographs were taken with a stereo microscope and the micrographs with a light optical microscope (LOM). TEM samples were prepared by in-situ lift-out in a Fei Strata 235 dual beam FIB-SEM. The TEM investigation was performed in a Philips CM200 FEG instrument, operated at 200 kV, equipped with a Link Isis EDS system.

To study the thin metal dusting corrosion front in cross-section it is important that the sample is polished, but in unetched condition, since any kind of etching may dissolve/destroy the sensitive outer corrosion front with depleted metal and oxides. The analysis of the corrosion products, the coke, was made with a Guinier-Hägg powder diffraction camera, using Cu-radiation and Si as an internal reference.

2.5 ThermoCalc

The thermodynamic modelling was conducted with ThermoCalc (TC) [12] database and software. Two databases were combined for the calculations, the SSUB database for the gas phases and the FEDAT database for the phases in the steel with additional thermodynamic data for oxides (spinel).
3 GAS ATMOSPHERES; EFFECT OF TEMPERATURE AND PRESSURE ON THE CARBON ACTIVITY

The industrial environments normally connected to the metal dusting (MD)-problem contain CO, H₂ and sometimes also other gaseous components, i.e. synthesis gas mixtures. Gas mixtures of 20-50% CO + 47-80% H₂ + 0-3% H₂O were used in the laboratory exposures described in this thesis. These gas mixtures and another synthesis gas mixture of 14% CO + 6% CO₂ + 32% H₂O + 48% H₂ were both modelled with ThermoCalc (TC). By using TC it is possible to calculate the carbon activity and gas equilibria as a function of temperature and pressure in complex gas mixtures taken into account multiple gas reactions. The SSUB database was used for this modelling.

The carbon activity, aₐ, was calculated with solid carbon, graphite, as the reference state, i.e. aₐ = 1 for pure graphite. In order to calculate carbon activities higher than unity in the gas phase, all solid (and liquid) states of pure carbon were set in status suspended in the TC-modelling. The calculated equilibrium composition of the environments used in most of the laboratory exposures is seen in Table 2.

Table 2. Equilibrium compositions of the gas environments used in Paper 2-6.

<table>
<thead>
<tr>
<th>Input gas composition</th>
<th>Temp.</th>
<th>Graphite a) mole and %</th>
<th>aₐ</th>
<th>pO₂</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂O</th>
<th>H₂</th>
<th>gas composition in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>25% CO + 3% H₂O + bal. H₂</td>
<td>600°C</td>
<td>Suspended</td>
<td>32</td>
<td>10⁻²⁶</td>
<td>23</td>
<td>1.8</td>
<td>2.2</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08 of 0.12 moles; 65%</td>
<td>1</td>
<td>10⁻²⁴</td>
<td>6</td>
<td>4</td>
<td>19</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>650°C</td>
<td>Suspended</td>
<td>10</td>
<td>10⁻²⁵</td>
<td>23</td>
<td>1.6</td>
<td>2.5</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05 of 0.12 moles; 42%</td>
<td>1</td>
<td>10⁻²⁴</td>
<td>11</td>
<td>4</td>
<td>13</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>50% CO + 3% H₂O + bal. H₂</td>
<td>600°C</td>
<td>Suspended</td>
<td>129</td>
<td>10⁻²⁵</td>
<td>48</td>
<td>2</td>
<td>0.8</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.14 of 0.24 moles; 57%</td>
<td>1</td>
<td>10⁻²⁴</td>
<td>12.5</td>
<td>18</td>
<td>24</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>650°C</td>
<td>Suspended</td>
<td>39</td>
<td>10⁻²⁵</td>
<td>48</td>
<td>1.9</td>
<td>1</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11 of 0.24 moles; 45%</td>
<td>1</td>
<td>10⁻²⁵</td>
<td>21</td>
<td>15</td>
<td>16</td>
<td>48</td>
<td></td>
</tr>
</tbody>
</table>

1) Hydrocarbons like methane are excluded from the equilibrium calculations.
2) The theoretical (highest) carbon activity in the gas phase is calculated with graphite phase suspended in the calculation. At aₐ = 1 the amount of graphite is expressed in moles and per cent of the total amount of elementary carbon in the input gas, i.e. 0.12 and 0.24 moles respectively. The input gas composition is normalised to one mole of atoms.

The different states, with or without graphite, represent the range in which the gas composition may change during an exposure, i.e. the carbon activity is high initially, but drops asymptotically with time towards unity as more and more graphite (coke) forms. As a consequence, a high gas flow rate preserves a high carbon activity.

If all gas species are used in the calculation, i.e. all thermodynamically stable hydrocarbons (HC) are allowed in the equilibrium, the carbon activity drops rapidly at lower temperatures, as shown in Figure 3 with a dashed line. However, methane or higher HC`s, will not form in appreciable quantities during normal
conditions due to slow kinetics and are therefore excluded in most of the following calculations.

Figure 3. ThermoCalc modelling of the carbon activity \( a_c \) as a function of temperature in 20CO-80H\(_2\) atmospheres, but this is appreciable on synthesis gases in general. At lower temperatures, a drop in \( a_c \) is predicted due to hydrocarbon formation. However, slow kinetics mean that this is not observed in practice, instead the carbon activity continues to increase rapidly, as marked by the arrow.

Basically there are four reactions that bring about solid carbon or coke deposition in H\(_2\)-CO mixtures:

\[
2\text{CO(g)} \rightleftharpoons \text{C(s)} + \text{CO}_2(g) \quad \text{(Boudouard equilibrium)} \quad (3.1)
\]

\[
\text{CO(g)} + \text{H}_2(g) \rightleftharpoons \text{C(s)} + \text{H}_2\text{O(g)} \quad \text{(Steam-carbon equilibrium)} \quad (3.2)
\]

It may be concluded that during MD of high alloyed steels and Ni-base alloys, three additional reactions takes place which produce carbon from the gas phase according to the reactions;

\[
\text{CO(g)} + \text{Me(s)} \Rightarrow \text{C(s)} + \text{MeO(s)} \quad (3.3)
\]

\[
\text{CO}_2(g) + 2\text{Me(s)} \Rightarrow \text{C(s)} + 2\text{MeO(s)} \quad (3.4)
\]

or via a solid state reaction involving carbide dissolution as a result of selective oxidation. This mechanism is described in detail in Paper 2 and Chapter 4.2.2 as Type III. Olsson and Turkdogan [13] have measured the kinetics of reaction (3.1) and (3.2) as a function of CO/H\(_2\) content and temperature on pure iron. The results show that reaction (1) dominates at higher CO concentrations and (3.2) at higher H\(_2\) concentrations. With a 50\%CO-50\%H\(_2\) mixture at 600\degree C, the kinetics of
the two reactions are equal. It should be mentioned that this is true for pure iron as reaction surface. In the case of high alloyed materials, i.e chromia or alumina formers as reaction surfaces, reactions (3.1) and (3.2) seems to be suppressed, especially reaction (3.2), as no water is condensed at the cooled gas outlet.

3.1 Synthesis gas mixture 25%CO+72%H₂+3%H₂O

As described above, several gas species, for example methane or higher hydrocarbons, are not expected or detected in significant concentrations due to slow kinetics and were rejected in the calculations. In order to calculate carbon activities higher than unity in the gas phase, all solid (and liquid) states of pure carbon were suspended in the TC-modelling. The carbon activity as a function of temperature and pressures for two possible equilibria based on the same input composition are shown in Figure 4. If water vapour is excluded from the equilibrium as shown in Figure 4 (b), the CO₂ content increases from 1.6% (in 23%CO + 2.5%H₂O +73%H₂) to 4.1% (in 20,4%CO +75,5%H₂) at 650°C, but the carbon activity will still be high.

According to Grabke [11], small amount of water vapour is needed in the exposure gas, but the necessity of such additions in CO/H₂-mixtures is questionable, as reaction (3.2) will produce a few per cent H₂O at 650°C. Even if the steam-carbon reaction (3.2) is excluded from the equilibrium, the ability to deposit carbon will be maintained by the Boudouard reaction (3.1).
Theoretically, the carbon activity would be infinitely high in a dry CO/H₂ mix but in practice it is not that high as reactions (3.1) and (3.2) rapidly change the situation. In fact, comparing studies in the same gas with and without 3% H₂O gave virtually identical metal dusting attack on a AISI 304L steel after 1000h, albeit with slightly more coke formation in the latter case (to be published). The effect of high pressure (40 bar) is quite dramatic with an order of magnitude higher carbon activity, which may be explained by a shift of the reactions (3.1) and (3.2) to the right since this would lower the pressure (less gas molecules), as discussed in Paper 3.

3.2 Synthesis gas mixture 14%CO + 6%CO₂ + 32%H₂O + 48%H₂.

The carbon activity as a function of temperature and pressure for two possible equilibria based on the same input composition are shown in Figure 5.

From Figure 5 (a) it is seen that the C-activity at ~580°C /1 bar is around unity which means that the driving force for MD is weak, but at 40 bar the carbon activity reaches close to 100. This is an important observation since it explains why exposures in laboratories at ambient pressure results in less or no corrosion while the same environment in a pressurised plant give severe metal dusting and coking problems [14].
In Figure 5 (b), small amount of C5 and higher HC’s are included in the equilibrium calculation in order to simulate a real situation with small amount of methane, i.e. not close to equilibrium amount. As seen, this gives strong carbon activity drop at 40 bar. The formation of HC’s reduces the carbon activity but as mentioned, the kinetics are normally very slow.

3.3 Measurements of H₂O and CO₂ content in the exhaust gas

Measurements of H₂O and CO₂ formation in an initially dry synthesis gas mixture were conducted on the exhaust gas by IR-spectroscopy during an exposure of alumina-forming alloys (total surface area: ~22cm²). The measurements were conducted after 100h exposure at 600°C and the temperature/gas equilibrium change was stabilised for 6-24h before the analyses were performed. These are new results which are not included in any of the appended papers.

The results and comparison with calculated gas equilibria are shown in Table 3. The input gas composition consisted of a dry 50%CO+50%H₂-mixture. Data from two other experiments using pure iron instead of alumina–forming alloys are added in the two last rows, Ref. [13] and Paper 4.

Some conclusions may be drawn:

- Alumina-formers represent poor catalyst materials for reaction (3.1) and (3.2). In other words they are potentially high performance materials in metal dusting environments with slow coke formation, see further in sections 4.4 and 6.1. Actually, the per cent values of graphite relative equilibrium would probably even be lower if one of the samples would not have been severely attacked by MD.

- Pure iron gave as much as 28.9% coke formation although the surface area was around a tenth of that of the alumina forming alloys.

- Increasing the temperature lowers the equilibrium amount of H₂O, CO₂ and coke formation, but the faster kinetics result in higher relative amount of these compounds, at least up to 650°C.

- A high temperature and low flow rate with pure iron give coke formation closer to equilibrium amount. On the contrary, an alumina-forming alloy will maintain a high C-activity in the gas phase and experience a low level of coke formation.
### Table 3. IR-spectroscopy measurements of H₂O and CO₂ content in the exhaust gas when dry synthesis gas mixture is exposed to alumina-forming alloys or pure iron and comparison with calculated equilibrium values.

<table>
<thead>
<tr>
<th>Temp. (ºC)</th>
<th>Flow rate (ml/min)</th>
<th>H₂O (%)</th>
<th>CO₂ (%)</th>
<th>H₂O/CO₂ ratio</th>
<th>Coke form.</th>
<th>H₂O (%)</th>
<th>CO₂ (%)</th>
<th>H₂O/CO₂ ratio</th>
<th>Coke form.</th>
<th>Coke formation relative equilibr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>550ºC</td>
<td>100</td>
<td>0.099</td>
<td>0.079</td>
<td>1.25</td>
<td>7.4</td>
<td>34.2</td>
<td>17.9</td>
<td>1.91</td>
<td>1422</td>
<td>0.52%</td>
</tr>
<tr>
<td>570ºC</td>
<td>100</td>
<td>0.151</td>
<td>0.120</td>
<td>1.26</td>
<td>11.3</td>
<td>30.1</td>
<td>17.8</td>
<td>1.69</td>
<td>1348</td>
<td>0.84%</td>
</tr>
<tr>
<td>600ºC</td>
<td>100</td>
<td>0.228</td>
<td>0.178</td>
<td>1.28</td>
<td>16.9</td>
<td>24.4</td>
<td>17.1</td>
<td>1.43</td>
<td>1223</td>
<td>1.38%</td>
</tr>
<tr>
<td>600ºC</td>
<td>200</td>
<td>0.121</td>
<td>0.077</td>
<td>1.57</td>
<td>16.5</td>
<td>24.4</td>
<td>17.1</td>
<td>1.43</td>
<td>2446</td>
<td>0.67%</td>
</tr>
<tr>
<td>650ºC</td>
<td>200</td>
<td>0.349</td>
<td>0.194</td>
<td>1.80</td>
<td>45.2</td>
<td>16.1</td>
<td>14.0</td>
<td>1.15</td>
<td>1930</td>
<td>2.34%</td>
</tr>
<tr>
<td>800ºC</td>
<td>3000</td>
<td>0.394</td>
<td>0.187</td>
<td>2.06</td>
<td>58.0</td>
<td>1200</td>
<td>0.93</td>
<td>2.81</td>
<td>1.04</td>
<td>6738</td>
</tr>
<tr>
<td>650ºC</td>
<td>250</td>
<td>0.349</td>
<td>0.194</td>
<td>1.80</td>
<td>45.2</td>
<td>16.1</td>
<td>14.0</td>
<td>1.15</td>
<td>1930</td>
<td>2.34%</td>
</tr>
</tbody>
</table>

1) Calculated coke formation based on eq. (3.1) and (3.2).
2) Calculated with the SSUB-database (ThermoCalc). The gas equilibrium is calculated with graphite but with all hydrocarbons rejected. The amount of carbon (CO) in the gas volume (per minute) is related to the equilibrium amount of formed graphite (coke) in the same volume.
3) Pure iron granules spread evenly over 7cm² surface, exposed at 800º C in 50%CO+50%H₂-mixture with high flow rate, from Olsson et al [13].
4) Pure iron sample of 2cm² exposed in dry 25%CO+75%H₂ (Paper 4).
5) Water vapour formation measured as condensed water at ∼15ºC in the exhaust gas.
6) CO₂-content based on the calculated H₂O/CO₂-ratio of 3.56. Olsson et al [13], gives the same ratio experimentally, i.e ~3.5, under the same conditions for pure iron, albeit at 600ºC.
The phenomenon of metal dusting (MD) may be divided into three main mechanisms denoted Type I, Type II and Type III.

Type I, first described by Hochman et al. [8,10] and further detailed by Grabke [11,15], involves decomposition of metastable cementite.

Type II, may be described as disintegration of a carbon supersaturated phase by internal graphitization and was first described by Hultgren and Hillert [7] and studied in detail by Pippel et al. [16,17].

Type III, which operates on high alloyed steels and Ni-base alloys, was first proposed in Paper 2 and further detailed in Papers 3-6 and [18], and involves selective oxidation of alloyed carbides, i.e not pure Fe-carbides.

A secondary mechanism may be added, carbon nanotube formation, Type IV. It may be described as a continued fragmentation of the corrosion products and involves carbon nanotube formation, see further in Chapter 6.2. There is seldom only one MD-mechanism operating on a steel or a Ni-base alloy. For example, Types III and II operate in conjunction on austenitic stainless steels and Ni-base alloys, see Papers 2-6 and Ref. [18]. In the following sections the MD mechanisms and driving forces will be discussed in detail for each category of engineering alloys. The alloys are grouped firstly according to oxide type, since this is of vital importance for the MD resistance and operating mechanisms and secondly by the metal structure, i.e. ferritic or austenitic.

A summary of the alloys studied and operating mechanisms together with reference to the Papers in this thesis is shown in Table 4. A ranking is made with the most dominating mechanism in the steady state process listed first.

<table>
<thead>
<tr>
<th>Alloy type</th>
<th>Commercial grade</th>
<th>Operating mechanisms</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>(Ultra pure Fe)</td>
<td>II+I</td>
<td>4</td>
</tr>
<tr>
<td>FeCr</td>
<td>TP 446, 26Cr-steel</td>
<td>III+II +I</td>
<td>4</td>
</tr>
<tr>
<td>FeCrAl</td>
<td>APM, 0C404</td>
<td>III+II</td>
<td>1,4</td>
</tr>
<tr>
<td>FeNiCr</td>
<td>AISI 304L, 253MA</td>
<td>III+II</td>
<td>1,2,3,4</td>
</tr>
<tr>
<td>NiFeCrAl</td>
<td>Alloy 602CA</td>
<td>III+II</td>
<td>5,6</td>
</tr>
</tbody>
</table>

Table 4. The studied alloys with operating mechanisms together with reference to the Papers in this thesis.
This outline with increasing alloy content will be followed in this thesis with one exception, the FeNiCr alloys will be treated before the Fe-Cr alloys because the Type III mechanism was first identified and described in detail on a AISI 304L stainless steel.

4.1 Metal dusting on non protective oxide formers

Pure metals like Fe, Ni and Co do not form any protective oxides in synthesis gas mixtures since the oxygen partial pressure is typical in the range of $10^{-26}$ to $10^{-24}$ bar depending on the content of oxygen bearing gases like H$_2$O and CO$_2$, see Chapter 3. Typical MD environments are marked in an Ellingham-Richardsson diagram for oxides in Figure 6. The oxides within or below the marked area are thermodynamically stable which means that pure iron spinel may not necessarily form but if Cr is present in the alloy, chromia or Cr-Fe spinels will always form, as discussed further in Chapter 4.2.2. Pure Fe, Ni or Co do not form any protective oxides and all show (CO-) catalytic properties [18] which implies that their MD behaviour is likely to be poor. Nevertheless, these metals are of principal importance since the alloys used today in MD environments are based on Fe, Ni and Co.
Figure 6. Ellingham –Richardsson diagram for some oxides of importance in the high temperature oxidation of metals. The diagram is a plot of the standard free energy of formation of the oxides per mole of oxygen versus temperature. The shaded area represents typical metal dusting environments.

4.1.1 Metal dusting on iron

Metal dusting on iron has been known for more than 120 years, as described in the introduction, and has been studied in modern times particularly by Hochman et al. [8,10] and Grabke [11,15]. The suggested mechanism may be summarised as formation of metastable cementite and its subsequent decomposition into graphite and iron during metal dusting conditions, see Figure 7.
Figure 7. Schematic illustration of the metal dusting mechanism on iron and low-alloy steels from Grabke [11]: (a) supersaturation of the metal matrix by carburization, (b) formation of Fe$_3$C at the surface with growth from the interior, (c) deposition of graphite onto the Fe$_3$C surface, and (d) Fe$_3$C decomposition and outgrowth of coke by carbon deposition on the metal particles from the Fe$_3$C decomposition.

The mechanism is problematic from a thermodynamic point of view since it requires carbon diffusion in opposite direction to the carbon activity gradient, as seen in Figure 7 (c) and (d).

The newly proposed steady state process and the identification of the driving force of MD on iron was based on a study on ultra pure iron at 650°C in 25%CO+3%H$_2$O+72%H$_2$ (Paper 4).

The post exposure study showed that the sample surface was covered with porous coke mixed with dense graphite after 48h and the metallographic cross-section showed general MD-attack with metal fragments released from the 100% ferritic surface. SEM investigations after 100h exposure showed the same appearance, see Figure 8 (a). Less than one percent cementite was present in the bulk and no cementite was found in the reaction front, as seen in Figure 8 (b). Powder diffraction analysis of the coke gave graphite lines and some very weak signals, possibly cementite (JCPDS 35-0772). The latter identification is supported by the work of Zeng and Natesan [9], who demonstrated the presence of cementite in the coke during similar exposures of iron.
It is well known that it is difficult or impossible for graphite to nucleate directly from a gas phase even if the carbon activity is rather high. On the other hand, metals like Fe, Ni and Co are very efficient catalysts [13,19]. A CO-molecule can be adsorbed on the surface and dissociate into free C and O. The C atom may then dissolve in the iron and the O atom stay on the surface until it is combined with other atoms to form a gas molecule, e.g., H$_2$O or CO$_2$. As more and more C dissolves in the iron, the carbon activity increases in the material and carbon can precipitate as graphite at an activity over 1.0 and as cementite at a higher activity, the critical value depending on the temperature. From a thermodynamic point of view, one would thus expect graphite to form first, but it is difficult to nucleate and slow to grow, at least inside the iron. Usually, cementite will thus be the first phase to form. Eventually, graphite will form inside the material and it usually results in the cementite dissolving. This may occur via the eutectoid reaction; cementite $\rightarrow$ Fe(C) + graphite. When graphite forms within the surface layer, it happens by interstitial diffusion of carbon, which does not itself provide any volume for the growing graphite. Instead, the graphite will deform the Fe matrix, which results in fragments of iron breaking off [16,17], i.e. the Type II-mechanism. In the subsequent process cementite will play a lesser role because it is more difficult for the carbon activity to exceed the critical value for cementite formation once graphite particles are present inside the material. In fact, it is not possible to explain the driving forces of MD on iron if there is an inward growing cementite layer present during the steady state process since that would require carbon diffusion in the opposite direction to the carbon activity gradient. It is now proposed that the simple solution to this problem is that there is such a layer only during the initial stages of MD. These initial stages, studied by several researchers [8,9,11,16,20,21] seem to continue for more than 20h [21] but not more than 48-100h at 650°- 700°C, as seen in the reaction front in Figure 8. Low alloyed steels and mild steels with impurities and alloying elements such as Cr and Mn will form...
significant amount of cementite under MD conditions. However, as predicted, no massive or intact layer of cementite was observed during longer exposure times (steady state), instead ferrite and intergranular cementite coexists in the MD reaction front as observed by Schmid et al. [22].

The main steps of the MD-process on pure iron proposed in Paper 4 are shown in Figure 9. In the first step a cementite layer form on the surface (a) followed by a graphite layer on the cementite (b). As the graphite layer grows thicker and tighter the carbon activity drops towards unity and cementite starts to decompose, i.e. the Type I mechanism (c). The eutectoid reaction (Cementite $\rightarrow$ Ferrite + Graphite) may be fast enough to form an intermediate layer of ferrite and graphite (d). Cementite contains 25 at-% carbon and 75 at-% Fe which corresponds to an eutectoid structure with approximately 19 vol-% graphite and 79 vol-% iron. However, the carbon diffusion is fast at 650°-700°C and some of the carbon may diffuse to the existing surface graphite, resulting in a structure with locally less graphite. The likelihood of observing this intermediate “iron layer”-step [20], i.e. the degenerated eutectoid structure, should be favoured by lower carbon activities because the fragmentation process of the same layer by graphitization is slower under these conditions. This Type II-mechanism (internal graphitization) constitutes the steady state process with a well-defined driving force, so no more cementite forms in contact with the graphite (e). A close up from the coke shows the steady state situation of the corrosion end products with small catalytic cementite particles producing carbon nanotubes, i.e. the Type IV mechanism (f), see Chapter 6. As discussed, the carbon activity in the coke in contact with the gas is high enough to transform ferrite to cementite particles.
Figure 9. A consistent description of metal dusting on pure iron and low alloyed steels is proposed (Paper 4). Figs. (a-f) represents increasing exposure times.

a) Cementite formation on the ferrite surface.
b) Graphite formation on the cementite layer.
c) As the graphite layer grows thicker and tighter the carbon activity drops to unity and cementite starts to decompose, i.e. Type I mechanism.
d) The eutectoid reaction may be fast enough to form an intermediate eutectoid layer; Cementite → Ferrite + Graphite.
e) No more cementite forms in contact with graphite in the coke, i.e. the steady state process has started, the Type II mechanism.
f) Close up from the porous coke; corrosion of the corrosion products to a steady state size, i.e. Type IV mechanism.

The different steps of MD on pure iron may be summarised with thermodynamically-consistent activity curves, as seen in Figure 10. The final metal dust particles may consist of ferrite and/or cementite particles depending on the carbon activity in the gas, or more correctly, the local carbon activity in the porous coke, as shown in the last time step, t=t₅.
Figure 10. Carbon activity profiles and carbon flux (red arrows) for the different time steps of MD on pure iron.
The important conclusion is that it is not possible to explain the driving forces or the steady state process of MD by decomposition of metastable cementite (Type I). However, there can exist an intact or unbroken cementite layer during the initial stages of metal dusting, while the steady state process is governed by fragmentation due to grafitization (Type II).

4.1.2 Metal dusting on nickel and cobalt

The mechanism of metal dusting on Ni and Co is predicted to be the same, and involves formation of neither carbides [23] nor oxides in typical MD environments, as seen in the Ellingham diagram in Figure 6. Instead a direct fragmentation takes place by grafitization [17,23], i.e the Type II mechanisms which is previously described as the steady state mechanism for pure iron, see Chapter 4.1.1. This mechanism was first described by Hultgren and Hillert during the 1950’s in a study of binary Fe-Ni alloys [7].

Ni and Co have similar properties in typical metal dusting environments;
- no formation of protective oxides [17,23]
- no formation of carbides [17,23]
- dissolves carbon and stabilize graphite [18]
- have strong catalytic properties on CO-dissociation [10,13,19]

These properties promote the Type II mechanism; disintegration of a carbon-supersaturated matrix by internal graphite formation. Initially, larger metal fragments may be released from the metal dusting front. These larger metal pieces are subjected to continued fragmentation until they finally may be too small for inward growth of graphite or graphite nucleation in their interior and the continued formation of solid carbon will occur on their surface. The final metal dust is typically in the nanometer scale, see further in Chapter 6, resulting in carbon nanotube formation.

An additional mechanism, proposed by Pippel et al. for Fe and Ni [16, 17] and further discussed by Chun et al. for Fe [20] and Co [23], involves metal dissolution and diffusion in graphite. This mechanism seems less likely to the present author since it would depend on the solubility and diffusivity of metal atoms in graphite and on a driving force for outward metal diffusion, as discussed further in Chapter 4.2 (Figure 12) and in Chapter 6.

4.2 Metal dusting on chromia-forming austenitic alloys

The mechanism for MD on chromia-forming alloys is considered to be similar for austenitic iron base alloys (Paper 2) and Ni-base alloys (Paper 5). The newly
identified MD mechanism, Type III, will be described below, but first the current theories of MD on high alloyed austenitic materials will be discussed.

### 4.2.1 Mechanisms proposed by other researchers

In publications by Grabke [11,24] the MD of high alloyed steels and CrFeNi-alloys were described with the schematics seen in Figure 11.

![Schematic presentation of the MD mechanism on high alloyed steels and CrFeNi-alloys taken from Ref. [11] (a) and Ref.[ 24] (b).](image)

**Figure 11.** Schematic presentation of the MD mechanism on high alloyed steels and CrFeNi-alloys taken from Ref. [11] (a) and Ref.[ 24] (b).

The proposed mechanism includes following principal steps:

i. Carburization and formation of very fine Cr-rich $M_6C_3$-carbides (grey zone) and $M_23C_6$ carbides in the grain boundaries.

ii. Formation of metastable (?) $(Fe,Ni)_3C$ cementite in the Cr-depleted matrix, followed by cementite decomposition (Type I) and/or direct fragmentation by grafitization (Type II). The corrosion products would thus be cementite or Fe/Ni particles, graphite and Cr-rich carbide particles.

iii. Oxidation of the corrosion products in the coke, i.e. oxidation of the very fine Cr-rich carbides which subsequently would give very fine spinel/chromia particles in the coke.
The above proposed mechanism implies that oxidation is not involved in the metal dusting process, only in the subsequent breakdown of the corrosion products. This is contradicted by a number of metallographic observations on CrFeNi-alloys like stainless steels, Alloy 800 and Inconel 600:

- A carbide free austenite zone is normally observed in the reaction front of stainless steels, referred to as a Cr-depleted layer/zone or “white layer” [3,4,5,18,25,26,27]. Sometimes it is mistakenly denoted a “decarburized layer” but in fact it is supersaturated with carbon [27].
- No cementite (Fe,Ni)₃C has been detected or reported elsewhere in the literature.
- Intact spinel oxide layers or areas are observed in the reaction front [3,4,5,18,25,26,28,29,44] normally in connection to the carbide free zone/layer formed on stainless steels.

All these observations indicate that oxygen is active in the MD process. Pippel et al. [16] and Schneider et al. [30] propose a somewhat modified mechanism for Cr-containing Ni-base alloys as shown in Figure 12.

![Figure 12](image)

**Figure 12.** Schematic representation of the processes and reactions layers involved in metal dusting on Cr-containing nickel base alloys (Inconel 600) from Ref. [30].

This proposed mechanism include following principal steps:
i Chromia formation on the surface with subsequent formation of a Cr-depleted Ni-layer underneath.

ii Carburization and direct fragmentation of the Ni-layer by graphite tubes, i.e. the Type II mechanism.

iii The graphite tubes shows an oriented growth perpendicular to the surface and a metal dissolution mechanism in the graphite planes is suggested. The metal atoms diffuse to the graphite-gas interface, where they agglomerate to small particles.

iv The corrosion products would thus be Ni/Fe fragments, Ni/Fe atoms/nano particles, graphite and chromia particles.

Again, the oxygen is not taking part in the suggested metal dusting mechanism and it is unclear what happens to the Cr-atoms in the steady state corrosion process. The mechanism step (iii) seems less likely to the present author since it would depend on the solubility and diffusivity of Ni and Fe atoms in graphite and on a driving force for outward diffusion, as discussed further in Chapter 6.

It should be mentioned that nickel base alloys, typically of composition around 20Cr80Ni, may also be attacked by another high temperature corrosion phenomenon denoted “green rot”; the term has been coined because the fractured surfaces have a green appearance due to formation of \( \text{Cr}_2\text{O}_3 \). Although green rot is a very old problem, it is described in only a few literature references. This is largely because its occurrence is limited to a narrow range of environmental parameters and to the temperature range 900°-1150°C [31,32,33,34,35,36]. The gas environment must be reducing or at least periodically reducing with respect to the bulk metal (Ni and/or Fe) although oxidising for Cr [34].

The term green rot has also been applied to alloys exposed to oxidising and carburizing atmospheres, which result in internal oxidation of previously formed grain boundary Cr-carbides, giving the same appearance with green chromia on the fractured surfaces [31,32,33]. This form of green rot may thus show some similarities with metal dusting, see further in Chapter 5. However, in synthesis gas mixtures in the temperature range 540°-650°C, the overall corrosion process is far more complex. The corrosion attack described here, with hemispherical pit formation and dark/black corrosion products consisting of metal particles graphite and spinel oxides, is typical for metal dusting, see Chapter 1.2.

As pointed out in Chapter 1.1, the effects of oxygen and spinel oxide formation in MD of high alloyed materials were the subject of lively debate at the 1959 NACE conference. Several years later in 1976, Perkins et al. reported MD attacks on Alloy 800 heat exchanger tubes in a coal gasification plant, apparently associated with oxidation [37]. Recently, considerable attention has been paid to the role of oxygen...
during metal dusting. Schmid et al. [38] and de Bruyn et al. [25] discussed these effects in synthesis gases with low oxygen partial pressures. These ideas have been taken further in the present work and an active corrosion mechanism involving both carbon and oxygen is proposed.

4.2.2 Type III mechanism: Active corrosion by carbon and oxygen

The proposed mechanism is based on the concept of active corrosion by carbon and oxygen. Carbon reacts with metal and metal carbides are formed. These carbides dissolve and oxidise selectively and free carbon is released which forms carbides/graphite and so forth. This process may be compared to chlorine-induced active corrosion where metal chlorides are formed which oxidise and chlorine is released to form more metal chlorides [39].

The Type III mechanism was first identified on a AISI 304L type stainless steel exposed at 650°C in a CO-containing gas mixture (Paper 2).

The SEM-image of the MD reaction front in cross-section in Figure 13 is comparable with the sketch in Figure 14. This shows simultaneous operation of mechanisms III (oxidation of carbides) and II (graphitization). These two processes work in collaboration; the carbides dissolve since there is a decreasing Cr-gradient towards the Cr-containing oxide and the process is promoted by the fine structured austenitic layer with graphite flakes (Zone 4) which provide fast Cr-diffusion paths.
Figure 13. FEG-SEM-BSE cross-section image of the unetched MD-reaction front in an AISI 304L stainless steel. The etched insert shows the heavily carburized bulk. This shows the carbide dissolution driven by the Cr-gradient towards the Cr-rich spinel oxide, under formation of a carbide free and Cr-depleted layer with a black substructure, marked by arrows. As nickel is a graphite stabiliser, it is a strong indication that the fine substructure is a graphite network. This image is comparable with the sketch in Figure 14.
Figure 14. The mechanisms of metal dusting as it appears on stainless steels. It includes an active corrosion process with carbon and oxygen (Type III), in combination with fragmentation by graphitization (Type II). The fine grained austenite/graphite layer (zone 4) promotes the Cr-diffusion and consequently oxide formation. The corrosion products consist of Fe-Ni austenitic metal dust, spinel oxides and elementary carbon, but no carbides.

Starting with uncarburized AISI 304L steel the metal dusting steps may be divided into six zones as shown in Figure 14:
1 Carburized bulk with M_{23}C_6 carbides, which forms at lower carbon activities.
2 Carburized bulk with M_7C_3 carbides.
3 Dissolving carbide front with M_7C_3 and M_3C.
4 Cr-depleted zone (“white phase”), Fe-Ni austenite border with graphite flakes.
5 Corrosion products: Cr-Fe oxides, metal fragments in μm size and carbon.
6 Coke, continued corrosion of the corrosion products by the Type II mechanism, i.e. disintegration of the metal fragments in smaller and smaller metal dust and finally, nm-sized particles under formation of carbon nanotubes, see Chapter 6.

These observations and mechanism description are consistent with the known thermodynamics in the AISI 304L-C-O-H system as shown in Figure 15.
Figure 15a. Mole fraction of stable phases in the AISI 304L-C-O-H system as a function of oxygen partial pressure with a fixed carbon activity $a_c=1$ and graphite phase suppressed.

Figure 15b. Mole fraction of stable phases as a function of carbon activity with the graphite phase suppressed and a fixed oxygen partial pressure of $p_{O_2}=10^{-24}$.

For the equilibrated gas composition used in this study, with $p_{O_2} = 10^{-24}$, the stable phases will be FCC-austenite and a Cr-Fe spinel oxide. Schematically, the diagram in Figure 15a can be seen as a cross section of the thin metal dusting front from the metal interface (at low $p_{O_2}$) towards the gas phase (high $p_{O_2}$). Figure 15b demonstrates that the spinel oxide is thermodynamically stable, even at carbon activities above 100. M$_3$C is predicted to be stable at carbon activities above 2.1, but this was not detected in the corrosion products (coke), i.e. the carbon activity in the coke was lower than 2.1.

Active corrosion by carbon and oxygen is probably the major degradation mechanism in chromia-forming engineering alloys exposed in CO-containing atmospheres independent of the water vapour content. It is also shown that this mechanism is operative for Cr-containing alumina formers, see Chapter 4.4.

4.2.2.1 Principal reactions of the Type III mechanism

The principal reactions of the Type III mechanism are presented below. In order to point out the main solid state reactions, intermediate reactions in the gas phase are excluded. For instance, adsorbed oxygen may originate from H$_2$O or CO$_2$, as discussed in Chapter 3, but is schematically written as O (ad) in the chemical equation.

Consider ten atoms of AISI 304L steel of composition 18Cr-10Ni-72Fe in weight-%, i.e. an approximate atomic ratio of 2Cr:1Ni:7Fe. The following reactions show the steps involved in a fully equilibrated carburization and metal dusting process in
a CO/H sub{2} containing gas (a sub{c} ≥1). Schematically, the mechanism reactions may be divided into two stages: carburization (zones 1 and 2 in Figure 14);

\[(2\text{Cr-Ni-7Fe})\gamma_{304L}+1.29\text{CO(g)} \rightarrow (6\text{Fe-Ni})\gamma_{\text{matrix}}+0.43[(\text{Cr}_{14/3}\text{Fe}_{7/3})\text{C}_3]+1.29\text{O(ad)} \quad (4.1)\]

and carbide dissolution by selective oxidation (zones 3-5);

\[(6\text{Fe-Ni})\gamma_{\text{matrix}}+0.43[(\text{Cr}_{14/3}\text{Fe}_{7/3})\text{C}_3]+4\text{CO(g)} \rightarrow (6\text{Fe-Ni})\gamma_{\text{dust}}+(\text{Cr}_2\text{Fe})\text{O}_4 + 5.29\text{C(s)} \quad (4.2)\]

where \(\gamma_{\text{dust}}\) is austenitic particles, i.e. metal dust. As shown in Figure 14, the carbides do not oxidise directly, they dissolve first and Cr diffuses through the carbide free austenite (zone 4) and reacts with oxygen. The equilibrium corrosion products are thus, austenitic (Fe-Ni) metal particles, Cr-Fe spinel oxides and elementary carbon. The carbide is a necessary reaction intermediate and the overall reaction simplifies to:

\[(2\text{Cr-Ni-7Fe})\gamma_{304L}+4\text{CO} \rightarrow (6\text{Fe-Ni})\gamma_{\text{dust}}+(\text{Cr}_2\text{Fe})\text{O}_4 + 4\text{C} \quad (4.3)\]

The summary reaction will be identical in the case of oxidation of cementite or \(\text{M}_{23}\text{C}_6\)-carbides instead of \(\text{M}_7\text{C}_3\)-carbides; it is only the carbon and CO content in the reaction (1) and (2) that differ. From the overall reaction alone, it seems that metal dusting of stainless steels by CO is basically degradation by oxidation but as discussed above, a more correct description is to see metal dusting as active corrosion by carbon, since the carbon reacts and is then released but not consumed. There is one major difference between the two active corrosion processes. In the case of chlorine-induced corrosion, virtually all metal atoms react chemically to form corrosion products. In the case of metal dusting, according to the above reactions, only around 30 atomic-% of the steel reacts chemically to form corrosion products and the remaining 70% forms metal particles or dust without any chemical reaction. These proportions correspond surprisingly well with the SEM observations in the active reaction front in a metal dusting pit, see Figure 13. In fact, in some cases only a fraction of 30 atomic percent have to react when the attack (Type III) selectively penetrates sub-grain boundaries, see further Chapter 4.4. These principal reactions demonstrate that it is possible to understand and describe the mechanisms of MD in detail and elucidate the reactions and diffusion processes needed.
4.2.2.2 Diffusion processes in the Type III mechanism

Under the influence of ingressing oxygen and carbon the carbides dissolve and the graphite flakes and oxides grow inwards. It appears that Cr-diffusion is the rate-limiting factor of the type III mechanism, since this is required for Cr-depletion of the austenite boundary layer, zone 4, Figure 14. Since the Cr-content of austenite in equilibrium with spinel oxide is very low this will constitute the gradient driving the Cr-diffusion. Cr bulk diffusion is too slow to explain the rather fast kinetics of metal dusting, instead it seems to be required that Cr diffuses with a rate more consistent with that of grain boundary diffusion. The fine grained austenite with graphite flakes (zone 4) suggests that the type II mechanism with inward growth of graphite is operating in the active corrosion front; significantly, it also provides a more rapid diffusion path for chromium in the austenite/graphite phase boundaries.

Using these findings, it is possible to calculate the metal dusting kinetics based on the Cr-diffusion through the austenite boundary layer. A very simple approach is to use Einstein’s random walk model, \((d)^2 = 2Dt\), with the following assumptions:

- The presence of a Cr-depleted austenite boundary layer with a graphite substructure having a separation or equivalent grain size of approximately \(L = 0.5\mu m\), see Figure 13.
- Cr-diffusion comparable with that of grain boundary diffusion of Cr in austenite. At 650\(^{\circ}\)C, the diffusion coefficient is \(D_{G.B.} = 6.5 \times 10^{-23}/\delta\ m^2/s\) [40], where \(\delta\) is the grain boundary width. At relative low temperatures and with a fine grain sized substructure, the effective diffusion coefficient may be approximated to [40]:

\[
D_{\text{eff}} = \delta D_{G.B.}/L = 6.5 \times 10^{-23}/0.5 \times 10^{-6} = 1.3 \times 10^{-16} \text{ m}^2/\text{s}
\]

- The effective Cr-diffusion distance is set to \(d = 1\mu m\) (i.e. the approximate thickness of the Cr-depleted austenite border).

\[
t = (d)^2/(2D_{\text{eff}}) = (1 \times 10^{-6})^2/(2.6 \times 10^{-16}) = 3846 \text{ sec} \approx 1\text{h}
\]

(4.4)

This means that if chromium diffusion through the depleted austenite border is the rate-limiting step, metal dusting may progress at a rate of one \(\mu m/hour\). Since the thickness of the austenite border has been observed to be relatively constant it is not unreasonable to extrapolate the corrosion rate to longer exposure times. Thus, after a 1000h exposure at 650\(^{\circ}\)C, the metal dusting pit may reach 1mm in depth,
which is of the same order of magnitude as the deepest pits observed on the AISI 304L sample. This corresponds to a corrosion rate of around 9mm/year, which is not much compared with other reported data on 18/8 stainless steels of up to 50mm/year in cracking service at 760°C [2]. However, the important conclusion is that the thickness of the Cr and carbide depleted austenite border (zone 4) determines, or reveals, the metal dusting corrosion rate.

4.2.3 Metal dusting Type III at carbon activity < 1

The type I and II dusting mechanisms obviously require a carbon activity of \( a_c \geq 1 \) since graphite is formed. The active corrosion, Type III, would theoretically not need a higher carbon activity than that required to form substantial amount of chromium carbides in the specific alloy and an oxygen partial pressure high enough to form chromia or spinel oxides. It is therefore likely that the Type III mechanism may continue at carbon activities lower than unity, particularly if metal dusting pits are already initiated.

This provides one possible explanation why a synthesis gas with high water vapour and low CO content (14%CO + 6%CO\(_2\) + 32%H\(_2\)O + 48%H\(_2\)), is reported to cause severe metal dusting problems in reformer plants [25].

In pressurised equipment, the situation is exacerbated because the carbon activity in a synthesis gas increases rapidly with pressure as seen in Figure 5. At 40 bar all three types of mechanisms are possible at least up to 800°C \( (a_c \geq 1) \), depending on alloy composition. To reach corrosion rates of 9-50 mm/year on stainless steels, as discussed in Chapter 4.2.2.2, the carbon activity must probably be much higher than unity, or alternatively, the temperature must be high enough to achieve high metal diffusion rates. At high temperatures \( (T>800^\circ C) \) “metal dusting” of Cr-Ni alloys exposed to carbon activity lower than unity may be seen as “green rot”, as discussed in Chapter 4.2.1.

4.2.4 Initiation of metal dusting pits

Normally, the metal dusting corrosion process produces hemispherical pits on highly alloyed steels and Ni-base alloys due to localised breakdown of semi-protective oxide layers, as seen in Figure 16 (a). Occasionally, especially under stagnant conditions, a massive breakdown of the oxide layer may occur as seen in Figure 16 (b).
Figure 16. Stereomicroscope images of AISI 304L sample. Upper side (a) exposed to the gas flow resulting in 1-10 hemispherical pits/cm$^2$. Underside (b) of the same sample exposed to stagnant condition. The surface is attacked by more than 700 pits/cm$^2$, which corresponds to at least one growing pit/100 grains (from Paper 2).

The stagnant gas conditions between the furnace quartz tube and the sample have apparently prevented formation of a protective oxide layer and resulted in nucleation and growth of more than 700 metal dusting pits/cm$^2$. On the upper side, with free access to the gas, there are large numbers of initiated pits, i.e. a pit on every larger grain (see further below), but only 1-10 pits/cm$^2$ have started to grow during the 1000h exposure.

Virtually all grain boundaries were carburized and internally oxidised to a depth of 5-10µm, see Figure 17.

Figure 17. SEM backscattered electron of an image, ground (unetched) sample of AISI 304L. The specimen is tilted at 45º to permit viewing of both the surface and cross-section. An oxide with internally oxidised grain boundaries is seen on the surface (upper part) and the grain boundaries are visible in cross-section (lower part).
However, none of the metal dusting pits start in the grain boundaries but initiate instead in the middle of larger grains, see Figure 18. The smaller grains in Figure 18 (a) are covered by a protective chromia layer and have not developed pits.

Figure 18. SEM backscatter micrographs of AISI 304L sample showing the exposed surface on the upper side with free access to the gas phase. Grain centres show light contrast and are covered with a thin non-protective oxide, compared with the thicker oxides (darker contrast) around all grain boundaries. Metal dusting pits, black spots, have initiated at the centre of the larger grains.

The grain boundary diffusion of Cr appears to be fast enough at 650°C to support a more protective chromia layer at grain boundaries and on smaller grain surfaces, but not on larger grains. A schematic illustration of an initiated metal dusting pit in cross-section is shown in Figure 19.

Figure 19. Schematic illustration of a cross-section with typical position of an initiated metal dusting pit in AISI 304L.

The simultaneous processes of oxidation and carburization are apparent in Figure 20 in that there is a Cr-rich oxide border around the coke-filled pit. This adds
further weight to the argument in Chapter 4.2.1 that oxidation is an inseparable part of the metal dusting process.

![Early stages of a metal dusting pit on AISI 304L sample are shown with SEM-EDS analyses. The simultaneous processes of oxidation and carburization are apparent with a Cr-rich oxide border around the coke filled pit.](image)

**Figure 20.** Early stages of a metal dusting pit on AISI 304L sample are shown with SEM-EDS analyses. The simultaneous processes of oxidation and carburization are apparent with a Cr-rich oxide border around the coke filled pit.

The following conclusions may be drawn from pit initiation studies:

- The grain boundaries are all carburized and internally oxidised but no MD pit are found to initiate at these positions.
- At lower temperatures such as 650°C, the formation of a protective chromia layer is dependent on grain boundary diffusion and subsequently, the Cr supply to the surface of larger grains is insufficient. These weak areas constitute the initiation points of metal dusting pits.
- The dissociation of CO-molecules on the surface produces carbon and oxygen and the simultaneous effects of carburization and oxidation during metal dusting in CO-containing gases is apparent.

### 4.3 Metal dusting on chromia-forming ferritic alloys

As indicted in previous chapters, an important difference between iron and Cr-alloyed steels is that the former give metastable carbides, while the latter form stable carbides like M₇C₃, M₂₃C₆ or M₇C₃, which change the MD-process. These “alloyed” carbides are stable over a wide range of carbon activities but they
destabilise even at very low oxygen partial pressures and dissolve by selective oxidation. The MD of a Fe26Cr-steel (TP 446) by this carbide oxidation mechanism is described in detail in Paper 4. This process is also expected to be valid for many other stable carbides such as those containing Ti, Nb, V, W, Mo, Mn etc.

The oxygen partial pressure in a CO-containing metal dusting environment is always high enough to form Cr-rich oxides such as chromia and (Cr,Fe)-spinel on Fe-Cr-alloys. The important difference from the initially protective chromia layer on the surface is that the oxides formed from selective oxidation of carbides are non-protective, in fact the spinel oxide is totally mixed with coke, as seen in the cross-section of the MD reaction front in Figure 21.

**Figure 21.** SEM-micrographs of 26Cr steel exposed in a metal dusting environment for 3000h showing the cross-sections of the reaction front in bottom of a metal dusting pit.

(a) mechanically polished surface, backscatter electron image  
(b) after etching in nital to give deep etching of the ferrite phase, secondary electron image. EDS-analyses in atomic-% and normalised to 100% are shown in the Table below.

<table>
<thead>
<tr>
<th>Marker</th>
<th>Phase</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ferrite</td>
<td>4</td>
<td>93</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>M7C3-carbide</td>
<td>48-57</td>
<td>22-10</td>
<td>1</td>
<td>-</td>
<td>~30</td>
</tr>
<tr>
<td>3</td>
<td>M3C-carbide</td>
<td>7-12</td>
<td>78-73</td>
<td>0,4</td>
<td>-</td>
<td>~25</td>
</tr>
<tr>
<td>4</td>
<td>Oxide</td>
<td>25-45</td>
<td>14-26</td>
<td>0-2</td>
<td>40-50</td>
<td>Excluded</td>
</tr>
<tr>
<td>5</td>
<td>Particle</td>
<td>7-10</td>
<td>93-90</td>
<td>-</td>
<td>-</td>
<td>Excluded</td>
</tr>
<tr>
<td>6</td>
<td>Coke</td>
<td>0,7</td>
<td>3</td>
<td>-</td>
<td>3</td>
<td>93</td>
</tr>
</tbody>
</table>

The powder diffraction data from the coke indicated large amounts of graphite, with wide lines indicating a fine crystallite size and with d-values corresponding to JCPDS 1-0640. The second strongest lines correspond to Fe-Cr spinel (JCPDS 34-140). The widening of the spinel lines indicates variation in Cr-content. The third crystalline phase detected was cementite (JCPDS 35-0772), again with broad intensity peaks. The cementite lines were significantly lower in intensity compared with the spinel lines, indicating there is more spinel in the corrosion end products.
These findings correspond well to the Thermo Calc-modelling shown in Figure 22. The metal containing corrosion end products at $pO_2 = 1.6 \times 10^{-24}$ bar are predicted to consist of 60-70% spinel and 40-30% cementite or ferrite particles, depending on the carbon activity as shown in (c) and (d). During exposures in MD-environments, the carbon activity in the coke is normally high enough to stabilize unalloyed cementite as discussed in Chapter 4.1.1 and the Cr-alloyed cementite is even more stable.

**Figure 22.** Mole fraction of stable phases in the 26Cr-steel, with graphite excluded in the equilibrium calculations; 

a) as a function of temperature with $a_c = 1$.  

b) as a function of carbon activity with $pO_2 = 1.6 \times 10^{-24}$ at 650°C.  

c) as a function of oxygen partial pressure with carbon activity $a_c = 1$ at 650°C.  

d) as in (c), but with higher carbon activity, $a_c = 2$.  

37
A 26Cr-steel may form 100% carbides ($M_7C_3 + M_3C$) in the steady state reaction front (at low $pO_2$), as seen in the Thermo Calc modelling in Figure 22 (a,c). This is in contrast to low alloyed or mild steels, which forms a mix of ferrite and carbide in the reaction front in the steady state situation as discussed in Chapter 4.1.1. Schematically, the diagram in (c) and (d) can be seen as a cross section of the thin metal dusting front from the metal interface (at low $pO_2$) towards the gas phase (high $pO_2$). For the equilibrated gas composition used in this study, with $pO_2 = 1.6 \times 10^{-24}$, the stable phases will be bcc-ferrite if $a_c < 1.7$ (c), or more commonly, cementite at $a_c > 1.7$ (d) and Cr-Fe spinel oxide.

The mechanisms of MD on Cr-steels may be described by schematic Gibbs energy diagrams as shown in Figure 23.

**Figure 23.** Principal Gibbs energy diagram as function of carbon content at 650°C explaining the mechanisms and driving forces of metal dusting on ferritic Cr-steel. The positions 1-3 correspond to a movement towards the gas phase, i.e. towards higher carbon activity and higher oxygen partial pressure. The positions may also be seen as time steps during the metal dusting process.

- **a)** Position 1 represents the MD-reaction front on a ferritic Cr-steel.
- **b)** Position 2 shows the situation when cementite fragments are exposed to the higher oxygen partial pressure prevalent in the coke.
- **c)** Position 3 is in the coke, away from the surface and shows the situation when the cementite particles are sufficiently small to be in equilibrium with nanotubes.
Position 1 is at the metal dusting reaction front on a ferritic Cr-steel (a). Two equilibria are possible; ferrite – alloyed cementite and alloyed cementite-graphite. Since the cementite is alloyed with sufficiently amount of Cr (~12 atom-%, according to Figure 22 (a)) it is stable at carbon activities significantly lower than $a_c = 1$, as shown schematically with the extended line. The ferrite-graphite equilibrium is marked by a broken line at $G_m = 0$ J/mole as ferrite and graphite are set as reference states.

The alloyed carbides are more stable than unalloyed cementite and thus not subject to the Type I decomposition. However, the oxygen partial pressure is high enough to selectively oxidise the Cr-rich carbides, i.e the Type III mechanism can operate and results in spinel oxides and more or less pure Fe$_3$C particles (b). The cementite may now be subjected to the Type I mechanism; decomposition of metastable cementite into ferrite and graphite.

The fragmentation process continues until the particles cannot nucleate graphite flakes anymore. Instead the Type IV mechanism takes place (c), see Chapter 6.2. The carbon activity in the porous coke is normally high enough to transform ferrite back into nm-sized cementite particles, as discussed above.

The steps and operating mechanisms during MD on ferritic Cr-steels can be summarised as follows;

i) Carburization and carbide formation; Initially $M_{23}C_6$ carbides, then $M_7C_3$ and $M_3C$ carbides at higher carbon activity up to a phase fraction of 100% (In steels with high Cr content).

ii) Partial $M_3C$-carbide dissolution by selective oxidation. $M_7C_3$-carbides may oxidise completely under (Cr-Fe)-spinel formation. (Type III-mechanism).

iii) Release of $M_3C$-carbide fragments due to oxidation (Type III-mechanism) and by graphite inward growth.

iv) The $M_3C$-carbide fragments with high Cr-content continue to dissolve under more Cr-Fe spinel formation until an equilibrium Cr-content (low) is reached in the cementite, depending on $pO_2$ and carbon activity, see Figure 22.

v) Local decomposition of iron cementite fragments in contact with graphite into smaller and smaller cementite fragments and graphite/ferrite eutectoid (Type I).

vi) The carbon activity in the porous coke is normally high enough to stabilise cementite and these nano-particles act as catalysts for carbon nanotube formation (Type IV, see section 4.1.1).

Inward graphite growth in a ferrite phase in stage (iii) refers to the Type II-mechanism whereas inward “growth” of graphite in sufficiently low alloyed and therefore metastable cementite refers to the Type I mechanism. In the latter case it is believed that the cementite decomposes locally where it is affected by surface graphite. Crystallographic preferred orientations in both cementite and graphite
might guide the decomposition process. It is proposed that this decomposition process may result in graphite with intercalation of Fe-atoms in the growing “decomposition” front [22]. Simultaneous inward supply of more graphite in the “crevice” or reaction front would explain the very high graphite fraction observed, which considerably exceed those resulting from a solely eutectoid decomposition as described for pure iron, see Chapter 4.1.1.

The corrosion end products are thus, Cr-Fe spinel oxides, cementite metal dust, and carbon in different forms.

An estimation of the MD corrosion rate of 26Cr-steel was made in Paper 4 and gave a corrosion rate of 0.45µm/h, or 4mm/year, which is about half the corrosion rate of austenitic stainless steels under similar conditions, see Chapter 4.2.2.2. The metal dusting process may be summarised as oxidation of alloyed carbides, decomposition of metastable cementite and fragmentation by graphitization of ferrite, in other words, all three mechanisms Type I, II and III may operate on Cr-steels.

4.4 Alumina forming alloys

Steels and Ni-base alloys high in Cr, Al and Si may form protective oxide layers, which prevent the ingress of carbon, thus providing improved resistance. However, the oxide scale is never perfect so a protective oxide can only extend the time for the onset of MD, i.e extend the incubation period. It has been shown that Al alloying in Fe- and Ni-base materials results in long incubation periods during severe MD-conditions, see Refs. [26,41,42,43,44] and Paper 4. However, the alumina-forming binary systems with nickel aluminides and iron aluminides exhibit relatively poor MD resistance [14]. This implies that the most protective oxides against carbon penetration are mixed oxides containing both Al and Cr.

4.4.1 Oxide formation on FeCrAl- and NiCrAl-alloys

It is generally believed that temperatures in the range 540°-650°C are too low for formation of an alumina layer [45]. This it is true for atmospheres with high oxygen partial pressures, as exemplified by the identification of a Cr-rich oxide on a FeCrAl-alloy at 560°C [46]. However, at low oxygen partial pressure, such as in low pressurised water vapour (10⁻⁵ bar), Al rich oxide may dominate at 560°C [46].

From a thermodynamic point of view it is predicted that both Cr-rich oxides and alumina would form on FeCrAl and NiCrAl alloys during MD conditions as seen
in the Thermo Calc modelling in Figure 24. The modelling cannot take into account Al$_2$O$_3$-Cr$_2$O$_3$ solid solution and Al-containing spinels, but nevertheless virtually all Cr and Al in the alloy is predicted to form oxides if the prevailing oxygen partial pressure in the gas could interact with the metal through an unprotective oxide layer.

However, it has been observed experimentally that a protective Cr-doped alumina can form on NiCrAl and FeCrAl alloys in MD environments at relatively low temperatures, 540°C-650°C [47] and Paper 6. The study in Ref. [47] showed that a 0.15µm thick alumina layer doped with some per cent Cr was formed on Alloy 602CA exposed two years in a methanol plant.

![Figure 24. Mole fraction of stable phases in the NiCrAl-C-O-H system at 650°C as a function of oxygen partial pressure with a fixed carbon activity $a_c=1$ and graphite excluded from the calculations. For the equilibrated gas composition used in this study, with $pO_2=10^{-24}$, the stable phases will be oxides (alumina, Cr-Fe spinel, chromia) and Ni-rich FCC. Schematically, the diagram can be seen as a cross section of the thin metal dusting front from the metal interface (virtually at lower $pO_2$ than $10^{-38}$) towards the gas phase (high $pO_2$).](image)

Rf-GDOES analysis on a FeCrAl-alloy exposed in 25%CO+72%H$_2$+3H$_2$O at 650°C showed that the surface oxide was rich in Al and low in Cr after 1000h, see Figure 25 (a). The oxide was perfectly smooth and shiny with violet-blue interference colour, indicating that no oxide had spalled off. The analysis after the 7600h exposure, Figure 25 (b), was somewhat smeared due to a rough and graphite “contaminated” surface, but shows a similar picture of Cr-containing alumina. A similar Al-enriched oxide on FeCrAl was reported in Paper 1 at 750°C.
Figure 25. Rf-GDOES analysis on a FeCrAl-alloy exposed in 25%CO+72%H₂+3%H₂O at 650°C. after 1000h exposure of a 600 grit surface (a) and after 7600h exposure of an 80 grit surface (b).

The diffusion of Al and Cr in a Ni-base alloy is discussed in Paper 6 at 540°C and the typical bulk diffusion lengths calculated with Einstein’s random walk model, $(d)^2 = 2Dt$, after a two year exposure are:

\[ d_{Cr} = 0.17\mu m. \]
\[ d_{Al} = 0.41\mu m. \]

This may be compared with the study of FeCrAl alloy in similar environment.
The bulk diffusion coefficient of Cr and Al at 650°C in ferrite are 6.1×10^{-18} \text{ m}^2/\text{s} and 3×10^{-17} \text{ m}^2/\text{s}, respectively [40,48]. Corresponding diffusion lengths for FeCrAl alloy at 650°C are calculated for a diffusion time selected to give the same Cr-diffusion length as above (d_{Cr} = 0,17\mu m);

\[ d_{Cr} = 0,17\mu m, \text{ gives } t = (d_{Cr})^2/2D_{Cr} = 40 \text{ min}, \text{ which gives the Al-diffusion length;} \]

\[ d_{Al} = (2D_{Al}t)^{0.5} = 0,38\mu m. \]

The diffusion length of Cr is thus the same for a Ni-base alloy at 540°C for 2 years or a FeCrAl alloy at 650°C for 40 minutes. These exposure times also give virtually the same diffusion length for Al. This implies that these two different cases may result in quite similar oxides in a selectively oxidising atmosphere, such as a MD environment, albeit at different exposure times. This is supported by the GDOES results shown in Figure 25.

Since the Cr-content is significantly higher than the Al-content in both types of alloys, it is inevitable that some chromia will form during the initial stages of oxidation. However, Al diffuses faster than Cr and can thus cause a transition to an alumina after a relative short period. If this happens, chromia will not form again, because the oxygen activity is too low under the alumina and subsequently only a slow alumina growth will occur. An additional effect that would promote this proposed scenario is the formation of volatile Cr-oxyhydroxides [49]. However, the formation of volatile Cr-containing compounds under metal dusting conditions has not yet been studied, or at least not published.

The important conclusion is that a highly protective Cr-doped Al$_2$O$_3$ oxide forms on FeCrAl and NiCrAl alloys under Cr and Al selective oxidation conditions, even at relatively low temperatures (540°-750°C). This explains the superior behaviour compared to chromia forming alloys in atmospheres with low oxygen partial pressure like MD-environments.

### 4.4.2 Metal dusting on NiCrAl-alloys

The same metal dusting mechanisms operate on austenitic NiCrAl alloys as on austenitic stainless steels in synthesis gas, see details in Paper 5 and 6. Field and laboratory exposures of Alloy 602CA revealed some new features which can explain the relative fast MD process at lower temperatures, 540°C.

A two-year field exposure was conducted at 540°C in a methanol plant, i.e. in a synthesis gas rich in water vapour. The same material was exposed in a comparative laboratory study at 650°C in a gas mixture with higher CO and lower H$_2$O content than in the field exposure; 50%CO + 3%H$_2$O + 47%H$_2$.  

43
The post exposure metallography showed two different morphologies of the MD-degradation which could often be observed in the same metal dusting pit, one with a fine uniform structure and one more coarse lamellar structure as seen in the overview in Figure 26. Both morphologies originate from the same metal dusting mechanism, i.e. Type III which involves selective oxidation of Cr-containing carbides.

The fine uniform substructure, seen in Figure 26 (c,d), is typical for cellular growth of discontinuously precipitated carbides, resulting in a carbide network, i.e. the reaction C-saturated (Cr,Ni)-austenite → Cr-carbide + (Cr,C)-depleted austenite. The mechanism and kinetics of this reaction is described in Chapter 7.1.

The inserted detail (a) in Figure 26 shows the coarse structure, which comprises of alternating lamellae of Ni-enriched austenite and a mixture of spinel oxides and carbon. The inserted details (a,b) show a ~0.5µm semi-protective Cr-rich oxide layer at the bottom of the pit. The presence of Cr-rich oxides here is in notable contrast to the more or less pure Al₂O₃ formed on the unattacked surface, see Chapter 4.4.1. The oxide at the base of the pit is penetrated by ~200nm thick Ni-austenite bands surrounded by dark flakes, ~50nm in thickness. The latter are believed to be graphite flakes in analogy with earlier finding, see Chapter 4.2.2. However, at the moment at which the MD-process was interrupted, there were no discontinuous precipitated carbides under this semi-protective oxide layer, and subsequently no active MD reaction front. In other words, it seems that at least a part of the MD-pit may undergo slow growing or “idling” periods. If or when discontinuous precipitated carbides start to form under the semi-protective oxide layer, the situation will change rapidly. This is a strong indication that the metal dusting process has an intermittent or cyclic feature resulting in variations in the corrosion rate and structure of the corrosion product, at least in less aggressive synthesis gas mixtures.
Figure 26. NiCrAl-alloy exposed in synthesis gas at 540°C/2 years. Metal dusting pits show both a banded structure with alternating lamellae of Ni-enriched austenite and spinel oxides/ carbon (a,b) and a more active reaction front with finer structure marked with a broken line to the right (c,d). A semi-protective oxide layer (spinel) at the bottom of the pit is seen (a,b,c) and indicates that the metal dusting process has an intermittent or cyclic feature resulting in periods with low corrosion rate, i.e. “idling” periods. The maximum pit depth detected was around 45µm.
There appear to be a number of parallels between the MD-process on stainless steels and Ni-base alloys. For stainless steels, Cr carbides dissolve, resulting in a Cr-gradient towards the spinel oxide in the reaction front. The difference for Ni-base alloy examined here is that a discontinuous carbide precipitation process precedes the MD attack and that Cr–carbide dissolution and direct Cr-carbide oxidation appear to take place at the reaction front. Ni-rich lamellae are thought to become included in the reaction products, because clusters of austenite sub-grains are released from the reaction front.

A graphitization process (Type II) probably operates in conjunction with these oxidation processes (Type III) and disintegrates the Ni-rich metal lamellae and flakes to metal dust. In a synthesis gas with a carbon activity not much higher than unity, it is expected that the disintegration by graphitization is quite slow and therefore, Ni-lamellae are still visible in the MD-pit, as seen in Figure 26.

It is not possible to explain the relatively fast MD-process in the Ni-base alloy 602CA, considering the low temperature (540°C), by bulk or even static grain boundary diffusion. The solution to the problem is found in the cellular structure with discontinuous precipitated carbides. All metal diffusion takes place in the moving cellular boundaries, which results in a fast growing carbide network. The fast MD-process operates only on the cellular structure with a discontinuous precipitated carbide network, which results in direct fragmentation into Cr-rich oxide (spinel), Ni-enriched particles and carbon.

There are three processes that could be rate limiting for the Type III MD-corrosion in this case, all of which require movement of substitutional atoms:

i) Cellular growth of discontinuous precipitation
ii) Carbide dissolution by selective oxidation
iii) Direct oxidation of carbides in the cellular sub-boundaries

Direct oxidation of Cr-rich carbides in a high water vapour environment, such as synthesis gas, is not considered likely to be the rate limiting reaction. An attempt to estimate the rate of the cellular growth of discontinuous precipitation (i) is presented in Chapter 7.1. An estimation of the selective oxidation (ii) is treated in Paper 6 and is based on the idea that the discontinuous precipitated carbide structure in the active MD-front, see Figure 26 (c,d), may be treated as a fine sub-grained metal layer with a grain size of 0.2µm.

The Cr-transport is governed by grain boundary diffusion in the phase boundaries towards the metal/oxide interface. This modelling of the MD-process may be compared with cyclic oxidation in that the oxide and metal particles are “spalled” away from the reaction front by oxide and graphite/coke formation. Hence, it can be assumed that after Cr-depletion and Cr-oxidation of a layer with a thickness of a sub-grain diameter, i.e 0.2µm, it spalls away and the cyclic process starts again.
It is concluded that the cellular growth rate (Chapter 7.1) is 4-8 times faster than the selective oxidation process. This implies that the Type III mechanism, carbide dissolution by selective oxidation, is rate-determining.

The metal dusting rate, from measurements of pit depths, of 602CA was estimated to be at least 550µm/year at 650°C and an order of magnitude lower in the field exposure at 540°C, where the carbon activity was much lower.

The rate 550µm/year at 650°C may be compared with the corrosion rate of austenitic steels, e.g. AISI 304L, 9000µm/year (Paper 2) or with FeCrAl alloys, 1300µm/year (Paper 4), during similar conditions with high carbon activity at 650°C. In this perspective, NiCrAl-alloys seem to have a superior metal dusting resistance. However, another degradation mechanism, micro crack formation, was also detected in this study and accelerates the corrosion process. These micro-cracks may explain the relatively low metal dusting resistance of 602CA (compared to other Ni-base alloys) during cyclic MD-conditions, as has been reported by other researchers [50]. It may be concluded that the micro-crack formation represents the major part of the metal loss, although the deepest attack is related to the MD-pits. This process is described in detail in Chapter 7.2.

The degradation process of MD on austenitic stainless steels and Ni-base alloys may be summarised with the following mechanism chart, Figure 27, based on the results from Papers 2, 5 and 6. The selective oxidation, Type III mechanism, changes somewhat when operating on a Ni-matrix compared to a Fe/Ni-matrix. On the former it results in carbide free Ni-lamellae or fine Ni-subgrains and on the latter it results in a carbide free (Fe/Ni)-austenite border in the steady state process. It may be added that the Type IV-mechanism causes a continued disintegration of the corrosion products under formation of austenitic nanoparticles and carbon nanotubes, see Chapter 6.2. Thus, the coke, or final corrosion product consists of carbon in different forms, austenitic nano-sized particles and oxides, primarily spinel oxides.
The identification of the role of discontinuous precipitated carbides is of principal importance since it explains high metal dusting corrosion rates at relatively low temperatures on Ni-base alloys and probably on austenitic steels stainless as well.

### 4.4.3 Metal dusting on FeCrAl-alloys

The metal dusting process on FeCrAl alloys resembles more MD on austenitic steels than on other ferritic materials in that FeCrAl-alloys form a thin carbide free and Cr-depleted layer in the reaction front. The study in Paper 4 is based on results from exposures at 650°C/4000h + 600°C/1000h in a synthesis gas low in water vapour, 25%CO+3%H₂O +H₂. FEG-SEM studies on a metal dusting pit are shown in **Figure 28. Figure 29 and Figure 30** are from a STEM investigation to identify the carbide phases [51].

A line analysis of the phase fractions in the outermost reaction front (**Figure 28**) gave approximate 34% M₇C₃-carbide, 35% of the dark plate-shaped κ-carbide and 33% ferrite.
According to the TC-modelling in Paper 4, up to 40% M₇C₃-carbide is expected. No ternary FeCrAl-carbide is described in the TC-database. However, a stoichiometric calculation of the maximum carbide content in a carbon-saturated FeCrAl-alloy gives approximately the following volume fractions: 35 vol-% M₇C₃-carbid, 40 vol-% Fe₃AlCₓ and 25 vol-% ferrite, which fits quite well with the observations. A carbide-free ferrite border is evident and comparable with the carbide-free and Cr-depleted austenite border observed on austenitic stainless steels.

**Figure 28.** FeCrAl-alloy exposed in a metal dusting environment for 5000h. FEG-SEM backscatter electron image, polished cross-section of the reaction front in bottom of a metal dusting pit. Average EDS- and for carbon, WDS-analysis of the different phases in atomic-% and normalised to 100% are shown below. The values are somewhat “smeared” because of the fine structure.

<table>
<thead>
<tr>
<th>Marker</th>
<th>Phase</th>
<th>Cr</th>
<th>Al</th>
<th>Fe</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Ferrite + M₇C₃</td>
<td>14</td>
<td>6</td>
<td>65</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>b</td>
<td>Grey contrast (M₇C₃)</td>
<td>30</td>
<td>4</td>
<td>40</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>c</td>
<td>Dark: (\kappa)-carbide</td>
<td>13</td>
<td>13</td>
<td>55</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>d</td>
<td>Ferrite</td>
<td>10</td>
<td>5</td>
<td>83</td>
<td>-</td>
<td>Excluded</td>
</tr>
<tr>
<td>e</td>
<td>Oxide</td>
<td>5-15</td>
<td>5-15</td>
<td>40-60</td>
<td>10-30</td>
<td>Excluded</td>
</tr>
<tr>
<td>f</td>
<td>Coke</td>
<td>1</td>
<td>0,5</td>
<td>10</td>
<td>6</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>FeCrAl-bulk comp.</td>
<td>20,4</td>
<td>10,6</td>
<td>69</td>
<td>-</td>
<td>0,03</td>
</tr>
</tbody>
</table>
**Figure 29.** FeCrAl alloy exposed 5000h at 650°/600°C, overview showing the sample removal with FIB (Focused ion beam) technique.

**Figure 30.** Bright-field STEM image close to the reaction front. EDS points are summarised in the Table below. Diffraction pattern from κ-carbide and ferrite are shown to the right. The κ-carbide has a hexagonal symmetry with lattice parameters: $a \approx 8.5$ Å, $c \approx 10.8$ Å.

<table>
<thead>
<tr>
<th>Point</th>
<th>Phase</th>
<th>Al</th>
<th>Cr</th>
<th>Fe</th>
<th>O</th>
<th>C</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M-C$_3$</td>
<td>-</td>
<td>50,5</td>
<td>49,1</td>
<td>Low level</td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ferrite</td>
<td>8,33</td>
<td>1,13</td>
<td>90,5</td>
<td>Low level</td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Oxide</td>
<td>-</td>
<td>73,4</td>
<td>22,6</td>
<td>High level</td>
<td>Background</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Fe$_3$AlC$_x$</td>
<td>19,8</td>
<td>4,26</td>
<td>75,8</td>
<td>Low level</td>
<td>Background</td>
<td></td>
</tr>
</tbody>
</table>

The diffraction pattern and the EDS analysis in *Figure 30* show that two phases, κ-carbide (Fe$_3$AlC$_x$) and M-C$_3$, were formed close to the MD reaction front. The outermost reaction front was unfortunately removed during the sample preparation. However, a small region with a “tongue” of chromia surrounded by ferrite and dissolving carbides where detected closer to the reaction front.
The mechanism of MD is similar to that of austenitic stainless steels and involves dissolution of carbides by selective oxidation to give a carbide-free ferritic surface layer with a decreasing Cr and Al gradient towards the (Cr, Al, Fe)-oxides on the surface. The ferritic surface layer is thinner than the corresponding (Fe/Ni)-austenite layer on austenitic steels and also without graphite channels, indicating a lower metal flux and slower metal dusting kinetics. A very simple approach is to use Einstein’s random walk model, \((d)^2 = 2Dt\), to calculate the diffusion times required. The effective metal diffusion distance is set to \(d = 0.3\mu m\), i.e. the approximate thickness of the carbide free and (Cr-Al)-depleted ferrite border. The bulk diffusion coefficient of Cr and Al in ferrite is \(6.1 \times 10^{-18} m^2/s\) and \(3 \times 10^{-17} m^2/s\) respectively, at 650°C [40,48].

\[
\begin{align*}
t_{Cr} &= \frac{(d)^2}{(2D_{eff})} = \frac{(0.3 \times 10^{-6})^2}{(2 \times 6.1 \times 10^{-18})} = 7353 \text{ sec} \approx 2h \quad (4.5) \\
t_{Al} &= \frac{(d)^2}{(2D_{eff})} = \frac{(0.3 \times 10^{-6})^2}{(2 \times 3 \times 10^{-17})} = 1500 \text{ sec} \approx 0.4h \quad (4.6)
\end{align*}
\]

This means that chromium diffusion through the ferrite border is the rate-limiting step and MD-corrosion may progress at a rate of \(0.3/2 = 0.15 \mu m/hour\). This is about 7 times slower than the metal dusting rate on AISI 304L austenitic steel, see Chapter 4.2.2.2 (Paper 2). The ferrite border has probably defects and grain boundaries, which enhance the Cr-diffusion and corrosion rate, but FeCrAl–alloys are nevertheless expected to exhibit much lower MD-corrosion rates compared to austenitic steels.

The steps and operating mechanisms during MD on FeCrAl-alloys can be summarised as follows;

i) Carburization and carbide formation, initially \(M_{23}C_6\) carbides, then \(M_7C_3\) and \(Fe_3AlC_x\) (\(\kappa\)-carbide) at higher carbon activity to an observed carbide fraction of \(\sim 70\%\mbox{ } (M_7C_3 + \kappa\)-carbide).

ii) Complete dissolution by selective oxidation of all carbides formed, i.e. a ferrite-border forms, through which Cr and Al diffuse under subsequent Cr-Al-Fe-oxide formation (Type III).

iii) Simultaneous fragmentation of the ferrite border due to the graphitisation process (Type II).

iv) The metal dust may act as a catalyst for filamentous carbon formation (Type IV), see Chapter 6.2. The corrosion products are thus Cr-Al-Fe oxides, ferritic metal dust, and carbon in different forms. Al is a ferrite stabiliser, which is in accordance with the observed ferritic border and the ferritic metal fragments. However, at a later stage, when Cr and Al are consumed in the ferritic fragments by oxidation, the ferrite may transform to cementite dust as the corrosion end product.
The alloy composition and exposure temperature determine which type of metal dusting mechanism is dominant. A principal change occurs around $750^\circ C$, as metastable cementite will not form above this temperature during metal dusting conditions [20]. A tentative schematic approach to visualise the operating metal dusting mechanisms as a function of alloy composition in a CO containing atmosphere are shown in Figure 31. The different types of metal dusting mechanisms are, as previously described,

Type I: Decomposition of metastable cementite.
Type II: Decomposition by graphitization.
Type III: Active corrosion by carbon and oxygen.

![Figure 31. Schematic ternary chart of the operating metal dusting mechanisms as a function of alloy composition at lower temperatures (a) and at higher temperatures (b). Modified results from [18] and Paper 3.](image)

It was shown in Paper 4 that Type I, cementite decomposition, only occurs during the initial stages of MD on iron and may not represent a steady state process. Types II and III constitute the steady state process of MD in all situations for thermodynamical reasons.

Empirically it is found that the kinetics become slower with the different mechanisms in the order I > II > III. This is in quantitative agreement with observations of the relative corrosion kinetics in metal dusting environments. Basically, moving from the Fe-rich corner of the Fe-Ni-Cr ternary towards the Ni-rich corner retards the metal dusting kinetics and moving from the Ni-rich corner towards the Cr-rich corner, has a further retarding effect.
However, it is predicted that the synergistic effect of the Type II and III mechanisms together, especially for alloy compositions far away from the Cr-rich corner in Figure 31, may give rather fast metal dusting kinetics, as is observed for AISI 304L or Alloy 800H. In these cases, the Cr-diffusion through the carbide free zone or layer is of vital importance, since it determines the corrosion rate (Type III). The graphite enhances the Cr-diffusion by forming a substructure and also causes fragmentation of the layer (Type II).

In a study by Ref. [52], pure Cr was studied in CO at ~900°C and the corrosion product was analysed by X-ray diffraction and identified as Cr$_3$C$_2$ and chromia, i.e only Type III. Pure chromium or alloys with a high Cr-content suffer from metal dusting but with relatively slow kinetics of the Type III mechanism. Furthermore, a high Cr-content prolongs the incubation period for the initiation of metal dusting. The positive effect of elements with high affinity to oxygen such as Cr, Al and Si is expected to be due to their influence on the incubation period, i.e. the time before the metal dusting attack starts. High levels of these elements enhance the protective/self healing properties of the oxides against carbon penetration and thus increases the incubation time.

Another attempt to summarise the mechanisms as a function of alloy composition and temperature is in terms of a schematic binary diagram for several interchangeable elements, as shown in Figure 32.

![Figure 32](image)

**Figure 32.** A tentative binary mechanism chart for several elements as a function of temperature. Basically, Fe Ni and Co are interchangeable elements, exception that Ni and Co do not form metastable cementite, i.e the Type I mechanism. In a similar way, Cr may be substituted with Al to some extent without changing the operating metal dusting mechanism.
Green rot may be included as a special case of the Type III-mechanism at higher temperatures, as shown in the binary chart with a shaded area. Green rot is basically a high temperature oxidation process, which results in green fractured surfaces as discussed in Chapter 4.2. In combination with carburization it may be seen as a special case of the Type III mechanism.

Basically all high alloyed materials are expected to suffer from a MD-process which is a combination or collaboration of Type II and III mechanisms. A summarising metal dusting mechanism flowchart for ferritic and austenitic stainless steels and Ni-based alloys are shown in Figure 33.

![Figure 33](image)

**Figure 33.** A summarising metal dusting mechanism flowchart for ferritic and austenitic stainless steels/Ni-base alloys. The marked carbon activity is calculated at 650°C, however, the principles are applicable in a wide temperature range.

Al is a ferrite stabiliser and, subsequently, ferritic dust is formed on FeCrAl-alloys. Cr is a cementite stabiliser and cementite dust is preferentially formed on Cr-steels. However, the carbon activity is normally high enough to form cementite nanoparticles even in the case of pure iron. Ni is an austenite stabiliser and, subsequently, austenitic metal dust is formed on stainless steels and Ni-base alloys.
It appears that all engineering alloys used today may suffer from metal dusting as they all can form oxides, carbides and/or graphite. It is only a question of time, temperature and environment before metal dusting starts. All alloys based on Fe, Ni, Co, even those alloyed with Cr, Al and Si, are more or less susceptible to metal dusting. The incubation time may differ but once a metal dusting pit starts to grow the kinetics are catastrophic, at least from an engineering point of view. It seems that the solution to the metal dusting problem should be found in new alloy systems free from carbide formers (such as Fe and Cr) and graphite formers (such as Ni and Co).
6 COKE AND CARBON NANOTUBE FORMATION

It is well known that it is difficult or impossible for graphite to nucleate directly from a gas phase even if the carbon activity is rather high. An exception may be soot formation during imperfect combustion of hydrocarbons, but it can be argued that soot probably consists of amorphous carbon. On the other hand, metals like Fe, Ni and Co and their oxides are very efficient catalysts [13,19,53].

6.1 Catalytic coke formation

A summary of catalytic data for CO dissociation on some metals and oxides at the maximum coke formation temperature are shown in Table 5.

Table 5. Relative catalytic activity of various materials for the decomposition of carbon monoxide after Ref. [53].

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature of maximum carbon deposition, °C</th>
<th>Approximate maximum deposition in 1/2 h, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>550</td>
<td>0.75</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>550</td>
<td>0.74</td>
</tr>
<tr>
<td>Fe</td>
<td>550</td>
<td>0.40</td>
</tr>
<tr>
<td>NiO</td>
<td>450</td>
<td>0.30</td>
</tr>
<tr>
<td>Co₄O₆</td>
<td>650</td>
<td>0.25</td>
</tr>
<tr>
<td>Co</td>
<td>650</td>
<td>0.15</td>
</tr>
<tr>
<td>Ni</td>
<td>750</td>
<td>0.15</td>
</tr>
<tr>
<td>Ni₂O₃</td>
<td>450</td>
<td>0.09</td>
</tr>
<tr>
<td>Mn</td>
<td>850</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>650</td>
<td>0.005</td>
</tr>
<tr>
<td>Al</td>
<td>550</td>
<td>0.002</td>
</tr>
<tr>
<td>Al₂O₃, Cr₂O₃, Cu, CuO</td>
<td>(Highest temp. examined)</td>
<td></td>
</tr>
<tr>
<td>Mn₃O₄, Zn and ZnO</td>
<td>No appreciable deposition</td>
<td></td>
</tr>
</tbody>
</table>

A CO-molecule can be adsorbed on the surface and dissociate into free C and O. The C atoms may then form graphite on an oxide surface or on and inside a carbon supersaturated metal phase. The O atoms stay on the surface until they combine with other atoms to form gas molecules, e.g., H₂O or CO₂ or form metal oxides like chromia, alumina or spinels if the oxygen partial pressure is high enough.
As metal dusting forms active metal particles and often also iron rich spinels, the total catalytic surface area increases rapidly during the corrosion process resulting in large amount of solid carbon in different forms.

### 6.2 Carbon nanotube formation, the Type IV mechanism

The coke from pure iron consist in certain regions of 100% carbon filaments or carbon nanotubes which are attached to small cementite particles. Typical examples are shown in Figure 34. Recently, both rods [54] and tubes [55,60] have been reported during metal dusting corrosion. However, the discovery of the tubular nature of these filaments was originally made by Hillert and Lange in the 1950’s [56].

The metal fragments broken off from the bulk material during MD will still act as catalysts and dissolve carbon and precipitate it as graphite. The fragmentation may thus continue and the particle size will decrease gradually. It is proposed that they finally may become too small to allow further precipitation in their interior and the continued formation of solid carbon will occur on their surface. For energetic reasons one could primarily expect that the graphite lattice would be oriented with its hexagonal planes more or less parallel to the surface of the metallic particle. The growth will occur at the interface where carbon atoms can attach themselves to the edge of a hexagonal plane. This would result in a tendency of the graphite to shoot out from the particle more or less tangentially.

It is proposed that this is the mechanism behind the formation of nanotubes on the very small particles and would explain why the diameter of the nanotubes corresponds to the diameter of the particles. This growth mechanism of nanotubes is shown in Figure 35.
Figure 34. Carbon nanotubes/rods formed in the coke after exposure of iron in a CO/H₂/H₂O gas mixture. (a) Region with 100% carbon filaments. (b) A catalytic particle associated with a tube or a rod. (c) The end surface, of a carbon nanotube. (d) A thin nanotube, around ~10nm in diameter is visible.

A catalytic particle is seen in Figure 34 (b) and an end view, or a fracture surface of a carbon filament is shown in (c) with the tubular shape clearly visible. The thin filament in (d), around 10nm in diameter may typically contain 5-10 graphite layers [19].
Figure 35. The proposed mechanism for nanotube formation in CO/H₂-containing gases at high carbon activities. CO-molecules dissociate at the cementite surface, carbon diffuses towards the lower carbon activity at the carbon nanotube growth zone and oxygen reacts with hydrogen to form water vapour (a). Two nanotubes may grow from one particle, as seen in (b).

The same micromechanism as described above may occur on the metallic surface of the bulk of the specimen but there it would not result in nanotubes for geometric reasons. Instead, a much more irregular structure would form, which normally is referred to as coke. The Type IV-mechanism actually represents a self-assembling system; the larger metal fragments are subjected to the Type II mechanism with irregular graphite formation until reaching a suitable size for nanotube formation.

Coke from the same exposure of pure iron was also studied by TEM and as shown in Figure 36, a carbon nanorod, or possibly a multi-walled nanotube with a wall-thickness close to the tube radius, was detected as well.
Figure 36. TEM image of carbon nanorod and associated nanoparticle observed on a TEM lacy grid. The diffraction pattern taken from the nanoparticle is consistent with the [312] zone axis of cementite.

In case of a single-walled nanotube the growth could be dependent solely on carbon surface diffusion on a particle, but obviously, the formation of rods or thick multi-walled tubes would need carbon bulk diffusion in cementite or in austenite depending on the alloy system.

It is difficult to find reliable diffusion data for carbon in cementite, however data for austenite is readily found. In the case of MD on AISI 304L steel, carbon filaments are associated with austenitic particles with a typical composition of 86Fe-14Ni. As shown in chapter 6.3, the maximum carbon activity difference in such nanoparticles should be $1.7 < a_c < 2.1$ at 650°C. This corresponds to a carbon concentration difference of 0.28 atomic-%, as shown in Figure 37.
Figure 37. Carbon content in (86Fe-14Ni)-austenite as a function of carbon activity at 650°C. An activity difference of 1.7 to 2.1 corresponds to a concentration difference of 0.28 atom-%.

A typical austenitic particle and associated carbon filament have a radius, \( r = 25\text{nm} \). Approximating the filament with a homogenous graphite rod it is possible to calculate the filament growth rate by using Fick’s first law:

\[
\frac{dm}{dt} = -D \Lambda \rho \frac{\partial C}{\partial x}
\]  

which in general can be approximated as:

\[
\Delta m/\Delta t = D \times \Lambda \times \rho \times \Delta C_C/\Delta x \quad \text{or;}
\]  

\[
\Delta m/(\Delta t\times \Lambda \times \rho) = D \times \Delta C_C/\Delta x 
\]  

\( \Delta t \) = diffusion time.
\( \Delta m \) = amount of carbon that diffuses through an austenite particle and forms a filament.
\( \Delta C_C \) = The difference in C-content in the austenitic particle expressed in mole fraction, \( \Delta C_C = \Delta X_C = 0.0028 \).
\( \Delta x \) = diffusion length, approximated to the particle radius, \( \Delta x = r = 25\text{nm} \).
\( \Lambda \) = diffusion cross-section area.
\( \rho \) = density of the diffused element.
\( D_C \) = Carbon bulk diffusion coefficient in austenite at 650°C, \( 2 \times 10^{-13} \text{ m}^2/\text{s} \) [40].
The expression in (Eq.6.3) corresponds to the growth rate, $v$:

$$v = D \times \Delta C_r / \Delta x$$  \hspace{1cm} (7.4)

$v = 2 \times 10^{-13} \text{m}^2/\text{s} \times 0.0028 / 25 \times 10^{-9} \text{m} = 2.2 \times 10^{-8} \text{m/s}, \text{or 22nm/s}$

This fits surprisingly well with the observed growth rate of thick multi-walled carbon nanotubes during MD; 3-20nm/s, albeit at 680°C[55].

A different hypothesis about the formation of the small particles acting as catalysts for the formation of nanotubes has been proposed elsewhere [17,20,28]. This suggests that Fe- or Ni-atoms dissolve in the graphite that grows on and into the specimen. These atoms are proposed to diffuse outwards and finally precipitate and agglomerate to nano-sized particles inside, or at the outer side, of the surface layer of graphite (coke). To the present author this mechanism seems less likely. It would depend on the solubility and diffusivity of metals in graphite and on a driving force for outward diffusion, which has not yet been identified.

The Type IV-mechanism, the nanotube process, represents only a secondary MD-effect, i.e. further disintegration of the corrosion products. However, there is an interest in these small tubes in material science in general and particularly in nanotechnology.

### 6.3 Carbon activity in the coke

It is relevant to discuss the carbon activity of the various types of carbon mentioned here. Perfectly developed graphite should by definition have a carbon activity of 1.0 and higher values are expected as a consequence of imperfections. The type here described as coke, which contains a mix of defect graphite, amorphous carbon and/or nanotubes, should thus have an activity considerably higher than 1.0. A compact graphite layer is observed to initiates decomposition of cementite, indicating that the carbon activity is in not higher than 1.7 at 650°C, as discussed in Chapter 4.1.1. However, the ferritic fragments released during the steady state MD-process, form catalytic nano-particles consisting of cementite, indicating that carbon activity is higher than 1.7 in the now prevalent porous coke.

Since nanotubes are only observed to be associated with cementite and not ferrite particles, it seems that the carbon activity needed for carbon nanotube formation may be 1.7 or higher. The nanotubes have a very high surface-to-volume ratio, which will increase the carbon activity.
By comparing pure iron and AISI 304L stainless steel exposed in the same MD environment it is possible to evaluate the effective carbon activity in the coke, see Figure 38. As mentioned above, the carbon activity in the case of iron must be at least 1.7 in order to form cementite. This is shown in the Gibbs energy diagram in Figure 38 (a). The particles found in connection to the carbon nanotubes in the case of AISI 304 were austenitic (not Ni-alloyed cementite) as shown in Figure 38 (b). Thus, the carbon activity in the coke which gives nanotube formation must be between the stability limits of unalloyed cementite and Ni-alloyed cementite, i.e. $1.7 < a_c < 2.1$ at 650°C.

Figure 38. Principal Gibbs energy diagram as function of carbon content at 650°C showing prevailing equilibria under carbon nanotube formation on iron, i.e. cementite (a), and on austenitic stainless steels (b).
7 EFFECTS OF CARBURIZATION

During carburization of metals additional effects may occur besides from carbon inward diffusion, carbide precipitation and metal dusting. Discontinuous precipitation, micro-crack formation and volume expansion due to carburization will be discussed next.

7.1 Discontinuous precipitation

Cahn [57] and Hillert [58] described the growth of discontinuously precipitated carbides during the 1950-60’s. Many solid state reactions such as eutectoid transformations like pearlite formation, and discontinuous precipitation result in a lamellar structure. In the case of discontinuously precipitated carbide in austenite, Cr-diffusion occurs in the austenite/austenite grain boundary as the boundary of the growing cell moves through the supersaturated austenite. In the Alloy 602CA described in Paper 5 and 6, a fine substructure of carbides (probably M₇C₃) and a new Ni-enriched, Cr-depleted austenite was formed from the carbon saturated austenite. The carbon supersaturation decreases discontinuously as the carburized austenite/ newly formed austenite cell boundary advances. The carburization thus constitutes the driving force for the phase transformation which occurs by a discontinuous co-operative growth of carbide and Cr- and C-depleted austenite. This type of reaction represents a fast precipitation process at lower temperatures where bulk diffusion is slow. It has been suggested that the force, actually pulling the cellular boundary of discontinuous precipitation, is the difference in atomic size, which gives rise to strain energy in the concentration gradient ahead of the growing new austenite grain. This mechanism was originally proposed by Sulonen [59].

Two different morphologies of the discontinuously precipitated carbides were detected in the active reaction front in the Ni-base alloy 602CA. A fine uniform substructure, seen in Figure 39(a) and a coarser structure with distinct cellular boundaries in (b).
Figure 39. FEG-SEM images of Alloy 602CA exposed in synthesis gas at 540°C/2 years. BSE-images from two pits, showing a fine- (a) and a coarse (b) discontinuous precipitated carbide structure at the respective active MD-fronts. The contrast is maximised in (b) to permit imaging of the newly-formed low alloyed Ni-austenite with discontinuous precipitated carbides.

Discontinuously precipitated carbides were detected in AISI 304L as well, see Figure 40 (Paper 2) and in Ref. [60]. It should be mentioned that the authors of Ref. [60] observed a similar microstructure but denotes the discontinuous precipitated structure as “carbide zone 3”.

Figure 40. SEM backscatter image of AISI 304L sample, unetched. Discontinuous precipitated carbides in the former austenite grain boundaries. The precipitates, dark in contrast, are probably M23C6-carbides, and the precipitates, grey in contrast, are probably M7C3-carbides. The phase, white in contrast, is the newly formed Cr-depleted Fe-Ni austenite.

The identification of discontinuously precipitated carbides is of principal importance since it explains high metal dusting corrosion rates at relatively low temperatures on Ni-base alloys and probably on austenitic stainless steels as well.
An estimation of the cellular growth rate of discontinuous precipitated carbides in Alloy 602CA, based only on diffusion limitations is discussed below. In this particular case it means that the advancement of the cellular boundary is governed by the rate at which a sufficient amount of Cr can move to the carbide phase via the cellular boundary.

Every Ni atom has a very short diffusion distance between the carburized bulk (old austenite) and the newly formed low alloyed austenite while Cr has orders of magnitude longer diffusion distances towards the nearest Cr-carbide. This means that the average Ni-atom has a very short dwell time in the cellular boundary while the average Cr-atom has order of magnitude longer dwell time and, as a consequence, the average Cr-fraction in the boundary could be much higher than the bulk fraction of 0.25. The cellular growth in this case is characterised by a small fraction of discontinuous precipitates and both the new phases formed are close to equilibrium, i.e the Cr-diffusion process and subsequently, the Cr-carbide formation, is almost accomplished.

It is possible to estimate the cellular growth rate based on diffusion limitations. It is assumed that the cellular boundary can move forward in steps of the boundary thickness and before it moves forward, all metal transport needed to reach equilibrium must be accomplished. Consider a segment of the cellular boundary, as shown in Figure 41:

![Figure 41. Principal sketch of the growing cellular structure with discontinuous precipitated Cr-carbides, where the grey area represents the modelled segment with a characteristic diffusion length of S/2.](image)

The thin segment of unit length in the normal direction having the thickness and properties of an austenite grain boundary, has a volume \( V = \delta \times S/2 \) per unit length, where \( \delta = \) cellular boundary thickness, i.e segment thickness.
S = lamellar spacing in the cellular structure and S/2 is the characteristic diffusion distance.

Fick’s first law:

$$\frac{\partial m}{\partial t} = -DA\rho \frac{\partial C}{\partial x} \quad (7.1)$$

which in general can be approximated as:

$$\Delta m/\Delta t = \delta D_{G,B}/L \times \Lambda \times \rho \times \Delta C_{Cr}/\Delta x \quad \text{or;}$$

$$\Delta t = (\Delta m \times \Delta x) / (\Lambda \times \rho \times \Delta C_{Cr} \times \delta D_{G,B}/L) \quad (7.2)$$

$$\Delta t = \text{time for one segment of cellular growth.}$$

$$\Delta m = \text{amount of Cr-metal in the segment that diffuses and forms carbide,}$$

$$\Delta m = \rho \times V \times X_{Cr}, \text{ where } X_{Cr} \text{ is Cr-fraction.}$$

$$\Delta C_{Cr} = 2X_{Cr} \text{ The Cr-content in the cellular boundary may be much higher than the bulk content (X}_{Cr}\text{) and the difference in Cr-concentration towards the carbide may therefore be estimated as } \Delta C_{Cr} = 2X_{Cr}.$$

$$\Delta x = \text{diffusion length; half the lamellar spacing, S/2.}$$

$$\Lambda = \text{diffusion cross-section area, } \Lambda = \delta \text{ per unit length}$$

$$\rho = \text{density of the diffused metal, i.e Cr.}$$

$$\delta D_{G,B}/L = \text{The effective grain boundary diffusion coefficient of the Cr-atoms with } L \text{ as a characteristic size of the structure, in this case } L = \delta.$$ 

Thus (Eq. 7.2’) gives:

$$\Delta t = \frac{(\rho \times S/2 \times X_{Cr} \times \delta \times S/2)}{(\delta \times \rho \times 2X_{Cr} \times \delta D_{G,B}/\delta)} = \frac{\delta S^2}{(8\delta D_{G,B})}$$

The growth increment or movement of the cellular boundary is set to the grain boundary thickness, \(\delta\), and thus the diffusion controlled velocity of the cellular boundary \(v\), may be written as:

$$v = \delta/\Delta t = 8\delta D_{G,B}/S^2 \quad (7.3)$$

Grain boundary (G.B) diffusion data for Cr in Inconel 600 (73Ni-16Cr-9Fe) is available [23] and for Cr at 540\(^\circ\)C, \(\delta D_{G,B}=1,22 \times 10^{-25} \text{m}^3/\text{s}\). The interlamellar spacing is evaluated as 0,2\(\mu\)m from Figure 26 (d), which gives a cellular growth rate:

$$v = 8 \times 1,22 \times 10^{-25}/(0,2 \times 10^{-6})^2 = 1,22 \times 10^{11} \text{m/s, or 760\(\mu\)m/year.}$$
This can be compared with another model for cellular growth by Hillert [58]. Applying the results from Fig. 22 in that paper to the present case, it gives the maximum growth rate, \( v \), for \( S_{rev} = S/3 \):

\[
vS_{rev}^2/\delta D_{G,B} = 1.8 \quad \text{for } S_{rev} = S/3 \quad (7.4)
\]

\[
v = 1.8 \frac{\delta D_{G,B}}{(S/3)^2} = 16 \frac{\delta D_{G,B}}{S^2} \quad (7.5)
\]

Where \( \delta D_{G,B} \) and \( S \) are the same quantities as in (Eq. 7.3).

The constant 16 in (Eq. 7.5), is directly comparable with the constant in (Eq. 7.3), i.e. the value 8. This means that Hillert’s model predicts two times faster growth rate of the discontinuous precipitated carbide structure. However, both these estimations suggest that if the cellular growth is rate limiting for the MD-process it may progress with a rate of 760-1500µm/year. This implies that the MD corrosion rate could be much higher if the atmosphere was more aggressive, i.e. with higher carbon activity. The cellular structure is thus of vital importance and facilitates the relatively fast MD-kinetics at lower temperatures.

### 7.2 Micro-crack formation

Carburization during metal dusting conditions of Al-containing Ni-base alloy may result in low ductility and micro-cracks, as seen in Figure 42 and Figure 43. These cracks form flat metal fragments on the surface in different sizes up to approximately 200×60×10µm, where 10µm represents the typical crack depth. The crack configuration suggests that the carburized surface metal developed compressive stresses, which could result in shear cracks parallel to the surface, favoured by a ductility drop.
Figure 42. FEG-SEM, BSE-images from cross-sections of 602CA exposed at 540°C. Micro-cracks are evenly distributed all over the carburized surface which accelerates the corrosion process. Al-rich oxides are formed in the cracks and opens them up, as seen in (a). An earlier stage of crack development is shown in (b) which reveals the crack propagation path through the carbide-network.

The attack at 540°C thus involves general surface carburization, oxidation and micro-crack formation in addition to the MD-pits. All these features are discussed in detail in Paper 6. The Al-rich oxide formed at 650°C/1600h appears to be more protective than the Al₂O₃-oxide formed at 540°C, since only some small MD-pits were found on the exposed surface. However, again, micro-cracks were found in connection to these pits, see Figure 43.
Figure 43. FEG-SEM, BSE-image on the mechanically polished surface. Micro-cracks are formed around a larger pit found on the 602CA sample exposed 1600h at 650°C. WDS-analysis in atomic-% is shown in the Table below. In the cracks (and on the sample surface) Al₂O₃ is detected, see marker A.

<table>
<thead>
<tr>
<th>Marker</th>
<th>Phase</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Al-oxide in crack</td>
<td>4-7</td>
<td>10-15</td>
<td>10-12</td>
<td>23</td>
<td>7</td>
<td>35</td>
</tr>
<tr>
<td>B</td>
<td>Bulk</td>
<td>2-3</td>
<td>0</td>
<td>2.5-4</td>
<td>24-25</td>
<td>9.5-10.5</td>
<td>58-59</td>
</tr>
<tr>
<td>C</td>
<td>Coke with oxides</td>
<td>35-40</td>
<td>~20</td>
<td>6-7</td>
<td>12-18</td>
<td>4</td>
<td>21-22</td>
</tr>
</tbody>
</table>

The carburization gives rise to compressive stresses due to volume expansion [61] but at higher temperatures such as 650°C, stress relaxation may take place fast enough to avoid crack formation. An additional effect may be that micro-cracks form during cooling because of different thermal expansion in the carburized layer and the bulk. If the uncarburized bulk “shrinks” somewhat more during cooling than the carburized surface layer, the result would be cracks parallel to the surface, as are observed.

The micro-crack formation during cooling may explain the surprisingly low metal dusting resistance for 602CA during cyclic conditions as pointed out by Toh et al. [50]. None of the exposures in this study were performed under cyclic conditions. Nevertheless some shutdowns were made in the methanol plant and three cycles down to RT were performed during the 1600h lab-exposure, which obviously is enough to accelerate the corrosion by crack-formation.
It may be concluded that the micro-crack formation represents the major part of the metal loss in 602CA, although the deepest attack is related to the MD-pits.

### 7.3 Volume expansion due to carburization and metal dusting

Several phases, such as oxides and carbides, that will form in an AISI 304L steel during metal dusting conditions, give rise to a substantial volume expansion. This may contribute to the rather rapid degradation process which characterises the metal dusting phenomenon. Some possible phases and calculated volume expansions, when formed in the steel matrix, are given in Table 6. These extended Pilling Bedworth Ratios (E.PBR) for different phases are based on density changes for the metal during phase transformation. The phase stability conditions are calculated with ThermoCalc.

**Table 6.** Possible phases formed in AISI 304L at 650°C during metal dusting conditions and calculated volume expansion

<table>
<thead>
<tr>
<th>Phase formed in the steel matrix</th>
<th>Phase stability conditions regarding carbon and/or oxygen content</th>
<th>Phase density [g/cm³]</th>
<th>Calculated volume expansion when the phase is formed in a AISI 304L steel, E.PBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference (304L)</td>
<td></td>
<td>7.9</td>
<td>1.00</td>
</tr>
<tr>
<td>304+1at%C</td>
<td></td>
<td>7.9</td>
<td>1.0087 1)</td>
</tr>
<tr>
<td>M₂₃C₆</td>
<td>≤2.3w%C</td>
<td>6.97</td>
<td>1.20</td>
</tr>
<tr>
<td>M₇C₃</td>
<td>≥1.2w%C</td>
<td>6.9</td>
<td>1.25</td>
</tr>
<tr>
<td>Graphite</td>
<td>≥3.5w%C (a_c ≥1)</td>
<td>2.26</td>
<td>∞ or 1.062)</td>
</tr>
<tr>
<td>(Fe,Cr)₃C</td>
<td>a_c ≥2.1</td>
<td>7.66</td>
<td>1.11</td>
</tr>
<tr>
<td>Ni₃C</td>
<td>a_c ≥39</td>
<td>7.96</td>
<td>1.06</td>
</tr>
<tr>
<td>Cr₃C₂</td>
<td>a_c ≥600</td>
<td>6.68</td>
<td>1.35</td>
</tr>
<tr>
<td>Cr₅O₃</td>
<td>10⁻³ ≤ pO₂ ≤ 10⁻²⁸ (a_c ≤ 1800)</td>
<td>5.21</td>
<td>2.17</td>
</tr>
<tr>
<td>(Cr₅Fe)O₄</td>
<td>pO₂ ≥ 10⁻²⁸ (a_c ≤ 190)</td>
<td>4.8</td>
<td>2.28</td>
</tr>
<tr>
<td>FeO</td>
<td>pO₂ = 10⁻²³ (a_c ≤ 2.1)</td>
<td>5.7</td>
<td>1.79</td>
</tr>
<tr>
<td>NiO</td>
<td>pO₂ ≥ 10⁻¹⁸ (a_c ≤ 39)</td>
<td>6.67</td>
<td>1.53</td>
</tr>
<tr>
<td>(Fe₂Ni)O₄</td>
<td>pO₂ ≥ 10⁻²² (a_c ≤ 10¹⁶)</td>
<td>5</td>
<td>2.19</td>
</tr>
<tr>
<td>Cr₂N</td>
<td>≤1.8w%C</td>
<td>6.8</td>
<td>1.31</td>
</tr>
<tr>
<td>CrN</td>
<td>≥1.8w%C</td>
<td>6</td>
<td>1.65</td>
</tr>
</tbody>
</table>

2) When related to M₇C₃.

The extended PBR are calculated by the virtual volume expansion or density change of the metal component during phase transformation, i.e. as if C, O or N had zero mass;
\[ E.PBR = \frac{\rho_{304}}{\rho_{\text{Phase}'}} = \frac{\rho_{304}}{\rho_{\text{Phase}} - \rho_{\text{Phase}} \left( \frac{m_i}{m_{i'之外}} \right)} = \frac{\rho_{304}(m_{\text{me}} + m_i)}{\rho_{\text{Phase}}' m_{\text{me}}} \quad (7.5) \]

\( \rho_{304} \) = Density of the AISI 304L steel

\( \rho_{\text{Phase}} \) = Density of the phase formed in the steel

\( \rho_{\text{Phase}}' \) = \( \rho_{\text{Phase}} \) with reduction of the mass contribution of the element C, N or O

\( m_i = n_i M_i \) = (Number of C, O or N atoms in the empirical phase formula) x (Molar weight)

\( m_{\text{me}} = n_{\text{me}} M_{\text{me}} \) = (Number of metal atoms in the empirical phase formula) x (Molar weight)

Once formed chromia or spinel oxide are very stable even at extremely high carbon activities, as seen in Table 6. As the carbide content in the reaction front, zone 2 and 3, may reach 50% or possibly up to 85% (Paper 2), it results in a total volume expansion of at least 15%. In zone 4, the Cr-depleted zone, a volume reduction would be expected since the carbides have dissolved, but depending on the carbon flux the reduction may be (over-) compensated by the graphite formation. In zone 5, where 30at% of the metal has formed spinel oxide, the total volume expansion would be about 40%. During the coke (and filamentous carbon) formation in zone 6, the volume expansion or dilution by the filamentous carbon would reach 200% at a position 2 mm from the reaction front. It is obvious that these volume expansions will create stresses and finally eject the corrosion products, which most likely accelerate the metal dusting corrosion process. An especially detrimental “grain pick out” process occurs when the grain boundaries are selectively attacked and complete grains are ejected (by the type III mechanism) as observed by de Bruyn et al. in reformer plants at 540°C [25]. This effect was also observed at higher temperatures as “Green rot” by Dovey and Jenkins [36].
As shown in Ref. [18] the slopes of the Coffin-Manson curves were less in the carburizing atmosphere for all alloys tested. The lifetimes in the carburizing environment were shorter than those in air at high strain amplitudes (shorter testing times), particularly for 253MA and AISI 304L. On the other hand the lifetimes were longer than those in air at low strain amplitudes (longer testing times) particularly for Kanthal APM and AISI 304L. A tentative explanation for this behaviour is that the crack propagation rate is lower, but the crack initiation time is shorter (fewer cycles to crack initiation), in the carburizing atmosphere compared to the oxidizing atmosphere.

As the metallographic examination in Paper 1 shows, the austenitic chromia formers AISI 304L and 253MA display rapid carbon pickup during the short LCF exposure times (25-35h) indicating that a chromia layer does not heal during metal dusting conditions. However, the ferritic alumina former, APM, showed no signs of carbon pickup even during the 350h exposure. This suggests that the crack initiation times for AISI 304L and 253MA in the carburizing environment may be reduced by carbon pickup.

The crack propagation rate may be affected by oxide formation in the cracks, which can act as a lever during cyclic load. Since the oxygen partial pressure in the carburizing atmosphere is low enough to prevent formation of bulky oxides, the crack propagation may be slowed down. It is thus possible to explain the LCF behaviour during the relatively short exposure times employed in Paper I by the difference in oxygen partial pressure. It is nevertheless expected that the influence of carburization will play a significant role at longer exposure times, i.e. at even lower strain ranges. The slope of the Coffin-Manson curves are expected to drop as the bulk material eventually will be carburized resulting in reduction of the mechanical properties [62].

To conclude, a damaged chromia layer on an austenitic stainless steel does not heal during metal dusting conditions, but an oxide formed on a ferritic alumina former, such as APM, may heal. This supports the discussion in Chapter 4.4.1, i.e formation of a superior Al-Cr oxide on FeCrAl and NiCrAl-alloys.
CONCLUDING REMARKS

Previously, two main mechanisms have been used to explain the phenomenon of metal dusting, decomposition of metastable carbides (Type I) and graphite formation into and inside a carbon supersaturated phases (Type II). However, this work has shown that a further mechanism must be added in order to make a consistent description of metal dusting as it appears on engineering alloys in CO-containing atmospheres: an active corrosion induced by carbon and oxygen (Type III).

The mechanism involves carbides as reaction intermediates. The equilibrated corrosion end products consist of carbon (graphite and filamentous carbon), spinel oxides and Cr-depleted austenite particles in the case of an AISI 304L steel. Both the mechanisms and the type of corrosion products were consistent with the thermodynamic conditions of the material under the influence of a carbon and oxygen gradient.

Schematically, the Type III corrosion mechanism may be divided into two stages:

i) Carbonisation: 
   \[ \text{AISI 304L} \rightarrow \text{Cr-depleted austenite} + \text{carbide} \]

ii) Carbide dissolution by selective oxidation and metal dust formation:
   \[ \text{Cr-depleted austenite} + \text{carbide} \rightarrow \text{Cr-depleted metal dust} + \text{oxide} + \text{carbon} \]

The carbide is a necessary reaction intermediate and the overall reaction is;
\[ \text{AISI 304L} \rightarrow \text{Cr-depleted metal dust} + \text{oxide} + \text{carbon}. \]

The driving force and steady state MD process for pure iron and low alloyed steels have been identified. The process is explained by separating the initial stage, intact cementite layer formation (Type I), from the steady state stage, metal dusting disintegration of supersaturated ferrite by graphite formation, denoted the Type II mechanism.

The important conclusion is that there is no unexplainable step or phenomenon included in the different metal dusting processes that occur on pure metals or engineering alloys. In fact, all the observed and reported observations are readily explained with four fundamental mechanisms, Type I, II, III and IV, which follow the known thermodynamics in the Me-C-H-O systems. The Type IV mechanism, may be described as continued disintegration of the corrosion products resulting in nanoparticles and carbon nanotube formation.
Furthermore, an explanation is proposed for the surprisingly fast MD process on a Ni-base alloy at such low temperatures that metal bulk and even static grain boundary diffusion are too slow to explain the corrosion process. The solution to the problem is found in the fast growing cellular structure with discontinuous precipitated carbides, in which all metal diffusion takes place in the moving cellular boundaries, and which results in a fast-growing carbide network. The total corrosion rate in this case may also be accelerated by micro-crack formation.

All engineering alloys based on Fe, Ni, Co, even those alloyed with Cr, Al and Si, are more or less susceptible to metal dusting, although the incubation time may differ. When a metal dusting pit starts to grow, the kinetics is catastrophic at least from an engineering point of view. A solution to the metal dusting problem may be found in new alloy systems free from carbide formers, such as Fe and Cr, and free from graphite formers, such as Ni and Co.

10 OUTLOOK

With a detailed knowledge of the mechanisms of metal dusting it is possible to improve the high-performance alloys of today. For instance, development of Ni-base alloys that are not prone to discontinuously precipitated carbides is feasible. It has been demonstrated that it is not possible to rely on chromia-forming alloy in metal dusting environments, instead alumina- or Cr-doped alumina-forming alloys will probably represent one of the future alloy categories for metal dusting environments.

With the new knowledge now available, it is possible to predict which kinds of alloy systems have the potential to be immune to pure “chemical” degradation by metal dusting. Confidential work is now in progress on completely new categories of materials designed to be immune to metal dusting.
I would like to express my sincere gratitude to the following:

-SIMR for encouraging postgraduate studies within the framework of research at the Institute.

-my colleague and group leader Rachel Pettersson, for excellent scientific support and with critical reading of my manuscript, also for letting me have the freedom to do my research on metal dusting despite the periodic lack of both funding and time.

-my former departmental head, Staffan Hertzman for many fruitful discussions and for always encouraging me in my work.

-my formal supervisor, Prof. Christofer Leygraf, Division of Corrosion Science (KTH) for all support and critical reading of my manuscript. Also for providing a grant from the Division and office space, which has been very valuable.

-Prof. Mats Hillert, KTH, for sharing his amazing knowledge in this quite exclusive topic, and for having answers to questions/theories asked or debated for decades.

-the High Temperature Corrosion Centre (HTC) and the director of HTC, Lars-Gunnar Johansson for supporting this work.

-the companies which sponsored the research projects which constitute the basis of this work; Sandvik Materials Technology (SMT), Kanthal and Outokumpu Stainless.

-the company representatives in the research committee; Mats Lundberg (SMT), Bo Jönsson (Kanthal) and Bo Ivarsson (Outokumpu Stainless) for all support and valuable discussions in general and in addition to Mats Lundberg for critical reading of my manuscript.

-Gunnar Hultquist (KTH) and Prof. Bevis Hutchnsson (SIMR) for valuable scientific discussions.

-my Norwegian colleagues, Bernd Schmid and Hennie De Bruyn at Statoil Research Centre in Trondheim for valuable discussions and fruitful joint research.
- Johan Angenete (HTC and MACH, Material Analysis at Chalmers) for advanced STEM studies and fruitful collaboration.

-Ulla Gustavsson (SIMR), Rein Vainik, Lars Göthe (SU) for various analyses and to Joacim Hagström and Jacek Komenda for assistance with the FEG-SEM analysis.

-Alexandra Kusoffsky and Johan Bratberg for help with the thermodynamic calculations and for answering my endless questions about the Thermo-Calc software…

-the SIMR librarian, Anders Mårtensson, for locating obscure references and papers published more than 100 years ago.

-Henrik Andersson and Joachim Lindblom for collaboration on the LCF exposures.

-my colleagues and former colleagues at SIMR and the Division of Corrosion Science for providing such a nice working atmosphere.

-my family, which I have been neglecting lately. Thanks for your support and understanding.

-last but not least, I would like to thank Prof. Dr. rer. nat. Hans Jürgen Grabke for introducing me to the research area of high temperature corrosion at Max-Planck Institut für Eisenforchung, Düsseldorf. Also for encouraging the Scandinavian research on metal dusting by delivering critical comments about newly proposed theories.
REFERENCES


733-749 (1976).

[38] B. Schmid, Ø. Grong, R. Ødegård, “Coke formation in metal dusting

[39] E. Reese, H.J. Grabke, “Effects of chlorides on the oxidation of the 2.25Cr-

[40] I. Kaur, W. Gust, L. Kozma, Handbook of Grain and Interphase Boundary


oxygen on the metal dusting of nickel-base alloys in carbon monoxide-rich
gas at high temperature”, Proc. of 2nd Int. EDMCCM Symp., Vancouver,

[44] C.H. Toh, P.R. Munroe, D.J. Young “Metal dusting of heat resistant alloys”,


[46] Q. Lu, G.Hultquist, T.Åkermark, “In-situ SIMS analysis of the initial
oxidation of a commercial FeCrAl alloy in H2O/O2 gas at 600-850K”, Proc.

korrosionsreaktioner i ulike nikkelbaserte legeringer”, Diploma Thesis,


vapour and flow rate on the High- temperature oxidation of AISI 304L;
54, Nos. 1 /2 (2000).

[50] C.H. Toh, P.R. Munroe, D.J. Young, K. Foger “High temperature carbon
corrosion in solid oxide fuel cells”, Mat. at high temperatures Vol. 20, No 2,


at elevated temperatures”, Proceedings of the 3rd Int. Congress on Met. Corr,
Moscow, USSR The Netherlands, 1966, Univ. Of Moscow Press, pp. 119-133