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# Metal Dusting

*Recent progress and industrial experience*

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## Abstract

The metal dusting is one of major failure mechanisms of equipment in producing process of hydrogen, ammonia, and syngas, as well as methanol reforming. Although it has been recognized for the decades, there are still controversies in its mechanism. With the recent development in metal dusting research, industries are having better understanding and may develop practical approaches to combat this type of failure.

In this report, the recent research of metal dusting mechanism is summarized. It is reasonable to group these mechanisms in 3 types per Szakálos' proposal:

- Type 1: decomposition of metastable carbides (e.g. cementite),
- Type 2: decomposition of graphitization
- Type 3: active corrosion by carbon and oxygen

The report also outlined the progress of metal dusting monitoring techniques, *i.e.*, coupon and acoustic monitoring are the most practical and promising monitoring practices.

The industrial practices to mitigate metal dusting are discussed in this report as well. It is commonly believed that not a single alloy is absolutely immune to the metal dusting. However, material selection, proper coating and optimum operation envelop are the key to mitigate the metal dusting risk. Various of industrial experience and failure cases provided the valuable information for future design, operation and inspection to mitigate such risks.

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## Introduction

Metal dusting is a rapid form of carburisation that leads to metal loss, which is characterized by the formation of fine metal carbide or pure metal and carbon dust (ZENG, NATESAN, & MARONI, 2001). This phenomenon occurs in syngas (Asia Industrial Gases Association, 2016), hydrogen and ammonia production, petrochemical and metal processing industry (Herring, 2003). It is a combining factor of temperature, pressure, and fluid composition (e.g., carbon monoxide content). Metal dusting is one type of high temperature corrosion phenomenon in strong carburizing gas atmosphere. Almost all Fe, Cr, or Ni base alloys are affected at carbon activities ( $a_c$ ) > 1 in the temperature range of 400 to 900°C. The local pits and holes are the most likely forms of metal loss. However, general / uniform metal loss is also observed. Although all been generally termed as metal dusting, recent research demonstrated that different alloys experienced different mechanisms. Therefore, the mitigation practice for different types of alloys are quite different.

With the recent development in metal dusting research, industries could develop an approach to better combat the failure (Mulaudzi, Cornish, & Slabbert, 2013).

## Metal Dusting Mechanisms

There is various type of metal dusting mechanisms proposed for different types of alloys. Szakálos grouped all metal dusting mechanisms into three genres based on the kinetic reactions (Szakálos, 2004);

- Type 1: decomposition of metastable carbides (e.g. cementite),
- Type 2: decomposition of graphitization
- Type 3: active corrosion by carbon and oxygen

The author further explored the relationship of metal dusting mechanisms and alloy phase diagram (Figure 1).

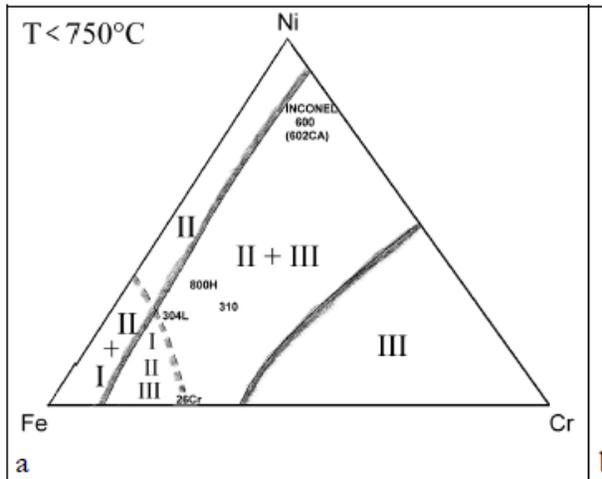


Figure 1 Metal dusting mechanisms in relation to alloy composition (Szakálos, 2004);

It demonstrate that metal dusting mechanism is closely related to the phase diagram of the alloys, in fact, it determines the overall metal dusting kinetics on stainless steels and Ni-base alloys.

### Type 1: Metal dusting through metastable carbides

The metal dusting mechanism of iron proposed by Hochman (Hochman 1977) is the typical Type 1 mechanism, in which decomposition of metastable carbides is the critical step for the metal dusting. The mechanism was further supported by Gruabke and Pippel's research (Pippel, Woltersdorf, & Schneider, 1998) (Grabke et al. 1998; Pippel et al. 1995). The mechanism is illustrated in Figure 2.

- 1) Carbon is deposited on the metal surface and is dissolved in the metal;
- 2) Cementite ( $Fe_3C$ ) forms as carbon diffuses into the iron and the metal becomes oversaturated;

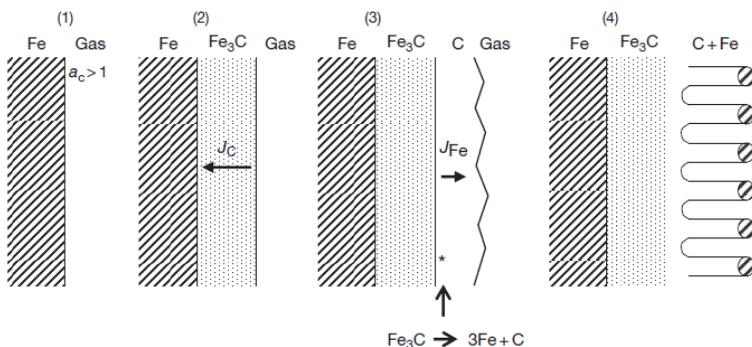


Figure 2 Hochman-Grabke Mode for dusting of pure iron (Pippel, Woltersdorf, & Schneider, 1998)

- 3) Metastable  $Fe_3C$  decomposes to Fe and graphite

The essential of this mechanism is the production of Chromium carbides, which are the expected reaction products and their formation within the alloy is the outcome of competition between rival processes. Scale formation is favored by rapid diffusion of chromium from the alloy to its surface, whereas internal precipitation is favored by rapid carbon ingress. (Young, 2010)

Zeng *et al* (ZENG, NATESAN, & MARONI, 2001) proposed a slight different mechanism in which iron and carbide rather than carbon plays the important catalytic role in the metal dusting process. Metal dusting is only a by-product of the catalytical crystallization of carbon (Natesan & Zeng, 2006). The model is illustrated in Figure 3.

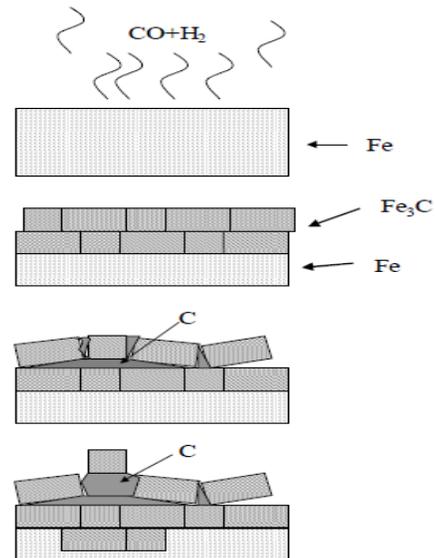


Figure 3 Metal dusting mechanisms proposed by Zeng *et al* (ZENG, NATESAN, & MARONI, 2001)

- 1) Carbon deposit on iron surface and supersaturates the iron;
- 2) Cementite forms at the surface of the iron, and the volume expansion creates defects;
- 3) Carbon diffuses through the cementite and precipitates at cementite defects;
- 4) Accumulation of carbon at cementite defects causes the cementite particles to separate into small particles and move away from the metal;
- 5) Gas penetrates into cracks in the metal and continues further carbon deposition and

metal dusting. At high temperature, cementite decomposes quickly.

## Type 2: Metal dusting through graphitization

The Type 2 mechanism is different to the Type 1. Rather than forming the metastable carbides, metal and graphite act as a catalyst to metal dusting process.

### Natesan model

Natesan *et al* proposed a new mechanism for nickel based alloy. It was nickel rather than nickel carbides acting as a catalyst for carbon deposition, which leads to further disintegration of base metal in nickel based alloys (Natesan & Zeng, 2006).

Since the graphite rather than the carbide is more critical for nickel based alloy metal dusting, Hwang investigated graphite deposition rate on nickel based alloy Inconel 601 with the variables of CO exposure time and oxidizing pretreatment temperature. It is not surprising to understand that long exposure to have more carbon deposition. However, the impact of temperature is less obvious. (Hwang, 2015).

Unlike iron and low alloy steels, the metal dusting process in nickel and nickel-based alloys does not involve the formation of metastable carbides. Instead, the alloy disintegrates by direct inward growth of graphite into the supersaturated structure.

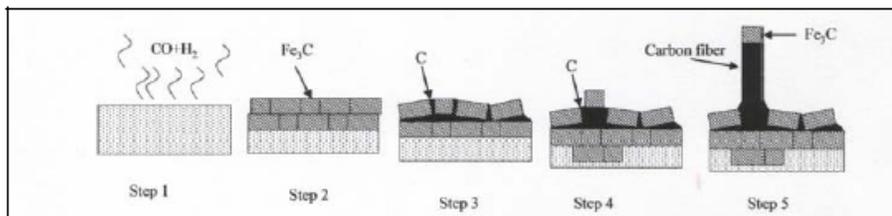


Figure 4 Metal dusting mechanism in low alloy steel (Natesan & Zeng, 2006).

## Type 3: Metal dusting through active corrosion by carbon and oxygen

### Chun model

Chun *et al.* outlined metal dusting mechanism for Austenitic 304 stainless steel (Chun & Ramanarayanan, 2005). The mechanism was

illustrated in the following diagram. Different to the Fe and low alloy steel, the oxides are playing important role in preventing of the metal dusting

- 1) Oxide film formation  
Surface oxidization leading to a spinel  $M_3O_4$ , which is effectively protecting the steel from carbon ingresson
- 2) Direct carburisation  
Cr is not sufficient to form oxide or grain size is too large to transport the Cr. This lead to  $M_7C_3$  type of carbide precipitation

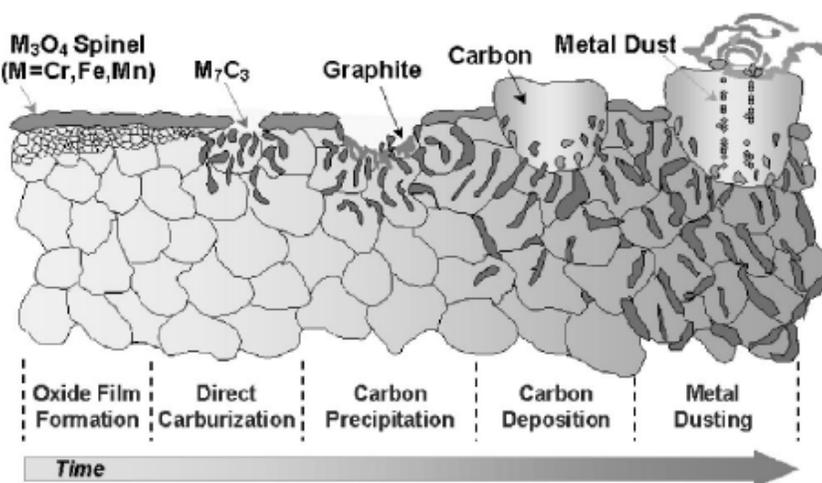


Figure 5 Role of surface metal oxide on metal dusting (Chun & Ramanarayanan, 2005)

- 3) Carbon precipitation  
Carbon from the gas phase is transferred to the surface of Cr-depleted steel, it is further dissolved and diffused into the steel.
- 4) Carbon deposition

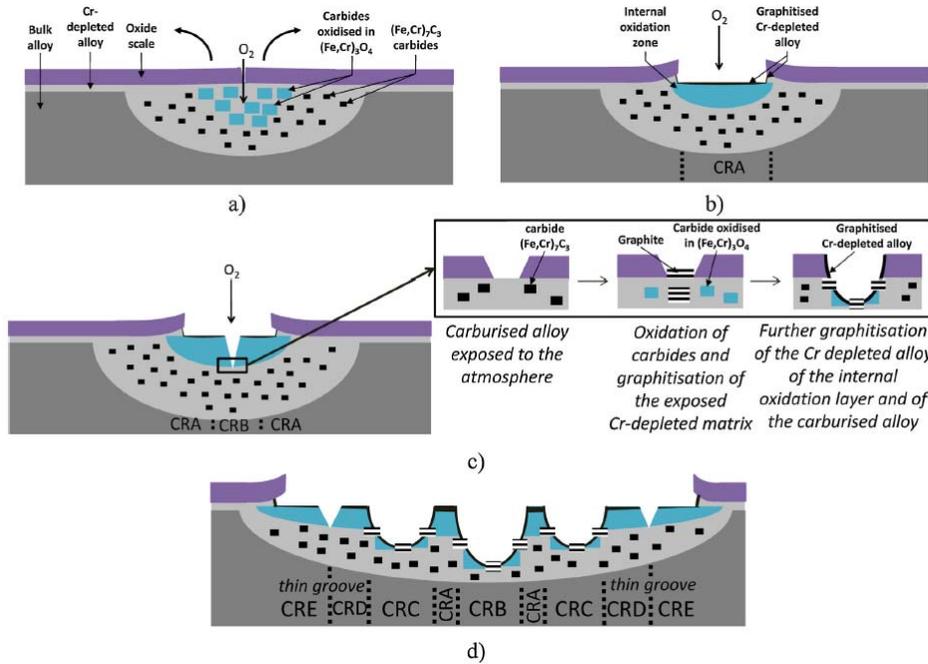
Graphite and larger metal particles deposit on the low Cr high Ni alloy surface

5) Metal dusting  
The metal atoms spall away from alloy surface through intergraphitic plane

There is more focus on carbon deposition on nickel and nickel base alloys, since it is the critical precursor of the nickel metal dusting. Gunawardana *et al* studied the effect of Ni -based alloy (Inconel® 601)'s surface condition on metal dusting corrosion initiation. It revealed that alloy surface condition has important impact on carbon formation due to the composition and structure of alloy surface. The surface treatments lead to iron or nickel oxide, which either reduce or catalyse the

carbon deposition. (Gunawardana, Walmsley, Holmen, Chen, & Venvik, 2012)

stemmed from the external oxide scale formation.



- 3) Enhanced graphitisation due to a microclimate atmosphere with lower oxygen and higher carbon activities at the bottom of a crack induced by tensile stress in the internal oxidation zone during cooling.
- 4) Pit lateral growth controlled by the kinetics of oxidation of the carbides whereas the pit inward growth is controlled by the enhanced graphitisation at the bottom of the crack (whose merging results in an inner deep

Figure 6 High alloy metal dusting mechanism proposed by Fabus *et al* (Fabas, Monceau, Josse, & Vande Put, 2016)

corrosion disk).

### Fabus model

Ni and Ni-base alloys showed different mechanisms of metal dusting. For example, it was reported that 'carburation' occurred by ingress of carbon into high alloy steels and subsequent internal carbide formation, which embrittles the steels and causes crack formation and loss of oxidation resistance (Grabke, 2002). Fabus *et al* proposed a model similar to Chun model, however, it includes a step of oxide scale breakdown and oxidization of carbides (**Error! Reference source not found.**):

- 1) Pit nucleation and growth due to the breakdown of the oxide scale induced by the large volume expansion resulting from the oxidation of previously formed carbides. The localisation of the attack is due to the presence of defects in the protective oxide scale.
- 2) Graphitisation of the Cr-depleted matrix of the internal oxidation zone and the one that

Austenitic alloy 29Ni-45Fe-21Cr-1.3Si-0.9Al-0.7Ti-0.3C-0.2Cu-0.2Mo-0.2P is utilised to study the metal dusting corrosion mechanism (Fabas, Monceau, Josse, & Vande Put, 2016). Even this is still an iron base alloy, however, high chrome and nickel content have significant impact on its high temperature corrosion, Alloy 800 (rolled 20Cr-32Ni-steel) or HK40 (cast 25Cr-20Ni-steel). the chromium is precipitated in the carbides  $M_{23}C_6$  and  $M_7C_3$  ( $M = Cr, Fe, Ni$ ).

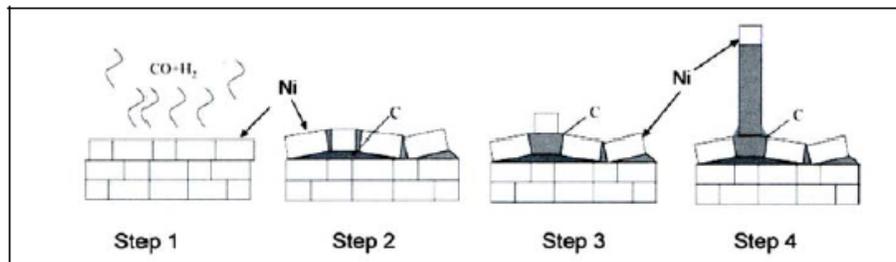


Figure 7 Metal dusting mechanism in nickel alloys (Natesan & Zeng, 2006).

Pippel *et al* demonstrated that base metal disintegration leads to larger metal particles in nickel base alloys (Pippel, Woltersdorf, & Schneider, 1998). They decompose directly by graphitization rather

than through an instable carbide. The attack sites are both grain boundaries and Cr-depleted metal. The metal particles contain mainly Ni and Fe. The authors believed both nickel based alloys (e.g. Alloy Inconel® 600) and pure nickel have the same disintegration metal dusting mechanism (Hwang, 2015).

## Monitoring

### Coupon testing

Corrosion coupon is a conventional way of monitoring for process conditions. Weight loss coupon as an indicator is not reliable in low temperature exposure. However, deposits analysis is an indicator of potential metal dusting. For example, samples contained carbon, metal, oxide, and probably carbide particles suggests the onset of metal dusting. The carburisation on alloy surfaces led to a volume increase and created internal stresses on the non-carburised areas is an indicator of unfavourable metal dusting process condition (Al-Meshari A. I., 2008).

### Acoustic emission

Acoustic emission is utilised to monitor the metal dusting of 13CrMo44. (DE LOO, WOLFERT, SCHELLING, SCHOORLEMMER, & KOOISTRA, 2002). Two clearly distinctive metal dusting activities were identified in the trial: oxide dusting in the range of 380 to 420°C, and metal (bulk) dusting most reactive at temperatures from 425 to 500°C. It is reported that noise and relevant signals can be distinguished. It is demonstrated that acoustic emission technique can be utilised to identify the dusting processes and gained the detail information of process dynamics, incubation times etc.

## Metal dusting mitigation

### Materials selection

#### Metal dusting mechanisms flow chart

Szakálos mapped a flow chart for the different types of alloys and their metal dusting mechanism, which provides useful guideline in understanding the metal dusting mechanisms under the process condition for different types of alloys, which is helpful on mitigating the metal dusting corrosion in design stage (Szakálos, 2004);

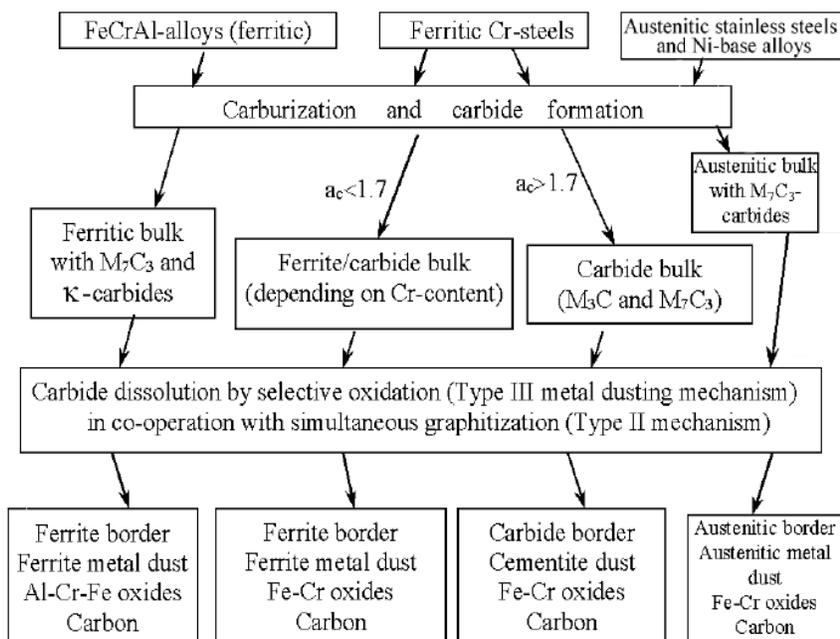


Figure 8 Metal dusting mechanisms guideline for different types of alloys (Szakálos, 2004);

### Effect of alloy element addition

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 (Söderström, 2010).

There are some recent reports on alloy element relating to the metal dusting resistance. For example, Kelly et al reported Industrial carburising furnace experience with dusting problems with different content of elements. Aluminum up to 4.5%

as an alloy addition is not effective (Kelly, 99). High chromium and silicon are beneficial. Neither high chromium nor high nickel without other alloying additions are sufficient. Tungsten may be helpful. However, there is no systematical understanding the role of individual elements for each alloy.

Some empirical equations are established for the effect of addition of common elements (BAKER & SMITH).

The best fit for Austenitic nickel-base alloys and Fe-Ni-Cr alloys was produced using the following summation (multiples of weight percentage):

$$(Ni + Co) + 2Cr + 5Mo + 9Ti + 11Si + 23Al - 1Fe.$$

This same regression technique was used to characterize the variation in the log of the mass loss of austenitic nickel-base and Fe-Ni-Cr alloys

$$(Ni + Co) + 5Mo + 11Cr + 15W + 52Ti + 54Al + 83Si - 1.5Fe.$$

Nishiyama *et al* established an empirical metal dusting resistance equation for high alloy metals, 696 Ni-Base Alloy (NISHIYAMA, OKADA, OSUKI, KURIHARA, & OGAWA, 2011)

$$Cr_{eq} = Cr\% + 2 \times Si\% > 22$$

$$Cr_{eq} = Cr\% + 3 \times (Si\% + Al\%) > 24$$

Söderström investigated carbon deposition on the surface of iron based Fe-Cr-Ni alloys (SS316, SS-308H, Fe-2.25Cr-1.0Mo, Fe-1.25Cr-0.5Mo) in syngas process. It is found that composition of the alloy has large influence on the carbon formation rate. It was shown that the poorer the alloy, the higher the carbon formation rate (Söderström, 2010).

### Chrome

Chrome is the most important element for improving metal dusting resistance as a carbide forming element (Roberge, 2006) (Kelly, 99). In high alloy, the chrome forms oxide scale, which is also beneficial to the metal dusting resistance (NISHIYAMA, OKADA, OSUKI, KURIHARA, & OGAWA, 2011). However, in the low alloy steel, the chrome may have detrimental effect on metal dusting. Its content is not sufficient to mitigate the metal dusting. The metal dusting of pure iron and 2.25Cr-1Mo alloy steel under CO-H<sub>2</sub>-H<sub>2</sub>O atmosphere at 650°C (Yin, 2006) is a good example. The content of chromium and molybdenum cannot stabilise the carbide but accelerate its disintegration process. It is suggested that Cr<sub>2</sub>O<sub>3</sub> fine particles in the cementite layers provide more nucleation sites in the cementite layer on steel, explaining its more rapid dusting kinetics. The cementite rather than iron particles is the catalyst for the carbon deposition. It is surprise to find chrome having detrimental effect

on metal dusting resistance. It is contradicted to other's finding and author tends to believe that chromium oxide supplies more sites for carbon nucleation in the cementite layer resulting in worse metal dusting.

### Titanium, Niobium and Molybdenum

Gideon *et al* believed that alloys containing carbide-forming elements initially degrade to a lesser extent. However, once the corrosion initiates, the metal wastage is much severer with the alloys containing carbide forming elements than the corresponding alloys without such elements. The study compared the alloy Type 304L against 321 (which uses titanium as carbide stabiliser); Type 316L against Type 316 Ti (which use Titanium as carbide forming elements); and Type 430 against Type 441 (Type 430 with Titanium and Niobium as carbide stabiliser). It is believed that the improved initial resistant coming from the carbide stabilisers. Once stabilised carbides are further oxidized in the later stage, the metal dusting is alleviated for those carbide-stabilised alloys. In addition, the ferritic alloys (Type 430) were initially more metal dusting resistant than austenitic alloys (Type 316L). It is due to the greater chromium mobility in a ferritic structure comparing to the austenitic structure. It is concluded that addition of carbide-forming elements such as Titanium, Niobium and Molybdenum is not preferable for metal dusting resistance (Slabbert, 2012). Other reports also find Molybdenum (over 4%) has detrimental effect at elevated temperature (Roberge, 2006)..

### Columbium

Columbium may be beneficial in reducing the rate of parent material carburisation. This is due to its effect on the carbon diffusivity; therefore, the introduction of T91 to the catalytic reforming processes to give better creep strength could also have benefits in minimising the risk of metal dusting (Roberge, 2006).

### Silicon

Silicon addition are beneficial to high temperature for metal dusting resistant. Normally up to 2% Si addition to mitigate metal dusting (Roberge, 2006).

### Nickel Sulfidation

Although nickel is beneficial to metal dusting resistance in general, however, it has detrimental effect in the sulfur containing environment. The sulfide-eutectic melting temperature frequently will constitute a limit to the upper service temperature of the metal or alloy, whereas only rarely does this occur with an oxide. The fact that pure nickel is much more susceptible to sulfur attack than pure iron (Roberge, 2006).

### *Copper in Nickel based alloy*

For a Cu-containing Ni-base alloy, excellent metal dusting resistance may be expected. A solid solution of Cu in the metal matrix plays the role of a surfactant-mediated resistance on the metal surface where any defects of the oxide scale have occurred, leading to a complete healing of the protective oxide scale (Kelly, 99).

### *Vanadium*

Entrained tiny particles of vanadium pentoxide and other impurity particles can be deposited on hot metal surfaces and result in extremely severe corrosion attack. metal dust is the combination factors of hot gaseous corrosion in the form of carburisation, oxidation, sulfidation, and nitridation (Roberge, 2006).

## Coating and Scales

### Coatings

Coating is the most economical way to mitigate the metal dusting in practical (Pond & Shifler, 2002). Chauhan suggested solutions to inhibit metal dusting by preventing coking deposition by a silicon based ceramics or chromium/ silicon oxide using pulsed laser deposition (PLD). PLD is preferred over others coating techniques, as the source of laser is independent of the deposition system (Chauhan, 2007). In this study, Fe-Cr-Ni and Cr-Ni based such as HK40, HP, HPM, 35Cr-45Ni and 36X alloys are investigated. However, the researcher didn't show conclusive evidence how this coating is beneficial to mitigate the metal dusting in ethylene pyrolysis service environments (1100°C)

Thermal sprayed coatings have been investigated to mitigate the metal dusting issue of Alloy 800H and Alloy 600. The coatings act as a physical barrier to carbon ingress, although the effectiveness of the coatings can be limited by the presence of interconnected porosity typical of thermally sprayed coatings. It is also found that laser-melting further improved the metal dusting resistance of the thermally sprayed coated samples. This is due to improving the effectiveness of the coating as a barrier to carbon ingress by elimination of interconnected porosity (Voisey, Liu, & Stott, 2006).

### Aluminizing

The other approach is to use aluminum-rich surface pretreatment to improve the thermal corrosion resistance with relatively little effect on mechanical properties. This surface treatment technique is so

called aluminum impregnation or aluminizing. This high-temperature cementation process is the diffusion of aluminum into iron and has been known for many years to produce an effective surface for exposure in air or sulfur dioxide fumes to temperatures in the neighborhood of 1095°C. The commercial process of calorizing or aluminizing has been in use for almost a century and has definite advantages for certain high temperature applications (Roberge, 2006).

### Oxide scale

Tight oxide scale is another approach to mitigate metal dusting by intermediate oxidation of the partially metal dusted alloys. If alloys can form a continuous oxide scale on their surface, carbon diffusion through the oxide scale is slowed, and carbon accumulation in the alloy diminishes (Natesan & Zeng, 2006).

A considerable effort is often made in industry to produce an initial scale on the interior that has the optimum properties. Centrifugally cast tubing is often bored to remove porosity near the inner surface, honed to provide a smooth surface profile, and then steamed heavily to produce a thin, continuous, dense, resistant oxide layer on the interior (Roberge, 2006). Such a procedure has remarkably increased the life of tubing sections in some services. As an example, forming of stable protective surface oxide film of Cr<sub>2</sub>O<sub>3</sub> on Alloy 800 has been proven an potential way to mitigate the metal dusting corrosion (Ojha & Dhiman, 2010)

### Surface finish

There is controversial report on surface finish on metal dusting prevention. Some found it effective in preventing the initiation of metal dusting with a difference of two orders of magnitude in the number of pits per unit area formed on an electropolished sample when compared with a sample with a 120 grit finish (Roberge, 2006). However, other suggested that surface finish modification (i.e., preoxidised surface) offers no extra benefit and may be counterproductive (Kelly, 99).

### Operating Envelop

Metal dust is the combination factors of hot gaseous corrosion in the form of carburisation, oxidation, sulfidation, and nitridation (Roberge, 2006). Managing the operating envelop is an effective way to mitigate the metal dusting.

### Sulfur addition in process fluid

Smith study the effect of H<sub>2</sub>S on nickel and Nickel alloys Inconel® 600 with the presence of oxygen. It was suggested that tens to hundreds ppm H<sub>2</sub>S is sufficient to inhibit the metal dusting (Smith, 1977). Additions of sulfur bearing compounds is used in the ethylene production by cracking of hydrocarbons to inhibit the metal dusting. Grabke *et al* demonstrated that carburisation and internal carbide formation is suppressed at pH<sub>2</sub>S/pH<sub>2</sub> at 10<sup>-4</sup> for Alloy 800 at 1000°C. (Grabke, 2002). Grabke also believes the benefits of sulfur in remedy against metal dusting by retarding the carbon transfer and nucleation of graphite, as well as stabilising the metastable carbides. This eventually improves the metal dusting resistance. Sulfur has an inhibition effect on metal dusting. It was reported that over 1000 10<sup>-4</sup>/10<sup>-3</sup> H<sub>2</sub>S/H<sub>2</sub> ratio is sufficient, while in lower temperature, lower ratio down to 10<sup>-6</sup> is sufficient (Lant & Tomkings, 2001).

### Ethylene

Söderström investigated syngas process parameters to determine the carbon free operation limits. It is identified that the presence of ethylene rather than its concentration increased the carbon formation rate significantly. The incubation time of carbon deposition is constantly varied due to the composition. This may have an impact on when



carbon starts to grow, hence the carbon free operation limits for syngas process (Söderström, 2010)

### Temperature

Increasing the exposure temperature generally caused less carbon deposition and more oxide formation on the alloy surfaces leading to a reduction in the aggressiveness of the attack (Roberge, 2006). Söderström pointed out that

temperature is the major factor in the catalytic reformer tubes (low alloy steel) (Söderström, 2010)

## Industrial Failure Cases

Metal dusting is a high temperature corrosion of materials, which often leads to catastrophic mechanical failure (Pond & Shifler, 2002). There are number of cases, which are invaluable for future design, operation and inspection.

### Failure of Alloy 800, HP40 and HK40 in ethylene production

Carburisation of high alloy steels Fe-20Cr-32Ni (Alloy 800), Fe-25Cr-35Ni (HP40) and Fe-25Cr-20Ni (HK40) leading to internal carbide formation, is a problem in the 'cracking' of hydrocarbons for ethylene production. At 900 - 1100 °C hydrocarbons and water vapor are passed through the cracking tubes. In the pyrolysis process, carbon is deposited on the tube walls and this 'coke' must be removed repeatedly by decoking with water vapor and air. The tube materials should form protective Cr<sub>2</sub>O<sub>3</sub> scales which hinder the ingress of carbon into the steels. Carbon is virtually insoluble in chromia and can be transferred into the steel only by diffusion of molecules through pores and cracks of the scale. (Grabke, 2002)

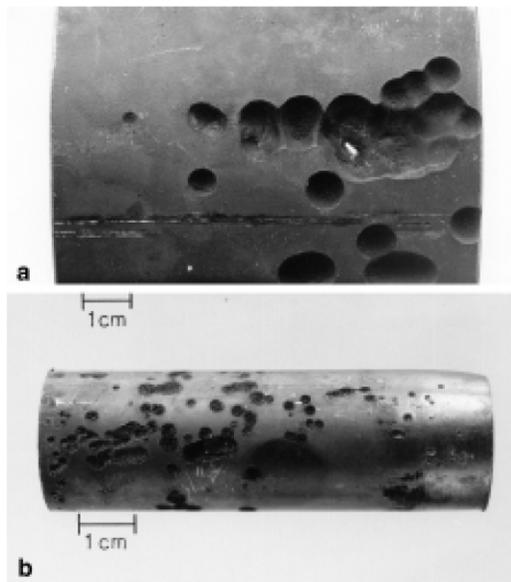


Figure 9 Failure of Alloy 800, HP40 and HK40 in ethylene production (Grabke, 2002)

### Failure of Alloy 800HT in ethylene production

The analysis was performed on a pipe and a plate that were made of Alloy 800HT from ethylene production. Several holes are shown on the pipe and a large hole (≈10 cm in diameter) on the plate (Figure 10), after the material was attacked by metal

dusting corrosion. SEM and Raman scattering methods are utilised to analyse specimens cut from the two components (Natesan & Zeng, 2006). A tightly adhering coke layer is identified on the surface, which cannot be removed by ultrasonic



cleaning and acetone washing.

Figure 10 Failure of Alloy 800HT for ethylene production in syngas plant (Natesan & Zeng, 2006)

### Failure analysis of a reactor in ethylbenzene unit

The material of the cone was found to be ASME A240 Type 304H which was severely corroded at elevated temperature. The study of the microstructure of the material showed the occurrence of carburisation which led to sensitization and resulted in corrosion of the material. The result of the microhardness testing and double-loop electrochemical polarization investigation proved the diffusion of carbon through the material and occurrence of sensitization. (Javidi & Ghassemi, 2017)

### Alloy 800 metal dusting failure in ammonia plant

The burner liner is intended to protect the refractory lining from erosion by the incoming gas stream may be susceptible to metal dusting if improper material is used. Holland and Bruyn [17] described one such failure of Moss gas secondary reformer in which 200 mm hole was formed.

They observed that the stable protective surface oxide film of  $\text{Cr}_2\text{O}_3$  on Alloy 800 was able to resist metal dusting but only slight changes would be

required to cross the boundary of  $\text{Cr}_3\text{C}_2$ , chrome carbide stability zone to initiate metal dusting (Ojha & Dhiman, 2010)

### SA-335-P5 failure in crude heater tube

Although crude process are not known for their high carbon activity (Figure 11) and normally would not fall into the metal dusting temperature range, the metal dusting may still happen with meeting the certain conditions:

- 1) Localized coke deposition, thus with high local carbon activity
- 2) Local temperature surge.

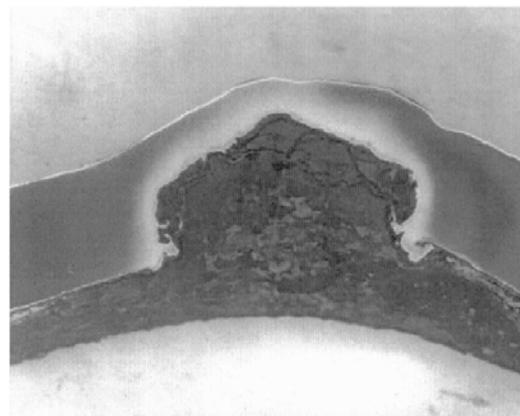


Figure 11 Failure of crude heater tube due to local carbon activity and high temperature (Lant & Tomkings, 2001)

### A-335-P11, A-335-P9 and A-335-P22 failure in catalytic reforming unit

Metallographic examination showed extensive carburisation and cracking of the carburized layer in reforming unit heater tubes (Figure 12). For these low and high alloy ferritic steels, there is no continuous chromia layers are formed. This is due to low  $\text{H}_2\text{S}/\text{H}_2$  ratio.

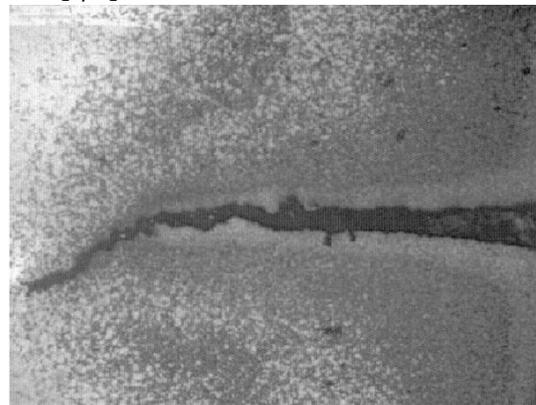


Figure 12 Failure of crude reformed tube with crack in carburized layer (Lant & Tomkings, 2001)

## Low alloy steels, 300 Series SS, nickel base alloys and heat resisting alloy in downstream

Low alloy steels, 300 Series SS, nickel base alloys and heat resisting alloys are commonly used in downstream process. there is currently no known metal alloy that is immune to metal dusting under all conditions (American Petroleum Institute, 2011). API Recommended Practice 571 outlined the critical factors of the metal dusting including

- 1) Process stream composition, operating temperature and alloy composition are critical factors.
- 2) Metal dusting is preceded by carburisation and is characterized by rapid metal wastage.
- 3) Metal dusting involves a complex series of reactions involving a reducing gas such as hydrogen,
- 4) methane, propane or CO.
- 5) It usually occurs in the operating temperature range of 900°F to 1500°F (482°C to 816°C). Damage
- 6) increases with increasing temperature.
- 7) The mechanism of metal dusting is considered to be:
  - i) Saturation of the metal matrix by carburisation;
  - ii) Precipitation of metal carbides at the metal surface and grain boundaries;
  - iii) Deposition of graphite from the atmosphere onto the metal carbides at the surface;
  - iv) Decomposition of the metal carbides under the graphite and metal particles; and
  - v) Further deposition of graphite catalyzed by the metal particles on the surface.”

## Alloy 602CA for better metal dusting performance

Alloy 602CA is a grade steel with higher nickel chromium, aluminum and silicon content, which is beneficial for carburisation resistance. The study compared the behavior of alloy 602CA with alloy 601, alloy 690 and alloy 600. It is found that Alloy 602CA with improved metal wastage rate. Alloy 602CA even with 1% strain still maintained its passive oxide layer thus preventing any further carbon ingress (Wilson & Agarwal, 2005).



Figure 13 Metal dusting of a 304H stainless steel pipe (American Petroleum Institute, 2011)

## Inconel® 601 metal dusting in syngas process

The laboratory test found that the oxidation layer is critical to metal dusting resistance. The formation of oxide layer is depending on the process condition, as well as metal surface. It appears that both structure and the composition of oxide are important to the initial stage of metal dusting (Gunawardana, Walmsley, Holmen, Chen, & Venvik, 2012).

## Inconel 601, 601H, 625 metal dusting failure in Ammonia plants

Inconel® 601, 601H, 625 and similar alloys in ammonia plant is reported . It is at least possible to reduce the attack to a level which is tolerable in practical operation. Conventional carburisation is a familiar problem with high-temperature alloys in steam reforming furnaces caused by inward migration of carbon leading to formation of carbides in the metal matrix.

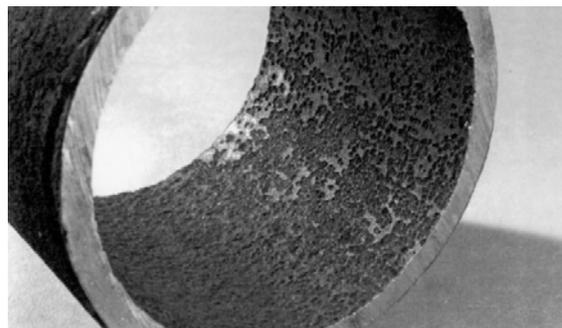


Figure 14 Metal dusting of a Inconel® 601, 601H, 625 in ammonia plant (Aly)

It happens at high temperatures, typically above 800°C, and the carbon originates from cracking of hydrocarbons. In contrast, metal dusting occurs at

500 - 800°C on iron -nickel and iron - cobalt based alloys with gases containing carbon monoxide.

## KHR35C HiSi, KHR45A LC and UCX<sup>®</sup> metal dusting failure in furnace tube application

KHR35C HiSi<sup>®</sup> suffered localised metal dusting at 650 and 750°C. The attack became less aggressive with higher temperature. The least attack on KHR35C HiSi<sup>®</sup> was however observed after exposure at 850°C.

KHR45A LC<sup>®</sup> after exposure at 650°C but to a lesser degree compared to KHR35C HiSi<sup>®</sup>. Moreover, a few pits were observed on KHR45A LC<sup>®</sup> exposed at 750°C with the least took place at 850°C. UCX<sup>®</sup>, which contained the highest concentrations of chromium and nickel, exhibited the best resistance to metal dusting at the test temperatures (Al-Meshari & Little, 2009).

## Conclusion

The recent research progress on metal dusting has improved understanding on its mechanism. It is reasonable to group the metal dusting into three different types:

- Type 1: decomposition of metastable carbides (e.g. cementite),
- Type 2: decomposition of graphitisation
- Type 3: active corrosion by carbon and oxygen

The metal dusting monitoring is still under development, coupon monitoring and acoustic monitoring are most practical and promising techniques. It is commonly believed that no a single alloy is absolutely immune to the metal dusting. However, material selection, coating and operation envelop are the key to mitigate the metal dusting risk. Various of industrial experience and failure cases are also provided the valuable information for future design, operation and inspection to mitigate such risk.

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