Advanced Materials for Utilization in Metal Dusting Environments

Metal dusting is an extremely dangerous corrosion phenomenon described as a catastrophic form of carburization which attacks nearly all kinds of steels in the temperature range between 750-1400°F (~400°C-760°C) where metals are exposed to atmospheres having high carbon activity (due to the presence of carbon monoxide or hydrocarbons) combined with a low oxygen potential. Metal dusting can produce rapid and unpredictable metal wastage, producing pits and grooves as the affected metal disintegrates into a mixture of powdery carbon and metal particles. Most materials are very susceptible to metal dusting with material selection limiting process efficiency. Here we review the performance of INCONEL® alloy 693 in aggressive environments supported by both long term laboratory testing and industrial references.

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Introduction

Steam reforming of natural gas for the production of synthesis gas being utilized in plants producing hydrogen, ammonia and methanol is well known. It is a highly endothermic process which is equilibrated at high temperatures to reach a sufficient conversion. The need for greater efficiency has reduced the quantity of steam used for the reforming process resulting in lower steam-to-hydrogen ratios. Higher front-end pressures have also increased the CO content of the syngas. When such gas mixtures are present in the process stream in the critical temperature range metal dusting can occur. Failures of iron-base alloys as well as nickel-base alloys which contain insufficient levels of key alloying elements have prompted equipment designers to seek materials that are more resistant to metal dusting. Special Metals INCONEL® alloy 693 and INCONEL® Filler Metal 53MD offer a combination of properties which make them attractive choices for application in severe metal dusting environments and have been successfully employed in many applications; being used for heat exchanger tubing and baffle plates, for ferrules, burner nozzles, thermocouple protection tubes and syngas bypass duct linings.

Metal Dusting

Metal dusting is one of the biggest challenges in the cooling of CO-containing process gases and has been responsible for considerable losses in equipment and production time across numerous industries. Failures have been reported in ammonia plants as reduced energy requirements results in a lower steam-to-hydrogen (H₂O/H₂) ratio while CO/CO₂ ratios have tended to increase. Failures have also been reported in methanol reforming plants and in other industries such as refining and heat treating. The phenomenon, termed “metal dusting” is a process
of highly accelerated material wastage which is preceded by the saturation of a material with carbon. The phenomenon is typified by the disintegration of a material (iron or nickel-based) to a mixture of carbon dust, metal particles and possibly carbides and oxides. This is usually a localized form of attack, resulting in pits or grooves.

The production of synthesis gas (syngas), a mixture of CO, H2, CO2 and H2O from natural gas via steam reforming is a common step to begin production of hydrogen, ammonia, methanol and liquid hydrocarbons. The need for greater efficiency has driven producers to reduce the amount of steam used for the reforming process, thereby lowering the H2O/H2 ratio. Trends towards higher front end pressures have also increased the CO content of the syngas. Lower H2O/H2 ratios in combination with higher CO/CO2 ratios result in lower oxygen partial pressures and higher carbon activities. This combination of factors greatly accelerates the propensity for metal dusting.

Carbon activity (ac) reflects the potential for carbon to deposit from carbon-bearing gases. If there is a potential for graphite formation by decomposition of CO and the carbon can diffuse into the metal, metal dusting might occur. Several reactions are suggested as being the mechanism for producing the carbon, namely:

- Boudouard reaction: \(2\text{CO} \leftrightarrow \text{C} + \text{CO}_2\)
- CO reduction reaction: \(\text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{C}\)
- Methane decomposition: \(\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2\)

The Boudouard and CO reduction reactions are carbon producing only below the equilibrium temperature. Methane decomposition is endothermic meaning carbon formation occurs above the equilibrium temperature. Methane decomposition is not discussed further as the kinetics of this reaction are much slower than for the Boudouard and CO reduction reactions. However practically this means that there is a critical temperature range between ~400 and 815°C (~750 and 1500°F) where metal dusting is a concern.

Whether an alloy is likely to be carburized or decarburized depends on the carbon activity (ac). The carbon activity is calculated using the following equations, dependent on the carburization reaction\(^4\).

\[
2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \quad \text{ac}=\frac{\text{K}_{\text{Boudouard}} \cdot P_{\text{CO}_2}}{P_{\text{CO}}} \\
\text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{C} \quad \text{ac}=\frac{\text{K}_{\text{COred}} \cdot P_{\text{H}_2} \cdot P_{\text{CO}}}{P_{\text{H}_2\text{O}}} 
\]

The equilibrium constants K\text{Boudouard} and K\text{COred} are given by the following, where T is the temperature in Kelvin.

\[
10^{\log(K_{\text{Boudouard}})} = 9.071-8817/T \\
10^{\log(K_{\text{COred}})} = 7.469-7100/T 
\]

Figure 1 shows the variation of the carbon activity as a function of CO/CO2 and H2O/H2 ratios for the reduction of CO by hydrogen at 627°C (1160°F) and a pressure of 1 atmosphere with the H2O content fixed at both 1% and 10%. It is interesting to compare Figure 1 with a chart published by Parks and Schillmoller (Figure 2) relating not the carbon activity but the observed severity of metal dusting attack of alloys 800 and 304 to the CO/CO2 and H2O/H2 ratios within critical zones of ammonia plant waste heat boilers.

It is now well understood that metal dusting occurs in environments that exhibit high carbon activities (i.e. ac>1)\(^4, 5\). When such gas mixtures are present in the process stream in the critical temperature range metal dusting can be a severe corrosion problem for standard materials\(^6\).
Figure 1. Contour plots showing variation of the carbon activity as a function of CO/CO$_2$ and H$_2$O/H$_2$ ratios for the reduction of CO by hydrogen at 627 °C (1160 °F) with the H$_2$O content fixed at 1% (top graph) and 10% (bottom graph).

Figure 2. Chart relating the observed severity of metal dusting attack of alloys 800 and 304 to the CO/CO$_2$ and H$_2$O/H$_2$ ratios within critical zones of ammonia plant waste heat boiler$^{[4]}$. 

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$^{[1]}$ Information on page 221 of AMMONIA TECHNICAL MANUAL.
The mechanism for metal dusting of iron-base alloys begins with oversaturation of the metal matrix with dissolved carbon. Metastable Fe₃C is formed at the surface which the decomposes according to the reaction Fe₃C = 3Fe + C \[7\]. The mechanism of metal dusting for nickel-base alloys begins with saturation of the alloy matrix with carbon/carbides. The saturated matrix directly decomposes into metal particles and graphite. Figure 3 illustrates the equidistant diffusion (assuming a material which exhibits uniform behavior) of carbon from a point defect in the protective oxide scale which results in saturation of a hemispherical region with carbon. Subsequent decomposition of this saturated area results in disintegration of the alloy matrix, producing a pit having the same hemispherical shape as the carbon saturated region (Figure 4).

Two commonly used alloys that offer good overall corrosion resistance as well as high temperature strength under a wide range of conditions are INCONEL® alloy 600 and INCOLOY® alloy 800H. Metal dusting failures of alloy 800 are well documented \[8,9\] and problems with alloy 600 have been reported as well; the combination of higher gas pressure, temperatures and lower H₂O/H₂ ratios and higher CO/CO₂ ratios limiting the suitability of these commonly used alloys. Figure 5 shows metal dusting attack of an alloy 600 piping connecting ring from a reformer pigtail. Figure 6 shows an alloy 800HT pipe taken from a syngas plant exhibiting severe metal dusting attack where pits in the thin wall have developed to through thickness holes.

The need to maximize the efficiency of steam reforming technology has led to the development of equipment which must be capable of operating within the range of temperature and carbon activity which can promote metal dusting. This ne-
cessitates the use of materials which exhibit excellent resistance to metal dusting attack.

The materials subject to gases with a metal dusting potential are protected from attack if a good and stable oxide is formed and continuously maintained as the oxide prevents the diffusion of carbon into the material. Chromium and aluminum are considered to be elements developing impermeable and protective oxide layers. Nickel-chrome alloys promoting chromium oxide and aluminum oxide development in the relevant temperature ranges and atmospheres are expected to perform best. INCONEL® alloys 690 and 693 exhibit beneficial contents of chromium and aluminum, INCONEL® 693 containing 29 wt% and 3.3 wt% respectively (see Table 1). Extensive testing coordinated by the Materials Technology Institute in the USA and the TNO Institute of Industrial Technology in Europe confirm the superior metal dusting resistance of INCONEL® alloy 693[10,11].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>Ti</th>
<th>C</th>
<th>Other</th>
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<td>INCOLOY 800</td>
<td>32</td>
<td>21</td>
<td>45</td>
<td>0.9</td>
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<td>0.4</td>
<td>0.4</td>
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<td>-</td>
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<td>36</td>
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<td>0.4</td>
<td>0.4</td>
<td>0.08</td>
<td>-</td>
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<td>15.5</td>
<td>8</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td>INCONEL 601</td>
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<td>13</td>
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<td>1.4</td>
<td>0.4</td>
<td>0.05</td>
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<td>INCONEL 625</td>
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<td>3</td>
<td>0.3</td>
<td>-</td>
<td>0.3</td>
<td>0.2</td>
<td>-</td>
<td>9 Mo</td>
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<td>INCONEL 690</td>
<td>59</td>
<td>29</td>
<td>9</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.3</td>
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<td>-</td>
</tr>
<tr>
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<td>30</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>0.3</td>
<td>-</td>
<td>0.6Nb</td>
</tr>
<tr>
<td>INCONEL filler 53MD</td>
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<td>3</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>0.3</td>
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<td>0.6Nb</td>
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Table 1. Nominal chemical compositions (wt%) for materials presented

Alloy performance in metal dusting environments

Table 1 shows the chemical composition for each alloy tested. Test specimens were prepared from commercially available material; testing procedures have been described elsewhere[12]. The carbon activity of the gas (80% CO-20% H₂ at 1150 °F (621 °C)) has been calculated as 57.9; a very aggressive metal dusting environment. Maximum pit depth and mass loss rate as functions of time are plotted in Figures 7 and 8. Figures 9 and 10 show three-dimensional plots illustrating the significant correlation of the summation in weight % (%Cr + 3 %Al) and the iron content (weight % also) with both the pitting depth and the mass loss rate. These plots were based upon analysis of data from 28 alloy compositions some of which were experimental.
Figure 7. Max. pit depth measurements for samples exposed to 80% CO-20% H₂ at 1150 °F (621 °C)

Figure 8. Mass loss rate vs exposure time for samples exposed to 80% CO-20% H₂ at 1150 °F (621 °C)
Figure 9. Plot showing 3D mesh generated using metal dusting data for 28 alloys from exposure to 80% CO-20% H2 at 1150 °F (621 °C). Log pit depth rate (microns per hour) vs (% Cr + 3 %Al) and %Fe.

Figure 10. Plot showing 3D mesh generated using metal dusting data for 28 alloys from exposure to 80% CO-20% H2 at 1150 °F (621 °C). Log mass loss rate (mg/cm² per hour) vs (% Cr + 3 %Al) and %Fe.

Statistically favorable correlations were obtained leading to the development of a “Metal Dusting Equivalency Number” to compare metal dusting resistance and rank the common alloys used in metal dusting service as shown in Table 2. The alloy INCONEL® 693 which contains a high combination of nickel, chromium and aluminum performs best in both resisting pitting attack and
resisting mass loss. The protection of the material is enhanced by the very high level of scale forming elements which form a dense, adherent and self-healing protective oxide layer. The plateau in the maximum pit depth measurements (Figure 6) for INCONEL® alloys 690 and 693 is evidence of oxide healing behavior. Based upon these observed pitting rates and mass loss rates in laboratory testing and the results of in situ field exposures INCONEL® alloy 693 shows excellent metal dusting resistance by forming a thin adherent oxide film and offers the most promising performance to end users seeking metal dusting-resistant materials.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Fe</th>
<th>Cr + 3Al</th>
<th>Mass loss</th>
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<tr>
<td>INCONEL 600</td>
<td>74</td>
<td>15.9</td>
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<td>INCONEL 601</td>
<td>58</td>
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<td>15.8</td>
<td>26.5</td>
<td>2.8</td>
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<tr>
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<td>0.6</td>
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<tr>
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<td>29.1</td>
<td>3.3</td>
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<td>0.0033</td>
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</table>

Table 2. “Metal Dusting Equivalency Number” (Cr + 3Al) ranking and mass loss rates. Tests were conducted in CO+H₂ at 1150 °F (621 °C). Mass loss reported in mg/cm²/hour.

Welding

Fabrication of most equipment and components require some degree of welding and the weld can be the most vulnerable area to metal dusting attack. In applications where corrosion resistance is as important as strength a matching welding consumable or weld overlay should be considered. The filler metals FM72 (ERNiCr-4, UNS N06072) and 53MD (ERNiCrFeAl-1, UNS N06693) have been developed as complementary compositions to the highly resistant INCONEL® alloy 693. In applications requiring higher strength and stability a welding consumable selected for its mechanical properties can be capped with a more corrosion resistant consumable. Combined weldments using filler metal 617 (ERNiCrCoMo-1, UNS N06617) and FM52 (ERNiCrFe7, UNS N06052) capped with FM72 or FM53MD have been used to provide an optimum combination of strength, stability and corrosion resistance.

Industrial experience

The Haldor Topsoe Exchanger Reformer (HTER) is a proven technology and has been in successful commercial operation since early 2003 in a synthesis gas plant in South Africa with great success (Figure 11). The HTER installed was of the double-tube type and by applying this technology the syngas production from the plant was increased by more than 30% [13]. The technology has since been expanded and adapted for use in both syngas and ammonia processing applications. A major challenge related to the HTER heated by reformed process gas is corrosion by metal dusting. Special Metals alloy INCONEL® 693 has a long incubation time and low corrosion rate which is why it has been utilized to great effect in the HTER design enabling the increased efficiency and output[14,15,16].
Conclusions

Due to efforts to increase the efficiency of processes involving the production of syngas and development of advanced catalysts metal dusting corrosion has become more prevalent. Failures of iron-base alloys as well as nickel-base alloys which contain insufficient levels of key alloying elements have prompted equipment designers to seek materials that are more resistant to metal dusting. Field and laboratory data confirm the desirability of addition of certain scale-forming and possibly anti-carbide-forming elements in conjunction with a nickel-base alloy matrix to limit pit progression rates. INCONEL® alloy 693 offers a combination of properties which make it an attractive choice for resistance to harshly corrosive high temperature environments, particularly those conditions which promote metal dusting. The material has been shown to be readily weldable and to exhibit desirable engineering properties in addition to its excellent corrosion properties. INCONEL® alloy 693 has been successfully employed under severe metal dusting conditions in many applications; being used for heat exchanger tubing and baffle plates, for thermocouple protection tubes, ferrules, burner nozzles and syngas bypass duct linings.

INCONEL® alloy 693 is approved under ASME Boiler and Pressure Vessel code 2481.

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References

[13] S.G. Thomsen (Haldor Topsøe A/S Denmark) and S. Loock and W. Ernst (Sasol Technology (Pty) South Africa), “The First Industrial Experience with the Haldor Topsøe Exchange Reformer”
[14] L. Nieberg et al. (Butting GmbH, Germany) and S.G. Thomsen and M. Boe (Haldor Topsøe A/S, Denmark), “Development and Production of an Innovative Steam Reformer”