

## 4. METAL DUSTING

As defined in the Introduction, metal dusting is a severe form of corrosion that occurs when susceptible materials are exposed to environments with very high carbon activities. It results in uniform metal loss and/or severe pitting. The rate of degradation is significantly influenced by alloy composition and condition, the particular gas environment, temperature, and pressure. According to Hochman,<sup>2</sup> this type of degradation was first observed in 1876 in the form of deterioration of iron in refractory brick used in blast furnaces (see the discussion of CO disintegration of refractories in the Introduction). However, it has only been within the last 35 years that much attention has been paid to metal dusting and, even then, the number of investigators who have devoted a significant amount of effort to its study is small. Nevertheless, systematic studies of this phenomenon (see, for example, the reviews in references 2 and 21) have shown that the manifestation of the typical metal dusting process results from a series of steps that occur in the following order:<sup>3</sup>

1. rapid uptake of carbon into the metallic phase leading to supersaturation of carbon in the alloy,
2. formation of metastable carbides (for steels,  $\text{Fe}_3\text{C}$ ),
3. decomposition of these carbides (which are stable only at  $a_c > 1$ ) when localized deposition of carbon occurs ( $a_c = 1$ ), and
4. development of a loosely adherent mixture of filamentary carbon and metallic particles, which then act as catalysts for further carbon deposition.

These steps are shown schematically in Fig. 5. Carbide formation and decomposition continues until the supersaturated region is consumed, but, if the reaction products are removed by erosion or other means, the process could start again.<sup>2</sup> At longer times and following significant metal consumption, pitting is usually observed.<sup>2,3,17,22,27</sup>

Metal dusting for any given material tends to occur in a relatively narrow range (100–200°C, 180–360°F) of the temperature regime from 400 to 900°C (750 to 1650°F). The particular temperature window of susceptibility depends on the material, the gas composition, thermodynamic considerations, and kinetics.<sup>2,3,22,28,29</sup> A schematic representation of the temperature dependence of reactivity for iron, cobalt, and nickel is shown in Fig. 6. The severity of the reaction does not necessarily increase with temperature,<sup>2,22</sup> as many factors influence the process either directly or indirectly. The kinetics of the process for low-alloy steels have been recently studied by Grabke et al.,<sup>17</sup> who showed that the rate of metal wastage by  $\text{Fe}_3\text{C}$  decomposition is linearly proportional to time ( $t$ ) and, as this reaction provides the catalysts for the carbon deposition, the mass of carbon increases in proportion to  $t^2$ .

Metal dusting can be inhibited by forming and maintaining a barrier layer between the gas phase and the reactive solid. Such a barrier would, by definition, be unreactive in the carburizing environment and would prevent rapid transport of carbon. Oxides of chromium, silicon, and aluminum appear to have the appropriate properties to protect underlying surfaces from reaction with carbon.<sup>2,22,23</sup> The presence of less stable oxides (such as  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ ) on the outer surface of these protective scales can promote carbon deposition. (This could be of concern with the use of weathered steel as a containment material.) However, under the nominal conditions of these gasifiers, the prevailing low oxygen activities preclude the formation of these higher iron oxides. As described in Sect. 2,  $\text{FeO}$  and, under certain conditions,  $\text{Fe}_{0.877}\text{S}$  are thermodynamically favored over  $\text{Fe}_3\text{C}$  and, therefore, should prevent metal dusting.

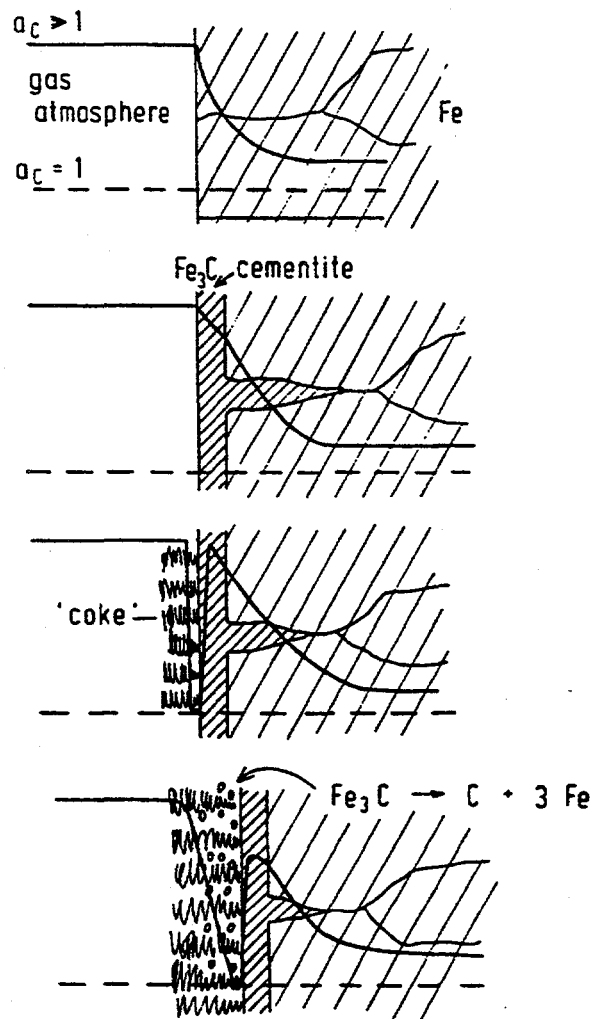


Fig. 5. Schematic representation of the steps involved in degradation by metal dusting. [From J. C. Nava Paz and H. J. Grabke, "Metal Dusting," *Oxid. Met.* 39, 437-56 (1993)].

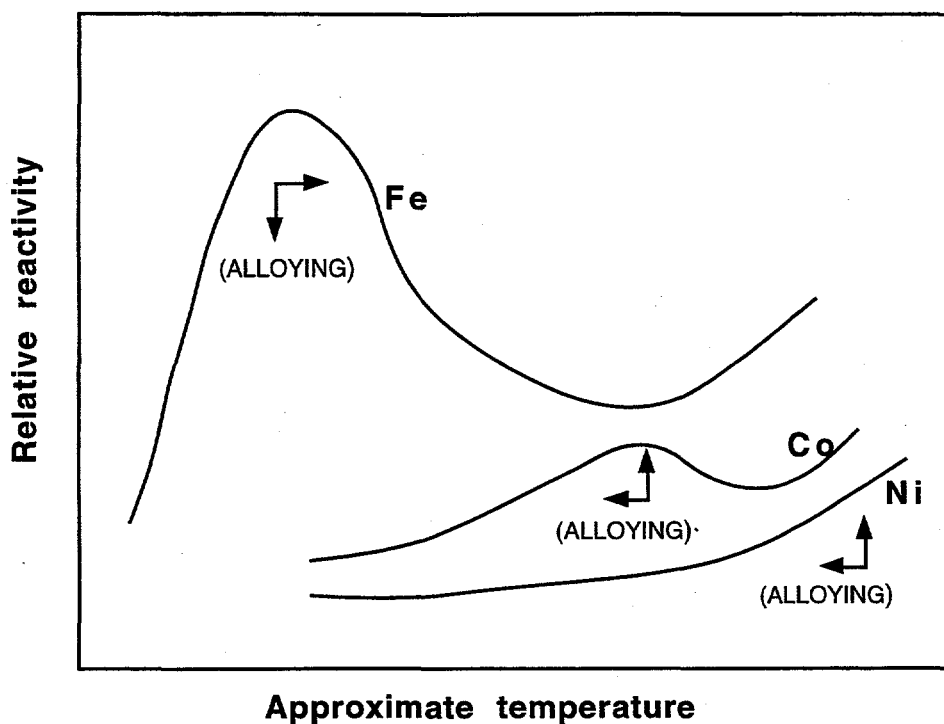


Fig. 6. Schematic representation of reactivity vs temperature for pure iron, nickel, and cobalt in 1 atm of pure CO. The arrows indicate the shift in relative reactivity caused by most alloying additions. [From R. F. Hochman and J. H. Burson III, "The Fundamentals of Metal Dusting," *API Division of Refining Proc.* 46, 331-44 (1966)].

Most of the metal-dusting experience with protective oxides relates to chromia, as chromium is the principal protective scale-forming alloying addition to stainless steels and heat-resistant alloys.<sup>2,22,27,28</sup> For these materials, the resistance to metal dusting is principally governed by the ability of the alloy to develop a continuous chromia scale. When chromia formation is enhanced by compositional or microstructural modifications that increase chromium activity or diffusivity and/or by environmental manipulation, resistance to metal dusting can be significantly increased.<sup>2,22</sup> On the other hand, when the tendency to form chromia is purposely suppressed, metal dusting of the same alloys can occur.<sup>22,28</sup>

It is known that the presence of  $H_2S$  suppresses the attack of iron and low-alloy steels by metal dusting.<sup>2,17-19</sup> The amount of  $H_2S$  in the gas phase need not be large; additions on the order of 20 to 200 ppm can effectively eliminate metal dusting.<sup>2,17</sup> This effect may be due to an inhibiting effect of  $H_2S$  on the carbon deposition rate.<sup>15,16,28</sup> However, it could also relate to suppression of the formation of  $Fe_3C$ . As discussed in Sect. 2, the formation of iron sulfide can compete with the nucleation and growth of  $Fe_3C$  and, at higher  $H_2S$  concentrations,  $Fe_{0.877}S$  can exist to the exclusion of the carbide. Alternatively, sulfur may be incorporated into  $Fe_3C$  and will effectively stabilize it so that it does not decompose when  $a_c \leq 1$  (see Fig. 5).<sup>2</sup> Ammonia has also been reported to inhibit metal dusting, but not as effectively as sulfur.<sup>2</sup> The beneficial effect of water vapor can probably be ascribed to the ability to oxidize an appropriate alloy to form an oxide layer.<sup>2</sup> As shown in Sect. 2, significant concentrations of water vapor can stabilize  $FeO$  rather than  $Fe_3C$  on iron or low-alloy steels under gas conditions that normally would lead to formation of the carbide.

Susceptibility of a particular alloy to metal dusting can usually be explained on the basis of the tendency for carbon deposition on its native surface, the formation of the appropriate metastable carbide, and the ability to form a protective surface oxide. Using iron or low-alloy steels as the reference point, addition of nickel decreases the rate of carbon deposition (see, for example, Fig. 7) and, therefore, the susceptibility to metal dusting.<sup>2,4</sup> To a lesser extent, alloying with cobalt has a similar influence.<sup>2</sup>

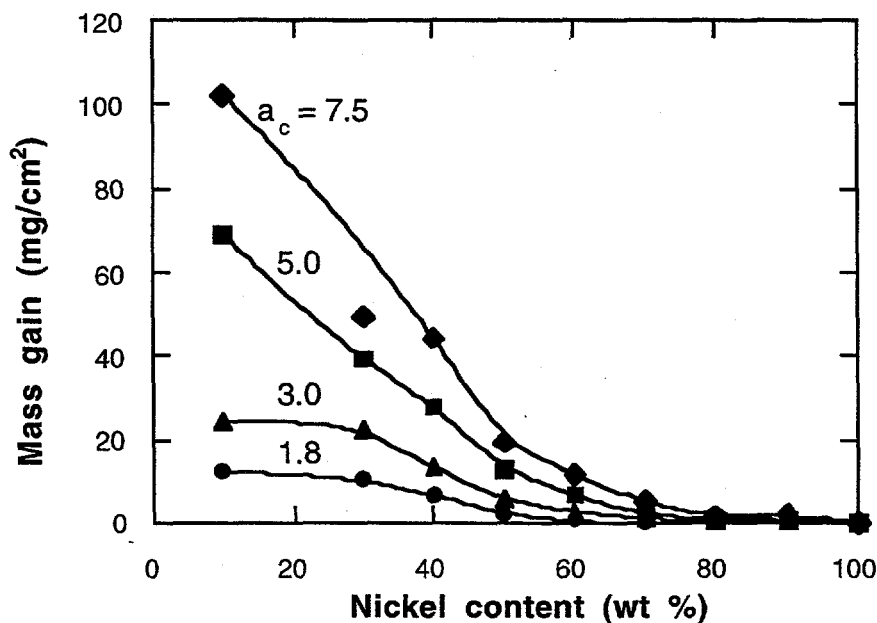


Fig. 7. Deposits on Fe-Ni alloys after 24 h of exposure in CO-H<sub>2</sub>-H<sub>2</sub>O at 0.1 bar CO and 650°C as measured by mass gain as a function of nickel concentration. [From H. J. Grabke, R. Krajak, and J. C. Nava Paz, "On the Mechanism of Catastrophic Carburization: Metal Dusting," *Corros. Sci.* 35, 1141-50 (1993).]

As indicated in Fig. 6, alloying additions to iron generally decrease its susceptibility to metal dusting and increase its temperature of maximum reactivity, while additions to nickel or cobalt normally result in the opposite behavior. As already noted, alloys containing a large concentration of chromium show improved resistance to metal dusting because a continuous protective layer of chromia can form. Furthermore, in this regard, alloys in which chromium has a higher solid-state diffusivity are preferred, as the higher diffusivity aids the rapid development of the Cr<sub>2</sub>O<sub>3</sub>.<sup>22</sup> Based on these factors, high-alloy steels are better than low-alloy versions (because of their higher chromium contents), and ferritic stainless steels are better than austenitic ones (because of higher chromium diffusivity). If metal dusting occurs on higher-chromium alloys, degradation tends to be in the form of pits rather than general metal wastage. Silicon additions also show a beneficial effect on resistance to metal dusting by providing the means to form a protective layer of SiO<sub>2</sub>.<sup>2,28</sup> Hochman concluded that, as a rule, an alloy with  $A$  wt % Cr and  $B$  wt % Si would show reduced susceptibility to metal dusting if  $A + 2 \cdot B > 24$  and if a stable surface oxide could be maintained.<sup>2</sup> Comparative metal dusting results for a number of metals and alloys can be found in refs. 1, 2, 20, 22, and 30.

Very few results for alumina-forming alloys are available. However, if an alloy can form a sound, stable Al<sub>2</sub>O<sub>3</sub> surface layer, it should be resistant to metal dusting in a manner similar to the way steels are protected by chromia films. Hochman reported some general, preliminary results showing such an effect.<sup>2</sup> Furthermore,

alumina scales are thermodynamically stable at even lower oxygen activities than chromia.<sup>11</sup> Initial tests with an iron aluminide revealed susceptibility to metal dusting, probably through the formation of metastable  $\text{Fe}_3\text{AlC}$ .<sup>31</sup> However, it may be possible to use preoxidation treatments (such as those discussed in Sect. 5) to establish an alumina layer on the iron aluminide and prevent such degradation.

For a given alloy, microstructural manipulation can also affect susceptibility to metal dusting. This can occur directly through effects on carbon deposition or carbide stability or, indirectly, through microstructural influences on the formation of a protective oxide layer. For example, grain size, internal stresses, and dislocation structure can all influence the rate of carbon deposition.<sup>25</sup> During the early stages of metal dusting, a heavily worked material can nucleate the metastable carbides sooner because of its higher density of dislocations.<sup>2</sup> On the other hand, deformation can aid the development of a protective chromia layer under the appropriate environmental conditions; dislocations can serve as paths for chromium to diffuse to the alloy surface to react with oxygen to form a barrier layer of  $\text{Cr}_2\text{O}_3$ .<sup>22</sup> In this way, cold work can have a beneficial effect on resistance to metal dusting for alloys with sufficient chromium activity. For the same reasons, refining the grain size of a chromia-former (by deformation or other means) can also impart improved resistance to carburization and metal dusting by facilitating the formation of a  $\text{Cr}_2\text{O}_3$  layer.