Metal Dusting Corrosion of Steels with Varying Chromium Content

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Metal Dusting is a very deleterious form of high temperature corrosion experienced by Fe, Ni and Co-based alloys at temperatures in the range, 350-900°C in carbon-supersaturated (carbon activity > 1) environments having relatively low oxygen partial pressures. This form of corrosion is characterized by the disintegration of bulk metal into powder or dust. The present study focuses on the metal dusting behavior of ferritic steels as a function of Cr content ranging from 1.25 to 20 wt.% Cr in carbon-supersaturated environments (CO-H₂) over the temperature range, 350-600°C.

For pure iron, the metal dusting mechanism involves the initial formation of a metastable Fe₃C carbide on the alloy surface in the carbon-supersaturated environment. Subsequently, graphite deposits on the metastable carbide whereby it is destabilized and decomposes to iron particles and carbon, thus triggering the corrosion process. All low chromium ferritic steels (e.g. 1/4Cr-1/2Mo and 5Cr-1/2Mo) in an overall sense disintegrate by metastable M₇C₃ formation and growth and its subsequent decomposition upon carbon deposition in good agreement with the mechanism for pure iron.

While the presence of a continuous M₇C₃ layer is characteristic of general metal dusting corrosion of ferritic steels having less than 5 pct. Cr, the metal dusting of higher chromium ferritic steels (e.g. 9Cr, 13Cr and 20Cr) is more involved. High-resolution electron microscopy of such steels reveals, in addition to metal particles, a mixture of graphitic and amorphous carbon, and M₇C₃ carbide particles in the corrosion product. The mechanistic aspects of metal dusting of high Cr ferritic steels are discussed with particular attention to stages of microstructure evolution as degradation proceeds, as illustrated in figure 1. Five distinct stages are proposed: Oxide film protection, Direct carburization, M₇C₃ formation, Carbon deposition and Metal dusting.

In high Cr ferritic steels, the Cr diffusion rate is about one order of magnitude larger than in austenitic steels. Thus, as long as the Cr content in the ferritic steel remains above about 9 pct., a protective chromium rich oxide film is established (stage I, figure 1). High Cr austenitic steels, on the other hand, are more prone to metal dusting corrosion because carbon can diffuse in before a chromium oxide film is fully formed. As shown in figures 2 and 3, upon exposure to a 50CO-50H₂ gas mixture at 600°C for 160 hours, ferritic Fe-20Cr steel is fully protected by a surface oxide film, while austenitic 304 stainless steel undergoes metal dusting. The importance of rapid Cr diffusion is further discussed along with findings on the effects of surface finish.

Figure 1. Schematic representation of the progression of low Cr ferritic steels degradation.

Figure 2. Surface and cross sectional secondary electron images obtained by FIB system showing a surface chromium oxide film of ferritic Fe-20Cr steel.

Figure 3. Surface and cross sectional secondary electron images obtained by FIB system showing a pit are of austenitic 304 stainless steel.