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A VIEW FROM THE PENTHOUSE: USEFUL INFORMATION FOR THE WORLD OF BOILERS

CARBURIZATION CORROSION OF STAINLESS STEELS

In an effort to improve air quality and reduce acidic emissions, power-plant operators have been forced to change their combustion technology. Reductions in emissions of sulfur oxides (SO_x) have been achieved mainly by using lower-sulfur fuels. Reductions in nitrogen oxide (NO_x) levels have been achieved principally by reducing combustion-flame temperatures. Of course some new power plants have installed scrubbers to remove these harmful oxides.

While some nitrogen oxides are present within the fuel in the form of nitrates, most NO_x comes from the reaction of atmospheric nitrogen and oxygen at combustion-flame temperatures. Under normal firing conditions, as the flame temperature increases, so does the formation of nitrogen oxide. Thus the simplest way to reduce combustion-formed NO_x is to reduce the flame temperature. The schemes for achieving this are to use off-stoichiometric or staged combustion firing. Combustion air is divided. Primary air is mixed with the fuel and is less than required for complete combustion. Secondary air is added through over-fire air ports. Other schemes may use concentric ducts with the primary air port along the center and secondary air in a concentric ring displaced from the center by some distance. The intent is to burn the fuel in stages. The first stage combustion would burn the hydrogen to water vapor, and carbon to carbon monoxide. Later in the combustion sequence, the carbon monoxide would be burned completely to carbon dioxide. However, the formation of carbon monoxide leads to reducing atmospheres in the vicinity of the burners.

The advantage to this combustion technique is to reduce flame temperatures and thus prevent or at least reduce the formation of any nitrogen oxides. The drawback is to form reducing conditions in the vicinity of the burners, and this topic was discussed in VOL. IV, No. 1 of <u>A View from the Penthouse</u>. What may not be fully appreciated is the damage that these reducing conditions can do to stainless-steel burner components.

Burner parts of austenitic stainless steel, coal nozzles, gas burner rings, ignition tubes, coal spreaders, oil-burner tips and air nozzles all operate at high metal temperatures, temperatures in the neighborhood of perhaps 1500°or 1600°F. The use of austenitic stainless steel for these parts provides adequate oxidation and corrosion resistance at these elevated temperatures. However under reducing conditions, the corrosion of stainless steel may proceed at unexpectedly and unacceptably high rates due to the carburization of these alloys.

Under fully oxidizing conditions of combustion, the fuel would be burned completely to water vapor and carbon dioxide. All fuels contain both hydrogen and carbon. To illustrate the principle consider methane, CH_4. Complete combustion is as shown in Equation 1.

$$CH_4 + 2O_2 = 2H_2O + CO_2 \qquad \text{EQ 1}$$

Usually a small amount of excess oxygen, perhaps 2% or so, is added to assure complete combustion to carbon dioxide (CO_2) and water (H_2O). Flame temperatures under these firing conditions would be in the neighborhood of 3000°F or higher, and the combustion would be said to be "stoichiometric".

Staged combustion would reduce the amount of oxygen available in the primary flame so that the combustion would be accomplished in several steps, as shown in Equations 1, 2, 3, & 4.

$$CH_4 + O_2 = 2H_2O + C \qquad \text{EQ 2}$$

$$C + {}^1/_2O_2 = CO \qquad \text{EQ 3}$$

$$CO + {}^1/_2O_2 = CO_2 \qquad \text{EQ 4}$$

Note that the final product is still water vapor and carbon dioxide but the carbon dioxide is formed in three steps. The advantage from a NO_x formation viewpoint is that flame temperatures are considerably lower and the formation of nitrogen oxides is considerably reduced. Note also, however, that in two stages of this combustion sequence, carbon (C) and carbon monoxide (CO), both reducing elements, are formed.

Austenitic stainless steels, similar to 304, readily form carbides at temperatures as low as 1400°F, but more typically, 1500°F. The addition of carbon to a steel is called "carburization." The reaction of soot, or unburned carbon, directly with the surface of the stainless steel, will form a chromium carbide by the reaction shown in Equation 5.

$$23Cr + 6C = Cr_{23}C_6 \qquad \text{EQ 5}$$

The chromium carbide is quite complex and has the chemical composition of $Cr_{23}C_6$. Carbon monoxide can also react on the surface of stainless steel to form carbon dioxide and elemental carbon, as shown in Equation 6.

$$2CO = CO_2 + C \qquad \text{EQ 6}$$

Either unburned carbon or carbon monoxide thus are available to carburize the surface of these burner components.

The formation of these chromium carbides depletes the surface of the stainless of chromium and thus reduces the corrosion resistance. Stainless steels get their excellent resistance to high-temperature oxidation by the addition of more than 12% chromium. When the chromium content is reduced to below 12%, the oxidation resistance is more ordinary. Thus the formation of chromium carbides by the reaction of stainless steels with carbon monoxide or elemental carbon leads to a depletion of chromium along the surface of the steel. With the chromium content reduced to below 12%, the oxidation resistance falls and the result is a rapid loss of material. Burner components can fail in only a few months rather than several years.

The microstructures that result can be quite striking. Figure 1 shows the normal, austenitic, stainless-steel microstructure, as would be expected in a 304 stainless-steel burner component after several thousand hours of operation. Here the grain size has grown and there is essentially an all-austenite microstructure. Figure 2 shows the microstructure at the surface to be composed of austenite with a myriad of fine carbide particles. Depending on the time and temperature, these microstructures can also form structures that are similar to pearlite in a plain-carbon steel, as shown in Figure 3. These microstructures are all taken from a coal nozzle made of 304 stainless steel. Other examples have been seen in gas-burner rings and stainless-steel castings for oil-burner service.

In order to prevent this form of rapid degradation to burner components under staged-combustion conditions, alloys more resistant to carburization need to be used.

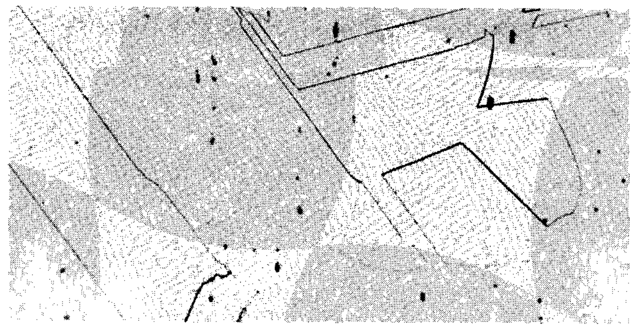

Fig. 1. Normal austenitic, stainless-steel microstructure is equiaxed grains. 500x, etched.

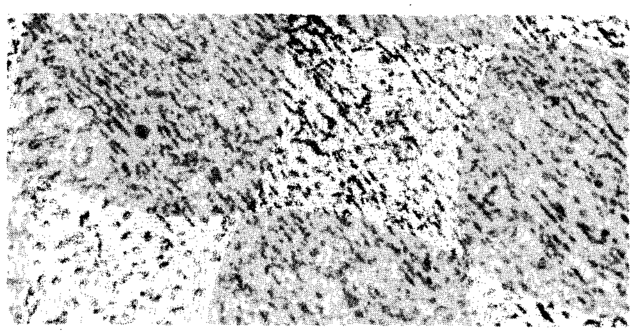

Fig. 2. Carburization of 304 stainless leads to the formation of tiny carbide particles. 500x, etched.

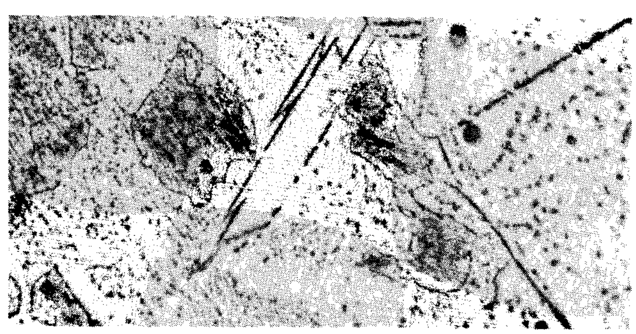

Fig. 3. Depending on the temperature of carburization, the microstructure can resemble a pearlitic steel. 500x, etched.