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

## **GRAPHITIZATION**

Graphitization occurs only in plain carbon and carbon  $+\frac{1}{2}$  molybdenum steels, for example the SA192, SA210, SA209 tubing grades. The initial microstructures are ferrite and pearlite, a mixture of cementite (iron carbide) and ferrite. The shape of the carbide phase in the pearlite is small platelets, large in two dimensions and quite thin. Under elevated temperature, longterm, operating conditions, the cementite is unstable and decomposes into ferrite and graphite. The addition of about 1/2% chromium stabilizes the iron carbide and prevents its decomposition into graphite.

The shape of the iron carbide can undergo two transformations at elevated temperatures: 1) change in shape from a blade to a sphere, a process known as spheroidization, and 2) change from iron carbide to ferrite and graphite, a process known as graphitization. Figure 1 shows the normal lamellar pearlitic structure of SA178 Grade A material.

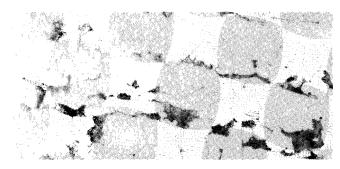


Figure 1, 500x

This structure is stable to approximately 825-850°F.

Spheroidization and graphitization are competing processes. At low temperatures, graphitization will occur before the pearlite colonies have completely spheroidized and disappeared. At elevated temperatures there will be spheroidization before graphitization. In both cases a temperature of at least about 850°F for carbon steel, and 875°F for carbon-½Mo steel, are necessary to alter the pearlitic structure. Stress will lower the temperature at which spheroidization and graphitization occur or decrease the time for transformation at a given temperature. Small amounts of aluminum will also promote graphitization, hence boiler steels are usually deoxidized with silicon.

The heat-affected zone in welds is a rapidly cooled or quenched structure. Such structures will graphitize more quickly than normal ferrite and pearlite. Thus, it is not unusual for heat-affected zones (either tube or attachment welds) to contain graphite while the rest of the component is still ferrite and iron carbide.

The microstructures can be variable.

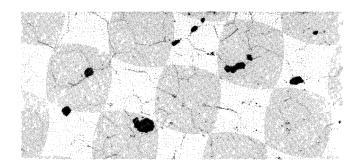


Figure 2, 500x

Figure 2 shows a completely graphitized structure from an SA178 Grade A superheater tube. The structure is ferrite and graphite, with very little iron carbide remaining.

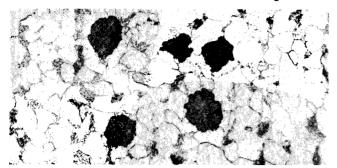


Figure 3, 500x

Figure 3 shows ferrite, spheroidized carbides and graphite, but with the pearlite colonies still well defined. This tube was from a lowtemperature superheater, SA209 tube.

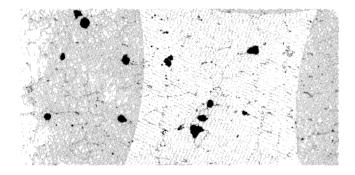


Figure 4, 500x

In Figure 4 the microstructure is ferrite, spheroidized carbides and graphite, but the iron-carbide particles are dispersed throughout the ferrite; and it is impossible to discern the original pearlite colonies, SA178A.

The difference between Figs. 3 and 4 is the average temperature of operation. For plain-carbon steels,

the transition point in the competing processes of spheroidization and graphitization is about 950°F. Above this temperature spheroidization occurs before graphitization, Fig. 4; and below this temperature, graphitization occurs before complete spheroidization, Fig. 3. In both cases, the final microstructure will be similar to that shown in Fig. 2, if the time is long enough. However, the time for the complete graphitization at temperatures below 950°F is extremely long, longer than most boiler-tube components would last, as failures usually occur before a fully graphitized structure develops.

One final factor in the transformation of iron carbide: a cycling of the metal temperature between safe limits of say, 800°F and 900-1000°F will hasten the formation of graphite. At start-up these high temperatures may not cause failures, as the unit is not up to full pressure so the hoop stress is low.

In summary, the long-term microstructural degradation of carbon steel ends with the formation of graphite. Depending on the average operating temperature, the graphitized structures will contain a uniform dispersion of iron carbide, a spheroidized structure, or an <u>in-</u> <u>situ</u> spheroidization with the pearlite colonies still well defined, along with the ferrite and graphite.

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