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

EQUILIBRIUM MICROSTRUCTURES

Plain-carbon and low-alloy steels are the most common and useful engineering materials. They are strong, weldable, corrosion and oxidation-resistant, have good high-temperature properties, and are inexpensive. Unalloyed iron (or ferrite) is, by comparison, too weak to be useful. Additions of alloying elements (usually manganese, silicon, chromium, and molybdenum) increase the ferrite strength. Small additions (<0.3%) of carbon further improve the strength of these alloys by the formation of metastable microstructures based on iron carbide. During elevated-temperature boiler service these metastable structures change over time to equilibrium structures, some quite unusual and uncommon.

Ferrite is an interstitial solid solution of carbon and the low-temperature form of iron. Carbon is a small atom and fits into the "holes" between iron atoms, hence the term "interstitial." Alloying elements substitute for iron atoms within ferrite also. Iron carbide has a specific composition, Fe_3C, but iron may be replaced by other elements, especially chromium, which is a potent carbide former on its own. Both chromium and molybdenum with iron form a complex carbide, $M_{23}C_6$, where "M" is the metal atom.

From a thermodynamic or internal energy viewpoint, for plain carbon steels, the stable or equilibrium structure is ferrite and graphite. The addition of about 1/2% chromium stabilizes the Fe_3C so that decomposition into ferrite and graphite does not occur.

There are other metastable structures that form during rapid cooling of these alloys from metal-working temperatures of 1700°-1800°F to room temperature. At these elevated temperatures, the structure is all austenite, a solid solution of carbon in the high-temperature form of iron, which transforms on cooling to ferrite and iron carbide at temperatures below 1340°F. The rate of cooling determines the final microstructure: a quench will form martensite or bainite, depending on the cooling rate. Since these metastable structures are not found in boiler components (except perhaps in heat-affected zones of welds or in high-temperature failures), no further discussion is necessary.

The usual heat treatment is to cool slowly to room temperature. This is known as a "normalizing heat treatment" and the final structure would be "normalized." The "normal" structure, following such a treatment, is ferrite and pearlite, see Figure 1. This structure of ferrite and pearlite is characteristic of plain-carbon

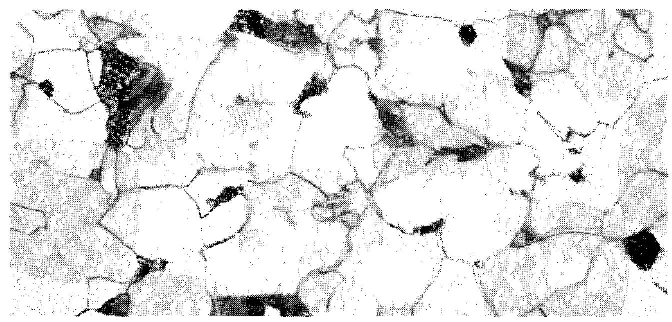

Figure 1

steels, SA-178, SA-210, or SA-106, for example.

The amount of pearlite depends on the % carbon: the higher the carbon content, the larger the amount of pearlite. Pearlite is made up of alternate layers of ferrite and iron carbide. The Fe_3C shape in pearlite is a blade or plate, large in two dimensions and small in the third. Such a shape has a large surface to volume ratio. By changing shape to spherical particles, this S/V ratio is reduced, and the internal energy tends toward a minimum.

The fully annealed condition for a plain-carbon steel would have the iron carbide in a spheroidized form. This same structure occurs in boiler steels after prolonged operation. The internal energy of Fe_3C is reduced by the change from a plate shape to a spherical one, see Figure 2. The microstructure is still ferrite and iron carbide, but the large surface to volume ratio has been reduced.

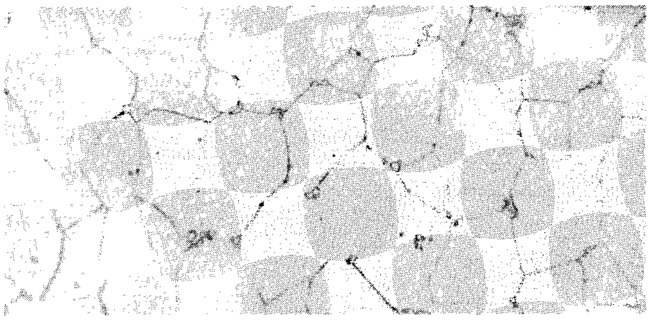

Figure 2

These structures are still considered metastable for plain-carbon steels in that the lowest-internal-energy form has still not yet been reached.

The true equilibrium microstructure of plain-carbon and carbon +1/2 molybdenum steels is the formation of ferrite and graphite. The transformation of iron carbide to ferrite and graphite further reduces the internal energy, see Figure 3.

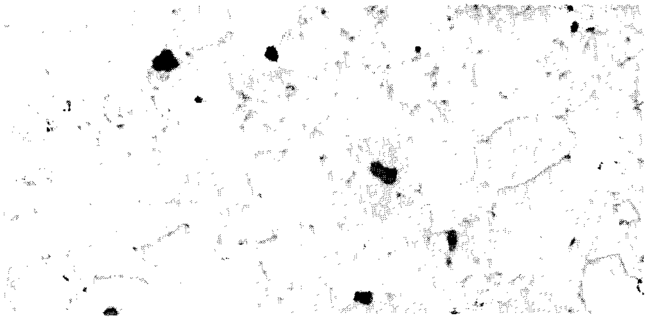

Figure 3

Graphite does not form in low-carbon steels during cooling from 1800°F because the nucleation of iron carbide is more easily accomplished than the nucleation of graphite. Thus the formation of ferrite and metastable iron carbide occurs rather than the stable graphite because the nucleation kinetics favor Fe_3C formation.

The decomposition of iron carbide into ferrite and graphite occurs in plain-carbon and carbon-molybdenum steels similar to SA-209. 1/2% chromium prevents the decomposition of the carbide into ferrite and graphite.

Thus for the chromium-molybdenum steels similar to T-11 and T-22 the equilibrium microstructure is one of ferrite and spheroidized carbides, similar to Figure 2.

One further but unusual change in microstructure occurs at low-operating temperatures, after a very long time. Ferrite is a solid solution of iron and carbon. At 1350°F, 0.02% carbon will dissolve in ferrite. At room temperature, the solid solubility in ferrite is estimated to be <0.0005% C. Thus ferrite is usually supersaturated relative to carbon. This presents no unusual microstructural features when the operating temperatures are in the 700°or 800°F temperature range. Carbon atoms are sufficiently mobile that equilibrium between the carbon dissolved in ferrite and iron carbide is relatively quickly achieved. For steam piping that has been in operation for many years at a temperature of 300°F, the circumstance is slightly different.

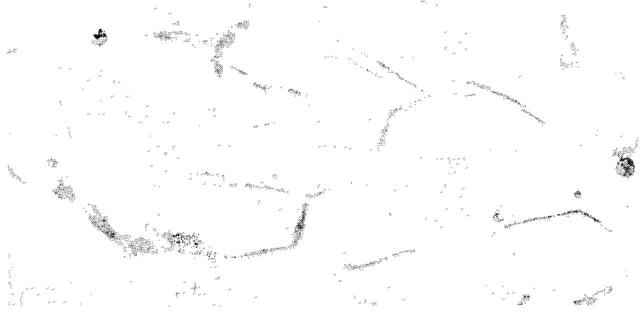

Figure 4

Figure 4 shows the equilibrium structure from a plain-carbon steel pipe in service since about 1915. The steam temperature was about 300°F. The structure here is ferrite, with tiny graphite particles within each ferrite crystal, and grain-boundary carbides. The graphite forms along particular crystallographic planes and so appears as rows or lines within each ferrite grain. If the temperature is higher, the carbon mobility is great enough to form large blocks of graphite, as shown in Figure 3. It is only after very-long service at temperatures of 200°-300°F that the structure of Figure 4 is developed.

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