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

GRAIN BOUNDARIES

Metals, like everything else, are made up of atoms. For our purposes, atoms within a metallic crystal are regularly arranged over great distances, distances that are huge when compared with atomic dimensions. There is, then, long-range atomic order within individual crystals. Where adjacent crystals join is a crystal boundary, a zone of short-range disorder. These crystal boundaries determine in no small way the useful properties of engineering materials.

All boiler alloys are made up of many crystals of various orientations. These individual crystals are called "grains." In any one grain all atoms are arranged with one particular orientation and one particular pattern. The juncture between adjacent grains is called a "grain boundary." The grain boundary is a transition region in which the atoms are not exactly aligned with either grain.

Grain size can vary greatly depending on the alloy and heat treatment. For reference, a typical grain size is about 1 mil (0.001"). Thus, there may be a billion (10^9) grains per cubic inch of alloy. The ASTM grain-size number is one standard for determining the average grain size. the ASTM grain-size number "N" is defined by:

$$n = 2^{N-1}$$

where "n" is the number of grains per square inch when viewed at 100x. The usual range is from 1 to 9; note that as the grains get smaller, the grain-size number gets larger. The usual way of reporting grain size is to give the average and the range; say, ASTM 6 with some as large as 4½ and as small as 7. The shape of a grain is governed by its neighbors. Although no grain is ever a sphere, but an irregular polyhedron that when packed together with others completely fills space, its characteristic length is referred to as a "diameter." At equilibrium the shape tends to minimize the grain-boundary surface area for a given volume. For example, this minimization of the surface to volume (S/V) ratio is the driving force for the spheroidization of iron carbide in pearlitic steels. Grains are said to be "equiaxed" when the characteristic dimensions are the same in all directions. Grains are said to be "elongated" when the characteristic dimensions are not the same but one direction is much longer than the others.

Grain boundaries are usually considered two dimensional but are actually of finite thickness, 2-10 atomic distances. The mismatch of the orientation of neighboring grains leads to a less efficient atomic packing within the grain boundary. Hence the atoms in a boundary have a less ordered structure and a higher internal energy. The disordered atomic arrangement and higher energy can explain several features associated with materials degradation found in boilers. The next several examples will describe the role that grain boundaries play.

ETCHING: In order to observe the microstructure, a piece of the metal is smoothly polished to a plane, mirror-like finish. The prepared surface is chemically attacked with dilute acid, a process called "etching," for a short period. The grain-boundary atoms are more easily and rapidly dissolved than atoms within the grains. A small groove is left at the grain boundaries. Since a groove will not reflect light as do the flat, polished grains, the grain boundaries appear as black lines and the structural details are visible.

DIFFUSION: Grain boundaries are regions of atomic mismatch and less dense atomic packing. Less density on an atomic scale implies bigger, atom-size holes through which atoms can more easily move. Such atomic mobility is called "diffusion." Thus grain boundaries will oxidize or corrode more rapidly, usually referred to as "grain-boundary penetration." Oxygen diffuses along the grain boundaries, reacts with the steel and forms iron oxide in the grain boundary. Since the volume of oxide is greater than the volume of metal from which it forms, a wedging action results. The tip of the grain-boundary oxide wedge is in tension, forcing open the material at the crack tip. The high stress enhances the oxidation or corrosion which also drives the grain-boundary penetration.

Figure 1. Oxide penetration along grain boundaries of a T-22 reheater tube sample after 19 years operation. Oxygen diffusion along grain boundaries is much easier than through the crystal lattice of a grain. Hence the oxide formation at the grain boundary. Note also the carbide particles at the ferrite grain boundaries and the fully spheroidized structure. 500x

In the austenitic and ferritic stainless steels, diffusion of an atom along the grain boundary leads to the formation of chromium carbides. As these carbides form, they deplete the region immediately adjacent to the grain boundary of chromium. As the chromium content decreases, the grain-boundary region becomes less corrosion resistant, a condition referred to as "sensitization." Once these steels have been sensitized, they are subject to an intergranular-corrosion attack known as "IGA."

HYDROGEN DAMAGE: Hydrogen damage, see Vol. II, No. 4 of this newsletter, is a circumstance where, due to corrosion, hydrogen reacts with iron carbide to form methane. The methane collects at grain boundaries; and when the pressure build-up is large enough, cracks will form. The strength of the steel is destroyed by the destruction of the grain boundaries.

CREEP: At elevated temperatures the strength of a grain is greater than the strength of a grain boundary. At room temperature the strength of a grain boundary is greater than the strength of a grain. Where the grain-boundary strength equals the grain strength is known as the "equi-cohesive temperature." Elevated-temperature failures follow grain boundaries and are referred to as "intergranular" (between the grains) failures. Room-temperature failures are usually "transgranular" (across the grains) failures. Elevated-temperature deformation occurs by one grain moving past its neighbor, a process known as "creep." Voids first form where several grains join, where grain-boundary sliding is limited. Individual voids then link up to form grain-boundary cracks, often referred to as "grain-boundary separation."

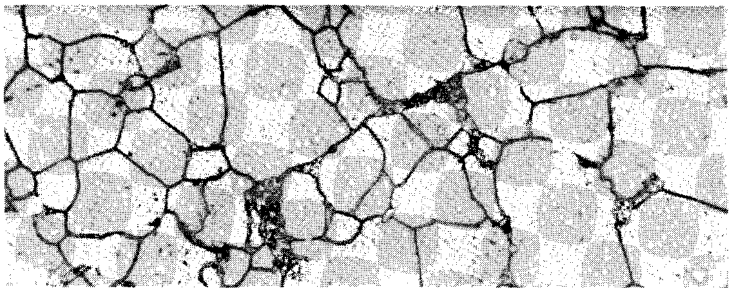

Figure 2. Microstructure of 347H stainless steel after nearly 26 years of operation in a secondary superheater. Note grain boundaries are clearly etched. Along grain boundaries are carbide particles, thus the structure is said to be "sensitized." 500x

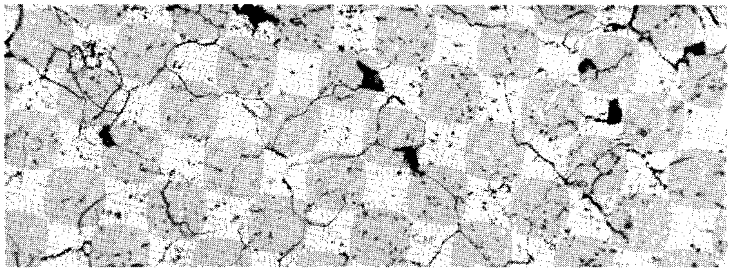

Figure 3. Creep voids along ferrite grain boundaries and at triple points where three grains come together. Note that the ferrite grain boundaries contain carbides and the structure is fully spheroidized. The microstructure is from a T-22 superheater which failed after 37 years. 500x

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