BY DAMIAN J. KOTECKI

Q: What is "sensitization" in a stainless steel weld?

A: *Note: This is a follow-on to my September 2007 Stainless Q+A column that discusses "sugaring." Sensitization is entirely unrelated to sugaring, and it occurs in a different region of the weldment.*

Sensitization in a stainless steel weldment occurs in that part of the weld heat-affected zone (HAZ) that is heated to a peak temperature of between about 900° and 1600°F (480° to 870°C) when there is enough carbon available to produce precipitation of chromium-rich carbides along grain boundaries. Higher peak temperatures than 1600°F either allow chromium to diffuse fast enough to keep up with the carbon in forming carbides, or actually cause the carbides to dissolve. Peak temperatures below about 900°F don't allow enough carbon diffusion to form significant chromium carbides during welding. The carbides have the general formula $M_{23}C_6$, where M is any metallic element, but chromium is by far the most concentrated metallic element in the carbides. The carbon atom is a very small atom that can diffuse rapidly through the stainless steel matrix to the grain boundaries, so that carbon from anywhere in a grain can reach the grain boundary in this temperature range. But the chromium atom is a large atom that diffuses slowly, so that only chromium from very close to the grain boundary participates in formation of the carbides. Formation of the carbides then tends to produce a chromium-depleted zone beside the grain boundary. This chromium-depleted zone, if exposed to a corrosive medium, is preferentially attacked and dissolved. The corrosion follows the chromium-depleted zones beside the grain boundaries and a continuous network of corrosion along grain boundaries causes grains to separate from the weldment.

In order to illustrate sensitization, a $\frac{3}{16}$-in. (4.8-mm) E309L-17 electrode was used to produce a single bead-on-plate deposit on a ¼-in. (6.4-mm) Type 304 stainless plate. Most 304 stainless produced today can be dual classified as 304L as well. The important feature of this 304 plate is that it is not dual classified as 304L — it actually contains 0.066% carbon, double the 0.03% maximum allowed for 304L. At this carbon level, the weld HAZ is easily sensitized by the bead-on-plate weld. After the weld was deposited, the weldment was sectioned transverse to the welding direction. The cross section was then polished and etched to reveal the chromium carbides along grain boundaries in the HAZ.

Figure 1 shows the HAZ in the region that was heated by the weld to a temperature in the sensitization range. Actually, the carbides have been almost entirely removed by the etching process and only their original locations can be seen in either the optical microscope, or the scanning electron microscope, as microscopic ditches along the austenite grain boundaries.

The damage that can be done to a weldment by exposure of the sensitized HAZ to even a weak corrodent can be very severe. Figure 2 reproduces a frequently published example of a cross section of a weld in a 304 stainless steel pipe that contained hot dilute nitric acid. The dilute

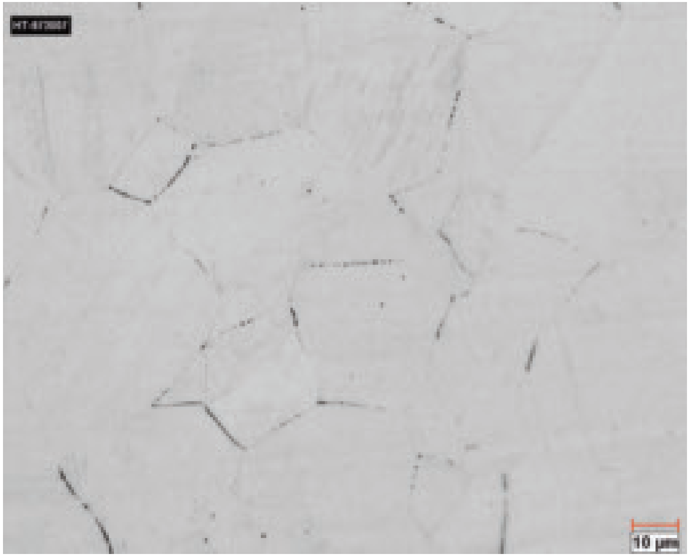

Fig. 1 — Sensitized HAZ of 304 stainless steel plate. Chromium carbides are indicated by chains of dark particles along austenite grain boundaries.

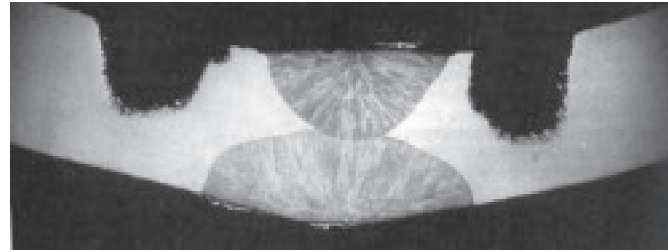

Fig. 2 — Sensitized 304 stainless steel pipe after service in dilute nitric acid. Note that the weld metal and the HAZ closest to the weld metal are unaffected, but the region of the HAZ that reached peak temperatures in the range of 900° to 1600°F (480° to 870°C) is severely attacked. *Photo from* Welding Handbook, *8th Edition, Vol. 4, p. 273.*

acid attacked the sensitized part of the HAZ, dissolving areas around grain boundaries and causing the individual grains of austenite to loosen and be carried off by the dilute acid. But the weld metal, base metal, and hottest part of the HAZ are unaffected by the dilute acid. If one looks carefully at Fig. 2, one can see, along the corroded surface, individual grains that appear separated from the HAZ in this picture but remain in place because they are still partially attached to the HAZ below the visible surface. If the corrosion were allowed to continue, these grains too would detach and be carried away by the dilute acid.

There are two main cures for sensitization. One is to choose a "stabilized" stainless steel base metal, such as Types 321 or 347 stainless steel. These steels are stabilized against chromium carbide precipitation by the addition of alloy elements that have a much stronger tendency to form carbides than chromium has. Type 321 stainless contains titanium as an alloying element for this purpose, and is otherwise identical in composition to 304. Type 347 contains niobium (columbium) for this purpose and is otherwise identical in composition to 304.

The other main cure, which is most commonly applied today, is to select a low-carbon grade of stainless, such as 304L instead of 304, as the base metal. The low-carbon grades are generally limited to 0.03% carbon maximum. At this low level, continuous networks of carbides generally do not form during welding, so welding does not compromise the corrosion resistance. Today, there is very little cost difference between 304 and 304L stainless, while there is significant cost difference between 304 and 347 or 321 stainless.

There is a third cure for sensitization, which consists of a solution annealing heat treatment after all welding is completed. However, this is costly, involves severe size limitations, and introduces distortion and scaling issues, so it is seldom used.

It should be noted that, while it is possible to also produce chromium carbide precipitation in multiple-pass weld metal by thermal cycles associated with subsequently deposited weld metal, the ordinary stainless steel weld metals that are not low carbon, such as 308 and 316, are not as easily sensitized as their corresponding 304 and 316 base metals. The weld metals generally contain a small amount of ferrite in the otherwise austenitic deposit. The ferrite is richer in chromium than the austenite matrix, and chromium diffuses in ferrite on the order of one hundred times as rapidly as it diffuses in austenite. Chromium carbides that form in ferrite-containing weld metal tend to form at the ferrite-austenite interface, where the ferrite can easily "pump" additional chromium to the precipitation area, thereby usually averting sensitization.

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