

Electrochemically Induced Surface Annealing of Austenitic Stainless Steel

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ABSTRACT

This paper describes a new process by which the surface of austenitic stainless steel is transformed electrochemically.

When austenitic stainless steels are deformed by cold work, they harden. One of the mechanisms of hardening is the metallurgical transformation of the austenite phase into martensite, a diffusionless displacement of the face-centered cubic (fcc) austenite lattice. The martensite phase is itself hard and brittle, and susceptible to hydrogen entry and embrittlement. Removal of the martensite phase normally requires heat treatment to high temperature, an annealing procedure, at which martensite decomposes spontaneously back to austenite with accompanying softening. Because the austenite phase is relatively soft, austenitic stainless steels with designations such as 304 and 316 are often unsuitable for use in circumstances where wear, erosion or galling may be a problem. This is despite their high degree of corrosion resistance.

The present paper describes an electrochemical process by which the brittle martensite phase is removed from a previously cold-worked 304 stainless steel surface. The process consists of subjecting the cold-worked metal to a series of anodic and cathodic pulses in potential while the alloy is immersed in a fairly concentrated solution of sodium nitrite (8 mol dm^{-3}) at a temperature of $80 \text{ }^\circ\text{C}$ (1-3). The pulses are set so that in the anodic part, the metal is passive, and the current density is low. In the cathodic part of the pulse, a high cathodic current density is evolved. It is easy to observe that reduction of the nitrite anion occurs in the cathodic part of the treatment. The surface structure of the metal has been analyzed by x-ray diffraction (XRD). The XRD pattern shows a progressive loss of the martensite phase during heat treatment over several hours. It is believed that the martensite phase is not dissolved in the electrolyte, but is transformed back to the austenite phase. This is rationalized by the fact that stainless steel is quite passive in this electrolyte. Indeed, as the processing treatment continues, the initially pH-neutral electrolyte becomes progressively alkaline. Passivity is borne out by the low anodic current density. The loss of martensite is therefore brought about by a metallurgical transformation in the surface layers; since no other phases are detected, this must occur to austenite.

Normally, one would expect the loss of the hard martensite phase from an otherwise austenitic steel to

result in softening of the alloy; this is what occurs during thermal annealing. It is indeed the loss of the martensite phase from the surface layers of the alloy that we have coined the term "surface annealing" for this electrochemical processing treatment. However, testing for the hardness of the surface treated in nitrite solution does not result in softening; to the contrary, some further hardening of the surface layers is achieved. Moreover, by heat-treating the stainless steel after electrochemically induced surface annealing, the surface is rendered still a little harder.

Analysis of the structure of the electrochemically annealed surface using XRD shows a simultaneous change in the lattice parameter of the austenite phase as well. The fact austenite lattice contracts a little as a consequence of the annealing process, and so the surface densifies relative to the bulk austenite lattice.

The results cannot be understood in terms of the hydrogen reduction reaction. Although the cathodic component of the potential pulse induces large cathodic current densities, these are not due to a high rate of hydrogen evolution. Inspection of the surface during the cathodic pulse shows in fact that very little hydrogen is evolved. The main reduction current must therefore be due to the reduction of the nitrite anion. This reduction can produce nitrogen or ammonia; the latter is the favored reaction, again because very little gassing is seen at low potentials where the cathodic current is high. The lack of hydrogen evolution is an important observation for this process. The question arises whether the electrochemical annealing process could be due to the ingress of cathodically reduced hydrogen in the alloy. Hydrogen permeation of austenitic stainless steels causes martensite to be formed, not destroyed. In addition, we used the same potential programme on stainless steels in other electrolytes, such as carbonate and hydroxide, which did not contain nitrite. In each case, the surface gained martensite as expected from earlier work. Pulse electrolysis in non-nitrite solutions also caused the lattice parameter of the austenite phase to expand a little, in contrast to the behavior in nitrite solution.

We therefore are led to the conclusion that it is uniquely the reduced nitrogen atom that enters the metal lattice and gives rise to the observations of electrochemically induced surface annealing.

REFERENCES

1. G.T. Burstein, I.M. Hutchings and K. Sasaki, *Nature*, **407**, 885 (2000).
2. G.T. Burstein, I.M. Hutchings and K. Sasaki, USA patent no. US10/039728 (2003).
3. G.T. Burstein, K. Sasaki and I.M. Hutchings, *Electrochem. Solid State Comm.*, **5**, A80 (2002).

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