Cautionary Tale XXIX

Oxide on Stainless Steel

Without its oxide, which grows naturally when the surface of stainless steel is exposed to air, stainless steels would not be corrosion resistant. This applies to all the stainless steel grades that are regularly used for manufacture of springs, whether they be of the austenitic type 302, 304, 316 or 17/7PH, martensitic type 420 or duplex austenitic / ferritic type.

It might therefore be presumed that a great deal is known about this oxide that confers such valuable service. It is known that the corrosion resistant properties of the oxide appear when there is >12% chromium in the alloy. Indeed this was how stainless steels were first invented in Sheffield in 1913 - Harry Brearley was examining the effects of alloy additions to carbon steel to improve the wear resistance of gun barrel steels, when discarded steel with >12% Cr did not go rusty when left out of doors, whereas all his other discarded trial steels did go rusty.

The multi-layer oxide formed in air comprises Cr_2O_3 that is about 3nm thick (0.120 x 10^{-6}in. or 10 - 15 atomic layers) with various layers over the Cr_2O_3 inducing a top layer of Fe_2O_3.

This oxide can be made thicker by heating springs in air or by acid passivation to ASTM A380(1), but is this thicker oxide better than the thin one, and why is an acid passivation oxide better than that formed when springs are stress relieved in air? Indeed why has 316 stainless steel better corrosion resistance than 304 stainless when there is no molybdenum incorporated into this protective oxide? Partial answers to these questions are available from academics who use X-ray photo-electron microscopy(2), but it would be very interesting to have a more complete answer to the questions. Fundamentally it would be interesting and informative to know if the thickness or structure of the Cr_2O_3 layer is affected by stress relief or passivation, but IST don’t think results of this study has ever been reported.

Notwithstanding the point of this cautionary tale is that the oxide that grows during stress relieving is not detrimental. If temperatures of 350°C (660°F) are used for stress relieving 302 stainless steel springs they go yellowy brown in colour - slight yellow at 350°C and darker at 480°C (900°F). This colour arises due to refraction of incoming light by the translucent multi-layer oxide - the colour is not real, it is a trick of light.

This yellow-brown oxide is corrosion resistant and will not harm the function of the springs. Yet, some customers still insist that they don’t want their springs this colour, but still want good functionality. In these circumstances IST recommend that the oxide is cleaned off by pickling and passivating to ASTM A380. Indeed this passivation confers better corrosion resistance (as measured by hours to onset of red rust in an ASTM B117 salt spray test) to stainless steel springs than the former brown oxide. This is thought to be because the chromium oxide structure is more tightly adherent (epitaxial).

As an aside, during the writing of this cautionary tale, a colleague was load testing two batches of stainless steel springs that had large cracks on the inside surface. He observed that the spring rate and load values were only very slightly reduced when the cracks were transverse and only 10 - 15% reduced when the cracks were longitudinal. It is surprising how little difference big cracks (to half way through the wire section) make to the load / deflection characteristics of compression springs. The point of this cautionary observation is that load testing springs as a means to sort cracked from non-cracked requires a greater degree of precision than might be expected. The cracking in both instances was nothing to do with the state of the oxide on the springs, but was associated with residual stresses.

References (1) Technically Speaking, Luke Zubek, Springs Oct 2005.
(2) Stainless Steel, Susan J Kerber and John Tverberg, Advanced Materials and Processes, Nov 2000.

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Corrosion resistance of these two springs is the same.

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