Advice & Counsel

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Stain-Less: Part 2

Continuing from last month, we cover the passivation process:

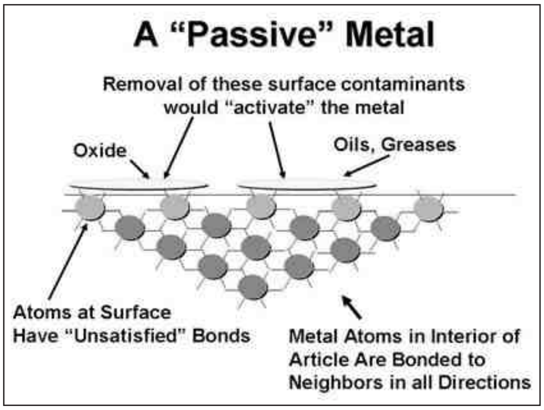
Defining passivation:

On a basic level, metals may exist in one of two surface conditions; active and passive. Consider the metal atoms shown in the figure. Each of the atoms within the bulk of the metal is bonded to neighboring atoms. However, the very last atoms at the surface of the metal are not bonded by neighboring atoms of the same metal, as on one side, there is only "air" available.

When a metal has surface atoms that are not (yet) bonded to other atoms, we conclude that the metal is in the "active" state. Converting a metal to the active state by stripping all surface atoms of any materials/compounds present from the surface is a process that generically is called "activation." A metal must typically be in the active state prior to any electroplating process, for example. A metal in the active state is prone to react with any convenient atoms available for bonding. That is why freshly electroplated nickel can not stay in a rinse tank too long, as the nickel will bond with oxygen present in the rinsewater, and then it will no longer be "active." Oxygen, sulfides and various organics are common compounds that are at least partially bonded to active metal surfaces, rendering them in the "passive" state. In general, (some precious metals are exceptions), metals react with whatever environment they are exposed to and given enough time, they will convert to a passive state.

Based on the above definition, "passivation" can be considered to be a generic term for any process that converts an active metal to the passive condition. Such processes include chromating, black oxide and phosphating, but most often the term passivation is used to describe a process in which stainless steel is treated in a chemical solution that will produce metallic oxides on the surface and at the same time dissolve any free iron that could galvanically produce electrolytic cells that can re-activate (on a local basis) the stainless steel, yielding corrosion spots.

We covered numerous types of stainless steel alloys last month and all of these were in the "active" state when produced by the steel mill. As the metal cooled it became passive and may even have grown a thick layer of oxide "scale."



Also, as parts are manufactured via stamping, cutting, forging, casting, etc., various lubricants and other organic materials will be either physically present on the surface or bonded to the surface atoms. In fact, if present, we need to remove the oxide scale prior to true passivation. The surface condition of stainless steel exhibiting the presence of scale and other residuals may generically be referred to as a passive condition. However, these materials are unsightly, promote the corrosion of stainless steel in various environments and are not suitable for use in typical applications such as food service or medical instruments. Therefore, we would not call such a condition truly passivated. In passivating stainless steel, we need to remove scales, machining/grinding fines and lubricants from the surface, rendering the steel in an active state, then treat the steel in a chemical solution specifically designed to passivate the surface under controlled oxidative condition(s).

Process steps

As just discussed, before we passivate a stainless steel, we need to remove oxide scales and all other surface impurities that can impede or prevent the formation of a controlled oxidative process. We won't discuss the details of conventional cleaning and descaling cycles employed, but here are a few general "tips":

- Parts that have intricate shapes that may make descaling/cleaning a difficult proposition should be processed through ultrasonic cleaning as part of the preparation cycle. Incomplete descaling and cleaning will result in poor corrosion resistance. For food/medical utensils this can be a huge problem, as the residuals can act to retain bacteria in service. For the same reason, any food/medical utensils should be thoroughly inspected after descaling to make certain that the process did not produce pitting.
- Solvent cleaning (vapor degreasing) using chlorinated solvents can lead to poor corrosion resistance if the part has an intricate shape or crevices that can trap solvent residuals, which in turn can be converted to chlorides by the passivation process. Trapped chlorides can produce corrosion spots, given enough time.
- Abrasive blasting should be conducted using iron-free media.
- Do not descale welded austenitic stainless steel in nitric-hydrofluoric acid mixtures, as these solutions can attack the weld areas.
- Visually inspect (at least some) descaled/cleaned parts before passivation. According to ASTM A380, the visual inspection should be carried out with general lighting at 100 foot candles and 250 foot candles on the surface that is being examined. Areas that can not be easily viewed should be wipe tested

using lint free cotton cloth or swabs. On the process line make sure that parts are water break-free before they go into the passivation solution.
- Since stainless steels are used in some highly critical application (nuclear, for example), the specification for such critical parts will include far more cleaning, descaling and handling do's and don'ts than we have here.

Passivating solutions

Nitric acid

Historically, nitric acid or nitric acid containing chromates have been employed to passivate stainless steel.

Nitric acid - 20 to 50 vol%

According to ASTM A380, this solution at 120 to 160°F (10 to 30 min) or 70 to 100°F (30 to 60 min) is suitable for annealed, cold-rolled, thermally hardened or work-hardened 200 and 300 Series, 400 Series, precipitation hardening and maraging alloys containing 16% or more of chromium, 400 Series, maraging and precipitation-hardening alloys containing less than 16% chromium, high-carbon-straight Cr alloys (except free-machining alloys), **IF** the surface is dull, as some light etching may occur. For bright surfaces, ASTM recommends a nitric-dichromate mix (see below).

Nitric acid - dichromate mixes

HNO_3 (20 to 40%) plus $Na_2Cr_2O_7 \cdot 2H_2O$ (2 to 6 wt%), 120 to 155°F, 10 to 30 min (or 70 to 100°F, 30 to 60 min) is preferred for the same alloys indicated above, if the surface is bright. Frankly, to avoid any chance of pitting, this would be my choice over straight nitric. For free machining 200, 300 and 400 series alloys, the temperature range for this solution changes to 70 to 120°F and immersion times are reduced to 25 to 40 min. An alternate composition for free machining 200, 300 and 400 series alloys is HNO_3 (1 to 2% plus $Na_2Cr_2O_7 \cdot 2H_2O$ (1 to 5 wt%). The temperature range and immersion time for this solution is 120 to 140°F and 10 min, respectively.

Nitric - copper sulfate mixes

This solution is an alternate for free machining 200, 300 and 400 series alloys. It contains HNO_3 (1 to 12 vol%) plus $CuSO_4 \cdot 5H_2O$ (4 wt%). Immersion temperature range and time are 120 to 140°F and 10 min, respectively.

Citric acid / citrates

Passivation of some alloys with citric acid-sodium nitrate mixtures has been commercialized over the past 10 years or so, but to date, it has not seen a high level of acceptance. One client that investigated the process declined its use due to long immersion times (60+ min) and poor corrosion resistance performance.

5 to 10 wt% ammonium citrate is also mentioned as an alternate to nitric acid-based passivating solutions. The processing time range is 10 to 60 min, but ammonium ions pose a wastewater treatment headache.

Other acids

Sometimes stainless steel requires passivation after assembly into a complex structure containing other metals. In other cases, the part is too massive to fit in a tank. Solutions have been developed to field passivate such problem parts.

Alternate 1. A solution containing hydroxyacetic acid (2 wt%) and formic acid (1 wt%) plus proprietary inhibitors at 200°F, for up to 6 hr, can be used when stainless steel parts are mated to steel parts.

Alternate 2. An ammonia-neutralized solution of EDTA containing proprietary inhibitors at 250°F for 6 hr followed by a hot-water rinse and a dip in a solution of 10 ppm ammonium hydroxide plus 100 ppm hydrazine can also be used for stainless steel / iron combinations.

For all solutions indicated, temperature, immersion time and chemical composition of the passivating solution are the three main operational parameters that must be in good control. Just because a range of temperature and time are given does not mean that the solution may fluctuate between those values during use. In general, once an operating temperature is chosen, it should be controlled within 2°F. Once an operational time is chosen, it should not fluctuate by more than about 10%.

The pH of the final rinse should be 6 to 8, preferably 6.5 to 7.5.

Before any large number of parts is processed, it is always a good idea to pre-test a sample or a section of a large part to make sure the chosen process chemistry and operating conditions will succeed and not aggressively etch the parts (all too often a result of rushing to the production line).

QC/QA

A common test employed to verify proper passivation of stainless steel is ASTM B177 (Salt Fog), with some specification for medical devices requiring 336 hr of exposure with no rust spots visible.

Other QA/QC tests described in ASTM B380 include:

Humidity

The part is exposed to 95 to 100% RH at 100 to 115°F (38 to 46°C) per ASTM D2247 for 24 hr. No visible signs of corrosion are allowed.

Copper sulfate spot test (aka, Preece Test)

This test does not work well on some 400 series stainless steels, especially those containing less than 16% chromium. On 200 or 300 series stainless steel, a drop of copper sulfate solution (4 g of copper sulfate pentahydrate plus 1 mL concentrated sulfuric acid in 250 mL of DI water) will galvanically displace free iron from the surface with metallic copper, producing a copper colored stain that does not readily wipe off. The solution has a shelf life of about two weeks. Unless conducted on a daily basis, it is best to make a new solution each time you test. For surgical and dental instruments made of hardened martensitic stainless steels, ASTM recommends an alternate copper sulfate solution be used. This mix contains 5.4 mL sulfuric acid and 4 g of copper sulfate in 90 mL of DI water. If the copper deposited from this solution wipes off, the part passes the inspection.

Solvent ring test

ASTM 380 describes this test as one to verify the "cleanliness" of the treated stainless steel. A drop of high purity solvent is applied to the test surface and allowed to dry. If the surface contains soluble residuals, then the solvent will dissolve them and re-deposit them as a "ring" as it evaporates. A black light may aid in the detection of the residue. The solvent is pre-tested for a "blank" by evaporating a drop on a glass slide.

Ferroxyl test

This is a classic test for the presence of free iron. A solution of potassium ferricyanide is made (3 wt% salts, plus 3 wt% nitric acid plus 94 wt% water). A drop of this solution will turn blue in the presence of free iron within a few seconds (usually less than 15).

Obviously, any parts that have been tested using the copper sulfate or Ferroxyl test need to be re-processed through the passivation line; especially if they are to go into the medical or food industry (ASTM and some specifications discourage the use of these tests for such parts). ***P&SF***