

Refinement of Citric Acid Passivation Methods and Comparison to Traditional Nitric Acid Based Chemistries

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ABSTRACT

Citric acid passivation offers a promising alternative to nitric acid passivation, particularly for free machining and precipitation hardened stainless steels where the latter requires the addition of sodium dichromate. While citric acid passivation is defined in industry specifications such as ASTM⁽¹⁾ A967 and SAE⁽²⁾ AMS2700, it is done with much less specificity than nitric acid passivation. This lack of specificity allows for conditions to be applied where inadequate passivation is achieved for some alloys. In this work, the citric acid passivation method has been explored and optimized for a range of common stainless steel alloys including a common austenitic alloy, AISI⁽³⁾ 304L (UNS S30403), an austenitic free-machining alloy, 303 (UNS S30300), a ferritic free-machining alloy, 416 (UNS S41600), and precipitation hardened alloy, 17-4 PH (UNS S17400). A series of commercially available chemistries have also been explored.

Key words: Stainless Steel, passivation, Nitric Acid, Citric Acid

INTRODUCTION

Traditional solutions for the chemical passivation of stainless steel are nitric acid based, with the addition of sodium dichromate as an inhibitor for precipitation hardened and free machining stainless steels. These passivation chemistries are difficult to handle from an environmental health and safety point of view, particularly the dichromate inhibited versions. Citric acid passivation has been pursued as a replacement for both nitric acid and inhibited nitric acid based chemistries for many years, and has been incorporated into consensus specifications such as ASTM⁽¹⁾ A967¹ and SAE⁽²⁾ AMS2700.² Adopting this process in a high-consequence production environment requires that the ability of the process to effectively passivate a contaminated surface (i.e., remove iron contamination, surface incident MnS inclusions, etc.) for a variety of stainless steels be demonstrated, particularly for free machining and precipitation hardened stainless steels. The primary driver for this work is the prevalence with which

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passivation of product by various vendors has been demonstrated to be deficient when using nitric acid passivation. As will be discussed below, the consensus specifications provide less guidance on appropriate combinations of solution concentration, temperature and time, raising the concern that changing the passivation methodology from nitric to citric acid could result in a greater number of performance issues due to errors when conducting citric acid passivation.

In AMS2700, while 8 different specific bath chemistries are presented for nitric acid passivation, for citric acid it simply states that *“an aqueous solution of 4 to 10 wt% citric acid with additional wetting agents and inhibitors as applicable”* be used. Temperatures are also recommended, but correlated only to the minimum passivation time, and not bath chemistry. ASTM A967 is similar, indicating that the solution chemistry be 4 to 10% citric acid, then varying the minimum time with the temperature of the bath. In both specifications, the minimum suggested immersion times are comparable, if not slightly shorter, than those recommended for nitric acid chemistries. It is worth noting that it is not uncommon for vendors to treat parts as close to the minimum time as practical, and that production issues, when they arise in nitric acid chemistries, are usually resolved by simply increasing the passivation time.

A review of the literature suggests that citric acid is as capable as nitric acid chemistries when it comes to passivating most stainless steels. Despite the apparent acceptance of citric acid in certain industries, and the availability of commercial solutions for citric acid passivation, there have been very few comprehensive reviews presented in the literature exploring the efficacy of citric acid passivation.³ However, some researchers have noted that certain free machining and precipitation hardened materials, in particular 416SS (a free machining martensitic stainless steel), are not readily passivated in citric acid.⁴ In terms of the resulting surface oxide, some studies have demonstrated a higher chromium to iron ratio in the resulting passive oxide layer for citric acid passivated relative to nitric acid passivated stainless steels.^{5,6,7} It has also been noted that while nitric acid is strongly oxidizing, citric acid is not – as a result, the citric acid solution may remove iron from the surface (which it readily chelates) but does not itself drive oxidation of the surface. This is supported by results obtained for 202SS exposed to various citric acid concentrations as a function of dissolved oxygen content in the solution, where a dramatically higher polarization resistance was observed when increased dissolved oxygen was present.⁸ While citric acid is very effective at chelating and removing iron from a stainless steel surface, it is much less effective at removing other metallic contaminants such as copper or nickel from drawing lubricants, etc.⁹ Although results in the literature demonstrating the effectiveness of citric acid passivation solutions are very positive, nearly all of the them have evaluated the ability of the citric acid passivation process to passivate sheet coupons of various stainless steels, without focusing directly on the ability of the passivation process to remove iron contamination deposited via machining, etc. onto the surface.

The lack of specificity in terms of bath chemistry in the consensus specifications suggests that chemistry is almost a secondary effect, provided there is sufficient citric acid present. This is supported by the work of Yasensky et al.¹⁰ where they noted that increasing the citric acid concentration beyond 4% had little effect on the passivation process, despite providing no technical basis. This assertion is also supported by work conducted by Murray evaluating the dissolution rate of iron in citric acid as a function of acid concentration which illustrated that at a fixed temperature, the dissolution rate of iron was not a strong function of concentration between 2.5 and 5 wt% citric acid.¹¹ However, Costa et al. explored the impact of citric acid concentration on the passivation of 316L stainless steel, demonstrating that passivation efficacy peaked at 20% citric acid (twice the concentration limit in the two consensus specifications), and further, that increasing the concentration to 30% resulted in chromium depletion of the passivation layer, an effect they referred to as over-passivation.¹²

In this study, the efficacy of citric acid passivation processes within the scope of the ASTM A967 and SAE AMS2700 specifications was explored for a series of alloys in an attempt to establish procedures that are applicable to each, while remaining cognizant of the need to minimize time in order to develop solutions that are workable at a vendor.

EXPERIMENTAL PROCEDURES

Sample Preparation

Samples of a workhorse austenitic stainless steel (304L (UNS S30403)), a free machining austenitic stainless steel (303 (UNS S30300)), a precipitation hardened stainless steel (17-4 PH (UNS S17400)), and a free-machining martensitic stainless steel (416 (UNS S41600)) in the form of sheet stock were prepared by first abrading the surface to a uniform 600 grit finish using SiC polishing media. The surfaces were then cleaned ultrasonically in an alkaline detergent for 15 minutes, rinsed ultrasonically in deionized water for 15 minutes, rinsed with flowing deionized water, and blown dry with filtered, dry air. Iron contamination was deposited by mechanically scoring the surface of each coupon using a similar coupon of high purity (99.99%) iron.

Nitric Acid Passivation

Nitric acid passivation was the baseline passivation method used to compare the various citric acid passivation methods to. Two procedures were used as noted in the text below. The first was AMS2700 Method 1, Type 2 (22.5 vol% HNO₃, 2.5 wt% Na₂Cr₂O₇·2H₂O, 125°F (51°C) for 20 minutes) and the second was AMS2700 Method 1, Type 6 (35 vol% HNO₃, 83°F (28°C), for 30 minutes). Passivation baths used American Chemical Society (ACS)⁽⁴⁾ reagent grade 70% (42° Baume) nitric acid and ACS reagent grade sodium dichromate in accordance with the specification. Upon completion of passivation, samples were rinsed in flowing deionized water for 2 minutes after which they were blown dry with filtered, dry nitrogen.

Citric Acid Passivation

Citric acid passivation was performed using ACS reagent grade citric acid added to deionized water. Compositions of 4, 7, and 10 wt% were used (covering the range of compositions specified in both ASTM A967 and AMS2700) and performed at temperatures of 60 and 70°C (140 and 158°F) for immersion times ranging from 20 to 60 minutes (longer times were not pursued as they would be difficult to implement in a production environment). Free machining stainless steels required the addition of an alkaline pre- and post-treatment in order to achieve satisfactory results, as will be discussed below. Both processes were accomplished by immersing the coupons in 5 wt% NaOH at 70°C (158°F) for 30 minutes. After passivation, samples were rinsed in flowing deionized water for 2 minutes, then blown dry with filtered dry nitrogen. For each combination of material and passivation methodology a total of 3 to 5 replicates were performed.

Passivation Validation

ASTM A967 provides a variety of methods through which the completeness of the passivation process can be assessed. Each of the methods in the specification rely on the formation of a stain, either iron oxides or deposition of other chemistries (e.g., copper) onto reactive sites on the steel surface. None of the practices indicate if the evaluation is to be performed with the unaided eye or if magnification is permitted. As such, these are qualitative in their determination of passivation effectiveness. In the work performed here, evaluation of if the iron had been removed was performed visually by performing a 5-hour ASTM B117¹³ salt spray exposure using 5 wt% NaCl (Practice C in ASTM A967). Any free iron present on the surface of the coupon is rapidly oxidized by the salt fog exposure, and the resulting iron oxide clearly visible on the sample surface.

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