SAND2021-12075C

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

David G. Enos and Derek Wichhart
Sandia National Laboratories
Materials Reliability
Albuquerque, NM 87185
USA

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 AMS2700 and ASTM A967, 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 austenitic and precipitation hardened stainless steels, with 304L, 303, 420, and 17-4 PH stainless steels. A series of commercially available chemistries have also been explored.

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

INTRODUCTION

Traditional solutions for stainless steel passivation are nitric acid based, with the addition of sodium dichromate as an inhibitor for precipitation hardened and free machining stainless steels. These chemistries are difficult to handle from an environmental health and safety point of view, particularly the dichromate inhibited solutions. 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 A967 and SAE AMS2700. Adopting this process in a 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 demonstrated, particularly for free machining and precipitation hardened stainless steels. The primary driver for this work is the prevalence with which 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.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

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. (Parsons, 2019) 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 (Peterson 2009). 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 (O’Laoire 2014, Kremer 2007, Luke 2006). It has 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. (Mulimbayan, 2015). 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. (Kremer, 1999). 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 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. (Yasensky, 2011) 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 (Murray, 2002). 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 overpassivation. (Costa 2020)

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.

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% HNO_3, 2.5 wt% $Na_2Cr_2O_7 \cdot 2H_2O$, 125°F (51°C) for 20 minutes) and the second was AMS2700 Method 1, Type 6 (35 vol% HNO_3, 83°F (28°C), for 30 minutes). Passivation baths used ACS 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. 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 B117 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.

Electrochemical Testing

While the methods in ASTM A967 are helpful in performing a quick assessment of passivation, they rely solely on the presence of free iron to determine the effectiveness of the passivation process. They do not assess the effectiveness at removing other reactive regions such as surface incident MnS inclusions or deposits of other metallic species, such as nickel or copper. In this work, anodic potentiodynamic polarization scans were used to provide a quantitative assessment of passivation efficacy, evaluating the impact on the passive current density, tendency for metastable pitting at elevated potentials, and the pitting potential of the material All scans were performed in 0.6M NaCl.

Experiments were performed in a glass cell exposing 1cm^2 of surface area, allowing the sample to come to steady state for a period of 10 minutes. Samples were initiated 50 mV cathodic of the open circuit potential at a scan rate of 0.1667 mV/s.

RESULTS AND DISCUSSION

Iron Contamination

As discussed above, the goal of the passivation process is first and foremost to remove active deposits from the surface of the stainless steel. Traditionally, these deposits are in the form of tool steel (iron) deposits left behind by machining operations. In order to assess the efficacy of citric acid in removing these deposits, each of the alloys was intentionally contaminated with iron. Evaluation of if the iron had been removed was performed visually by performing a 2 hour minimum ASTM B117 salt spray exposure using 5 wt% NaCl (Practice C in ASTM A967) in addition to electrochemically by performing anodic potentiodynamic polarization scans, paying particular attention to the passive current density, extent of metastable pitting, and the pitting potential. In Figure 1, a 304L coupon that has been iron contaminated then exposed to the salt fog exposure is shown, along with a similar coupon that was passivated via nitric acid (AMS2700, Method 1, Type 6). As can be seen, without passivation which removes the iron contamination, the surface iron results in iron oxide formation and staining of the surface.

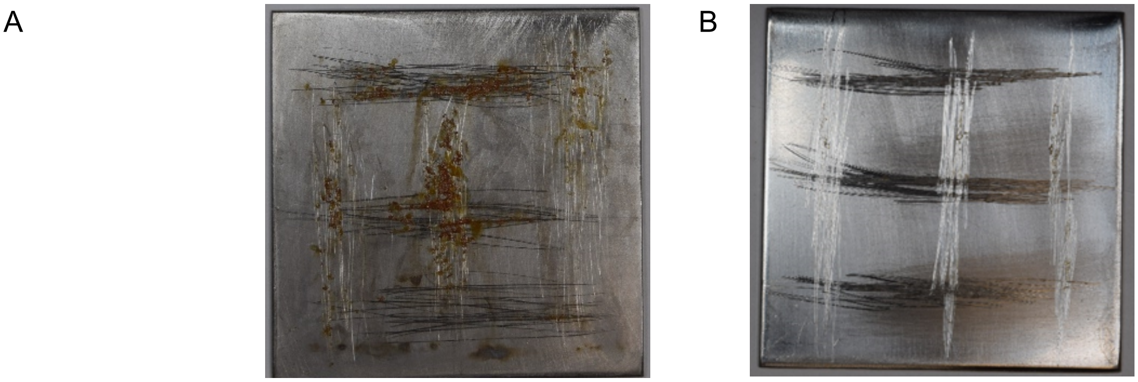

Figure 1: 304L surfaces contaminated with iron, then exposed to an ASTM B117 salt fog environment. The iron contamination readily oxidized if the material was not passivated (A), but if the material was successfully passivated, no iron oxide staining is observed.

In Figure 2, the electrochemical behavior of as-received 304L along with 304L that has been contaminated with iron is shown. In the as-received condition, 304L has an open circuit potential of approximately -200 mV vs. Ag/AgCl, then with anodic polarization of the surface exhibits spontaneous passivity. As the potential is increased in the anodic direction, the material remains passive until initiation of stable pitting. The presence of metallic iron on the surface has a dramatic impact on the resulting electrochemical behavior, driving the open circuit potential down to levels typical for metallic iron and eliminating the spontaneous passivity observed for 304L in the as-received condition. In addition, as the pitting potential is approached, significant metastable pitting events are visible in the data. The pitting potential is also reduced relative to the as-received material, as well as the apparent repassivation potential. Allowing the iron to oxidize (exposure to elevated humidity) removes the behavior characteristic of metallic iron (i.e., the low open circuit potential and lack of a passive region), but the metastable pitting is still present. The pitting potential was similar to that of the as received material, as well as the repassivation potential. Subsequently passivating the part, in this case using AMS2700 method Nitric 6, eliminates all of the behavior associated with the iron contamination. As the treated material is polarized anodically from the open circuit potential, it again exhibits spontaneous passivity with a consistently lower passive current density than the as-received material.

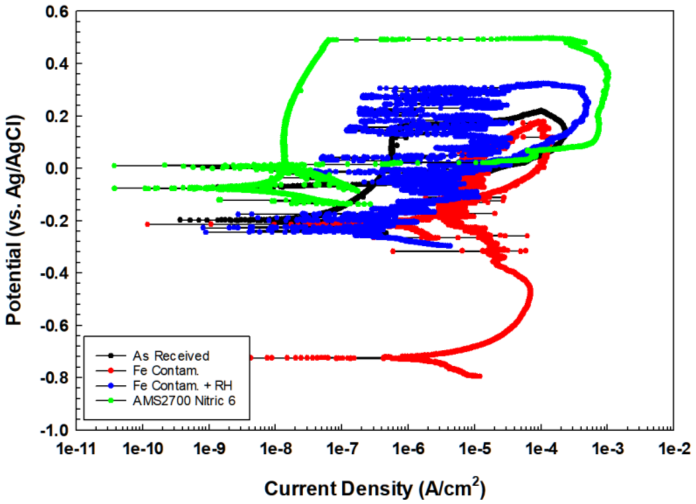

Figure 2: Anodic polarization behavior of an as-received 304L surface with a surface that was iron contaminated, one where the iron was partially oxidized at elevated humidity, and one where the surface is nitric acid passivated.

Passivation of 304L

Figure 3 illustrates representative polarization data for nitric and citric acid passivated 304L stainless steel. This alloy was readily passivated in 4% citric acid after 20 minutes, achieving results comparable to nitric acid passivation (AMS2700 Method 1, Type 6) in terms of the pitting potential achieved, and effective elimination of significant metastable pitting. The iron contamination was completely removed, and none of the characteristics of the contaminated surface are visible following salt fog exposure of the iron-contaminated then passivated coupons. The passive current density was consistently higher (approximately 1 order of magnitude). One potential explanation for the increased passive current density following citric acid passivation is the inability of citric acid to remove reactive metal contaminants such as iron and copper, as stated by Kremer (Kremer, 1999)..

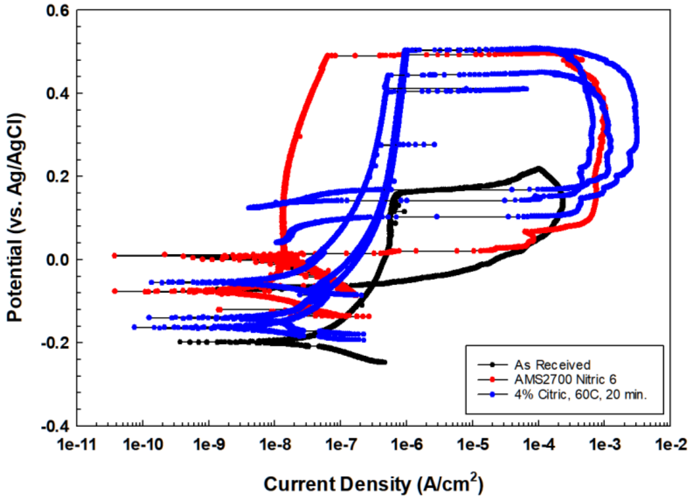

Figure 3: Anodic polarization of iron contaminated 304L stainless steel successfully passivated in nitric and citric acid, illustrating the performance relative to an as-received surface.

Passivation of 303

303SS is a free machining austenitic stainless steel containing a minimum of 0.15% sulfur. The sulfur results in the formation of a network of MnS inclusions in the alloy that serve to assist with chip formation during machining operations. These MnS inclusions are electrochemically active and it has been demonstrated conclusively in the literature that surface incident inclusions can result in localized corrosion initiation. As a result, nitric acid passivation of free machining stainless steels require the addition of a corrosion inhibitor, in this case sodium dichromate, to limit corrosion damage during the passivation process. Citric acid passivation, however, does not have this same requirement and is not as aggressive towards these defect sites. However, irrespective of the concentration, time, and temperature evaluated, citric acid formulations resulted in the formation of a blue surface oxide formed on the 303SS surfaces while in the passivation bath, as illustrated in Figure 4. This may have been the result of redeposition of components from the passivation bath. The redeposition was alleviated by implementing the alkaline-acid-alkaline technique developed to address flash-attack for free machining stainless steels (DeBold 2003). The 303SS samples were treated first by immersing the samples in 5 wt% NaOH at 70°C (158°F) for 30 minutes, after which the citric acid passivation process was performed. The samples were then treated again in 5 wt% NaOH at 70°C (158°F) for 30 minutes as a neutralization step. This procedure resulted in the elimination of the blue deposit and was also necessary for the free machining ferritic stainless steel discussed below.

Figure 4: Dark blue surface oxide that forms on 303 and 416 stainless steel surfaces from citric acid passivation. Formation of the dark layer occurs during the passivation process itself. Incorporation of an alkaline pre and post treatment resulted in the elimination of the discoloration, and surfaces that appeared similar to that illustrated in Figure 1B.

As expected, 303SS was more difficult to passivate than 304L. In Figure 5A, the behavior of 303 in 4% citric acid is shown. While for some samples, the surface was effectively passivated, in others it was not – this same behavior was observed in 7% citric acid for times less than 60 minutes as well as in 10% citric acid for times less than 60 minutes. Figure 5B illustrates the behavior observed after 60 minutes in a 7% citric acid solution, where all three samples were effectively passivated – this was also observed visually as no iron oxidation was observed after salt fog exposure of the passivated coupons. Increasing the temperature to 70C did not result in an improvement in the efficacy of the passivation bath.

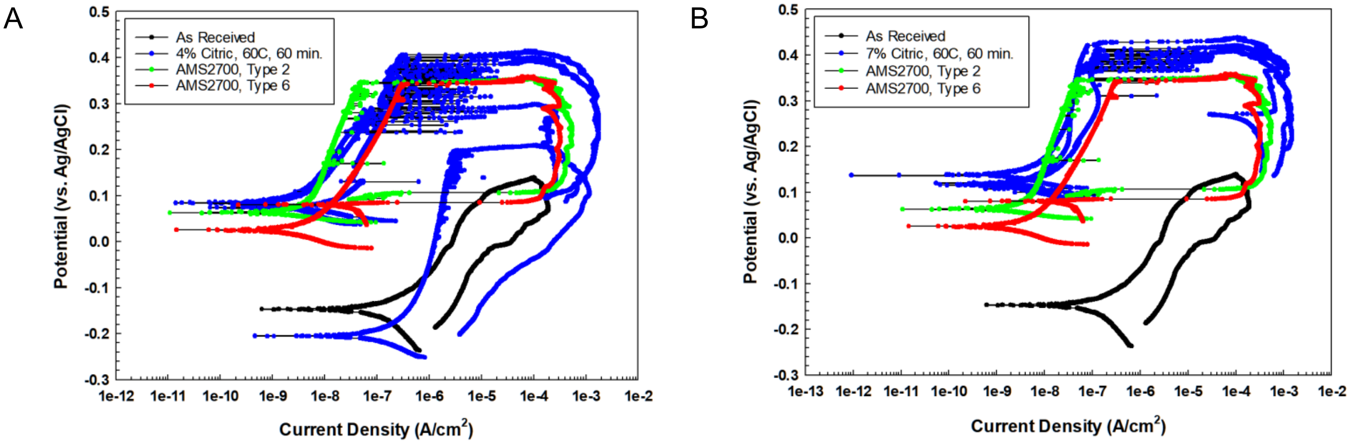

Figure 5: Anodic polarization of 303SS passivated in citric acid passivation. Passivation in solutions below 7% citric acid, for times less than 60 minutes resulted in erratic performance (A) where some samples passivated readily while others did not. Increasing the concentration to 7 or 10% and increasing the time to 60 minutes resulted in consistent passivation of the surface (B).

Passivation of 17-4 PH

70-4PH is a common precipitation hardened stainless steel. As with free machining stainless steels, the addition of a corrosion inhibitor (sodium dichromate) is required to effectively passivate precipitation hardened stainless steels. Unlike the free machining materials, the citric acid passivation solutions were able to be employed without resulting in the formation of the blue deposit on the metal surface. For concentrations below 10% citric acid, the passivation process resulted in increased passive current densities and lower pitting potentials as illustrated in Figure 6. At 10% citric acid for 60 minutes, reproducibly good behavior was achieved, as evidenced by electrochemical data as well as visual observation of passivated coupons following salt fog exposure. However, the resulting pitting potentials for all conditions were lower than the values readily achieved via traditional nitric acid passivation (AMS2700 Method 1, Type 2). As with 304L, the nitric acid passivation processes achieved substantially lower passive current densities, while the citric acid passivation resulted in a passive current density comparable to the as-received material.

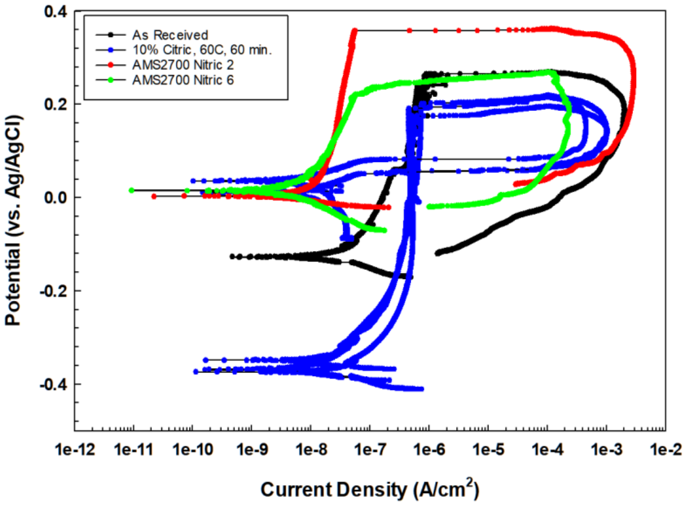

Figure 6: Anodic polarization of citric acid passivated 17-4 PH stainless steel. As with 303, erratic behavior was observed for concentrations below 10% at a time of 60 minutes. In addition, citric acid passivation resulted in a reproducibly lower pitting potential than an appropriate nitric acid passivation method.

Passivation of 416 SS

416SS is a martensitic free machining stainless steel with a low chromium (12-14 wt%) content and high sulfur content (0.15 wt% min), and as such is extremely difficult to passivate. While the material can be passivated in nitric acid based passivation solutions, it has been stated in the literature that citric acid is not able to address this material (Peterson, 2009). The results achieved in this study further support the assertion that citric acid is insufficient to address 416SS. As shown in Figure 6, at 7% citric acid after 60 minutes the behavior of the material was nominally identical to the unpassivated, as-received material. As with 303SS, the alakine-acid-alkaline procedure was used for the citric acid solutions, where the surface were treated in 5wt% NaOH both prior 2 and following the passivation process. Increasing the concentration to 10% yielded better performance after 60 minutes but was still significantly less effective than AMS2700 Method 1, Type 2 (sodium dichromate inhibited nitric acid) – however, salt fog testing combined with visual assessment of the coupon surface indicated that the surface deposited iron had been removed. To illustrate the importance of the inhibitor in nitric acid for free machining materials, AMS2700 Method 1, Type 6 was also performed. As illustrated in the figure, the omission of the dichromate inhibitor resulted in failure of the solution to effectively passivate the material.

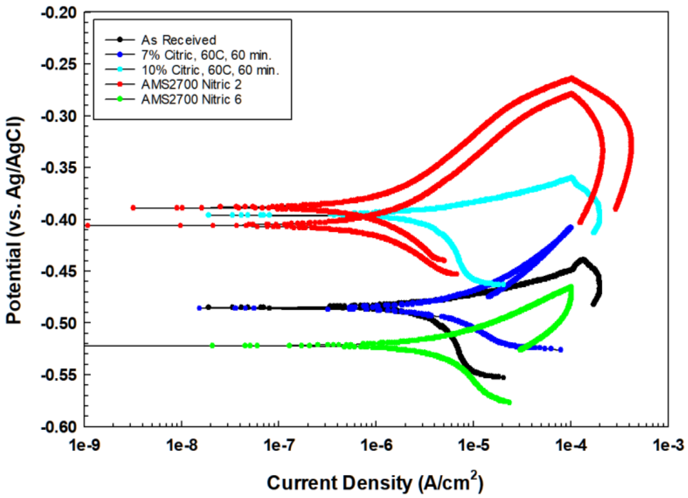

Figure 7: Passivation of 416SS in citric and nitric acid solutions, demonstrating the limitations of citric acid when working with this free machining, martensitic alloy.

SUMMARY/CONCLUSIONS

Citric acid passivation has been embraced by many in industry as an environmentally friendly alternative to nitric acid passivation solutions. Unlike nitric acid passivation procedures, the consensus specifications present provide no specificity in terms of what the appropriate combination of solution chemistry, temperature, and immersion time is appropriate as a function of alloy.

- Citric acid was effective at removing intentionally introduced iron contamination, but had difficulty addressing other contaminants and surface incident MnS inclusions.
- Citric acid passivation of free machining stainless steels was ineffective without the incorporation of an alkaline pre- and post-treatment
- 304L stainless steel was readily passivated by all conditions permitted by the consensus specifications
- 303L was not effectively passivated in some instances at citric acid concentrations below 7% for times less than 60 minutes
- 17-4PH was not effectively passivated in some instances for citric acid concentrations below 10% and times below 60 minutes
- 416 stainless steel could not be effectively passivated by the citric acid concentrations permitted by the consensus specifications, even with immersion times as long as 60 minutes.

ACKNOWLEDGEMENTS

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

REFERENCES

ASTM A967/A967M-17 "Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts", 2017.

SAE AMS2700-F, “Passivation of Corrosion Resistant Steels”, 2018

C. O’Laoire et al., “Analysis of the Acid Passivation of Stainless Steel”, Analytical Letters, Vol. 30 (2006), pp. 2255-2271.

L.V. Kremer, “Improvements in Passivation Using Citric Acid Formulations”, Galvanotechnik, Vol. 98, no. 2 (2007), pp. 333-339.

D. Luke et al., “The Pickling and Passivation of Stainless Steels, Part 2”, Galvanotechnik, Vol. 97, no. 7 (2006), pp. 1646-1653.

F.M. Mulimbayan et al., “Electrochemical Investigation of the Effects of Acid Concentration and Dissolved Oxygen on the Corrosion Behavior of Austenitic, Low-Nickel Stainless Steels in Citric Acid”, Applied Mechanics and Materials, Col 835 (2015), pp. 115-120.

L.V. Kremer “Citric Acid Passivation of Stainless Steel”, Products Finishing, Vol 63, No. 8 (1999), pp. 45-46

D. Yasensky et al., “Citric Acid Passivation of Stainless Steel”, Presentation from Aircraft Airworthiness and Sustainment Conference, April 19, 2011.

M. Murray “Using Surfactant Free Citric Acid to Passivate Stainless Steel”, Plating and Surface Finishing, Vol., 89, No. 11 (2002), pp. 54-55.

T.A. DeBold et al. “How to Passivate Stainless Steel Parts”, Modern Machine Shop, Vol. 76, No. 5 (2003), pp. 98-104

D.S. Peterson, “Parts Cleaning Clinic: Nitric vs. Citric Acid Passivation”, Product Finishing, Vol. 74, No. 1 (2009), pp. 34-35.

A.T. de Costa et al., “Interplay Between the Composition of the Passive Film and the Corrosion Resistance of Citric Acid Passivated AISI 316L Stainless Steel”, Surface and Interface Analysis, Vol. 53, no. 3 (2020), pp. 374-384.

S. Parsons et al., “Green Chemistry for Stainless Steel Corrosion Resistance: Life Cycle Assessment of Citric Acid versus Nitric Acid Passivation”, Materials Today Sustainability, Vol. 3-4 (2019), pp. 100005.