

Effect of Passivation Treatments on the Corrosion Resistance Properties of As-sintered 17-4 PH Additive-Manufactured by Binder Jetting Technology

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Binder Jetting (BJ) is an additive manufacturing technology that can produce alloy components at a higher speed and resolution than other systems. However, the localized corrosion resistance properties of BJ stainless steel are lower than those obtained with conventional manufacturing processes. This study aims to evaluate the effects of passivation treatments on the corrosion behavior of as-sintered 17-4 PH samples fabricated through BJ. The samples were treated with four acidic solutions: 15 %, 20 %, 40 % HNO₃, and 40 % HNO₃ + 1 % HF. The localized corrosion resistance properties were evaluated through Cyclic Potentiodynamic Polarization (CPP) tests in a neutral pH sodium chloride electrolyte. The treatments significantly enhanced the localized corrosion resistance properties of as-sintered BJ samples, determining the typical passive anodic behavior of the CPP curve, which was not shown in the untreated samples. Moreover, higher concentrations of HNO₃ (40%) improved the pitting corrosion resistance, while adding HF was ineffective. The study paves the way for broader industrial applications of additive-manufactured stainless steel, emphasizing the critical role of improving localized corrosion resistance properties through passive treatments.

KEYWORDS: LOCALIZED CORROSION; PASSIVATION TREATMENTS; BINDER JETTING; CYCLIC POTENTIODYNAMIC POLARIZATION;

INTRODUCTION

Additive Manufacturing (AM) technologies have gained significant attention in recent years as an innovative technology capable of printing complex metallic components with reduced fabrication time and cost [1]. Among the different AM technologies, Binder Jetting (BJ) has emerged as a promising technique due to its high printing speed of a wide range of alloys and the absence of residual stress, which is typically induced by high-energy beam-based processes [2–5]. In BJ, a liquid binder is selectively deposited into layers of metallic powder to generate a green part, which is subsequently cured, depowdered, debound, and finally sintered at high temperatures around 1300 °C [6,7]. Besides these benefits, one of the main limitations of BJ lies in the intrinsic heterogeneous microstructure produced during sintering, which directly affect both mechanical and corrosion resistance properties [8–11]. The precipitation hardened martensitic Stainless Steel (SS) 17-4 PH is widely used in aerospace, petrochemical, and biomedical industries because of its good balance

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of mechanical and corrosion resistance properties [12]. Conventionally manufactured 17-4 PH exhibits a primarily martensitic microstructure which provides high mechanical strength and acceptable corrosion resistance in moderately aggressive environments. On the other hand, BJ-fabricated and as-sintered 17-4 PH typically shows a mixed ferritic-martensitic microstructure with microporosities, secondary phases, and inclusions [13,14]. The samples investigated in this study were fabricated with the Shop System™ (Desktop Metal, Burlington, MA, USA) using a layer thickness of 75 µm and sintered at 1300 °C under an argon-hydrogen atmosphere, exhibit porosities up to 0.5% and compositional segregations at grain boundaries [14].

Localized corrosion is a significant aspect that arises from the breakdown of the passive oxide film, which typically provides protection to the metal surface. In BJ-fabricated alloys, porosities, inclusions, and secondary phases act as preferential sites for pit initiation. In particular, elemental segregation around inclusions and grain boundaries strongly influences local stability of the passive film. In a recent study [15] demonstrates that segregation of Cu and Sb at inclusion-matrix interfaces promotes localized corrosion during pit initiation, while co-segregation of Cr and solute atoms at grain boundaries can produce Cr-depleted zones, making the alloy highly susceptible to intergranular corrosion [16]. Moreover, limited oxygen diffusion in pore regions impairs repassivation, accelerating pit and crevice propagation. As a result, corrosion resistance properties of as-sintered samples fabricated by BJ technology are generally inferior to their wrought counterparts, as shown in previous studies [13,14,17,18].

Most of the passivation treatments commonly involve nitric acid (HNO₃) or nitric (HNO₃) and (HF) acids mixtures to restore and stabilize passive films on stainless steels, which enhance resistance against localized corrosion [19–22]. While these treatments are well established for conventionally manufactured stainless steels, their application to additive-manufactured stainless steels is marginally studied.

The goal of this study is to evaluate the effect of different passivation treatments on the localized corrosion resistance of as-sintered 17-4 PH fabricated by BJ technology. Comparisons are made between untreated

and passivated BJ samples and wrought counterparts through Cyclic Potentiodynamic Polarization (CPP) tests in neutral sodium chloride solution.

MATERIALS AND METHODS

Samples

Two sets of stainless-steel specimens were employed in this study:

1. Binder Jetting (BJ) 17-4 PH samples manufactured by using the *Shop System*™ (Desktop Metal, Burlington, MA, USA). The printing process was carried out with a layer thickness of 75 µm, and after curing and depowdering, the samples were sintered at 1300 °C under an atmosphere of 97% Argon and 3% Hydrogen. The samples obtained are square plates with dimensions of 25×25×10 mm as shown in figure 1.
2. Wrought (Wr) 17-4 PH samples, used as a reference.

Sample Preparation

Before conducting the corrosion test, the specimens were mounted in acrylic resin to have one flat exposed surface. Surfaces of the samples were ground by using Silicon Carbide (SiC) papers up to 1200 grit size and cleaned in an ultrasonic bath with deionized water for 5 minutes and then normal hexane for 15 minutes. Before performing an electrochemical test, the samples rested for 24 hours. Then the exposed area (2.01 cm²) was defined by using polyimide tape with a circular aperture.

Passivation Treatments

Passivation treatments were performed using four chemical solutions prepared as follows:

- P1:** 15 vol.% HNO₃ in deionized water
- P2:** 20 vol.% HNO₃ in deionized water
- P3:** 40 vol.% HNO₃ in deionized water
- P4:** 40 vol.% HNO₃ + 1 vol.% HF in deionized water

The samples were immersed in each solution for 30 minutes at room temperature. After the passivation treatment they were rinsed in deionized water in a sonicator for 5 minutes, to remove the residual chemical, and then dried with compressed air and lastly stored in a desiccator for 24 hours.



Fig.1 - Provini as-sintered di 17-4 PH ottenuti per Binder Jetting / *The 17-4 PH BJ as-sintered specimens.*

Electrochemical Testing

The CPP tests were carried out at room temperature in a neutral electrolyte having a concentration of 0.035 wt.% NaCl with the scan rate of 0.166 mVs^{-1} .

A typical three-electrode electrochemical cell setup was used in this study. The configuration included:

- Working electrode: the prepared stainless-steel sample
- Reference electrode: Saturated Calomel Electrode (SCE, +0.241 V vs SHE)
- Counter electrode: activated titanium wire

CPP scans were initiated 175 mV below the open circuit potential (OCP), sweeping towards positive values at $83 \mu\text{V/s}$ until a current density of $0.1 \text{ mA}\cdot\text{cm}^{-2}$ was reached. The scan was then reversed until current density returned to near-passivation conditions.

The tests were repeated at least three times for each

sample type, and the most representative curve will be shown. Concerning the characteristic parameters obtained from the CPP curves, such as corrosion potential E_{corr} , protection potential E_{prot} and pitting potential E_{pit} , average values and the corresponding standard deviations were calculated.

Microscopy

After electrochemical measurement, post-corrosion surface morphology was examined by using optical microscopy (OM) to identify localized corrosion (pitting and crevice attack) associated with the samples submitted to different passivation treatments.

RESULTS AND DISCUSSION

The average chemical composition (wt.%) of BJ-fabricated 17-4 PH and wrought sample measured by using Spark Analyzer (Spectrolab, Sylmar, CA, USA) at four different points is reported in table 1.

Tab.1 - Composizione chimica (% in peso) di un campione BJ as-sintered e wrought / *Chemical composition (wt.%) of an as-sintered BJ sample and wrought.*

	Cr	Cu	Si	Ni	C	Mn	Mo	Fe
17-4 PH Binder Jetting	16.54	3.35	0.54	4.77	0.02	0.46	0.21	Bal.
17-4 PH Wrought	15.55	3.10	0.34	5.15	0.03	0.77	0.12	Bal.

Although, a detailed microstructural characterization of untreated samples has been extensively reported in previous work [13, 14], a summary of the main

microstructural features is provided to support the discussion of the electrochemical tests. The XRD diffractogram of the as-sintered sample reveals only

peaks commonly attributed to the body-centered cubic (BCC) phase, which is found in both ferrite and martensite [14], despite the latter having a distorted BCC structure in terms of a higher lattice cell parameter in the z-axis. The presence of hydrogen gas within the sintering chamber, along with pores and compositional heterogeneities at the grain boundaries, promotes ferrite stabilization during cooling rather than retention of austenite at room temperature [23]. In addition, OM and Scanning Electron Microscopy (SEM) revealed significant residual porosities together with elemental segregations, mainly involving Cu and Nb, which are preferentially located at the grain boundaries. These microstructural features are responsible for influencing electrochemical behavior by promoting localized passive film instability and corrosion initiation sites.

On the other hand, the wrought sample displays BCC peaks and Face-Centered Cubic (FCC) peaks, which correspond to retained austenite (FCC), representing a small fraction in volume, as observed in a previous study [13]. Consistently, the microstructure of wrought 17-4 PH is characterized by a finer and more homogeneous martensitic matrix, with a limited amount of retained austenite and δ -ferrite stringers. This comparatively dense and uniform microstructure, in contrast to the as-sintered BJ condition, is known to promote a more stable passive film formation and plays a key role in the different

electrochemical response observed between wrought and BJ samples.

The most representative CPP curves of wrought specimens before and after passivation are shown in figure 2: it can be observed that the passivation treatments did not improve their localized corrosion resistance, as the untreated material already exhibited a relatively stable passive behavior due to its dense and homogeneous martensitic microstructure as shown in figure 2a, similar results were found in other studies [18]. This indicates that for wrought 17-4 PH, passivation treatments are not beneficial. The only beneficial effect of the passivation treatments that can be observed in figure 2 and 3 is the increase of the corrosion potential. Conversely, BJ as-sintered samples show a markedly different response. The untreated material does not display a well-defined passive region, owing to microstructural heterogeneities, residual porosities, and elemental segregation, other studies observed the similar results [14]. However, after passivation treatments, a well-defined passivation trait was observed in figure 3, especially at higher HNO_3 concentrations, indicating that passivation effectively stabilizes the passive film by mitigating the effects of porosity and microstructural heterogeneities and thus improves pitting corrosion resistance. These results confirm that the effectiveness of passivation treatments is strongly governed by intrinsic microstructural characteristics of the material.

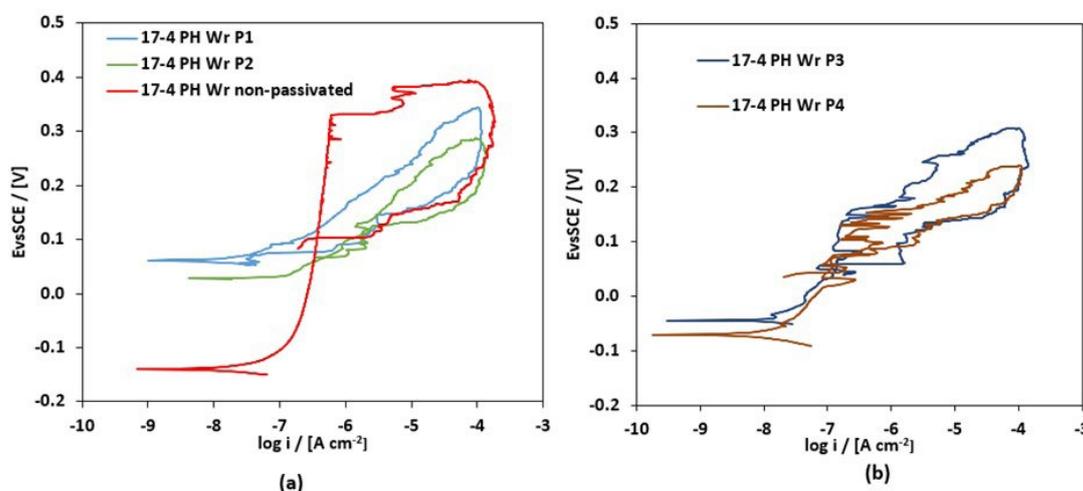


Fig.2 - Curve CPP dei campioni 17-4 PH wrought (Wr) dopo i trattamenti di passivazione: (a) campione non passivato, P1, P2; (b) P3, P4 / CPP curves of 17-4 PH Wr samples after passivation treatments: (a) non-passivated sample, P1, P2; (b) P3, P4.

All passivation treatments produced a well-defined passive region, which is more extended as the concentration of HNO₃ increase from 15% (P1) to 40% (P3, P4). In particular, BJ samples passivated by P3 and P4 treatments supplied

comparable CPP curves as figure 3 shows, thus the same localized corrosion resistance of the obtained samples. This means that the addition of HF (P4) did not give any particular benefit to the passivation treatment.

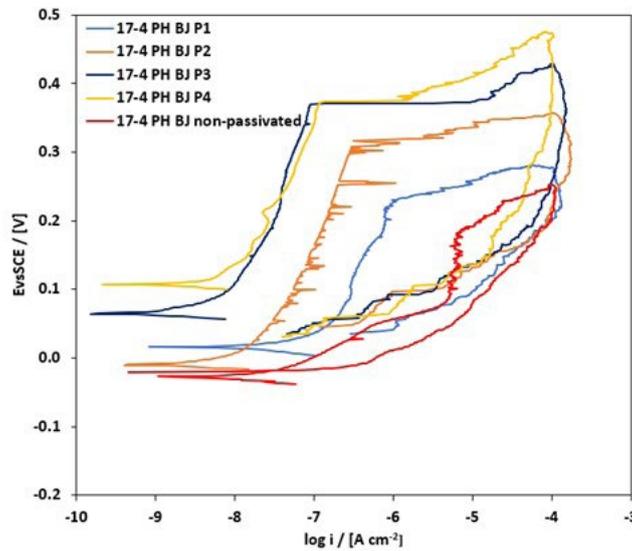


Fig.3 - Curve CPP dei campioni 17-4 PH ottenuti tramite Binder Jetting allo stato non passivato e dopo i trattamenti di passivazione / *CPP curves of 17-4 PH BJ-fabricated samples in the non-passivated condition and after passivation treatments.*

Figure 4 represents the characteristic potentials obtained from the CPP curves: E_{corr} , E_{pit} and E_{prot} . The passivation treatments produced a clear benefit in terms of corrosion resistance properties for BJ fabricated samples, particularly at high nitric acid concentrations, determining an increase of E_{pit} . In figure 4, the perfect passivity region

corresponds to potentials less positive than E_{prot} , where the pitting corrosion cannot initiate and, furthermore, existing pits cannot propagate; the imperfect passivity region is defined by the potential range between E_{pit} and E_{prot} , where pits cannot initiate but existing pits can propagate.

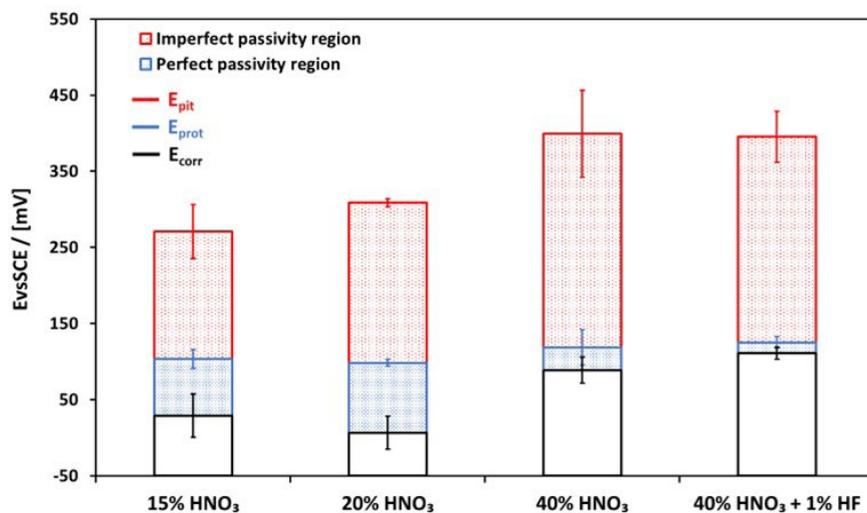


Fig.4 - Potenziali caratteristici (E_{pit} , E_{corr} ed E_{prot}) dei campioni ottenuti tramite Binder Jetting, dopo i trattamenti di passivazione / *Characteristic potentials (E_{pit} , E_{corr} and E_{prot}) of BJ-fabricated samples after passivation treatments.*

The OM was performed after the electrochemical tests. In a previous study [14], as-sintered BJ samples without passivation showed preferential initiation of localized corrosion, mainly in the form of pits and micro-crevice. However, after passivation treatments, the protective film significantly improved, resulting in a noticeable reduction in corrosion extension. Through OM observations, very few corrosion attacks were found like that shown in figure 5, for a sample treated with passivation P3, as an example, which is representative of the attacks found in the passivated samples: it affects a limited area of the sample and remains

very superficial because it does not seem to penetrate deeply, contrarily to what was previously observed in as-sintered samples. Although passivation effectively mitigates corrosion, based on these observations localized attacks may still occur at specific sites, in agreement with that is suggested by the anodic characteristics of the examined samples (figure 3).

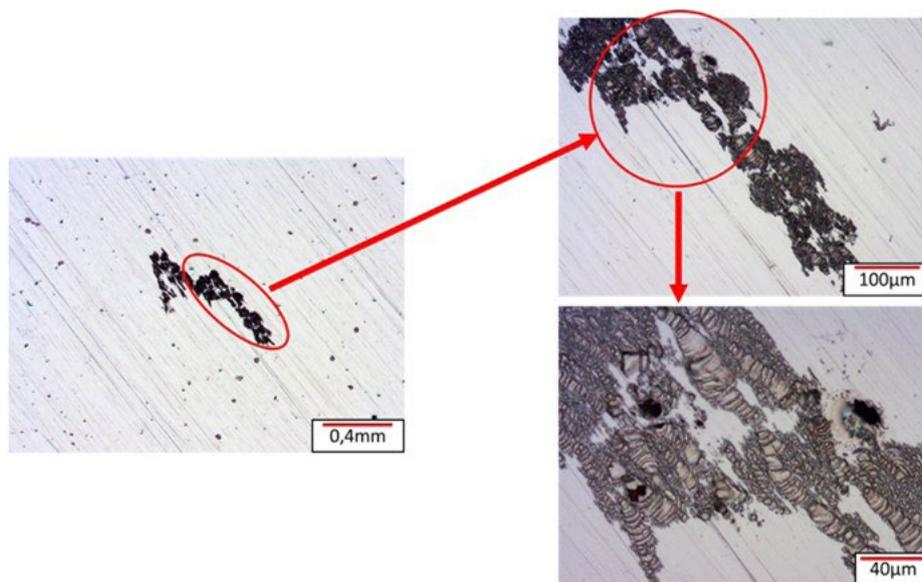


Fig.5 - Immagini di microscopia ottica dopo prove CPP: campione BJ passivato P3 con attacco localizzato /
Optical microscopy images after CPP tests: BJ sample passivated with P3 showing localized pitting.

CONCLUSION

From a previous study of the same authors, the as-sintered BJ-fabricated 17-4PH samples were found to be characterized by a heterogeneous microstructure, which was considered responsible of a limited ability to form a stable passive film. Therefore, solutions to improve the localized corrosion resistance of these materials are of paramount importance. For this reason, this study has been done, where 17-4 PH in as-sintered condition was submitted to passivation treatments by different solutions of HNO_3 , adding in one case a small amount of HF. The present work demonstrated that passivation treatments significantly improve the localized

corrosion resistance of BJ-fabricated 17-4 PH stainless steel, while their effect on wrought counterparts is negligible or slightly detrimental. Electrochemical characterizations showed that, after passivation, a well-defined passive region appeared, particularly with 40% of HNO_3 treatment. The addition of HF did not bring benefits.

These results underline the novelty of applying passivation to BJ-fabricated stainless steels, proving it as an effective strategy to mitigate their intrinsic corrosion limitation and extend their potential for industrial use.

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Effetto dei trattamenti di passivazione sulle proprietà di resistenza a corrosione dell'acciaio 17-4 PH as-sintered ottenuto con tecnologia Binder Jetting

Il Binder Jetting (BJ) è una tecnologia di additive manufacturing che consente di produrre componenti in lega con una velocità e risoluzione superiori rispetto ad altri sistemi. Tuttavia, le proprietà di resistenza alla corrosione localizzata dell'acciaio inox prodotto tramite BJ sono inferiori a quelle ottenute con i processi di produzione convenzionali. Questo studio si propone di valutare gli effetti dei trattamenti di passivazione sul comportamento alla corrosione dei campioni 17-4 PH as-sintered realizzati tramite BJ. I campioni sono stati trattati con quattro soluzioni acide: 15% HNO₃, 20% HNO₃, 40% HNO₃ e 40% HNO₃ + 1% HF. Le proprietà di resistenza alla corrosione localizzata sono state valutate tramite test di Polarizzazione Potenziodinamica Ciclica (CPP) in un elettrolita a base di cloruro di sodio a pH neutro. I trattamenti hanno migliorato significativamente le proprietà di resistenza alla corrosione localizzata dei campioni BJ as-sintered, determinando il tipico andamento anodico passivo della curva CPP, che non era stato osservato nei campioni non trattati. Inoltre, concentrazioni più elevate di HNO₃ (40%) hanno migliorato la resistenza alla corrosione per pitting, mentre l'aggiunta di HF si è rivelata inefficace. Lo studio svolto permette di rendere più ampia l'applicazione industriale dell'acciaio inox prodotto tramite manifattura additiva, grazie al miglioramento delle sue proprietà di resistenza a corrosione localizzata attraverso trattamenti di passivazione.

PAROLE CHIAVE: CORROSIONE LOCALIZZATA; TRATTAMENTI DI PASSIVAZIONE; BINDER JETTING; POLARIZZAZIONE CICLICA POTENZIODINAMICA;