La Metallurgia Italiana
International Journal of the Italian Association for Metallurgy

Study of corrosion resistance of 17-4 PH stainless steel as-sintered and heat-treated samples manufactured by Bound Metal Deposition™

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The corrosion resistance of 17-4 PH stainless steel samples additive manufactured by Bound Metal Deposition™ (BMD) has been investigated in neutral sodium chloride environments. The methods used in this study were based on long-term monitoring of the Open Circuit Potential and afterwards recording of Cyclic Potentiodynamic Polarization curves in the same electrolytic solution. The electrochemical investigations have been carried out on 17-4 PH wrought samples and on BMD as-sintered and H900 heat-treated samples. The BMD samples had different build-up orientations with respect to the build plate. The results showed that the susceptibility to localized corrosion of the 3D printed samples is higher than the wrought 17-4 PH, although the breakdown potential on the anodic curves was even higher in some of the former than the latter. A better corrosion behavior of the BMD printed samples was observed after heat treatment, in particular for those with build-up orientation of 0° and 45°.

KEYWORDS: 17-4 PH, BOUND METAL DEPOSITION, AS-SINTERED, PRECIPITATION HARDENING, BUILD-UP ORIENTATIONS, OPEN CIRCUIT POTENTIAL, CYCLIC POTENTIODYNAMIC POLARIZATION

INTRODUCTION

The 17-4 PH is a precipitation hardened martensitic stainless steel that combines good mechanical resistance properties and corrosion resistance behavior. This material is widely used among precipitation hardened steels in many fields such as chemical, oil and gas, food, paper and metal working industries. Despite the 17-4 PH is usually obtained by conventional metallurgy processes, in the past decades a growing demand in Additive Manufacturing (AM) techniques has occurred in the manufacturing industry, since they allow to obtain near net-shaped parts characterized by complex geometries [1, 2]. An emerging AM technology is Bound Metal Deposition™ (BMD) that has been developed recently and has found applications in the printing of components such as pumps, valves, fasteners, jigs and brackets. The BMD technology is defined as an AM process based on extrusion, where metal components are built by extruding a thermoplastic support filled with metal powder [3]. This technique is performed by a Studio System™ that is made up of a printer,

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a debinding chamber, and a sintering furnace. After the layer-by-layer extrusion, most of the thermoplastic resin is debinded, in a nonpolar solvent. The sintering is then required to obtain adequate functional and structural properties by consolidation of metal powders and thermal removal of the remaining binder. This process has many features in common with Metal Injection Moulding that consists of an injection phase of a mix of metal powders and organic binder; afterwards, the manufacts are debinded and finally they are sintered [4-6]. This study focuses on investigation of corrosion performances of as-sintered and heat-treated BMD and wrought (Wr) 17-4 PH samples during long-term exposure to neutral NaCl environment by means of Open Circuit Potential (OCP), followed by Cyclic Potentiodynamic Polarization (CPP). This approach has been used in previous study [7], which showed that a passive film is likely developed on the surface of BMD, even though the characteristic passive trait cannot be clearly observed in CPP tests.

MATERIALS AND METHODS

The 17-4PH martensitic stainless steel samples investigated in this study were obtained by BMD and consisted of 25x25x3 mm plates. The printing parameters selected for the 17-4 PH samples of this work are summarized in Tab. 1.

Tab.1 - Printing process parameters of BMD samples. / Parametri di stampa dei campioni BMD.

Build-up orientations	0° - 45° - 90°
Layer height	0.1 mm
Printing nozzle diameter	0.4 mm
Printing infill pattern	Concentric

The build-up orientation is defined as the angle between the build plate of the printer and the plane of the surface investigated in this work. A concentric infill pattern was selected for the extrusion, therefore the layers were printed by deposition of metal powders and binder starting from the center and towards the perimeter of the sample. Most of the binder was removed from the samples after the printing process by debinding cycle that took place up to 40 hours in a chamber filled with trans-1,2-dichloroethylene solvent. Finally, the sintering was performed in a furnace at temperature up to 1400 °C for 40 hours in an inert gas atmosphere of 97% argon and 2.9% hydrogen. The BMD samples were tested in as-sintered and heat-treated conditions. With more details the heat treatment (H900) consisted in the precipitation hardening obtained through two stages: 1 hour of solubilization at 1040 °C followed by 1 hour of ageing at 482 °C. The BMD precipitation hardened samples that underwent the solubilization and ageing process were labeled as "SA", while the as-sintered samples were not labeled.

Before tests, the samples were prepared by embedding the samples in acrylic resin and grinding their surfaces up to 1200 grit; then they were sonicated in deionized water for 5 minutes and n-hexane for 15 minutes. An insulating polyimide tape was applied on the surface of the embedded samples to obtain a circular area of 1.13 cm^2 exposed to the electrolyte. The corrosion resistance properties were investigated by means of long-term OCP monitoring followed by CPP tests. The OCP of the BMD as-sintered, SA and Wr samples was monitored up to 318 hours in a cell filled with an aerated solution of 3.5 wt% of NaCl at room temperature using a Saturated Calomel Electrode (SCE) as reference electrode and by means of an Agilent Data Switching Unit Mod. 34970A equipped with a multiplexer module 34901A. The potential was acquired every 5 minutes considering that in preliminary experiments there were not observed differences for lower acquisition times of 30 seconds and 1-2 minutes. The OCP data were analyzed after 6 hours of delay to ensure steady state conditions and by means of a routine in Visual

Basic (VB) running in Excel to evaluate the susceptibility to localized corrosion of each specimen. The algorithm of the routine determined the negative drops toward more active OCPs, attributed to metastable localized corrosion events, applying a threshold of 10 mV below a baseline, which was calculated from the points where these events were not present. The metastable drop event has been considered finished when the potential reached a value above the 10 mV threshold from the baseline. The area of each drop in the OCP curve was determined by the trapezoidal rule using the experimental points and the baseline. The summations of the areas of each event of potential drop were calculated for each sample and compared among them. The summation of the areas expressed in [V h] represents a quantitative index of the frequency, duration and the magnitude of the drops in potential, thus reflecting the instability of the passive film during the long-term exposure to the electrolyte. Immediately after the long-term OCP monitoring, the CPP tests were performed on the same samples by means of a Gamry Reference 600 in the same 3.5 wt% of NaCl electrolyte of the OCP. The curves were recorded by an electrochemical cell with a three-electrode configuration using a SCE as reference electrode, an activated titanium wire as counter electrode and the samples under investigation as working electrodes. Before starting the CPP, an OCP was recorded to ensure steady state conditions, then the Electrochemical Impedance Spectroscopy was performed in a range of frequency from 100 kHz to 1 Hz to estimate ohmic loss due to testing solution resistance for the correction of the CPP curves. The CPP tests were performed starting from -15 mV below the corrosion potential ($E_{corr)}$ and an increasing potential toward anodic direction was applied by a scan rate of 0.083 mV s^{-1}. The scan was reversed when the current density reached the threshold of 0.1 mA cm^{-2} and the reverse scan was stopped when the current density reached values in the range of the forward passive trait. The corrosion potential (E_{corr}), breakdown potential (E_{br}) and repassivation potential (E_{prot}) were estimated from the CPP curve obtained for each tested sample.

All electrochemical tests were repeated at least twice and the most representative results are reported in the next section.

RESULTS AND DISCUSSIONS

All the samples showed a positive and increasing trend of the OCP curves with many drops in potential. The results of the routine in VB performed on OCP curves are shown in Fig. 1; for the sake of brevity, only those corresponding to as-sintered 45° (Fig. 1a) and SA 45° (Fig. 1b) samples are displayed as representative data. Both BMD and Wr samples were characterized by an increasing trend in number and magnitude of drops in potential approximately after 100 h from the immersion in the electrolyte. Few drops in potential with relatively low magnitude were recorded before 100 h for the Wr and SA samples, if compared to the as-sintered samples, suggesting a more active behavior for the latter since the beginning of the experiment in neutral chlorides environment.

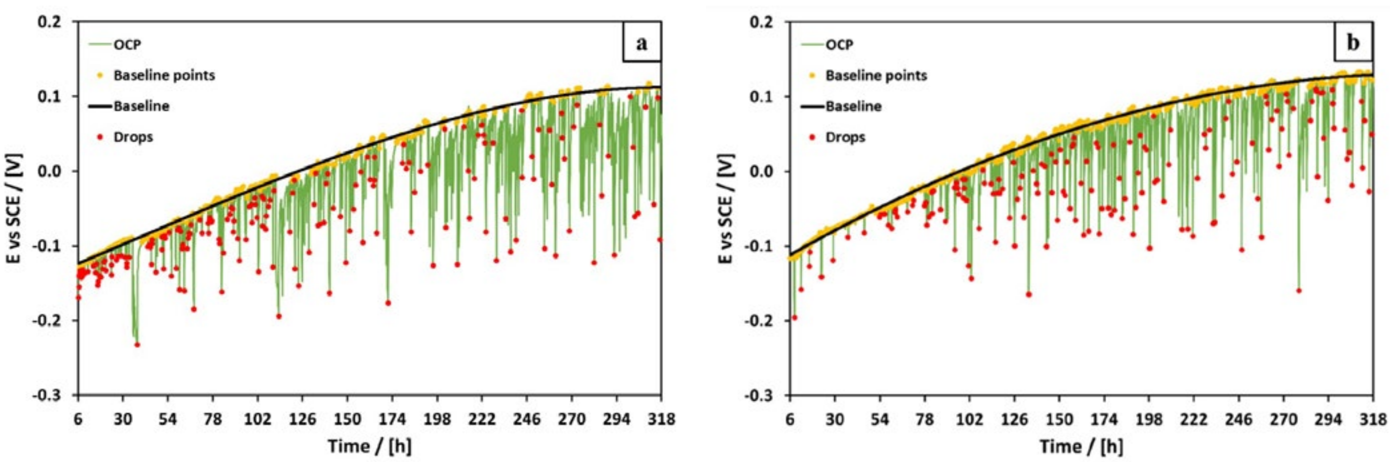

Fig.1 - Results obtained by the routine in VB performed on OCP curves: a) as-sintered 45°; b) SA 45°. / Risultati della routine in VB ottenuta dalle curve OCP: a) as-sintered 45°; b) SA 45°.

The summation of the areas calculated by means of trapezoidal rule and obtained by the routine in VB on OCP curves of the BMD and Wr samples are plotted in Fig. 2. The SA samples exhibited lower values of the area if compared to the as-sintered, thus indicating that the trend of the heat-treated samples was characterized by a less active behavior (less potential drop events and less corresponding areas) in chlorides environment. The SA 0° and SA 45° showed the lowest values of the area among the examined BMD samples and thus they were characterized by a low instability of the passive film, which corresponds to the lowest susceptibility to localized corrosion; in addition, the heat-treatment reduced the area of 30% and 40% compared to 0° and 45° as-sintered samples (Fig. 2), respectively. On the other hand, the area of 90° samples was the highest, indicating the high instability of their passive film. The area was reduced approximately by only 20% after the heat-treatment. These differences among build-up orientations could be explained by the higher amount of porosities formed in 90° samples during the printing process itself, as previously observed [7].

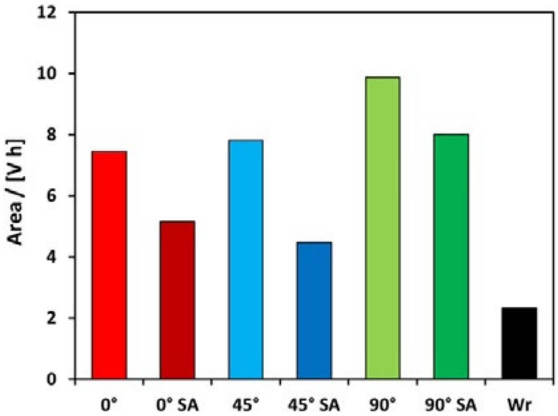

Fig.2 - Total areas calculated by the summation of all OCP drop areas for all tested samples. / Aree totali calcolate dalla sommatoria delle aree di tutte le cadute di OCP per tutti i campioni testati.

The increment in the summation of the areas of the samples is shown in Fig. 3. The trend of these curves confirmed what was observed in Fig. 1, where a rapid increase in the number and/or magnitude of the drops in potential was visible after 100 h of exposure for BMD specimens. The Wr also showed higher number of drops in potential after the same period even though they were of relatively lower areas if compared to the BMD. After 100-200 h of immersion, it can be seen that the slopes of the as sintered (Fig. 3a) samples are higher than the slopes of the SA, and in particular the 0° and 45° of both as sintered and heat-treated samples, which showed lower trends towards active behavior.

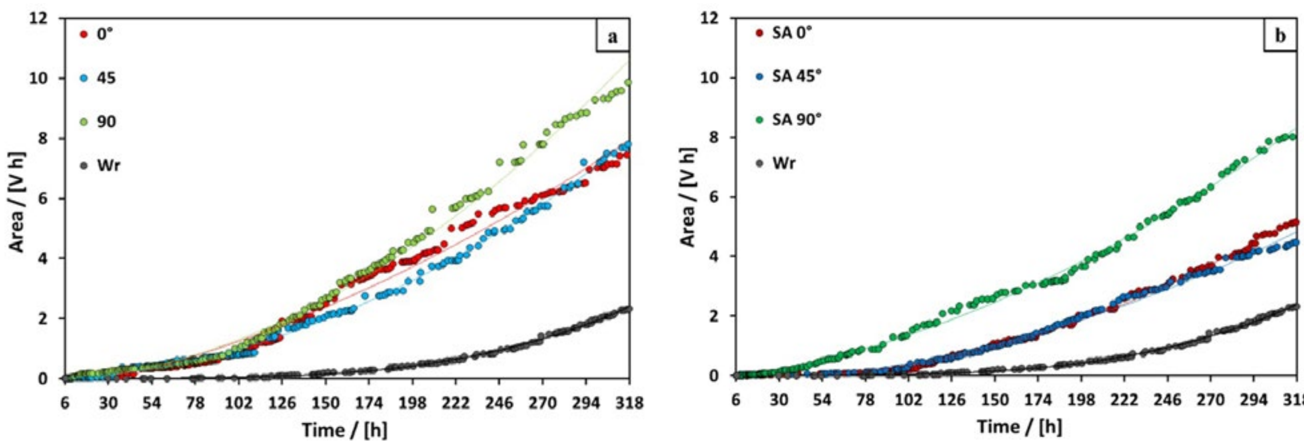

Fig.3 - Comparison of the increment in the summation of the area of each sample: a) as sintered and Wr; b) SA and Wr. / Confronto dell'incremento della sommatoria dell'area dei campioni: a) as sintered e Wr; b) SA e Wr.

In Fig. 4 the CPP curves of the BMD and Wr samples performed after the long-term OCP monitoring are shown. A passive trait of the anodic branch was observed in all the samples and ranged from 10^{-9} to 10^{-8} A cm^{-2}, while it was not showed at all in short-term CPP in neutral NaCl electrolyte performed on the as sintered 0°, 45° and 90° build-up orientations [7]. The E_{br} values for 0°, SA 0° and SA 45° were found higher than that of Wr sample, indicating that the passive film developed on the surfaces of BMD specimens can have even better corrosion resistance properties than those of Wr after long-term exposure, although during the OCP monitoring this traditionally manufactured material showed a more stable passive film, giving the lowest amount of potential drops (Fig. 2 and 3). So far, it can be concluded that the mentioned BMD samples did not show a worse corrosion behaviour compared to Wr sample. The 90° CPP curve (Fig. 4a) exhibited a short anodic passive trait since the E_{br} value was very close to the E_{corr}; moreover, the better passive behavior of SA 90° sample (Fig. 4b) suggested an improvement of the corrosion resistance properties compared to the as-sintered 90° attributed to the heat-treatment, even though the E_{br} value was lower than Wr. The higher values of E_{br} determined for both as-sintered and heat-treated 0° and 45° samples compared to those relative to 90° could be attributed to the presence of more porosities in these last samples. These results agree with the observations reported above on the areas calculated in correspondence of potential drops in OCP curves. None of the CPP curves in Fig. 4 showed a perfect passivity region since E_{prot} was always lower than E_{corr}; however, for 0°, 90°, SA 0° and Wr samples the E_{prot} ranged from -50 to -200 mV, which are values above or close to the corrosion potential measured at the start of the long-term OCP monitoring, suggesting that afterwards the CPP those surfaces may be able to repassivate.

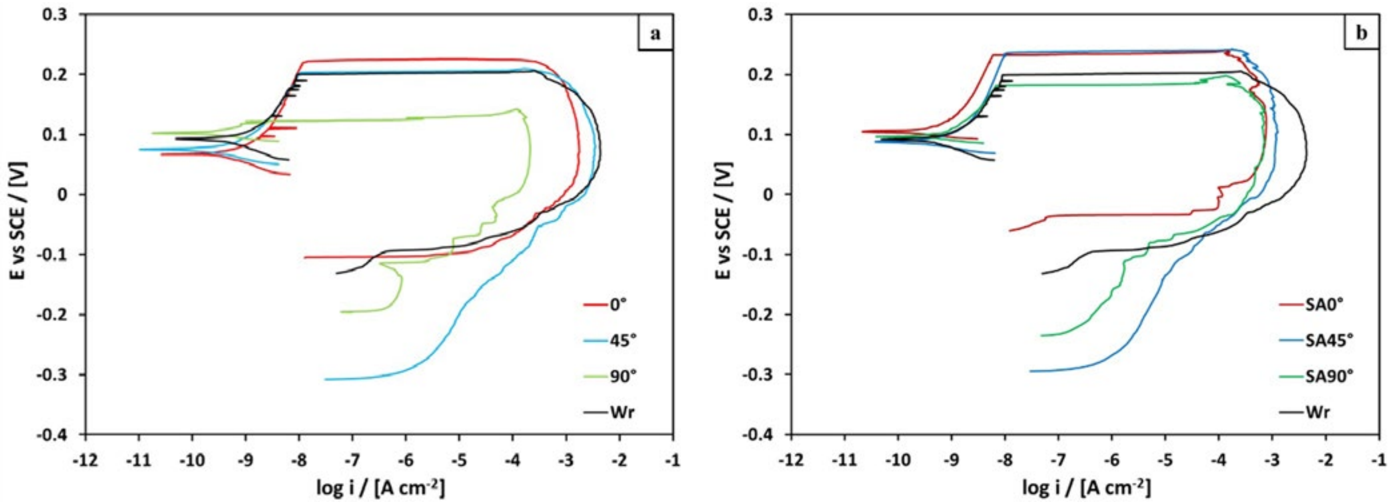

Fig.4 - Comparison of the CPP curves following the OCP of each sample: a) as sintered and Wr; b) SA and Wr. / Confronto delle curve CPP eseguite dopo l'OCP dei campioni: a) as sintered e Wr; b) SA e Wr.

CONCLUSIONS

In this work, the corrosion resistance properties of 17-4PH samples printed with different build-up orientations by Bound Metal Deposition technique in as-sintered and heat-treated (H900) conditions has been investigated by means of long-term Open Circuit Potential monitoring evaluated by a routine in Visual Basic; afterwards Cyclic Potentiodynamic Polarization curves were recorded in the same neutral sodium chloride electrolyte. The results of this investigation showed that the heat-treatment decreased the localized corrosion susceptibility for each build-up orientation and in particular for the 0° and 45°. The evaluation of drops in potential also indicated a higher tendency towards activation for the printed samples, thus the passive film in both as sintered and heat-treated conditions could be more unstable than a wrought 17-4 PH. Furthermore, the anodic polarization recorded after the long-term exposure in the NaCl solution confirmed that passivating properties were most likely well developed by the surface of each printed sample and that under steady state conditions the corrosion resistance properties can be even higher than wrought 17-4 PH; nevertheless, the breakdown potential of the 90° as sintered was significantly lower than the others.

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Studio della resistenza a corrosione di campioni sinterizzati e trattati termicamente di acciaio inossidabile 17-4 PH ottenuti per Bound Metal Deposition™

In questo lavoro sono state studiate le proprietà di resistenza a corrosione in soluzione neutra di cloruri di campioni in acciaio inossidabile 17-4 PH stampati con tecnologia Bound Metal Deposition™ (BMD) mediante tecnica di monitoraggio del potenziale a circuito aperto, seguita dalla registrazione di curve potenziodinamiche cicliche per lunghi tempi di immersione nell'elettrolita. Le indagini elettrochimiche sono state effettuate su campioni di 17 4-PH ottenuti sia con tecnologie convenzionali che BMD as-sintered e trattati termicamente H900. I campioni BMD avevano diverse orientazioni di crescita rispetto al piano di stampa. I risultati hanno evidenziato che la suscettibilità a corrosione localizzata è più elevata nei campioni BMD rispetto a quelli forgiati con tecniche di metallurgia convenzionali, sebbene in alcuni campioni dei primi è stato misurato un potenziale di breakdown nelle curve anodiche più elevato che nei secondi. Il miglior comportamento a corrosione dei campioni BMD è stato riscontrato nei campioni trattati termicamente e in particolare per quelli con orientazione di stampa di 0° e 45°.

PAROLE CHIAVE: 17-4 PH, BOUND METAL DEPOSITION, AS-SINTERED, INDURIMENTO PER PRECIPITAZIONE, ORIENTAZIONI DI CRESCITA, POTENZIALE DI CIRCUITO APERTO, POLARIZZAZIONI POTENZIODINAMICHE CICLICHE

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