Investigating the Effect of Energy Density on Corrosion Susceptibility of Additively Manufactured Thin-walled Cobalt Chrome Alloy

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Abstract
Metal additive manufacturing is an innovative technology based on fabricating near-net shaped metallic components from a digital model in a layer-by-layer manner. Although, it has many advantages over conventional subtractive methods, understanding the correlation between process parameters and properties of additively manufactured alloys is key to producing components with optimal performance. Hence, in this study corrosion susceptibility of laser powder bed fusion additively manufactured cobalt chromium alloy (CoCr) alloy produced with three different energy densities (0.58 J/m, 0.87 J/m, 2.26 J/m) was investigated. Some of the CoCr alloys produced were subjected to post-build heat treatment by hot isostatic pressing (HIP). Corrosion resistance of both as-built and HIP CoCr alloys in 0.5 M H_2SO_4 solution at room temperature was investigated using gravimetric method. The results indicated that additively manufactured (AM) CoCr alloy produced with energy density of 0.58 J/m and 2.26 J/m respectively were less susceptible to corrosion compared to that produced with energy density of 0.87 J/m which is the standard energy density recommended by the Original Equipment Manufacturer (OEM). This result was consistent with the trend observed in previously reported mechanical properties of the AM CoCr alloys.

Keywords: CoCr alloy, additive manufacturing, Corrosion, energy destiny, Hot Isostatic Pressing

1.0 INTRODUCTION

Cobalt-chrome (CoCr), an alloy of cobalt and chromium, is widely applied in the biomedical industry due to its excellent resistance to corrosion. Its high resistance to dissolution is attributed to its surface oxide, composed of mostly Cr_2O_3, and minor amounts of cobalt and other metallic oxides (Hyslop et.al., 2010, Lysaght and Webster, 2011). Besides, its high resistance to corrosion, CoCr alloys have good biocompatibility and excellent mechanical properties, similar to that of stainless steel. Its excellent mechanical properties originate from its multiphase structure and precipitation of carbides, resulting in significant increase in the hardness of the alloy (Klastrom et.al., 2018, Hong and Yeoh, 2020). Its excellent mechanical properties, high specific weight and oxidation resistance also make CoCr alloys candidate materials in the aerospace industry for aircraft components such as jet engine vanes, exhaust nozzles and gas turbines (Blakey-Milher et. al., 2021 and Ciobota et. al., 2019). In recent times, additive manufacturing of these alloys has been widely reported.

Additive manufacturing (AM), the layer by layer joining of materials to make end-usable products, offers the platform for swift production of complex, tailored structural materials and components. In contrast to conventional manufacturing techniques like machining and stamping which fabricates products by removing materials from the larger stock metal. AM produces components by the addition of materials with minimum amount of waste generated. Metal additive manufacturing has revolutionized how metallic components are designed and manufactured (Blakey-Milher et. al., 2021, Ciobota et. al., 2019 and DebRoy et. al., 2016). In recent times, there has been considerable research interest in powder based additive manufacturing systems based on electron and laser beam sources to produce metallic components. For laser powder bed fusion AM, characterized by rapid melting and cooling rates, process parameters such as laser power (heat input), scanning velocity, hatch distance, and layer thickness, (Gu et. al., 2012) dictates the microstructure of the alloy produced, which

in turn determines its corrosion resistance and mechanical properties. Amongst these process parameters, the combined influence of laser power and scanning speed, otherwise known as linear energy density, is well known to influence the quality of metal components produced in terms of porosity content and other densification related defects etc.

CoCr alloys find application in aerospace industries where fully dense components are critical for performance and safety. In aircraft engines, combustion of aviation fuel produces sulphur dioxide (SO_2) gas which is further oxidized to sulphur trioxide (SO_3) and later forms sulphuric acid vapor on reacting with moisture. Acid vapor is further converted to acidic solution when operating temperatures are favorable for condensation and low temperature corrosion becomes a challenge (Seljak et. al., 2016, Woodyard, 2009). Corrosion is also a challenge for CoCr alloys in biomedical applications, however, this has been the subject of much research (Singh et. al., 2024, Fay, 2021, Hong and Yeoh, 2020) whilst corrosion of CoCr alloys in other aggressive environments such as sulphuric acid is scarcely reported. Hence, this study, which is a continuation of previous investigations by the first author (Osoba et. al., 2018; Osoba and Ojo, 2020), is aimed at evaluating the influence of linear energy density on corrosion susceptibility of additively manufactured (AM) CoCr alloy in sulphuric acid solution.

2.0 MATERIALS AND METHOD

2.1 Materials and Charcterisation

Cobalt chrome alloy powder used in this study were as supplied to Precision ADM, Canada by the Original Equipment Manufacturer (OEM) with proprietary parameters information. Details of CoCr coupon production by laser powder bed fusion AM process have been reported in previous studies (Osoba et. al., 2018, Osoba and Ojo, 2020). In summary, the coupons were produced in three categories: (i) coupons produced using the manufacturers' recommended energy density parameters (designated as RED), (ii) coupons produced with lower energy density than that recommended by the manufacturer (designated as LED) and (iii) coupons produced using higher energy density than that recommended by the manufacturer (designated as HED). The production parameters were Scan power = 170 - 220 Watts, Scan speed: 400 -1200 mm/s, Energy densities were 0.58 J/m for LED, 0.87 J/m for RED, 2.26 J/m for HED. The thickness of the coupons was 7.62 x 10^{-4} m. The as-built samples were produced in duplicates, one set of as-built coupons from the three categories described above was subjected to hot isostatic pressing (HIP). Both as-built and HIP CoCr alloy samples were characterised using optical and scanning electron microscopes.

2.2. Corrosion susceptibility evaluation

Corrosion susceptibility of CoCr alloys in this study was investigated using gravimetric method. The coupons (as-built and HIP) were immersed in 0.5 M H_2SO_4 solution as schematically shown in Figure 1. The volume of H_2SO_4 solution used for the immersion test was 250 ml. The dimensions of all the test coupons were 100 mm x 50 mm x 0.762mm. Only selected coupons from the total production given in our precious studies (Osoba et. al., 2018, Osoba and Ojo, 2020) was investigated. Weight loss was recorded at an interval of 3-5 days for 45 days. For each weight loss measurement, the coupons were washed in water when brought out of the acid solution and examined for signs of corrosion and weighed. The measured weight loss was employed to calculate the corrosion rate as given in Equation 1.

$$Corrosion\ rate = \frac{K\Delta w}{D.A.T} \qquad Equ.1$$

Where w = weight loss (mg), D = density (g/cm^3), A = Exposed specimen area (cm^2),
T = Exposure time (hrs.) K is the conversion factor, and it is equal to 87.6 for mm/yr.

Pontentiodynamic polarisation was conducted on LED AM CoCr samples only to verify a part of the immersion test result. Other samples were not tested because the thickness of the samples was too thin for electrical connection. The electrochemical test was conducted using a conventional three electrode system consisting of the AM CoCr samples as the working electrodes, a graphite rod counter electrode, and a saturated calomel electrode (SCE) reference electrode. The working electrodes consisted of the AM CoCr samples embedded in epoxy resin with an exposed area of about 0.5 cm^2. The working electrode was immersed in the acidic solution for one hour after which open circuit potential (OCP) was measured and potentiodynamic polarisation scan was conducted from -0.5 V vs OCP to 1.8 V vs SCE at scan rate of 1 mV/s. A Gamry 1000E potentiostat was used for the electrochemical test.

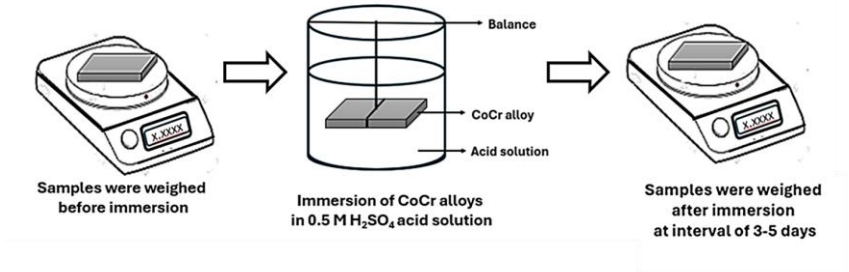

Figure 1: Schematic representation of the gravimetric method used to evaluate corrosion resistance in this study.

3.0 RESULTS AND DISCUSSION

Figure 2 presents the microstructures of as-built and HIP CoCr alloys produced in LED, RED and HED conditions. The SEM images of the samples revealed cellular dendritic solidification profile in the as-built conditions (Figure. 2(a) –(c)) typical of alloys produced by LBPF AM (Fay, 2021, Liu et al., 2023). When the samples were subjected to HIP the dendrites disappeared, and homogenized microstructures were observed (Fig. 2(d)-(f)). The optical images of the samples shown in the inset of the SEM images in Figure 2 showed that pores were observed in the CoCr alloy samples irrespective of the energy density. Other defects which ranged from porosity to partially melted powder was reported for all samples irrespective of the energy densities in previous publications (Osoba et. al. 2018 and Osoba and Ojo, 2020). Defects in LPBF produced AM alloys are generally attributed to unstable melt pool (keyhole) formation, causing the melt pool to collapse in, and resulting in pores of inert gas or voids (Gu et. al. 2012). The homogenized microstructure of the HIP CoCr alloys indicate that the simultaneous application of heat and pressure (HIP) reduces significantly the defects observed in the as-built samples. In the HIP process, components are subjected to high temperatures and isostatic gas pressure in a high-pressure containment vessel between 50.7 MPa and 310 MPa. During this process, surface oxidation of the metal is prevented by using an inert gas at high pressure is applied to the metal from all directions (isostatic). During HIP processing, soaking temperature ranges from 482 °C to 1,320 °C depending on the type of metallic alloy. The HIP process often reduces defects such as internal voids and micro-porosity through a combination of plastic deformation, creep and diffusion bonding resulting in improved mechanical properties and workability (Atkinson and Davies, 2000, Loh et. al., 1992).

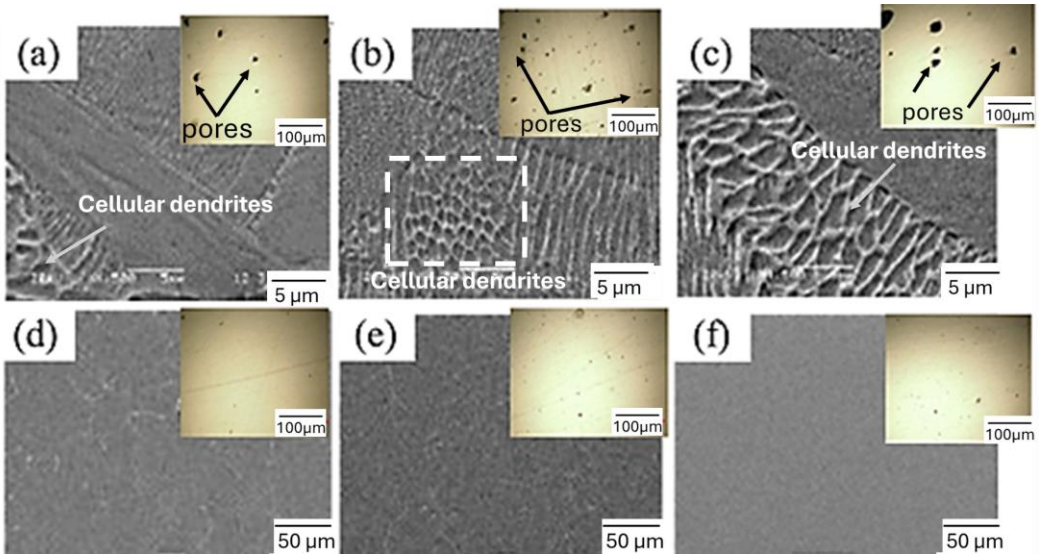

Figure 2: SEM images of CoCr alloy in As-built (a - c) and HIP coupons (d-f) at different energy densities LED (a, d), RED (b, e) and HED (c, f). Inset: optical images of as polished CoCr alloy samples

Figure 3 presents the corrosion rate of as-built and HIP CoCr alloys produced with variable energy densities in 0.5 M H_2SO_4 solution. Comparing the as-built samples, RED samples exhibited the lowest susceptibility to corrosion. However, when it was subjected to HIP, it exhibited the highest susceptibility to corrosion. Hence, based on energy densities, in the as-built condition corrosion susceptibility can be ranked as LED > HED > RED while in the HIP condition it is ranked as RED > HED > LED. In the LED condition, subjecting the samples to HIP reduced the susceptibility of the samples to corrosion. To further confirm this result, the LED samples were subjected to pontentiodynamic polarisation, and the result is shown in Figure 4. From the analysis of the result presented in Table 1, it was observed that HIP process reduced the corrosion suspectibility of LED as-built samples evidenced by its much lower corrosion current density(i_{corr}) and passive current density (i_{pass}) value compared to that of the as-built LED. Passive current density (i_{pass}) is a measure of dissolution within the passive film, hence, lower i_{pass} values indicates a more protective passive film with reduced dissolution within the passive film (Wood and Wharton, 2011). It is well known that HIP treatment results in homogenisation of as-built microstructure , in addition to reducing porosity, (as seen in Figure. 2) thereby reducing microsegregation typically associated with AM alloys. In AM CoCr based alloy, studies (Fay, 2021, Liu et al., 2023) have shown that Cr , the main element needed for passivation, segregates at the dendrites boundaries. When these alloys are subjected to HIP treament the dendrites diasppear (as seen in Figure. 2 (d-f)) and Cr is readily avaliable on the surface to improve passivation. Similar improvement in passivation after HIP as been reported by Fay (2021) and Wang et. al. (2023). Hence,the reduction in the susceptibility of LED CoCr alloy to corrosion in the HIP condition is attributed to the formation of a more protective passive film than that formed in the as-built LED.

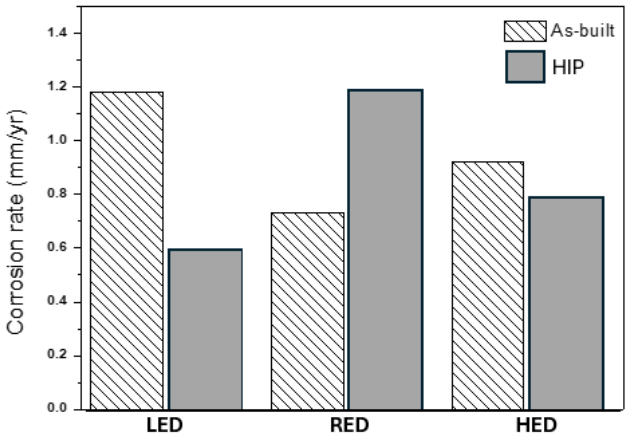

Figure 3: Corrosion rate of CoCr samples immersed in 0.5 M H_2O_4 solution for 45 days

For the HED samples HIP had negligible influence on the corrosion rate of the as-built HED samples. In our previous study (Osoba and Ojo, 2020) , it was reported that surface roughness was considerably high for HED both in the as-built and HIP conditions. A rough surface is known to be prone to corrosion. Also, grain size of as-built HED was increased compared to that of LED and RED. The grain size coupled with the rough morphology accounts for the insignificant effect of HIP on the susceptibility of the as-built HED samples. On the other hand, HIP did not reduce susceptibility of RED samples to corrosion rather its increased it. Further charcaterisation to ascertain the reason for the poor corrosion performance of RED samples subjected to the HIP process would be necessary. As HIP is known to reduce the defects such as pores and cracks, which should invariably lead to improvement in its resistance to corrosion.

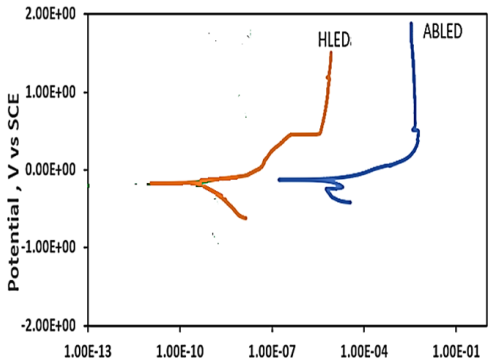

Figure 4: Potentiodynamic polarisation of AM CoCr alloys in 0.5M H_2SO_4 solution at a scanning speed of 1mV/s. HLED- HIP LED, ABLED – as-built LED

Table 1: Corrosion parameters obtained from the pontentiodynamic plot of AM CoCr alloys in 0.5M H_2SO_4 solution

Specimen	Energy Density (Ws/m)	Corrosion rate (mm/year) (Immersion test)	Corrosion potential, E_{corr} (V)	Corrosion current density, i_{corr} (μA/cm^2)	Passive current density, i_p (A/cm^2)
ABLED	0.58	1.180	-0.127	10.98	≈ 10^{-4}
HLED	0.58	0.590	-0.197	0.01	≈ 10^{-6}

4. CONCLUSION

The susceptibility of CoCr alloy produced with different energy densities (LED, RED , HED) to corrosion was investigated before and after subjecting the samples to hot isostatic pressing (HIP). The results showed that :

1. In the As-built condition samples produced with RED was most resistant to corrosion compared to LED and HED. Subjecting RED to HIP, however, worsened the corrosion resistance.
2. In the HIP condition, samples produced with LED exhibited the most significant improvement in corrosion rate. HED samples also showed improvement in corrosion resistance, but it was insignificant, this observation was attributed to its rough morphology n the as-built and HIP conditions.
3. The trend of LED and HED exhibiting better corrosion properties in the as-built and HIP conditions than RED was also the observed trend for mechanical properties reported for the same alloy in an earlier publication.

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