Effect of energy density on corrosion susceptibility of additive manufactured thin-walled cobalt chrome alloy

L.O. Osoba[1], A.M. Oladoye[1], C.O Folorunsho[2], Y.O Abiodun[3] and B.O. Alenkhe[1]
[1]Department of Metallurgical & Materials Engineering, University of Lagos, Nigeria
[2]Department of Systems Engineering, University of Lagos, Nigeria
[3]Department of Civil Engineering, University of Lagos, Nigeria
Email: *losoba@unilag.edu.ng*

Abstract
Metal additive manufacturing is an innovative technology based on fabricating three dimensional metallic objects from a digital model in a layer-by-layer manner. Although, it has many advantages over conventional subtractive methods, there are still major challenges to be addressed. Hence in this study the effect of energy density on the corrosion susceptibility of Laser Powder Bed Fusion (PBF) additively manufactured cobalt chromium alloy (CoCr) alloy was investigated. The alloy was also 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 of the gravimetric test indicated that the CoCr alloy produced with high and low heat energy density coupons in the as Built and HIP conditions were less susceptible to corrosion compared to the standard energy density coupons recommended by the Original Equipment Manufacturer (RED). This result was consistent with the trend observed in previously reported mechanical properties evaluation of the CoCr AM alloy.

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 resulting from its surface oxide, which is 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 good mechanical properties result from its multiphase structure and precipitation of carbides, which increase the hardness of the alloy significantly (Klastron et.al., 2018; Hong and Yeoh, 2020; Sims et. al.,1987). Its excellent mechanical properties, high specific weight and oxidation resistance also make CoCr alloys are also candidate materials in the aerospace industry for jet engine vanes, fuel nozzles and gas turbines (Blakey-Milher et. al., 2021; 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; Huang et. al., 2013). Recently, there has been considerable research interest in powder based additive manufacturing systems based on electron and laser beam sources to produce metallic components and parts. For laser powder bed fusion, process variables include laser power (heat input), scanning velocity, hatch distance, and layer thickness (Gu et. al., 2012). These process variable dictates

the microstructure of the alloy produced, which in turn determines its corrosion resistance. While the application of AM technology is gaining wide acceptance and commercialization, corrosion resistance of these AM CoCr alloys in non-biological electrolytes is scarcely reported. Hence in this study, which is a continuation of two other reported investigations by the first author (Osoba et. al.,2018; Osoba and Ojo, 2020), is aimed at evaluating the corrosion susceptibility of the additively manufactured (AM) CoCr alloy coupons in sulphuric acid solution.

2.0 MATERIALS AND METHOD

2.1 *Materials and Charcterisation.*

Cobalt chrome alloy coupons used in this study were produced by Laser metal powder bed fusion process from cobalt-chromium (Co-Cr) powder with proprietary chemical composition sourced from Original Equipment Manufacturer (OEM). Details of the production process have been reported in our previous studies (Osoba et. al.,2018; Osoba and Ojo, 2020). In summary, the CoCr alloy coupons produced were in three categories: coupons produced using the manufacturers' recommended energy density parameters (designated as RED), coupons produced with lower energy density than that recommended by the manufacturer (designated as LED) and 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 P/V for LED, 0.87 P/V for RED, 2.26 P/V for HED. The thickness of the coupons was 7.62×10^{-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 dimensions of all the test coupons were of equal length and breadth. 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 intervals 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.

$$\text{Corrosion Rate} = K \Delta w / D.A.T \qquad \text{Eq. (1)}$$

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.

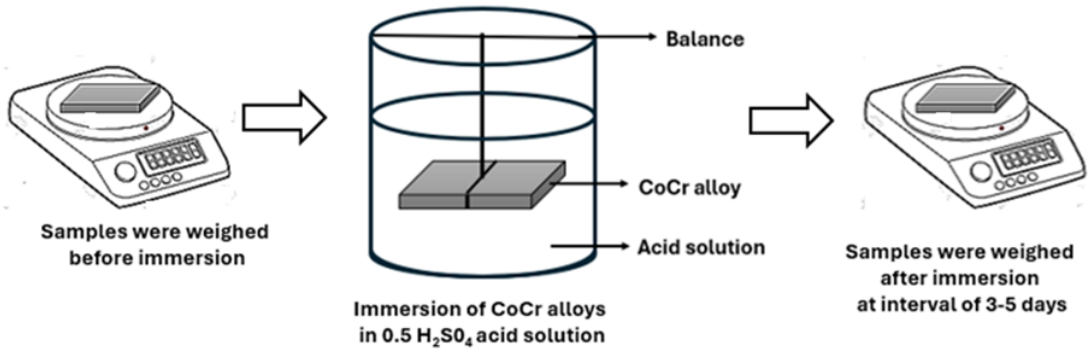


Figure 1: Schematic representation of the gravimetric method used to evaluate corrosion resistance in this study

Pontentiodynamic polarisation was conducted on selected AM CoCr samples to verify a part of the immersion test result. All samples were not subjected to electrochemical test because the sample thickness 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 was measured and potentiodynamic polarisation scan was conducted from -0.5 V vs open circuit potential (OCP) to 1.5 V vs SCE at scan rate of 1 mV/s. A Gamry 1000E potentiostat was used for the electrochemical test.

3.0 RESULTS AND DISCUSSION

Figure 2 presents the microstructures of As-built and HIP CoCr alloys produced in LED, RED and HED conditions. It can be observed that the SEM images and the optical images in the inset of the samples revealed dendritic solidification profile in the As-built conditions. When the samples were subjected to HIP the dendrites disappeared, and smooth morphologies was observed. Defects ranging from porosity to incompletely un-melted powder were observed in all coupons (LED, RED and HED), irrespective of the energy density process employed in the production process.

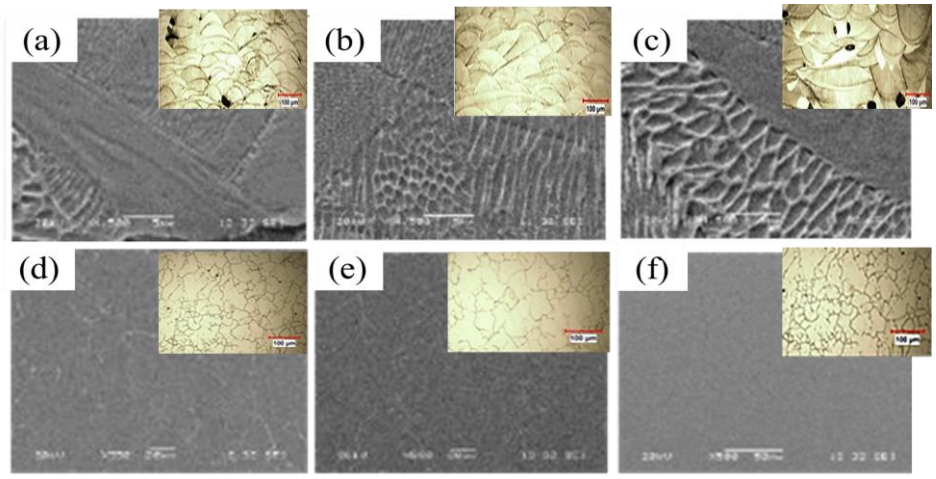


Figure 2: SEM images of CoCr alloy in As-built and HIP coupons at different energy densities LED (a, d), RED (b, e) and HED (c, f). Inset: optical images of the microstructure.

This observation has been 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). CoCr samples subjected to HIP, however, exhibited a smooth morphology indicating 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 temperatures range 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 3 presents the corrosion rate of As-built and HIP CoCr alloys produced with variable energy densities in 0.5M 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 samples were subjected to pontentiodynamic polarisation, and the result is shown in Figure 4. From the analysis of the pontentiodynamic polarisation result presented in Table 1, it is obvious that the HIP process reduced the corrosion rate of LED as-built samples. The reduction in the susceptibility of LED CoCr alloy to corrosion in the HIP may be attributed to the formation of a more protective passive film as can be seen in the passive current density of the latter in Table 1. The passive current density (ip) is a measure of dissolution within the passive film, hence, lower ip values means a more protective passive film with reduced dissolution within the passive film (Wood and Wharton, 2011).

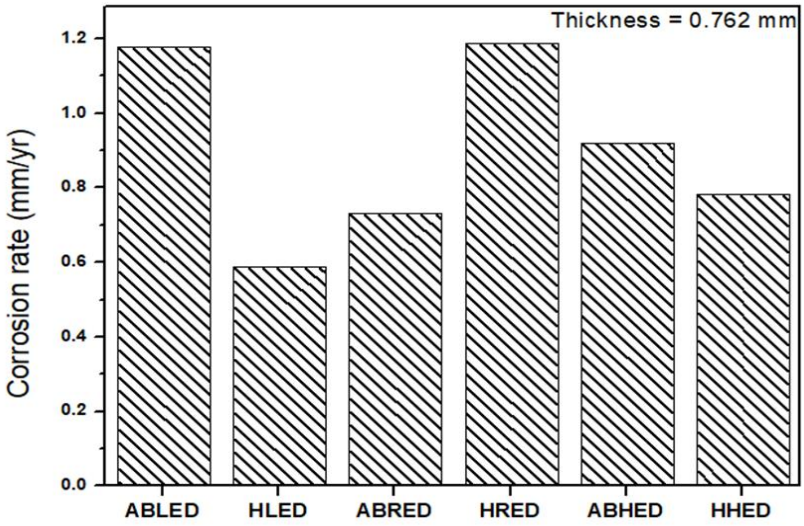


Figure 3: Corrosion rate of CoCr samples immersed in 0.5 H_2O_4 solution for 45 days (*AB for As-built, H for HIP)

For the HED conditions, HIP had negligible influence on the corrosion resistance 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 or 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 samples. On the other hand, HIP

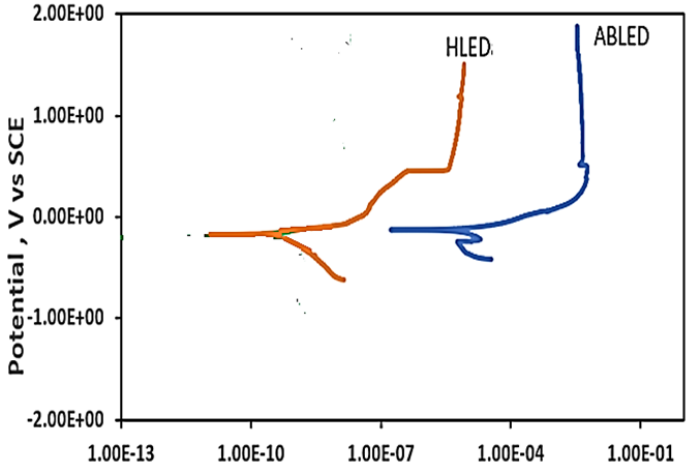


Figure 4: Potentiodynamic polarisation of AM CoCr alloys in 0.5M H_2SO_4 at a scanning speed of 1mV/s.

did not reduce the susceptibility of RED samples to corrosion rather its increased it. There may be need for further charcterisation to ascertain the reason for this. As HIP was reported to reduce the defects, which should invariably lead to improvement in its resistance to corrosion.

Table 2: 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} (A/cm^2)	Passive current density, i_p (A/cm^2)
ABLED	0.58	1.180	-0.127	1.098×10^{-5}	$\approx 10^{-4}$
HLED	0.58	0.590	-0.197	1.281×10^{-8}	$\approx 10^{-6}$

4. CONCLUSION

The susceptibility of CoCr alloy produced with different energy densities (LED (0.58 Ws/m), RED (0.87 Ws/m), HED (2.26 Ws/m) 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 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 in the as-built and HIP conditions.

(3) The findings in this study were consistent with that repoerted earlier for mechanical properties

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