

Corrosion Characterization and Performance Evaluation of Co-Cr alloys by Laser Powder Bed Fusion and Suitability of their use for Pressure Containing Down-hole Wear Components

Krutibas Panda
Halliburton Energy Services
3000 N. Sam Houston Pkwy. E.
Houston, Texas 77032
USA

Brendan Voglewede
Halliburton Energy Services
3000 N. Sam Houston Pkwy. E.
Houston, Texas 77032
USA

Reece Goldsberry
Halliburton Energy Services
3000 N. Sam Houston Pkwy. E.
Houston, Texas 77032
USA

ABSTRACT

Tungsten containing Cobalt based alloys (Co-Cr-W-C) possess an attractive combination of corrosion resistance, erosion resistance and heat resistance properties. This property combination coupled with their low magnetic permeability values make them suitable for many flow components in the measurement and logging while drilling (M/LWD) systems in the oil and gas industry. However, flow components manufactured from investment cast Stellite 6 alloy (Co-Cr-W-C) have shown that they are susceptible to cracking under operating conditions due to the brittleness of the material and the complex geometry of these parts. One possible solution was to produce the same part through additive manufacturing (AM) with a Co-Cr-Mo-C system which exhibits significant ductility enhancement compared to cast Stellite 6. The current study evaluated parts fabricated using a laser powder bed fusion additive manufacturing using a Cobalt 28 (Co-Cr-Mo-C) alloy. These AM parts, when put under pressure, led to a loss of pressure/failure of the component because of a network of interconnected pores. Microstructural evolution and defect density of these AM parts are characterized in this study. The role of chemistry in the microstructure has been studied using energy dispersive spectroscopy mapping and porosity quantification is studied using computed tomography scanning. The difference in the wear behaviors of these two families are characterized using low-high angle dry erosion tests. Comparison of their corrosion performance was performed by exposing them to alkaline brines with high concentration of chlorides typically seen in the drilling environment. The corrosion properties were studied using electrochemical methods such as open circuit potential, linear polarization resistance, and cyclic potentiodynamic polarization along with high temperature immersion testing. Optical microscopy techniques were further utilized to characterize the microstructures of the samples pre/post corrosion testing to further assess the role of microstructural defects on corrosion rate of the AM parts compared to investment cast Stellite 6 parts.

Key words: Cobalt based alloys, Additive manufacturing, Laser powder bed fusion

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INTRODUCTION

Cobalt (Co) - Chromium (Cr) based alloys are known for exhibiting a superior combination of corrosion resistance, erosion resistance, galling resistance, and high temperature strength.¹⁻⁴ They have found a wide variety of applications in automotive, aerospace, chemical and biomedical applications. They are frequently known as the Stellite[†] grade of families (ex: Stellite[†] 1, Stellite[†] 6, Stellite[†] 12, Stellite[†] 21, etc.) and are broadly classified into the Co-Cr-Mo-C and the Co-Cr-W-C systems.⁵⁻⁶ The relatively high Carbon (C) and Tungsten (W) containing (Co-Cr) alloys are mostly used for their high wear properties.⁶⁻⁷ This attractive wear properties when combined with their non-magnetic behavior makes them suitable for a variety of flow components in the oil & gas industry. Hence, Stellite 6 is commonly employed as a wear resistant material for a variety of components such as flow manifolds, flow diverters and erosion sleeves.

Both these alloy families derive their hardness and wear properties from the carbide precipitates in their microstructure. Carbon content and the carbide forming elements in these alloys drive the type and morphology of these carbides. The low C-containing Co-Cr-Mo-C alloys have sparsely distributed M_6C , $M_{23}C_6$ type of carbides in a σ -phase while increasing the C-content will result in greater precipitation of these carbides in the Co-Cr-W-C family.⁶⁻⁷ These grades exhibit a range of hardness from the low 30 HRC to all the way to 60 HRC.⁶ The microstructure is more akin to a composite material with fine and uniformly distributed very hard carbides in a ductile Co-Cr matrix. This gives these family of materials the beneficial wear performance for their use in adhesive, abrasive as well as erosive applications. The Co-Cr matrix provides the additional benefits of corrosion performance against a broad range of drilling fluids.

A wide variety of processing routes are employed to manufacture these alloys including castings (sand casting, investment casting), powder metallurgy as well as metal forming.⁸⁻¹² These are also available as hard facing wire/rod shapes to be applied using conventional welding technique or in the powder form to be deposited by plasma transfer arc (PTA) as well as laser applied process of hard facing for high wear situations.¹³⁻¹⁸

The superior wear resistant Co-Cr-W-C grades, however, suffer from much lower ductility, especially in the casting and hard facing applications. This trendline continues as we move towards the higher hardness grades within this family of alloys (Stellite[†] 1, Stellite[†] 12, Stellite[†] 190 etc.). In applications involving aggressive down-hole conditions there has been known cracking issues with the Stellite[†] 6 grades. Much of that issue come from the ductility / toughness limitations these grades exhibit. Using wrought form (Stellite[†] 6B) as well as powder metallurgy-based hot isostatically pressed (HIP)-consolidated processing techniques, Stellite[†] 6 ductility behavior can be improved significantly. However, for many components, there are size limitations in applying these aforementioned techniques. In addition, those processing routes are significantly more expensive and don't lend themselves to many of the complex components used in down-hole applications.

Recent advances in additive manufacturing (AM) have successfully demonstrated the use AM techniques to both Cr-Co-alloy families. Most of the fusion based techniques using Co-Cr-Mo-C alloys, such as selective laser sintering (SLS), selective laser melting (SLM), electron beam melting (EBM) as well as binderjet processing has been quite widely used in the biomedical applications.¹⁹⁻²³ The fusion based techniques are currently not applied to the Co-Cr-W-C grades because of their susceptibility to cracking. These grades primarily utilize binderjet process to fabricate the structure in the green stage that is subsequently sintered.²⁴

In contrast to legacy manufacturing techniques, the AM processes are known to address complex geometries quite well. Most down-hole flow components such as flow manifolds are typically quite complex, hence AM techniques provide an interesting opportunity to address the limitation of the Co-Cr-W-C family by moving to the fusion based AM processes in the Co-Cr-Mo-C family. Careful control of

[†]Trade Name

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material (powder size, chemistry), the processing parameters (laser powder, layer thickness, scan patterns etc.) and post weld treatment could yield material properties that will have equivalent corrosion resistant, wear resistant properties while exhibiting similar or better mechanical properties compared to the Co-Cr-W-C families.

EXPERIMENTAL PROCEDURE

Material

The Stellite[†] 6 (Co-Cr-W-C) flow diverters and test specimens were investment casted and subsequently HIPed. The HIP treatment was performed at $2,125^{\circ} \pm 25^{\circ}$ F and $15,000 \pm 500$ psi for 3-4 hours. The AM Cobalt 28 (Co-Cr-Mo-C) flow diverters and test coupons were processed using a powder bed fusion (PBF) technique. A multi-laser AM system was used to print the Cobalt 28 flow diverters and test samples. The component as well as the test specimens were printed in the Z direction. The AM part along with the test samples were further HIP treated using the same vendor and with the same process parameters. The chemical composition of the Co-Cr-W-C was as per AMS 5387²⁵ while the powder chemistry of the Cobalt 28 was as per ASTM F75 / ASTM F3213^{26,27}. Chemical composition of test samples was determined by using an optical emission spectroscopy (OES), X-ray fluorescence (XRF) and inductively coupled plasma – mass spectrometry (ICP-MS). The porosity and density of the materials were determined from the test coupons produced simultaneously with the flow diverters. Porosity of both Co-Cr-W-C and Co-Cr-Mo-C were determined by examining at the cross section of test coupons, after polishing to $1\mu\text{m}$ surface finish, at high magnification. Table 1 and 2 include both the allowable range and the actual chemistry of the cast specimen and the powder chemistry of the Co-Cr-W-C and Co-Cr-Mo-C samples, respectively.

Table 1. Chemical composition of cast Stellite[†] 6 (wt.%)

Sample ID	Carbon (C)	Chrome (Cr)	Nickel (Ni)	Iron (Fe)	Tungsten (W)	Molybdenum (Mo)	Silicon (Si)	Cobalt (Co)
Co-Cr-W-C AMS 5387	0.9 – 1.4	27 -31	3.0 (Max)	3.0 (Max)	3.5 – 5.5	1.5 (Max)	1.5 (Max)	Bal.
Actual	1.18	29.96	2.68	2.60	4.73	0.10	0.89	Bal.

Table 2. Chemical composition of AM Cobalt 28 (wt.%)

Sample ID	Carbon (C)	Chrome (Cr)	Nickel (Ni)	Iron (Fe)	Manganese	Molybdenum (Mo)	Silicon (Si)	Cobalt (Co)
Co-Cr-Mo-C ASTM F 75/F 3213	0.35 (Max)	27 - 30	0.5 (Max)	0.75 (Max)	1.00 (Max)	5 - 7	1.0 (Max)	Bal.
Actual	0.09	28.23	0.19	0.36	0.19	5.76	0.26	Bal.

Wear Testing

The wear response of these two grades was characterized using low - high angle dry erosion testing following ASTM G76.²⁸ Erosion testing was performed with an apparatus consisting of a compressed air prime mover, precision powder feeder, gas pressure and velocity meters, containment chamber, and sample fixturing. The test set-up is shown in Figure 1. Testing was done on cast Co-Cr-W-C samples and the AM Co-Cr-W-C test sample. Dry erosion testing was done at three different angles: 30°, 45°, and 60°. Two tests were carried out for each of these angles at two randomly selected areas. The abrasive medium used was Reade[†] Advance Materials F-75 unground SiO₂. The mean particle size was 100 mesh or approximately 150 microns diameter. The erodent particle velocity was averaged at 339.9 ft/sec. The duration of erodent delivery was at 15 ± 2 seconds and for the test duration a total of 855.6 g of silica

abrasive was delivered to each test samples surface. Erosion rates were measured in mass loss to the nearest milligram. Surface topography of the wear scars were also characterized using Keyence[†] wide area 3D measurement system.



Figure 1: (a) ASTM G76 erosion testing set-up (b) nozzle and sample holder inside containment cabinet

Corrosion Testing

Electrochemical and immersion test methods were used to characterize and compare the corrosion response of cast+HIP Co-Cr-W-C and AM+HIP Co-Cr-Mo-C. A simulated drilling environment was used for testing consisting of an alkaline brine with 4 molar (M) chloride concentration and a pH of 8. Test solution was produced with reagent grade sodium chloride (NaCl) for chloride addition and sodium hydroxide (NaOH) and phosphoric acid (H₃PO₄) for pH balance.

Immersion testing was performed with cylindrical samples 1.27 cm (0.5") in diameter by 3.81 cm (1.5") long. 1.27 cm of each end of the cylinder were coated in high temperature epoxy giving a total exposure area of 10.84 cm². Co-Cr-W-C and Co-Cr-Mo-C samples were tested in the as-machined condition. Samples were exposed for 168 hours at 350°F inside of a pressure cell with glass liners to protect the cells and prevent any galvanic interactions. Cells were purged with nitrogen (N₂) to remove oxygen from the solution and followed by pressurization to 500 psi with N₂ to prevent test solution from boiling. After testing the samples were cooled to room temperature and cleaned with distilled water and lightly brushed to remove any corrosion product followed by cleaning with ethanol and air drying. To evaluate the corrosion resistance of alloys corrosion morphologies and depth of corrosion attack were studied using optical microscope.

Electrochemical testing was performed using a Gamry[†] Instruments Interface 1000E potentiostat. A three-electrode set up was used including the polished Co-Cr-W-C/Co-Cr-Mo-C piece as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and a graphite rod as the counter electrode.

Electrochemical samples were mounted in epoxy and ground in subsequent steps from 240 grit to 1000 grit silicon carbide paper, polished to a 1μm finish with diamond suspensions. The exposed surface area of the electrochemical samples was 1.27 cm² (0.20 in²). Open circuit potential (OCP), linear polarization resistance (LPR) and cyclic potentiodynamic polarization (CPP) methods were used to characterize and compare the corrosion response. All electrochemical testing was performed at room temperature and with the solution purged with nitrogen (N₂). To purge the solutions, N₂ was bubbled through the solution for 1 hour before samples were immersed and N₂ continuously bubbled throughout testing as well as filling the head space of the electrochemical cell. OCP measurements were made for 55 min before LPR

and CPP. LPR was measured by varying the voltage from -30 mV vs OCP to $+30$ mV vs OCP with scan rate of 0.1667 mV/s. CPP curves were created by polarizing the samples anodically by -150 mV vs OCP to $+1200$ mV vs OCP or an apex current of 5 mA/cm². Once the peak voltage or apex current was reached the voltage was reversed to -100 mV vs OCP. The forward and reverse scan rate was 0.1667 mV/s. All electrochemical tests were run in triplicate to test the reproducibility of the data. After corrosion testing the surface of the samples were investigated using optical microscopy and SEM/EDS techniques.

RESULTS

Microstructure and Mechanical Properties

The microstructure of the cast Co-Cr-W-C and the Co-Cr-Mo-C is shown in Figure 3 along with their energy dispersive spectra (EDS). Figure 2a shows a well distributed carbide network throughout the microstructure while the carbide precipitates are sparse in Figure 2b. The high C and W containing Stellite[†] 6 drives the precipitation of a network of Cr- and W- carbides within the matrix. The Co-Cr-Mo-C have a very few of these carbides because of their much lower C content.

Figure 3a shows the different carbides (white and dark gray) in a Co-Cr matrix for Co-Cr-W-C samples. The compositionally biased image shows the different carbide in a CoCr matrix. The elemental mapping further illustrates the chrome carbide and the tungsten carbide in Figure 3c and 3d in a CoCr matrix. These carbides play a dominant role in the beneficial wear resistance behavior of these materials while at the same time adversely impacting the machinability of these Co-Cr-W-C grades.

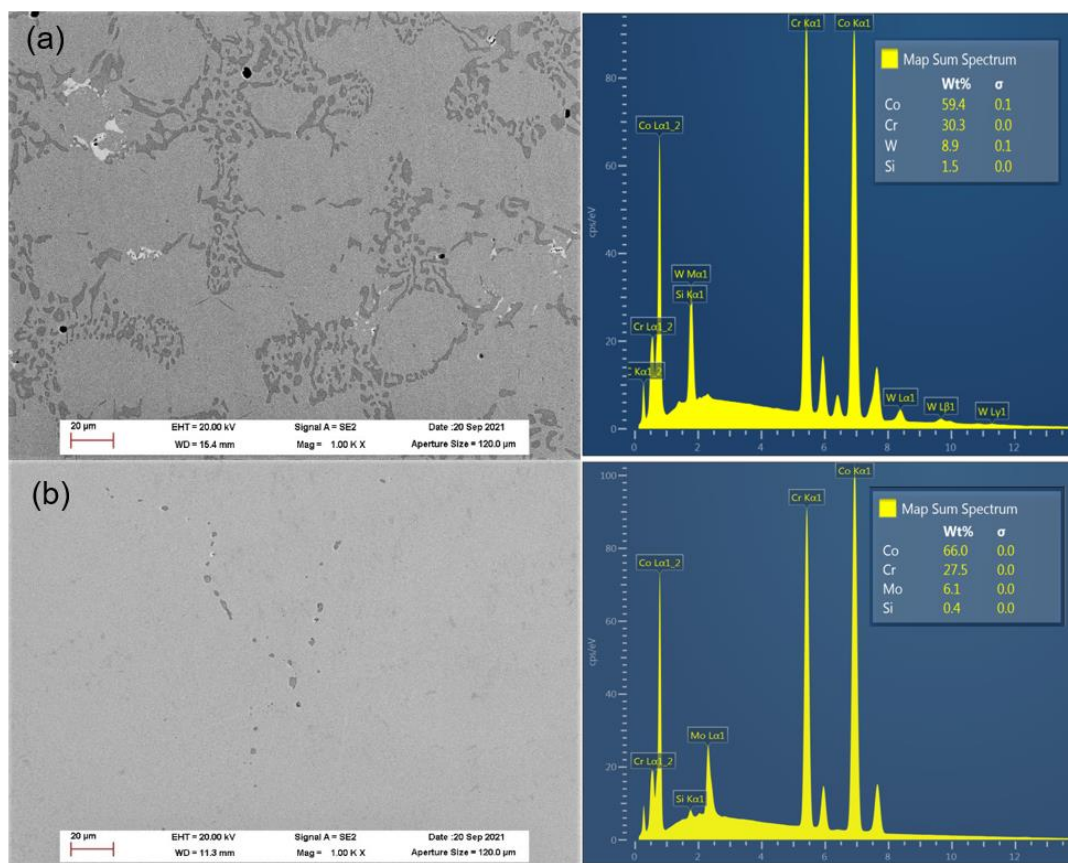


Figure 2: Microstructure and elemental mapping of (a) Co-Cr-W-C & (b) Co-Cr-Mo-C