Microstructural and mechanical characterization of Mo-containing Stellite alloys produced by three dimensional printing

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Abstract

Stellite materials are widely used in demanding conditions such as corrosion and high-load wear components. The ability to develop cobalt-chrome based components by means of three-dimensional printing may increase their performance as well as enable the use of these wear-resistant materials in new applications. In this study, we use the binder jetting method to manufacture cobalt-chrome based articles using powders with various characteristics. The final components showed theoretical densities above critical limits, which correlated well with the microstructural characterization and mechanical properties. In addition, abrasion experiments showed higher wear resistance for the 3D printed parts compared to as-cast components, which was attributed to differences in the microstructure.

1. Introduction

Stellite materials exhibit superior corrosion and tribological (i.e. wear resistance) behavior at a wide range of contact and environmental conditions [1-3]. Thus, these materials are a desired choice for extreme contact applications in industries such as aerospace, oil & gas, forging, and power generation [4-7]. Stellite components are typically produced by various casting methods (e.g. investment casting, sand casting, etc.), as well as powder metallurgy processes which may include a compaction step such as isostatic pressing, die pressing, or automatic pressing. Due to the complexity of these processes, the design of Stellite components is limited by the shape and size of the mold or die and thus, these materials are limited to the applications mentioned above. In addition, the post processing (e.g. surface finishing, cutting, shaping) of such materials is extremely difficult due to their hardness and high wear resistance.

With the recent advances in the technology, additive manufacturing has certain benefits compared to traditional manufacturing. For instance, additive manufacturing eliminates the time and production cost of molds and dies that are required to develop Stellite components with certain traditional methods. In addition, additive manufacturing makes efficient use of the material by using the required powder to develop a specific component and recycling the residue. In the view of Stellite components, this technology offers improved design freedom, which provides two main benefits for wear resistant materials: 1) enabling the use of wear resistant materials in new applications (e.g. by minimizing the component weight, increasing reliability with surface modifications, etc.) and 2) eliminating a large portion of the post-machining.

In general, metal additive manufacturing systems can be classified into powder bed (e.g. SLM, E-beam), powder feed (e.g. LENS), and wire feed (e.g. EBFFF)[8], with each technique having advantages and disadvantages[9]. The
binder-jetting method uses a binder to create a ‘green’ component in a layered fashion followed by post-process consolidation (e.g. infiltrating, sintering). Thus, this process offers some benefits in terms of the microstructural control and printing velocity. In this study, we use different Stellite powder in the binder-jetting method to manufacture nearly-fully dense components, which can be used in certain demanding wear conditions (e.g. high contact pressures and sliding velocities). We suspect the use of this three-dimensional printing technique for such components will allow us to develop parts with complex features for functionality, to improve the mechanical properties and wear resistance, to decrease the total weight (i.e. by eliminating unnecessary material), and to decrease the manufacturing time and costs.

2. Materials and Methods

In this study, Stellite powder is used to manufacture a three-dimensional part using the binder-jetting method. The Stellite powders are atomized in gas atomization towers at Kennametal Stellite (Goshen, IN, USA), producing predominately spherical powders. The chemical composition of the powder is shown in Table 1 and comprises primarily of Co-Cr-Mo. The 3D printing instrumentation used in this study is Innovent (ExOne) with a chamber size of 160x65x65mm. More details on this process are found elsewhere [10-12]. Briefly, the powder is loaded into the chamber of 3D printing system and a binder is applied onto the powder bed to develop a component cross-section. Subsequently, the green three-dimensional part is manufactured in a layered fashion. The components printed for this study consisted of cylinders and rectangles (i.e. in the parallel and perpendicular direction), as well as flat tensile bars and flat wear coupons. After printing, the component is carefully removed from the chamber and the “green” component is sintered in high vacuum using previously reported temperatures and conditions [13]. Hot Isostatic Pressing (HIP) is then performed at Bodycote Thermal Processing on the sintered component using their standard conditions. While in this study we use standard temperatures and conditions, the effects of varying these sintering conditions is currently being investigated and will be reported in a future study.

| Table 1 Elemental composition of Stellite powder used in additive manufacturing |
|---|---|---|---|---|---|---|---|
| Cr | Mo | C | Ni | Fe | Co | Mn | Si |
| 27.96 | 5.35 | 0.28 | 2.69 | 1.15 | Balance | 0.53 | 1.52 |

Microindentations are performed on the cross-sections in order to investigate the strength of the final components. A Tuchon 2500 microindentation system with a diamond tip (R=150 nm) is used for the indentations. Tensile tests were performed at Westmoreland Mechanical Testing & Research Inc. (Youngstown, PA, USA) using the ASTM E8-13a procedures (i.e. speed of testing = 0.05in./min). The abrasive wear tests were performed using ASTM G65 wear tests at 200 rpm, with a 30lb load under ambient conditions (i.e. 70.7°F, 22%RH). Transmission electron microscopy of the final components is performed using a FEI Titan (G2 80-300 TEM/STEM) instrument in the Carnegie Mellon University Materials Characterization Facility. The samples are prepared using a Focus Ion Beam at Clemson University.

3. Results and Discussion

SEM analysis of the Stellite 21 powder as well as cross-sectional images of the same powder is shown in Figure 1. The images of the Stellite powder show predominantly spherical shape with few satellites. The spherical shape is typical for the gas atomization process and has been previously reported [14]. The cross sections of the powder (lower right panel) reveal low porosity of the powder. Correspondingly, the pycnometric density of the Stellite powder is measured to be 8.13 g/cm³.

![Figure 1](image)

Figure 1 (a) SEM images of Stellite 21 powder with the corresponding cross-sectional analysis used to manufacture a Stellite three-dimensional article by means of binder jetting. Cross-sectional (b) optical and SEM image (xy-axis) of the 3D printed Stellite component subsequently to sintering and HIP showing high density components.

Figure 1 (b) shows cross-sectional images of the 3D printed components after the sintering and HIP process. The density of the final component, printed using the Stellite powder, showed a density of 8.22 g/cm³. It should be noted that the component prior to HIP obtained a density of 8.20 g/cm³, which indicates that the HIP process had no significant influence on the density. Accordingly, the cross-sectional images (Figure 1b) show a high-density microstructure with a homogeneous grain size distribution. The microstructure is similar to cast F75 alloys, which consist of solid cobalt matrix with interdendritic phases and carbides. The carbides, distinguished by the darker region, are in the form of M₂₃C₆ and possibly M₆C. The cobalt matrix grains are found to range between approximately 50 and 150 µm in diameter, without any evidence of abnormal grain growth, which has been previously observed with traditional manufacturing methods (i.e. casting, sintering) [15].

With the current state of the technology, components manufactured by three dimensional printing processes typically require some surface finishing to obtain the near net
shape and reduce the high roughness. However, such post-processing techniques can lead to microstructural changes in the near-surface region. Thus, here we use Transmission Electron Microscopy (TEM) to provide a better understanding of the influence of the surface finishing on the microstructure of the three dimensional part produced using the Stellite 21 powder. Figure 2 (a) and (b) shows cross-sectional TEM images of the near-surface region and closer to the surface, respectively. Figure 2 (a) reveals stacking faults in the subsurface region, which are likely formed due to the shearing from the polishing process. This type of stacking fault formation due to wear or plastic deformation is common with Stellite 21 and has been previously reported [16] and can be attributed to the low stacking fault energy [17]. The cross-sectional image closer to the surface, on the other hand (Figure 2b), does not reveal any evidence of stacking faults. Instead, the image reveals evident grain refinement, as confirmed by the diffraction pattern. Such grain refinement is also caused by the polishing and for metals can be attributed to the nucleation of dislocations at the surface and rotation of clusters [18-20].

The low porosity observed with the microstructural analysis of the 3D printed Stellite components correlated well with the mechanical properties (i.e. tensile strength and micro-hardness), as shown in Table 2. The ultimate tensile strength, in the parallel and perpendicular direction to the printing, exceeded the required value of the ASTM F75-07 (i.e. 95,000psi) and compared well with that of PM Stellite 21 [21]. In addition, the abrasion resistance of the 3D printed components was nearly double compared to cast Stellite 21 specimen (i.e. volume loss of 89.4mm³), which was tested separately as a reference. Similarly, the hardness value here was higher compared to that of cast Stellite 21 (i.e. HV\textsubscript{250N} = 311.8±6.3) [22]. It should be noted that the hardness value of the sintered components (i.e. prior to HIP) was similar to the ones after the HIP process.

Table 2 Hardness, tensile properties, and abrasion wear of 3D printed component using Stellite 21 powder

|                   | VHN | Parallel | Perpendicular | Abrasive Wear* (volume loss – mm\(^3\)) |
|-------------------|-----|----------|---------------|---------------------------------------|
| Stellite 21       | 332±14 | 105±2 | 105±3 | 47.8 |

*ASTM G106 test for 2000 revolutions at 700 lbf load

In order to enhance the tensile strength of the three dimensional components, we used modified Stellite powder with increased Molybdenum content (i.e. up to 18 wt.%). SEM analysis as well as cross-sectional imaging of this powder is shown in Figure 3(a), revealing spherical shape with low porosity. The cross-sections of the final component (i.e. printed, sintered, and HIPed) are shown in Figure 3(b) in the parallel and perpendicular direction to the printing, respectively. The microstructure (i.e. after etching) was different compared to the Stellite 21, consisting of a cobalt solid matrix and metal carbide phases (i.e. in the form of primary M7C3 and possibly M6C as well as secondary M23C6), as shown in Figure 3 (b). These microstructural observations are common with the addition of Molybdenum, where the increased Mo content enhances the carbide formation. Correspondingly, the hardness value of this 3D printed material is 838±38 VHN, which is significantly higher compared to the Stellite 21 alloy.

4. Conclusion

In this study, we use Stellite powder to manufacture nearly fully dense components by means of three dimensional printing. The overall additive manufacturing process we used consists of the three dimensional printing step (i.e. where the binder is deposited onto the powder in a layered fashion), the sintering process, and the hot isostatic pressing. The final components created using the Stellite 21 powder exhibit tensile strength exceeding that of as cast components, which was attributed to the high density and difference in microstructure. Similarly, abrasion experiments showed higher wear resistance for the 3D printed parts compared to as-cast components. The effects of the surface finishing on the microstructure were also investigated by means of TEM.
addition, altered Stellite powder was used for the printing process, which resulted in an increased hardness of the final components.

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