Electron Beam Melted (EBM) Co-Cr-Mo Alloy for Orthopaedic Implant Applications

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Abstract

The Electron Beam Melting (EBM) manufacturing process is emerging as an additional method for producing orthopaedic devices in several materials, including Co-Cr-Mo Alloy. This work presents the chemical, microstructural and mechanical properties of several test specimens produced by the EBM process before and after a post-EBM Heat treatment. Comparisons are made to the properties of Co-Cr-Mo materials used within the orthopaedic implant industry processed by conventional methods such as investment casting and machining from wrought. The results of the work are promising, and demonstrate that EBM produced Co-Cr-Mo material has comparable, and in several cases superior microstructural and mechanical properties to those found in the traditionally-processed materials used today.

Introduction

The last several years have seen many advances towards realizing the goal of additive manufacturing for medical and aerospace applications. The additive manufacturing industry has focused its efforts on producing 'higher end' metals including medical grade stainless steels, titanium, titanium alloys and cobalt-chrome alloys. The availability of these materials within the scope of additive manufacturing technology opens the door for many applications in the field. One of the industry-leading additive metal manufacturing processes is the Electron Beam Melting (EBM) Process. The EBM process is an additive fabrication process, which utilizes a scanning electron beam to melt pre-alloyed metal powder in a layered fashion and build a three-dimensional construct, based on input generated from a computer model.

The EBM process is quite different than conventional production techniques, thus it is anticpated that the properties and mirctostructure of EBM produced materials will differ from what is currently seen today. The EBM process intruduces several processing variables which do not exist in currrent manufacturing methods. It is important to identify these variables, and come to understand their effect on the metallurgical characteristics of the material.

The goal of this paper is to present the metallurgical properties of a particular alloy produced by the EBM process; Co-Cr-Mo. Results of chemical, microstructural, and mechanical evaluations will be presented. The results of these evaluations will be used to compare EBM produced Co-Cr-Mo material to several similar materials used today in the medical industry. In addition, key processing variables that may influence the properties of the material are identified, and their effects on the material are investigated.

The Electron Beam Melting Process

Like many rapid manufacturing techniques, the EBM process creates a physical component from digital CAD models by building the component in a series of layers. The EBM process starts by distributing a 70 μm layer of fine metal powder onto a steel platform. An electron beam is produced by passing current through a Tungsten filament. The electron beam scans areas of the metal powder layer, in an x-y coordinate system (as defined by the computer model) fully melting the powder in the areas scanned. Once the beam has scanned the appropriate areas, the steel platform is lowered by 70 μm and a new layer of powder is distributed on top of the previously melted layer. This process continues, layer by layer, until a complete part is produced. During processing the entire build chamber maintains a temperature of approximately 800°C. Once the part has been completed, the build chamber is flooded with He gas to expedite cooling. A schematic of the EBM process is shown in **Figure 1**.

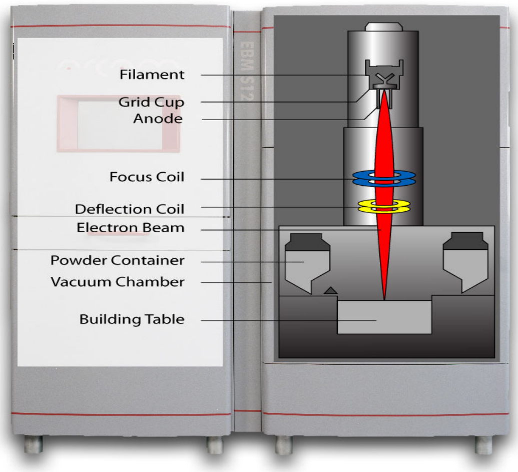


Figure 1: Schematic of an EBM production system.

The use of an electron beam to supply the energy necessary to melt the metal powder mandates that the process be done in a vacuum chamber, which minimizes chemical reactions between the melting metal powder and the surrounding atmosphere. Currently the EBM process is capable of producing parts up to 200x200x200 mm, with a dimensional accuracy of 0.4 mm.

Post EBM Heat Treatment

In addition to evaluating as-produced Co-Cr-Mo samples directly out of the EBM process, samples were also evaluated following a two-stage heat treatment. The heat treatment consisted of a hot isostatic pressing (HIP) cycle and a homogenization treatment. The goals of the heat treatments were to dissolve carbides present in the as-produced material and improve isotropy of the microstructure. **Table A** outlines the parameters used for each heat treatment cycle.

Table A: Heat treatment parameters

Heat Treatment Cycle	*Time*	*Temperature*	*Pressure*	*Atmosphere*	*Quench*
HIP	**4 hrs**	**1185**	**25 ksi**	**Argon**	**N/A**
Homogenization	**4 hrs**	**1190**	**N/A**	**Argon**	**75°C/Minute**

Procedure for Metallurgical Evaluation

The goal of this research was to provide basic matallurgical data from evaluation of EBM produced Co-Cr-Mo alloys, and to compare the results of these evaluations to data in literature and conventionally used standards and specifications. To accomplish this goal, several test specimens were produced to evaluate the chemical composition, microstructure, and mechanical properties of EBM produced material.

Sample Production & Orientation:

Mechanical testing was conducted on samples whose gauge-section was both parallel (Z orientation) and perpendicular (XY orientation) to the beam direction. Z orientation samples were produced as cylinders, where as XY samples were produced as large slabs which were sectioned into several specimens.

Chemical Composition:

Chemical composition analysis was conducted on virgin Co-Cr-Mo alloy powder prior to EBM production. Solid specimens produced from the same powder were analyzed following EBM production to understand changes in chemical composition during solidification. The analyses were conducted in accordance with ASTM E 354 [1].

Microstructure:

Cross-sections of specimens created by the EBM process were prepared for metallographic examination. The gross microstructure of material was evaluated in two orientations, parallel to the build direction (Z orientation), and horizontal to the build direction (XY orientation). Samples were taken from the mid-section of each specimen, approximately 25mm from the bottom of the build platform. In addition to the EBM produced Co-Cr-Mo alloy, a custom Co-Cr-Mo implant component investment cast in accordance with ASTM F 75[2] was also sectioned and prepared for metallographic examination to allow for a comparison of microstructures. All samples were evaluated by light microscopy and were electrolytically etched in a 5% HCl solution.

Mechanical Properties:

The mechanical properties of EBM produced Co-Cr-Mo material were evaluated by static tensile testing, rotating bending fatigue testing, Rockwell hardness testing, and facture analysis. The mechanical testing specimens were machined to the appropriate dimensions for each test from the near-net shapes.

The static tensile properties of the EBM produced material were evaluated in accordance with ASTM E 8, using the round powder metallurgy specimen geometry (*Figure 20 of ASTM E8-08*) [3]. Rockwell hardness was measured on cross sections of the grip area on tensile samples following testing. Rotating bending fatigue (RBF) samples were surface polished in the gauge area prior to testing to prevent premature failures. The tests were conducted at a frequency of 100 Hz at room temperature. A run-out value of 10 million cycles was chosen.

Results and Discussion

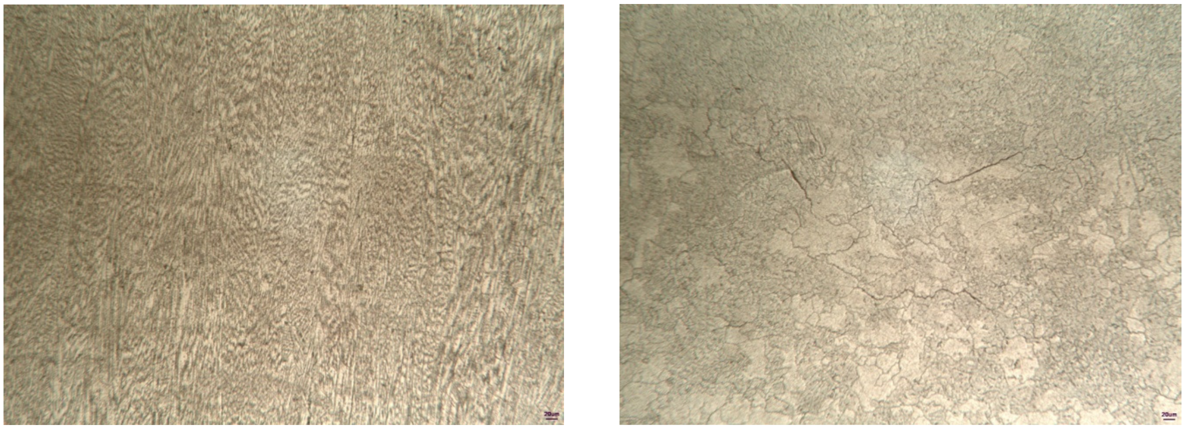
Table B contains the chemical composition of the virgin powder prior to production as well as the chemical composition of solid test specimens following EBM production. The results indicate that no significant changes in material composition occur during the melting and re-solidification of the pre-alloyed powder during the EBM process. Of particular note, are the consistent levels of interstitial elements such as O, N, C and H. The high vacuum level in the build chamber of the EBM equipment limits the amount of these gasses available for diffusion into the material during production, allowing for tight control on interstitial elements. Alloys containing elements with greatly differing melting points have shown a propensity to ‘burn off’ a fraction of the low melting point element during the EBM process. This phenomenon has been observed with a loss of Al during the EBM production of Ti6Al4V alloys [4].This does not appear to be the case for the Co-Cr-Mo alloy system, as all alloying elements remain relatively constant throughout the process.

Table B: Chemical compositions of Co-Cr-Mo powder and EBM solidified material

State	*Al wt%*	*B wt%*	*C wt%*	*Cr wt%*	*Fe wt%*	*Mn wt%*	*Mo wt%*	*N wt%*	*Ni wt%*	*P wt%*	*Si wt%*	*Ti wt%*	*W wt%*	*Co wt%*
Powder	**<0.010**	**<0.001**	**0.24**	**28.29**	**0.60**	**0.59**	**5.74**	**0.16**	**0.14**	**0.009**	**0.37**	**0.026**	**<0.01**	**Bal.**
EBM Solidified	**<0.010**	**<0.001**	**0.22**	**27.69**	**0.23**	**0.40**	**5.96**	**0.14**	**0.09**	**0.009**	**0.38**	**0.011**	**<0.01**	**Bal.**

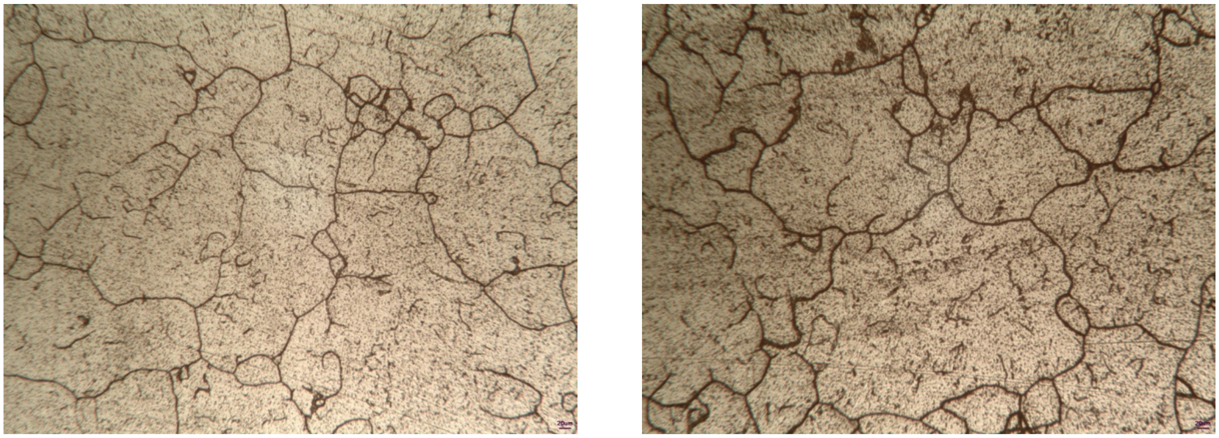
The microstructure of the Co-Cr-Mo alloys resulting from EBM solidification is unique to the process. Micrographs of as-produced EBM Co-Cr-Mo alloy for both XY and Z orientations are shown in **Figure 2**. These micrographs are representative of the microstructure typical seen in EBM produced Co-Cr-Mo alloys. The microstructure consists of columnar grains orientated along the z-axis. A large number of carbides are also present in both micrographs. It is suggested that the combination of high carbon content along with the elevated 800^{o}C chamber temperature during EBM production encourage the precipitation of carbides out of the matrix material.

Figure 3 contains micrographs of EBM Co-Cr-Mo alloy for both XY and Z orientations following hot isostatic pressing and a homogenizing heat treatment. The heat treatments result in several significant changes in the material microstructure. Heat treatment appears to re-dissolve a portion of the carbides back into solution, increase the overall grain size of the material, and most importantly, results in a much more isotropic microstructure.



a) **b)**

Figure 2: Micrographs of EBM produced Co-Cr-Mo alloy in the as-produced condition orientated in a) the Z direction and b) the XY direction.



a) b)

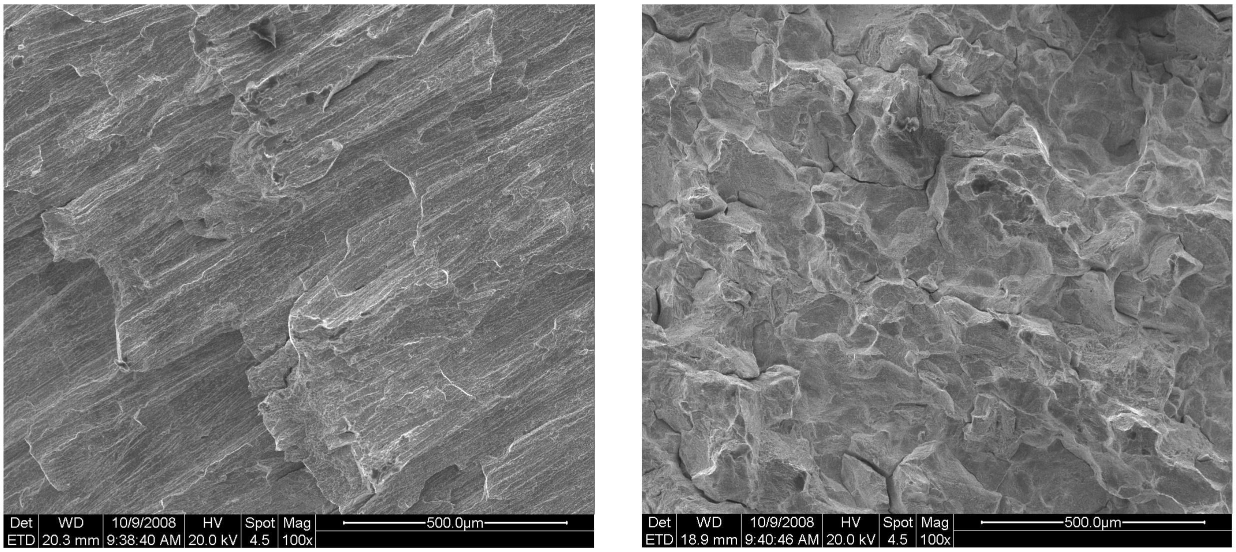
Figure 3: Micrographs of EBM produced Co-Cr-Mo alloy in the HIP and homogenized condition orientated in a) the Z direction and b) the XY direction.

Table C contains the static tensile property results of EBM produced tensile bars in both the as-produced condition and the HIP and heat treated conditions. Test bars from each condition were tested in both the Z orientation as well as the XY orientation. The results indicate that as-produced EBM Co-Cr-Mo material is extremely brittle, especially when stressed along the Z orientation. The low ductility measured in the as-produced material is likely due to large quantity of carbides present in the microstructure. The mechanical property dependence on orientation can be explained by the columnar grains orientated parallel to the beam direction. Heat treatment following EBM production has quite a drastic effect on the mechanical behavior of Co-Cr-Mo material. The 2% offset yield strength is significantly lower and the material exhibits much higher elongation following heat treatment when compared to the as-produced material. The heat-treated samples all exhibited similar mechanical behavior independent of orientation. The average hardness of the heat-treated samples was measured at 33 HRC.

Table C: Static Mechanical Properties of EBM produced Co-Cr-Mo material

State	*Orientation (XY or Z)*	*Number of Samples*	*Avg. YS ksi (MPa)*	*Avg. UTS ksi (MPa)*	*Reduction of Area (%)*	*Avg. Elong. (%)*
As-Produced	**XY**	**5**	**104 (717)**	**161 (1110)**	**7.2**	**5.0**
As-Produced	**Z**	**5**	**114 (786)**	**126 (869)**	**N/A**	**0.8**
HIP & HT	**XY**	**5**	**85 (586)**	**166 (1145)**	**24.3**	**30**
HIP & HT	**Z**	**5**	**85 (586)**	**167 (1151)**	**24.0**	**30**

Fracture analysis was conducted on failed samples following tensile testing utilizing a SEM. **Figure 3a** shows the fracture surface of an as-produced XY orientated tensile sample. The fracture follows the grain boundaries of the columnar grains, and is indicative of a brittle fracture mechanism. **Figure 4b** shows the fracture surface of a XY orientated tensile that has been heat treated. The fracture can be characterized as intergranular, which typically indicates a brittle fracture with little deformation during failure. This sample, however, exhibited approximately 30% elongation which is rather unique. The microstructures in **figure 3** do show a high concentration of carbides at the grain boundaries, which are likely responsible for the intergranular fracture mechanism.



a) b)

Figure 4: Fracture surfaces of failed static tensile XY orientated samples of EBM produced Co-Cr-Mo alloy in the a) as-produced and b) HIP and homogenized conditions.

The fatigue performance of EBM produced Co-Cr-Mo material is summarized as an S-N curve in **Figure 5**. Two groups of specimens were tested; samples orientated in both XY direction and the Z direction. Both sample groups underwent HIP and homogenization treatments prior to testing. The number of samples in each group is not sufficient to accurately predict the 10 million cycle stress level, however it appears the value will be between 400 and 500 MPa. The data also indicates that samples tested in the Z direction have a slightly lower fatigue limit. This may be a consequence of the layering in the Z direction which could provide crack initiation sites.

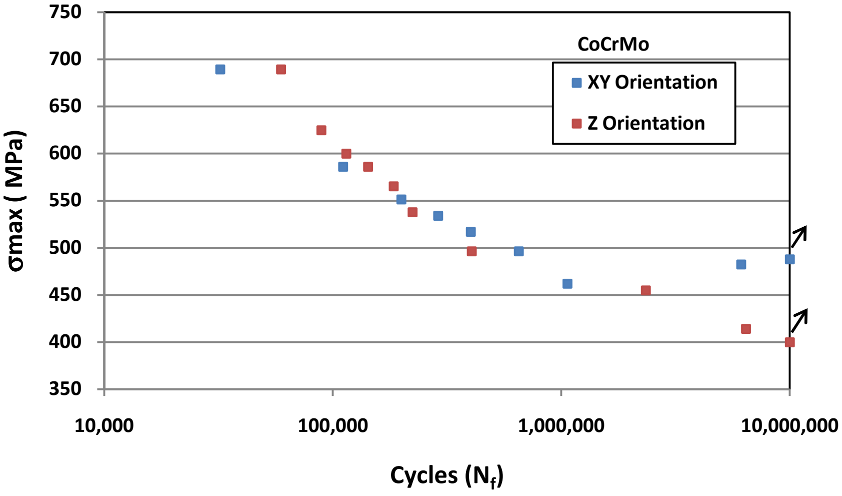


Figure 5: S-N curve for EBM produced C-Cr-Mo material tested in rotating bending fatigue.

If EBM produced Co-Cr-Mo material is going to be used in the medical field it is important to understand how all of the characteristics presented in this study compare to the characteristics of the Co-Cr-Mo materials currently used in the medical industry. **Table D** summarizes the most commonly used Co-Cr-Mo materials in the medical industry today [2]. The main difference between these alloys is the method of production; forging, casting or wrought alloys. Each alloy has slightly different chemical composition requirements set at the necessary levels to enable proper manufacture and result in the desired mechanical performance. The powder used in this study was produced with the intention of meeting the ASTM F-75 chemical composition requirements. **Table E** compares the chemical composition of the solid EBM Co-Cr-Mo alloy with that of each of the standard materials listed in **Table D**. The ASTM F799 and F1537 standards designate three (3) separate alloys; 1) Low carbon, 2) High Carbon and 3) Dispersion Strengthened. The EBM produced material meets the chemical requirements of ASTM F 75 as well as high carbon (Alloy 2) material.

Table D: Conventional standards for Co-Cr-Mo alloys in the Medical Industry

Specification Designation	*Title*
ASTM F 75	Standard Specification for Cobalt-28 Chromium-6 Molybdenum Alloy Castings and Casting Alloys for Surgical Implants
ASTM F 799	Standard Specification for Cobalt-28 Chromium-6 Molybdenum Alloy Forgings for Surgical Implants
ASTM F 1537	Standard Specification for Wrought Cobalt-28 Chromium-6 Molybdenum Alloys for Surgical Implants

Table E: Chemical composition comparison of EBM produced material and conventional Co-Cr-Mo Alloys

Material	*Alloy*	*Al wt%*	*B wt%*	*C wt%*	*Cr wt%*	*Fe wt%*	*Mn wt%*	*Mo wt%*	*N wt%*	*Ni wt%*	*P wt%*	*Si wt%*	*Ti wt%*	*W wt%*	*La wt%*	*Co wt%*
EBM Solidified	......	**<0.010**	**<0.001**	**0.22**	**27.69**	**0.23**	**0.40**	**5.96**	**0.14**	**0.09**	**0.009**	**0.38**	**0.011**	**<0.01**	**N/A**	**Bal.**
ASTM F 75	....	**<0.10**	**<0.010**	**<0.35**	**27.0-30.0**	**<0.75**	**<1.0**	**5.0-7.0**	**<0.25**	**<0.50**	**<0.020**	**<1.0**	**<0.10**	**<0.20**	......	**Bal.**
ASTM F 799 & F 1537	**1**	......	......	**<0.14**	**26.0-30.0**	**<0.75**	**<1.0**	**5.0-7.0**	**<0.25**	**<1.0**	......	**<1.0**	......	......	......	**Bal.**
ASTM F 799 & F 1537	**2**	......	......	**0.15-0.35**	**26.0-30.0**	**<0.75**	**<1.0**	**5.0-7.0**	**<0.25**	**<1.0**	......	**<1.0**	......	......	......	**Bal.**
ASTM F 799 & F 1537	**3**	**0.30-1.00**	......	**<0.14**	**26.0-30.0**	**<0.75**	**<1.0**	**5.0-7.0**	**<0.25**	**<1.0**	......	**<1.0**	......	......	**0.03-0.20**	**Bal.**

Figure 6 compares the mechanical properties of EBM produced Co-Cr-Mo material following HIP and heat treatment with the mechanical requirements of the alloys listed in **table D**. There are several important conclusions that can be drawn from the comparison. The elongation and reduction of area properties of the EBM produced materials exceed the requirements for all conventionally produced materials. The EBM produced material also meets or exceeds all mechanical strength requirements for both ASTM F75 and ASTM F1537 Annealed material.

Although none of the ASTM standards for implantable Co-Cr-Mo alloys require a specific microstructure, it useful to compare the the microstructure of EBM produced materials to that of a conventionally produced implantable device. **Figure 7** is a optical light micrograph of an investment cast commercially available implantable Co-Cr-Mo device which was obtained and sectioned for microstructural evaluation. It is obvious that the microstructure of this implant is quite different than the microstructures presented in **figure 3**. The microstructure in **figure 7** is what one would expect from an investment cast material that experiences a slow solification rate [5]. EBM produced material solidifies very quickly after melting, and experiences an entirely different thermal history through out its production and subesequent heat treatments, resulting in an entirely different microstructure.

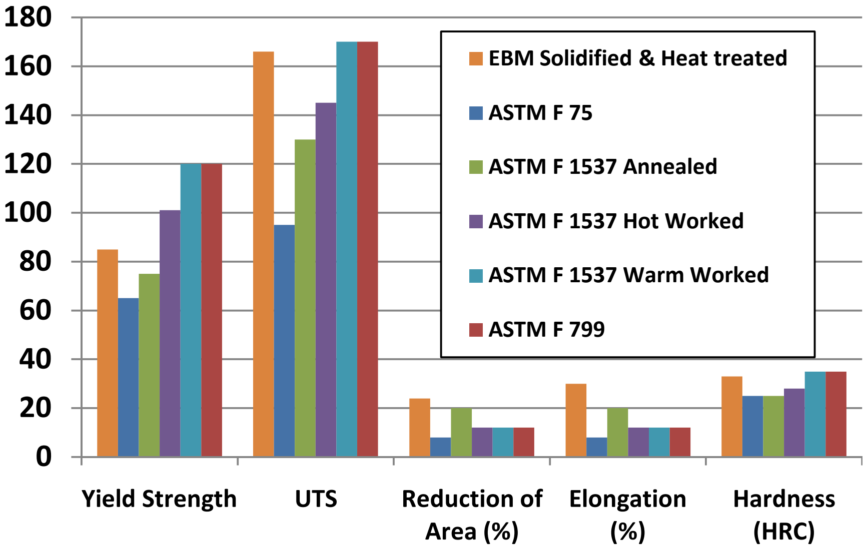


Figure 6: Comparison of mechanical properties of conventional medical grade Co-Cr-Mo alloys and EBM produced Co-Cr-Mo alloy.

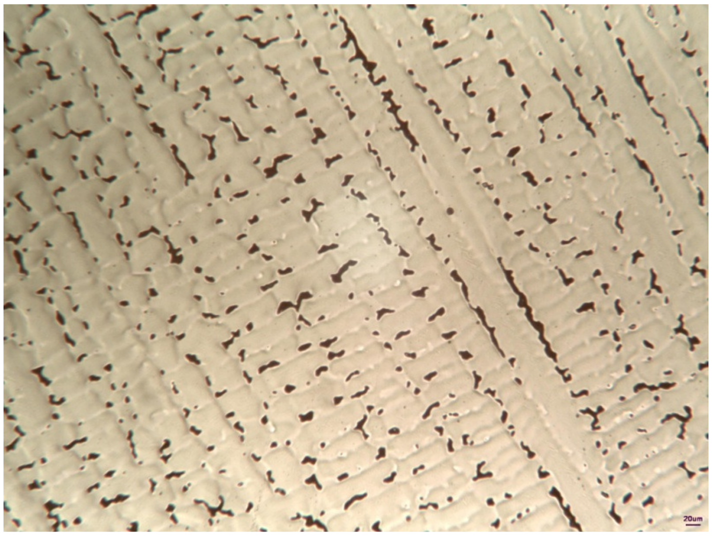


Figure 7: Microstructure of a commercially available investment cast Co-Cr-Mo implant.

Summary and Conclusions

The purpose of this research was to investigate whether EBM produced Co-Cr-Mo alloys exhibit adequate chemical and mechanical properties to be considered acceptable alloys for surgical implant applications. The results demonstrate that as-produced Co-Cr-Mo alloy is quite brittle and exhibits anisotropic mechanical behavior. For these reasons, as-produced Co-Cr-Mo material needs to undergo a two-stage heat treatment in order to satisfy the requirements of standard Co-Cr-Mo medical grade standards. The heat treatment has the effect of dissolving carbides which precipitate out of the matrix during EBM solidification, and removing the anisotropic behavior from the material. Although the microstructure of EBM produced Co-Cr-

Mo alloy is unique when compared to material manufactured by conventional means, its mechanical performance exceeds or meets the requirements for both ASTM F75 material and annealed ASTM F1537 grade material.

References

1. ASTM Standard: E 354 Standard Test Methods for Chemical Analysis of High-Temperature, Electrical, Magnetic, and Other Similar Iron, Nickel, and Cobalt Alloys, 2006.
2. Book of ASTM Standards, Vol. 31.01 Medical and Surgical Materials and Devices, 2006.
3. ASTM Standard: E 8-08 Test Methods for Tensile Tension Testing of Metallic Materials, ASTM, 2008.
4. Christensen, A., Lippincott, A., Kircher, R., *Qualification of Electron Beam Melted (EBM) Ti6Al4V-ELI for Orthopaedic Applications*, MPMD, Palm Desert, CA, 2007.
5. Mishra, A., et al., “Metallurgy, Microstructure, Chemistry and Mechanical Properties of a New Grade of Cobal-Chromium Ally Before and After Porous-Costing”, Cobalt-Based Alloys for Biomedical Applications, ASTM STP 1