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<th>Selective electron beam melting of Co-Cr-Mo: microstructure and mechanical properties</th>
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ABSTRACT: As an emerging powder-bed fusion additive manufacturing technique, selective electron beam melting (SEBM) attracts numerous attentions due to its great potential applications in orthopaedic implants and aerospace components. The microstructure and mechanical properties of SEBM-built Co-Cr-Mo alloy have been investigated. Microstructural characterisation was carried out using scanning electron microscopy, and X-ray diffraction techniques. Its microstructure consists of face-centred cubic columnar grains with <001> preferred orientation and continuous carbide thin films at grain boundaries. Each columnar grain is comprised of parallel dendrites with short secondary arms and sparse carbides within interdendritic regions. Two sorts of carbides were identified in terms of their compositions, i.e. $\text{C}_2\text{M}_6$ and $\text{C}_6\text{M}$ (where M = Co, Cr and Mo). In addition, anisotropic mechanical properties were found to exist in SEBM-built Co-Cr-Mo parts. The microstructure-property relationship for SEBM-built Co-Cr-Mo parts is discussed.

KEYWORDS: additive manufacturing, EBM, Co-Cr-Mo alloy, microstructure, mechanical properties

INTRODUCTION

Selective electron beam melting (SEBM) is a promising powder-bed fusion additive manufacturing (AM) technology for metals and alloys, and it is being increasingly used in producing complex orthopaedic implants and aerospace components (Tan et al. 2014; Kok et al. 2015). In addition to some process-induced defects, such as internal pores and rough surface, another critical issue that may obstacle its wide applications is the limited material library for SEBM process. Ti-6Al-4V is still the most investigated material in SEBM and its microstructure and mechanical properties have been extensively reported [Wang et al. 2016; Tan et al. 2015; Tan et al. 2016]. However, only limited studies were involved in SEBM processing of Co-Cr-Mo alloys [Kircher et al. 2009; Gaytan et al. 2010; Sun et al. 2014; Sun et al. 2015; Kok et al. 2018; Tan et al. 2018]. Co-Cr-Mo alloys are widely used in both biomedical and aerospace applications where require good biocompatibility, high wear resistance, and superior high-temperature creep properties [Davis 2000].

In recent years, microstructural consistency, i.e. anisotropy and homogeneity of microstructure, has become another important concern when seeking practical applications of SEBM as well as other metal AM techniques. Sun et al. [Sun et al. 2014] reported the build direction and build height dependent microstructure and their effects on high-temperature tensile and creep properties for SEBM-built Co-Cr-Mo. Kircher et al. [Kircher et al. 2009] suggested that as-SEBM-built Co-Cr-Mo has significantly better mechanical properties as compared to its wrought and as-cast forms. The SEBM-built Co-Cr-Mo, however, was found to be more brittle with a markedly lower elongation before failure. This is especially so when the load was applied normal to the z-direction.
due to the high concentration of carbides along the grain boundaries. Recently, Tan et al. [Tan et al. 2018] studied the carbide precipitate behavior in SEBM-built Co-Cr-Mo alloy which can help to better understand its mechanical performance.

In this work, Co-Cr-Mo block samples were fabricated by SEBM. Microstructures of SEBM-built Co-Cr-Mo on X-Y plane and X-Z (or Y-Z) were examined. Moreover, both tensile and compressive tests were carried out along horizontal and vertical (or build) directions. This work presents preliminary results on microstructure and mechanical properties of SEBM-built Co-Cr-Mo parts.

**EXPERIMENTAL**

EBM A2XX system (Arcam EBM, Mönadal, Sweden) was used to fabricate Co-Cr-Mo samples. The schematic of A2XX EBM system can be seen in Fig. 1a. Its build envelop is 420 × 380 mm³. A standard build theme recommended by Arcam AB was applied. The nominal compositions of ASTM F75 pre-alloyed Co-Cr-Mo powder is 28.50Cr-6.00Mo-0.25Ni-0.20Fe-0.22C-0.70Si-0.50Mn-0.15N-Bal. Co (in wt.%). The powder size ranges from 45 to 106 μm as seen in Fig. 1b, which was supplied by Arcam EBM. Co-Cr-Mo block parts with a build length of 100 mm and build height of 30 mm with varying build thicknesses (Fig. 1c) were fabricated on a start plate of 210 × 210 × 10 mm³. The detailed SEBM processing can be found elsewhere [Tan et al. 2014; Kok et al. 2015].

![Fig. 1. (a) schematic of A2XX EBM system. (b) SEM image of ASTM F75 Co-Cr-Mo powder. (c) Photo of SEBM-built Co-Cr-Mo block parts with varying build thicknesses.](image)

SEBM-built Co-Cr-Mo blocks with a build thickness of 10 mm were chosen to study in this work due to its typical build thickness. Scanning electron microscopy (SEM; JEOL JMS-5600; 20 kV) and X-ray diffraction (XRD; PANalytical Empyrean; Cu Kα; step size of 0.01°) were used to examine the microstructure of as-built Co-Cr-Mo samples. Co-Cr-Mo blocks were sliced into squares of 10 mm and then were hot mounted. Metallographic samples’ preparation was carried out with a Struer’s Tagamin 25. 320# SiC papers were firstly used to grind the surface of as-built samples. Struer’s MD-Largo disc was then employed with Allegro/Largo 9μm suspension. It was followed by MD-Dac disc accompanied with Dac 3 μm suspension. The final polishing was conducted using a MD-Chem disc with OP-S active oxide polishing suspension. Electro-etching was performed using a 5% HCl solution under 2 V for ~10 s.
Tensile pieces with a gauge dimension of $12.5 \times 3 \times 1 \text{ mm}^3$ and cylindrical compressive pieces with a dimension of $\Phi 5 \times 7.5 \text{ mm}^3$ were extracted from both horizontal and vertical directions. In terms of the build thickness of 10 mm, the specimens of these two directions were termed 10mm_H and 10mm_V, respectively. Both tensile and compressive tests were carried out on the Instron Static Tester (model 5569) at room temperature. The tensile tests were conducted using a test rate of 0.1 mm/min while a test rate of 1 mm/min for the compressive tests. Engineering stress versus engineering strain curves were plotted for both tensile and compressive tests.

RESULTS AND DISCUSSION

The relative build density for the Co-Cr-Mo samples fabricated by SEBM in this work was measured to be higher than 99.2%. Fig. 2 shows the columnar grains along the build direction from both X-Z and X-Y planes. Columnar-grained microstructure is preferred in SEBM process owing to its rapid solidification rates coupled with high thermal gradients along the build direction. Each columnar grain consists of parallel dendritic structures with constrained secondary arms. Carbides were found to precipitate at both columnar grain boundaries and interdendritic regions. They became continuous thin films with a thickness of ~200 nm for the carbides appeared at grain boundaries, separating the adjacent columnar grains [Tan et al. 2018]. While the carbides existing at interdendritic regions tend to form long chains or clusters in morphology along the primary dendrites. It can be seen from the regular distribution of carbide particles that are separately with a nearly constant spacing of dendrites in Fig. 2b. Transmission electron microscopy (TEM) and atom probe tomography (APT) studies [Tan et al. 2018] have shown that two sorts of carbides (M$_6$C and M$_{23}$C$_6$) exist and both of them remain a cube-on-cube crystallographic relationship with face-centred cubic (fcc) γ-Co matrix, i.e. (100)$_{M_6C}$//(100)$_y$, [100]$_{M_6C}$//[100]$_y$, where M$_6C_y$ denotes the carbides. Furthermore, these two types of carbides can be distinguished in chemical composition, because M$_6$C is rich in Mo while M$_{23}$C$_6$ contains a high amount of Cr.

![Fig. 2. SEM images showing columnar grains carbides on (a) X-Z plane and (b) X-Y plane.](image)

Fig. 3 shows that the hexagonal close-packed (hcp) ε-Co phase also exist inside the microstructure of SEBM-built Co-Cr-Mo sample in addition to the popularly seen fcc γ-Co phase. That is because SEBM processing is a long-term high-temperature layerwise deposition process (>800 °C for Co-Cr-Mo) which favors the transformation from meta-stable fcc γ-Co phase into stable hcp ε-Co phase. Moreover, this fcc→hcp transformation would result in the formation of equiaxed ε-Co grains [Sun et al. 2015]. Due to the limited SEBM processing time, this transition in grain
morphology is usually incomplete and it presents a gradual trend from bottom to top along the build direction. It is noted that the quantity of equiaxed $\varepsilon$-Co grains is still limited in this 10 mm thick Co-Cr-Mo block samples according to both microscopy observation and XRD detection. In addition, no obvious carbide peaks were found in the XRD data in Fig. 3, meaning that the quantity of carbides within microstructure is still below 3-5% in volume fraction.

![XRD profile of SEBM-built Co-Cr-Mo sample.](image)

In order to examine the anisotropy in mechanical properties for SEBM-built Co-Cr-Mo parts, tensile and compressive testings were conducted in both horizontal and vertical directions. Fig. 4a shows the representative tensile stress-strain curves of horizontal and vertical specimens. It can be seen that both strength and elongation of the vertical specimens are much better than those of the horizontal specimens. Obviously, it still yet reaches the yield point for the horizontal specimen. Fig. 4b displays the representative compressive stress-strain curves of horizontal and vertical specimens. It is observed that the horizontal specimen has a higher yield strength but lower elongation and ultimate compressive strength compared to the vertical specimen.

There are two critical reasons for the mechanical anisotropy for SEBM-built Co-Cr-Mo specimens. Firstly, it is due to the orientation of the columnar grain boundaries in the $<001>$ direction which causes weaker grain boundaries for horizontal specimens as compared to vertical specimens. Horizontal specimens experience dislocation propagating along columnar grain boundaries which are parallel to them. The presence of grain boundaries thus allows a faster rate of crack propagation. In contrast, vertical specimens experience dislocation which are propagating perpendicular to the columnar grain boundaries. In this case, the grain boundaries hinder the propagation of dislocation instead. Secondly, the severe brittleness of SEBM-built Co-Cr-Mo specimen along horizontal direction is attributed to the thin carbide film precipitated at grain boundaries. Previous study [Tan et al. 2018] has shown that carbides precipitated at grain boundaries via the discontinuous mode and they were coherently grown with one columnar grain but incoherently with the other one. It is thus supposed that the weak incoherent carbide/$\gamma$-Co interface may cause the disastrous fracture when subjecting to the horizontal stress. Moreover, the
grain-boundary carbides have much less influence on the compressive properties. Regarding the tensile and compressive fracture mechanisms, fractography is needed to conduct in the future.

![Fig. 4. (a) Tensile stress-strain curves and (b) compressive stress-strain curves of SEBM-built Co-Cr-Mo samples.](image)

From the experimental results stated above, it is demonstrated that as-SEBM-built Co-Cr-Mo parts may not be directly employed in practical applications due to the significant anisotropic mechanical properties. Columnar $\gamma$-Co grain and continuous thin carbide film at grain boundary are supposed to be the two critical microstructure features that results in its poor mechanical performance at some certain direction. Post heat treatment is required to modify the microstructure with favourable equiaxed grains and discrete carbide precipitates for SEBM-built Co-Cr-Mo parts.

CONCLUSIONS

ASTM F75 Co-Cr-Mo samples were additively manufactured by SEBM method. The microstructure and mechanical properties of SEBM-built Co-Cr-Mo samples were investigated. The following conclusions can be drawn.

1. Anisotropic microstructure mainly consists of columnar $\gamma$-Co grain and continuous carbide thin film at grain boundary was observed in SEBM-built Co-Cr-Mo samples.
2. Anisotropic tensile and compressive properties were obtained for SEBM-built Co-Cr-Mo samples. The strength and ductility along vertical direction are better than those along horizontal direction. Severe brittleness fracture occurred when tensile stress was applied in horizontal direction.

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