Study of the Pore Formation on CoCrMo alloys by Selective Laser Melting Manufacturing Process

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ABSTRACT
Cobalt-base alloys are widely used in medical applications as is the hardest known biocompatible alloy with wear and/or corrosion resistance. The manufacturing process used on these alloys strongly influences the features produced, therefore it should be carefully controlled to attain the desired quality. Selective laser melting (SLM) is a novel process proposed for the fabrication of biomedical implants with cobalt alloys. In this technique, density is the most important concern as it has a direct influence on the component performance. Due to its different energy inputs given by its processing parameters, it has the potential to control porosity. In this work, SLM experiments were carried out on a CoCrMo alloy to study the formation of pores. The analysis showed that the SLM technique enables the building of high dense samples up to 99%, resulting in a mean of porosity of 5.77% and a pore mean size of 0.759 µm².

Keywords: selective laser melting; additive manufacturing; cobalt alloys; porosity.

1. Introduction
Over the years cobalt-chromium-molybdenum (CoCrMo) has demonstrated a remarkable level of versatility and durability as an orthopaedic implant material. These alloys are widely used in biomedical applications as is the hardest known biocompatible alloy with wear and/or corrosion resistance. Originally they were adopted for dental applications and lately they have been employed for body joints and fracture fixation applications. How these alloys are processed or manufactured can markedly affect the mechanical and metallurgical properties of the resulting components, therefore it should be carefully controlled to attain the desired quality. Investment casting and closed die forging remain the traditional processes used to manufacture cobalt-chromium-molybdenum alloy implants. Nevertheless, additive manufacturing (AM) is the novel candidate process for the fabrication of customized biomedical implants with cobalt alloys [1, 2].

Additive Manufacturing (AM) is one of the most developed technologies in recent years, it includes techniques as stereolithography (SLA), Selective Laser Sintering (SLS), Layer Object Manufacturing
Among them, SLM is now being demanded since it offers a lower time-to-market, a near-net-shape production, a higher material utilization rate, along with its ability to produce functional metallic parts with mechanical properties comparable to those in bulk materials [4, 5].

The SLM technology consists of building three dimensional objects layer by layer through melting selectively a powder using laser radiation. SLM, compared to the classical laser sintering, requires higher energy levels, which are normally achieved by applying a high laser power and by using thin powder layer thickness. Therefore, it suffers from several issues associated with the melting and consolidation phenomena of the metallic powders [5]. Typical concerns from the melt instability and large thermal stresses generated in the material include balling effect, porosity, lack of fusion, part distortion, cracks and delaminations. Among these defects, porosity is the most frequently reported in many metallic pieces manufactured by SLM. Moreover, it is the most important concern in this process as it is well known that it is detrimental to the mechanical properties, since pores act as stress concentrators leading to an earlier onset of plasticity and localizations of strains. Both morphology and distribution of pores in the component can have a significant effect on the mechanical behavior, and in turn, on the component performance [6-8].

The ideal objective in SLM is to obtain 100% dense parts, which means zero porosity, which is a challenge in the field due to a lack of mechanical pressure, as in moulding processes. By its counterpart, SLM is only characterized by temperature effects, gravity and capillary forces. In fact, porosity in the final part still remains a challenge even for conventional production techniques [6].

Previous studies have shown that SLM has the potential of controlling porosities according to the capacity of providing different energy inputs by its processing parameters [9]. In this work, SLM was applied on a CoCrMo powder to study the formation of pores and its relation with the processing conditions in order to understand its development and to control this setback.

2. Experimental Methodology

2.1 Material

Cobalt-chromium-molybdenum powder was used for the SLM experiment. The powder particles exhibited predominantly spherical morphology (Figure 1b) with a diameter sizes between 20 to 50 µm (Figure 1a).

![Figure 1. SEM images showing the CoCrMo powder particle morphology (a) Mag. 200x (b) Mag. 1000x.](image)

Table I. Chemical composition of the CoCrMo powder

<table>
<thead>
<tr>
<th>Element</th>
<th>Cobalt</th>
<th>Chromium</th>
<th>Molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt. %)</td>
<td>60.25</td>
<td>31.62</td>
<td>8.14</td>
</tr>
</tbody>
</table>
2.2 Equipment

In this experiment, a self-develop SLM machine was used, depicted in Figure 2. The system consisted on a vertical milling centre equipped with an Ytterbium-fiber laser type (FL x50s, Rofin) with a maximum power of 500W in continue wave, which operates at a wavelength of 1080nm. The welding head was equipped with a focal length and collimator of 125mm producing a minimum spot size of 150μm. The powder layers were deposited on a building platform, which consisted on a plate of Steel AISI 1045 with a built inclined plane in order to evaluate the process at different layer thicknesses.

![Vertical milling centre equipped with an Ytterbium-fiber laser type](image)

Figure 2. Vertical milling centre equipped with an Ytterbium-fiber laser type

2.3 Single track forming process

To simplify the interpretation, samples were built using a straight laser scan, as shown in Figure 3. Each experiment consisted on a single track of 230 mm in length, where the powder layer thickness was varied continuously from 40 to 500 mm. The building process was specified under four families or groups of experiments. Each family corresponded to a different scan speed value, and within each family the straight tracks were produced under different laser power values. The summary of the factorial design of experiments (DOE) used on the deposition are listed on Table II. The SLM process was performed without a controlled atmosphere.

![Scanning strategy used on SLM experiments Based from [4, 10]](image)

Figure 3. Scanning strategy used on SLM experiments Based from [4, 10]

<table>
<thead>
<tr>
<th>Runs</th>
<th>Parameters</th>
<th>Min</th>
<th>Max</th>
<th>Increment</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>P [W]</td>
<td>25</td>
<td>500</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>SS [mm/s]</td>
<td>33.3</td>
<td>83.3</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>LT [μm]</td>
<td>40</td>
<td>500</td>
<td>Continuous</td>
</tr>
</tbody>
</table>
2.4 Porosity Characterization

The outcome of the SLM testing was a platform containing 80 samples. The samples were then prepared by standard metallographic technique; the plate was cut from a cross section view by Wire Electrical Discharge Machining (WEDM), mounted on epoxy resin RSF 816 and ground using a SiC paper through fine 2000 grit size. After grinding, polishing was done with alumina suspension on 9.5, 3 and 1 µm synthetic cloths. In order to quantify the porosity and the pore mean size cross section images performed on Leica microscopy were used. The images where binarized using a threshold value. Then the porosity was calculated as the ration of the black to white pixels (shown in Fig. 4), which represented the fraction of the surface voids over the total surface. The pore mean size was acquired by particle analysis in ImageJ software.

Finally, the obtained data was statistically studied by analysis of variance (ANOVA) to determine the effect of the laser power (P), scanning speed (SS) and layer thickness (LT) and its interaction, on the porosity and pores formed during the experimental study.

![Image](binary_treated_image.png)

*Figure 4. Binary treated image, (SS= 50 mm/s, LT= 100 µm and P=425 W). Mag. 200x*

3. Results and Discussion

During the sintering, the total solid volume may be maintained and to reach this constant value, the shape and size of each particle change with the formation of grain boundaries. This change in solid particles is accompanied by the change of shape, size and fraction of pores in a unit volume. Therefore, since the aim of this research is to describe and study the pore characteristics formed on CoCrMo during SLM, the porosity along with pore morphology features as pore shape, size, and distribution will be presented in this section given that they have a profound impact on the mechanical behavior of the component. Furthermore, the presented results were analyzed to encounter the controllable relation with some process parameters [6-8].

3.1 Porosity

Primary porosity is due primarily by powder packing characteristics. The densification of these powder particles is the main purpose of the sintering. Therefore, the final primary porosity depends on the particle sizes of the initial CoCrMo powder, given that the compaction process starts with the rearrangement of these particles. Consequently, it can be said that using a distribution of diverse size particles (from 20 µm to 50 µm) on the present experiment ensured a good interdiffusion of the components into one another through vacancy movements and a large contact surface, which permitted to overstep from an initial porosity of 39.63% (Figure 5a) [11-13] to a lowest value of 0.9% and a 5.77% mean of porosity.

3.2 Pore Shape

Figure 6, a micrograph of the SLM sample cross section, shows the shapes of the present pores. Two different shape types of pores are distinguishable: round pores, which are formed during the sintering process; and irregular pores, which are formed during the compacting process.

The predominant shape encountered were the round pores, where its circularity resulted from 0.79 to 0.919; this can reflect the regularity of the shape in the pores formed. In general, the literature states
that irregular pores have a higher stress than perfectly round pores [12]. Moreover, irregular pores are a matter of serious concern as they show the faulty powder deposition and/or abrupt changes in powder environment, geometry or scanning conditions requiring a bigger effort for process optimization.

The contour of the round pores was also analyzed, and it can be observed rough and smooth walls in them. Pores found with smooth walls came from the final stage of sintering, were pores become isolated and any gas remaining becomes trapped, the rough walls can be derived by dendrite contraction.

3.3 Pore Distribution

In pore distribution studies, the structures are characterized in two main categories: regular porous structures and irregular porous structures. In this experiment, the pore architecture does not exhibit an orderly geometry and the pore formation was random, therefore exhibiting irregular porous structures. In Figure 7 is presented a section of a part produced by SLM in which it can be seen that the pore formation is arbitrary and homogeneously distributed in each cross section.
3.4 Pore Size

Depending on the size, pores are classified as micro-pores (<0.002 µm), meso-pores (0.002 – 0.05 µm) and macro-pores (>0.05 µm) [14]. The total amount of pores developed in the experiment belongs to the category of macro-pores, as the mean pore diameter was 0.9454 µm and the size, 0.759 µm². Statistically 95% of the pores had a diameter between 0.9199 and 0.9710 µm.

3.5 Influence of Processing Conditions

A statistical analysis was performed to calculate the variation and the influence of all the process parameters during the experiments. In the current study, the process parameters considered were: the laser power (P), the laser scan speed (SS), and the layer thickness (LT). Porosity and pore mean size of sintered parts were analyzed and evaluated as output variables. Moreover, as the interactions between the input parameters also resulted in variations on the porosity and pore mean size, they were also quantified as influential effects of the experiment.

The general factorial DOE analysis states that the mean of all the measured porosities (%) and pore mean size (µm²) of tested parts were 5.77 and 0.759 µm², respectively. The above results and the calculated effects are presented in Tables III and IV.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LT</td>
<td>9</td>
<td>0.122</td>
<td>0.0135</td>
<td>24.54</td>
<td>2.42E-16</td>
</tr>
<tr>
<td>SS</td>
<td>3</td>
<td>0.004</td>
<td>0.0015</td>
<td>2.778</td>
<td>0.0494</td>
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<tr>
<td>P</td>
<td>14</td>
<td>0.009</td>
<td>0.0006</td>
<td>1.236</td>
<td>0.2762</td>
</tr>
<tr>
<td>LT*SS</td>
<td>27</td>
<td>0.113</td>
<td>0.0009</td>
<td>1.747</td>
<td>1.1E-09</td>
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<tr>
<td>LT*P</td>
<td>118</td>
<td>0.100</td>
<td>0.0008</td>
<td>1.457</td>
<td>0.0934</td>
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<tr>
<td>SS*P</td>
<td>42</td>
<td>0.033</td>
<td>0.0008</td>
<td>1.457</td>
<td>0.0934</td>
</tr>
<tr>
<td>LT<em>SS</em>P</td>
<td>159</td>
<td>0.167</td>
<td>0.0010</td>
<td>1.906</td>
<td>0.0031</td>
</tr>
<tr>
<td>Error</td>
<td>56</td>
<td>0.030</td>
<td>0.0005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>428</td>
<td>0.582</td>
<td>0.0228</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table IV. ANOVA Table – Pore size

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LT</td>
<td>9</td>
<td>2.994</td>
<td>0.332</td>
<td>2.133</td>
<td>0.0414</td>
</tr>
<tr>
<td>SS</td>
<td>3</td>
<td>9.714</td>
<td>3.238</td>
<td>20.76</td>
<td>3.5E-09</td>
</tr>
<tr>
<td>P</td>
<td>14</td>
<td>3.597</td>
<td>0.256</td>
<td>1.647</td>
<td>0.0945</td>
</tr>
<tr>
<td>LT*SS</td>
<td>27</td>
<td>21.04</td>
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<td>4.997</td>
<td>1.9E-07</td>
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<tr>
<td>LT*P</td>
<td>118</td>
<td>26.53</td>
<td>0.224</td>
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<td>0.0635</td>
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<tr>
<td>SS*P</td>
<td>42</td>
<td>8.614</td>
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<td>1.315</td>
<td>0.1677</td>
</tr>
<tr>
<td>LT<em>SS</em>P</td>
<td>159</td>
<td>27.348</td>
<td>0.172</td>
<td>1.102</td>
<td>0.3423</td>
</tr>
<tr>
<td>Error</td>
<td>56</td>
<td>8.733</td>
<td>0.1559</td>
<td></td>
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</tr>
<tr>
<td>Total</td>
<td>428</td>
<td>108.57</td>
<td>5.3652</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As seen in the tables and in the statistical analysis, the main effects are highly significant, being LT for most influential factor for porosity and SS for pore size. Although not as high as the main effects, the interaction LT*SS, also presented evidence of substantial effect on both, porosity and pore mean size. The results showed that the porosity is reduced by increasing the layer thickness; and that is almost independent of the scanning speed. The latter trend can be seen visually on the Figure 8. This phenomenon may be explained as with a high layer thickness, a good particle packing is more likely to occur. Consequently, a greater contact area take place and in consequence, a more effective thermal conductivity, a Fuller densification and at last, a successful pore removal or shrinkage.

By the counterpart, the pore mean size remained equal under different layer thickness and laser power conditions, while at lower scanning speeds the pore mean size increased a noticeable 41.17%
Changes like recrystallization and grain growth, during sinterization may explain this occurrence. Based in the latter, the grain growth permits the densification and the removal or shrinkage of the pores. However, if high temperatures are maintained for extensive long times during sintering, as with lower scanning speeds, the pore growth can be promoted. As it was reported in [15], low scan rates can also decrease the density by contributing to the formation of large cracks and delamination of the sintered layers.

Initial efforts of the research were concentrated on determining the processing window for optimizing porosity issues. In the case of porosity, considering only the significant factors, the minimum porosity (2.00%) was acquired with the SS level of 50-66.6 mm/s interacting with the highest layer thickness, 500 µm (shown in Figure 9a). The smallest pores (0.197 µm²) were formed by a high level of scanning speed, 83.3 mm/s, interacting with a 500 µm layer thickness (Figure 9b).

4. Conclusions

In this study porosity features and its relation with SLM were systematically studied. The following conclusions can be made based on the results:

- The image analysis shows mainly round pores with smooth walls which came from gas entrapment. These were found in random allocation and all over the cross section of the sample.
- The SLM technique enabled the building of high dense samples, reaching a lowest 0.9% of porosity, and a mean of 5.77%.
- The minor porosity was produced by the highest layer thickness, which provided a better particle packing enhancing then the thermal conductivity among the particles and subsequently permitting a successful densification and finally the pore removal or shrinkage.
- The pore mean size, 0.759 µm², remained equal under different layer thicknesses and laser power conditions; while at lower scanning speeds the pore mean size increased a noticeable 41.17%. The literature states that if high temperatures are maintained for long times during sintering, pore growth will occur. This condition is fulfilled with lower scanning speeds, by which the exposure time to the laser radiation extends and therefore pore growth occurs.
- The optimized process window stated that minimum porosity was obtained with a scanning speed level of 50 mm/s interacting with the highest layer thickness, 500 µm. The smallest pores (0.197 µm²) were formed by a scanning speed level of 83.3 mm/s, and a 500 µm layer thickness.
5. Acknowledgements

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6. References


