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3D Printing of Biocompatible PM-materials

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Abstract

The fabrication of complex-shaped parts out of Co-Cr-Mo alloy and 316L stainless steel by three-dimensional printing (3DP) was studied using two grades of each alloy with average particle size of 20 and 75 µm, respectively. To produce sound specimens, the proper 3DP processing parameters were determined. The sintering behavior of the powders was characterized by dilatometric analysis and by batch sintering in argon atmosphere at 1280°C for 2h. The 3DP process has successfully produced complex-shaped biomedical parts with total porosity of 12-25% and homogenous pore structure, which could be suitable for tissue growth into the pores.

Keywords : biomaterials, 3D printing, rapid prototyping, Co-Cr-Mo alloy, 316L

1. Introduction

Rapid prototyping technologies can create physical parts directly from CAD models by generating a number of layers of a given material [1]. One of these flexible processes is three-dimensional printing (3DP) in which, a polymeric binder is used as glue to bound layer by layer powder particles together [2,3]. Regarding the potential of the process in manufacturing of complex-shaped parts out of both, metals and ceramics, there is much attention on extending materials and applications.

This technology creates a great opportunity in manufacturing biomaterial parts like implants and instruments. No much work can be found on fabrication of biocompatible PM-materials by 3DP process in literature. This paper deals with 3DP of Co-Cr-Mo and 316L stainless steel. The Co-Cr-Mo alloys have applications in fabrication of medical implants such as hips, knees and shoulders [4]. Although this alloy has very good corrosion and wear resistances, its toughness and fatigue strength is not as much as the medical-grade stainless steels. Therefore, both materials are still in use, and fabrication of functional prototypes out of these alloys is of importance. In this paper, the viability of 3DP in generating tailored implants with individual shape, specific porosity and material composition is addressed.

2. Experimental and Results

Co-28Cr-6Mo (nominal composition in wt%) and 316L stainless steel (Fe-17Cr-13Ni in wt%) gas atomized spherical powders with two different average particle sizes of 20 and 75 µm, respectively, were used in the present study. The sintering behavior of the powders was studied through sinter dilatometry (TMA 801, Behr, Germany).

Small cylindrical test specimens (15 mm diameter and 10 mm height) were generated by a 3D-Printer (RX-1, Prometal, USA) in order to find proper processing parameters including the drying time of a printed layer, speed of powder spreading and the layer thickness. Sound parts, were dried in a small oven at 230°C for 60 min in air and sintered at 1280°C in argon atmosphere. The heating and cooling ramps were 5 and 10 °C/min, respectively.

The sintered density was determined. Microstructural study was performed on the cross-sections of the sintered parts perpendicular to the printing direction. The amount of carbon pick up upon debinding and sintering was also analyzed.

Fig. 1 shows the dilatometric curves of the examined powders. In the case of Co-Cr-Mo powder, the shrinkage starts at ~1000°C and the maximum shrinkage rate occurs at 1260°C and 1270°C for the fine and coarse powders, respectively. The result of DSC showed that the solidus temperature of the alloy is 1266°C. Therefore, if sintering is performed at the higher temperatures, the materials turns mushy and rapid densification is attained by particle rearrangement and grain shape accommodation. Nevertheless, since in supersolidus liquid phase sintering the amount of the liquid phase strongly depends on the sintering temperature, part slumping is very susceptible. Therefore, a sintering temperature of 1280°C is reasonable to achieve a high densification without the danger of loosing the dimensional accuracy. In contrast to the Co-Cr-Mo alloy, solid state sintering is responsible for the densification of the stainless steels powders. Therefore, the amount of shrinkage is slightly, i.e. ~2%, lower than that of the Co based alloy. It means that for achieving higher densities, higher sintering temperatures must be afforded.

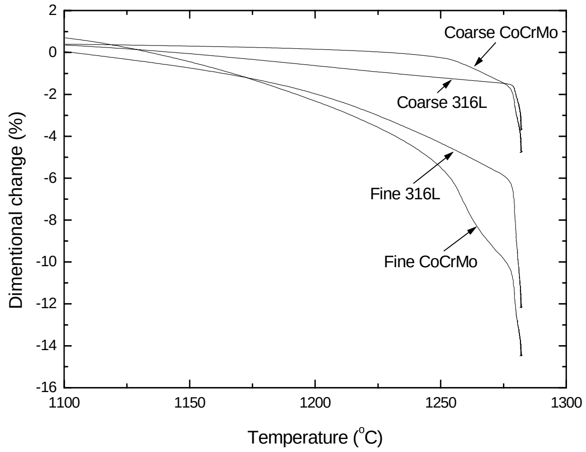

Fig. 1. Dilatometeric curves of Co-Cr-Mo and 316L powders sintered at 1280 °C for 120 min in argon.

By comparison of the results of process optimization tests, it was found that applying a high layer thickness leads to unbounded layers whilst a low layer thickness results in pushing away of the printed layers during spreading. The proper layer thickness was determined at 75 and 150 μm for the fine and coarse powders, respectively. On the other hand, the duration time for the binder curing should be high enough to achieve sufficient green strength. It was found that 60 s with a powder spreading speed of 10 mm/s yield reasonable result.

Fig. 2 shows the green and sintered (at 1280°C for 120 min) density of the 3D printed cylinders produced at the conditions reported above. The green density of the printed coarse powders is nearly equal to the tap density whilst the fine powders yielded lower density. This suggests that during 3D Printing, agglomeration of the fine particles is likely to occur. The agglomeration of powder particles influences the densification of the green part during subsequent sintering. One can notice the higher densification of 3DP parts compared to the tapped powders when the coarse particles were used. It seems that the agglomerated particles cause a network of large pores, which in fact, cannot be removed during sintering.

By metallographic studies, large pores in the microstructure of the Co-Cr-Mo part produced from 20 μm powder were found. In contrast, the microstructure of parts made from the coarse powder consists of relatively homogenous large pores that could be suitable for biomedical application (Fig. 3). When fine 316L powder is used, the amount of porosity is low, i.e. ~12%, whilst most of the pores are relatively small. Using coarse 316L particles resulted in a higher porosity (~20%) with a significant amount of large (~100-300μm) pores.

In addition, the amount of carbon pick up during debinding and sintering is very important concerning the effect of carbon on the corrosion behavior. The measured carbon pick up is 0.2 and 0.07 wt% for the fine and coarse powders, respectively. This is attributed to the lower layer thickness used for 3DP of the fine powders, which directly influences the amount of binder used for printing. Additionally, the debinding of green parts composed of finer particles needs more attention since the pore channels are smaller.

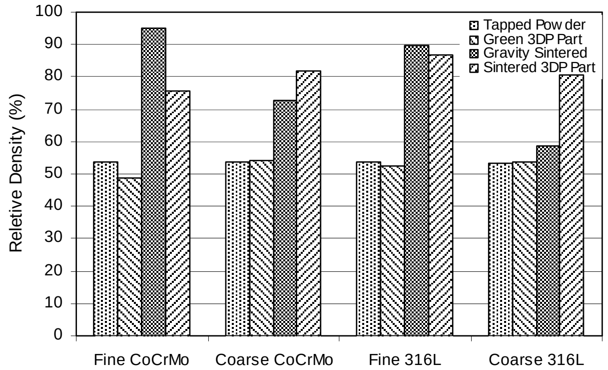

Fig. 2. Green and sintered density of 3DP cylinders and tap density of raw powders.

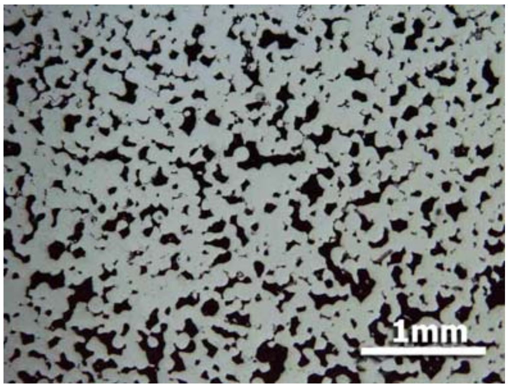

Fig. 3. Cross-sections of printed part from coarse Co-Cr-Mo, after sintering at 1280 °C for 120 min.

3. Summary

The 3DP process was used to fabricate biocompatible P/M components using Co-Cr-Mo and 316L powders. It was shown that powders with average particle size of 75 μm by utilizing the layer thickness of 150 μm, spreading speed of 10 mm/s, and drying time of 60 s, can be used for successful manufacturing of complex-shaped parts. Sintering at 1280°C for 120 min yields sound parts with ~20% porosity. The pores are open and large to get tissue the possibility of in growth. By controlling the sintering condition, the amount of porosity can be tailored dependent on the application.

4. References

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