

DEVELOPMENT OF INJECTION MOULDED CO-CR-MO ALLOY POWDER USING PALM BASED BINDER

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ABSTRACT

Metal Injection moulding (MIM) is an advanced near net shape forming process for high quality of complex shapes combined with high properties of materials. For economic reasons, it is necessary to have demand for a large quantity of parts. This paper presents the attempt to manufacture metallic implant using CoCrMo alloy powder by MIM process. The CoCrMo alloy powder with the median particle size of 15 μm and a binder consisting of palm stearin and poly ethylene were mixed at 160°C using a sigma-blade mixer for one hour to prepare the feedstock of the test bar. The test bar was injection moulded using vertical injection moulding machine with the nozzle temperature of 200°C. Prior to sintering, the specimens were debound using a combination of solvent extraction and thermal pyrolysis method. The specimens were then sintered under vacuum at the temperature between 1350°C to 1390°C. The properties of the sintered bar such as physical appearance and densities were presented and discussed.

Keywords: Metal Injection moulding; CoCrMo; feedstock; solvent extraction; sintering;

INTRODUCTION

Cobalt based alloy may be generally described as a non magnetic, wear , corrosion and heat resistant. Today, the use of Co based alloy for surgical applications is mainly related to orthopedic prostheses for the knee, shoulder and hip as well as to fracture fixation devices. Joint endoprotheses are typically long term implants and the applied implant materials must therefore meet extremely high requirements with regards to biocompatibility with the surrounding body tissue material and corrosion resistance to body fluids. Materials properties for various Co-Cr-Mo compositions and processing routes are covered by a number of ASTM specifications [1]; such as ASTM F75 for common composition and can be cast, ASTM F1537 for wrought and forged by ASTM F799. At least three methods of manufacture are used to make Co-Cr-Mo implants: precise (lost wax) casting, hot forging and powder metallurgy [1-7]. Casting is often selected for surgical implants processing route while for high volume applications, metal injection molding (MIM) is applied. The purpose of this study is to investigate the processing characteristics of injection molding of Co-Cr-Mo alloy for medical applications using MIM process.

EXPERIMENTAL DETAILS

The 90 %-22 μm F75 Co-Cr-Mo powder used in the present study was obtained from Sandvik. The mean particle size distribution was determined using HELOS Particle Size Analysis WINDOX 5 and around 9 micron. A scanning electron micrograph showing the powder morphology is indicated in Figure 1. The powder was mixed with a natural polymer based binder (palm stearin) at a solid loading of 65-volume % for injection molding. The binder system consists of 70-weight % of palm stearin and remaining 30-weight % of polyethylene, which represent the remaining 35-volume %. Mixture of powder and binder were dry mix followed by the entry into the Z-Blade mixer heated to 160 °C. The mixing was left for 1 ½ hour. After mixing has completed, the heater was shut off and the feedstock was allowed to cool with the mixing blade still in motion. This procedure gives a granulated feedstock.

The granulated feedstock then injected into tensile bars using a simple, vertically aligned and pneumatically operated plunger machine, MCP HEK-GMBH. Feedstock was fed into the barrel and then injected through the nozzle in the mold cavity. Test bars were successfully molded at temperature of 220 °C at pressure 65 psi. The dimensions and weight including density were measured in order to determine the solvent removal and shrinkage after sintering. The densities of the specimens were measured using water immersion method.

The test bars were debound by a two-step process where at the first stage the samples were solvent debound in order to remove all the wax portion of the binder, in this case palm stearin which is consist the major fraction of the binder. Molded samples termed the green body were arranged in a glass container, which then immersed in heptane and held at temperature 60 °C for 5 hours. The glass container was covered to prevent evaporation of the heptane during extraction. Subsequent thermal pyrolysis was performed in Lynn Furnace. The thermal debinding cycle consisted of 1 °C/min to 450 °C and soaking for 1 hour before furnace cool. Sample that completely undergoes thermal debinding termed the brown body. The components were sintered in vacuum furnace with the heating rate at 10°C/min to the sintering temperature 1390 °C, and held for 1 hour at this temperature before cooled down by furnace cool. The dimensions, density and weight of the sintered specimens were measured to calculate sintered shrinkage and final density. Tensile properties of the sintered samples were determined using an Instron Series IX Automated Materials Testing System. The yield strength, ultimate strength and elongation were measured at strain rate of 0.1/s [7]. Finally, the microstructure analysis carried out using optical microscopy and scanning electron microscopy.

RESULTS AND DISCUSSION

Powder Characterization

The volume ratio of solid powder to the total volume of powder and binder is defined as the powder loading. In general, it is expected that MIM feedstock has a higher powder loading. Higher powder loading means smaller volume shrinkage of moulded specimen and easier for dimension tolerance control. Nevertheless, too high powder loading is also unacceptable because it will lead to a too high feedstock viscosity and results in failure during injection moulding. Consequently, a suitable powder loading has to be established. A curve of torque evolution for CoCrMo is depicted in Figure 1. The point of addition of oleic acid can be observed as an increase of torque reading as shown in Figure 1. The shape of torque curve is typical of mixing done with sequential addition of oleic acid in metal powder.



Figure 1: The torque curve for determination of powder loading

All the particles were approximately spherical, as indicated in Figure 2. Some particles are large spheres and some are very small. Easier molding and a high solids loading are favored by spherical particles [5]. The spherical shape of the particles will result in higher packing density, easier molding. Small particles agglomeration is a common problem.

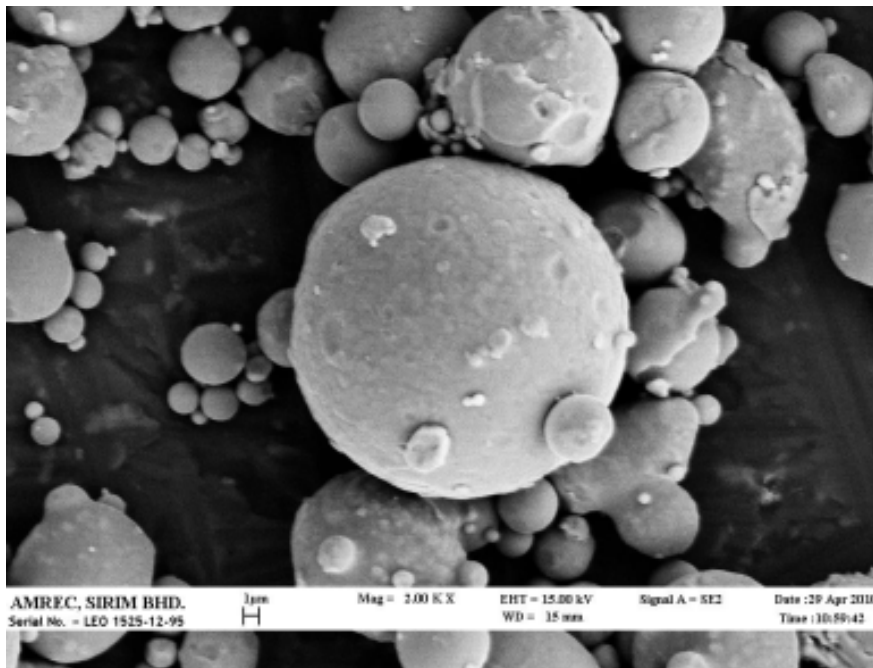


Figure 2: Scanning Electron micrograph of the CoCrMo alloy powder

Injection Moulding of the Feedstock

The detail of the processing parameters during injection is in Table 1. All the injection parts were good and free from normal defects such as short moulding, obvious flashes at the parting surfaces and obvious separation between the powder and binder.

Table 1: Moulding parameters (optimum) for producing fracture fixation plates component

Moulding parameters	value
Injection temp	200- 210°C
Injection pressure	300 bar
Cycle time	10-15 sec
Mould temperature	Room temperature

Figure 3 clearly shows the SEM of the green specimens at two different regions; at the fracture surface and on the outer surface for three different particle sizes. It can be seen that, the binder fills practically all the interstitial spaces between the powder particles. The outer surface is filled with more binder than those of fracture surface. This is due to a greater contact of feedstock flow to the cavity wall and also that was the area to solidify first.

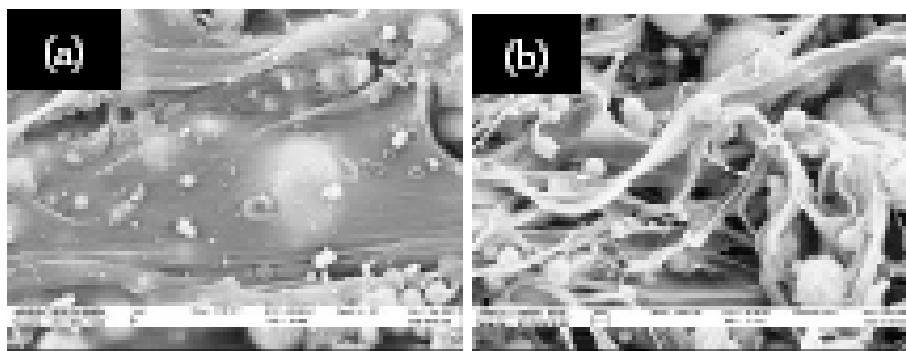


Figure 3: Scanning electron micrographs of the green specimen. a) surface and b) fracture

Solvent Extraction Process

Figure 4 shows the effect of solvent temperature on the rate of binder extraction. It shows that the rate of extraction increase with increasing solvent extraction temperature.

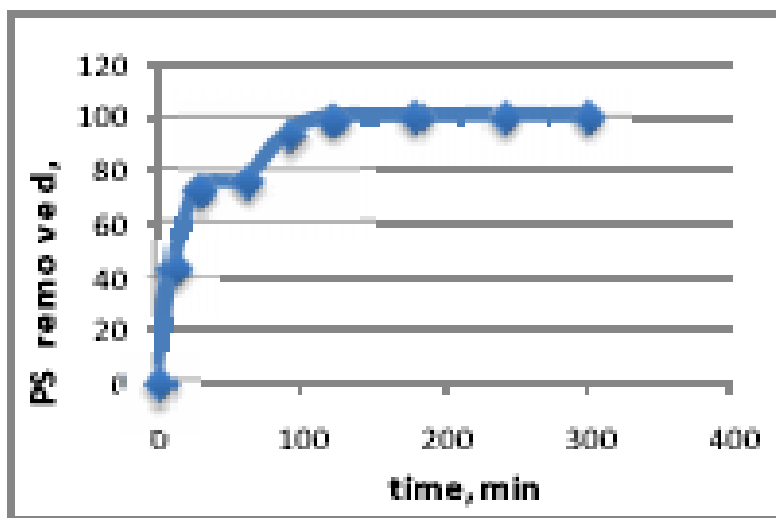


Figure 4: The effect of solvent temperature on the rate of solvent extraction process

For the first 2 hours, the slope of the curves are steep, which apply that the removal rate of palm stearin are fast because of more interconnected pore channels through which dissolved solution can diffuse to the surface. Moreover, the solvent is easy to leach the soluble binder component since the binder phase is on or near the compact surface, thus the debinding rate is faster. Dissolution is the rate-determining in the first step. After 2 hours, the slope of the curve is slightly horizontal which mean that the removal rate of the palm stearin is slow down. As debinding proceeds, the core portion of the compact containing binder recedes from the surface, making diffusion is the rate-determining

step. The removal rate of palm stearin becomes smaller as a solvent extraction time increases owing to the increased length of porous channels through which the polymer diffuse out.

The binder distributions and evaluation of interconnected porosity with time during solvent extraction for various temperatures in heptane were observed using scanning electron microscopy (SEM). Different areas of the debound components were examined, including the outer and the central regions of fractured surface in order to monitor the progress of the solvent extraction process. Figure 4 shows the formation of the open pore channels as the palm stearin is extracted from the moulded specimens at different time.

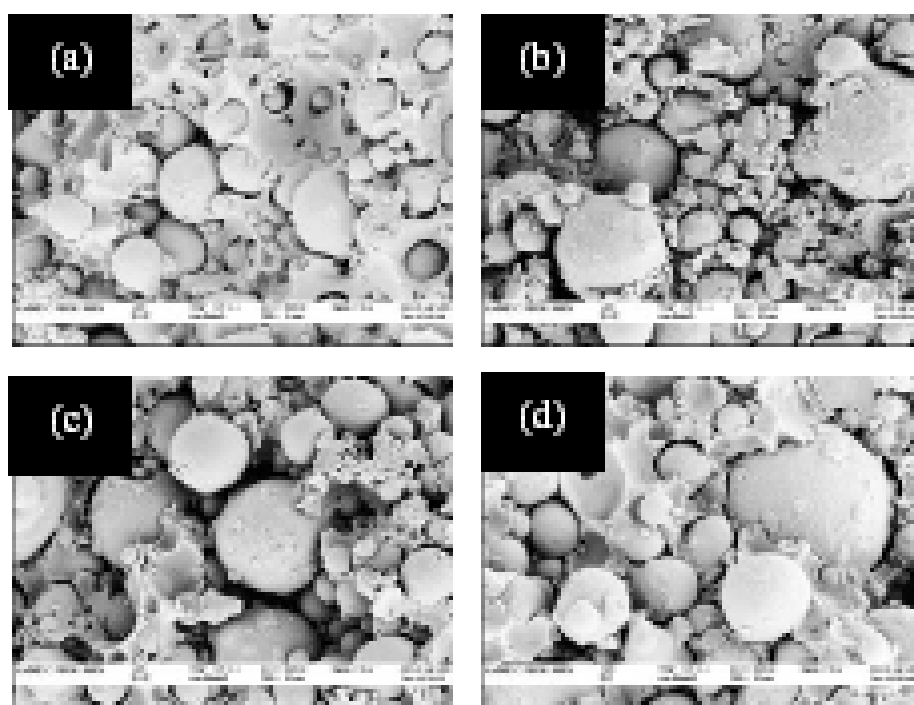


Figure 5: SEM morphology of solvent extracted fractured surface: (a) 10, (b) 90, (c) 180 and (d) 300 minutes

These samples were immersed in the heptane bath at 60 °C. As the time increased, the weight loss of palm stearin increased and the pore channel enlarged. SEM of debound specimen with extracting time of 10 minutes (Figure 5(a)) showing that there are much amount of binder left interstices between the powder particles. But small amount of palm stearin left between the powder particles after 120 minutes (Figure 5(c)) while Figure 5(d) indicates all the palm stearin was removed after 240 minutes. It is clearly seen that a network of porous polyethylene ligaments remained, binding and holding the powder particles together to provide the moulding with sufficient brown strength to be handled.

Thermal Pyrolysis Process

SEM micrograph of the samples heated to 450 °C is shown in Figure 6. The rate of degradation of polyethylene is low at lower temperature and increases as the temperature increases. Moreover, the diffusivity of the thermal degradation products will increase with rising temperature. After aqueous extraction of the palm stearin there are sufficient pore channels in the extracted compacts to allow for the rapid escape. Thus the rate of formation of the volatile products is the rate controller factors. When the temperature reached about 300 °C, it was observed that almost of the polyethylene had decomposed. At 450 °C, its removal was completed.

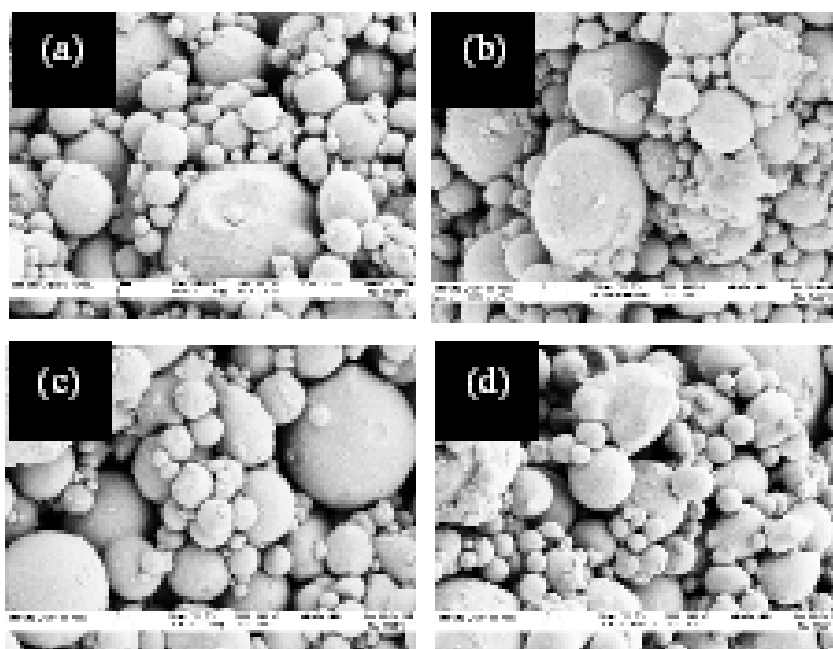


Figure 6: SEM morphology of different heating rate thermal debound fractured surface of: (a) 1 °C/min; (b) 3 °C/min, (c) 5 °C/min and (d) 10 °C/min

Sintering Process

No defects such as cracks, distortion which might affect the properties were observed in the sintered samples. Figure 7 shows the relationship between sintering temperature and the density. As the sintering temperature increased, the sintered density, as expected, increased. The pores become more rounded. Consistent with increasing density, the measured linear shrinkage increased with increasing sintering temperatures.

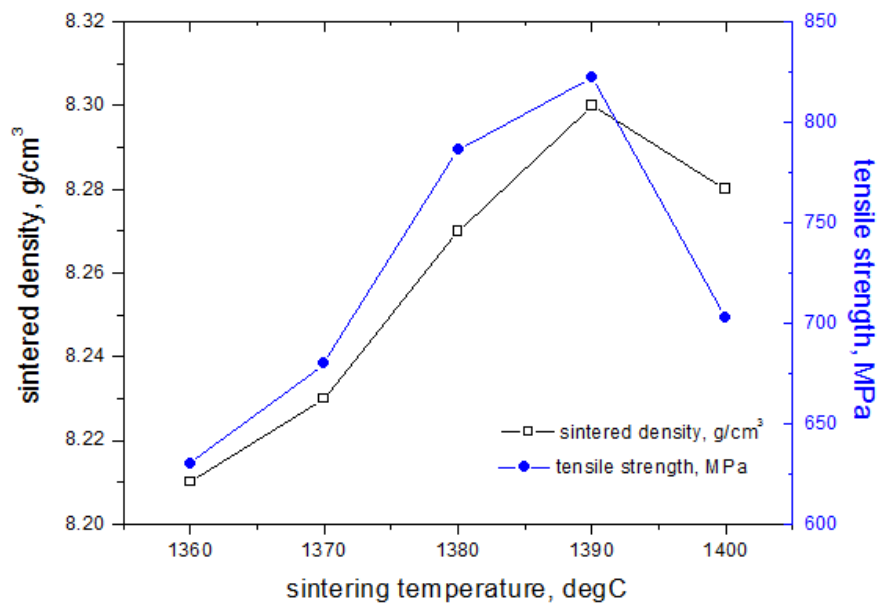


Figure 7: The effect of sintering temperature on sintered densities and ultimate tensile strength

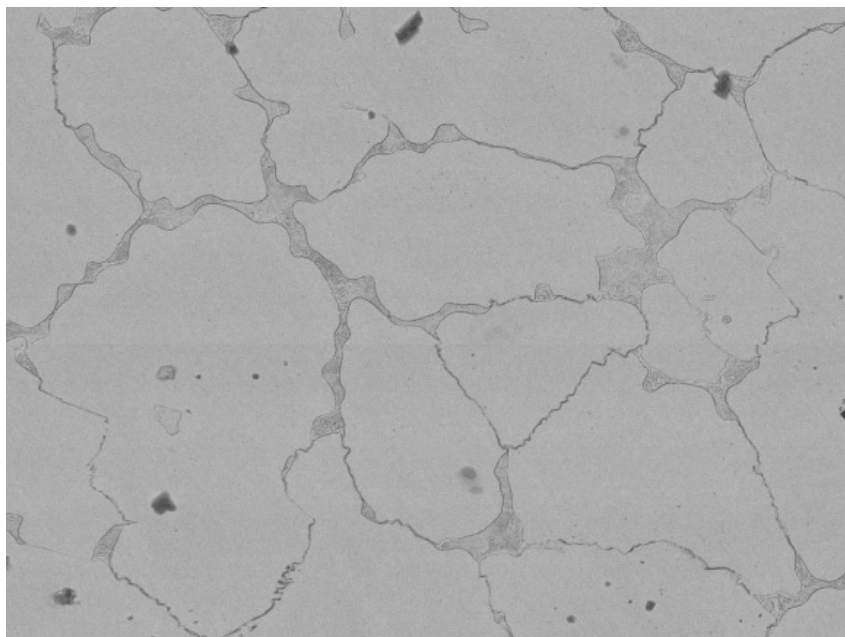


Figure 8: The microstructure of CoCrMo alloy after etching

This powder is usually sintered slightly above its solidus temperature; however, the solidus temperature varies depending on composition, especially carbon content [1]. The high packing density of the F75 powder resulted in high final density that is 8.3

g/cm³. As can be seen, the samples average density is almost the same as ASTM F75 density, which is more than 8.20 g/cm³. As expected with the decreasing in porosity, increased the sintering temperature improved the sintered density and ultimate tensile strength. The optimal sintering temperature was 1390 °C. After this, the properties of the sintered sample decreased.

Microstructure of the etched samples sintered at 1390 °C in vacuum is shown in Figure 8. Etching results in clearly defined grain boundaries, indicating that they are chemically different from the grains.

CONCLUSION

It was shown in this study that the CoCrMo alloy powder was successfully injection moulded using the palm based binder using a temperature of 210 °C with maximum injection pressure of 300 bar. The moulded samples were good and free from normal defects such as short moulding, flashing and parting surfaces. The highest final sintered densities were about 99.9% of theoretical maximum value with good mechanical properties which comply to the standard ASTM F75.

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