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Original Research Article

Processing and In-Vitro Study of Injection Moulded Cocrmo Alloy Hip Stem for Orthopedic Applications

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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. The concept of the MIM is based on mixing of the fine powders with a small proportion of polymer to form a feedstock that can be moulded. The granulated feedstock is then giving shape using injection moulding machine. After shaping, the polymer binder is then removed from the moulded part without significant disturbing the powder particles. Then, the powder is sintered at high temperatures. This paper discussed the mechanical properties and in-vitro evaluations of injection moulded cobalt based alloy for potential orthopedic applications. The CoCrMo alloy powder with the median particle size of 15 □m and a binder consisting of paraffin wax and poly ethylene were mixed at 160□C using a sigma-blade mixer for one hour to prepare the feedstock. 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 of 1380ºC. The properties of the sintered bar such as physical appearance and densities were presented and discussed. In-vitro evaluation of the sintered bar also has been conducted and discussed.

Keywords: Metal Injection moulding, CoCrMo, feedstock, sintering, in-vitro.

INTRODUCTION

Cobalt-chromium alloys are commonly used for surgical implants because of their high strength, superior corrosion resistance, non-magnetic behavior and biocompatibility [1]. Applications include prosthetic replacements of hips, knees, elbows, shoulders, ankles and fingers, bone plates, screws, staples, and rods; and heart valves [1]. Joint endoprostheses are typical long-term implants, and the applied implant material must therefore meet extremely high requirements with regard to biocompatibility with the surrounding body tissue material and corrosion resistance to body fluids [1]. Various in vitro and in vivo tests have indicated that the alloys are biocompatible and suitable for use as surgical implants [4].

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 [4]. Casting is often selected for surgical implants processing route while for high volume applications, metal injection molding (MIM) is applied.

Metal injection molding (MIM) is a novel process, which combines plastic injection molding and conventional powder metallurgy technologies. It is a combination of four sequential technological processes which is mixing - compounding the metal powder and organic powder into feedstock, injection molding – shaping the parts from feedstock as in plastic injection molding, debinding – removing the binder in the molded parts by pyrolysis or solvent extraction and sintering – densifying the debound parts to a high final density. Every process involved in MIM has significant impacts on the characteristics of the final parts. The feedstock has to be as homogeneous as possible made by intensive mixing of metal powder and the binder. In the next phase, a green body is made by injection molding. Then the binder is removed from the green body in various debinding processes. The brown body produced retains its shape due to friction between the metal powder particles. This part is very fragile and need to be sintered carefully to achieve its final density

and the desired mechanical, chemical and dimensional properties. A high final density is important for optimization of the desirable attributes. The final properties of the product can be further improved with additional heat and mechanical treatments [5-7].

The purpose of this study is to investigate the processing characteristics of injection molding of CoCrMo alloy for medical applications using MIM process. In addition, in-vitro study also has been investigated and discussed**.**

MATERIALS AND METHOD

The 90 %-22 µm F75 Co-Cr-Mo powder used in the present study was obtained from Sandvik, UK. The mean particle size distribution was determined using HELOS Particle Size Analysis WINDOX 5 and around 15 micron. A scanning electron micrograph showing the powder morphology is indicated is Figure 1The 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^{o}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 200^{o}C at pressure 300 bar. 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 removed 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^{o}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^{o}C/min to 450^{o}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^{o}C/min to the sintering temperature 1390^{o}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 [8]. Finally, the microstructure analysis carried out using optical microscopy and scanning electron microscopy.

For in-vitro study, the test material is extracted for 24 hours in Minimum Essential Medium (MEM). An extract is prepared from the test material which is then placed on cell monolayers. The cells are examined for morphologic changes, malformation, degeneration and cytolysis to determine a toxicity score ISO 10993-5(E). Biological evaluation of medical devices – Part 5: Tests for *in vitro* cytotoxicity. 2009.

RESULTS AND DISCUSSION

Debinding Process

To minimize the possibility of defects with safe and fast binder removal, solvent debinding followed by thermal debinding was used in this study. The multi-component binder chosen includes the lower stability components of palm stearin wax which is removed in early stage of debinding and generate pore channels inside of the part that allow gaseous products of degradation of remaining binder harmlessly diffuse out of the structure while PE has a function of holding particles together during and after extracting lower stability components to maintain the part shape. Solvent debinding was carried out by means of heptane as a solvent at 60 °C only for 5 hours. It is considered that after removing 40% of binder, there exists some interconnected capillary porosity inside of samples which makes leaving of gaseous products in subsequent thermal debinding easy in short time. Since nearly 70% of palm stearin was removed in solvent debinding step, subsequent thermal debinding can be performed with higher speed in comparison with usual thermal debinding process.

Different heating rates and sintering environment were performed to optimize the suitable heating rate can used later. The test samples were thermally debond successfully at temperature 450°C and dwell time 1hr. The reason of selecting this temperature was complete decomposition of binder in the previous study. Five different heating rates were used from 1ºC/min to 10 ºC/min to select for debinding process.

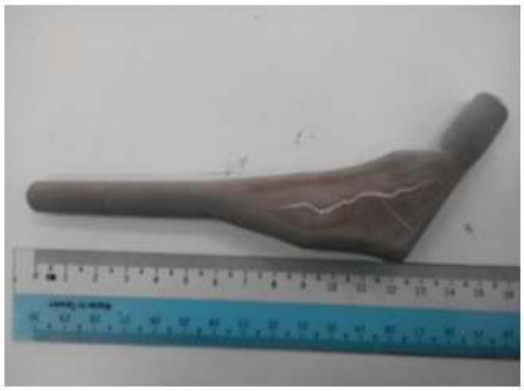


Fig-1a

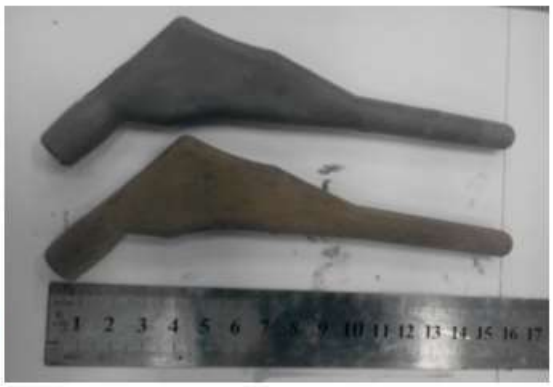


Fig-1b

Fig-1a Comparison of dimensions of test samples after solvent extraction and thermal pyrolysis. Test samples subjected to heating rate 0.1˚C/ min at temperature 450°C for 1 hr show no defects. Fig-1b Thermally debound test sample subjected to heating rate 1˚C/ min at temperature 450°C for 1hr shows swelling and cracks

It was observed that at heating rates 1°C/min, 0.5°C/min, 0.3°C/min and 0.1°C/min were study to optimise the thermal pyrolysis stage. It was shown that only 0.1°C/min gave the best appearance without any blistering on the surface, as shown in Fig-1. However, when the heating rate was increased to 0.5 to 1°C/min the swelling and cracks appeared on the surface of the test samples as shown in Figure-1. Based on these results, it was considered that the most suitable heating rate for debinding rate is 0.1°C/min. From room temperature to 450°C, the temperature increased by 5°C/min and held at that temperature for 1 hour, which removed the binder system used.

Sintering Process

A sintering temperature of 1380^{o}C was chosen for densification of the test bar in vacuum atmosphere. Pores are eliminated as part of particle bonding during high-temperature sintering [5]. Sintering densification normally take place close to the me melting temperature of the material, where the bonds of the particles are bonding together by the atomic motion of the individual atoms via either solid state or liquid phase. As the temperature arises, the atomic motion occurs faster. Likewise, sintering temperature differs for each material. This powder is usually sintered slightly above its solidus temperature; however, the solidus temperature varies depending on composition, especially carbon content [2, 3].

The fracture surfaces of the specimen are shown in Figure-2 reveal clearly the different morphology between the stage of pre-sintering process to sintering process. Sinter bonding is evident as bonds grow at the particle contact. The establishment of interparticles bonds by partial fusion is clearly seen. Increasing the temperature up to 1100°C extends the fusion bonding further with a substantial reduction in porosity. The particles take many paths to form the bonds. The original shape of the powders can still be discerned, although the particles have been fused together. As the bonds become larger, they impinge on each other and form a network of pores as shown in Figure-2 at sintering temperature of 1380°C.

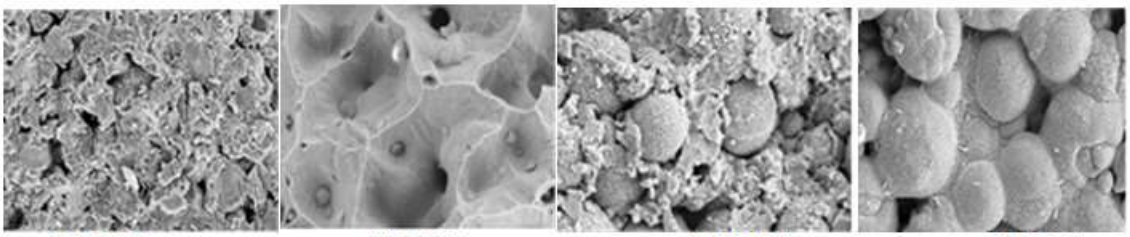


Fig-2: The fracture surfaces of the specimen reveal clearly the different morphology between the stage of pre-sintering process to sintering process

Sintered sample properties are shown in Table-1 as sintered at 1380°C in vacuum. The high packing density of the CoCrMo powder resulted in high final density that is 8.20 g/cm^3. As can be seen, the samples average density is almost the same as ASTM F75 density, which is 8.28 g/cm^3. Figure-3 shows the sintered hip stem prototype after sintering and polishing.

Fig-3: Sintered hip stem produced using MIM process after polishing

The sample indicated ductile fracture during tensile test. High rate of densification during sintering resulted in high packing density due to less porosity remain in the sintered body.

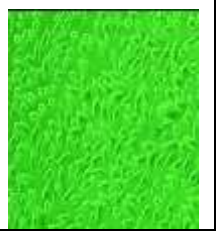
Table-1: Sintered properties of injection moulded CoCrMo alloy powder

Samples	MIM process	ASTM F75-07
Density (g/cm^3)	8.20	8.28
% from theoretical	99.0	100
Ultimate tensile strength (MPa)	822	655
Elongation (%)	10.4	>8
Hardness,	42 HRC	35

Cytotoxicity Study
(MEM Elution)

The hip stem is extracted for 24 hours in Minimum Essential Medium (MEM). An extract is prepared from the test material which is then placed on cell monolayers. The cells are examined for morphologic changes, malformation, degeneration and cytolysis to determine a toxicity score. L929 mouse subcutaneous connective tissue fibroblast cells (*Mus musculus*, NCTC clone 929, CCL-1™) was used as a cell line.

Table-2: Grading of test material CoCrMo alloy

	control	200 mg/ml	100 mg/ml	50 mg/ml	25 mg/ml
Grade	0	0	0	0	0
	0	0	0	0	0
	0	0	0	0	0
	0	0	0	0	0
Mag: 100x					

The results of grading is shown in Table-2. It was shown that the cells morphology are not much different from that of the control and this indicates that there is no morphological abnormalities taking place. Cells growth towards the material under test demonstrates good biocompatibility, particularly on longer incubation time which also indicates good material-tissue integration. Grade 0 mean that discrete intracytoplasmic granules, no cell lysis and no reduction of cell growth. All concentration tested exhibited 'none' reactivity. From the inverted light micrographs, it can be observed and seen the appearance of discrete intracytoplasmic granules, no cell lysis and no reduction of cell growth. All concentration tested exhibited 'none' reactivity. The hip stem samples produced by MIM process shows that the materials tested is not cytotoxic and should be considered for further in vitro testing.

This assay is a proven cell viability indicator that uses the natural reducing power of living cells to

convert resazurin to the fluorescent molecule, resorufin. The active ingredient of Alamar Blue (resazurin) is a nontoxic, cell permeable compound that is blue in color and virtually nonfluorescent. Upon entering cells, resazurin is reduced to resorufin, which produces very bright red fluorescence. Viable cells continuously convert resazurin to resorufin, thereby generating a quantitative measure of viability

To evaluate the cytotoxicity of test material CoCrMo alloy by determining the percentage of cell viability. L929 cells demonstrated good cell viability on all four different batches of CoCrMo alloy. More than 90% cells viable on all concentration tested showing no toxic effects released from the test materials. The test materials induced cell viability and cell growth increment.

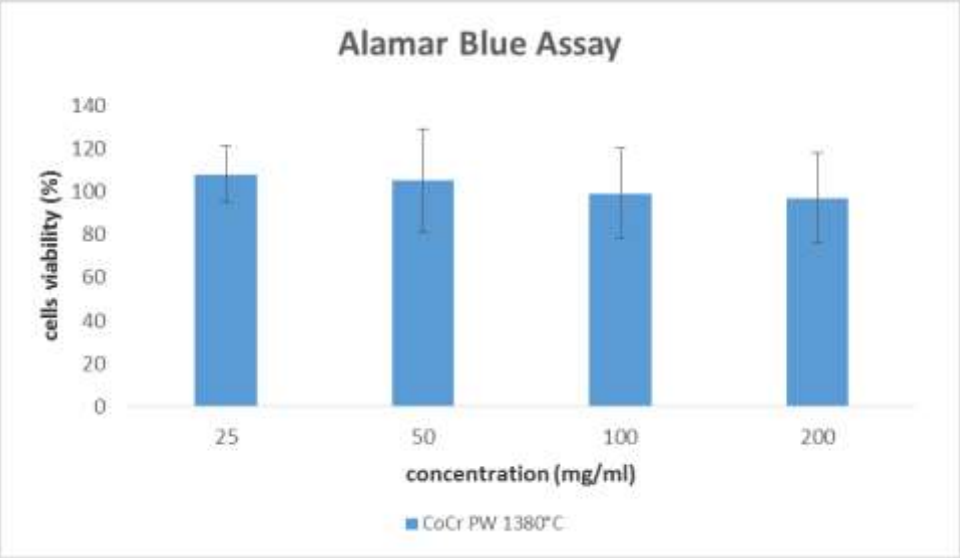


Fig-4: The percentage of cell viability

CONCLUSIONS

Through some modification on some MIM processes, the MIM process has successfully implemented the F75 CoCrMo alloy 22 um powder. Powder characteristics, mixing and molding is quite a critical stage in MIM for cobalt based powder. The physical and mechanical properties achieved comply with the International Standard, ASTM F75. The hip stem samples produced by MIM process shows that the materials tested is not cytotoxic and should be considered for further in vitro testing

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