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Net-shape Forming of Porous 17-4PH Stainless Steel via Metal Injection Molding-Space Holder Technique

Nor 'Aini Wahab[1], Nik Rozlin Masdek[1], Anizah Kalam[1], Fauziah Mohd Yusof[1], Rosniza Rabilah[2]*
[1]Faculty of Mechanical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[2]Faculty of Mechanical Engineering, Universiti Teknologi MARA, 13500 Permatang Pauh,Pulau Pinang, Malaysia
**norainiwahabitm@yahoo.com*

ABSTRACT

Porous metal which displays unique combination of properties such as excellent biocompatibility, good corrosion resistance and decent mechanical strength near human cellular bone has huge potential in biomedical applications. This paper presents fabrication of porous 17-4PH stainless steel via a combination of Metal Injection Molding and space holder technique (MIM-SH) by incorporating saccharose as the space holder at the feedstock preparation stage; followed by injection molded the feedstock at injection temperature and pressure of 160°C and 7 bar. The study was performed by replacing the 17-4PH stainless steel (17-4PH SS) with 20wt% saccharose at powder loading of 65 vol% and utilizing a binder system consisting of palm stearin (PS) and low-density polyethylene (LDPE). The results obtained clearly demonstrated that saccharose is a promising space holder material that could be employed in production of a near net-shape porous 17-4PH SS with a network of interconnected open pores which are separated by dense cell walls.

Keywords: *17-4PH stainless steel, saccharose, Metal Injection Molding, space holder, porous.*

Introduction

Owing to its high strength and high apparent hardness whilst exhibiting superior corrosion resistance, the 17-4PH SS is extensively utilized in various applications such as metal working, aerospace, chemical and medical industries [1]. Nevertheless, the mismatch of Young's Modulus between bone (10-20 GPa) and bulk metallic material which is around 205 GPa for Fe-based alloys results in an inhomogeneous load transfer between the dense metallic implant and the surrounding tissue or bone. The inhomogeneous load transfer leads to stress shielding of the host bone which has been identified as the major cause for implant loosening [2-5]. The presence of highly interconnected open pores structure in porous metal that may promote bone ingrowth and enhance the osseo-integration of the implant is capable to offer solution to problems associated with the stress shielding effect [6].

Porous metallic implants that promote a better fixation of the implants to the bone host can be produced by a variety of industrially applied techniques. The resulting porous structure such as the quantity, geometry and pore arrangement are greatly affected by the manufacturing technique employed. It is interesting to note that the Powder Metallurgy technique is capable to offer a near net-shaped products with a porous structure with tailored porosity, pore size and pore distribution [7]. Additionally, powder metallurgy could be beneficial when dealing with metallic biomaterials which are hard to machine by conventional technique such as Ti, Mg and Nitinol.

A combination of Metal Injection Molding and space holder (MIM-SH) technique has the potential to offer a cost-effective route that can be employed to produced high production of small, near net-shaped intricate geometry of metallic implant which possessed a well-controlled pores structure. The MIM-SH technique starts with blending of metal and space holder powders with a multi-component binder system prior to produce the feedstock, then injection molding of the feedstock into the desired shape, continued with removal of the spacer and binder components and finally sintering process in order to provide sufficient strength to the part [8]. The key issue in this technique is the proper choice of the space holder (spacer) as the porous structure is greatly influenced by the type of spacer utilized. The space holders which ranging from metallic to non-metallic could be removed from the injection molded part via leaching or burning depending on the removal technique employed.

In fabrication of porous metal, it is also equally crucial to take into consideration the properties and geometrical characteristics of the space holder particles such as biocompatibility and non-cytotoxicity, chemical stability, removal capability and mechanical properties. Numerous studies have shown that food-grade powders such as sodium chloride

[9,10,11], saccharose [12,13,14] corn starch [15] and tapioca starch [16] have been devised as safe space holders in order to minimize the adverse effects on the resultant porous metallic implant. Sodium chloride and saccharose are removed by dissolution in water whilst removal of the starch space holders is realized by thermal decomposition before the sintering stage.

Owing to its low price and good solubility in water, saccharose has been employed as a space holder material in this research work with the aim to produce the 17-4PH SS foam via metal injection molding process. In addition, the effects of sintering temperature on the properties of the 17-4PH SS foam was investigated and the structure of the foam was examined via Scanning Electron Microscopy analysis.

Methodology

Materials

In this research work, a pre-alloyed, water atomised 17-4PH SS obtained from Sandvick Osprey Powder (Figure 1) was used. Saccharose was chosen as the space holder due to its good solubility in water whilst a composite binder system comprising of palm stearin (PS) and low-density polyethylene (LDPE) was employed to provide sufficient green strength to the injection molded part. The morphological analysis for the 17-4PH SS and saccharose was performed using FESEM machine. The characteristic of the materials which were obtained from density, Differential Scanning Calorimetry (DSC) and Thermogravimetric (TGA) analysis are tabulated in Table 1.

Table 1: Characteristics of materials

Materials	**Density (g/cm³)**	**Melting Temperature ^{0}C**	**Degradation Temperature ^{0}C**
17-4PH SS	7.76	-	-
Saccharose	1.61	186	-
Palm Stearin (PS)	0.89	59.93	446.64
Low-density polyethylene (LDPE)	0.93	114.42	382.09

Sample Preparation

The feedstock was prepared by mixing the 17-4PH SS, saccharose and binder components using a Z-blade mixer with a speed of 50 rev/min at a temperature of 160^{0}C for 2 hours. The volume fraction of the binder system was kept constant at 35% volume fraction whilst the remaining 65% volume fraction is a combined volume fraction of 17-4PH SS and saccharose. As displayed in Table 2, as the volume fraction of saccharose increases from 0% to 20%, the corresponding volume fraction of 17-4PH SS reduces from 65% to 45%.

Table 2: Fraction by volume of the materials

Volume fraction of saccharose (vol %)	Volume fraction of 17-4PH SS and binder (vol %)	Binder formulation (PS : LDPE)
0	65 : 35	80:20
20	45 : 35	

The feedstock was injection molded into tensile test specimens using MCP HEK-GMBH vertical injection molding machine. Appropriate set of injection molded parameters that capable to offers defects-free molded parts must be established.

The green injection molded part was immersed in the distilled water bath at 60°C for 2 hours to leach the saccharose. The water leached part was dried in an oven at 60°C for 12 hours before the solvent debinding stage was conducted. The soluble binder component, PS was removed via solvent debinding stage which was performed using a bath of n-heptane at 60°C for 5 hours. The final stage of forming porous 17-4PH SS was accomplished by integrating the removal of the backbone binder component, LDPE, and densification of the part in a single step sintering process with the parameters depicted in Table 3.

Table 3: Sintering Parameters

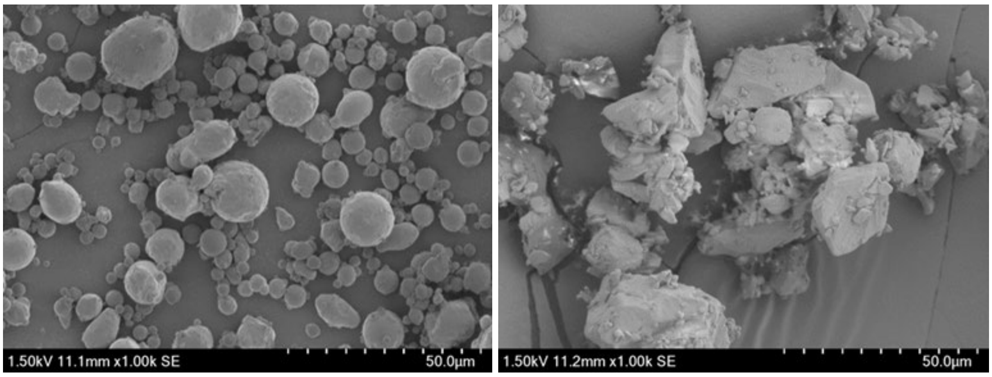
Stage	Parameters	Value
Thermal Debinding	Temperature	450°C
	Heating rate	1°C/min
Sintering	Temperature	1370°C
	Heating rate	3°C/min

The thermal debinding which aims to remove the LDPE consists of heating to 450°C with a heating rate of 1°C/min. the subsequent sintering was conducted at temperatures of 1370°C in argon gas environment. The heating rate used was 3°C/min, followed by soaking for an hour before the part was furnace cooled.

Both green and sintered parts were characterized by employing density determination, HRC hardness measurement, tensile test in accordance with MPIF standard 42, MPIF standard 43 and MPIF standard 10 respectively. In addition, Scanning Electron Microscopic (SEM) and X-Ray Diffraction (XRD) analysis was performed to evaluate the morphology and phases of the part.

Results and Discussion

Figure 1 displays typical morphologies of 17-4PH SS powder and saccharose particles used in the study. As can be seen from Figure 1(a), the 17-4PH SS was approximately spherical and had a relatively wide particle size distribution. These characteristics are well aligned with the requirement of MIM that may promotes high efficiency of particles packing during the injection molding stage. As depicted in Figure 1(b) the saccharose particles powder on the other hand possessed irregular shape.



(a) (b)

Figure 1: Morphology of (a) 17-4PH SS Powder and (b) Saccharose particles

The 17-4PH SS, saccharose and binder components were all successfully blended to form a homogenous feedstock. Several trials had been performed to injection molded the prepared feedstock into a defects-free tensile test specimen using a vertical injection molding machine. It has been observed that the presence of saccharose particles in the feedstock did not caused interference with the feedstock flow into the mold cavity. The optimum moulding parameters that capable to produced injection moulded part which was free from normal defects such as short shot, flashes and binder separation are tabulated in Table 4.

Table 4: Injection Molding Parameters

Parameters	Value
Injection temperature	160º C
Injection pressure	7 bar
Injection time	10 seconds
Holding time	25 seconds

The properties of the green injection molded part as a function of saccharose content are tabulated in Table 5. In the feedstock formulation, saccharose was replacing the 17-4PH SS particles whilst the volume fraction of binder was kept constant at 35 vol%. Based on the apparent density of saccharose which is 1.61g/cm^3 compared to 17-4PH SS which is 7.76 g/cm^3, the density of the green injection molded part was expected to be lowered with the increasing vol % saccharose added. As can be clearly observed in Table 4, both density and flexural strength decrease with addition of saccharose.

Table 5: Properties of green part

Saccharose (%vol)	Flexural Strength (MPa)	Density(g/cm^3)
0	1.77	4.7
20	0.744	3.5

German and Bose [17], suggested that the density and the fracture strength of a green injection molded part which is near 5 gm/cm^3 and 5MPa for typical ferrous MIM part are needed to allow easy handling of the part before the sintering process. Despite the values which were lower compared to the one which had been outlined by German and Bose, handling of the green part to other subsequent stages encountered no complications. Typical pore structure for the sintered parts with 20 vol % saccharose which was sintered at 1370^{0}C is displayed in Figure 2.

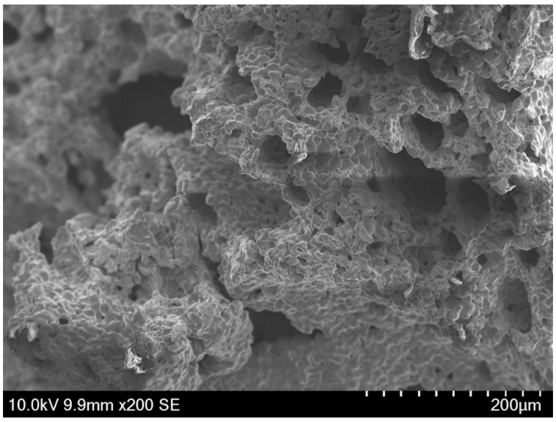
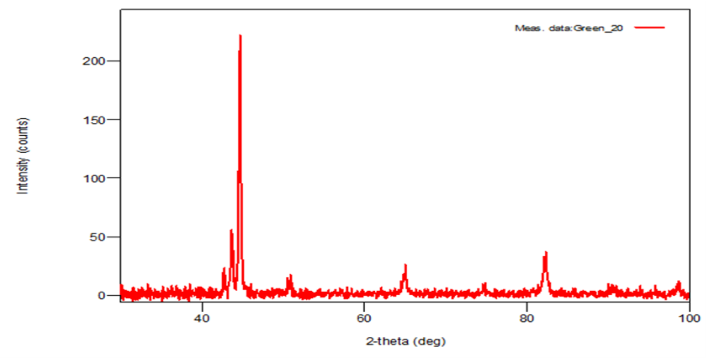


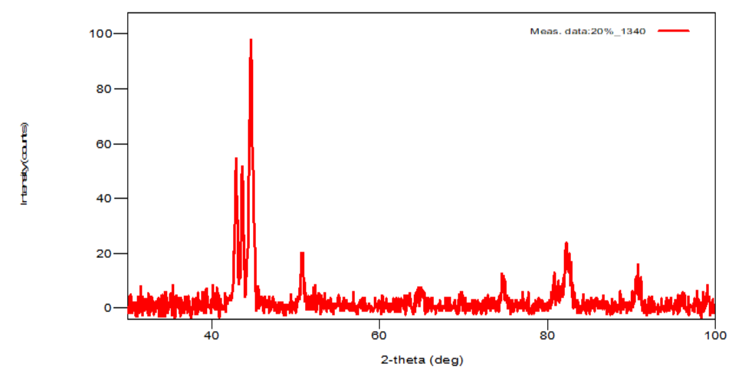
Figure 2: Pore structure by Scanning Electron Micrograph (SEM)

From the SEM image depicted in Figure 2, it is evident that the pores are homogenously distributed in the part and the walls are reasonably smooth. The SEM micrograph also reveals that most of the pores are connected to one another. The presence of the interconnected channels between the pores can be clearly observed. This could be due to the fact that the saccharose crystals were completely leached during dissolution in water, resulting in well-defined pores. The open pores which are extending from the surface to the centre of the part are beneficial for osseointegration [12].

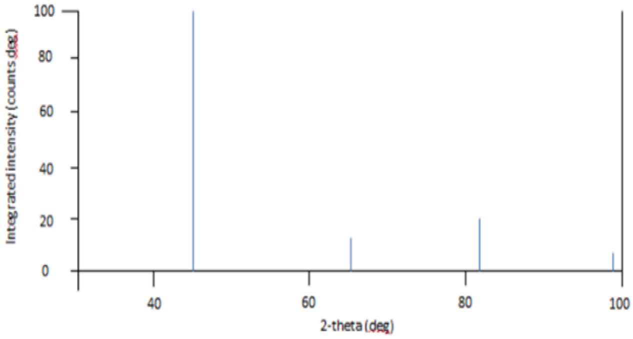
Figure 3 compares the corresponding XRD spectra for the part containing 20 vol % saccharose (a) green part, indicating the presence of saccharose and the (b) sintered part which clearly suggests the absence of the saccharose. Figure 3(b) shows, in comparison with 3(a), that the sintered part did not exhibit the presence of saccharose. This feature is confirmed on comparing the corresponding XRD spectra for sintered part with the XRD spectra for both **17-** 4PH SS (PDF Card No. 01-087-0722) and Saccharose (PDF Card No. 00-024-1977) as shown in Figure 3(c) and (d) respectively.



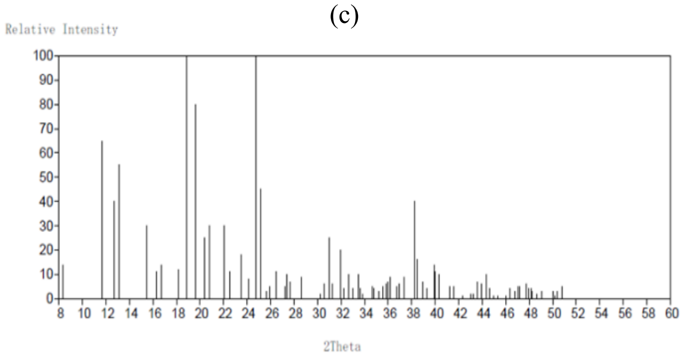
(a)



(b)



(c)



(d)

Figure 3: XRD spectra for (a) 17-4 PH SS green part (b) 17-4 PH SS (20%SH) sintered part (c) 17- 4PH SS PDF Card No. 01-087-0722 (d) Saccharose PDF Card No. 00-024-1977

Complete removal of saccharose during the water leaching stage is crucial in order to prevent contamination by the space holder residue. The advantage of saccharose is that it has solubility of 2000 g/L at room temperature. Hence it was removed from the injection molded part by immersing the part in the distilled water bath at 60°C. A similar approach was taken by Jakubowicz et.al [12] whereby the water bath temperature utilized to remove saccharose from Titanium compact range from 20^0C to 80^0C.

Density, tensile strength and Young's Modulus of the 17-4PH SS foams which possessed porosities between ~ 10.30% and 26 % are in the range of 6.95 g/cm^3 and 5.73 g/cm^3, 474.4 MPa and 168.6 MPa and 4.2 GPa and 2.7 GPa respectively. It is clear that the strength and stiffness which characterized the extrinsic bone properties are influenced by the presence of porosities in the foam. It has been also demonstrated that the mechanical properties of the foams were closed to cancellous bone.

Conclusions

The findings in this study has demonstrated that 17-4PH SS foam with tailored porosities content and morphology was successfully obtained by metal injection moulding-space holder route. The pores which were created by removing the saccharose via water leaching process resulted in 17-4PH SS foam with experimentally measured mechanical properties comparable to human cancellous bone.

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