Effect of sintering temperature and time on the mechanical properties of Co–Cr–Mo/58S bioglass porous nano-composite

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Abstract. In the present study, Co–Cr–Mo/58S bioglass porous nano-composite samples were successfully produced using 30 wt% carbonate hydrogen ammonium and polyvinyl alcohol solution as space holder and binder, respectively. The cold compacted samples were heated at 175°C for 2 h and then were heated to sinter at 1100, 1150, 1200 and 1250°C for 3, 6, 9 and 12 h. True porosity of samples was measured and the samples were characterized using the X-ray diffraction (XRD) technique, scanning electron microscopy (SEM) and compressive test. Although the results of compression test for samples sintered at 1200 and 1250°C showed that the shape of stress–strain curves were similar to each other, compacted powders sintered at 1100 and 1150°C exhibited some fluctuations. Moreover, the compressive strength increased by decreasing the true porosity, indicating the role of high temperature on the sintering process. In addition, volume diffusion was predominant mechanism for these samples at sintering temperature of 1250°C. SEM images of the porous sample sintered at 1250°C for 3 h showed an appropriate range of pore sizes and interconnectivity. The XRD results showed that there are no contaminations and new phase is detectable in the sintered porous samples.

Keywords. Porous; compressive strength; nano-composite.

1. Introduction

Among biomaterials used for load-bearing conditions, ceramics and polymers cannot meet the mechanical requirements. On the other hand, metallic materials such as Co–Cr–Mo are widely used for orthopaedic applications.¹

The Co–Cr–Mo as-cast alloys conforming to the ASTM F75 standard have been widely used for many years to produce medical implants such as hip, knee and dental prosthesis.^{2,3} Although this alloy exhibits high strength, excellent corrosion and wear resistance, one of the major problems is the mismatch between Young's modulus of the bone (cancellous: < 3 GPa and cortical bone: 3–20 GPa) and this alloy (~210 GPa).^{4–6} This large stiffness mismatch results in stress-shielding and micro-movement between the implant and the adjacent bone and the following implant loosening. Previous investigations have indicated that these phenomena retard the bone remodeling and healing and inhibit bone formation, which result in the loss and even implant separation from the surrounding tissues after implantation (fibrous tissue encapsulation).^{7,8}

Using the porous metals is a way to overcome 'stress-shielding' and weak interfacial bonding between the bone

and the implant. By adjusting the porosity of the implant, the stiffness can be reduced to reach to that of the natural bone. In addition, open-cellular structure allows the ingrowths of the new bone tissues and transport of body fluids,⁹ leading to the mechanical interlocking of the bone with the implant and therefore provides a system that enables stresses to be transformed from the porous implant to the surrounding bone tissue.¹⁰

The production methods of porous metals are categorized into four groups: liquid, gas, aqueous solutions and solid state porous through powder metallurgy.⁹ Space-holder technique, which was first employed by Zhao and Sun,¹¹ is a production process that can produce porous metal of greater porosity.¹² This technique includes five main steps: the process starts by powders selection and mixing the metal powders with an appropriate selected space-holder material. Next step is compaction of the powders into a mould to form a green body. Produced samples, depending on the kind of space holders, are then heated to low temperature to remove the space holder. Finally, sintering at higher temperature increases sinter neck growth. In this method, size, shape pores and the amount of porosity were controlled using the spacer.¹³

In spite of the appropriate selection of spacer, desired porosity levels with open-cellular structure using powder metallurgy can be achieved in low pressure compaction and a partial sintering technique.¹⁴ Hence, in this investigation it was tried to produce porous nano-composite of

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Co–Cr–Mo powder with 58S bioglass using solid NH_4HCO_3 space holder followed by cold pressing and then sintering at high temperatures. Moreover, the structural and mechanical characteristics of fabricated samples as a function of time and temperature have been investigated in detail.

2. Experimental

2.1 Raw materials

Spherical Co–Cr–Mo powder (Co–28 wt% Cr–5.3 wt% Mo) according to the ISO standard 58342-4 (E) (ISO-1996) was supplied by Carpenter Co. (Sweden).

Ammonium hydrogen carbonate with nearly cubic shapes supplied by UNI-CHEM and polyvinyl alcohol (PVA) solution (5 wt% PVA + 95 wt% water) have been used as space holder and organic binder, respectively. The size of space-holder particles was selected to be 250–500 μm , approximately. The average size of ammonium hydrogen carbonate powder is three times more than the average size of the metal powder. This ensures that the smaller metal powders will locate themselves surrounding the larger spacer powders when these are blended uniformly.

The 58S bioglass nano-powder with the composition of 58% SiO_2 –38% CaO –4% P_2O_5 (all in mol%) was synthesized by the sol–gel method.¹⁵ Figure 1 illustrates the

Figure 1. TEM image of 58S bioglass nano-particles showing a narrow distribution of quasi-spherical morphology. The scale bar is equal to 200 nm.

transmission electron microscopy (TEM; CM120, Philips) image of this powder showing their nanosized quasi-spherical morphology.

2.2 Sample preparation

Firstly, the metal prealloyed and 58S bioglass powders were weighed to give a nominal composition of Co–28Cr–5.3Mo/15 wt% 58S bioglass. The blending process was carried out in a shaker-mixer. Next, the blended powder was mixed with ammonium hydrogen carbonate as a space-holder material. Finally, in order to supply sufficient green strength to compact, 2 wt% of PVA solution was added to powder mixtures prior to compaction. The final mixture was blended together for 15 min to ensure the homogeneous distribution of Co–28Cr–5.3Mo, 58S bioglass and ammonium hydrogen carbonate particles. The powder mixture was cold pressed at around 200 MPa and crosshead speed of 5 mm min^{-1} in a cylindrical die of 5 mm diameter. Pressure was applied for 3 min in order to ensure effective and uniform compaction. The cold compacted samples were heated in two steps. The first step was carried out in an air atmosphere at 175°C for 2 h to burn out the space-holder particles. In the second step, for debinding and sintering, the compacts were heated to 1100, 1150, 1200 and 1250°C and held for 3, 6, 9 and 12 h under high-purity argon gas.

2.3 Characterization

2.3a Porosity: The general porosity of the porous samples is calculated by the formula

$$P = (1 - \rho/\rho_{th}) \times 100, \quad (1)$$

where P is the general porosity, ρ the density of porous sample measured by dividing the weight by the volume of the sample and ρ_{th} the theoretical density calculated by the following equation

$$\rho_{th} = 100/(P_1/\rho_1 + P_2/\rho_2 + \dots + P_n/\rho_n), \quad (2)$$

where ρ_{th} is the theoretical density, P_n the mass percentage of respective composition and ρ_n the density of the respective composition in pure form.

According to the above equation, the theoretical density is 6.2 g cm^{-3} .

2.3b Mechanical properties: Compressive tests of samples (5 mm diameter and 7.5 mm height) were carried out using a universal testing machine (UTM) (Universal HOUNFIELD, H25ks, England) with control software according to ASTM : E9-09. Three samples were tested at a strain rate of 0.5 mm min^{-1} to obtain the average value of the mechanical properties.

2.3c Structure and morphology investigation: Microscopic analysis was performed using scanning electron

microscope (SEM, Philips XL 30) with energy-dispersive spectrometer (EDS). From the micrographs, pore size and neck growth of the initial point contact at 1250°C with increasing sintering time were determined by quantitative image analysis using commercially available software (UTHSCSA Image tool, version 3). For these measurements around 15 selected contacted particles were used randomly.

2.3d X-ray diffraction (XRD) analysis: XRD was used for two purposes (1) to consider that the samples were without any contamination or oxidation and (2) to consider whether phase transformation has occurred or not. For these purposes, powders (the metal powder and 58S bioglass) and sintered samples were tested using a Philips X'pert-MPD in the range of $30^\circ < 2\theta < 100^\circ$ ($\lambda_{\text{CuK}\alpha} = 0.154186$ nm, step size: 0.05 and time per step: 1 s).

3. Results and discussion

Porous samples were successfully produced by adding 30 wt% space holder. Visual inspection reveals a good integrity of the sintered samples, which indicates the homogeneous porosity and acceptable sintered strength for further characterization. For each temperature and time, seven samples in the same level of space holder were produced and all of them were used for different analyses.

The compressive stress–strain curves of composite porous samples sintered at 1100 and 1150°C for 3 h are shown in figure 2. Figure 3a, b and c shows SEM images of compacted powders sintered at 1100, 1150 and 1200°C, respectively. It is evident from figure 2 that at the constant sintering time, stress increases significantly by raising the sintering temperature. In each curve, the stress reaches a maximum and then exhibits some

Figure 2. Stress–strain curves of samples sintered at 1100 and 1150°C for 3 h.

fluctuations that are repeated in a nearly similar manner. This continuous decrease and increase of stress could be related to the repetitive fracture and resistance of interparticle bonding. It is worth mentioning that, due to the poor interparticle bonding, the compressive strength is low for using in load-bearing application as shown in figure 2. Therefore, improvement in the compressive strength is necessary. For this purpose, the strength of cell walls or on the other hand, the interparticle contact areas must be improved by using higher sintering temperature.

The compressive stress–strain curves of composite porous samples sintered at 1200°C for different holding times are shown in figure 4. It is clear that increase in time from 3 to 12 h at sintering temperature of 1200°C leads to an increase in compressive strength from 6.8 to 29 MPa. The compressive stress–strain curves of the composite porous samples sintered at 1200°C for 12 h

Figure 3. SEM images of interparticle region of samples sintered at (a) 1100, (b) 1150 and (c) 1200°C for 3 h.

and 1250°C for 3 h are shown in figure 5. The compression tests for all porous samples sintered at 1200 and 1250°C show that the shape of stress–strain curves are similar to each other and smooth. The smooth character of curves indicates the ductile behaviour of samples during compression test.¹⁶ In addition to repetitive fracture of interparticle bonding in samples sintered at 1100 and 1150°C, the serrations in their stress–strain curves confirmed the brittle behaviour of these samples without plastic deformation. Figures 4 and 5 show that the stress–strain curves have an initial linear region where the cell walls deform elastically (stage I), an yield point (stage II), a plastic yield stage up to a peak stress as the cells deform plastically (stage III) and finally, the fracture of the porous struts due to collapse of the walls (stage IV).¹⁷ Although holding time is an important process parameter for sintering, as shown in figure 4, figure 5 demonstrates

Figure 4. Stress–strain curves of samples sintered at 1200°C for different times.

Figure 5. Stress–strain curves of samples sintered at 1200°C for 12 h and 1250°C for 3 h.

that the sintering temperature has the higher influence on the compressive strength of sintered samples. The temperature of sintering depends on the type of particles. This temperature should be high enough to form an interparticle bonding and initiate fusion and should be lower than melting point of particles.¹⁸

The necking phenomenon between the particles at sintering temperature of 1250°C at different sintering times is shown in figure 6. This figure clearly shows the occurrence and growth of the necks. Figure 7 shows the dependence of true porosity of the samples on sintering time and temperature. It is clearly observed that the true porosity decreases with the increase in the sintering time and temperature. Furthermore, it can be seen that the true porosity slope increases with the increase in the sintering temperature. On the other hand, by increasing the sintering temperature, samples become denser and rapid densification occurs. These results could be related to the formation and growth of necks between the particles. A comparison between figures 3 and 6 shows that with the increase in the time and temperature, the particles start to weld together and formed necks at the particle interface, and it can increase density and consequently reduce the true porosity.¹⁹ Indeed, the compacted powders have a large surface area and the driving force during the sintering is the reduction of surface energy.²⁰ Moreover, an increase in the input energy through the higher sintering temperature caused a more sintering neck growth, resulting in faster sintering and the lower porosity.

The relationship between the true porosity and compressive strength for all samples sintered at different temperatures and times is shown in figure 8. The compressive strength at each porosity is the average value of samples having the same time and temperature of sintering. It could be observed that the compressive strength of the samples is decreased with the increase in the true porosity. On the other hand, in lower true porosity or in lower sintering time and temperature, the bonding between the particles are not satisfied and the sintered samples have lower compressive strength, which is in good agreement with the microstructure that has been observed by SEM, as shown in figures 3 and 6. Moreover, the increasing trend of compressive strength increases, with the decrease in the true porosity indicating the role of higher temperature on the sintering process. According to the microstructural evolution, a large number of parameters affect the mechanical properties of the sintered compact. The morphology, size and distribution of pores throughout the sample and necking size between the particles have a major effect on the compressive strength.¹⁹ Also, sintering temperature causes the changes in structural characteristics that are phase transformation, crystallite size increase and decreasing the structural defects.²¹ However, briefly, the mechanical properties will be affected by simultaneous strengthening of bonds between the particles on the one hand, and recrystallization and

Figure 6. SEM images showing structure, pores and pore walls of samples sintered at 1250°C for (a) 3, (b) 6, (c) 9 and (d) 12 h.

Figure 7. Dependence of true porosity on the temperature and time of sintering.

grain growth and softening of the individual particles on the other hand. In this research, as will be discussed in latter section, the XRD results showed that with the increase in the temperature, the crystallite size of grain increases. Also, SEM images show that the neck grows between the particles. Totally, the increase trend of compressive strength reflects the higher effect of interparticle bonds than grain growth and softening. In previous research that has been done by Dunmore and Smith²² on

sintered copper powder specimens, the results show that after about 600°C the tensile strength decrease, due to grain growth and expansion of gas trapped within closed powders.

According to the obtained equation of fit curve in figure 8, the relationship between the true porosity and compressive strength is expressed to be as following equation

$$\sigma = 1179 + (-1325.78 \times 10^2/\theta) + (3726.726 \times 10^3/\theta^2), \quad (3)$$

where σ is the compressive strength and θ the true porosity. On the other hand, the true porosity is a function of temperature and can be written as follows

$$\theta = -0.062T + 125.6. \quad (4)$$

This equation is calculated from available data in figure 7. By substituting equation (4) into (3), the compressive strength as a function of temperature is given as

$$\sigma = 1179 + (8219.9T - 1292 \times 10^4)/T^2. \quad (5)$$

For instance, based on the above equation to reach the compressive strength value 150 MPa, the temperature is estimated to be 1357.5°C. Although this temperature seems to be approximately true, validity of this equation needs more investigations and further experimental work must be performed.

Figure 8. Experimental values and fit-curve of compressive strength as a function of true porosity.

As well known, diffusion coefficient increases exponentially with temperature according to the Arrhenius law, as below

$$D = D_0 \exp(-Q/RT). \quad (6)$$

According to previous sections, the influence of temperature on the neck growth and compressive strength was shown; also this equation indicates the importance of this parameter on the sintering process. Indeed, bonding between the particles requires a diffusion transport of material from the volumes of the particles to the points and regions where they are in contact with one another. According to equation (6), higher temperatures of sintering caused a more atomic diffusion, resulting in faster interparticle neck growth. However, based on previous works,²³ there are different material transport mechanisms for diffusion of atoms into the points between particles. In order to find out which mechanisms are dominant during sintering, according to a theoretical model, (n) and (m) constants are determined²⁴

$$(x^n/a^m) \sim t, \quad (7)$$

where x , a and t are the neck width, particle diameter and time, respectively. Figure 9 shows that x^5/a^2 vs. time is a reasonably straight line, indicating (n) and (m) constants are equal to 5 and 2, respectively. Considering these values for (n) and (m), it can be concluded that temperature volume diffusion is predominant mechanism for this powder metal.

Pore size and morphology of the fabricated sample sintered at 1250°C for 3 h is shown in figure 10. It is clear that there are two types of pores: macropores or interconnected (i.e., above 100 μm) pores and micropores which are below 100 μm . The interconnected macropores are a result of decomposition of ammonium hydrogen carbonate particles and the micropores are the result of

Figure 9. Relationship between neck width (x), particle diameter (a) and time.

partial sintering of the alloy particles on the cell walls. Pore size and pore interconnectivity are critical factors in porous material for tissue engineering. Micropores are scale to provide pathways for body fluid and nutrient transportation, needed for bone regeneration and growth.²⁵ In addition, these kinds of pores provide locations for cell attachment given that mammalian cell typically are 10–20 μm in size.²⁶ Although there is hardly consensus about the optimal macropore size for efficient bone ingrowths, it is believed that macropores should be suitably large for tissue function. Here, as can be seen in figure 10, the size of macropores are in the range of 200–500 μm , that is in good agreement with the pore size suggested by other researchers.^{27,28}

The EDS analysis shown in figure 10, as would be expected, demonstrates that no trace of nitrogen and carbon was found. As mentioned before, this confirmed that ammonium hydrogen carbonate particles were completely removed. Also, there was no oxygen contamination after sintering that is in good agreement with XRD patterns.

The patterns shown in figure 11 were selected as reference patterns for comparison. Figure 11a and c shows the XRD patterns of the starting pre-alloyed powder and as-produced 58S nano-powder, respectively. Figure 11c displays no crystalline peaks and confirms the disorder and amorphous nature of particles. Figure 11b shows that after thermal treatment, sharp peaks have been appeared and amorphous structure has been transformed into crystalline structure; during the sintering process. The patterns shown in figure 12 are related to the porous samples sintered at 1100, 1150, 1200 and 1250°C for 3 h. Compared with pre-sintering patterns, figure 12 shows that there are no contaminations and new phase formation is detectable in the sintered porous samples. But these patterns show that positions of some peaks have been slightly shifted towards lower diffraction angle at sintering temperature

Figure 10. SEM image and EDS spectrum of the porous samples sintered at 1250°C for 3 h.

Figure 11. X-ray diffraction patterns of (a) as-received metal powder, (b) fully crystallized and (c) amorphous 58S bioglass.

Figure 12. X-ray diffraction patterns of porous samples sintered at (a) 1250°C, (b) 1200°C, (c) 1150°C and (d) 1100°C.

1200 and 1250°C. Also with increasing the sintering temperature, some pre-alloyed peaks became more observable and stronger.

Previous investigations have shown that the as-cast microstructure depends on the solidification process and chemical composition mainly includes FCC structure (cobalt-rich matrix) with primary carbides ($M_{23}C_6$).^{3,29} It has been reported that partial carbide dissolution positively affects some mechanical properties such as ductility.³⁰ But the temperature range to achieve carbide dissolution is significantly narrow.³¹ Clemow and Daniell³² have mentioned that no carbide dissolution occurred at 1165°C and dissolution of carbides occurred at 1210°C. However, according to previous literatures,^{3,29} the slight shift of peaks could be related to the dissolution of carbides. Also, the obvious change in the relative peak's heights could be attributed to the grain growth and the presence of grain crystallographic orientation. It is worth mentioning that

the main aim of the use of 58S nano-bioglass was improvement of bioactivity properties of this composite.

4. Conclusions

Visual inspection of fabricated samples reveals a good integrity, indicating the homogeneous porosity and acceptable sintered strength. Although the compression tests for samples sintered at 1200 and 1250°C show that the shape of stress–strain curves are similar to each other and smooth, compacted powders sintered at 1100 and 1150°C exhibit fluctuations that are repeated in a nearly similar manner. Due to poor interparticle bonding of samples which have been sintered at 1100 and 1150°C, their compressive strength is considerably low to being used for load-bearing application. The dependence of true porosity of the samples on sintering time and temperature shows that the slope of true porosity increases with the increase in the sintering temperature. Moreover, the increasing

trend of compressive strength increases, with the decrease in true porosity, indicating the role of higher temperature on the sintering process. In addition, among different mechanisms, volume diffusion is the predominant mechanism for this powder metal at sintering temperature of 1250°C. SEM images of the porous sample sintered at 1250°C for 3 h show an appropriate range of pore sizes and interconnectivity. The XRD results show that there are no contaminations and new phase formation is detectable in the sintered porous samples. Also, the obvious change in the relative peak heights could be attributed to the grain growth and the presence of grain crystallographic orientation.

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