Mechanical Properties of Porous Ti-Mo and Ti-Nb Alloys for Biomedical Application by Gelcasting

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Abstract

In this study, we have introduced gelcasting for prepared near-shape porous Ti-Mo and Ti-Nb alloys implants. The microstructure and the total porosity of the vacuum sintered porous Ti alloys were analyzed by using electronic microscopy (SEM) and X-ray diffraction (XRD). Moreover, compression and bending tests were conducted to investigate their mechanical properties. The results shows that three-dimensional pore morphologies and total porosity range from 39% to 50% can be achieved. The microstructure of Ti-Mo and Ti-Nb alloys contained a mixture of α and β phase. The compressive strength was significantly increased with adding Mo and Nb element. The Young's modulus ranging from 5-18 GPa. In conclusion, from a mechanical strength viewpoint, we have found that the porous Ti-12.5Mo and Ti-25Nb alloys prepared by gelcasting present a promising efficient process for the direct fabrication of customized implants for personalized medicine.

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1. Introduction

Bone repair or reconstruction addressing degenerative disease or catastrophic injury often involves the application of bone implants. The total number of hip revision surgery is expected to increase by 137% and knee revision surgery by 607% between the years 2005 and 2030 [1]. Titanium and its alloys have been used extensively in the last several decades as materials for orthopedic implants, dental implants, and medical devices. This is due to the excellent surface oxide biocompatibility, high mechanical strength and corrosion resistance [2, 3]. But stress shielding effect where reabsorption of natural bone and implant

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loosening arises because of the difference in stiffness between natural bone (10-30 GPa) and hard tissue implant (110 GPa for Ti), is one of the primary causes requiring revision surgery. Another problem with metallic implants lies in the interfacial bond between the tissue and the implant [4]. This has led to the development of low modulus beta titanium alloys that consist of non-toxic β-stabilising elements (such as Mo, Nb, Zr and Ta) and have modulus closer to that of bone. The new potential alloys that are currently under research with interest are Ti-Mo alloys [5, 6] and Ti-Nb-Ta-Zr Alloy [7, 8].

In addition, porous titanium is an exceptional material for bioapplications, the bulk modulus of which could be reduced to values more compatible with natural tissue. The introduction of porosity into the implant may also promote the entrapment of specific proteins such as vitronectin and fibronectin and thus enhance osteoblastic cell attachment, proliferation and differentiation on the implant surface [9]. The rough surface morphology of the porous implant also promotes bone ingrowth into the pores and provides not only anchorage for biological fixation but also a system which enables stresses to be transferred from the implant to the bone [4]. A number of approaches to the fabrication of porous surface or implants have been reported, including powder metallurgy, plasma spray coating [10], self-propagating-high-temperature synthesis (SHS) [11] and the void-metal composite method. Nugroho [12] investigated the use of solid state isothermal foaming technique in the manufacture of porous titanium alloys from elemental powders, the resulting alloys were found to contain porosity amounts and sizes ranging between 20-40 vol% and 20-200 μm, respectively. However, complex-shaped porous implants cannot be fabricated using the above-cited traditional methods and the properties of the samples made are mechanically inadequate. Over the past few years, direct fabrication process of metallic components such as direct laser metal sintering (DLMS) [13], laser-engineered net shaping (LENS) [4] and electron beam melting technology (EBM) [14], which uses metal powders to create functional parts have gradient porosity and cellular structures that can be used in very demanding applications, however, there are disadvantages such as high cost and low efficiency.

Therefore, the present work has introduced the use of gelcasting process [15] for fabricated porous titanium alloys. Gelcasting process can be easily adjusted the porosity and mechanical properties of porous titanium parts by altering the parameters. Furthermore, easy preparation of complex-shaped products with low costs of the molds make gelcasting more appropriate for the fabrication of porous titanium implants especially in personal medical treatment areas. We have used gelcasting to prepare porous Ti-Mo and Ti-Nb alloys with appropriate porosity and good properties. The microstructures and properties of porous alloys by gelcasting are mainly discussed in this paper.

2. Experimental

Commercially pure titanium, molybdenum and niobium powder was used in this study. The characteristics and chemical composition of elemental powder are shown in Table 1. The Ti+Mo and Ti+Nb powders were weighed to give a different compositions (7.5, 12.5 and 17.5 wt.% of Mo, 10, 25 and 35 wt.% of Nb) and then placed into a stainless steel can. Following this, approximately 600 g of alloy powder was mixed by high energy vibration ball milling at frequency of 23.2 Hz for at least 2h. Figure 1 shows the SEM morphology of high-energy ball milling Ti +12.5 wt.% Mo and Ti +35 wt.% Nb powder, in which the added Mo and Nb powders evenly dispersed around the irregular Ti powder, some fine powder also attached to the titanium surface.

The aqueous system gelcasting are as follows: acrylamide (AM) was used as the monomer, N, N'-methylene-bisacrylamide (MBAM) as a cross-linker, N, N, N’, N’- tetramethylethylene- diamine (TEMED) as a catalyst, and ammonium persulphate ((NH4)2S2O8) as an initiator. All reagents were analytically pure. Schematic representation of the gelcasting process is shown in Fig. 2. The monomer and the cross-linker were mixed at a fixed ratio to make gel former. At room temperature, the gel former
was dissolved in deionized water in different proportion to make a premixed solution. Titanium mixed powder was then added to make metal slurry with fixed solid loading. In addition, a suspending agent was used to obtain uniform slurry. After ball-milling for 24 h in N₂, the slurry was de-aired under vacuum, and then the initiator and the catalyst were added. Finally, the slurry was poured into a non-porous mould and held at 60°C for 2 h to ensure that the gelatin reaction processed effectively and the slurry was solidified into parts of required shape and size. After demoulding, the wet green body was dried in vacuum at room temperature. In view of the porosity requirement of porous materials, gelcasting green body was sintered at lower temperatures in a vacuum furnace (<2.0×10⁻² Pa).

Table 1. Characteristic and chemical composition of pure powder.

| Powder   | Average particle size (µm) | O    | H    | N    | C    | Fe   | Cl   | Si   | Ni   | Ti   | Mo   | Nb   |
|----------|----------------------------|------|------|------|------|------|------|------|------|------|------|------|------|
| Pure Ti  | 46.6                       | 0.25 | 0.02 | 0.04 | 0.02 | 0.06 | 0.05 | 0.02 | 0   | Bal. | 0    | 0    |
| Pure Mo  | 38                         | 0.4  | 0.07 | 0.05 | 0.03 | 0.06 | 0.01 | 0.02 | 0.01 | 0    | Bal. | 0    |
| Pure Nb  | 45.6                       | 0.25 | 0.07 | 0.05 | 0.05 | 0.05 | 0.05 | 0.01 | 0.02 | 0    | 0    | Bal. |

Fig. 1. SEM image (a) Ti+12.5 wt.% Mo and (b) Ti+35 wt.% Nb powder by ball milling.

The main gelcasting parameters were solid loading, monomer content of the premixed solution, monomer and cross-linker mixed ratio (AM: MBAM) and sintering conditions. By changing the parameters, the volume of polymeric network between the powder particles can be varied, resulting in more porous or dense structures. Moreover, the pores can be smooth and oriented by changing the sintering condition, leading to a three-dimensionally interconnected porosity. Solid loading between 30 and 35 vol. % were chosen to create the desired porosity. Sintering temperatures of 900 to 1050°C for 2 h were used to fabricate Ti alloys with varying porosity.

Microstructures of mixed powders and the amount and morphology of any porosity of sintered porous titanium alloy samples were examined using scanning electron microscope (Cambridge S-250MK2). Constituent phases of porous sample were identified using a D/MAX RB X-ray diffractmeter with Cu Kα radiation. The porosity of porous titanium alloys was determined using Archimedes principle. Compression test of cylindrical specimens of φ10×20 mm (GB 7314-87) in size were performed using an Instron material test system (CMT4305) at a loading rate of 0.5 mm/min, respectively. The modulus of samples was determined from the nominal stress–strain response.
Fig. 2. Schematic representation of the gelcasting process.

3. Results and Discussion

3.1. Porosity and Microstructure

Ti-Mo and Ti-Nb alloys with the solid loading varied from 31 to 35 vol.% were prepared by gelcasting. For the same volume of green body, the higher the solid loading means that the denser green body and the less organic additives, therefore, the lower porosity of samples has been sintered in the same process. The total porosity of titanium samples decreased with increasing the solid loading, between 39.15%–48.4% for Ti-Mo and 39.2%–50.1% for Ti-Nb alloys respectively. The porosity of Ti-Mo alloys decreased and pores closed gradually when the solid loading up to 35%. Microstructural study indicated that the pores were irregular in shape with uniform pore size distributed in all the samples processed under same processing parameters (Fig. 3). It is important to note that the porous Ti-Mo and Ti-Nb alloys prepared by gelcasting are promising for load-bearing implant, since the optimal porosity of implant materials for ingrowths of new bone tissue is in the range 20–50%. Figure 3(a-c) shows that the open and closed porosity was observed in the Ti-7.5Mo, Ti-12.5Mo and Ti-17.5Mo samples, the size and connectivity of pores were low in the Ti-7.5Mo alloys samples fabricated at solid loading of 32% compared to Ti-17.5Mo alloy. When the Mo content is less than 7.5wt.%, the densification of Ti-7.5Mo alloys was more sufficient due to its relatively high diffusion and solution compare with Ti-17.5Mo alloys during sintering, which leaving smaller pore size and less three-dimensional connectivity porosity. However, densification will be affected when the solid solution reaches a certain level, therefore with the increase of Mo contents, the pore diameter and its connectivity were increased for Ti-Mo alloys when the Mo content up to 17.5wt.%. In addition, it also found the few closed-cell pore structure distributed on the wall and edges of macro pores. The pore diameter of Ti-7.5Mo, Ti-12.5Mo and Ti-17.5Mo alloys were 98 μm, 102 μm and 110 μm respectively.

Figure 3(d-f) shows that the open interconnected porosity was observed in the Ti-10Nb, Ti-25Nb and Ti-35Nb samples processed at 32% solid loading. It shows that the pores of Ti-Nb alloy were irregular in shape and didn’t appear closed-cell structure differ from porous Ti-Mo alloy. The mean pore diameter of Ti-10Nb alloy and Ti-25Nb alloy reduced from 120μm to 32μm and 113μm to 28μm respectively. The pore structure has not changed significantly with the Nb content increased. It was also found that uniform porosity and thicker pore walls structure in Ti-25Nb alloys, which benefit to improve its mechanical properties. Along with its roughed surface, the interconnected irregular pores of porous titanium implant increased its contact with human tissue after the implantation of the human body. Experiments show that this rough surface and pore structure can capture the cellulose and expand the cell adhesion, and then accelerate the osteoblast aggregation and bone ingrowth, which result in the bonding strength between
bone and implant was improved. Moreover, the macro-porous surface area can provide a large number of nucleation centers for calcified tissue, which also accelerate bone ingrowth and the tissue healing.

![Figure 3](image-url)

**Fig. 3.** SEM image of pore morphology and distribution in porous titanium alloys processed at 32% solid loading: Ti-7.5Mo (a), Ti-12.5Mo (b), Ti-17.5Mo(c), Ti-10Nb (d), Ti-25Nb (e) and Ti-35Nb (f) alloys.

The densification of titanium alloy by gelcasting includes binder removal and alloying stage during sintering. The organic additives gradually burnout first with increasing temperature from the green body and left the pore between the powders, and then into the high temperature stage, the Mo or Nb atoms are activated and then diffused into the Ti substrate in the high temperature, meanwhile, the mass transfer and vacancy exchange occurs. In order to obtain good porosity and mechanical properties, the sintering temperature was constant and fixed as 1050°C for Ti-7.5Mo and Ti-10Nb alloys based on previous research. The backscattered electron morphology of gelcasting-processed Ti-Mo and Ti-Nb alloys has been shown in Figure 4. It can be seen that added 7.5% Mo and 10% Nb powder has been completely diffused into the Ti matrix, but the alloy is not fully densified. Dark area in the figure was irregular pores, white light-colored area was rich in molybdenum, while the remaining adjacent gray areas are rich in titanium. It can be seen from the figure, apart from macro-and micro pores, which benifit to implants, the microstructure of Ti-Mo and Ti-Nb alloys contains a mixture of α (dark gray) and β phase (white and light gray), and the structure did not change with gelcasting parameters. This observation is supported by X-ray diffraction (XRD) results, as shown in Figure 5. It can be found that the sintered porous Ti-7.5Mo and Ti-10Nb alloys indicated that the microstructure consisting α phase and fewer β phases, furthermore, the amount of β phase increased with increasing Mo and Nb contents.

Molybdenum and niobium are the β-phase stabilizing element, which can be more solid solution in the β phase and lower phase transition temperature. In addition, it belong to the same crystal elements in the infinite solid solution in Ti, when β isomorphous elements in the β phase of solid solution concentration reaches a critical value, the balance can prevent the transformation of β-phase. Thus, with increasing Mo and Nb content, the β-phase content of porous Ti-Mo and Ti-Nb alloys increased at the same sintering temperature. Therefore, Mo and Nb are the most suitable alloying elements that can be added to decrease
the modulus of elasticity of bcc Ti without compromising the strength. It is also interesting to note that molybdenum and niobium fall into the category of non-toxic elements, which make it more suitable for implant applications. The results from XRD results (Fig. 5) Porous Ti-17.5Mo and Ti-35Nb alloys containing higher amounts of $\beta$ stabilizers is needed for biomedical applications. In porous titanium implant materials, only the well-organized uniform distribution of pore structure and phase composition can obtain the best mechanical properties to meet the needs of biomedical implant, therefore, both higher amounts of $\beta$ stabilizers and uniform pore structure were needed to prepared porous Ti-Mo and Ti-Nb implants.

Fig. 4. SEM image of porous titanium alloy, (a) Ti-7.5Mo and (b) Ti-10Nb alloy.

Fig. 5. XRD pattern of porous (a) Ti-Mo and (b) Ti-Nb alloys by gelcasting.

3.2. Properties of Porous Ti-Mo and Ti-Nb Alloys.

For applications in bone replacement it is desirable to match the Young’s modulus of the bone itself. This prevents stress shielding and bone desorption, and leads to longer implant life. The mechanical properties of various porous titanium alloys and bones are shown in Fig. 6. In contrast to porous Ti by gelcasting available before, the compressive strength and the bending strength was significantly increased with adding Mo and Nb element, which attribute to its microstructures and phase composition. The compressive strength and Young’s modulus increased with decreasing porosity of the samples. The goal
is to be near the Young’s modulus of bone which is 10–20 GPa depending on bone type and location. The experimental data indicate that the strength and modulus of Ti-Mo and Ti-Nb alloy samples can be tailored by changing the gelcasting process parameters. In addition, the modulus of samples (5–18 GPa) having a porosity in the range 39–50 vol.% is almost the same as that of human cortical bone. As shown in Fig. 6, these porous Ti-Mo and Ti-Nb alloys have compressive strengths in the range 141–286 MPa, which match the strength of the adult bones. Porous Ti-12.5Mo and Ti-25Nb alloys with matching properties with bone and total porosities in the range 39–48 vol. %, which sintered at 1050°C for 2 h, can significantly improve bone-implant interaction. Moreover, the necks between the powder particles have high strength due to the fine, homogeneous structure, thus improving the brittleness of alloys. The bending strengths in the range 89–131 MPa for Ti-Mo alloys and 79–120 MPa for Ti-Nb alloys demonstrate that it is capacity for load bearing orthopedic implants by improve sintering and post heat-treatment. Even though we are not able to archive the high strength and low modulus for ideal implant, when compared to fully dense titanium that is currently used, the addition of porosity offers a significant improvement.

The near-net shape titanium implants can directly prepared by gelcasting with macro and micro-porosities. It can reduce the bulk density of alloy and the modulus by introducing porosity. Therefore, gelcasting can be used to produce personal implants with tailored properties depending on the patient’s need. For use as a bone replacement material, the fatigue properties and biocompatibility of porous titanium alloys become very important for further studies.

![Fig. 6. Compressive strength and Young’s modulus of porous Ti alloys and bones.](image)

4. Conclusions

The porous Ti-Mo and Ti-Nb alloys with three-dimensionally interconnected porosities were prepared by gelcasting and subsequently sintering. The results show that total porosity range from 39.15% to 49.66% and the pore size range from 5–120 μm can be achieved by changing the gelcasting parameters, especially solid loading and monomer content. The microstructure of Ti-Mo and Ti-Nb alloys contains a mixture of α and β phase. In contrast to porous Ti by gelcasting available before, porous Ti-Mo and Ti-Nb alloys present excellent properties. The compressive strength was significantly increased with adding Mo and Nb element. The Young’s modulus ranging from 5–18 GPa, which match the properties of bones. In addition, the compressive strength and Young’s modulus increased linearly with decreasing porosity of the samples. In this study, porous Ti-12.5Mo with 40–45% porosity and Ti-25Nb alloy with 39–48%...
porosity, which sintered at 1050°C for 2 h which have great properties close to those of human cortical bone, therefore being suited for medical applications.

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