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Review

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Current developments of biomedical porous Ti–Mo alloys

As a biomedical hard tissue implant candidate, porous Ti–Mo alloy has received considerable attention because of its special porous structure, appropriate Young's modulus and compressive strength as well as good corrosion resistance. As a bioactive coating, hydroxyapatite is commonly used to cover the surface of bioinert metallic prostheses due to its excellent biocompatibility, bone-like structure and composition. This article reviews the current developments and the relationships between the fabrication methods, porous structure, mechanical properties, bioactive surface modification and corrosion behavior of porous Ti–Mo alloy used for hard tissue implant application. Furthermore, the future research directions are discussed to optimize the porous structure and improve the properties of porous Ti–Mo alloys.

Keywords: Porous Ti–Mo alloy; Fabrication; Mechanical properties; Surface modification; Corrosion behavior

1. Introduction

Metallic biomaterials have been widely used to fabricate load bearing hard tissue implants such as dental roots, hip prosthesis and so on recently because the need for replacements increase with the rapidly growing aging population in the world [1–3]. Titanium alloys, stainless steel and Co–Cr–Mo alloys have become the commonly used hard tissue prostheses. The reasons for choices of these metals include high specific strength and fracture toughness, good corrosion resistance, etc. [1–4]. However, the recent investigations reveal that two major drawbacks involve the mechanical properties and cytotoxicity of the conventional solid metals. The former is related to biomechanical compatibility. The latter is relevant to biochemical compatibility. The Young's moduli of the aforementioned metals ranging from 120 to 232 GPa are substantially larger than those of cancellous (1–2 GPa) and cortical (20–27 GPa) bones [5]. Therefore, stress shielding, a critical issue in hard tissue replacement, which originates from the mismatch of Young's modulus, may cause osteoporosis of the surrounding bone tissue. These metals have poor biomechanical compatibility [1, 2]. Furthermore, toxic elements such as Al, V, Ni or Cr present in the aforementioned metals may result in neurological disorder, Alzheimer's, allergic reaction or other diseases. From the viewpoint of cytotoxicity, these metals have poor biochemical compatibility [1, 2]. Accordingly, two commonly used approaches have been adopted to resolve the aforementioned problems. One involves developing new β type solid titanium alloys with low Young's modulus such as Ti-29Nb-13Ta-46Zr, Ti-10Mo-7Nb, Ti-35Zr-10Nb, Ti-15Mo and so on using nontoxic alloying elements including Mo, Nb, Ta, Zr, etc. [1–3]. Recent studies have demonstrated they have great potential for implant application [6–19]. The other involves suitable design of the architecture by introduction of porosity. Recently, porous titanium alloys like porous Ti–Mo and Ti-Nb alloys with the following advantages have become the research focus in the field of hard tissue prostheses [2, 20, 21]. The interconnected porous structure may facilitate the transportation of body fluid and nutrients, and attachment of the implant to the surrounding bone tissue. Moreover, the Young's modulus and strength altered by ad-

justing the processing parameters match those of bone tissues [22–27]. Generally speaking, artificial metallic prostheses implanted are encapsulated by fibrous tissue and isolated from the bone tissue because of the bio-inertness [1, 2]. Bioactive ceramics like hydroxyapatite (HAP) can't be solely used for load-bearing hard tissue implants because of their brittleness although HAP possesses good bone-bonding ability [5]. Therefore, an effective method to make ideal hard tissue implants may be the combination of porous titanium alloy with non-toxic alloying elements and surface modification with deposition of bioactive HAP [1, 2].

Ti–Mo alloys have drawn much attention among biomedical titanium alloys due to the following characteristics of using molybdenum. Firstly, Mo exhibits a stronger β-stabilizing effect on Ti alloys compared with commonly used Nb, Ta or Zr elements [6–8]. Secondly, it has a significant economic saving since the prices of the above-mentioned three metallic β-stabilizers are relatively high [9–12]. Thirdly, Mo is expected to improve strength and corrosion resistance with lower Young's modulus [6, 7, 10–12]. Lastly, as an essential trace element in human nutrition, Mo is beneficial in regulating the *pH* balance in the body, etc. [18]. Some reports are available on microstructure, mechanical properties, corrosion behavior, surface modification and biocompatibility of solid binary Ti–Mo alloys [6–19]. But there is less information regarding porous Ti–Mo alloys and their potential use as biomaterials. It is recognized that a minimum of 10 wt.% Mo is necessary to stabilize the beta phase in Ti–Mo alloys. Therefore, porous Ti-*x*Mo ($x \geq 10$) alloys will hereinafter be reviewed.

The objective of this article is to review the status and understand the relationships between the fabrication method, porous structure, mechanical properties, surface modification and corrosion behavior of biomedical porous Ti–Mo alloy.

2. Fabrication of porous Ti–Mo alloy

It is convenient to alter the mechanical properties including Young's modulus and compressive strength, improve corrosion behavior and in-vivo biological behavior by adjusting the porosity of porous Ti–Mo alloy. Several researchers have proposed methods of powder metallurgy, selective laser sintering and gelcasting to fabricate biomedical porous Ti–Mo alloys [22–27].

2.1. Powder metallurgy

Powder metallurgy (PM) is a conventional technique for producing solid or porous metallic or ceramic materials from powders. It is generally performed by three basic steps of powder blending, compaction and sintering. The powders mixed according to the nominal composition are blended in a chamber. Compaction is generally carried out at ambient temperature. After compaction, neighboring powder particles are held together by cold welds, which give the compact sufficient "green strength" to be handled. Powder sintering is a heat treatment applied at elevated temperature to a powder compact in order to impart strength and integrity. At sintering temperature, diffusion processes cause necks to form and grow at these contact points [22, 23]. In order to fabricate porous metals, ammonium hydrogen carbonate NH_4HCO_3 can be considered as a candidate for a space holder because it may be decomposed to gaseous components by heating below 473 K without polluting the sample [23].

Porous Ti-15Mo alloy has been fabricated from TiH_2 and Mo powders by the PM technique. The hydride decomposes into titanium and hydrogen, which acts as a protective atmosphere. The substitution of Ti with TiH_2 may accelerate the sintering process and decrease the oxidation of titanium [23]. Ball milled elemental Ti and Mo powders have been used to produce porous Ti-10Mo alloy by PM [22]. The blended metallic powders and space holder of NH_4HCO_3 are conventionally cold pressed to green compact and then heated between 448 and 473 K to remove the space holder. After that, the compacts are sintered between 1 373 K and 1 473 K. X-ray diffraction (XRD) patterns of the sintered porous alloy indicate that there is no elemental Mo phase because of the physical diffusion and complete solid solution of Mo in the alloy. Meanwhile, XRD results show that space holder has little influence on the phases of the sintered alloy [23]. Figure 1 presents a scanning electron microscopy (SEM) image of the sintered porous Ti-15Mo alloy with porosity of 68.5 %. The porous structure of sintered porous Ti-(10–15) Mo alloys is characterized by small and irregular closed pores located on the walls of interconnected open pores. Porosity and mean pore size (100–400 μm) of the sintered porous Ti-(10–15) Mo alloys increase and the pore distribution becomes uniform with the increasing amount of added NH_4HCO_3. The interconnected porous structure with mean pore size larger than 100 μm is the preliminary requirement to allow bone tissue ingrowth and body fluid transportation [5, 23].

Advantages of the PM technique include simplicity, good maneuverability and low capital investment of equipment. The shortcomings include inhomogeneous pore distribution and mechanical properties because the distribution inhomogeneity of the blended metallic and space holder powders.

2.2. Selective laser sintering

As an additive and rapid prototyping manufacturing technology, selective laser sintering (SLS) involves the use of

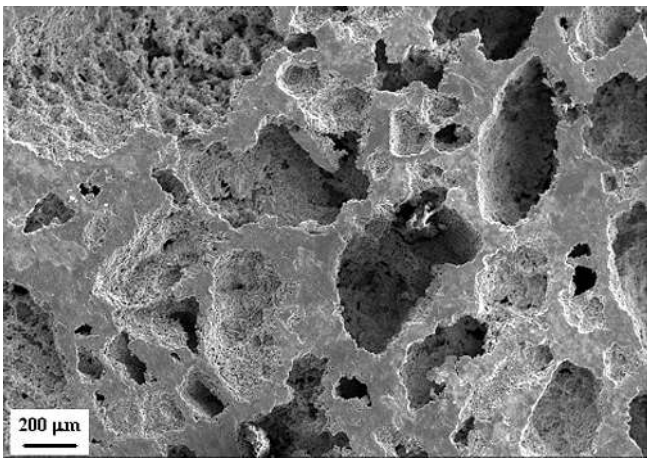

Fig. 1. SEM image of sintered porous Ti-15Mo alloy with porosity of 68.5 %.

a laser to sinter the powders, focusing the laser automatically at points in space defined by a three-dimensional model, binding the material together to create a solid structure in a layer-by-layer manner [24, 25].

Porous Ti-10Mo alloy was fabricated via the SLS route from mixed hydride-dehydride titanium, gas atomized molybdenum and epoxy resin powders. The porous structure of Ti-10Mo alloys prepared by SLS is characterized by irregular shaped pores and uniform pore distribution. A pore size of 120 to 130 μm of porous Ti-10Mo alloy with porosity of 61 to 63 % is favorable to bone tissue ingrowth [24, 25].

Distinct advantages of SLS over conventional methods like powder sintering include high material utilization rate, fast time-to-market, high flexibility, simultaneous implementation of sintering and patterning, ability to produce custom-designed components with complex geometrical features and so on. The disadvantages include high capital investment of SLS equipment and low production efficiency.

2.3. Gelcasting

Gelcasting is an attractive and new near net shaping technique to form metals or ceramics. The procedures of gelcasting are shown in Fig. 2 [26–28]. During the gelcasting process, a slurry formed by dispersion of metallic powders in an aqueous monomer solution is subsequently de-aired and mixed with catalyst and initiator and then gelled in a mold. Macromolecular gel networks from the polymerization of organic monomers in the suspensions bind the metallic particles together. After demolding, drying, binder removal and sintering, the products are available. Average pore size of 102 to 110 μm of porous Ti-(12.5–17.5) Mo alloys with porosity ranging from 40.15 to 46.32 % prepared by gelcasting would allow bone tissue to grow inside the foam [26, 27].

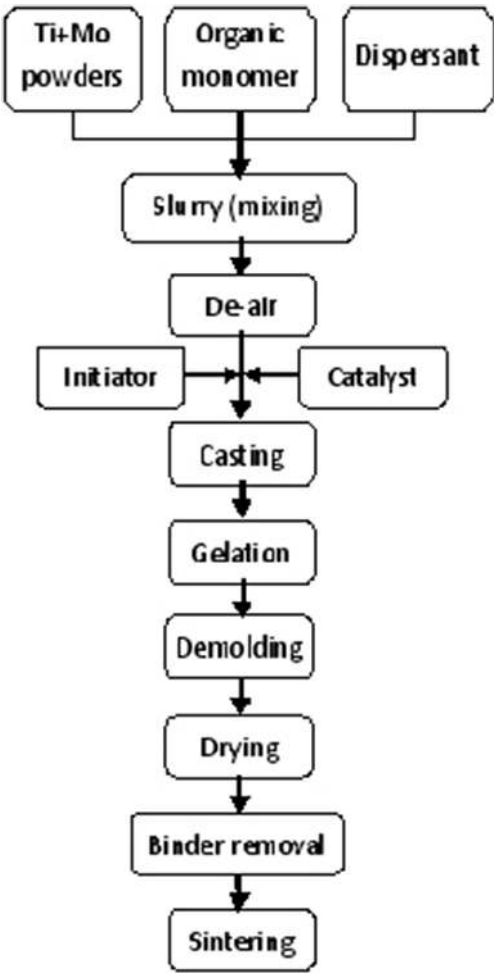

Fig. 2. Flowchart of gelcasting procedures [26–28].

The advantages of gelcasting over other approaches such as injection molding and slip casting include near net shape capacity, homogeneous properties and versatility in controlling the properties by adjusting process parameters. The shortcoming of gelcasting is complicated procedures.

In terms of pore size of porous implants, an ideal range between 100 and 300 μm is recognized to provide better osteoinduction and osteointegration of new bone tissue inside the open pores or cavities [5, 22–27]. In general, pore size of porous Ti–Mo alloys adjusted by the fabrication process variables can meet the preliminary pore size demand for porous implants. However, SLS is superior to PM and gelcasting in respect to homogeneous pore distribution and regular shaped pore morphology because the custom-designed pore architecture can be gained through the former method. But the inevitable inhomogeneous distribution and irregular shape of the space holder and organic binder in the green sample used for the latter two methods can result in inhomogeneous pore distribution and irregular shaped pore architecture. Moreover, the different porous structure may exert significant influence on the mechanical properties, corrosion resistance and surface modification of porous Ti–Mo alloys.

3. Mechanical properties

For application in hard tissue replacement, it is imperative to match the Young's modulus of the implant to that of bone tissue. Mechanical properties of porous Ti–Mo alloys with given compositions depend mainly on the porosity, which can be adjusted by process parameters. The Young's moduli of porous Ti–Mo alloys prepared by different methods are shown in Fig. 3, which is plotted from the available data [22–24, 26, 27]. The Young's moduli decrease dramatically with the increase in porosity of Ti-(10–17.5) Mo alloys prepared by PM, SLS or gelcasting. Furthermore, the modulus decreases with increasing Mo content, exhibiting a significant dependence on the composition of porous Ti–Mo alloy. Young's moduli (4.6–38.5 GPa) of the porous Ti-(10–17.5) Mo alloys with porosity of (18–70 %) are comparable to those of cancellous and cortical bones [5, 29]. The tailored Young's modulus can lessen the stress shielding effect, and allows bone/implant biological fixation by mechanical interlock between the bone and the porous implant.

The dependence of compressive strength on the porosity of porous Ti–Mo alloys with given compositions prepared by different methods is presented in Fig. 4, which is plotted from the available data [22–24, 26, 27]. Compressive strength decreases substantially with the increase in porosity of Ti-(10–17.5) Mo alloys prepared by PM, SLS or gelcasting. Moreover, the strength decreases with increasing

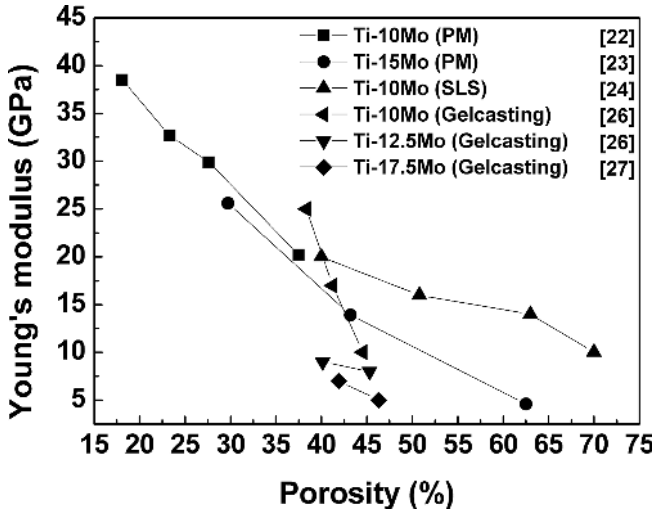

Fig. 3. Young's modulus of porous Ti–Mo alloys produced by different methods [22–24, 26, 27].

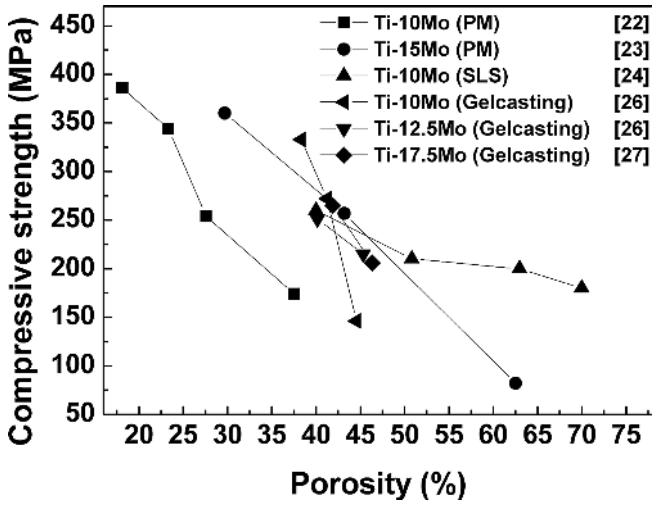

Fig. 4. Compressive strength of porous Ti–Mo alloys produced by different methods [22–24, 26, 27].

Mo content. Compressive strength (82–386 MPa) of porous Ti-(10–17.5) Mo alloys with porosity of (18–70 %) matches that of bone tissues [5, 29].

As an alternative route, multi-element alloying can be used to enhance compressive strength while maintaining low Young's modulus of Ti–Mo based alloy [30, 31]. The investigations demonstrate that the distinct strengthening effect of Fe and effective β-stabilizer of Mo could provide a good combination of adequate strength and ductility as well as relatively low Young's modulus in porous Ti-10Mo-(2–5)Fe alloys fabricated by powder metallurgy. The compressive strength (500–800 MPa) of porous Ti-10Mo-(2–5)Fe alloy is much larger than that (260 MPa) of porous Ti-10Mo alloy. Young's modulus of porous Ti-10Mo-(2–5) Fe alloy is less than 10 GPa [30].

The enhanced compressive strength (405 MPa) and low Young's modulus (9.19 GPa) of porous Ti-14Mo-2.1Ta-0.9Nb-7Zr alloy with porosity of 38.9 % prepared by powder metallurgy match those of cancellous bone [31].

To clarify and establish the quantitative relationship between porosity and mechanical properties is critical to design porous metallic implants with controlled Young's modulus and strength. The relationship between mechanical properties and relative density (ρ/ρ_s) or porosity (P) of porous Ti–Mo alloys with a given composition can be expressed based on the following Gibson-Ashby model, which obeys a power law relation [23]:

$$E/E_s = C_1\,(\rho/\rho_s)^m \tag{1}$$

$$\sigma/\sigma_s = C_2\,(\rho/\rho_s)^n \tag{2}$$

where E, σ and ρ denote the Young's modulus, strength and density of porous alloy while E_s, σ_s and ρ_s represent the Young's modulus, strength and density of the corresponding solid Ti–Mo alloy, respectively. Meanwhile, C_1 and C_2 are constants related to material and experimental condition; m and n are exponentials related to porous structure. The correlation between P and ρ/ρ_s of a cellular solid can be expressed as

$$P = (1 - \rho/\rho_s) \times 100\ \% \tag{3}$$

In general, the tailored Young's modulus and adequate compressive strength of porous Ti–Mo alloy are comparable to those of natural bones. Pore size distribution, pore architecture, pore distribution and so on, aside from porosity, are also responsible for the mechanical behavior of the porous alloy. Therefore, much attention should be paid on the stress concentration and uncertain fluctuation of the mechanical properties data that may arise from the inhomogeneously distributed, irregular and sharp-cornered pores in porous Ti–Mo alloys.

4. Bioactive surface modification

Deposition of HAP coatings on the surface of porous Ti–Mo alloys is an optional surface modification to improve the surface bioactivity, interface bonding between the film and the substrate. HAP coating can be conveniently deposited on the surface of porous metals with complex architecture by the biomimetic method whose common procedures consist of alkali treatment, heat treatment and simulated body fluid (SBF) soaking [22]. Gao et al. have deposited HAP coating on the surface of porous Ti-10Mo alloys using this route [22]. The alkali treatment refers to the immersion of the porous sample in 10 M NaOH solution at 323 K for 24 h. The heat treatment involves heating the alkali treated porous sample to 873 K for 1 h in vacuum and furnace cooled. The SBF soaking means the immersion of the heat treated porous sample in 1.5 SBF at 310 K for 5, 7, 14 and 28 days, respectively. After being dried at 323 K for 5 h, the HAP coating can be deposited on the surface of porous Ti-10Mo alloy by this approach [22].

The mechanism of apatite deposition on the surface of porous Ti–Mo alloy may be similar to that proposed for solid Ti alloy. A sodium titanate hydrogel layer could form on the surface of the alkali treated sample. After immersion in SBF, the exchange between Na^+ ions from the sodium titanate and H_3O^+ ions from the surrounding fluid would result in the formation of Ti-OH functional groups, which can in-

duce apatite nucleation on the surface. The HAP nuclei grow spontaneously by adsorbing Ca^{2+} and HPO_4^{2-} ions from the SBF solution and then a HAP layer can be deposited on the surface of porous Ti–Mo alloy [22].

In fact, porous structures including pore distribution, pore size, architecture of inner and outer pores, the surface condition, i.e. roughness and so on, play important roles in controlling the thickness, morphology, distribution and fixation of the HAP coating deposited on porous Ti–Mo alloys. Therefore, it is crucial to understand the correlation between the HAP coating characteristics and porous structure of porous Ti–Mo alloys by further investigations.

5. Corrosion behavior

The corrosion behavior of porous metallic implants is of great concern because the release of ions from the implant to the surrounding tissues may affect cell metabolism or cause other problems. The biomedical titanium alloys implanted inevitably corrode in the body fluid environment that contains some corrosive species, e.g. chloride ions, etc. The corrosion resistance of solid Ti–Mo alloys can be enhanced by addition of Mo [10–12]. However, the corrosion resistance of porous Ti–Mo alloys may degrade due to the larger surface area exposed to the body fluid. Corrosion behavior of metals is commonly characterized by means of electrochemical tests including potentiodynamic polarization and electrochemical impedance spectra (EIS). Electrochemical tests of porous Ti-10Mo alloys have been performed using a traditional three-electrode system by Xie et al. [25]. A saturated calomel electrode serves as a reference electrode, a platinum electrode as a counter electrode, and the polished porous alloy specimens as a working electrode. The tests were conducted in 0.9 % NaCl solution at 310 K. The polarization curve experiences a short passivation subsequent to active dissolution. Large and interconnected open pores can provide enough room to entrap electrolyte, resulting in accelerated crevice corrosion attack.

Comparative investigations of electrochemical tests for compact and porous Ti-20Mo alloys have been performed by Bolat et al. [32]. The corrosion current densities of both compact and porous Ti-20Mo alloys increase with the increase of the NaCl concentration in solution. The corrosion current densities of the porous Ti-20Mo alloy samples were about 25–30 times higher compared to the compact samples. Uniform oxidation without visible signs of deterioration has been observed on the surface of compact Ti-20Mo alloy. Conversely, corrosion pits randomly distributed on the surface characterized by local breakdown of the protective oxide layer have been observed on porous Ti-20Mo alloy. These results confirm the significant effect of chloride ions on the corrosion resistance of porous Ti-20Mo alloy. Meanwhile, porous Ti-20Mo alloy is more susceptible to corrosion than the compact form, indicating that the porous structure may exert a distinct effect on the corrosion resistance [32].

The equivalent circuit models used to fit the EIS data assume that duplex layers composed of a dense inner barrier layer and a porous outer layer may be formed on the surface of porous Ti–Mo alloys. Furthermore, the inner barrier layer is responsible mainly for the corrosion resistance of the alloy. The outer porous layer may contribute more to osteointegration after the biomaterial implantation. The outer passive layer is always found during the electrochemical tests. Much attention should be paid to the interaction between the surface chemistry of the alloy and corrosion behavior in the bone tissue, although it is not expected to change the mechanical properties. Porous Ti–Mo alloy is not only attacked on its surface but also the inner pores. Breakdown of the passive film and degradation of the corrosion resistance accelerate with the porosity of porous Ti–Mo alloys because the pitting and crevice corrosions occur simultaneously [25, 32].

In short, the corrosion behavior of porous Ti–Mo alloy is associated with factors such as porosity, architecture of outer and inner pore, pore size, pore distribution, etc. Consequently, it is important to clarify the relationships between the corrosion behavior of porous Ti–Mo alloy and its influencing factors. Deposition of a bioactive HAP coating may be an alternative measure to improve the corrosion resistance of porous Ti–Mo alloy in SBF.

6. Future directions and concluding remarks

Recent investigations of porous Ti–Mo alloys for hard tissue implant applications have achieved great progress, but more efforts should be made to realize practical application. More comprehensive studies in the following future directions are required to fabricate ideal biomedical porous implant candidates.

1. Porous Ti–Mo alloy can be fabricated using the approaches of PM, SLS and gelcasting. SLS is superior to other methods with respect to custom-designed components with complex geometry. Therefore, as an additive manufacturing technology, 3D printing will become the ideal route to synthesize porous Ti–Mo alloy.
2. Open porous structure with pore size larger than 100 μm can facilitate the ingrowth of bone tissue, transportation of body fluid and nutrients and firm fixation of the implant. It is imperative to optimize the fabrication approach to obtain controlled porous structure including surface condition, ideal pore size and porosity, homogeneous pore distribution and regular shaped open pores.
3. Young's moduli (4.6–38.5 GPa) and compressive strength (82–386 MPa) of the porous Ti-(10–17.5) Mo alloys with porosity of (18–70 %) match those of bones. Multi-element alloying can be used to enhance the compressive strength while retaining low Young's modulus of porous Ti–Mo based alloys.
4. It is important to establish the quantitative correlation between mechanical properties and the porous structure of porous Ti–Mo alloy for given compositions. Extensive investigations including bending, abrasive and fatigue tests should be performed to evaluate the bending behavior, wear resistance and fatigue resistance.
5. Bioactive HAP coatings on the surface of porous Ti–Mo alloys can be deposited using a biomimetic method. In the future, Zn-, Ag-, and Sr-doped bioactive HAP coatings with antibacterial properties should be deposited on the surface of porous Ti–Mo alloy to resolve the implant-related infection problems.
6. Electrochemical measurements indicate that porous Ti–Mo alloy is less corrosion resistant than the solid form. Further investigations should be carried out to evaluate its corrosion behavior and affecting factors.

7. In-vitro and in-vivo investigations of porous Ti–Mo alloys with deposited HAP coatings should be performed to evaluate the long-term biocompatibility.

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