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In-situ formed graded microporous structure in titanium alloys and its effect on the mechanical properties

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ABSTRACT

A simple method to fabricate porous titanium was developed, with which the graded microporous titanium alloys could be prepared by simply casting. The in-situ formed graded microporous structure and its effect on the mechanical properties of the titanium alloys were investigated. The results indicated that the mechanical properties of such graded microporous titanium alloys were superior to the porous titanium fabricated by other methods. This work provides a bright prospect for the production of graded porous titanium alloys with low-cost and high properties. This method can also be applied to synthesize other porous metallic biomaterials.

1. Introduction

Porous metals or metallic foams exhibit some novel properties, such as low density, low elastic modulus, and unique thermal, electrical and acoustic properties, which can be extensively used as functional and/or structural materials [1]. Among these applications, the porous metals as biomaterials, e.g., bone substitute material, have revealed their attraction and superiority [2]. For example, the connective porous structure in the material allows the ingrowth of the new-bone tissues and the transport of the body fluids. The low elastic modulus of the porous metals just meet the requirement of the metallic implants because the porous metals with bone-comparable elastic modulus can simulate the nature bone and improve bone remodeling and healing [3]. Recent years, Ti and Ti alloys used as implants have become increasingly prevalent because of its good biocompatibility, high strength/weight ratio and excellent corrosion resistance in the body environment [4]. However, its comparatively high elastic modulus has been a major problem. One way to solve this problem is to fabricate porous Ti and Ti alloys that can be produced through the following methods: (a) powder metallurgical process by sintering the simple metallic powder or the mixture of metallic powder and polymer resin [5–9]; (b) liquid-state process by injecting and mixing gas into a vat of molten metal or alloy followed by cooling [10–13]; and (c) solid–gas eutectic solidification process [14]. The porous titanium produced by different methods reveal some differences in homogeneity and quality. For example, by powder sintering one can get more homogeneous porous structures. However, the processing of powder sintering is complicated and high-cost compared with the other two methods. As for the liquid-state process, it requires that the injected gas do not react with the liquid metals. This process is also difficult to be controlled and the porous structure is more likely inhomogeneous. Recent years, 3D printing has been a quite popular method for fabricating biomaterials [15–17]. When this method was used to fabricate porous titanium [18,19], the metallurgical problems involved in the processing, such as impurity containment and metallurgical defects, might severe deteriorate the mechanical properties, which needs further investigations.

In this paper, we report a new route to fabricate the porous titanium alloys, which can be directly realized by simply casting. The indispensable conditions for achieving this aim are the large liquid–solid mushy zone and the dendritical solidification. The solid solution primarily nucleates and grows with dendritic morphology upon cooling. The developed branches isolate the interdendritic regions from the liquid melts and form micropores during solidification due to the liquid–solid shrinkage and the cooling contraction. Thus, the porous structure can be in-situ formed. Such solidification process can be adjusted and controlled by changing the composition of the alloy and/or by changing the cooling conditions applied. For example, by changing the composition one can get an expected porosity, or by changing the composition and the cooling condition one can obtain different porous sizes and

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distributions. The principles and the methods involved in the in-situ formed porous alloys will be explained and demonstrated in the following sections.

With this method the as-cast titanium alloys generally exhibit a graded porous structure due to the gradient solidification process along the radius of the cylindrical castings, in which the central zone of the cylinders has larger porosity, but the surface layer of the cylinders is dense. Such graded porous titanium alloys just can imitate the natural bone. It is obvious that the direct cast method to fabricate the graded porous titanium alloy described in this paper is much simple and convenient compared to the other methods [20–22].

2. Alloy design strategies

In order to develop the titanium alloy with large liquid–solid mushy zone, the composition of the alloy generally contains the high melting point components (melting temperature: larger than 1668 °C) and the low melting point components. The former usually can infinitely mix with titanium in the liquid state, and form beta-Ti solid solution that can primarily solidify during solidification. The latter can form low melting point eutectics with titanium, which disperse in the interdendritic region and lead to micropores after solidification. To meet these requirements, some refractory metals, such as Nb, Mo, Hf, Ta, and W, are candidates as the high melting point components; and some transition metals, such as Co, Cr, Fe, Ni, Zn, and Cu, are candidates as the low melting point components. To our knowledge, Ti–Cu–Ni–Sn quaternary alloy can form low melting point eutectic [23]. It is highly possible to construct the porous titanium alloy in the following form:

$$(Ti_aR_b)_x(Ti_cCu_dNi_eSn_f)_{1-x} \tag{1}$$

where the first parenthesis indicates the components for forming the high melting point solid solution; and the second parenthesis indicates the components for forming the eutectic phase. R indicates refractory metals. The subscript a–f indicate the atomic percentages; and x is the ratio of the solid solution and the eutectic phase, $0 < x < 1$. The values of c–f could be determined according to the Inoue's empirical rule for forming bulk metallic glass [23], which results in an eutectic composition with low melting temperature (lower than 1000 °C). The combination of R and Ti is arranged for getting a primary solidified phase (*bcc*-β-Ti solid solution) with relatively high melting temperature (about 1900–2500 °C) during solidification.

The phase diagram of such porous titanium alloys can be illustrated by Fig. 1. When cooling the liquid alloy, the *bcc*-β-Ti solid solution primarily nucleates in the melts at/below T_l (T_l corresponds to the liquidus temperature of the alloy with composition of C_0). With decreasing temperature, the nuclei grow preferentially along {001} directions of the *bcc* structure, leading to form a dendritic morphology in the melts. The size and the volume fraction of the dendritic phases can be adjusted by changing the alloy composition and/or by changing the cooling rate. As the dendrites grow, the remaining melts contract in volume because of the decrease in temperature. Since the liquid-feeding and the shrinkage cavities-refilled are restricted by the rapidly growing up of the dendritic branches, the shrinkage of the remaining melts in the interdendritic regions must lead to porous structures. The pore size (d) is in proportion of the total shrinkage of the remaining melts, which includes the thermal shrinkage and the liquid–solid transformation shrinkage, i.e.,

$$d \propto \alpha(T_l - T_e)V + \Delta V_{L-S} \tag{2}$$

where α is the coefficient of thermal contract of the remaining melts. T_e is the eutectic temperature (see Fig. 1). V is the volume

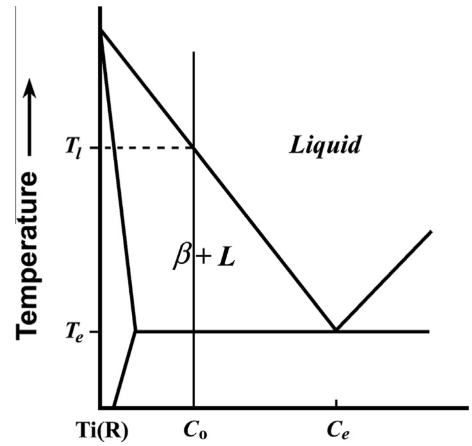

Fig. 1. Illustration of the phase diagram of the graded microporous titanium alloys.

of the remaining melts. ΔV_{L-S} is the liquid–solid transformation shrinkage of the remaining melts. Since the very large difference in melting temperature between the dendrites and the eutectic phase, i.e., T_l–T_e is very large (~1000 °C), the pore size must be remarkable. The forming process of the porous structure in the alloy can be illustrated in Fig. 2. When the alloy melts were cooled down to the temperature below (but near) the liquidus, the bcc-beta-Ti(R) phase primarily nucleates (Left in Fig. 2). As the temperature decreases from the liquidus to the eutectic, the primary phase grows dendritically (Middle in Fig. 2). When cooling down below the eutectic temperature, micropores form in the interdendritic regions (Right in Fig. 2). Since the shrinkage holes are restricted by the dendritic arms and branches, the pore sizes and distributions also depend on the morphology, the size and the volume fraction of the dendrites in the alloy. Therefore, we can adjust the porous structure by adjusting the dendrites.

3. Experiments and methods

Several graded microporous Ti alloys, named A, B, C, D, E, F and G as listed in Table 1, were demonstrated in this study. Master alloys with different compositions were prepared by arc melting of 99.9% pure metals. Copper mold casting was employed to cast cylinder and sheet samples with different sizes. In this paper, ϕ 3 mm × 50 mm and ϕ5 mm × 50 mm cylinders and 2 mm × 3 mm × 60 mm bars were cast. The as-cast cylinders were machined into ϕ3 mm × 6 mm specimen for compression tests and the as-cast sheets were machined into dog-bone shaped specimens with a gauge zone section of 1.5 mm × 2.5 mm × 40 mm for tensile testing. Both the compression and the tension tests were carried out with an Instron 8562 testing machine at a strain rate of 1×10^{-4}/s at room temperature. The characterization of the as-cast microstructures was carried out by using a JEOL-JSM6400 scanning electron microscope (SEM). The melting temperature of the alloys was determined by differential scanning calorimetry (NETZSCH DSC 404) using a constant heating rate of 20 °C/min. Observations on the porosity were made by using SEM. The porosity was evaluated from the SEM images. The average porosity of each alloy is the mean of the value determined on at least five images.

4. Results and discussion

4.1. Graded microporous structure in the titanium alloys

In the practice, Nb, Ta and Mo were used to configure the porous titanium alloys. As expected the dendritic *bcc*-Ti(R) phases