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Preparation of porous titanium materials by powder sintering process and use of space holder technique

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ABSTRACT

It is shown that an adapted powder sintering process can successfully prepare a 24.0%—35.5% porous titanium composite using 20 μm Ti powder and rice husk particles ranging in size between 250 μm and 600 μm. The phase constituents of the porous Ti composite samples were determined by X-ray diffraction (XRD) pattern sintered at 1250 ℃. The generation of silicon in the form of a $TiSi_2$ solid solution, injected into the substrate, illustrates the solid solution strengthening effect. The average grain size of the tested sample and the grain boundary area increase along with the silicon content. This indicates that silicon is dispersed within the green compact of Ti. As the distance from a hole becomes greater, the nanohardness increases until it reaches a maximum hardness of 3.5 GPa at approximately 1.5 mm. This may be due to the solid solution strengthening of SiO_2. However, nanohardness is 3.3 GPa at a distance of approximately 0.5 mm from a hole′s edge. The compressive strength is measured to be in the range of 440—938 MPa. The strain reaches 14.8%—16.6% under compression testing. A large number of cleavage steps appear following a fracture. The observed fracture is a brittle fracture. Porous Ti composites with about 36% porosity have promising potential biomaterial applications, specifically related to bone implants and biological bearings.

1. Introduction

Rice husks (RHs) are a rich and renewable crop genetic resource though great harm is done to the environment in China′s rural areas as the vast majority of RHs are incinerated. Only a small number of RHs are treated as feed. There are currently three major problems with how RHs are utilized. The first is a low utilization rate; only about 20% of RHs are recycled. The second is a low utilization level; RHs applications are limited to power generation and the manufacturing of low value-added industrial products such as industrial water glass, activated carbon and feed additives. The third is an inefficient recycling method that results in secondary pollution.

Porous titanium materials exhibit good mechanical properties, biocompatibility and corrosion resistance[1,2]. As these are favorable properties for medical applications[3-6], porous Ti and Ti composites are widely used as load-bearing implants for bone tissue engineering[7].

Porous Ti preparation methods, such as powder metallurgy sintering, diffusion bonding, slurry foaming sintering, freeze casting, polymer sponge template impregnation sintering, gel casting and powder injection molding, have been extensively studied[8-18]. The space holder method has been an area of research of significant activity, specifically the use of KCL[19], NaCl[20], Carbamide[21] and NH_4HCO_3[22] as the space holder.

In the present study, the use for presently wasted rice husks was explored. Namely, the use of rice husks in the preparation of porous Ti composites. Rice husks are composed primarily of carbon, oxygen, hydrogen and silicon, and have a low impurity content. Si is amorphous and has relatively high reactivity while C allows for carbon-thermal reduction. This provides favorable conditions for low temperature preparation of porous materials.

A powder metallurgy sintering process was used. First, a series of powder compaction experiments were carried out to investigate the compression behaviors of a variety of Ti and RHs powder mixtures under compressive stresses. Mixtures with several different volume fractions of RHs were tested. Ensuring data allowed for the analysis of compression be-

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haviors. Additionally, possible compression mechanisms responsible for the observed compression behaviors were established. Critical compacting pressures, which resulted in the geometrical change or fragmentation of RHs space holding particles in the titanium scaffold, were determined. The effects of the sintering temperature on phase constituents, pore characteristics, internal microstructures and mechanical properties of porous Ti composites were also measured.

2. Experimental Materials and Methods

The RHs used in this experiment were sourced from the Wuhan Rice Mill. The chemical composition of these RHs is shown in Table 1.

Table 1
Chemical composition of rice husks from Wuhan Rice Mill (wt. %)

Elemental analysis				Proximate analysis			
O	C	H	N	Volatile	Carbon	Ash	H_2O
55.58	38.55	5.32	0.55	61.23	14.96	17.08	6.73

Firstly, RHs were cleaned for 30 min in a deionized water and citric acid solution (10 vol. %) to remove organic compounds. The RHs were then dried in a stoving chest at 80 ℃. The dried RHs can be seen in Fig. 1(a). Ti powder (20 μm, 99% purity) served as a raw material. A scanning electron microscope image of titanium powder is shown in Fig. 1(b).

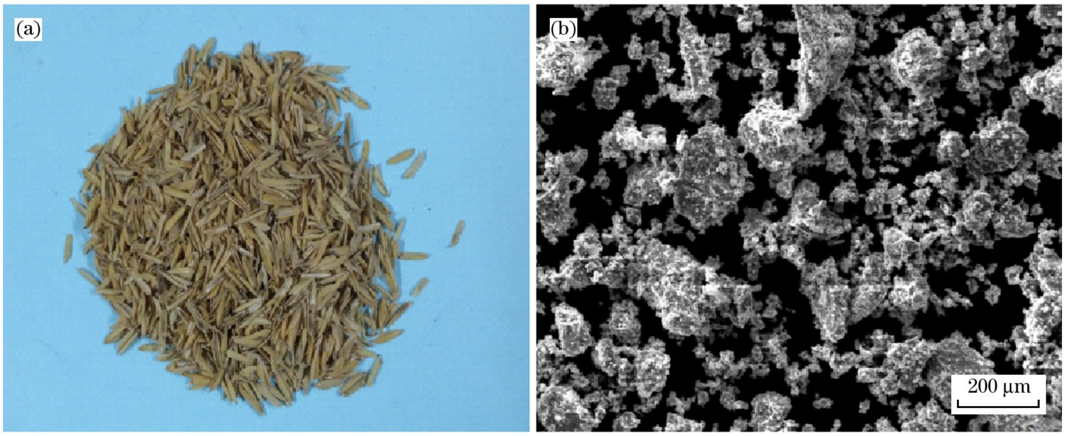

Fig. 1. Cleaned and dried rice husks (a) and scanning electron microscope image of Ti powder (b).

The chemical composition of Ti powder is shown in Table 2.

RHs particles with different sizes were added as space holder to the Ti samples in order to obtain different porosities and pore sizes. To achieve these different sizes, dried RHs particles were placed into a blender. Several standard sieves were used to sort the blended particles according to their size. RHs particles were classified as R1-R3 sample types, as shown in Table 3.

To prepare the samples, RHs with a particular size were mixed with the Ti powder at a weight ratio of 1 ∶ 5 in a specialized blender for 2 h. A hydraulic universal testing machine with pressure of 500 MPa

Table 2
Chemical composition of Ti powder (wt. %)

Ti	O	Si	C	Other
99.9	0.006	0.002	0.002	0.036

Table 3
Sample type and particle size

Sample type	R1	R2	R3
Particle size/μm	550-600	400-450	250-300

and one-way compression was employed. A cylindrical green compact test sample using a steel mold (ϕ15 mm×10 mm) was then prepared. Three types of green compacts were placed into a vacuum sintering furnace, and vacuum degree was set to 10^{-3} Pa. The vacuum sintering furnace was heated to 700 ℃ from room temperature at a minimum rate of 10 ℃ · min^{-1}. Full insulation was then ensured for 2 h to allow for the carbonization of the RHs. After that, the vacuum sintering furnace was heated to 1 250 ℃ and insulated for 3 h to allow for the thermal reaction between the Ti and the carbonized RHs. Finally, the samples were cooled at a rate of 10 ℃ · min^{-1}. The resulting porous Ti composites served as test samples.

The phase constituents of the porous samples were determined by X-ray diffraction (XRD) patterns exposed by an X-ray diffractometer (model 7000) with CuKα radiation and a Ni filter. The powder sample for XRD was prepared by smearing a thin layer of powder on a glass plate. The glass plate had previously been coated with paraffin wax to allow for good adhesion. The XRD analysis was carried out at a voltage of 40 kV and 40 mA within diffraction angles ranging from 20° to 80° at a scanning speed of