Preparation of Porous Fe from Biomorphic Fe$_2$O$_3$ Precursors with Wood Templates

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Porous iron with woodlike microstructures was prepared from two kinds of wood templates through a developed biotemplating method in the present work. The biomorphic iron oxide was first produced through infiltration and sintering procedures, and was then reduced to the biomorphic iron in a hydrogen atmosphere at high temperatures (600°C and 1000°C). The morphologies of iron and iron oxide products were observed using SEM and FESEM, and their crystal structures were identified using X-ray diffraction. The results indicate that the pure iron phase can be obtained after the reduction process and the products faithfully retained the microstructures of the corresponding wood templates.

1. Introduction

In recent years, there has been great interest in the preparation of porous metals owing to their low density as lightweight structural and multifunctional materials with nice thermal conductivity, acoustic, energy absorption characteristics and so on. Different methods have been utilized in the synthesis of porous metals or metallic foams including traditional powder metallurgy,\(^1\) a unidirectional solidification method,\(^2\) CVD technique,\(^3\) natural convection,\(^4\) and electroleass deposition method.\(^5\) However, most of these methods should be performed with special equipment and under high pressure to improve the porosity.

The synthesis method (biotemplating technology), which uses organism as template to prepare new materials, has concentrated intensive efforts due to the unique, exquisite and highly ordered structures of templates, large amount and low cost of raw materials, and simple operation conditions. Wood is a principal organic structural material with high strength, stiffness, toughness and damage tolerance at low density.\(^6\) Its outstanding mechanical properties originate from its hierarchical porous structures with cylindrical pores of vessels in millimeter scale, fibers and tracheids of micrometer in diameter and millimeter in length, and molecular fiber and cell membrane in nanometer scale. In previous researches, biotemplating technologies were concentrated on converting biological structures into ceramic materials. Carboide ceramics (SiC and TiC\(^{7-11}\)), oxide ceramics (ZnO, NiO, Al$_2$O$_3$, and TiO$_2$\(^{12-16}\)), and carbon composites (TiN/C, SiOC/C, Al/C, and C+SiC/Al\(^{17-20}\)) have been prepared successfully with various wood templates and retained the morphologies of templates faithfully.

In the present work, biotemplating method was developed to prepare porous Fe for overcoming the disadvantages of complex traditional methods for porous Fe. We employed a simple but effective biotemplating method using biomorphic Fe$_2$O$_3$ ceramics as precursor to prepare porous Fe. Here, wood was chosen as the porous template for Fe product due to its regular and diverse porous configuration. Two kinds of woods, fir and paulownia woods were used as template because they represent typical categories of wood: softwood and hardwood. Hardwood is composed by several kinds of cells, such as visible vessels, fibers and multiseriate rays at \(\mu\)m scale. Softwood has much simpler structure, which consists of tracheid cells accounting for over 90% of the volume. It’s hoped that Porous Fe products can retain hierarchical pores and high porosity from both wood templates.

2. Experimental

Cuboid preforms with the size of 20 × 10 × 3 mm$^3$ were cut by fir wood and paulownia wood along the cross sections. The preforms were extracted by boiling 5 mass % ammonia solution to remove the wood extractive compounds such as resins, salts and so on. The preforms were washed by deionized water, and dried at 80°C for 24 h. The ferric nitrate precursor solution was prepared by ferric nitrate (Fe(NO$_3$)$_3$, 9H$_2$O, analytically pure, >98.5%), ethanol and deionized water as the ratio of 48 mmol/30 ml/10 ml. The preforms were infiltrated in the precursor solution at 60°C for 72 h and subsequently dried at 60°C for 12 h. In order to realize the well-connected porous structures in biomorphic Fe product after lose weight and thermal contract during reducing Fe$_2$O$_3$ precursors at high temperature, we have to increase the infiltration rate and weight gain when preparing Fe$_2$O$_3$ precursor. So the infiltration/dry processes were repeated for 5 times to improve the infiltration rate of the wood preforms. The infiltrated preforms were sintered at 600°C for 2 h in air to remove the wood’s original components and obtain biomorphic Fe$_2$O$_3$ ceramics. Finally, the Fe$_2$O$_3$ ceramics were used as precursor to produce biomorphic Fe through

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Reduction in hydrogen at 600°C or 1000°C in normal atmosphere for 2 h. The fabrication process of biomorphic iron is summarized in Fig. 1.

The wood templates were pyrolyzed into char templates at 600°C for 2 h and were observed in SEM images by PHILIPS EDAXPV9900 for investigating the morphologies of the original wood. The biomorphic iron oxide and iron were observed in FESEM images by FEI SIRION200. The crystal structures of the preforms were examined by X-ray diffraction (XRD, Cu Ka radiation, BRUKER-AXS).

3. Results and Discussion

The crystalline phases in the biomorphic products before and after the last reduction procedure were detected by XRD as shown in Fig. 2(a) and (b, c), respectively. After being sintered at 600°C, before reduction, iron ions adsorbed on the cell walls of woods through capillary adsorption were converted to α-Fe₂O₃, which was the only phase detected according to the peaks in Fig. 2(a). After the Fe₂O₃ ceramic was reduced at 600°C for 2 h, the coexistence of the peaks (see Fig. 2(b)), which were belonging to α-Fe₂O₃ or cubic Fe, illustrated that the reduction procedure was incomplete. When the reducing temperature increased to 1000°C, with the same reducing time of 2 hours, all the Fe₂O₃ ceramics have been converted to Fe because only three peaks were detected, which correspond to the (110), (200) and (211) diffraction peaks of Body-centered cubic Fe as shown in Fig. 2(c).

Figure 3(a) shows SEM image of the char template of fir wood. The fir wood is a kind of softwood that is composed of single rectangular type of cells. They are called as tracheids that run longitudinally and resemble long, straight tubes of about 20 μm in diameter and several mm in length. The cross section of biomorphic Fe₂O₃ ceramics through infiltration/dry processes five times was observed with FESEM as shown in Fig. 3(b). Another kind of Fe₂O₃ ceramics through infiltration/dry processes only once was also fabricated for comparison. Fig. 3(c) shows the cross-section morphology of this sample. The fir’s well-aligned porous structures were retained by both Fe₂O₃ ceramics. The features of tracheid cells were well reproduced after removing the wood’s organic components by oxidation. The product infiltrated only once had some cracks, thin cell walls about 1 μm, and low density. In comparison with Fig. 3(c), the product infiltrated five times had more intact structure, thicker cell walls of about 1.5 ~ 5 μm and higher strength. The difference of wall thickness came from the difference of weight gain during infiltration process, which were about 67 wt % for once infiltration and 169 wt % for five times infiltrations. So the biomorphic Fe₂O₃ ceramics infiltrated five times was chosen to produce biomorphic porous Fe due to its better structure. Fig. 3(d) shows the FESEM image of porous Fe product after reduction in hydrogen at 1000°C for 2 h. Rectangular pores were originated from the fir’s tracheid cells, although the pores have shrunk to about 10 μm, and the cell walls were thickened to about 3.5 ~ 6 μm by the thermal contraction and grain growth at high temperature.

Paulownia wood, as a typical hardwood, was also used as template to prepare biomorphic Fe₂O₃ and Fe to certify the effect of our fabrication process on the hardwood. The morphology of the char paulownia template is shown in SEM image (see Fig. 4(a)). In contrast to softwood, the structure of hardwood is more complicated, due to more cell types existing in hardwoods. The large pores represent the vessel cells with the diameter of about 100 μm, and the small ones are the fibers with the diameter of 10 ~ 25 μm. In some vessels, tyloses are visible, which are ingrowths of adjoining parenchyma cells into the vessel cells. The morphologies of biomorphic Fe₂O₃ and Fe products are shown in Fig. 4(b) and (c) with FESEM images, respectively. Biomorphic Fe₂O₃ ceramics has preserved both vessel pores and fiber pores. In comparison with char template, its vessel pores enlarged and flattened slightly to ellipse due to the large size.

Fig. 1 Flow chart of the fabrication process.

Fig. 2 XRD patterns of fir-templated products: (a) sintered at 600°C for 2 h without reduction process; (b) sintered at 600°C for 2 h and then reduced at 600°C for 2 h; (b) sintered at 600°C for 2 h and then reduced at 1000°C for 2 h.
Fig. 3  (a) SEM image of char template of fir wood. FESEM images of fir-templated Fe₂O₃ ceramics sintered at 600°C: (b) infiltrated once; (c) infiltrated five times. (d) FESEM image of biomorphic Fe reduced at 1000°C.

Fig. 4  (a) SEM image of char template of paulownia wood. FESEM images: (b) biomorphic Fe₂O₃ ceramics infiltrated five times and sintered at 600°C; (c) biomorphic Fe reduced at 1000°C.
difference between vessels and fibers during sintering process. Several lumps were observed in the vessels because of two reasons: one is to preserve the tyloses’ structures, and the other is that Fe$_2$O$_3$ multilayer was deposited on the cell walls during repeated infiltration and then a few layers curled up toward vessels during high-temperature sintering. When the biomorphic Fe$_2$O$_3$ was reduced, well-aligned and connected structure of Fe product was obtained. The biomorphic Fe retained both two kinds of pores with smaller size than Fe$_2$O$_3$ product because of thermal contraction at 1000°C. The vessel pores preserved cylindrical shape with the diameter of 50 ~ 100 μm while the fiber pores with the diameter of about 10 μm. During reduction, creation and escapement of a large amount of water vapor caused many micro pores on the cell walls, which can improve the connectivity of the Fe product.

4. Conclusion

Porous iron has been successfully prepared through a simple biotemplating method. Biomorphic iron oxide was first fabricated by infiltration with a ferric nitrate precursor solution and subsequent oxidation at 600°C in the air atmosphere. Then, the biomorphic iron can be obtained through reducing its biomorphic iron oxide precursor. Both Fe and Fe$_2$O$_3$ products retained the porous structures of wood templates. Depending on choosing different wood template’s pore size and pore distributions, biomorphic Fe and Fe$_2$O$_3$ with various porous morphologies can be smoothly designed and fabricated.

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