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Communication

Complex-Shaped Porous Cu Bodies Fabricated by Freeze-Casting and Vacuum Sintering

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Abstract: Porous Cu bodies with complex shapes were fabricated by freeze-casting and vacuum sintering water-based CuO slurry. The sintered bodies showed no noticeable macroscopic defects and good shape tolerance. The interconnected pore tunnels were observed by electronic microscopy. The pore size became smaller and the porosity and volume shrinkage of sintered porous bodies decreased with the increase of solid content in the slurry. XRD results showed the CuO was fully decomposed by vacuum sintering into Cu without any second phases. This new fabrication method may be especially economical when small quantities of porous parts are required.

Keywords: porous materials; microstructure; copper; freeze-casting; vacuum decomposition sintering

1. Introduction

Porous metals are regarded as a potential engineering material in various industrial fields because of their unique properties, such as good sound absorption, being light-weight, high damping and impact energy absorption, gas and liquid permeability, thermal conductivity, electrical insulating properties, *etc.* [1] Therefore, many fabrication techniques have been developed to produce porous metals, such as electrodeposition, vapor deposition or powder metallurgy, directional solidification, *etc.* [2] Pore structures of various types can be produced according to the fabrication process used: e.g., closed-cell, open-cell, and lotus-type structures [3]. However, it is difficult to control the macroscopic shape of the porous bulk metals. Therefore, it is necessary to develop a flexible technique to fabricate complex-shaped porous metal bodies with controlled pore characteristics.

The porous ceramic bodies can be fabricated via freeze-casting. Freeze-casting [4,5] is a forming technique where ceramic slurry, which is usually aqueous, is frozen in a mold at an extremely cold temperature, followed by demolding and vehicle removal by sublimation, *i.e.*, freeze-drying, to obtain a green body with porous structures. Deville and Bouville *et al.* reported a bioinspired, material-independent approach based on the freeze-drying method [6]. The pore size, volume and morphology are dependent on variables such as freeze temperature, slurry concentration, and nature of solvent and solute [7].

However, the freeze-casting process has been restricted to the fabrication of porous ceramics due to difficulties in the preparation of homogeneous slurry with metal particles [8]. In order to fabricate porous metals, metal oxide can be used instead of metal powder, and then pure metal is obtained by thermal decomposition or hydrogen reduction sintering [8–10]. Cuba Ramos and Dunnad *et al.* have fabricated directional copper foams by hydrogen reduction using CuO powder as a precursor for Cu; however, hydrogen is dangerous [10]. Compared with metal powder, metal oxide is a low-cost, chemically stable and abundant raw material. The complex-shaped porous metal oxide bodies can be fabricated using freeze-casting or machining of the green compacts (after freeze-drying). Many researchers have recently focused on the preparation of porous ceramics by freeze-casting [4,5,11], but preparation of porous metal using this method is rare. In particular, the green compact can easily be further machined into complex shapes and machined chips can be reused to prepare new slurry.

In this work, we demonstrate the possibility of using water as an alternative freezing vehicle for the production of the complex-shaped porous bulk Cu. CuO powder was selected as the source for the formation of Cu via thermal vacuum decomposition. The dependence of the CuO content in the slurry on microstructure and porosities of porous Cu is described.

2. Experimental Section

Commercially CuO powder (−200 mesh, 99.0% purity, Tianjin Zhiyuan Chemical Co., Ltd, Tianjin, China) was used as the source of Cu. Deionized water was used as a solvent, and PVA industrial grade (polymerization degree ~2000; hydrolysis degree 99 mol%; Sinopec Shanghai Petrochemical Co., Ltd, Shanghai, China) was chosen as binder. The CuO/aqueous slurries with various solid contents (from 20% to 40% with a gap of 5%, volume fraction) were prepared by ball milling. The slurries were then poured into polyethylene molds at −20 °C for 3 h. After the slurries were completely solidified, the frozen bodies were followed by moving into a freeze-drier (Shanghai Bilang Co., Ltd, Shanghai, China), freeze-drying at 5 Pa vacuum for 20 h. Figure 1 shows the schematic diagram of fabrication procedure of complex-shaped porous Cu. The green bodies were heated up to 900 °C in a vacuum atmosphere (<4 × 10^{-2} Pa) for 2 h to induce the complete decomposition of ceramics CuO to metallic Cu, also consolidation of the Cu powder.

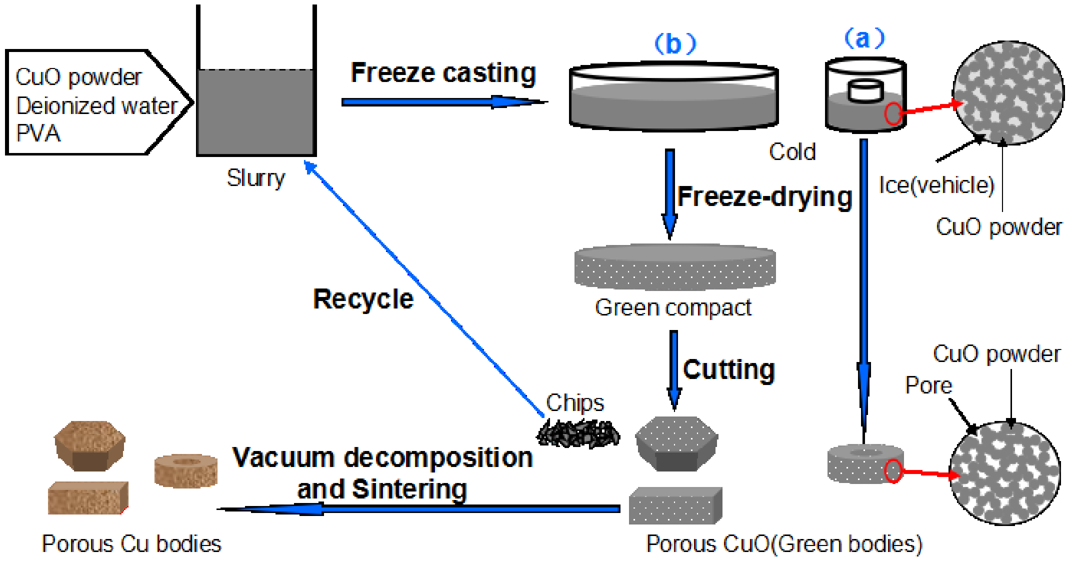

Figure 1. Schematic diagram of fabrication procedure of complex-shaped porous Cu bodies.

PVA (3 wt%) aqueous solution was prepared first. CuO powders were mixed with the PVA aqueous solutions at the desired volume ratio, ball milled for 2 h. The CuO slurry was then poured into polyethylene molds placed into a freezer at −20 °C. The frozen bodies were removed from the mold and transferred to a freeze-dryer where the ice was removed by sublimation. The freeze-dried CuO green bodies were decomposed into porous Cu bodies by vacuum sintering. The porous CuO green body, such as hollow cylinder body in present work, can be prepared directly using freeze-drying by route (a). Different shaped porous CuO green body can be obtained by machining the freeze-dried compacts by route (b). Meanwhile, the machined chips can be recycled for preparation of slurry (Figure 2).

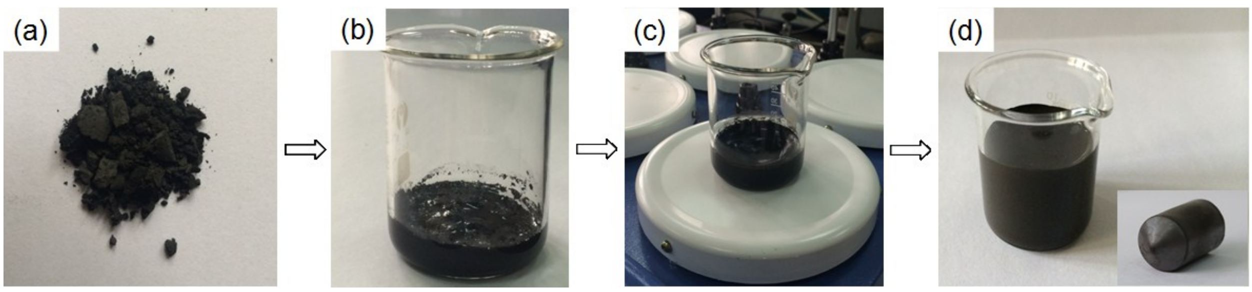

Figure 2. Schematic diagram of fabrication procedure of secondary slurry: (**a**) chips; (**b**) adding solvent; (**c**) heating and stirring; (**d**) secondary slurry and green body (bottom right in Figure 2d).

Phase identification was determined by X-ray diffractometry (XRD, D8 ADVANCE, Bruker, Karlsruhe, Germany). The Quanta 250 SEM (FEI, Hillsboro, OR, USA) was employed to observe and analyze the microstructure of the sintered bodies. The porosities were determined by Archimedes method. Compressive tests were carried out on a CSS-44300 electronic universal testing machine

(Changchun New Testing Machine Co. LTD, Changchun, China) with a compression rate of 0.1 mm/min. The sintered porous Cu was machined by precision cutting saw (SYJ-200, MTI Corporation, Shanghai, China).

3. Results and Discussion

Figure 3 shows the macro photograph and XRD patterns of the porous bodies (30 vol.%) before and after sintering. The graceful complex-shaped porous Cu bodies are fabricated using the described technology, as shown in Figure 1. The color change shows that CuO is fully decomposed into Cu by sintering (Figure 3a), and these observations are also in good agreement with XRD results (Figure 3b). The sintered bodies show no noticeable macroscopic defects, such as cracking or distortion. The complex shape is due to the slurry having good fluidity which can flow into all corners of the molds. In addition, the basis of the freeze-dried CuO green compact is powder which bonds with a PVA binder and is easy to machine into different shapes with a knife.

XRD patterns show only the peaks associated with the CuO phase before sintering, indicating that the additives did not react with CuO powders. Moreover, the CuO powder decomposition at 900 °C for 2 h in vacuum was composed only of Cu phase without any second phases in porous Cu bodies. This indicated that CuO can transform to Cu metal via thermal vacuum decomposition [9]. The weights of porous bodies were measured before and after vacuum sintering, and the mass loss was calculated at around 23.3%, which is consistent with the results of CuO to Cu (loss of 20.1%) and decomposition of additive (loss of 3%), including a little water. On the basis of these results, the vacuum decomposition of CuO green body was established.

Figure 3. Macro photograph (**a**), and XRD patterns (**b**) of the porous bodies (30 vol.%) before and after vacuum sintering.

The microstructures of sintered bodies are shown in Figure 4. The sintered bodies preserved their highly porous structures with interconnected pore tunnels. These pores were generated from sublimation of the ice and the pore morphologies were controllable by the solid content in the slurry. Note that the walls of the tunnels are dense, without any noticeable cracks; the surface of the walls facing tunnels is also smooth. In other words, the fine CuO particles were effectively repelled by growing ice crystals and became concentrated as the slurry solidified, resulting in the formation of highly packed CuO walls; consequently, allowing the preservation of the porous structure without the disintegration of the sample after freeze-drying and heat-treatment. As shown in Figure 4, as the initial CuO content increased, the porosity of porous Cu decreased, the pores became smaller and the compressive strength increased (Figure 5); as is often the case with the freeze-casting method [8]. In this case, more nucleation sites were available for the aqueous crystals to grow, leading to the pore structure becoming homogenous with solid loading. These pores exist homogenously throughout the sintered body, and the pore tunnels have flat. ellipsoidal. and nearly circular cross-sections.

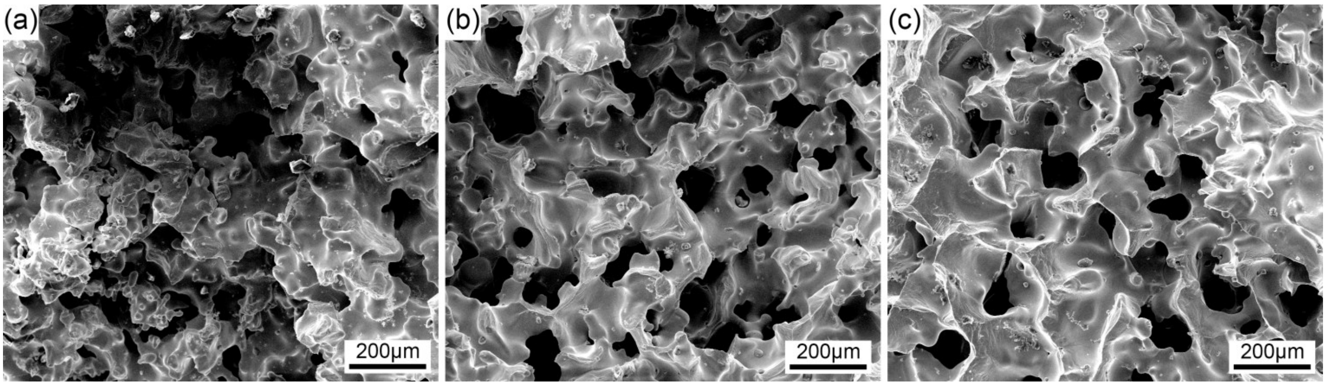

Figure 4. SEM of porous Cu bodies produced using different CuO contents: (**a**) 20 vol.%; (**b**) 30 vol.%; (**c**) 40 vol.%.

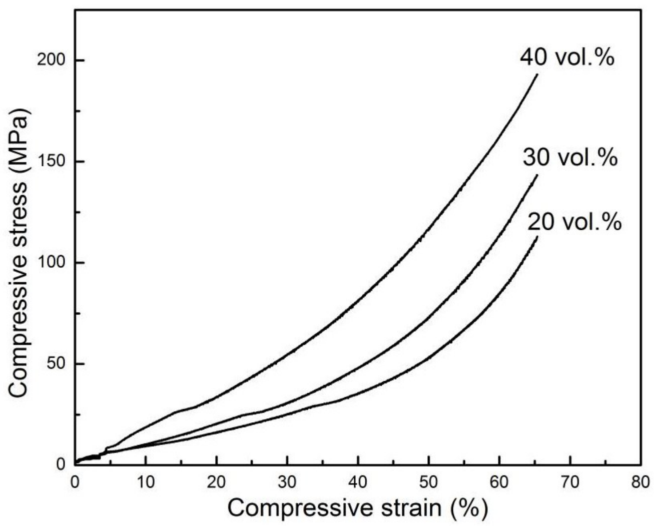

Figure 5. The stress-strain curves of porous Cu bodies with various solid content.

Table 1. Porosity and volume shrinkage of the porous Cu bodies as a function of the solid content in the slurry.

Solid content (vol%)	Porosity (%)	Volume shrinkage (%)
20	49.7	60.2
25	44.3	55.1
30	38.3	51.4
35	34.9	46.2
40	30.8	42.2

Table 1 shows the porosity and volume shrinkage of the sintered body. The porosity is controllable by the solid content in the slurry, and decreases from 49.7% to 30.8% with the increase in solids content from 20 to 40 vol.%, in agreement with the microstructure (Figure 4). On the other hand, shrinkage during sintering mainly occurs because of densification of the metal framework, and the degree of shrinkage is also affected by solid content. Table 1 shows that the volume shrinkage decreases with the increase in solids content, and reaches a minimum 42.2% when the solids content is 40 vol.%. The solids content determines the porosity and volume shrinkage levels of the material.

Figure 6 shows the surfaces of porous Cu (20 vol.%) in different machining conditions. The machining of green freeze-dried porous body was found to be more promising compared with that of sintered porous metal. The machining of sintered porous Cu bodies leads to partial closure of surface pores due to plastic deformation of Cu and to rapid wear of the tool. Also, the residues of lubricants or grinding media mark the porous structure. Owing to the disadvantages of machining of sintered porous metal, the machining of green freeze-dried porous body becomes especially economical for fabricating porous parts with special geometry, and the machined chips can be reused for preparing slurry. This process may be applicable to many other metal oxide slurries for the preparation of porous metal, and the procedure is low-cost and simple.

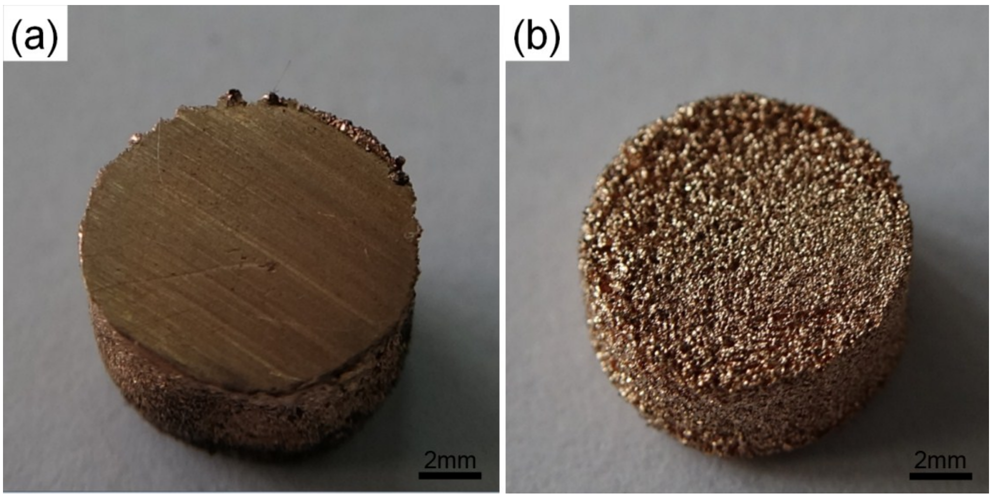

Figure 6. The surfaces of porous Cu in different machining conditions: (**a**) machined in the sintered state; (**b**) machined in the green body state.

4. Conclusions

Porous Cu bodies with complex shapes were fabricated by freeze-casting and vacuum sintering water-based CuO slurry. After vacuum sintering, the CuO powder was completely converted to metallic Cu. Pores were generated from sublimation of the ice during freeze-drying, and the interconnected pore tunnels were observed. As the CuO content increases from 20 to 40 vol.%, the porosity of the porous Cu body decreases from 49.7% to 30.8%, the pore size becomes smaller and the compressive strength increases. Complex shapes can be obtained directly using freeze-drying, or machining the freeze-dried compacts, whilst the machined chips can be recycled for preparation of new slurry. Our study opens a way to prepare complex-shaped porous metal bodies from metal oxides slurry by freeze-casting, followed by thermal vacuum decomposition sintering.

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Author Contributions

Huashen Ran: Sample preparation, and writing the manuscript. Zhangsheng Liu and Jinan Niu: Data analysis. Xiaohong Wang: Development of the process. Peizhong Feng and Haifei Zhang: Supervision of the first authors and writing the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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