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# Low temperature solid-phase sintering of sintered metal fibrous media with high specific surface area

TANG Biao, TANG Yong, ZHOU Rui, LU Long-sheng, LIU Bin, QU Xiu-ming

Key Laboratory of Advanced Manufacturing Technology of Surface Functional Structure of Guangdong Higher Education Institutes, South China University of Technology, Guangzhou 510640, China

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**Abstract:** A procedure of low temperature solid-phase sintering (LTSS) was carried out to fabricate sintered metal fibrous media (SMFM) with high specific surface area. Stainless steel fibers which were produced by cutting process were first plated with a coarse copper coating layer by electroless plating process. A low-temperature sintering process was then completed at about 800 °C for 1 h under the protection of hydrogen atmosphere. The results show that a novel SMFM with complex surface morphology and high specific surface area (>0.2 $m^2/g$) can be obtained in this way. The effect of sintering temperature on the surface morphology and specific surface area of SMFM was studied by means of scanning electron microscopy and Brunauer-Emmett-Teller. The damage of micro-structure during the sintering process mainly contributed to the loss of specific surface area of SMFM and the optimal sintering temperature was 800 °C.

**Key words:** sintered metal fibrous media; low temperature solid-phase sintering; electroless copper plating; surface morphology; specific surface area

## 1 Introduction

Porous metallic materials with three-dimensional internal pore structure can be used as both structural materials and functional materials. As a kind of porous metallic material, sintered metal fibrous media (SMFM) has many promising characteristics, such as high mechanical strength, high specific surface area, high porosity and low manufacturing cost. So it has been widely applied in absorption [1], filtration and separation [2], catalyst carrier [3], biomedical materials [4], fuel cells [5], metal electrodes [6] and so on. Studies show that the specific surface area of SMFM is closely related to its performance on filtering, absorption, capillary function and catalyst adhesion. SMFM with high specific surface area is widely needed.

ZHOU et al [7] and TANG et al [8] obtained metal fibers with plenty of micro-structure by cutting method. Fibers with relative high specific surface area are good raw materials to manufacture SMFM. However, WEI et al [9] found that the microstructure on metal fibers would be remarkably damaged during traditional sintering process because the employment of high sintering temperature leads the decrease of specific surface area of SMFM. Thus, further increase of the specific surface area of raw fibers and decrease of the sintering temperature should be considered to obtain SMFM with high specific surface area.

It is found that activated sintering process is a viable method for lowering sintering temperature of metal [10−12]. MENG et al [13] and HE et al [14] confirmed that the existence of copper additive in stainless steel matrix phase could increase the diffusion of atomic sintering system and lower the sintering temperature. MARKAKI et al [15] achieved metallurgy forming of stainless steel fibers at a low temperature (1 100 °C) by plating copper coating on stainless steel fibers as sintering activator. They proposed a feasible method for low-temperature sintering of stainless steel based SMFM. However, the surface morphology and specific surface area of sintered materials were not considered.

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**Corresponding author:** TANG Yong; Tel: +86-20-87114634; E-mail: ytang@scut.edu.cn
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A novel LTSS route which combined electroless plating with sintering process was proposed in this work to fabricate SMFM with high surface area. It should be noted that the low-temperature sintering concept mentioned was relative to the melting point of stainless steel material. The effects of sintering temperature on the surface morphology and specific surface area of SMFM were studied.

## 2 Experimental

### 2.1 Preparation of SMFM by LTSS route

The LTSS route was employed to fabricate stainless steel based SMFM, which was composed of three steps, the fabrication of stainless steel fibers, the plating process and the sintering process.

First, stainless steel (Cr18Ni9Ti) fibers were fabricated by cutting process with multi-tooth tool [16]. Dry cutting was conducted on a lathe CM6140 and continuous stainless steel fibers with coarse surface morphology were efficiently produced. The cutting parameters were: back engagement of 0.2 mm, feed rate of 0.1 mm/r and cutting speed of 13.19 m/min.

Second, electroless plating [17] was carried out to plate a copper coating on stainless steel fibers. The electroless plating process was carried out in an alkaline bath. The temperature of alkaline bath was maintained at 60 °C. The reagent formula of plating solution was comprised of $CuSO_4·5H_2O$ (10 g/L), EDTA (12 g/L), $C_4H_4KNaO_6·4H_2O$ (40 g/L), NaOH (10 g/L), HCHO (10 g/L) and $NiSO_4·6H_2O$ (2 g/L). The thickness of copper coating was controlled by plating time. In this work, in order to get a uniform thickness of copper coating, all the as-plated fibers were plated for a fixed time of 20 min.

Third, sintering samples (A, B, C and D) with the same porosity (80%) were prepared and sintered in a box-type furnace (FXL-12-11) with hydrogen protection atmosphere. Copper coated fibers were cut into short fibers of about 10 mm in length and the fibers were put into a packing chamber of a mold pressing equipment (as shown in Fig. 1). After the mold pressing equipment was assembled and put into furnace, the sintering procedure was imposed on the samples. The samples A, B, C and D were sintered at 800, 700, 900 and 1 000 °C for 60 min, respectively. Thus, SMFM sample $A_s$, $B_s$, $C_s$ and $D_s$ were obtained respectively.

### 2.2 Surface morphology analysis and BET-area test

The surface morphology of stainless steel fiber, copper coating and SMFM samples were characterized by scanning electron microscopy (QUANTA 400/INCA/HKL).

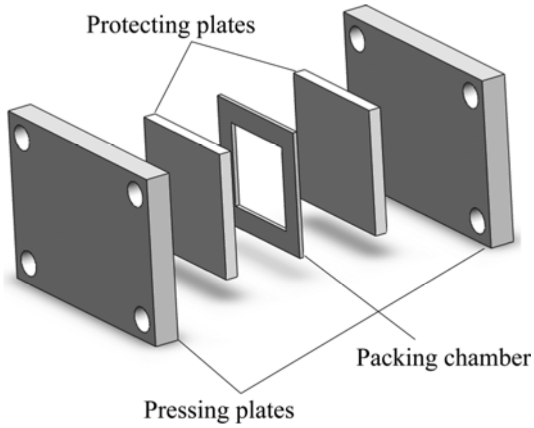


**Fig. 1** Illustration of mold pressing equipment

The specific surface area of samples $A_s$, $B_s$, $C_s$, $D_s$ and a piece of commercial SMFM $L_s$ were tested according to the operation standards of BET-area testing for porous solid materials [18]. The samples were firstly degassed at 200 ℃ for 60 min. Then, multi-point BET-nitrogen tests were carried out on a automatic specific surface area and porosity test machine (Micromeritics Tristar II). The nitrogen adsorption temperature was −196.15 °C.

## 3 Results and discussion

### 3.1 Morphology analysis of copper coating

Figures 2 and 3 show the surface morphology of stainless steel fiber before and after electroless plating process. From figure 3, the copper coating well covers the surface of stainless steel fiber. Plenty of micro-scale cell body-like copper particles, as marked with arrows, distribute randomly on the surface of coating layer.

During the electroless plating process, the coating layer grows by nucleation. Crystal nucleuses form with

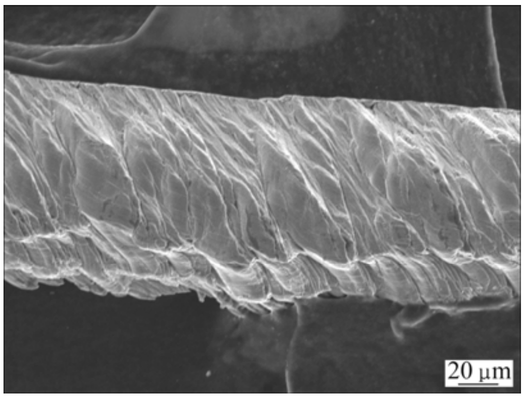


**Fig. 2** SEM image of stainless steel fiber fabricated by multi-tooth tool

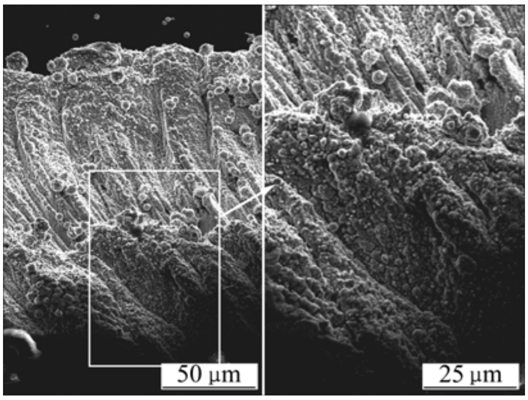


**Fig. 3** SEM images of copper coating layer

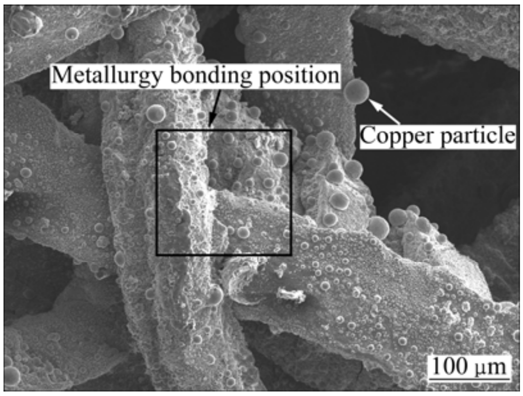


**Fig. 4** SEM image of SMFM sample $A_s$

gradually increasing the deposition of metal atoms. Then, crystal nucleuses grow into cell body-like particles. The growth of cell body-like particles is due to the crystallographic properties and defects of material. The dislocations, pores, cracks and scratches on the surface of substrate are the deposition centers of plating coating layer [19]. The plating substrates employed in this experiment are stainless steel fibers manufactured by multi-tooth tool. As shown in Fig.2, there are lots of grooves, groove edges and other rough microstructures on the surface of fibers. In the vicinity of these surface microstructures, there are some deposition points of strong activity. Consequently, the crystals of these points quickly grow into randomly distributed cell body-like particles with various sizes.

It is confirmed that a copper coating with random distribution of micro-particles on surface can be generated on stainless steel fibers by electroless plating process. The micro-structure generated during the cutting process on fibers plays an important role in the forming process of copper micro-particles on coating layer. These copper micro-particles can not only greatly increase the fiber surface area, but also enhance the surface energy of the fiber. It is noticeable that the parameters of electroless plating process such as the temperature of bath, time of plating and reagent formula of plating solution can affect the surface morphology and thickness of coating layer, which should be discussed in further study.

### 3.2 Morphology analysis of SMFM made by LTSS route

Figure 4 presents the surface morphology of SMFM $A_s$ made by LTSS route. It is observed that compared with the surface morphology of the fiber before-sintered (Fig. 3), less microstructure distributed on the surface of as-sintered fiber. Many micro-particles, particularly relatively small particles on the coating layer disappear. Some spherical copper particles with random distribution can be found on the surface of as-sintered fiber. Additionally, metallurgy bonding positions can be found in the fiber-fiber contact regions.

The small size of microstructures and micro-particles on the coating layer are in high surface energy state, so they are firstly evaporated or melted during the sintering process. The loss of microstructure can decrease the specific surface area of SMFM. However, at a low sintering temperature (800 °C), the loss of microstructure on fibers is not obvious. As shown in Table 1, SMFM $A_s$ made by LTSS route has a higher specific surface area of 0.219 0 $m^2/g$ in comparison with commercial stainless steel fibrous felt which possesses a specific surface area less than 0.01 $m^2/g$.

**Table 1** Results of BET-area test

| Test samples | Sintering temperature/°C | BET-area/($m^2 \cdot g^{-1}$) |
|---|---|---|
| $A_s$ | 800 | 0.219 0 |
| $B_s$ | 700 | 0.231 6 |
| $C_s$ | 900 | 0.083 4 |
| $D_s$ | 1 000 | 0.035 |
| $L_s$ | 1 300 | <0.01 |

Due to its low melting temperature of about 1 083 °C, copper can be more easily melted and sintered compared to stainless steel, the melting temperature of which is about 1 450 °C. The copper coating layer which well covers the surface of substrate forms a copper interface between the stainless steel fibers in the contact region of fibers. This copper interface can lead to the metallurgy bonding of fibers at relative low sintering temperature (≤800 °C) [9]. Furthermore, there is a limited solid solubility between stainless steel and copper. Due to the mass transfer between fiber substrate and copper coating layer during the sintering process, alloy layer may be generated at the interface of fibers [14]. The existence of metallurgical bond area can greatly increase the link strength of fibers and demonstrate that SMFM can be formed at low temperature by LTSS route.

The result proves that low temperature (800 °C) sintering of stainless steel based SMFM with high specific surface area can be realized by LTSS route. The coarse copper coating not only directly contributes to the enhancement of specific surface area of SMFM, but also plays a key role in lowering its sintering temperature. From Table 1, compared with commercial SMFM $L_s$, SMFM samples fabricated by LTSS route have great advantage on specific surface area. This material with many characteristics, such as high mechanical strength, high specific surface area, high porosity and low manufacturing cost, has a wide application prospect.

### 3.3 Effect of sintering temperature on surface morphology of SMFM

The mass transfer during sintering process leads to the changes of surface morphology of sintered materials. The enhancement of sintered temperature or the addition of liquid mass transfer channels can speed up the mass transfer during sintering process of metallic materials.

According to the mass diffusion transfer theory, the diffusion coefficient of atomic during sintering process can be expressed as:

$$D = D_0\exp(-\Delta G/RT) \quad (1)$$

where $D$ is the self-diffusion coefficient; $D_0$ is the pre-exponential factor; $\Delta G$ is the self-diffusion activation energy; $R$ is gas constant; $T$ is the thermodynamic temperature.

As indicated in Eq. (1), the increase of sintering temperature leads to exponentially increase of atomic diffusion coefficient, which can rapidly accelerate the velocity of mass transfer. Moreover, the copper coating layer on stainless steel matrix can be easily melted to liquid-phase copper at a relatively high temperature, which could further increase the diffusion of atomic sintering system and accelerate the mass transfer process. Since the convex microstructures on fiber have higher surface energy than fiber substrate, they could be more easily evaporated or melted, and then condensed at the depressions during a high-speed mass transfer process. This can result in the planarization of fiber surface, which will significantly reduce the specific surface area of SMFM.

As shown in Fig. 5, sample $B_s$ sintered at 700 °C has a rich surface morphology. The microstructure of stainless steel fiber is well conserved. Few spherical copper particles can be found on the fiber surface and copper sintered necks can not be observed at fiber-fiber contact regions. Figure 6 presents the fiber surface morphology of sample $C_s$ which experienced a sintering process at 900 °C. From Fig. 6, further deformation of microstructures on the fiber surface can be observed. The regular spherical copper particles can be hardly found, while some traces of liquid copper can be observed on the fiber surface.

Figure 7 shows the surface morphology of SMFM sample $D_s$ which was sintered at 1 000 °C. The copper microstructure on sample fibers disappears and large area of trace of liquid-phase copper covers the surface of fiber. The existence of large area of trace of liquid-phase copper is a characteristic of liquid-phase sintering. The liquid-phase copper can provide fast diffusion channels

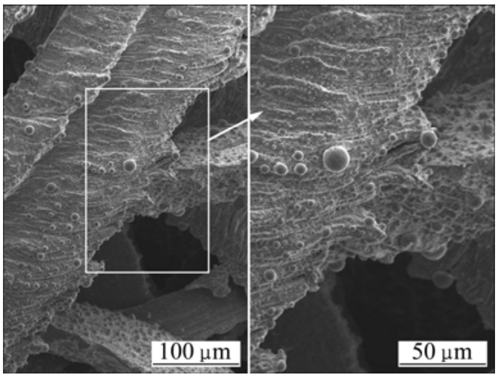

**Fig. 5** SEM images of SMFM sample $B_s$

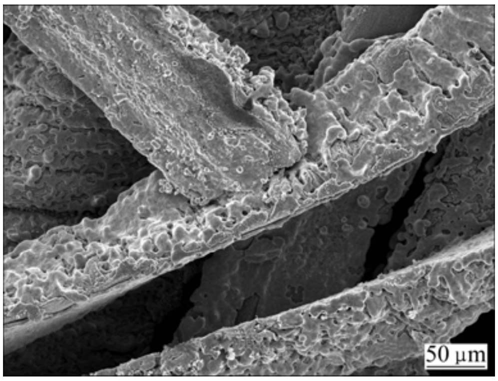

**Fig. 6** SEM image of SMFM sample $C_s$

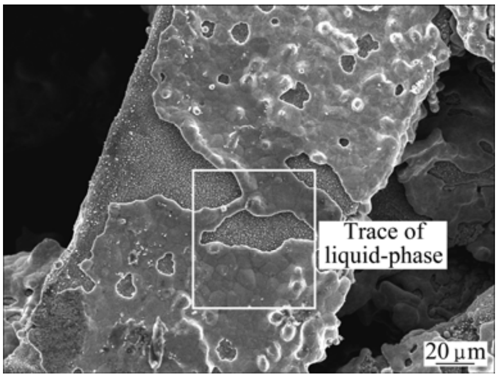

**Fig. 7** SEM image of SMFM sample $D_s$

for sintering process [20], which accelerates the dissolution of microstructure on the fiber surface, such as edges and corners, convex and fine particles during the mass dissolution-precipitation stage of liquid-phase sintering. Thus, the SMFM sample $D_s$ has a smooth surface morphology.

The study confirms that sintering temperature can significantly influence the surface morphology of SMFM, which is consistent with the mass diffusion transfer theory and the research results studied by WEI et al [9]. The damage of micro-structure on SMFM surface during the sintering process is a main reason for the loss of specific surface area of SMFM. 800 °C as a suitable sintering temperature is recommended when link strength of fibers is concerned.

## 4 Conclusions

1) The novel SMFM with high specific surface area (higher than 0.2 $m^2/g$) is obtained by means of LTSS route. The coarse copper coating layer not only directly enhances the specific surface area of SMFM, but also benefits lowering the sintering temperature of SMFM.

2) The sintering temperature can significantly influence the surface morphology and specific surface area of SMFM. The damage of microstructure on the surface of SMFM during the sintering process is a main reason for the loss of specific surface area of SMFM.

3) The loss of specific surface area of SMFM during sintering process is not obvious until the sintering temperature is above 800 °C. A sintering temperature of 800 °C in this LTSS route is recommended.

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# 高比表面积金属纤维多孔材料的低温固相烧结成形

唐 彪, 汤 勇, 周 蕤, 陆龙生, 刘 彬, 屈修明

华南理工大学 表面功能结构先进制造广东普通高校重点实验室，广州 510640

**摘 要**：采用低温固相烧结工艺 LTSS 制备一种高比表面积金属纤维多孔材料。首先，采用化学镀铜工艺在切削加工的不锈钢纤维表面镀覆一层具有粗糙表面形貌的铜，然后将该镀铜纤维在氢气保护氛围下于 800 °C 保温 1 h 完成低温固相烧结成形。结果表明，采用该工艺可以获得一种具有复杂表面形貌以及高比表面积(>0.2 $m^2/g$)的新型金属纤维多孔材料(SMFM)。 利用 SEM 及 BET 表征手段研究 LTSS 工艺中烧结温度对烧结样本表面形貌以及比表面积的影响规律，发现烧结过程中对纤维表面微结构的破坏是造成 SMFM 比表面积损失的重要原因。实验得出理想的烧结温度为 800 °C。

**关键词**：金属纤维多孔材料；低温固相烧结；化学镀铜；表面形貌；比表面积

**(Edited by FANG Jing-hua)**