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Tape casting and lost carbonate sintering processes for production of heat sinks for portable electronics

Mosalagae Mosalagae[1, 2*], Russell Goodall[1], Mohammed Elbadawi[3]

[1]*Department of Material Science and Engineering, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield, S1 3JD, UK*
[2]*Department of Mechanical and Energy Engineering, College of Engineering and Technology, Botswana International University of Science and Technology, Plot 10071, Boseja Ward, Palapye, Private Bag 16, Botswana, UK*
[3]*Department of Mechanical Engineering, University of Sheffield, Mappin Building, Mappin Street, Sheffield, S1 3JD, UK*

*Corresponding author: Tel.: (+44) 7910744502; E-mail: mmosalagae1@sheffield.ac.uk

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Abstract

Porous copper was fabricated by means of a powder metallurgy process applied to tape casting. Lost Carbonate Sintering (LCS) was employed to control porosity within the component during processing. The weight ratio of the potassium carbonate introduced into the matrix ranged from 30-40 wt%. Additives such as; plasticizers, binders, dispersant and solvents were utilized to control the properties throughout the processes and ease fabrication. The component was debinded and sintered at 400 °C and 900 °C respectively, under vacuum. The potassium carbonate was removed from the sintered component via dissolution in water. By using X-ray Florescence (XRF) and Energy Dispersive X-ray Spectrometry (EDS) techniques, the effectiveness of the dissolution route at removing the space holder was investigated. The results show that porous copper produced in this way has porosity ranging from 75-85 % and pore size from 500-766 μm. The component produced has thickness ranging from 1300 -1800 μm. Copyright © 2017 VBRI Press.

Keywords: Tape casting, lost carbonate sintering, porous copper, heat sinks, dissolution.

Introduction

Open-cell porous metals with large surface area and high permeability for fluids are good candidates for heat sink and heat exchanger applications, especially in small electronics where high efficiency and small size are often required **[1, 2, 3].** However, the design of the heat sink in portable electronic devices is dependent on the physical space, cooling needs and manufacturing cost and frequently a thin porous layer could provide a significant benefit. Lost Carbonate Sintering (LCS) is one of the techniques commonly used for fabrication of porous metals, combining powder metallurgy with the use of a leachable carbonate space-holder **[1, 4, 5, 6, 7]**. The porous copper produced from this technique is mainly for heat sink applications **[4, 8]**. Recent studies have shown that a combination of LCS with common processes such as hot pressing are favorable, but these have limitations in terms of the thickness range and flexural strength that can be achieved **[5, 7].** On the other hand, some research has been performed on tape casting of copper composites such as copper/diamond **[9]** and copper/carbon **[10],** mainly for heat sink applications where minimum thicknesses are required. Other researchers attempted to tape cast copper alloys from powder state, mainly for tribological applications **[11].** Here, the process of tape casting is adapted for the creation of a thin copper sheet with a well-controlled porosity, using a blend of copper powder, potassium carbonate and polymeric binders allowing the use of LCS. Combining LCS and tape casting processes is novel for production of porous copper for heat sink applications. This combination has been successful and shows a great promise based on the trials recently performed under this research. A porous copper tape of thickness down to 1350 μm was successfully produced after rigorous examination of the manufacturing process, which shows suitable behavior for heat exchangers in simple assessments of the properties. The processing technique and characterization of the material produced is reported, with Scanning Electron Microscopy (SEM) employed to investigate the change in structure throughout the processing steps. Thermal analysis techniques such as thermo-gravimetric analysis are utilized to study the efficiency of the de-binding and sintering processes. The porosity and density of the finished copper product will also be reported. Different variations of the manufacturing route are employed to obtain a good pore distribution for the application of the product, and different trials of manufacturing routes have achieved the flexural strength needed for application on curved surfaces. There are two carbonate removal routes; a decomposition route and a dissolution route. This report will concentrate on the dissolution route, where the effectiveness of carbonate removal and characteristics of the dissolution route will be studied by employing XRF and EDS (SEM) techniques.

Experimental

Materials/ chemicals details

Two primary powders were used in this approach; dendritic copper (Cu) powder (see **Fig. 2 (a)**) (av. particle diameter ≈ 50 µm) from *Goodfellow, Cambridge, UK* and potassium carbonate (K_2CO_3) from *Alfa Aesar, Lancashire, UK* (see **Fig. 2.(e)**) The copper powders had a purity of more than 99% and was used as the main matrix of the tape during processing. Potassium carbonate is a leachable space holder, used to introduce and control porosity, pore size and shape of the final product. It has a solubility of 111 g per 100 g of water at 20 °C and melting temperature of 891 °C.

The density of copper and potassium carbonate was 8.96 g/cm^3 and 2.43 g/cm^3, respectively. The images in **Fig. 2. (a)** and **(e)** below show both powders as received from the suppliers imaged by Scanning Electron Microscope (SEM).

Solvent

Azeotropic mixture of ethanol and 2-butanone at a ratio of 40:60 **[10, 12]** was used in this study because it has low temperature of vaporization and a low dielectric constant promoting a good wettability of both the copper powder and potassium carbonate. The mixture has a low boiling point and is also nonreactive to both primary powders.

Triphenyl phosphate

To ensure the best de-agglomeration and dispersion of the powders in a slurry, triphenyl phosphate was used as a dispersant. It leads to good dispersion of primary powders in the slurry by introducing repulsive forces between the particles **[9].** This occurs by electrosteric mechanics but some dispersants use an electrostatic mechanism for repulsion depending on their chemical composition.

Poly (methyl meth acrylate) (PMMA)

The binder transfers its mechanical strength to the green tape by forming organic bridges between the primary particles during evaporation of the solvent. Molecules of the binder bond to each other avoiding crack propagation during solvent evaporation from the tape. Removal of the binder has to be easy, without having to reach high temperatures. PMMA was selected as a binder, with a high molecular weight (ranging from 120, 000 – 150, 000 g.mol^{-1}) and a low boiling point of 160 °C.

Dibutyl phthalate (DBP)

DBP was used as a plasticizer to ensure a good flexibility of the tape by lowering the glass transition (T_g) of Poly (Methyl Meth acrylate) (PMMA). It decreases the T_g of PMMA by 45 °C, from 110 °C (PMMA only) to 65 °C (PMMA/DBP). Refs. **[3]** and **[4]** have shown that a mixture of PMMA/DBP ratio of 1:2 leads to excellent combination of green tape flexibility and mechanical strength. It has a low molecular weight of 300 g/mol and a boiling point of 340 °C.

Material synthesis / reactions

Powders and additives in the proportions required for the formulation of the slurry were put together and mixed with the addition of 30-40 wt% potassium carbonate (**Fig. 1**). Powders and additives were then mixed together in polypropylene mixing cups with a *SpeedMixer^{TM}* at a speed of 1800 rpm for 45 min to obtain a homogenous slurry for casting. After mixing, the slurry was tape cast into a thin tape following three different manufacturing routes presented in **Table 1.** One of these routes involve casting directly onto a copper foil tape. The purpose of this is to create a thin porous sheet of copper integrated with a dense copper layer, which can provide a superior contact to a surface where additional heat transfer is required.

Table 1. Three types of manufacturing routes for fabricating green copper tape.

Manufacturing Routes	**Descriptions**
Manufacturing Route A	Tape casting directly on to copper foil, partial drying at 40ºC then sintering at 900 ºC.
Manufacturing Route B	Tape casting on Siliconed Mylar carrier film, partial drying at 40 ºC then flipping on to copper tape and sintering at 900 ºC
Manufacturing Route C	Tape Casting on Siliconed Mylar carrier, partial drying at 40 ºC, then flipping and pressing against copper tape with a rubber roller, and sintering at 900 ºC

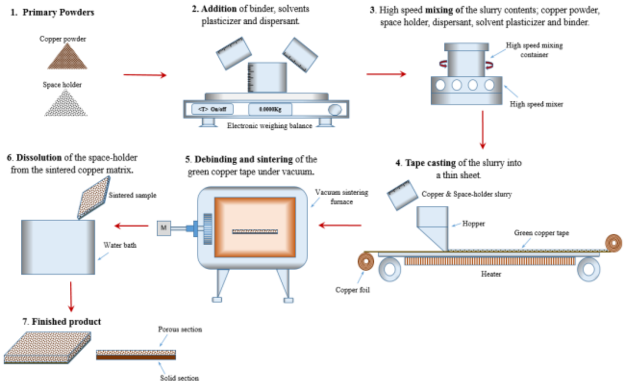

Fig. 1. The fabrication process of porous copper tape by lost carbonate sintering technique applied to tape casting.

The green tapes were partially dried at 40 °C under air. Then, partially dried tapes were taken thorough a debinding and sintering process at 400 °C and 900 °C respectively under vacuum. The samples were allowed to cool down to room temperature within the vacuum sintering furnace. Sintered copper samples were then taken through some dissolution tests to remove the potassium carbonate, resulting in a porous medium. The dissolution test results are presented in **Fig. 5.**

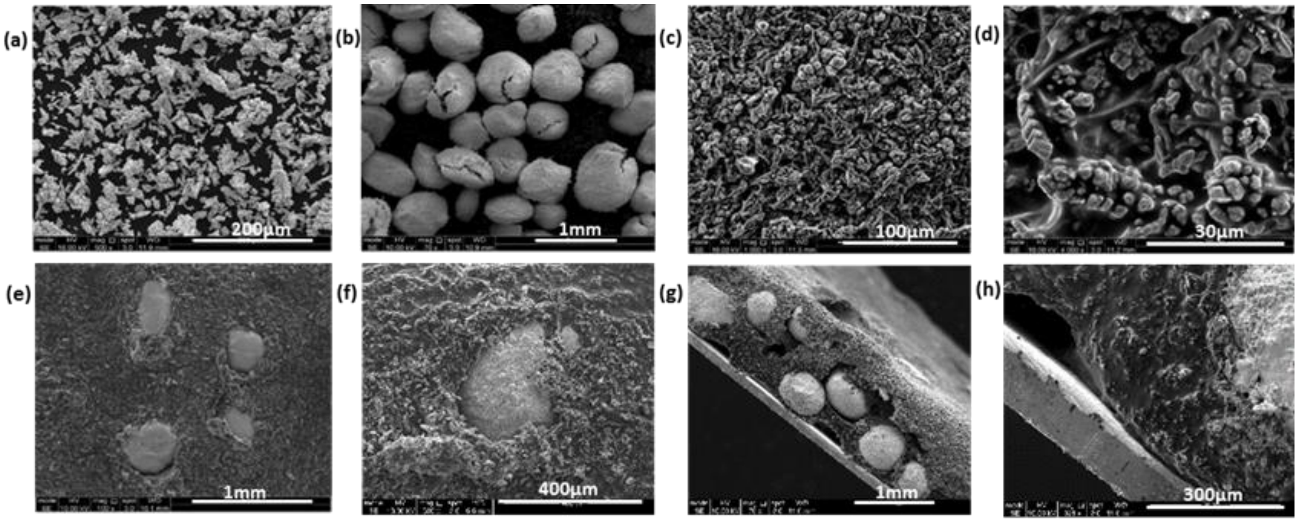

Fig. 2. Primary powders; (a) As received copper powder before processing with average size of 50 µm. and (e) potassium carbonate used as leachable space holder during fabrication of porous copper The SEM images of the green copper tape after tape casting. It shows copper powder and potassium carbonate bonded together by polymeric binders, tape cast on copper foil just before taken through sintering stage.

Thermogravimetric analysis (TGA)

Thermogravimetric studies were carried out in a thermogravimetric analyzer (Pyris 1 TGA). All samples were heated from room temperature to 400 °C at 10 °C/min for 3 hours then scanned to 900 °C at 10 °C/min for 2 hours under argon atmosphere. The mass loss against temperature and time was obtained from the TG curves.

Dissolution study

In order to determine the appropriate method to dissolve the potassium carbonate from the sintered copper matrix, three methods were investigated. Firstly, by stirring the distilled water the samples were immersed in at approximately 1 rpm, secondly by using an ultrasonic bath and lastly by dipping in stagnant distilled water. The outcome of these three methods is presented under the results and discussion section (**Fig. 5.)**

Scanning electron microscopy (SEM)

Samples were firstly sectioned and mounted on aluminum sample holder with carbon sticker pad. The samples were then imaged by SEM using secondary electron mode. The SEM images are presented under results and discussion section **(Fig. 2, Fig. 4 and Fig. 6.).**

Porosity measurements

Porosity of the samples was measured using two different techniques. The first technique used is quantitative stereology metallography, which was used to determine the porosity distribution across the thickness of the porous tape. A counting grid was superimposed onto a micrograph of the selected area of the sample. *ImageJ* image analysis software was used to process the micrographs. The second technique used to obtain the porosity of the whole sample was by measuring the density of the porous copper. First, the mass of the sample was measured using an electronic balance. The length, width and height of each sample were measured four times at difference position to obtain averages. The gas pycnometer (AccuPyc II 1340) in the Dept. of Materials Science and Engineering, University of Sheffield, UK was employed to measure the true volume and density of the solid part, therefore allowing calculations of the porosity of the samples.

Results and discussion

The selection of the additives used for the mix was based on the reasons outlined under *experimental section*. The images presented in **Fig. 2** below shows primary powders and a green body, which was successfully fabricated by tape casting. Potassium carbonate is held within the tape by a mixture of copper particles and additives as observed in the **Fig. 2 (c), (d) & (g)**. A reasonably high number of potassium carbonate particles were exposed on the surface of the green tape prior to sintering. The binder penetrates the space in between the primary particles as clearly shown in **Fig. 2 (d),** forming a good linkage between the powders as well as bonding the green body to the copper foil. The combination of both additives allowed tape casting of the powders into a thin tape as observed in **Fig. 2** (**d) and (h**). The tape maintained its shape and was reasonably flexible, allowing it to be taken through the next steps of processing.

The efficiency of the debinding process was confirmed by carrying out Thermogravimetric analysis on a green tape of copper before heat treatment. The first mass loss on the curve corresponds to the burn out of Poly (Methyl Meth Acrylate) (PMMA) from the tape and the second mass loss corresponds to the burn out of dibutyl phthalate (DBP). It was demonstrated by the TGA analysis that both PMMA ($T_{melting}$ = 160 °C), DBP ($T_{melting}$ = 340 °C) and other organics ($T_{melting}$ < 80 °C) are eliminated from the green tape after 400 °C. The debinding treatment is therefore expected to be effective on the green tape of copper from 400 °C. At 400 °C, all organics are completely burned out under argon. Therefore, 400 °C was chosen as the debinding temperature throughout the debinding and sintering process of the green tapes. At 900 °C, there was a small mass loss on the curve corresponding to the burn of potassium carbonate. As observed from **Fig. 3**, both processes took 6 hours to complete.

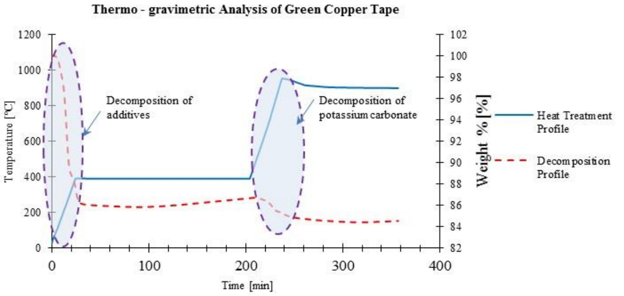

Fig. 3. A graph showing Thermo-gravimetric analysis results of green copper tape, decomposed following the heat treatment profile used in vacuum sintering process.

Ideally, the porosity across the thickness of tape will decrease towards the component base, in order to provide a better surface to bond to the component or the copper foil if present. To achieve this, three different manufacturing routes were studied. These three manufacturing routes were briefly explained in **Table 1** above. **Fig. 4** above shows green tapes from three different routes, as they were observed under SEM. The tape obtained from manufacturing route A **(Fig. 4 (a) and (b))**, green body bonded very well to the copper foil. The slurry was directly fabricated on copper while still reasonably viscous, therefore, it bonded well to the foil by means of gravity. In manufacturing route B **(Fig. 4 (c) and (d))**, the green body was found to detach from the foil during sectioning and shaping. It should be noted that the green body was not rolled down onto the copper. Therefore, in this route, the binders in the green body were not forced to bind with the copper foil hence giving rise to a weaker bond. In Manufacturing Route C **(Fig. 4 (e) and (f)),** the green body was forced down to the foil by a rubber roller. The bond was relatively good, with no gaps at the barrier.

The graph in **Fig. 5** below shows the dissolution tests of potassium carbonate on sintered sample. As clearly observed from the graph, stirring the sample in the distilled water bath emerged as the fastest method to dissolve the potassium carbonate from copper matrix. It is then followed in terms of speed by dipping in the ultrasonic bath and lastly, dipping in stagnant distilled water. After 60 seconds, potassium carbonate was dissolved from the tape in both techniques (**Fig. 5**). Dissolution speed is dependent on the temperature and the concentration of any other species dissolved in the water, but in both approaches, here, the temperature of water was kept constant throughout the tests. In this case, it is also dependent on the permeability of the porous sample to water or the accessibility of potassium carbonate (within the sample) to water.

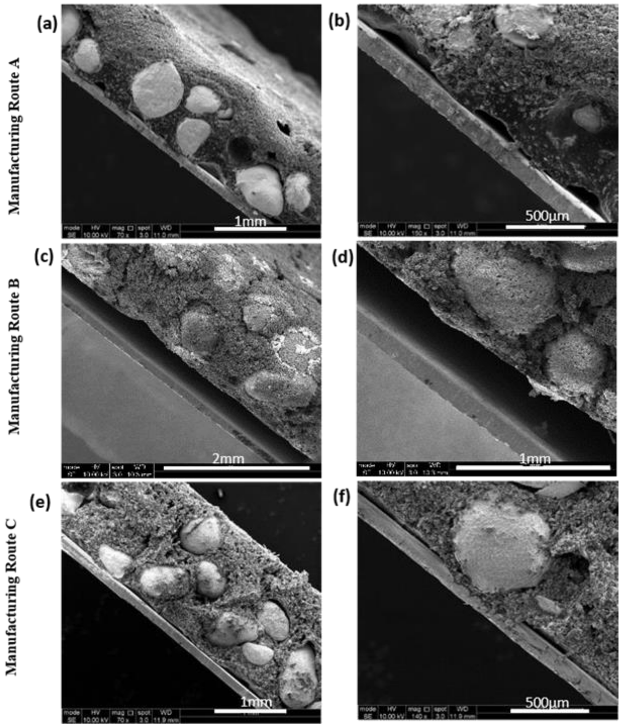

Fig. 4. SEM images of three different tapes fabricated by three different manufacturing routes; (a) and b) Manufacturing route A, (c) and (d) Manufacturing route B and lastly (e) and (f) Manufacturing route C.

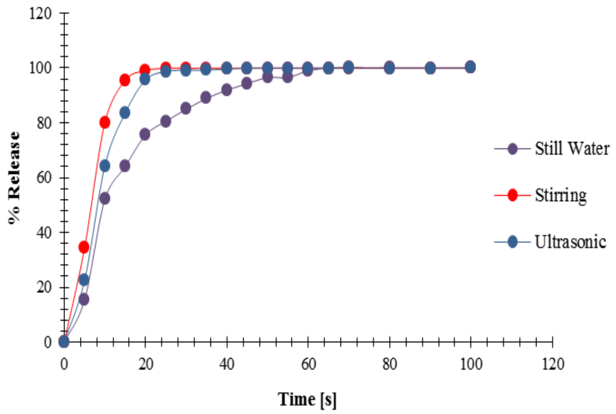

Fig. 5. Dissolution of potassium carbonate from the sintered copper tape by three different techniques; dipping the tape in still distilled water, stirring in distilled water and dipping in ultrasonic bath.

Dissolution involves breaking down of the intermolecular bonds in the potassium carbonate at the same time, separation of water molecules therefore providing space for potassium carbonate. Stirring somehow influences molecules from the potassium to diffuse much faster into water. At the same time the flow rate of water through or/and around the samples is a factor in the observed dissolution rate. Hence, the faster the flow rate of water through the sample the higher the dissolution rate of potassium carbonate from the sample. It was observed during the test that the water turned milky, showing dissolution of potassium carbonate into the water. However, the water was evenly milky for stirring technique during the test. In the other two techniques, the milky colour of the water was most distinct around the sample, and less obvious away from the sample. Ideally the water around the sample becomes more concentrated during the test compared to the rest of the water in the container as it was observed during the test. This observation confirmed that concentration of potassium carbonate within the water around the sample was increasing as the test proceeded. Therefore, mixing water will promote close an even distribution of potassium carbonate concentration hence increasing the dissolution rate of potassium carbonate from the sample. Less stirring will results in higher concentration of potassium carbonate within the water the sample, hence lower concentration gradient which would be expected to reduce the dissolution rate of potassium carbonate, as seen from the graph in **Fig. 5**. The comparison leads to a conclusion that dissolution of potassium carbonate by stirring is the best method between the three methods.

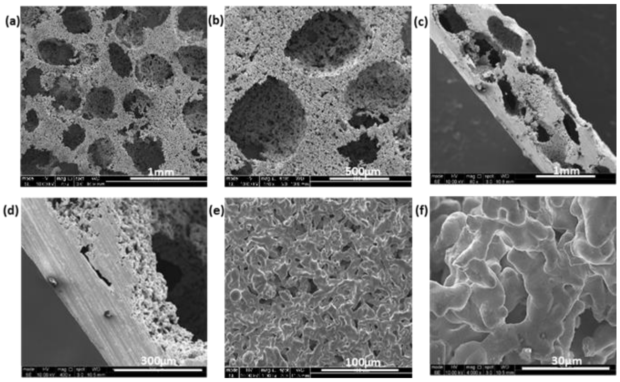

Fig. 6. Sintered copper tape as observed under SEM. Images in (a) and (b) shows the pore structure on the top surface of the tape; (c) and (d) is the cross section of the tape, porous section well bonded to copper foil after sintering; (e) and (f) represent copper particles perfectly bonded together within the tape, after sintering at 900°C.

Table 2 below shows the results of the pore distribution across the thickness of the sintered tape. In the first approach; manufacturing route A, the sample was more porous on the bottom section (64.4 %) compared to the top section (35.6 %). This is likely to be due to gravity-induced settling and segregation in the mixture after tape casting but before it becomes solid. The last two approaches have the opposite results; higher porosity was obtained on the top section compared to the bottom section. However, the porous section and the foil did not bond well in manufacturing route B. Therefore, manufacturing route C offered a fairly good porosity distribution of 61.7 % at the top half section and 38.3 % at bottom half section. Also, the porous section and the foil bonded relatively well.

Table 2. Pore distribution across the thickness of the porous tapes produced by three different manufacturing routes.

Manufacturing routes	**Pore distribution**	
	Top half section (%)	**Bottom half section (%)**
A	35.66 ± 3.3	64.46 ± 3.5
B	60.26 ± 3.2	39.86 ± 3.1
C	61.76 ± 3.4	38.36 ± 2.9

The green tapes in **Fig. 4** were taken through debinding and sintering processes at 400 °C. and 900 °C consecutively followed by dissolution of potassium carbonate. Images in **Fig. 6** shows the finished components of the sintered copper tape. During sintering, copper particles appears to have adhered very well to each other (see **Fig. 6 (f)**), as well as to the copper foil by diffusion, to such an extent that the distinction between powder and foil is not apparent (**Fig. 6 (e)**). The finished sintered tape had porosities and thickness ranging from 75-85 % and 1300-1800 µm respectively.

Conclusion

In conclusion, the study explores the possibility of fabricating a thin heat sink from tape casting combined with lost carbonate sintering. Porous copper tape was successfully produced by tape casting combined with lost carbonate sintering. The tape had porosity and pore size ranging from 75-85 % and 500-766 µm respectively. The electron microscopy revealed that sintering process results in a good bonding between the porous section and copper foil resulting in a one rigid component. Expectedly, manufacturing route C offered a relatively good porosity distribution across the thickness of the component, as well as a fairly good bond between the porous section and the copper film. The thickness of the tape ranged from 1300-1800 µm. Finally, dissolution of potassium carbonate from matrix of the sintered component was successfully achieved. Stirring in distilled water at 1rpm provided a faster dissolution of potassium carbonate from the sintered copper matrix.

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Author's contributions

Conceived the plan: MM, RG; Performed the expeirments, Data analysis and Wrote the paper: MM, ME; Guidance: RG.

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Supporting Information

The setup of tape casting

Fig. S1. The Setup of casting of copper slurry into a copper tape using tape caster. The slurry is fabricated into a copper foil of 0.1mm thickness by 150mm width.

Sintered porous copper tape

Fig. S2. Sintered copper tapes.