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Production of porous copper with high surface area for efficient water purification

Nikolaos Michailidis [a,*], Fani Stergioudi [a], Panagiotis Seventekidis [a], Alexander Tsouknidas [a], Dimitrios Sagris [b]

[a] Physical Metallurgy Laboratory, Mechanical Engineering Department, School of Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece
[b] Department of Mechanical Engineering, Technological Education Institute of Serres, Serres, Greece

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ABSTRACT

Porous copper of controllable and uniform pore distribution was produced by a space holder technique, yielding to an attractive combination of properties like high surface area, ductility and thermal conductivity, rendering favourable its use in industrial applications such as filters, fuel cells and heat exchangers. The pore characteristics (size, shape and porosity) defining the surface area, as well as the surface integrity of the cells were defined by micro computed tomography and profilometry. The mechanical properties of porous copper was determined by uniaxial compression, while their high efficiency in purifying water were correlated with porosity (wetting surface) characteristics.

Introduction

The attractive combination of properties offered by porous copper, i.e. ductility, high thermal and electrical conductivity, renders them excellent candidates for potential use in a wide range of industrial applications. Porous electrodes in rechargeable batteries, fuel cells, heat exchangers for electronic components, catalytic substrates for chemical reactions and filtration applications are some of them. Pore quality is considered as a key factor for sustainable design of high performance porous components and therefore, pores are imperative to exhibit a high degree of uniformity and controllable distribution [1–4].

Copper tends to act as an electron donor and participate in redox reactions, thus drawing attention to possible applications of copper foams in drinking water treatment and purification. Its ability to remove a number of heavy metals, decompose organic pollutants and provide antimicrobial properties is mainly based on the occurrence of a reducing mechanism. For instance, common methods for the uptake of hexavalent chromium Cr(VI), usually introduce a reduction step of Cr(VI) to the Cr(III) oxidation state, which appears in the form of an insoluble hydroxide. Commercial available solutions are based on the adsorption of Cr(VI) in a filter column setup filled with a powder material, offering advantages like simplicity and compactness. Zero-valent metals (Fe, Al, Cu, Mg, Ni, Zn) and iron oxides (Fe_3O_4) in the form of powders or granulated materials are the most important class of adsorbents utilized in Cr(VI) removal from drinking water [5]. However, their efficiency is restricted by the surface passivation, as well as by flow blocking, sometimes even after a short-term use.

Several space holder materials have been reported for the production of porous copper, with NaCl particles being the most popular ones [6]. However, any residual NaCl particle can cause undesirable corrosion to the metal matrix. Powder metallurgical porous copper structures have been produced using naphthalene [7]. The main limitations of this approach are related to the low rate of the space holder material removal. Carbonate particles or polymeric materials [8] have been also used to produce porous copper, with the space-holder material removal being facilitated through heating. This, however, leads to environmental concerns arising from the release of dangerous gases during the decomposition process of the space-holder. In addition, the porous metal structure is prone to collapse before strong bonding between the metal particles is formed during sintering.

In this study copper foams have been manufactured by a dissolution and powder sintering process using crystalline raw cane sugar, as a novel leachable pattern. The method involves powder-mixing, compaction, leaching and sintering of the green product. The influence of several process parameters (particle size of the sugar, powder size of copper along with porosity and sintering temperature) on the resulting porosity and the wetting

* Corresponding author at: Aristotle University of Thessaloniki, Physical Metallurgy Laboratory, Mechanical Engineering Department, School of Engineering, Uni. Campus, 54124 Thessaloniki, Greece. Tel.: +30 2310995891; fax: +30 2310996069.
E-mail address: nmichail@eng.auth.gr (N. Michailidis).

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surface (resulting from the pore network) of the produced foams is investigated towards optimizing the production of efficient copper foams for applications in water purification. From an engineering perspective, it is important to understand the effect of manufacturing parameters on the mechanical strength of the produced foams, in order to exploit their potential for industrial applications. To gain information on the mechanical properties of the copper foam, uniaxial quasi-static compressive tests were performed. Stress–strain curves are reported in relation with sintering temperature, pore and powder size of copper. Finally, initial results on the effect of wetting surface on the foams Cr(VI) absorption capacity are introduced. The production method is cost-effective and environment friendly, providing adequate control on the uniformity of the porous structure and on the surface area available for reaction with the flowing medium.

Experimental details

Two elemental copper powders (purity of 99%) possessing different particle size (fine powder with mean size <75 μm and coarse powder with mean size ranging between 250 and 400 μm) were used as starting material. To control the cell size of the final foam within desired range, the commercial raw cane sugar applied as a space holder material was divided by a series of sieves into three size groups: 1.0–2.0, 0.5–1.0 and 0.125–0.5 mm, with nominal mean sizes of 1.35, 0.70 and 0.35 mm, respectively. The production method is described in detail in [9,10].

Initially, the copper powder is mixed thoroughly with the crystalline raw cane sugar at a pre-specified volume or weight ratio, depending on the desired relative density of the final product. The mixture was uniaxially compacted in a stainless steel cylindrical mould with a diameter of 16 mm and height of 80 mm. The applied pressure depends on the ratio of the initial powders and the powder size of the parent material. The crystalline raw cane sugar was removed from the green compact by water leaching at room temperature. The final stage involves sintering performed in a vacuum furnace ($p = 10^{-3}$ Torr). Sintering temperatures were varied between 780 and 940 °C, while the holding time was fixed to 4 h. The density ρ_f of the final Cu-foam was calculated by dividing the mass of the foam by its volume, based on Archimedes principle. The porosity of the as-manufactured Cu-foam P_f can be estimated by $P_f = 1 - \rho_f/\rho_{Cu}$, ρ_{Cu} being the density of Cu (8.96 g/cm^3).

Optical microscopy was used to characterize the structure of the as-produced foam using an Olympus BX 60 microscope. Compressive response was determined by uniaxial static testing (on an electric INSTRON Testing system) at a crosshead speed of 0.13 mm/s, corresponding to a strain rate of approximately 0.0085 s^{-1} for all samples. Cylindrical samples were used having a diameter of about 15.5 mm and height of about 16.8 mm. The axis of compression was parallel to the compaction direction. The recorded force–displacement data were converted to engineering stress and strain values, based on the measured sample dimensions. A minimum of three tests was performed per testing condition to guarantee the reliability of the results.

Micro Computed Tomography (μCT) was utilized to gain access into the three-dimensional (3-D) structure of the foam. An X-ray computed tomography apparatus (Werth TomoScope® HV Compact-225 3D CNC) with a 5 μm focal spot, reflection target X-ray tube source and digital sensor analysis of 1024 × 1024 pixel operating in the absorption mode was used to acquire the 2D images of the Cu-foam samples used before and after the Cr(VI) removal experiments.

In order to obtain the maximum accuracy during the measurement, the specimens' region of interest has to be placed exactly on the rotation axis of the rotary table. To obtain comparable results, all the measurement parameters were kept stable. A voxel of about 25 μm side length was chosen. The intensity (current) and frequency (voltage) of the X-ray source were selected after several trials and eventually were set to 200 μA and 120 kV, respectively, leading to an X-ray power of 24 W. Thus, a long time (2000 ms) of exposure to the X-rays is required in order to get measurable X-ray absorption on each 2D radiographic image. The reconstruction of the 3D object by means of three processing steps (data preparation, filtering, back projection) requires several 2D radiographic images of different orientations for a whole rotation of the object. For all the conducted measurements, 1600 rotational steps are used and for each orientation 8 radiographic images are received to increase the quality of the final 2D image.

In order to obtain a morphological representation of the foam from reconstructed X-ray computed tomography data and to quantify pore-scale parameters such as surface area, a binarization process is commonly implemented to separate images into discrete phases (e.g. solid particles and void space). The 3D volumetric data were processed using the VG Studio Max software. A global thresholding was used, based on the histogram of the tomogram to highlight regions of interest in order to obtain the 3D model of the foam. Thresholds were deduced from the higher intensity inflection point of the pore distribution versus the lower intensity inflection point of the solid distribution, by analyzing the concavity points on the convex curve of the histogram. Geometrical convergence is tested by comparing the measured porosity of the Cu-foam sample with the volume porosity of the corresponding 3D model (i.e. deviation <2%).

Upon the determination of the 2D outline within each given cross-section (scan) of the foam, the 3D data sets were generated by overlaying consecutive scans and reverse engineering the volume through the segmented profiles. The basic morphological characteristics of the foams used were also obtained by image analysis.

Results and discussion

Establishment of production conditions

A small amount of binder was required during the mixing process to create a homogeneous distribution of Cu powders and raw cane sugar, as well as to ensure that high-quality foams with uniform pore size distributions are obtained. Therefore, mixing was carried out in two stages: First, a small amount of water (weight ratio of Cu powder to water: ~17) was sprinkled on the Cu powders and secondly the raw cane sugar particles were gradually added to ensure homogenous mixing. The use of water facilitated the creation of a stable and easy to handle compact, having a length of about 15–16 mm.

Uniaxial cold pressing was employed to form the green compacts, using a stainless steel cylindrical die with a diameter of 16 mm and height of 80 mm. The optimum compaction pressure lies in the range of 210 MPa, when using sugar particles with a mean size of 0.7 mm. The compaction pressure was slightly decreased when using sugar particles with a mean size of 0.35 mm. Coarser copper powder require higher compaction pressures by 25–50 MPa. The variation of the optimum compaction strongly depends on the powder size ratio (Cu/sugar) of the starting materials in the mixture and the compressibility of the parent material, which in turn is affected by the mean size of the copper powder. These foam samples exhibited the highest qualities, retained their original shapes and had satisfactory strength. At lower compaction pressures, severe spalling of Cu powders was observed when the space-holder material was removed from the water bath after the dissolution stage. At higher compaction pressures, the samples often crack, sometimes leading to a total