Lost carbonate sintering process for manufacturing metal foams

Y.Y. Zhao *, T. Fung, L.P. Zhang, F.L. Zhang

Department of Engineering, The University of Liverpool, Brownlow Hill, Liverpool L69 3GH, UK

Abstract

This article describes a lost carbonate sintering process for manufacturing open cell metal foams. Cu foams with porosity in the range 50–85% and cell sizes in the range 53–1500 μm have been manufactured.
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1. Introduction

Metal foams have recently attracted considerable attention in both academia and industry because of their exceptional mechanical, thermal, acoustic, electrical and chemical properties [1–4]. For structural applications, such as energy absorption, the most important considerations are porosity, specific strength, ductility in compression and cost. The overwhelming majority of metal foams in the market are therefore closed-cell Al foams manufactured by liquid or semi-liquid foaming technologies. For functional applications, such as sound absorption, thermal insulation, heat dissipation and catalyst support, the cells need to be open and small. The metal matrix may be Cu-, Fe-, Ti- or Ni-based. These metals have much higher melting points than Al. Solid route manufacturing technologies are then often adopted.

Sintering a compact of metal powder incorporating removable salt particles is a cost-effective route for producing metal foams with controlled cell shape, cell size and porosity. Zhao and his colleagues [5–8] developed the SDP process for manufacturing Al foams. SDP uses NaCl powder as the filler material. The main limitations

of SDP are that it is time consuming to eliminate NaCl completely and any residual NaCl can lead to contamination or corrosion of the base metal. Laptev et al. [9] used ammonium bicarbonate and carbamide powders as the filler materials for producing porous Ti parts. As both carbamide and ammonium bicarbonate decompose at 200 °C, the porous metal structure is prone to collapse before strong bonding between the metal particles is formed at the sintering temperature. It is also hard to control the cell shape because of the significant shrinkage involved. Another problem of this method is that the decomposition of the filler materials releases environmentally damaging gases.

This paper describes a lost carbonate sintering (LCS) process for manufacturing metal foams, and reports the structural characteristics of Cu foams manufactured by LCS.

2. Experimental procedure

The raw materials used in LCS for manufacturing a metal foam are the metal and a carbonate in powder form. The particle size of the carbonate powder needs to be selected according to the intended cell size of the final foam. The particle size of the metal powder is not critical but the metal particles must be considerably

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* Corresponding author. Tel.: +44 151 794 4697; fax: +44 151 794 4675.
E-mail address: y.y.zhao@liv.ac.uk (Y.Y. Zhao).

smaller than the carbonate particles. The process is shown schematically in Fig. 1.

Fig. 2 shows the morphology of the Cu powder and the K_2CO_3 powder used in this study. The Cu powder was supplied by Ecka Granules (UK) Ltd at Luton, UK. The Cu powder has spherical particles with sizes <75 μm. The K_2CO_3 powder was supplied by E&E Ltd of Widnes, UK. The K_2CO_3 powder has rounded granular particles with sizes in the range 53–1500 μm. The carbonate powder was further divided into different size groups by sieving to produce Cu foams with different cell sizes.

The Cu and K_2CO_3 powders were mixed with a volume fraction of Cu ranging from 0.15 to 0.5 of all solid materials excluding pores in the mixture. Ethanol was used as the binder and a small amount, roughly 1 vol.% of the Cu–K_2CO_3 mixture, was added during mixing. The Cu–K_2CO_3 powder mixture was poured into a mild steel tube and both ends were sealed with a layer of iron powder in order to protect Cu from extensive oxidation. Compaction of the mixture was carried out by a hydraulic press at 200 MPa. In some cases, the debinding was carried out at 200 °C for 1 h in order to evaporate the ethanol in the preform. In others, the debinding was achieved by heating the samples slowly (10 °C/min) to the sintering temperature.

The melting point of K_2CO_3 is 891 °C, at which it also starts to decompose. The sintering temperature and the carbonate removal temperature were therefore chosen as 850 and 950 °C, respectively. Three different routes of sintering and carbonate removal, as illustrated in Fig. 3, were investigated. In Route A, the preform was sintered at 850 °C for 4 h, cooled to room temperature and then placed in a running-water bath for 5 h to dissolve the carbonate. In Route B, the preform was sintered at 850 °C for 4 h, heated at 950 °C for 0.5 h to melt and decompose the carbonate and then cooled to room temperature. In Route C, the preform was heated to 950 °C and maintained at this temperature for 2 h before being cooled to room temperature.

The structure of the as-produced foam samples was examined by a Hitachi S-2460N scanning electron microscope (SEM). Energy dispersive X-ray analysis (EDX) and X-ray diffraction analyses and weight meas-
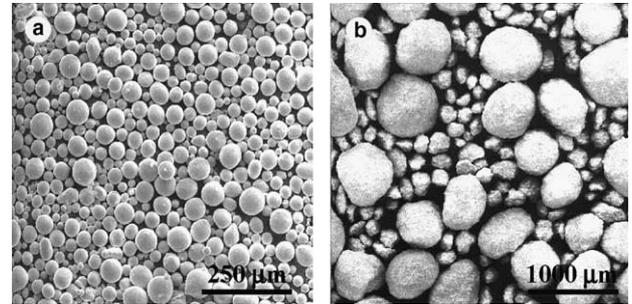

Fig. 2. SEM micrographs of (a) Cu powder and (b) K_2CO_3 powder.
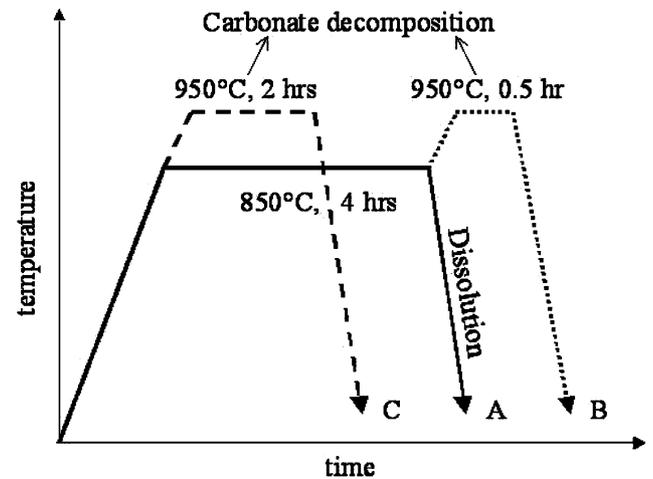

Fig. 3. Illustration of the three different sintering and carbonate removal routes.

urements were also carried out to determine the extent of carbonate removal.

3. Results and discussion

The typical cell structures of the Cu foams produced by Route A or Route B are shown in Fig. 4. Fig. 4(a) shows a SEM micrograph of the Cu foam produced by Route B. The foam exhibits uniformly distributed open cells and a network of well-bonded Cu particles. It has a porosity of 75% and cell sizes in the range 425–710 μm. The Cu foams produced by Route A have
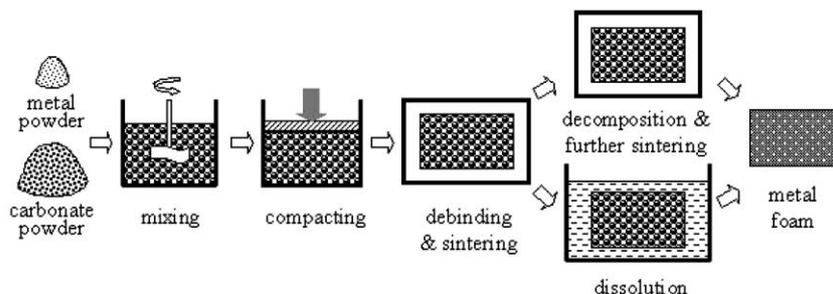

Fig. 1. Schematic of the LCS process for manufacturing metal foams.
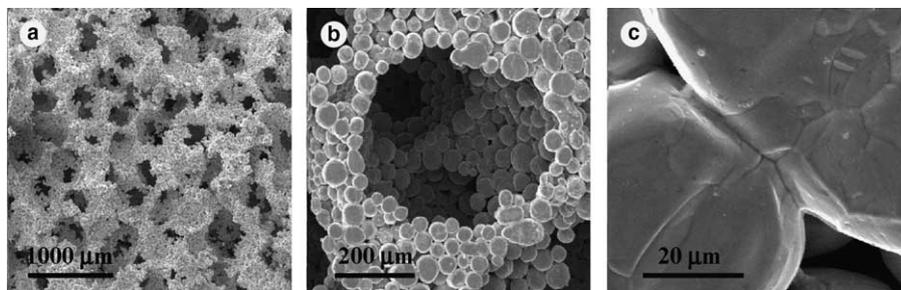
Fig. 4. SEM micrographs showing (a) typical structure of Cu foams, (b) a cell and its walls, and (c) bonding between the Cu particles.

similar cell structures to that shown in Fig. 4(a). Fig. 4(b) shows the structure of a typical cell and the cell walls of a Cu foam produced by Route A, which has a porosity of 80% and cell sizes of 53–1500 μm. The geometry of the cell closely matches that of the carbonate particles used in this study. The interconnecting cell channels are also clearly shown. Fig. 4(c) shows the bonding region between two Cu particles in the sample shown in Fig. 4(b), indicating that strong bonding has formed between the Cu particles.

Although all the sintering and carbonate removal routes, A, B and C, have produced Cu foams with acceptable quality, they showed different characteristics. In Route A, the preform showed very little shrinkage because the K_2CO_3 particles remained solid during sintering and held the metal particle network in place. The cells were virtually replicas of the K_2CO_3 particles used in the preform. Dissolution of the K_2CO_3 particles after sintering was very time-consuming, especially for a large preform with fine K_2CO_3 particles. Although the aqueous solution of K_2CO_3 does not react with Cu, it may chemically attack some metals such as Al. In Route B, the preform often shrank during the carbonate removal stage when very small K_2CO_3 particles were used. Using K_2CO_3 particles smaller than 125 μm resulted in a high shrinkage of 20% in volume. The main advantage of Route B is that the carbonate in the preform can be removed very rapidly, as long as the temperature throughout the preform is maintained above the melting point of the carbonate for a period of no less than 30 min. The resultant Cu foam was very clean. No residual carbonate was detected by X-ray diffraction and EDX analyses and the weight measurements. In Route C, the preform was cleared of the carbonate particles before strong bonding was formed between the Cu particles. The resultant foam was weak and often partly collapsed to form large cavities. Therefore, the sintering stage before carbonate removal was critical and Route C was not a good option.

Fig. 5 shows the compressive stress–strain curves of the Cu foams produced by Route A, with a porosity of 70%, 75%, 80% or 85%. The curves are generally characterised by three regions. In the low strain region, from 0 to about 0.05, the stress does not increase signif-
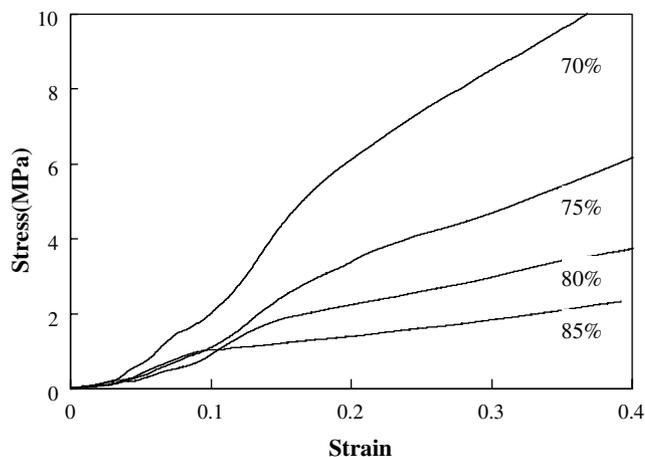

Fig. 5. Compressive stress–strain curves of Cu foams with different porosities.

icantly with strain. This is likely a result of initial misalignment of the test samples rather than an inherent characteristic of the foams. In the intermediate strain region, roughly from 0.05 to 0.15, the stress increases markedly with strain, showing a relatively strong resistance of the foams to elastic and plastic deformation. In the high strain region, roughly above 0.15, the stress increases less rapidly with strain, indicating that plastic deformation becomes dominant. At any fixed strain in this region, the strength of the foam decreases with increasing porosity. The gradient of the stress–strain curve in the high strain region also decreases with increasing porosity. The foams produced by LCS generally exhibit smooth stress–strain curves, because of small and homogeneously distributed pores.

In principle LCS can be used for manufacturing foams of any metals that can be sintered. In addition to Cu, iron foams have also been manufactured.

4. Summary

Cu foams with porosity in the range 50–85% and cell sizes in the range 53–1500 μm have been manufactured by blending, compaction and sintering of Cu and K_2CO_3 powders followed by removal of K_2CO_3. Either

dissolution or melting and decomposition can be chosen for the carbonate removal after sintering, depending on whether production time or shrinkage is the main concern.

Acknowledgments

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