

Fabrication of high melting-point porous metals by lost carbonate sintering process via decomposition route

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Abstract: Porous metals with high melting points can be manufactured by the lost carbonate sintering (LCS) process either via the dissolution route or via the decomposition route. In the current paper, porous copper and steel samples with porosity in the range of 50 to 85 per cent and cell size in the range of 50 to 1000 μm have been produced via the decomposition route. The effectiveness of carbonate loss and the characteristics of the decomposition route have been studied. In comparison with the dissolution route, the decomposition route can be applied to a wider range of conditions and often requires shorter times to achieve a complete carbonate removal. The porous metal samples produced by the decomposition route generally have higher tensile strength and higher flexural strength than those produced by the dissolution route.

Keywords: porous metal, lost carbonate sintering, decomposition, dissolution

1 INTRODUCTION

Porous metals, or metal foams, have found increasing applications in many areas [1–6]. These applications can be broadly classified according to the main properties utilized. Structural applications use the exceptional mechanical properties of porous metals, such as high specific stiffness and high energy absorption capacity. Examples of the applications include building and transport structures against buckling and impact. For structural applications, the most important property of porous metals is porosity or relative density. Although the morphology of the cells or pores also affects the mechanical properties, its effect is secondary. Very often, it does not matter whether the cells are open or closed. Functional applications use the geometrical, thermal, acoustic, and electrical properties of porous metals, such as high surface areas, multiple fine channels, and high electrical and thermal conductivities. Examples of the applications include sound absorbers, heat sinks for electronic devices, and catalyst supports. For most functional applications, the most important properties of the porous metals are the geometry and morphology of the cells as well as the intrinsic

physical properties of the matrix metals. The cells are normally required to be open and with controlled sizes.

There are many technologies available for manufacturing porous metals [1–6]. The liquid route methods, such as melt infiltration, investment casting, gas injection, and powder metallurgy (P/M) foaming, are more suited to metals of relatively low melting points, such as aluminium. The liquid route methods have also been applied to some metals of higher melting points. For example, a P/M foaming process has been used to produce steel foams with closed cells [7] and an investment casting method has been used to produce porous copper with large cells and a high porosity [8]. However, most porous metals of higher melting points, such as copper, steel, nickel, and titanium, often need to be produced by solid route technologies. This is partly because of the technical difficulties and high processing costs involved in handling liquid metals at elevated temperatures and partly because of some of the undesirable properties generally associated with liquid routes (such as inhomogeneous, large, and closed cells, which are not suitable for many functional applications). P/M solid route methods have been employed to manufacture porous titanium and stainless steel, where burnable particles are used as space holders and removed at low temperatures before sintering [9]. Because the space holders are removed before

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any strong bonding between the metal particles is formed, the networks of the metal particles may partially collapse before reaching the sintering stage. The porous metals produced by these routes can often show poor cell structure or morphology. Zhao and his colleagues have developed the lost carbonate sintering (LCS) process for manufacturing open-cell porous metals including aluminium, copper, and steel [10]. LCS is a simple, low-cost process with a good control over pore size and porosity and is suitable for a range of metals with high melting points.

The current paper reports the study on the manufacture of porous copper and steel by the LCS process via the decomposition route. The study is focused on the effectiveness of carbonate loss and the characteristics of the decomposition route in comparison with the dissolution route.

2 EXPERIMENTAL PROCEDURE

The general procedure of the LCS process was described in reference [10]. LCS involves four stages: powder mixing, compaction, sintering, and carbonate removal. In LCS, a metal powder and a carbonate powder are first mixed at a given volume ratio. The powder mixture is compacted and then sintered. A porous metal part is finally obtained by removing the carbonate particles from the sintered compact either by decomposition or by dissolution.

In this study, the raw materials were commercially pure copper (Cu), micro-alloyed steel, and potassium carbonate (K_2CO_3) powders supplied by Ecka Granules (UK) Ltd, Pometon Ltd, and E&E Ltd, respectively. The Cu powder consisted of spherical particles with particle diameters in the range 20–75 μm . The steel had a maximum carbon content of 0.01 per cent and was alloyed with 0.2% Ni and 0.15% Mo. The steel powder consisted of irregular granular particles with particle sizes in the range 40–150 μm . The K_2CO_3 powders consisted of granular particles with two different size ranges of 53 to 125 μm and 425 to 710 μm . The volume fraction of K_2CO_3 in the metal- K_2CO_3 mixture was fixed at 0.7. The compaction of powder mixtures were carried out under a pressure of 200 MPa. The compacts of the powder mixtures were cylindrical with a diameter of either 21 mm or 43 mm and a thickness of 5, 10, 15, or 20 mm. The heating temperatures and times of the sintering and carbonate removal stages are shown schematically in Fig. 1. The compacts were first sintered at 850 °C for 4 h. In the dissolution route, the sintered compacts were cooled to room temperature and the K_2CO_3 was dissolved in water. In the decomposition route, the sintered compacts were heated further to 950 °C to decompose the K_2CO_3 particles. To investigate the effect of time on the effectiveness of decomposition, the samples were

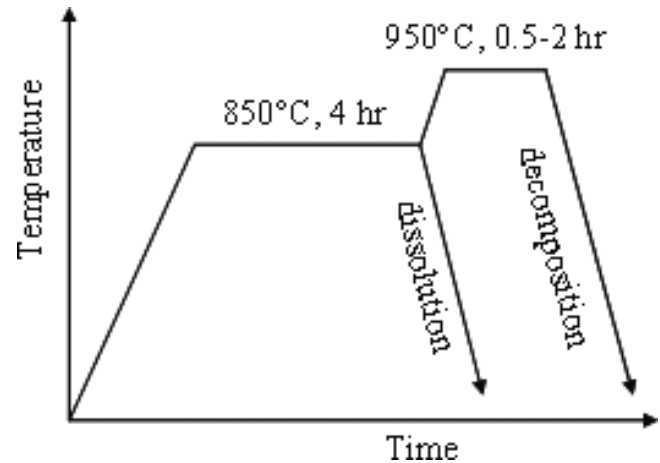


Fig. 1 Schematic of the sintering and carbonate removal stages of LCS

held at 950 °C for 0.5, 1, 1.5, or 2 h before being cooled to room temperature. The weights of the samples before and after the sintering and decomposition stages were measured by an electronic scale with a precision of 0.01 g.

A Hitachi S-2460N scanning electron microscope (SEM) equipped with an X-ray detector was used for microstructural and chemical analysis of the samples. The tensile and three-point bending tests were conducted on an Instron 4505 materials testing system at a crosshead speed of 1mm/min. The samples for the tensile and three-point bending tests were cut into 40×10×8 mm cuboids. Before the tensile test on a porous metal sample, both ends of the sample were impregnated with a cold mounting liquid and then left for 10 h for the liquid to set. The sample was thus strengthened at both ends so that it could be gripped by the tensile machine without being crushed. The flexural strength of the porous metal samples was obtained from the three-point bending tests in accordance with AMST standard E855 and was calculated by [11]

$$\sigma_b = \frac{3FL}{2bh^2} \quad (1)$$

where b is the width of the test sample, h is the thickness, L is the span length between the two supports, and F is the maximum load corresponding to the break of the sample. In this experiment, $L = 36$ mm, $b = 8$ mm, and $h = 10$ mm.

3 RESULTS AND DISCUSSION

3.1 Effectiveness of carbonate loss

K_2CO_3 melts and starts to decompose at 891 °C. A complete decomposition of the K_2CO_3 particles can be achieved by holding the particles at a temperature

above 891 °C for a certain period of time. In this study, a small amount of K_2CO_3 powder was heated at 950 °C for half an hour so that the decomposition proceeded to completion. The weight of the powder before decomposition and the weight of the solid product of the decomposition were measured using a scale with a precision of 0.01g. By comparing the weight change with those of the possible decomposition reactions, the decomposition reaction was confirmed to be



The X-ray diffraction analysis also confirmed that the solid product of the decomposition was potassium oxide K_2O .

The melting and decomposition of K_2CO_3 are likely to take place concurrently and progressively when a sintered metal- K_2CO_3 sample is raised to 950 °C. At 950 °C, one of the decomposition products, K_2O , is in the liquid state. The other decomposition product, gaseous CO_2 , bubbles through the melt of the mixture of undecomposed K_2CO_3 and its product K_2O . The K_2CO_3 - K_2O melt comes out of the sample mainly through drainage, either owing to gravity or owing to the high pressure generated by CO_2 . The CO_2 bubbles can also carry away small amounts of the melt into the atmosphere. These mechanisms of carbonate loss have been supported by experimental observations. In the decomposition stage of LCS, a white smoke was observed to come out of the sample. After the sample was cooled to room temperature, solid K_2O powder was found both at the bottom and top parts of the cylindrical sample container. The examination of the amounts of K_2O powder at the bottom and top parts indicated that melt drainage by CO_2 expansion was the dominant mechanism of carbonate loss.

The degree of carbonate loss in LCS can be expressed by the weight percentage of the decomposed carbonate with respect to the original carbonate in a sample and can be determined by weighing the sample before and after the decomposition. The degree of K_2CO_3 loss can be affected by several factors, including volume fraction of K_2CO_3 in the metal- K_2CO_3 mixture, size of the K_2CO_3 particles, thickness of the sample, decomposition temperature and decomposition time. A series of Cu- K_2CO_3 samples with a fixed K_2CO_3 volume fraction of 0.7 and with different K_2CO_3 particle size ranges or different sample thicknesses were used for studying the effectiveness of K_2CO_3 loss. These samples were all sintered at 850 °C for 4 h followed by further sintering at 950 °C for different times. For the samples containing K_2CO_3 particles larger than 125 μm and with a sample thickness up to 20 mm, half an hour was found to be sufficient to remove all the K_2CO_3 . The energy dispersive

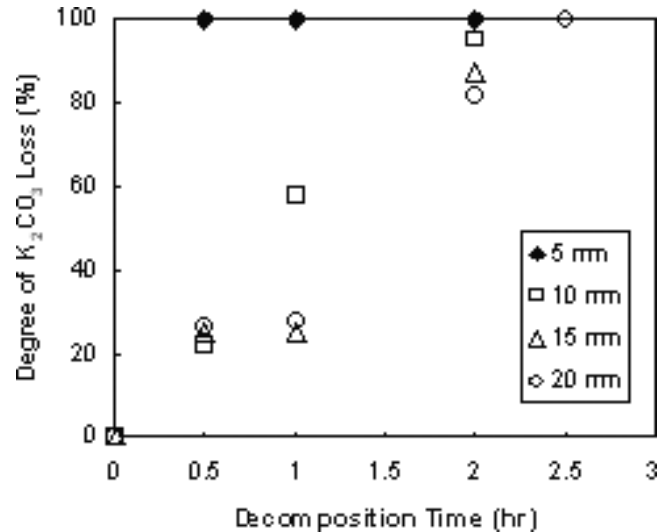


Fig. 2 Effects of sample thickness and decomposition time on degree of K_2CO_3 loss

X-ray (EDX) analysis of the resultant porous Cu samples also confirmed that no discernible residual K_2CO_3 or K_2O was left. For the samples with K_2CO_3 particles smaller than 125 μm , the degree of K_2CO_3 loss depended on the sample thickness and decomposition time. Figure 2 shows the degrees of K_2CO_3 loss of the samples, with K_2CO_3 particle sizes of 53–125 μm and K_2CO_3 volume fraction of 0.7, after different decomposition times for different sample thicknesses. It is shown that the degree of K_2CO_3 loss increased with increasing decomposition time and decreased with increasing sample thickness. For the samples with a sample thickness up to 20 mm, 2.5 h was found to be sufficient to remove all the K_2CO_3 . For a 5 mm thick sample, less than half an hour was needed for a complete removal.

The rate of K_2CO_3 loss, i.e. the change of the degree of K_2CO_3 loss with time, seems to be determined mainly by the rate of K_2CO_3 decomposition. This is because the rate of K_2CO_3 decomposition determines the rate of CO_2 release, which in turn determines the pressure of the CO_2 bubbles generated in the melt. The observation of the through-thickness cross-section of a sample sintered at 950 °C for 15 min showed that the undecomposed K_2CO_3 distributed evenly across the sample thickness. This phenomenon supported the previous statement that the dominant mechanism of carbonate loss was melt drainage by CO_2 expansion.

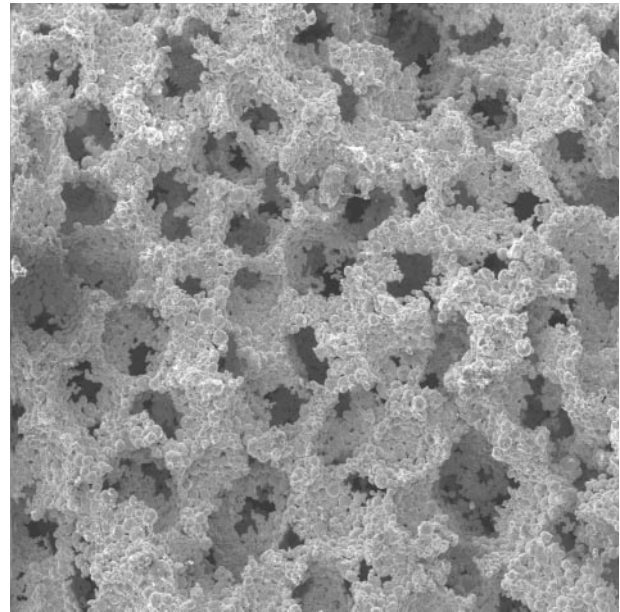
The rate of K_2CO_3 loss is also affected by the flow resistance of the metal matrix. The network of the K_2CO_3 particles is effectively the channels in the metal matrix for the K_2CO_3 - K_2O melt to flow out. Large K_2CO_3 particles lead to large open channels and thus small flow resistance. In this case, a small amount of released CO_2 can create a pressure great

enough to drive the melt out of the sample. When the K_2CO_3 particle sizes are below $125\ \mu\text{m}$, however, the flow resistance can become significant. A thicker sample has a higher flow resistance and requires a higher pressure of CO_2 to drive the melt out of the longer channels. In short, thick samples with small K_2CO_3 particles, i.e. small intended pore sizes, have lower rates of K_2CO_3 loss.

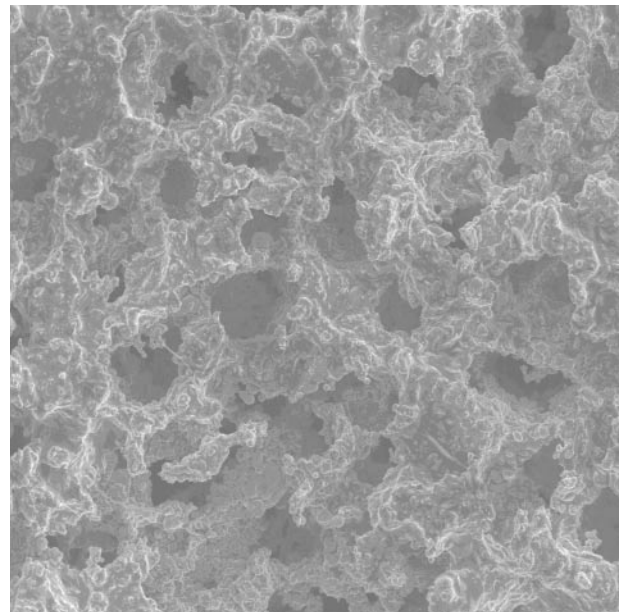
3.2 Comparison between decomposition and dissolution

The porous Cu and steel samples fabricated by LCS via the decomposition route show less oxidation compared with those fabricated by the dissolution route, because the caustic attack by the aqueous solution of potassium carbonate is prevented. Figure 3 shows the SEM micrographs of typical structures of porous copper and steel samples, with a porosity of about 75 per cent and cell size in the range of 425 to $710\ \mu\text{m}$. The structure of the samples is a well-bonded metal network of the metal particles with uniformly distributed open cells. The primary cells are largely equiaxed and rounded, which reflect the shapes and sizes of the K_2CO_3 particles used in the manufacturing process. The large primary cells are connected by smaller holes in the cell walls. The structure of the porous metals produced by LCS via the decomposition route is similar to that produced via the dissolution route. However, the porous metals produced by the decomposition route have a slightly lower porosity than that produced by the dissolution route for the same volume fraction of K_2CO_3 used, because of the higher shrinkage in the decomposition stage.

In comparison with the dissolution route, the decomposition route can be applied to a wider range of conditions and often requires shorter times to achieve a complete carbonate removal. The dissolution of K_2CO_3 requires direct contact between the water and the K_2CO_3 particles. The dissolution process proceeds gradually from the outer surface towards the centre of the sample. To remove the K_2CO_3 particles completely from the sintered sample, it is necessary for the fresh water to penetrate the entire depth of the open channels across the sample thickness and for the resultant aqueous solution of K_2CO_3 to flow out. The rate of dissolution is approximately proportional to the volume fraction of the salt in the initial metal–salt compact and inversely proportional to the square root of dissolution time [12]. For samples with very small K_2CO_3 particles, low K_2CO_3 volume fractions or large thicknesses, the dissolution times for complete removal of the K_2CO_3 particles from the samples can be unacceptably long. In contrast, the removal of the K_2CO_3 particles in the decomposition route relies upon the release



(a)



(b)

Fig. 3 SEM micrographs showing typical structures of (a) porous copper and (b) porous steel manufactured by LCS via the decomposition route

of CO_2 , which takes place evenly throughout the entire sample. The particle size and volume fraction of K_2CO_3 in the sintered sample and the sample thickness affect the flow resistance and thus the rate of carbonate loss. For samples with very small K_2CO_3 particles, low K_2CO_3 volume fractions or large thicknesses, however, the rate of carbonate loss in decomposition is often much higher than that in dissolution.

The different by-products of decomposition and dissolution may have significant implications in the

Table 1 Average tensile strengths and flexural strengths of porous copper samples produced by LCS via dissolution and decomposition routes

K ₂ CO ₃ removal route	Tensile strength (MPa)	Flexural strength (MPa)
Dissolution	1.2	4.1
Decomposition	2.1	6.0

commercialization of the LCS process, as environmental friendliness is concerned. The by-product of dissolution is an aqueous solution of K₂CO₃, which may pose a problem in recycling. The by-product of decomposition is solid K₂O ash, which is much easier and cheaper for collection and recycling. However, any residual K₂O ash left in the porous metal components or processing facilities can absorb moisture from the air and form a strong base that attacks many metals.

The porous metal samples produced by the decomposition route were found to have better mechanical properties. Table 1 shows the average tensile strengths and flexural strengths of several porous Cu samples produced by LCS via the dissolution and decomposition routes. The compacts used in making the porous copper samples have a K₂CO₃ volume fraction of 0.7 and K₂CO₃ particle sizes of 425–710 µm. It is shown that the strength of samples produced by the decomposition route was 1.5–2 times of that produced by the dissolution route. This was mainly a consequence of the additional sintering at 950 °C, which made the metal matrix denser and stronger.

However, the strength values of the samples are much lower than that estimated using the scaling relations reported in reference [1]. These scaling relations were largely established for metal foams manufactured by the casting routes. It seems these relations are not applicable for porous metals manufactured by the sintering routes.

4 CONCLUSIONS

Porous Cu and steel samples with porosity in the range of 50 to 85 per cent and cell size in the range of 50 to 1000 µm have been produced by LCS via the decomposition route. The rate of K₂CO₃ loss increases with increasing K₂CO₃ particle size in the metal–K₂CO₃ compact and decreases with increasing sample thickness. In all samples with a thickness up to 20 mm, K₂CO₃ can be removed completely in less than 2.5 h at 950 °C. In comparison with the dissolu-

tion route, the decomposition route can be applied to a wider range of conditions and often requires shorter times to achieve a complete carbonate removal. The porous metal samples produced by the decomposition route have higher tensile strength and higher flexural strength than those produced by the dissolution route.

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