Friction powder compaction process for fabricating open-celled porous Cu by sintering-dissolution process route using NaCl space holder

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Abstract

Open-celled porous metals have received considerable attention in various fields and are expected to be used as engineering materials where heat exchange, sound absorption and filtration are required. In this study, porous Cu specimens with NaCl volume fractions of 60, 70 and 80% were successfully fabricated by the friction powder compaction (FPC) process with the sintering and dissolution process (SDP) using NaCl as space holders. In the FPC process, no external heat source was used for fabricating porous Cu except for the friction heat generated by the rotating tool plunged into the die and powders. From the X-ray CT and SEM observation of the pore structures of the fabricated porous Cu, it was found that almost the entire specimen had a pore structure similar to the NaCl morphology, regardless of the NaCl volume fraction. This is mainly because the sintering process for Cu particles in the FPC process was achieved at a temperature lower than the melting point of NaCl. From compression tests of the fabricated porous Cu, porous Cu exhibited ductile fracture regardless of its NaCl volume fraction, which is considered to be attributed to the good bonding between Cu particles. The plateau stress and energy absorption decreased with increasing NaCl
volume fraction, indicating strong relationships between them. The porous Cu with the highest energy absorption per unit volume up to the specific stress changed from the high-NaCl-volume-fraction porous Cu to the low-NaCl-volume-fraction porous Cu with increasing compression stress. Consequently, it was shown that the mechanical properties of porous Cu can be controlled by adjusting the volume fraction of NaCl.

Keywords : cellular materials; powder metallurgy; sintering; tomography; mechanical characterization

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1. Introduction

Open-celled porous metals have received considerable attention in various fields and are expected to be used as engineering materials where heat exchange, sound absorption and filtration are required[1-3]. A novel sintering and dissolution process (SDP) was developed for the fabrication of open-celled porous metal on the basis of powder metallurgy by Zhao and Sun[4]. In this process, a mixture of a metal powder and a soluble powder as space holders, such as sodium chloride (NaCl), is compacted and sintered by applying appropriate pressure and heat using an electric furnace or by spark plasma sintering. Then, the sintered mixture is placed in water to remove the soluble particles and an open-celled porous metal is obtained. The SDP is promising for fabricating open-celled porous metals because pore structure parameters (i.e., porosity, pore size and pore morphology) can be easily and accurately controlled by adjusting the proportion of metal/soluble powders and selecting a soluble powder with particles of an appropriate shape. Also, the soluble powder in the sintered mixture can be easily removed simply by placing the sintered mixture in water at room temperature, that is, SDP is a simple process and, essentially, no heat source is necessary for the removal of soluble particles. In particular, using NaCl particles as soluble particles has additional advantages, such as low cost, ready availability, nontoxicity and fast dissolution in water.

Up to now, most porous metals fabricated via the SDP using NaCl as space holders have been limited to porous aluminum (Al) [4-10]. This is mainly due to the relationship between the melting points of the metal and NaCl. Namely, the melting point of Al (933 K) is below that of NaCl (1074 K); thus, it is considered that NaCl does not largely deform or melt during the sintering of Al particles and almost retains its original shape. Recently, open-celled porous Cu and porous Ti, which have higher melting points than NaCl, have been fabricated by the SDP using NaCl as space
holders[11-13]. However, heating to above the melting point of NaCl is necessary to sinter the Cu and Ti matrices simultaneously with and/or after the removal of NaCl.

Other soluble particles, such as potassium carbonate (K₂CO₃)[14], ammonium hydrogen carbonate (NH₄HCO₃)[15-17], carbamide[18], urea[19] and polymethyl methacrylate (PMMA)[20, 21], have been used as space holders for fabricating porous Cu and porous Ti. Even in these cases, a heating process to above the melting point of the space holders was necessary to sinter the Cu and Ti matrices simultaneously with and/or after the removal of the space holders.

Recently, a friction powder compaction (FPC) process has been developed for compacting a mixture of Al and NaCl powders to fabricate porous Al[22, 23]. The compaction of the powders is conducted by simply plunging a rotating tool into a metal plate with a hole filled with the powders. Namely, the sintering of the powders is mainly achieved by the friction heat and pressing load generated by the rotating tool plunged into the metal plate and powders. The FPC process is simple and requires an extremely short time. Also, it does not require an external heat source for the compaction of powders. Therefore, the FPC process is more environmentally friendly. Furthermore, it can be conducted using a conventional milling machine and does not require the use of any special equipment, making it a low-cost manufacturing process.

In this study, open-celled porous Cu was fabricated by the FPC process by the SDP using NaCl; i.e., no sintering process for the Cu matrix above the melting point of NaCl was necessary simultaneously with and/or after the removal of NaCl, which other process by the SDP using NaCl cannot be realized. Namely, this process requires no external heat sources for all the processes needed to fabricate porous Cu. The pore structure of the fabricated porous Cu was nondestructively observed by X-ray computed tomography (CT) and scanning electron microscopy (SEM) to confirm that its shape is similar to that of NaCl particles. In addition, the compression properties of the obtained
porous Cu were investigated in accordance with Japanese Industrial Standards JIS-H-7902[24].

2. Experimental procedure

2.1 Materials

Fig. 1 shows a schematic of the FPC process for fabricating porous Cu. Commercially available as-received Cu (99.99% purity, average diameter of 1 μm) and sieved NaCl (99.9% purity, diameter range from 300 μm to 425 μm) powders were used as the starting materials. Fig. 2 shows SEM images of the Cu and NaCl powders, which revealed that the Cu particles had an irregular, but relatively round shape, while the NaCl particles were cuboidal. These powders were thoroughly mixed at a specific weight ratio with NaCl volume fractions of $V_f = 60$, 70 and 80%. The NaCl powder was heated to 433 K for 30 min to remove the moisture from it before mixing. As shown in Fig. 1(a), the mixture was placed in a hole ($\phi = 15$ mm) previously drilled in a commercially available oxygen-free Cu plate of 10 mm thickness. If a low-melting-point Al plate is used, instead of an oxygen-free Cu plate, the Al plate is first softened by increasing the temperature during the compaction process, thereby reducing the increase in sintering temperature and pressure to some extent[23]. An SS400 back plate of 3 mm thickness was placed under the oxygen-free Cu plate, i.e., the bottom of the powder was placed in contact with the back plate. Next, as shown in Fig. 1(b), a rotating tool ($\phi = 25$ mm) was pressed into the hole filled with the mixture. The dimensions of the tool and hole were selected by trial and error because they depended on the capacity of the machine used. The central axis of the rotating tool corresponded to the center of the hole of the oxygen-free Cu plate. The tool used was made of tungsten carbide (WC) and had a cylindrical shape with a flat bottom. Note that, a tungsten-based alloy is conventionally used as the tool material in the FSW of Cu[25,
The rotation speed was 1000 rpm, the tool plunge load was constant at 34.3 kN and the holding time was set at 60 s. Cu has good heat conductivity; therefore, it was considered that the Cu powder temperature would vary with the position during the compaction process. The powder temperature was measured by a thermocouple placed at the center of the hole at upper, middle and lower positions, i.e., at the center of upper, middle and lower positions in the powder, respectively.

Finally, the sintered mixture was cut by electrodischarge machining (Fig. 1(c)), and, as shown in Fig. 1(d), the NaCl was removed by placing the mixture in a water bath for approximately 24 h, where the water temperature was 333 K. Although it is possible to remove NaCl at room temperature, warm water was used for the faster removal of NaCl. The weight of the sintered mixtures was obtained during NaCl leaching, to confirm that NaCl was completely removed. Before the weight measurement, the sintered mixture was removed from the water bath and placed in a preheated furnace of 433 K for 20 min to remove the water from the specimen. Eventually, three cylindrical compression test specimens with dimensions of $\phi = 12 \text{ mm} \times 5 \text{ mm}$ were obtained for each NaCl volume fraction.

2.2 Observation of pore structures

X-ray CT observations were performed on the compression test specimens using an SMX-225CT microfocus X-ray CT system (Shimadzu Corporation). The X-ray source was tungsten. A cone-type CT system, which produces three-dimensional images, was employed. In this system, only one rotation of the specimen was sufficient to obtain a three-dimensional volume image, which consisted of a set of CT images with a slice pitch equal to the length of one pixel in the CT image. The resolution of each CT image was $512 \times 512$, and the pixel length was $38 \mu\text{m}$. The X-ray tube voltage and current were
120 kV and 30 μA, respectively. A Cu plate filter of 2 mm thickness was placed in front of the image intensifier.

The pore structures and cell walls of the fabricated porous Cu were also observed by SEM at the cross section of the middle longitudinal section.

2.3 Compression tests

Compression tests were carried out at room temperature in ambient air using an Autograph AG-100kNG universal testing machine (Shimadzu Corporation) at a strain rate of $3.3 \times 10^{-3}$ s$^{-1}$. At the same time, the compression deformation of the specimen was recorded by a digital video camera.

The plateau stress $\sigma_{pl}$ was defined as the average stress for a strain of 20–30%[24]. The energy absorption per unit volume, $E_V^{50}$, was defined as the area under the stress–strain curve up to 50% strain as follows[24]:

$$E_V^{50} = \frac{1}{100} \int_{\varepsilon=0}^{\varepsilon=50} \sigma(\varepsilon) d\varepsilon.$$

3. Experimental Results and Discussion

3.1 Relationship between leaching time and NaCl removal rate

Fig. 3 shows the relationship between the leaching time and the removal rate of NaCl for the fabricated sintered mixtures with NaCl volume fractions of $V_f = 60$, 70 and 80%.

A large amount of NaCl had already been removed before the removal process due to the cutting process by electrodischarge machining (about 10 min). This is because running water was used in the cutting process. Therefore, NaCl was removed faster than in the case when the sintered mixture was simply placed in static water. Also the reduction of NaCl was achieved faster at the start of leaching[22] owing to the removal of NaCl from the outside of the specimen where water can directly come into contact with NaCl. During the removal process, it could be seen that NaCl was completely
removed at a removal time of less than approximately 10 h for all specimens. In particular, NaCl in the sintered mixture was removed faster with increasing NaCl volume fraction of the sintered mixture. This is because water can more easily come into contact with the specimen with increasing NaCl volume fraction.

3.2 Pore structures of fabricated porous Cu

Fig. 4 shows the compression test specimen of fabricated porous Cu with a NaCl volume fraction of $V_f = 80\%$. The average porosities of the obtained porous Cu in the three compression test specimens with $V_f = 60$, 70 and 80\%, which were evaluated by mass and dimension measurements, were 64.2, 72.8 and 80.6\%, respectively. The decrease in the difference between $V_f$ and the corresponding porosity with increasing $V_f$ is considered to be mostly due to the density of the cell walls of the porous Cu, i.e., the density of the Cu powder compact, being lower than the theoretical density. Therefore, the difference between $V_f$ and the corresponding porosity decreased with decreasing volume fraction of Cu.

Fig. 5 shows X-ray CT images of the pore structures of fabricated porous Cu with $V_f = 60$, 70 and 80\% taken at the upper, middle and lower positions. The upper position of the specimen corresponds to the vicinity of the surface, with which the rotating tool was in direct contact, and the lower position is the bottom part during sintering. Gray regions indicate cell walls of porous Cu, and black regions indicate pores. Fig. 6 shows SEM images of the pore structures of the fabricated porous Cu with $V_f = 70\%$ taken at the upper, middle and lower positions. Although, there was concern that the upper position would be subjected to intense plastic deformation due to its direct contact with the rotating tool, it can be seen that almost all the positions had a pore structure similar to the NaCl morphology, as shown in Fig. 2(b). This tendency was almost the same regardless of $V_f$.  

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Fig. 7 shows an enlarged SEM image of the cell wall shown in Fig. 6(b). It can be seen that the shape of the Cu particles shown in Fig. 2(a) remained unchanged. No voids can be seen at this magnification, and the particles were considered to be bonded properly.

3.3 Temperature during compaction process

Fig. 8 shows the relationships between the indentation time $t$ and powder temperature $T$ during the compaction of the upper, middle and lower positions for $V_L = 60\%$. $t$ is the time elapsed from when the tool first came into contact with the surface of the oxygen-free Cu plate and powder. First, the indentation of the tool caused a rapid increase in temperature until approximately $t = 20$ s. The temperature of the upper position, which is in the vicinity of the rotating tool and where friction heat was generated, initially increased. Heat generated in the vicinity of the rotating tool transferred to the high-heat-conductivity oxygen-free Cu plate caused a rapid increase in the temperature of the SS400 back plate. This induced a rapid increase in the temperature of the lower position. In the middle position, lower-thermal-conductivity NaCl existed and the difficulty of transferring the heat in the Cu powder caused a slow increase in its temperature. After approximately $t = 20$ s, the rate of temperature increase decreased, which is considered to be due to the amount of heat released from the oxygen-free Cu plate increasing with increasing temperature of the powder. In particular, the rate of the temperature increase of the lower position decreased because heat was released from the SS400 back plate. After approximately $t = 40$ s, the temperature became almost constant and reached a maximum of approximately 900 K. The temperature was higher closer to the rotating tool. After $t = 60$ s, the tool was moved upward and unloaded, causing the temperature to decrease rapidly. This tendency is almost the same regardless of the NaCl volume fraction.
Fig. 9 shows the maximum temperature $T_{\text{max}}$ achieved during the compaction of the upper, middle and lower positions for $V_f = 60$, 70 and 80%. It can be seen that the maximum temperature is achieved in the vicinity of the rotating tool and the farther the distance from the rotating tool, the lower the powder temperature, regardless of the NaCl volume fraction. The temperature of the powder with $V_f = 70\%$ was lower than that at the same position for the other $V_f$ values. By comparing the powders with $V_f = 60$ and 70%, it is considered that increasing the amount of endothermic NaCl decreases the powder temperature. By comparing the powders with $V_f = 70$ and 80%, it is considered that increasing the amount of Cu in the specimen, which has superior heat conductivity, decreased the powder temperature. Clearly, the amounts of NaCl and Cu have a complicated effect on the powder temperature. Therefore, much more extensive studies are necessary to clarify the relationship between the powder temperature and NaCl volume fraction.

3.4 Mechanical properties

Fig. 10 shows typical stress–strain curves of the obtained porous Cu with $p = 63.3$, 72.8 and 79.6%. Three specific regions, namely, the elastic region at the initial stage, the plateau region with a nearly constant stress up to a large strain and the densification region where the stress increased markedly, can be clearly observed. The low-porosity porous Cu had a higher plateau stress but a narrower plateau region than the high-porosity porous Cu. As the porosity became higher, the Young’s modulus (gradient of elastic region) and the rate of increase of stress with increasing strain in the plateau region became lower. This deformation behavior under compression was similar to that of open-cell porous Cu obtained by different sintering processes using an electric furnace or spark plasma sintering via the SDP[11, 15].

Fig. 11 shows deformation images for different strains during compression tests with
$p = 79.6\%$. The upper part of the images corresponds to the upper position of the specimen in the vicinity of its surface, which was in direct contact with the rotating tool. These porous Cu specimens exhibited ductile fracture, and no brittle fracture, which would have resulted in a decrease in plateau stress during the compression tests due to the poor bonding of Cu particles[7], was observed; namely, it is considered that the good bonding of Cu particles was achieved. This deformation behavior was observed for all the specimens examined in this study.

The deformation started from the lower position of the specimen; then moved to the upper position, regardless of the porosity of the specimen. It is considered that the upper position, where intense plastic deformation, high friction heat and pressing load were applied, achieved a higher bonding strength of Cu particles than the lower position, where little plastic deformation, relatively low friction heat and pressing load were applied. However, it is considered that this difference in the bonding strength of Cu particles between the upper and lower positions is too small to affect the stress-strain curve and cause multiple plateau regions to appear, which would indicate independent and different plateau stresses[27, 28]. Clearly, further studies are necessary to determine the relationship between the position of the specimen and the bonding strength of Cu particles, as well as the effect of the bonding strength on the mechanical properties of porous Cu fabricated by the FPC process.

Figs. 12(a) and (b) respectively show the relationships between the NaCl volume fraction $V_f$, and the plateau stress $\sigma_{pl}$ and the energy absorption per unit volume $E_V^{50}$ for the fabricated porous Cu. It was found that the plateau stress and energy absorption tend to decrease with increasing $V_f$, indicating strong relationships between them. Therefore, it is considered that the plateau stress strongly affects the energy absorption of porous Cu. From these results, it was indicated that $\sigma_{pl}$ and $E_V^{50}$ (i.e., mechanical properties of porous Cu) can be controlled by adjusting the NaCl volume fraction.
Figure 13 shows the relationship between the compression stress $\sigma$ and the energy absorption per unit volume $E_V$ (the area under the stress-strain curve up to a specific stress $\sigma$) for the fabricated porous Cu specimens with different porosities. The porous Cu with high porosity had a higher $E_V$ in the first stage of compression up to $\sigma \approx 40$ MPa. This is because the porous Cu with high porosity has a low plateau stress; therefore, it deforms with a large compression strain at a low compression stress. In contrast, the porous Cu with low porosity had a high plateau stress and therefore remained in the elastic region and exhibited a low $E_V$ at a low compression stress. As the compression stress increased and the compression behavior of the porous Cu with low porosity departed from the linear elastic region and transferred to the plateau region, $E_V$ increased rapidly owing to the higher plateau stress. Therefore, $E_V$ for porous Cu with low porosity became higher than that of porous Cu with high porosity at a high compression stress. Consequently, the highest $E_V$ was observed for the high-porosity porous Cu at a lower compression stress and for the low-porosity porous Cu at a higher compression stress. This tendency was also observed for the energy absorption per unit mass.

4. Conclusion

In this study, porous Cu specimens with porosities of 60% to 80% were successfully fabricated by the FPC process using NaCl as space holders. In the FPC process, no external heat source such as an electric furnace or spark plasma sintering was used for fabricating porous Cu except for the friction heat generated by the rotating tool plunged into the die and powders.

From the X-ray CT and SEM observations of the pore structures of the fabricated porous Cu, it was found that almost the entire specimen had a pore structure similar to the NaCl morphology, regardless of the NaCl volume fraction. Consequently, it was
shown that the morphology of the pores and porosity of the fabricated porous Cu can be easily controlled by adjusting the shape and volume fraction of NaCl particles. This is mainly because the sintering process for Cu particles in the FPC process was achieved at a temperature lower than the melting point of NaCl.

The fabricated porous Cu exhibited ductile fracture regardless of its porosity, which is attributed to the good bonding between Cu particles. The plateau stress and energy absorption decrease with increasing porosity, indicating the strong relationships between them. The porous Cu with the highest energy absorption per unit volume changed from high-porosity porous Cu to low-porosity porous Cu with increasing compression stress. Consequently, the mechanical properties of porous Cu can be controlled by adjusting the volume fraction of NaCl.

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References


Fig. 1. Schematic of FPC process for fabricating porous Cu.
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Fig. 9. Relationship between NaCl volume fraction $V_f$ and maximum temperature $T_{\text{max}}$ during sintering for upper, middle and lower positions.
Fig. 10. Stress–strain curves for fabricated porous Cu with porosities $p$ of 63.3, 72.8 and 79.6%.
Fig. 11. Deformation images for different strains during compression tests of fabricated porous Cu with $p = 79.6\%$. 
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Fig. 13. Relationship between compression stress and energy absorption per unit volume.