Relationship between Amount of Residual NaCl and Compressive Properties of Porous Al/NaCl Composites Fabricated by Sintering and Dissolution Process

Yoshihiko Hangai¹, Hiroaki Yoshida^{1,*}, Ryo Yamaguchi^{1,*},
Osamu Kuwazuru² and Nobuhiro Yoshikawa³

¹Graduate School of Engineering, Gunma University, Kiryu 376-8515, Japan

²Graduate School of Engineering, University of Fukui, Fukui 910-8507, Japan

³Institute of Industrial Science, The University of Tokyo, Tokyo 153-8505, Japan

In this study, a porous Al/NaCl composite was fabricated by a sintering and dissolution process, and the possibility of controlling the mechanical properties of porous Al by varying the amount and distribution of residual NaCl was investigated. It was shown that the range of the plateau region decreased and the stress-strain curves became similar to those of dense materials as the amount of residual NaCl increased. The deformation started from the layers where NaCl was removed, then the layers where NaCl remained started to deform. This indicates that the strength of each region can be controlled by varying the amount and distribution of residual NaCl. [doi:10.2320/matertrans.M2013023]

(Received January 21, 2013; Accepted February 8, 2013; Published March 23, 2013)

Keywords: cellular materials, sintering and dissolution process, functionally graded materials (FGM), foam

1. Introduction

Porous aluminum (Al) is expected to be used for automotive components owing to its light weight, good energy absorption properties and good sound insulation properties.¹⁾ However, there have been some difficulties in fabricating components with complicated shapes because the machining of porous Al is difficult owing to its thin cell walls.

The sintering and dissolution process is a promising process for fabricating porous Al.²⁻⁸⁾ In this process, a mixture of Al powder and soluble sodium chloride (NaCl) powder is compacted and sintered by applying an appropriate pressure and heat. Then, the sintered mixture is placed in water to remove the NaCl, thus obtaining open-cell porous Al. The sintering and dissolution process enables easy and accurate control of the pore structure (porosity, pore size and pore morphology) by adjusting the proportions of Al and NaCl powders and selecting NaCl powder with particles of the appropriate size and morphology. In addition, the NaCl powder in the sintered mixture can be easily removed simply by placing the sintered mixture in water.

It is considered that the sintered mixture (porous Al/NaCl composite) has mechanical properties superior to those of porous Al itself. Namely, the spacer (NaCl) particles of the porous Al/NaCl composite can act as strengthening particles of porous Al. Therefore, it may be possible to fabricate porous Al components with complicated shapes by first machining a porous Al/NaCl composite, and thereafter leaching NaCl from the composite with the complicated shape. Also, if such composites can be fabricated with a biocompatible metal as the base material and a biodegradable material as the spacer, for example, porous titanium and hydroxyl apatite, respectively, then the porous metal can be used in biomedical applications such as bone fixation

devices. These devices are expected to have mechanical properties superior to those of human bone when the operation is conducted, which gradually deteriorate *in vivo* as the healing progresses.⁹⁾ The deterioration of the mechanical properties of these devices is required to prevent the stress-shielding phenomenon, in which bone resorption occurs around the region of bone replacement.^{10,11)}

In this study, the relationship between the amount of residual NaCl in a porous Al/NaCl composite fabricated by a sintering and dissolution process and its compressive response was investigated. The amount of residual NaCl in the composite was tailored by changing the removal time of NaCl, i.e., the duration for which the composite was placed in water. In addition, X-ray CT inspection was conducted to observe the distribution of residual NaCl before compression tests to reveal the relationship between the deformation behavior and the distribution of residual NaCl. As a result of these investigations, the possibility of controlling the mechanical properties of porous Al by varying the amount and distribution of residual NaCl was demonstrated.

2. Experimental Procedure

2.1 Specimen preparation

Commercially available as-received pure Al (99.9% purity, average particle diameter: 20 μm) and NaCl (99.9% purity, particle diameter range: 300 to 425 μm) powders were thoroughly mixed at a specific weight ratio to obtain Al foam with porosity p of 74%. The mixture was then subjected to spark plasma sintering by SPS-515L spark plasma sintering (Sumitomo Coal Mining Co., Ltd.). The sintering temperature, sintering pressure and sintering time were fixed at 843 K, 20 MPa and 600 s, respectively, in accordance with previous studies.^{5,6)} As a result, six porous Al/NaCl composite specimens with a cylindrical shape of diameter 20 mm and height 13.8 mm were obtained.

*Graduate Student, Gunma University

2.2 NaCl dissolution

NaCl was removed from the porous Al/NaCl composite by leaching in a water bath. The water temperature was set at 333 K. The amount of residual NaCl ϕ was determined as the weight fraction of the residual NaCl in the porous Al/NaCl composite relative to the total amount of NaCl in the initial composite.

The six composite specimens were subjected to the dissolution process for different times. Thereafter, X-ray CT observation was conducted for all specimens to determine the distribution of residual NaCl in the composite.

2.3 X-ray CT observations

X-ray CT observations were conducted using an SMX-225CT microfocus X-ray CT system (Shimadzu Corporation). A cone-type CT system, which produces three-dimensional images, was employed. In this system, only one rotation of the specimen is sufficient to obtain a three-dimensional volume image, which consists of a set of CT images with the slice pitch equal to the length of one pixel in the CT image. The resolution of each CT image was 512×512 , and the pixel length was approximately $70 \mu\text{m}$. The number of slices was about 450. The X-ray tube voltage and current were 80 kV and $30 \mu\text{A}$, respectively. Figure 1 shows a representative cross-sectional X-ray CT image of the specimen with residual NaCl ϕ of 14%. Gray regions indicate

Fig. 1 Cross-sectional X-ray CT image of the specimen with residual NaCl ϕ of 14%.

NaCl and the cell walls of porous Al, and black regions indicate pores.

To obtain three-dimensional images of the distribution of residual NaCl in the specimens, a voxel model of each specimen was constructed. First, two-dimensional cross-sectional X-ray CT images were stacked using VOXELCON 2011 image-processing software (Quint Corporation). Next, an appropriate threshold was set to distinguish NaCl, Al and the pores, then an isosurface was established to obtain the voxel model.

2.4 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 $3.3 \times 10^{-3} \text{ s}^{-1}$. At the same time, the compression deformation of the specimen was recorded by a digital video camera.

3. Experimental Results and Discussion

Figures 2(a)–2(d) show the three-dimensional residual NaCl distributions in the porous Al/NaCl composite specimens used in the compression tests with residual NaCl ϕ of 77, 40, 14 and 7%, respectively. The size of the residual NaCl region gradually decreased with increasing leaching time. The reduction in the size of the residual NaCl region occurred from the outside of the specimen, where water can directly come into contact with NaCl, whereas NaCl remained at the center of the specimen. It is assumed that the mechanical properties are different between the regions where NaCl remained and NaCl was removed.

Figure 3 shows the compressive stress–strain curves for various values of ϕ . It can be seen that the mechanical properties of the porous Al/NaCl composite markedly changed with the amount of residual NaCl. The composite with $\phi = 0\%$ (i.e., porous Al without NaCl) exhibited the conventional stress–strain curve for porous Al,¹²⁾ which can be divided into three distinct regions, namely, the elastic region in the initial stage, the plateau region with a nearly constant stress over a large range of strain, and the densification region, where the stress increases markedly. For the composite with $\phi = 7\%$, the stress–strain curve is similar to that of the composite with $\phi = 0\%$ up to $\varepsilon = 0.2$, thereafter, the stress gradually increases to above that of the plateau region, i.e., the range of the plateau region decreased.

Fig. 2 Three-dimensional residual NaCl distributions in the porous Al/NaCl composite specimens used in the compression tests with residual NaCl ϕ of (a) 77%, (b) 40%, (c) 14% and (d) 7%.

For the composite with $\varphi = 14\%$, the increase in stress away from the plateau region started at a lower strain and the rate of increase of stress away from the plateau region was higher than that of the composite with $\varphi = 7\%$. This tendency became increasingly marked as φ increased. The decrease in the range of the plateau region with increasing φ is considered to be due to the decrease in the size of the region from which NaCl was removed, where the same mechanical properties as those for the $\varphi = 0\%$ specimen were observed, as can be seen from Fig. 2. The differences in the rate of increase of stress arise because the area perpendicular to the compression direction of the residual NaCl also decreased with decreasing φ . Namely, the area of residual NaCl is larger in the specimen with $\varphi = 14\%$ than in the specimen with $\varphi = 7\%$. For the composite with $\varphi = 100\%$, the stress–strain curve was that of a conventional dense material. Therefore, it is considered that the machining of the composite can be conducted similarly to that of dense materials.

Figure 4 shows deformation images of the porous Al/NaCl composite with $\varphi = 14\%$. Figure 4(a) shows a longitudinal cross-sectional X-ray CT image of the center of the specimen in the initial state before the compression test. Figure 4(b) shows the initial state of the specimen immediately before the compression test, and Fig. 4(c) shows the specimen subjected to a strain of $\varepsilon = 0.11$. Although there are difficulties in observing the deformation in detail owing

to the small pores of the obtained porous Al, the deformation started from the layers where NaCl was removed, as indicated by the dashed boxes. Thereafter, the layers where NaCl remained started to deform, which was accompanied by the deformation and densification of the layers where deformation first occurred, as indicated by the dashed boxes. This change in the deformation behavior approximately corresponds to the stress–strain curves shown in Fig. 3, where an increase in stress away from the plateau region occurred.

This deformation behavior, in which weaker layers (layers where NaCl was removed) deformed before stronger layers (layers where NaCl remained), is similar to that of functionally graded porous Al, for which the order of deformation of layers can be controlled by controlling the strength of each layer.^{13,14} It is considered that the strength of each region can be controlled by controlling the amount and distribution of residual NaCl, for example, by coating the surface of the composite to prevent or delay the removal of NaCl.

4. Conclusion

In this study, porous Al/NaCl composites were fabricated by a sintering and dissolution process. The dissolution process was stopped after various times to obtain porous Al/NaCl composites with various amounts of residual NaCl. The compressive properties of the obtained porous Al/NaCl composites were investigated. It was shown that the range of the plateau region decreased and the stress–strain curves became similar to those of dense materials as the amount of residual NaCl increased. The deformation started from the layers where NaCl was removed, then the layers where NaCl remained started to deform. This indicates that the strength of each region can be controlled by varying the amount and distribution of residual NaCl.

Acknowledgements

This work was partly financially supported by the Industrial Technology Research Grant Program in 2009 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan. The authors thank Professor K. Saito, Gunma University, for his helpful advice on conducting the experiments.

Fig. 3 Compressive stress–strain curves of porous Al/NaCl composites with various values of φ .

Fig. 4 Deformation images taken during compression test of porous Al/NaCl composite with residual NaCl φ of 14%. (a) Longitudinal cross-sectional X-ray CT image of specimen in initial state. (b) Initial state of specimen before compression test. (c) Specimen subjected to a strain of $\varepsilon = 0.11$.

REFERENCES

- 1) J. Banhart: *Prog. Mater. Sci.* **46** (2001) 559–632.
- 2) Y. Y. Zhao and D. X. Sun: *Scr. Mater.* **44** (2001) 105–110.
- 3) D. X. Sun and Y. Y. Zhao: *Metall. Mater. Trans. B* **34** (2003) 69–74.
- 4) C. E. Wen, M. Mabuchi, Y. Yamada, K. Shimojima, Y. Chino, H. Hosokawa and T. Asahina: *J. Mater. Sci. Lett.* **22** (2003) 1407–1409.
- 5) M. Hakamada, Y. Yamada, T. Nomura, Y. Q. Chen, H. Kusuda and M. Mabuchi: *Mater. Trans.* **46** (2005) 2624–2628.
- 6) M. Hakamada, T. Kuromura, Y. Chino, Y. Yamada, Y. Chen, H. Kusuda and M. Mabuchi: *Mater. Sci. Eng. A* **459** (2007) 286–293.
- 7) R. Surace, L. A. C. De Filippis, A. D. Ludovico and G. Boghetich: *Mater. Des.* **30** (2009) 1878–1885.
- 8) Y. Hangai, H. Yoshida and N. Yoshikawa: *Metall. Mater. Trans. A* **43** (2012) 802–805.
- 9) N. Nomura, K. Sakamoto, K. Takahashi, S. Kato, Y. Abe, H. Doi, Y. Tsutsumi, M. Kobayashi, E. Kobayashi, W. J. Kim, K. H. Kim and T. Hanawa: *Mater. Trans.* **51** (2010) 1449–1454.
- 10) M. E. Osullivan, E. Y. S. Chao and P. J. Kelly: *J. Bone Joint Surg. Am.* **71** (1989) 306–310.
- 11) R. Huiskes, H. Weinans and B. Vanrietbergen: *Clin. Orthop. Rel. Res.* **274** (1992) 124–134.
- 12) L. J. Gibson: *Ann. Rev. Mater. Sci.* **30** (2000) 191–227.
- 13) Y. Hangai, K. Takahashi, T. Utsunomiya, S. Kitahara, O. Kuwazuru and N. Yoshikawa: *Mater. Sci. Eng. A* **534** (2012) 716–719.
- 14) Y. Hangai, K. Takahashi, R. Yamaguchi, T. Utsunomiya, S. Kitahara, O. Kuwazuru and N. Yoshikawa: *Mater. Sci. Eng. A* **556** (2012) 678–684.