Fabrication of porous aluminium with directional pores through thermal decomposition method

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Abstract. Lotus-type porous metals were fabricated by unidirectional solidification in pressurized gas atmosphere. The elongated pores are evolved by insoluble gas resulted from the solubility gap between liquid and solid when the melt is solidified. Recently we developed a novel fabrication technique, in which gas compounds are used as a source of dissolving gas instead of the high pressure. In the present work this gas compound method was applied to fabrication of lotus aluminium. Hydrogen decomposed from calcium hydroxide, sodium bicarbonate and titanium hydride evolves cylindrical pores in aluminium. The porosity is about 20%. The pore size decreases and the pore number density increases with increasing amount of calcium hydroxide, which is explained by increase in pore nucleation sites.

1. Introduction
The porous and foamed metals exhibit various characteristics such as an inherent low density and large surface area, which are different from bulk metals. These metals are expected to be utilized as light-weight materials, catalysts, electrodes, vibration and acoustic energy damping materials, impact energy absorption materials etc.[1] Recently lotus-type porous metals, a new type of porous metals have attracted much attention because of the long cylindrical pores aligned in one direction, which are fabricated by unidirectional solidification process in pressurized gas atmosphere such as hydrogen[2,3]. The pores are evolved from insoluble gas when the molten metal dissolving the gas is solidified. The lotus-type porous metals have not only the properties of conventional porous metals but also the unique properties originating from their directional pores. In particular, these metals exhibit superior mechanical properties to the conventional porous metals whose pore shape is isotropic and nearly spherical[4]. Thus, the metals are attracting considerable attention for various industrial applications[3]. Shapovalov[2] and the present authors’ group[3] fabricated lotus-type porous metals with homogeneously distributed pores using the mold casting technique (Gasar method) in high pressure gas. Although this technique is a simple process, it is difficult to control the solidification velocity and as a result the pore structure with uniform pore size and porosity cannot be produced for the metals with lower thermal conductivity. In order to improve this shortcoming, the continuous zone melting technique [5] and continuous casting technique [6] were developed by the present authors. Since these techniques can control the solidification velocity, various kinds of lotus metals with homogeneously distributed long pores are fabricated.

Although such fabrication techniques were quite advanced, we still have a big technical barrier that high-pressure hydrogen gas must be used. The use of high-pressure hydrogen gas may be risky to lead to inflammable and explosive accidents if oxygen is mixed. Therefore, it is desirable not to use such high-pressure hydrogen when fabricating lotus metals. In order to solve this difficulty, we proposed an alternative but very simple method to fabricate such lotus-type porous metals by utilizing a thermal decomposition method (TDM) of
compounds containing gas elements in a non-hydrogen atmosphere under nearly atmospheric pressure [7]. The present paper reports to fabricate lotus-type porous aluminium to use the TDM.

1.1 Melting and solidification processes

Shapovalov and Nakajima et al. fabricated lotus metals containing homogeneously distributed pores using a mold casting technique (Gasar method) under a high-pressure hydrogen as shown Fig.1(a). Although this technique is a simple process, it is difficult to control the solidification velocity, which affects the pore morphology. Although the heat from the melt is easily dissipated to the water-cooled plate during the solidification process, the cooling becomes slow in the upper part of the solidified ingot, and thus the pores become coarse. Therefore, large-sized lotus metals with a uniform pore size and porosity, particularly metals and alloys with low thermal conductivity such as stainless steel, cannot be fabricated by this technique. In order to overcome this shortcoming, we invented a continuous zone melting technique [5].

Figure 1. Schematic drawings of fabrication apparatus for high-pressure gas method. (a) mold casting technique, (b) continuous zone melting technique and (c) continuous casting technique.

Figure 1(b) shows the schematic drawing of the continuous zone melting technique. By using this technique, we were able to fabricate lotus metals and alloys with a low thermal conductivity, which possess long cylindrical pores distributed homogeneously. A part of the metal rod is melted by an induction heating coil. Gas is dissolved into the melt from the surrounding atmosphere. When the melt is moved downward from the coil to be solidified, insoluble gas pores are evolved in the solidification direction. This technique has a benefit to control the solidification velocity by changing the transference velocity. However, this technique is not suitable for the mass production of the specimen rod because the size of the ingot that can be fabricated is restricted. Therefore, we considered the continuous casting technique [6] as a new fabrication method for the mass production of the lotus-type porous metals.

The continuous casting technique is extensively used as a mass-production method for ferrous and nonferrous metals and alloys. In this conventional continuous casting process, the solidified ingot can pass through the mold smoothly due to the solidification shrinkage from the melt. However, in the present process, a large volume expansion is arisen when the solidified ingot is passed through the mold. We initially thought that such an expansion would bring us a difficulty to stack the ingot to the mold and therefore this technique could not be applied to the fabrication of the lotus-type porous metals. However, we later realized that such a large expansion inherent from the pore evolution was released to push the volume toward the copper part of the molten metal; the melt can accommodate large strain of the solidified ingot. That is why the continuous casting technique is applicable for the fabrication of lotus-type porous metals.

Through this technique, the solidification velocity can be controlled by the transference velocity in the hydrogen gas atmosphere. Since the pore morphology of the lotus-type porous metal is related to the solidification velocity, it is suggested that the pore morphology of the lotus-type porous metals can be easily controlled by the technique. We successfully fabricated the lotus-type porous copper and reported the method for controlling its pore size and porosity [3].
1.2 Gas dissolution processes

(1) Gas dissolution from high pressure gas

As mentioned above, lotus metals can be fabricated by unidirectional solidification in high pressure gas atmosphere. The pores evolve by insoluble gas resulted from the solubility gap between liquid and solid when the melt is solidified. According to the Sieverts’ law, the concentration $C_x$ of gas (hydrogen, nitrogen or oxygen) soluble in the liquid and solid is expressed as

$$ C_x = K \sqrt{P_X} $$

(1)

where $K$ and $P_X$ are constant and the pressure of gas X. In order to obtain high porosity, the solubility gap

$$ \Delta C_x = C_x(\text{liquid}) - C_x(\text{solid}) $$

(2)

should be larger. Therefore, high pressure of the gas atmosphere is usually used.

(2) Gas decomposition from gas compounds

As mentioned, the use of high-pressure gas is indispensable for fabricating the lotus metals. Hydrogen gas is explosive when a small amount of oxygen is mixed so that its use is not convenient for industrial mass production. Thus, safety procedure must be necessary to fabricate the lotus metals. In order to avoid such difficulty, it is desirable to use an alternative technique.

It is noticed that some compounds containing gas elements are very useful to supply a gas source into molten metals. For example, hydrogen can be dissolved into molten metals through thermal decomposition reaction

$$ TiH_2 \leftrightarrow Ti + 2H $$

If hydrogen can be dissolved in the level as much as the saturated solubility in the melt, insoluble hydrogen evolves gas pores as a result of rejection of hydrogen solution in the solid/liquid interface during unidirectional solidification. Figure 2 shows a schematic drawing of the principle for fabricating lotus metals by the mold casting technique through thermal decomposition of gas compounds.

![Figure 2. Schematic drawing of the principle to fabricate lotus metals by thermal decomposition of gas compounds](image)

2. Experimental procedure

Pure aluminum (99.99%) about 100 g was melted in a graphite crucible by an induction heating coil in vacuum. The bottom of the mold was copper plate cooled down by circulated water chiller, while the side was made of stainless steel sheet. 0.2 g of the compounds as calcium hydroxide, sodium bicarbonate and titanium hydride were usually wrapped with aluminum foils and were set on the bottom plate of the mold.
The temperature of the liquid in the graphite crucible was monitored by an infrared pyrometer (model IR-AP, Chino Co.). After pouring the molten aluminum at 1023 K in the crucible into the mold, hydrogen decomposed from the compounds dissolves in the melt, which is then solidified so that insoluble hydrogen precipitates to evolve the hydrogen pores. In order to investigate dependence of the pore size and porosity on the mass of calcium hydroxide, the amount of the compounds was changed from 0.1 g to 1.0 g.

When the solidification was taken place unidirectionally, the lotus aluminum with directional cylindrical pores was fabricated. The size of the obtained ingot was about 25 mm in diameter and about 60 mm in height. The specimens were cut using a spark-erosion wire cutting machine (Model LN1W, Sodick Co.) in the both directions parallel and perpendicular to the solidification direction. Each cross-section was polished with a series of emery papers and was observed using an optical microscope. The pore diameter was measured from the cross-section perpendicular to the solidification direction. The porosity ($p$) was evaluated from the following equation:

$$p(\%) = (1 - \frac{\text{Apparent density of porous aluminum}}{\text{Density of nonporous aluminum}}) \times 100$$

(3)

The apparent density of the individual specimen was calculated by measuring both the weight and the apparent volume of each specimen. The shape and size of pores were observed with an optical microscope and evaluated with image analyzer (Win ROOF, Mitani Co.).

3. Results and discussion

Figure 3 shows the microstructure of lotus aluminum with aligned pore parallel and perpendicular to the solidification direction. The pore morphologies perpendicular to the solidification direction are shown in the upper photos, while those parallel to the solidification direction are shown in lower photos. In all specimens the aligned pores parallel to solidification direction were observed. It is considered that the cylindrical gas pores are evolved by TDM from the compounds during solidification of aluminum containing hydrogen gas.

Table 1 compiles the decomposition reactions of three compounds in the aluminum melt. Calcium hydroxide and sodium bicarbonate decompose into vapor and other compounds and then, the vapor decomposes to hydrogen and metallic oxide. On the other hand, titanium hydride decomposes into hydrogen and titanium. These decomposed gas element can dissolve in aluminum melt. When the melt is solidified, lotus aluminum can be produced.

![Figure 3. Optical micrographs of lotus aluminium fabricated by mold casting technique with different compounds in vacuum at 1023K.](image)
Figure 4 shows the pore size and porosity of lotus aluminum with different compounds using mold casting technique in vacuum. The porosity of lotus aluminum was similar, being as much as 20% regardless of kinds of the compounds. The pore size was small as much as 300-400 μm and its distribution was homogeneous in porous aluminum through TDM of calcium hydroxide and sodium bicarbonate, while the pore size was large as much as 1000 μm and its distribution is not uniform through TDM of titanium hydride.

Calcium hydroxide or sodium bicarbonate decomposes into compounds (CaO, Na₂CO₃+CO₂) and vapor, the latter of which furthermore decomposes into metallic oxide and hydrogen. Small pore size with homogeneous distribution was observed through these reactions. On the other hand, titanium hydride decomposes directly into titanium and hydrogen. Large pores with inhomogeneous distribution were observed. It is not clear at present, but evolution of small pores with homogeneous distribution may be attributed to existence of the oxide particles which may serve as the nucleation sites of the pores.

Figure 5 shows the pore size and porosity of lotus aluminum with different amounts of calcium hydroxide at 1023K. Although the porosity is almost constant, the average pore size decreases with increasing amount of calcium hydroxide. Figure 6 also shows that the number density of pores increases with increasing amount of calcium hydroxide. It is suggested from these results that high density of the nucleation sites for pores is resulted from the increase in the amounts of the compound; the number density of metallic oxide CaO increases by further addition of calcium hydroxide.

**Figure 4.** Pore size and porosity of lotus aluminium fabricated by mold casting technique using compounds

**Figure 5.** Change in porosity and pore size of lotus aluminium as a function of amount of calcium hydroxide in vacuum at 1023K.

**Figure 6.** Change in number of pores of lotus aluminium as a function of calcium hydroxide.
4. Conclusions
Lotus aluminum was fabricated through thermal decomposition method of compounds containing gas elements by unidirectional solidification in vacuum. The results are summarized as follows.

The pores with homogenous distribution were evolved by decomposition of the compound, calcium hydroxide and sodium bicarbonate.

The porosity of lotus aluminum is similar to about 20 % regardless of different compounds in vacuum. The pore size decreases and the number of pores increases with increasing amount of calcium hydroxide. For homogenous pore structure of lotus aluminium, the oxide particles are important for the pore nucleation sites.

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