Chapter 2
Fabrication of Porous Metals with Slender Directional Pores

Hideo Nakajima

Abstract Lotus-type porous metals with aligned slender cylindrical pores are fabricated by unidirectional solidification from the melt with a dissolved gas such as hydrogen, nitrogen or oxygen. The gas atoms can be dissolved into the melt via a pressurized gas atmosphere or thermal decomposition of gaseous compounds. Three types of solidification techniques have been developed: mold casting, continuous zone melting and continuous casting techniques. The last technique is superior from the viewpoint of mass production of lotus metals.

Keywords Hydrogen • Nitrogen • Porosity • Porous metals • Solidification

2.1 Principle of Fabrication of Lotus-Type Porous Metals

Porous and foamed metals exhibit various characteristics that differ from bulk metals, including possessing a low density and large surface area. These metals are expected to be used as lightweight materials, catalyst carriers, electrodes, vibration and acoustic energy damping materials, impact energy absorption materials, etc. [1]. However, porous and foamed metals all suffer from deteriorating mechanical properties such as strength, stiffness, and fatigue due to the inhomogeneous pore number density distribution and pore size. Many methods, including powder metallurgy and the melt route, have been used to develop porous materials. Among these materials, lotus-type porous metals have attracted much attention because their slender cylindrical pores aligned in one direction [2, 3]. These metals are fabricated by a unidirectional solidification process using gas from a pressurized

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gas atmosphere such as hydrogen (gasar method) [3] or thermal decomposition of gas compounds such as hydrides [4]. The pores evolved from the insoluble gas when the molten metal dissolving the gas is solidified. Compared to conventional porous metals, which have nearly spherical and isotropic pores, these metals exhibit superior mechanical properties [5].

This article reviews recent developments in the fabrication techniques of lotus metals. Our group also investigated various properties and applications of lotus metals, whose details are described in elsewhere [2, 5].

2.2 Mold Casting Technique

Figure 2.1 shows schematic drawings of the mold casting technique; a metal inside a crucible is melted by an induction heating in a high-pressure gas atmosphere [2, 3]. The gas is dissolved up to the equilibrium gas concentration into the molten metal under a given gas pressure according to the Sieverts' law. The melt saturated with gas is poured into the mold. When some part of the mold is cooled down by a chiller or circulated water, the melt can be solidified unidirectionally from the vicinity of the cooling part. The elongated pores can evolve and grow by the influence of the unidirectional solidification. The pore growth direction can be controlled by changing the location of the cooling part. When the bottom of the mold is water-cooled, the molten metal is unidirectionally solidified upwards from the bottom part so that the directional pores grow in the upward direction. When the lateral side of the mold is cooled down, the solidification takes place inwardly from the surrounding and thus, the pore distribution becomes radial.

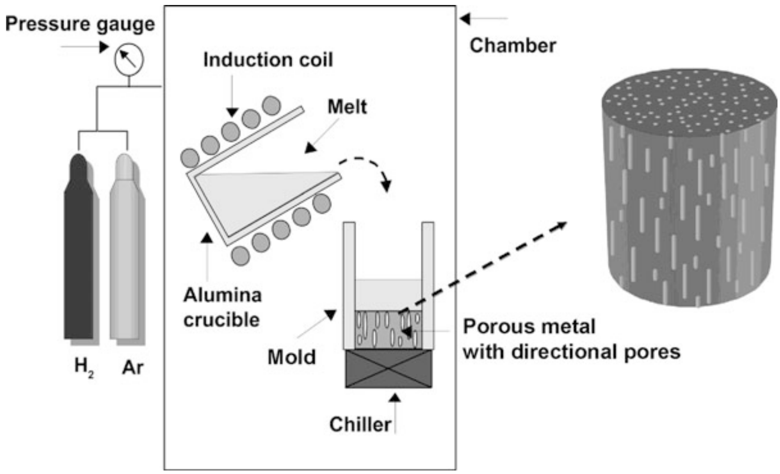

Fig. 2.1 Mold casting technique for fabrication of lotus and gasar-type porous metals. Reproduced from Nakajima H 2007 Fabrication, properties and application of porous metals with directional pores. Prog. Mater. Sci. **52**, 1091–1173, with permission from Elsevier

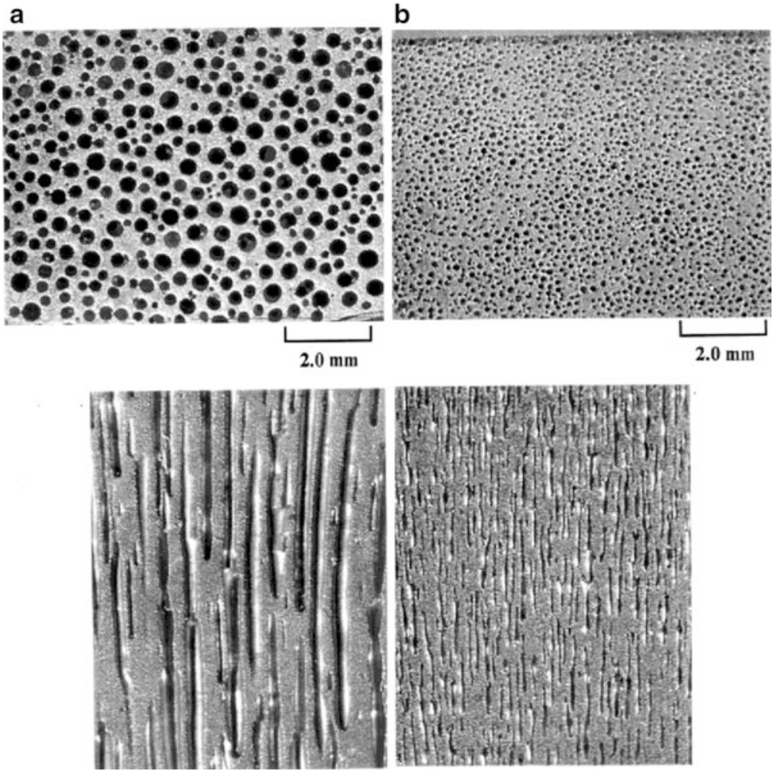

Fig. 2.2 Typical examples of optical micrographs on the cross-sections of lotus copper fabricated at different hydrogen pressure. The above is the cross-sections perpendicular to the solidification and the below is the cross-sections parallel to the solidification. (**a**) 0.4 MPa hydrogen, porosity 44.9%, and (**b**) 0.8MPa hydrogen, porosity 36.6%. Reproduced from Nakajima H 2007 Fabrication, properties and application of porous metals with directional pores. Prog. Mater. Sci. **52**, 1091–1173, with permission from Elsevier

The lotus metals are characterized by pore growth direction, pore size and porosity. The parameters to control the pore morphology can be listed up as

- The melt temperature
- The solidification rate
- The dissolving gas pressure during melting and solidification
- The inert gas pressure during melting and solidification.

Figure 2.2 shows typical examples of optical micrographs on the cross-sections (above) and the longitudinal sections (below) of lotus copper. The mold casting technique is usually used to produce copper and magnesium. Since these metals exhibit high thermal conductivity, the solidification proceeds with almost constant rate through the whole of ingot. Thus, lotus metals with uniform pore size and porosity can be produced by this technique.

2.3 Continuous Zone Melting Technique

The mold casting technique cannot be applied to fabricate lotus metals and alloys with low thermal conductivity such as stainless steel. For the metals and alloys with low thermal conductivity, although the heat from the melt is easily dissipated to the water-cooled plate during the solidification process the cooling becomes slower at the upper part of the solidified ingot where is far from the cooling part and thus the pores become coarse. As a result only lotus metals with non-uniform pore size and porosity can be produced as illustrated in Fig. 2.3. In order to overcome the shortcoming, a novel technique was invented by the present author to fabricate pore-elongated lotus metals even with low thermal conductivity [6]. Figure 2.4a

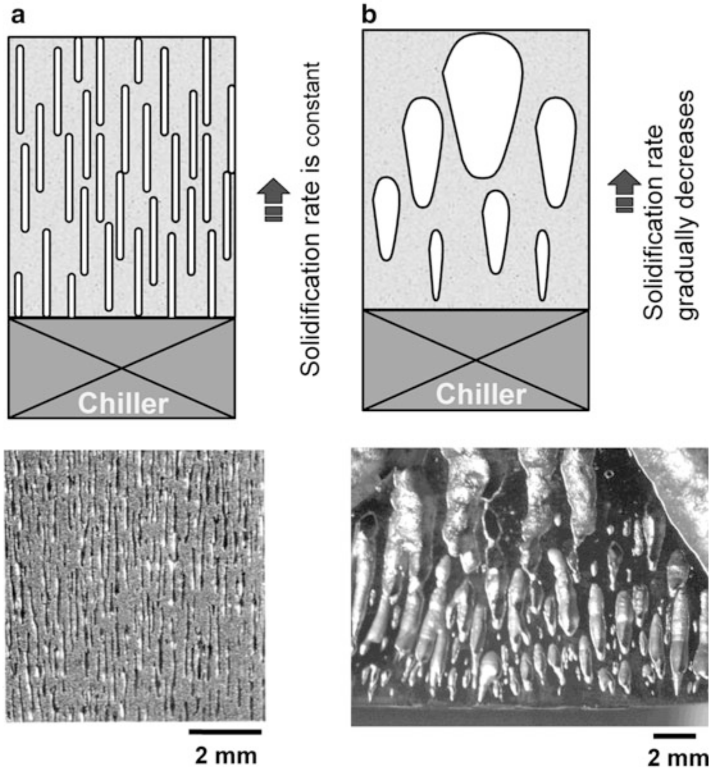

Fig. 2.3 Comparison of the evolution of pores in lotus metals fabricated by mold casting technique in gas atmosphere. The above is schematic drawings of pore evolution during the unidirectional solidification. The below is optical micrographs of the sectional views parallel to the solidification direction. The *left* is lotus copper and the *right* is stainless steel. (**a**) The uniform pore size and porosity are observed in copper and magnesium with high thermal conductivity, and (**b**) various pore size and porosity are found in stainless steel with low thermal conductivity. The magnitude of the thermal conductivity affects the solidification velocity of the melt. Reproduced from Nakajima H 2007 Fabrication, properties and application of porous metals with directional pores. Prog. Mater. Sci. **52**, 1091–1173, with permission from Elsevier

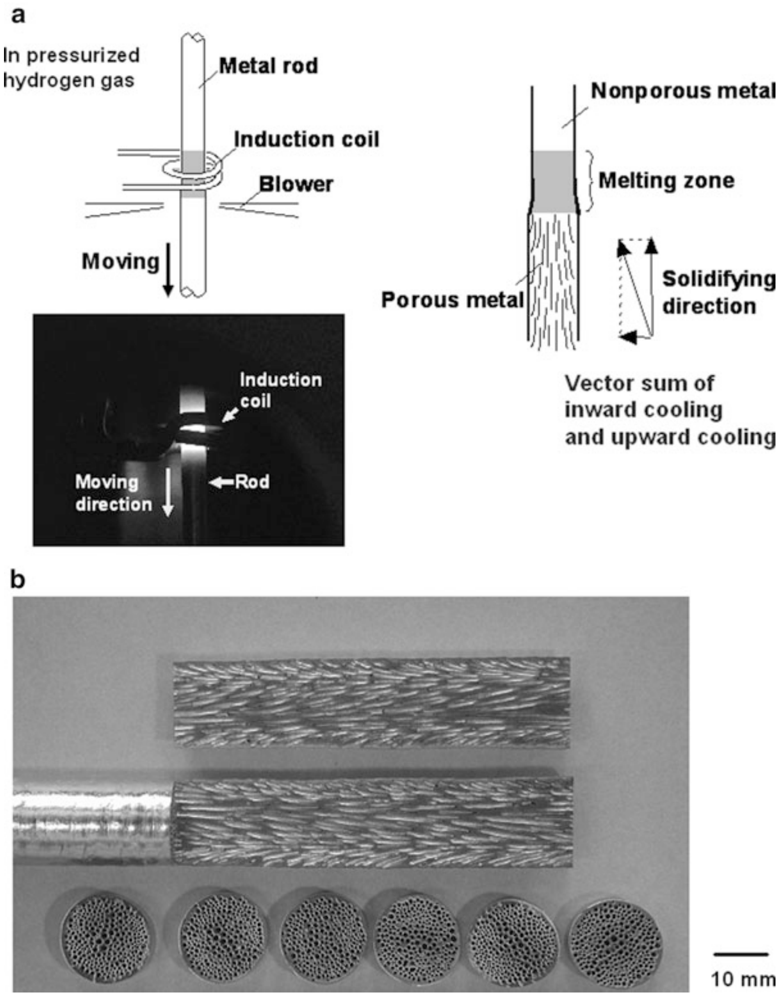

Fig. 2.4 (**a**) Schematic drawings and a photograph of the overview for the melting part of continuous zone melting technique. (**b**) Rod and sections of lotus stainless steel fabricated by the continuous zone melting technique in 2.0 MPa hydrogen atmosphere. The transference velocity of the rod is 330 μm^{-1}. Resulting porosity and average pore size are 40% and 320 μm, respectively, both of which are almost uniform in the whole part of the ingot. Reproduced from Nakajima H 2007 Fabrication, properties and application of porous metals with directional pores. Prog. Mater. Sci. **52**, 1091–1173, with permission from Elsevier

illustrates the schematic setup of the continuous zone melting technique, which consists of radio-frequency induction coil, blowers, specimen rod and movable specimen holders; the induction coil is used for zone (restricted) area melting of the rod specimen, while the blower is effective for further cooling of the melt metal. These components are placed into a high-pressure chamber filled with gases such as hydrogen (or nitrogen) and argon. While a part of the specimen rod is melted by induction heating, the hydrogen (or nitrogen) gas is absorbed into the melt up to the gas equilibrium solubility in the pressurized gas atmosphere according to Sieverts' law. Concurrently the specimen rod is moved downward at a given velocity. In the lower part of the melt zone, solidification takes place simultaneously. Then, directional elongated pores are evolved by precipitation of insoluble gas of hydrogen (or nitrogen) in the solidified specimen. If the transference velocity is kept constant, the solidification velocity becomes constant so that the pore size can be constant. Although the stainless steel exhibits a low thermal conductivity so that lotus stainless steel with homogeneous pore size and porosity is impossible by the mold casting technique as shown in Fig. 2.3, lotus stainless steel with homogeneous pore size and porosity is successfully fabricated by continuous zone melting technique. This technique has an advantage that the solidification velocity is controllable by changing the lowering speed of the specimen rod. Figure 2.4b shows a sectional view of lotus stainless steel fabricated by this technique.

2.4 Continuous Casting Technique

When lotus metals are put to practical use, mass production is indispensable. Since previous methods like mold casting and continuous zone melting techniques are not suitable, the present author et al. developed a new continuous casting technique, by which long plate or rod can be fabricated as shown in Fig. 2.5 [7]. This fabrication apparatus consists of a crucible with a rectangular hole on the crucible bottom, a dummy bar for preventing the melt flow through the hole, and induction heating coil and a mold with water-cooled plate. These are installed in a high-pressure chamber. The metal is melted in the crucible by radio-frequency heating in high-pressure mixture gas. After enough time to make hydrogen dissolve into the molten metal, the molten metal is pulled down through the cooled mold at a given velocity. In the mold, the molten metal is solidified simultaneously. Then, directional elongated pores are evolved by precipitation of insoluble gas of hydrogen (or nitrogen) in the solidified specimen.

The average pore diameter and the porosity are plotted against the transference velocity as shown in Fig. 2.6. The average pore diameter decreases with increasing transference velocity, while the porosity is not much different. The pores which are considered to nucleate heterogeneously grow by the hydrogen rejected in the solid–liquid interface and hydrogen diffusion from the solid copper to the pores. It can be understood that the amount of hydrogen diffusing from liquid to the pores increases with decreasing transference velocity. For this reason, the formed pores at lower velocity become larger than those at higher velocity. As the transference velocity increases, the pore size decreases but the number density of pores increases.

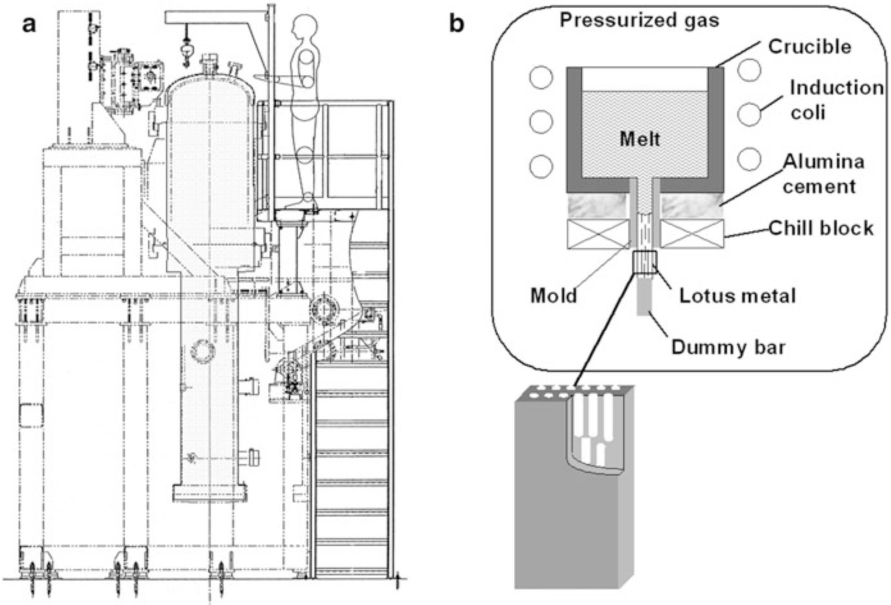

Fig. 2.5 Schematic drawings of fabrication apparatus of lotus metals by the continuous casting technique. (**a**) Large crucible and induction heating coil are located in the *upper part* of the chamber, while the mold with cooling part and movable mechanism of the solidified metal rod with pinch roll are installed in the *bottom part* of the chamber. (**b**) Schematic drawing of the details inside the chamber. The dummy bar is connected together with the melt at the mold. Reproduced from Nakajima H 2007 Fabrication, properties and application of porous metals with directional pores. Prog. Mater. Sci. **52**, 1091–1173, with permission from Elsevier

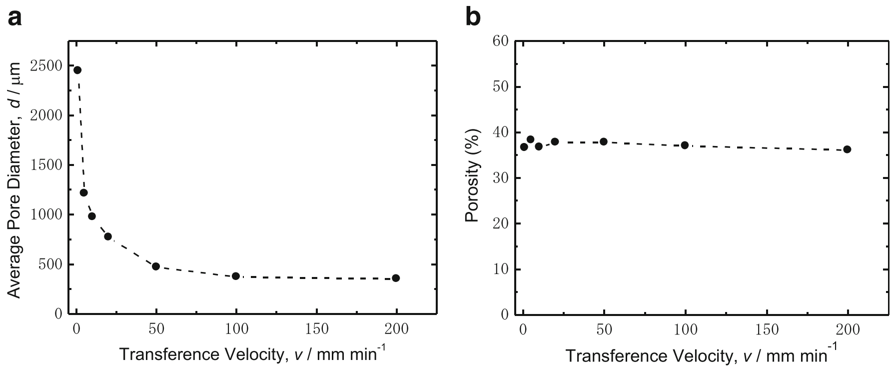

Fig. 2.6 (**a**) Average pore diameter and (**b**) porosity versus transference velocity of lotus copper fabricated in mixture gas of hydrogen 0.25 MPa and argon 0.15 MPa by continuous casting technique. Reproduced from Park JS, Hyun SK, Suzuki S, Nakajima H 2007 Effect of transference velocity and hydrogen pressure on porosity and pore morphology of lotus-type porous copper fabricated by a continuous casting technique. Acta Mater. **55**, 5646–5654, with permission from Elsevier

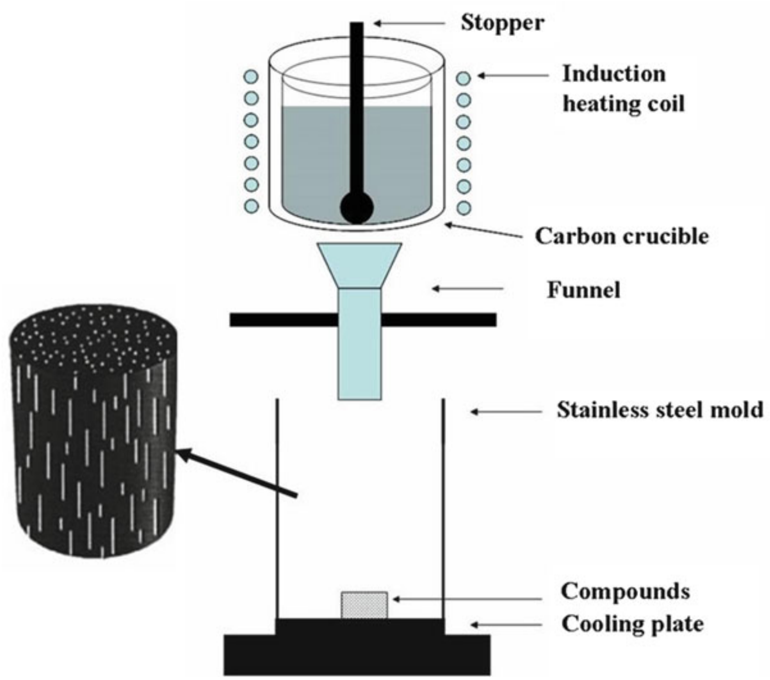

Fig. 2.7 Mold casting technique for fabrication of lotus aluminum by thermal decomposition technique

2.5 Thermal Decomposition Method

Although the fabrication techniques mentioned above are quite advanced, one large technical barrier remains; high pressure hydrogen gas must be used. Employing high pressure hydrogen gas has inherent risks because it may lead to inflammable and explosive accidents if oxygen is mixed. Therefore, a technique that does not require high pressure hydrogen to fabricate lotus metals is highly desirable. In order to overcome this difficulty, the present author et al. proposed an alternative, but simple method to fabricate lotus metals by a thermal decomposition method (TDM) of compounds containing gas elements in a non-hydrogen atmosphere under nearly atmospheric pressure or vacuum [4].

First a metal copper 200 g is melted by radio-frequency induction heating in a crucible under an argon atmosphere. Then the melt is poured into the mold, which has a copper bottom plate cooled by water. A few pellets of titanium hydride, which ranges from 0.075 and 0.25 g in mass, are set on the bottom plate of the mold. Unidirectional solidification occurs in the mold so that lotus copper is obtained, as illustrated in Fig. 2.7. Figure 2.8 shows the optical micrographs of the cross-sectional views of lotus copper parallel and perpendicular to the solidification direction. The pore growth direction is coincident to the direction of the

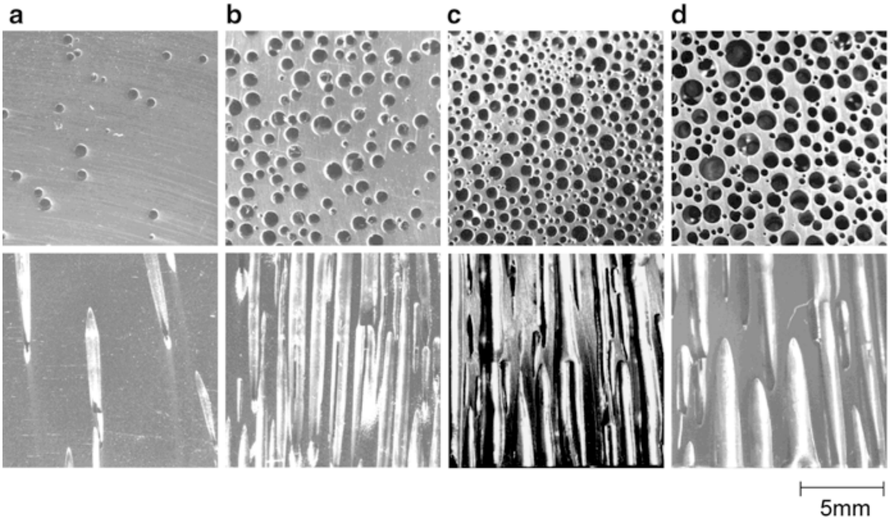

Fig. 2.8 Optical micrographs pf cross-sectional views of lotus copper (*upper views*) perpendicular and (*lower*) parallel to the solidification direction. Mass of titanium hydride added to the mold is (**a**) 0.075 g, (**b**) 0.10 g, (**c**) 0.125 g, and (**d**) 0.25 g. Melting and subsequent solidification were carried out in 0.1 MPa argon atmosphere. Reproduced from Nakajima H, Ide T 2008 Fabrication of porous copper with directional pores through thermal decomposition of compounds. Metall. Mater. Trans. **39A**, 390–394, with permission from Springer

unidirectional solidification, which is consistent with that of the conventional high pressure gas methods (PGM). This result suggests that the principle mechanism of this pore evolution is similar to that of PGM; when a molten metal dissolving a gas is solidified, the insoluble gas leaves the solid and evolves into gas pores in the solid metals. When titanium hydride is decomposed into hydrogen and titanium, the latter is very reactive element, which easily reacts with residual oxygen in the molten copper. Consequently, titanium oxide particles are formed and dispersed, which may serve as the nucleation sites for the hydrogen pores in the solid–liquid interface during unidirectional solidification. It is well known that the pores evolve by heterogeneous nucleation in metal melts in the presence of small amounts of foreign particles. Thus, it is expected that the pore size and porosity become homogeneous by uniformly distributed nucleation sites. Therefore, TDM exhibits another advantage to produce lotus metals with more homogeneous pore size and porosity than those by PGM, which does not provide intentional nucleation sites.

2.6 Fabrication of Lotus Aluminum Through Thermal Decomposition Method

Lotus metals are fabricated by using the gas solubility gap between liquid and solid. Although hydrogen in aluminum has a solubility gap at the melting point, the hydrogen concentration is low so that high porosity of lotus aluminum cannot be

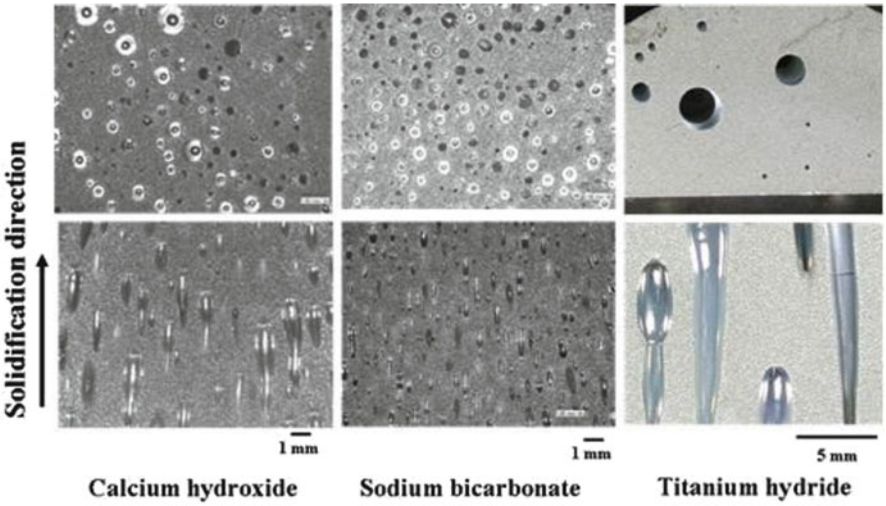

Fig. 2.9 Optical micrographs of lotus aluminum fabricated by mold casting technique with different compounds in vacuum at 1,023 K. The *upper* and *lower* micrographs are the cross sections perpendicular and parallel to the solidification direction, respectively. Reproduced from Kim SY, Park JS, Nakajima H 2009 Fabrication of lotus-type porous aluminum through thermal decomposition method. Metall. Mater. Trans. **40A**, 937–942, with permission from Springer

obtained by the conventional PGM of hydrogen. According to our recent investigation, lotus aluminum with a porosity as high as 10 pct can be fabricated by unidirectional solidification in hydrogen pressure less than atmospheric pressure [8]. The lower the hydrogen pressure is, the higher the porosity is. Kim et al. [8] was undertaken fabrication of lotus aluminum in vacuum using the thermal decomposition of gas-forming compounds.

Figure 2.9 shows the cross sectionals views of microstructure of lotus aluminum 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 the lower photos. In all specimens, the aligned pores parallel to the 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 2.1 compiles the decomposition reactions of three compounds in the aluminum melt. Calcium hydroxide and sodium bicarbonate decompose into vapor and 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 elements can dissolve in aluminum melt. When the melt is solidified, lotus aluminum can be produced.

Figure 2.10a shows the pore structure on cross sections of lotus aluminum perpendicular (upper) and parallel (lower) to the solidification direction. The lotus aluminum was fabricated using calcium hydroxide in vacuum or under argon

Table 2.1 Decomposition reaction and temperature of gaseous compounds. Reproduced from Kim SY, Park JS, Nakajima H 2009 Fabrication of lotus-type porous aluminum through thermal decomposition method. Metall. Mater. Trans. **40A**, 937–942, with permission from Springer

Reactions	Decomposition temperature [K]	Gas atoms or molecules to be dissolved and bubbled
$Ca(OH)_2 \rightarrow CaO + H_2O$	853	H
$H_2O \rightarrow$ metallic oxide + 2H		
$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$	473	H, CO, O
$H_2O \rightarrow$ metallic oxide + 2H		
$TiH_2 \rightarrow Ti + 2H$	723	H

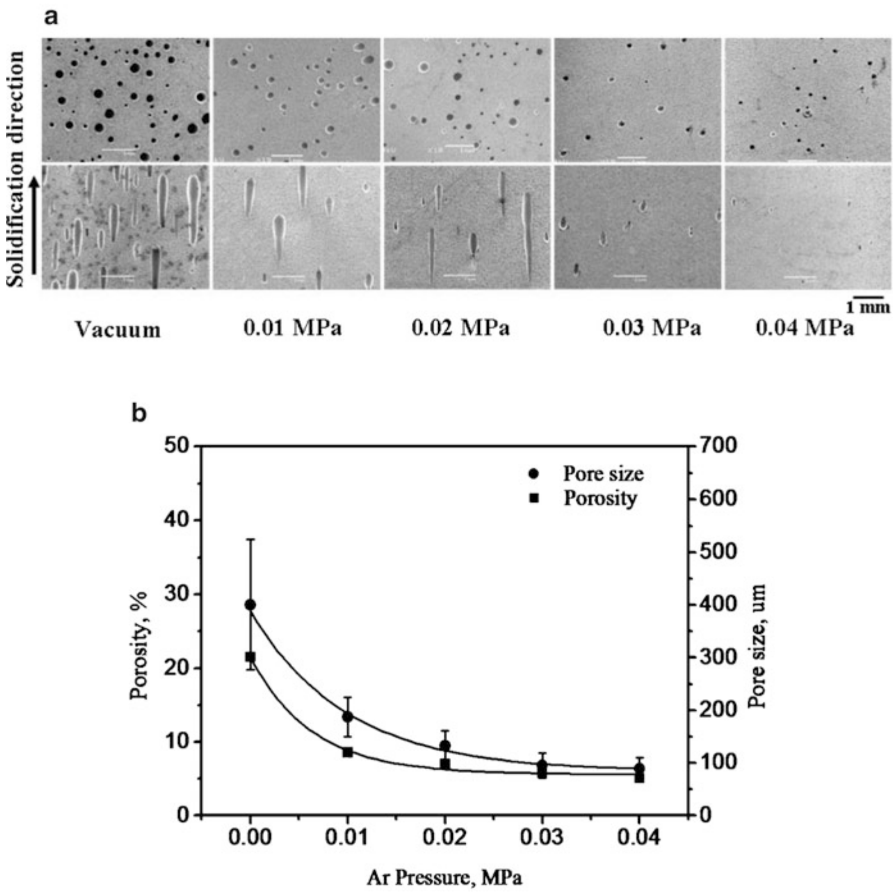

Fig. 2.10 Lotus aluminum fabricated using calcium hydroxide in vacuum or under argon pressure (0.01–0.04 MPa). The amount of calcium hydroxide was kept to be 0.2 g. (**a**) Pore morphology. The *upper* and *lower* micrographs are the cross sections perpendicular and parallel to the solidification direction, respectively. (**b**) Variation of the porosity and pore size as a function of argon pressure. Reproduced from Kim SY, Park JS, Nakajima H 2009 Fabrication of lotus-type porous aluminum through thermal decomposition method. Metall. Mater. Trans. **40A**, 937–942, with permission from Springer

pressure. The aligned pores formed under the pressure less than 0.03 MPa argon; however, spherical pores formed over 0.04 MPa argon. This may indicate that the applied pressure in the chamber reduces the driving force for pore nucleation and growth. Figure 2.10b shows the dependence of the porosity and the average pore size as a function of argon pressure. The effect of external pressure is obvious, and the pore growth is suppressed under higher pressure. Both the porosity and the average pore size decrease with increasing argon pressure. The pore volume v, which is equivalent to the porosity, is inversely proportional to the external argon pressure P, which can be described by the Boyle's law, $v = nRT/P$, where n, R and T are the hydrogen molar number, the gas constant, and the temperature, respectively. Therefore, the pore diameter d can be written as $d \propto P^{-1/3}$. The tendency of the pressure dependence of the porosity and pore size is explained by the law.

2.7 Summary

Lotus metals are fabricated by unidirectional solidification of the molten metals dissolving gas atoms. Three solidification techniques were developed: mold casting technique, continuous zone melting technique and continuous casting technique. The continuous casting technique is the most superior for mass production of lotus metals with uniform pore size and porosity. On the other hand, two different supply methods of gas source into the melt are shown: high-pressure gas method and thermal decomposition method. TDM is superior to the PGM, because PGM uses high pressure hydrogen gas with inflammable and explosive risks and gas pressurization in a high-pressure chamber.

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