Fabrication of Porous Iron by Unidirectional Solidification in Nitrogen Atmosphere

Soong Keun Hyun and Hideo Nakajima

The Institute of Scientific and Industrial Research, Osaka University, Ibaraki 567-0047, Japan

Porous iron whose long cylindrical pores are aligned in one direction has been fabricated by unidirectional solidification of the melt in a pressurized mixture gas of nitrogen and argon. Nitrogen dissolved in the molten iron is rejected at the solid-liquid interface during the solidification due to the solubility difference of nitrogen between the liquid and solid. The gas pores are evolved from the nitrogen insoluble in the solid iron, which grow unidirectionally. The porosity is controlled by the partial pressures of nitrogen and argon during melting and solidification. The porosity decreases with increase of the partial pressure of argon at a given nitrogen pressure according to the Boyle’s law. At a constant total pressure of the mixture gas, the porosity increases with increasing partial pressure of nitrogen and no pores are formed during solidification below a critical partial pressure of nitrogen. The nitrogen concentration in the solid iron increases with increasing partial pressure of nitrogen. The solid-solution hardening has been observed in as-cast porous iron, while more significant hardening has also been found in the porous iron quenched from a high temperature 1273 K, which is due to the martensitic transformation.

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1. Introduction

Interest is growing in fabrication of porous metals as it opens a path to the development of lightweight structural materials with thermal, acoustic and energy absorption characteristics. There have been several kinds of fabrication techniques for the porous metals; (1) bubbling gas through molten Al–SiC or Al–Al₂O₃ alloys, (2) by stirring a foaming agent (TiH₂) into a molten alloy, (3) consolidation of a metal powder with a foaming agent followed by heating into the mushy state when the foaming agent releases hydrogen, expanding the material, (4) vapor phase deposition or electro deposition of metal onto a polymer foam precursor which is subsequently fumed out, leaving cell edges with hollow cones, etc.\(^{(1,2)}\)

Recently porous metals whose long cylindrical pores are aligned in one direction have been fabricated by unidirectional solidification method at a pressurized hydrogen atmosphere.\(^{(3–14)}\) Many gas pores are evolved from insoluble hydrogen in solids while hydrogen dissolves significantly in liquids. Formation of elongated gas pores during solidification has been studied by Imabayashi \(^{(12)}\) by Svensson and Fredriksson\(^{(13)}\) and by Knäcke \(^{(14)}\). Furthermore Boiko \(^{(13)}\) and by Knäcke \(^{(14)}\).

2. Experimental Method

The fabrication apparatus of the porous iron consists of an alumina crucible (40 mm in outer diameter, 30 mm in inner diameter, and 100 mm in length) surrounded by an induction-heating coil and a mold with water-cooled bottom copper plate as shown in Fig. 1. These are installed in a high-pressure chamber. High purity iron “Atomiron-MP” was supplied from Showa-Denko Co., Ltd. whose chemical analysis is listed in Table 1. The iron was melted in the crucible with a foaming agent followed by heating into the mushy state when the foaming agent releases hydrogen, expanding the material, and leaving cell edges with hollow cones, etc.\(^{(1,2)}\)

Table 1 Chemical composition of “Atomiron-MP” (mass%).

<table>
<thead>
<tr>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0011</td>
<td>0.0008</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0005</td>
<td>0.0008</td>
</tr>
</tbody>
</table>
cible by radio-frequency heating in a vacuum, and then high-pressure mixture gas of nitrogen and argon was introduced into the chamber. The purities of both gases used for these experiments were 99.999%. The temperature of the melt in the crucible was monitored by an optical pyrometer and was set to be 1973 K. The pressure was measured by a pressure gauge sensor (Model GC61, Nagano Keiki Co.) and the pressures of nitrogen and argon were set in the range from 0 to 2.0 MPa. The crucible was rotated by 90 degree to pour the molten iron through an alumina-coated stainless steel funnel into the mold whose bottom copper plate was water-cooled by a chiller (Model CA-1100, Tokyo Rikakikai Co.). The lateral side was made of alumina tube, which is suitable for heat-insulating material in order to be solidified in one direction from the bottom to top. Thus the molten iron was solidified unidirectionally upwards. The ingots obtained were 35 mm in diameter and maximum 80 mm in height, and contained various levels of porosity that was controlled by the total and partial pressures of nitrogen and argon. The porosity is calculated from the following expression:

$$\text{Porosity} = 1 - \frac{\text{Apparent density of porous iron}}{\text{Density of nonporous iron}}.$$  

The apparent density of the individual specimens was calculated from measurement of its weights at air and in the water through Archimedes’ method.

The ingot of porous iron was sliced and the nitrogen concentration of each specimen was analyzed by means of Oxygen–Nitrogen Determinator (Model TC300, LECO Co.). The specimens having the size of about 10 × 10 × 2 mm³ were cut from the ingot by spark-erosion wire-cutting machine (Model A320D, Sodick Co.). Some of the specimens were sealed in an evacuated Pyrex glass tube, heated at 1273 K for 3600 s, and were, then, quenched by breaking the tube in brine in order to examine the martensitic transformation of the porous iron. The cross sections were observed under an optical microscope (Model DP50, Olympus Optical Co.), and micro Vickers hardness (Model MVK-E, Akashi Seisakusho Co.) was measured under a load of 0.98 N. Each data point presented is the average of at least ten measurements.

3. Results and Discussion

3.1 Dependence of porosity on mixture gas pressure

In the present work, depending on the partial pressures of argon and nitrogen, the pore diameter ranges from 100 to 800 µm, and the porosity ranges from 0 to 50%. However, it was observed that the pore size depends on height of the ingot; the pore diameter increases from bottom to top. Such the pore size change with position is much different from that for the lotus-structured porous copper,9–11 in which the pore size and the porosity are almost independent of the position. The increase of the pore size with increase of the height of the porous iron ingot may be attributed to the solidification velocity change which depends on the vertical position. Such velocity change may be due to the feature that the thermal conductivity of iron is much lower than that of copper. The velocity of the solidification front decreases while the solidification proceeds in the upward direction. As will mention below, the growth rate of pores is dominated by the rate of arrival of diffusing gas. Then, as the velocity of the solidification front becomes lower, the more amount of nitrogen can diffuse into the pores. As a result, the size of the evolved pores increases toward the upper part of the ingot.
Figure 2 shows the typical optical micrographs of the cross section at the bottom part of the ingot. The overall porosity was measured as functions of the partial pressures of nitrogen and argon as shown in Fig. 3. The porosity was found to be affected by the nitrogen and argon pressures. At a given nitrogen pressure, the porosity decreases with increasing argon pressure as shown in Fig. 4(a). At a given argon pressure, the porosity increases with increasing nitrogen pressure as shown in Fig. 4(b).

In order to obtain the criterion for the pore formation, it was considered the external gas pressure, \( P_e \), which suppresses the pore formation, and the internal gas pressure, \( P_i \), of the pore, which is in equilibrium with the supersaturated nitrogen in the solid. Neglecting the hydrostatic pressure of the melt above the pore, the external gas pressure of a pore is given by

\[
P_e = P_{N_2} + P_{Ar} + \frac{2\sigma}{r},
\]

where \( P_{N_2} \) and \( P_{Ar} \) are the pressures of nitrogen and argon in mixture gas atmosphere, respectively, \( \sigma \) is the surface tension of the melt, which is 1.872 N/m at 1809 K for iron melt,\(^{17}\) and \( r \) is the radius of the pore. \( 2\sigma/r \) is the capillary pressure which acts as resistance to the pore formation during the solidification.

According to the theory of pore nucleation\(^{18–20}\) if the gas pores are formed from liquid phase in solidification by homogeneous nucleation, the gas pressure required for the pore nucleation is evaluated to be a few ten thousand atmosphere. This magnitude of the pressure is not realistic. Therefore, the pores are considered to nucleate heterogeneously. It is certain that in practice nucleation of pores might occur on a foreign substrate, the solid surface of an impurity particle or by the presence of surface-active impurities in the melt.

On the other hand, the rate of growth of pores is considered to be controlled by nitrogen diffusion through the bulk
liquid and solid phases. After the evolution of the gas pores, the capillary pressure corresponding to pores diameter formed in the present work ranges approximately 0.01 to 0.07 MPa. Thus, the capillary pressure during the growth of pores is much lower than the total pressure of nitrogen and argon and is neglected. With increasing total pressure of nitrogen and argon, the internal gas pressure of a pore increases and then the porosity decreases according to the Boyle’s law; the pore volume (the porosity) is inversely proportional to the pressure.

The solubility of nitrogen in iron is proportional to the square root of the nitrogen gas pressure, \( \sqrt{P_{N_2}} \), according to the Sievert’s law

\[
C_N^L = K^L \sqrt{P_{N_2}},
\]

\[
C_N^\delta = K^\delta \sqrt{P_{N_2}},
\]

where \( C_N^L \) and \( C_N^\delta \) are the nitrogen concentration in the liquid and the \( \delta \)-iron, respectively, and \( K^L \) and \( K^\delta \) are equilibrium constants given by

\[
K = \exp \left( \frac{\Delta G}{RT} \right) = \exp \left( \frac{\Delta S}{R} - \frac{\Delta H}{RT} \right),
\]

where \( \Delta G \) is the Gibbs energy change for the solution of nitrogen, \( T \) is an absolute temperature, \( R \) is the gas constant, and \( \Delta H \) and \( \Delta S \) are the standard enthalpy and entropy of solution of nitrogen, respectively. The solubility of nitrogen in the different iron phases is usually evaluated from the slope of the decomposition pressure on logarithmic scale against \( 1/T \). Table 2 shows the solubility of nitrogen in the different phases of iron.\(^{21} \)

The solubility of nitrogen in the molten iron is much higher than that of \( \delta \)-iron as shown in Fig. 5. Therefore, nitrogen in the molten iron is rejected at the solidification and the pores nucleate and grow unidirectionally.

Considering the mixture gas of nitrogen and argon, although the solubility of nitrogen in liquid is determined by the partial pressure of nitrogen, the nitrogen solubility near the pores is related with the internal gas pressure \( (P_i) \) for satisfying with the equilibrium between solid phase around the pores and gas phase in the pores. Therefore, eq. (4) can be written as

\[
C_N^\delta = K^\delta \sqrt{P_i}.
\]  

From eq. (6), it can be seen that the solubility of nitrogen in solid is related with total pressure of nitrogen and argon. With increasing the partial pressure of argon at a given total pressure, the nitrogen solubility in liquid decreases but the nitrogen solubility in solid is almost constant.

The porosity is closely related with the difference of nitrogen solubility between liquid and solid. If the partial pressure of argon increases under the constant total pressure of the mixture gas, the nitrogen solubility in liquid will decrease and the nitrogen solubility in solid will be almost constant. Thus it can be explained qualitatively that the porosity decreases with increasing partial pressure of argon at a given total pressure of 2.0 MPa in Fig. 6.

### Table 2: Nitrogen solubility in different iron phases at 0.1 MPa of nitrogen pressure \([\log(\text{mass}%) = A + B/T]^{21}\)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature range (K)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>1809–2373</td>
<td>−0.91</td>
<td>−850</td>
</tr>
<tr>
<td>( \alpha, \delta )</td>
<td>723–1184, 1665–1809</td>
<td>−0.97</td>
<td>−1640</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>1184–1665</td>
<td>−2.14</td>
<td>723</td>
</tr>
</tbody>
</table>

### 3.2 Characteristics of iron matrix

#### 3.2.1 Nitrogen concentration in iron matrix

Figure 7 shows the nitrogen concentration in the matrix of lotus-structured porous iron as a function of the partial pressure of nitrogen when the total gas pressure of nitrogen and argon is kept constant at 2.0 MPa. It was found in the present work that the measured nitrogen concentration is in the range from 0.06 to 0.135 mass%. According to the solubility curve of nitrogen in iron,\(^{21} \) the nitrogen solubility in \( \gamma \)-iron decreases with increasing temperature and the maximum solubility is 0.135 mass% at the lowest temperature of the \( \gamma \)-phase. On the other hand, in \( \delta \)-iron, the nitrogen solubility increases with increasing temperature and the maximum solubility is calculated as 0.06 mass% at the temperature just below the melting point of iron. Thus, it is reasonable that the measured nitrogen concentration range as shown in Fig. 7 is in between these two limits of the solubility.

The reason why the measured nitrogen concentration is much higher than the nitrogen solubility in \( \delta \)-iron can be explained as follows. As shown in Fig. 8, when the molten iron is solidified in the pressurized mixture gas of nitrogen and...
Fig. 7 Nitrogen concentration in the matrix versus the partial pressure of nitrogen under constant total pressure of 2.0 MPa.

argon, the pores are formed by the evolution of the nitrogen insoluble in the solid iron. In the subsequent cooling process in the solid state, the nitrogen solubility in δ-iron gradually decreases with decreasing temperature. And then, the insoluble nitrogen atoms, \( C_{\delta}^{FeN} - C_{\gamma}^{FeN} \), diffuse into the pores from δ-iron matrix. However, in further cooling process in γ-iron, the nitrogen solubility abruptly increases at the \( \delta \rightarrow \gamma \) phase transformation temperature and continues to increase with decreasing temperature until the \( \gamma \rightarrow \alpha \) phase transformation temperature is reached. In this process the nitrogen gas in the pores dissolves into the γ-iron. Finally, two-phases of α (ferrite)-phase and Fe₄N compound are formed on the phase transformation from γ-phase to α-phase.

Figure 9 shows the microstructure of the specimen containing 0.137 mass% nitrogen in the matrix of as-cast porous iron which was fabricated in the mixture gas of \( P_{N_2} = 1.25 \) MPa and \( P_{Ar} = 0.75 \) MPa. The proeutectoid ferrite was observed on the grain boundaries and also inside the grains.

3.2.2 Martensitic transformation

In order to investigate an effect of martensitic transformation on the lotus-structured porous iron, the specimens having different nitrogen concentration were quenched from 1273 K into the brine. Table 3 shows the results of the nitrogen concentration and microstructure of as-quenched lotus-structured porous iron, where all specimens contain the phase of martensite. Figure 10 shows the typical microstructure of the as-quenched specimen, which contains mixed structure of massive α-phase and martensite.

3.2.3 Hardness

The micro Vickers hardness, \( H_v \), measured for the matrix of the as-cast and the as-quenched porous iron is shown in Fig. 11. The hardness increases with increasing nitrogen concentration in both specimens. The hardness of the as-quenched specimens is twice higher than that of the as-cast specimens at a given nitrogen concentration. It can be explained that the increase in \( H_v \) of the as-cast iron is due to solid-solution hardening with interstitial nitrogen, while the remarkable increase in \( H_v \) of the as-quenched specimens is attributed to the formation of the martensitic phase.
4. Conclusion

We successfully fabricated the lotus-structured porous iron having long aligned pores via melt-route process in a mixture gas of nitrogen and argon for the first time. The characteristics of this porous iron are as follows:

(1) The porosity depends on the pressure of nitrogen and argon gases. At a given nitrogen partial pressure, the porosity decreases with increasing argon partial pressure according to the Boyle’s law. At a constant total pressure of the mixture gas, the porosity increases with increasing partial pressure of nitrogen according to the Sievert’s law.

(2) The nitrogen concentration of the iron matrix depends on the partial pressure of nitrogen as well as the total pressure of argon and nitrogen. The measured nitrogen concentration increases with increasing partial pressure of nitrogen.

(3) Small amount of nitrogen dissolves in the matrix of the lotus-structured porous iron, which can undergo martensitic transformation on quenching from high temperature. The resulting microstructure is composed of massive $\alpha$ and martensite.

(4) The micro Vickers hardness increases which is due to the solid-solution hardening and the formation of martensite.

Acknowledgements

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