Fabrication of Porous Iron with Directional Pores through Thermal Decomposition of Chromium Nitride

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Lotus-type porous iron with long directional pores was fabricated by a continuous zone melting technique through thermal decomposition of chromium nitride $Cr_{1.18}N$. Nitrogen decomposed from the nitride powders dissolves in the molten iron. Insoluble nitrogen evolves the directional gas pores when the melt is solidified in a direction. The porosity increases with increasing transference velocity, while the pore diameter is almost constant. The porosity change with the transference velocity is attributed to the difference in decomposition rate of chromium nitride. The compound $Cr_{1.18}N$ is composed of CrN and Cr_2N, the latter of which is considered to evolve the pores because of the coincidence of heating rate of the continuous zone melting with that for the decomposition of Cr_2N.

I. INTRODUCTION

POROUS and cellular metals have attracted much attention because of their various characteristics different from those of nonporous metals, such as an inherent low density and a large surface area.[1] Although most of the porous metals have isotropic and spherical pores, lotus-type and Gasar porous metals have unique pore morphology with long cylindrical pores aligned in one direction. The porous metals can be fabricated by unidirectional solidification from the metallic melt dissolving gas through the gas-crystallization reaction.[2] These pores are evolved by precipitation of insoluble gas due to the solubility gap between liquid and solid state during unidirectional solidification.[3–5] Lotus metals were usually fabricated by unidirectional solidification in the pressurized gas atmosphere (pressurized gas method, abbreviated as PGM), because the gas is dissolved into the melt. In this case, higher pressure is better to have higher porosity of the lotus metals according to the Sieverts' law. However, there were two experimental difficulties. One is the need for a high pressure chamber, which is expensive and requires particular care in the handling procedures. Another is to use hydrogen gas, which is flammable and explosive gas when a small amount of oxygen is mixed. These are obstacles for mass production of lotus metals and alloys.

Recently, Makaya and Fredriksson[6] produced porous Fe-base materials by dissolving CrN compound into a metallic melt of Fe-base alloy in an argon atmosphere. The decomposition of the compound leads to dissolution of a gas into the melt. They solidified the melt in the crucible to produce porous metals with an isotropic pore structure. However, no investigations were carried out to produce porous metals with an anisotropic cylindrical pore structure until Nakajima and Ide performed theirs. Nakajima and Ide[7] studied fabrication of lotus-type porous copper using titanium hydride in an argon atmosphere instead of a pressurized hydrogen atmosphere. This method is called the "thermal decomposition method" (TDM): gas atoms can dissolve in the melt from the compound containing a gas element through endothermic reaction.

In order to fabricate the porous metals with unidirectional pores, unidirectional solidification was usually carried out using the mold casting technique. The bottom of the mold is cooled by circulated water and the melt is solidified from the bottom toward the top (Gasar process[5]). However, this technique cannot be applied to the metals and alloys with low thermal conductivity. The solidification rate changes from the bottom to the top: the cooling speed near the bottom is faster, while it becomes slower near the top where the pores are coarsened because the heat cannot be dissipated. Thus, the pore size significantly changes with the height: the pore size increases with the increasing height of the mold. In order to solve this problem, Ikeda et al.[8] developed a continuous zone melting technique. The partial melting zone is moved to retain the constant solidification rate so that uniform distributions of porosity and pore size are obtained. In the present work, this technique was adopted to fabricate porous iron.

The present article reports the fabrication of lotus-type porous iron by continuous zone melting technique through thermal decomposition of chromium nitride. Particular care was necessary to supply chromium nitride at a constant rate during the zone melting experiment. The details are described in this article.

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II. EXPERIMENTAL PROCEDURE

Iron rods (99.5 pct purity) of 10.0 mm in diameter and 80 mm in length were used as specimens. In order to supply a constant source of chromium nitride, a hole of 2.0 mm in diameter in a central part of the cross section was made by an electric drill. The hole was filled with the nitride compound. Figure 1 exhibits a 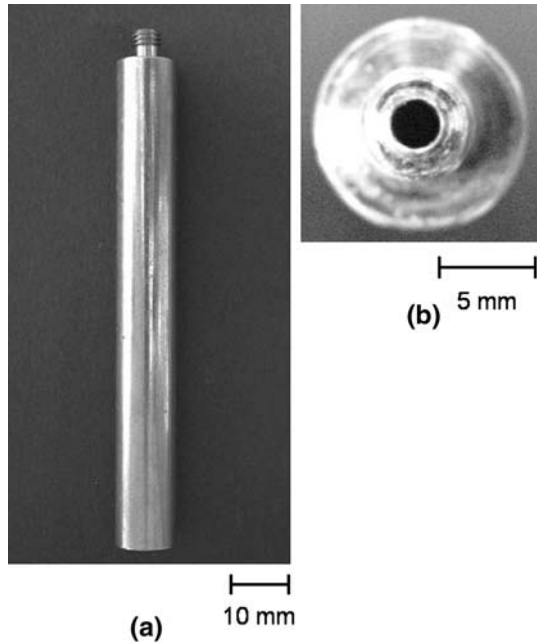view of a machined iron rod. Various kinds of compounds (titanium hydride TiH_2, calcium hydroxide $Ca(OH)_2$, iron nitride Fe_4N, and chromium nitride) were tested as a gas dissolving source into molten iron during continuous zone melting. Then, the chromium nitride was selected as a gas dissolving compound, since the temperature of gas releasing of chromium nitride is the closest to the melting temperature of iron. Since the gas from other compounds is released far below the melting temperature of iron, the gas cannot dissolve in the melt of iron.[9]

The $Cr_{1.18}N$ and Cr_2N powders were purchased from Furuuchi Chemical Corp. (Tokyo). The $Cr_{1.18}N$ powders were a mixture of 81.4 mass pct CrN and 18.6 mass pct Cr_2N. 1.0 mass pct of $Cr_{1.18}N$ powders was filled into the permeable straight hole of the iron rods. The continuous zone melting technique was adopted for unidirectional solidification of the rod in helium atmosphere of 0.5 MPa. The upper and lower edges of the iron rod were connected to the sample supporting devices. The rod was moved downward by controlling the transference velocity from 80 to 580 $\mu m\ s^{-1}$. The temperature distribution was measured by a pyrometer (XC-ST10, Tokyo Seiko Co., Tokyo). The length of the melted zone in the zone melting process was about 15 mm.

The specimens were cut using a spark-erosion wire cutting machine (model LN1W, Sodick Co., Yokohama, Japan) in both directions parallel and perpendicular to the solidification direction. The pore diameter was measured from the cross section perpendicular to the solidification direction. The porosity (p) was evaluated from the following equation:

$$p(\text{pct}) = \left(1 - \frac{\text{apparent density of porous metal}}{\text{density of nonporous metal}}\right) \times 100$$

[1]

Fig. 1—Outer view of iron rod: (a) longitudinal direction and (b) cross section perpendicular to the longitudinal direction.
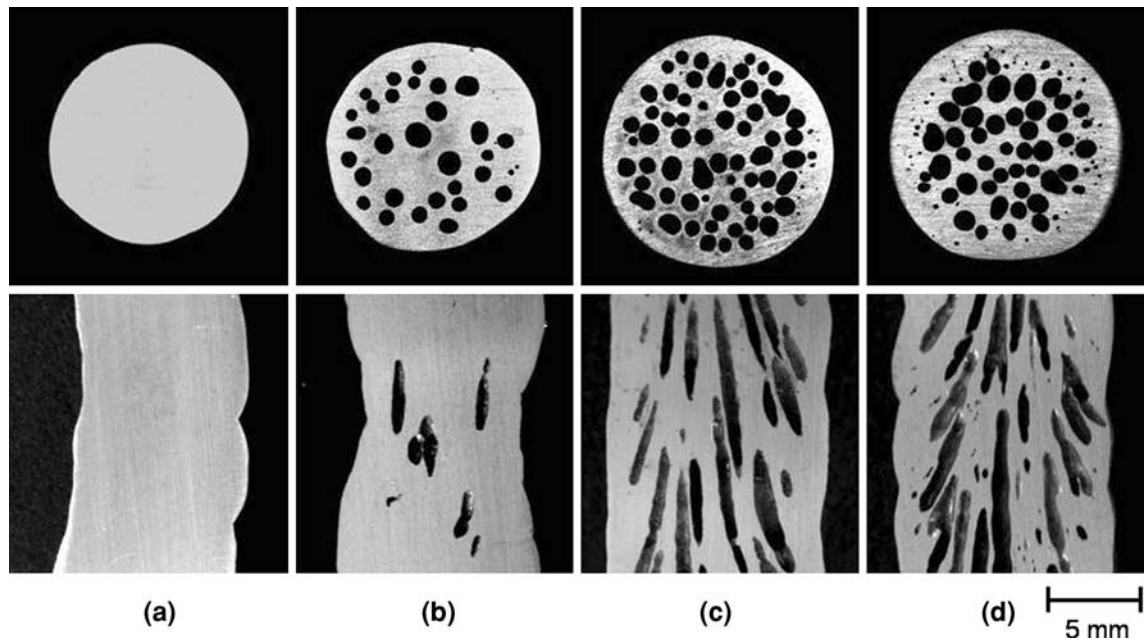

Fig. 2—Cross-sectional views of lotus iron perpendicular (upper) and parallel (lower) to the solidification direction. Transference velocity: (a) 80 $\mu m\ s^{-1}$, (b) 250 $\mu m\ s^{-1}$, (c) 410 $\mu m\ s^{-1}$, and (d) 580 $\mu m\ s^{-1}$. Atmosphere is 0.5 MPa helium.

The apparent density of the individual specimen was calculated by measuring both the weight and the apparent volume of each specimen. The pore morphology was observed with an optical microscope, and the pore size was evaluated with an image analyzer (Win ROOF, Mitani Co., Tokyo, Japan). Derivative thermogravimetry (DTG) of chromium nitrides of $Cr_{1.18}N$ and Cr_2N powders was carried out using a thermal analyzer (TG-DTA2000SA, Bruker-AXS Corp., Ibaraki, Japan). Fifty milligrams of the compounds were taken and the measurements were performed in an argon flow (150 mL min^{-1}) of 0.1 MPa in the temperature range from room temperature to 1773 K. The heating rate was changed from 10, 20, 30, and 40 K min^{-1}.

III. RESULTS

Figure 2 shows the cross-sectional views of lotus iron perpendicular and parallel to the solidification direction as a function of the transference velocity. No pores were observed in the ingot fabricated with the velocity of 80 μm s^{-1}; however, cylindrical pores were found in the lotus iron fabricated with the transference velocity higher than 250 μm s^{-1}. Figure 3 exhibits the transference velocity dependence of the porosity and average pore diameter. The porosity increases with increasing transference velocity, while the variation of the pore diameter with the velocity is relatively limited compared with previous results. For lotus stainless steel[8] and lotus copper[10] fabricated in pressurized hydrogen atmosphere, the porosity is almost independent of the transference velocity and the pore size decreases with increasing transference velocity. This suggests that the mechanism of pore formation obtained in the present study by the TDM is different from that obtained by the PGM.

Figure 4 shows DTG curves measured by the DTG with the heating rate of 10 K min^{-1} for $Cr_{1.18}N$ and Cr_2N powders. Two peaks for gas release from $Cr_{1.18}N$ were observed at 1240 K (T_{p1}) and 1570 K (T_{p2}), while one peak from Cr_2N was found at 1680 K. Thus, the 1570 K peak observed in higher temperature is attributed to the gas release from Cr_2N. Since $Cr_{1.18}N$ is composed of CrN and Cr_2N, the 1240 K peak of lower temperature is due to the gas release from CrN.

IV. DISCUSSION

In the continuous zone melting process, nitrogen released from chromium nitride dissolves in the melt of iron rod. Insoluble nitrogen precipitates to evolve gas pores when the melt is solidified subsequently. The pore evolution is dependent upon the transference velocity. In general, the behavior of thermal decomposition of compounds is strongly affected by the heating rate.[11] The possibility of forming pores by continuous zone melting will be discussed, taking into consideration the transference velocity dependence of the temperature distribution in the iron rod and the thermal decomposition of nitrides.
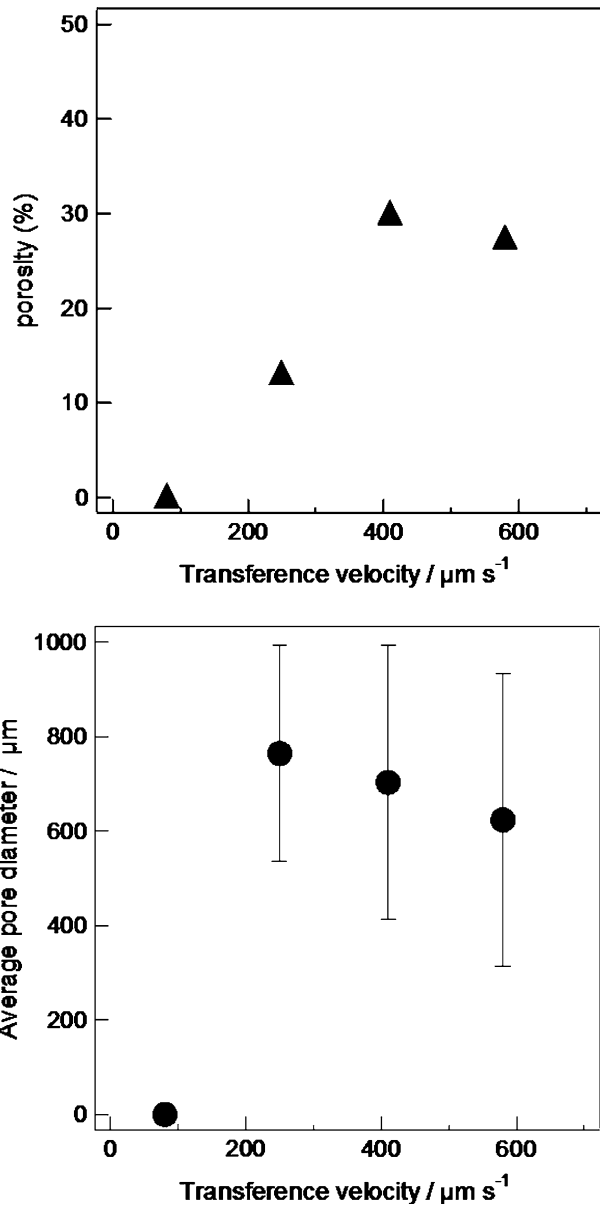

Fig. 3—Transference velocity dependence of the porosity and average pore diameter of lotus iron. Atmosphere is 0.5 MPa helium.

When the rod is solidified unidirectionally by the continuous zone melting technique, the rod is preheated by heat conduction before melting so that the rod has a temperature distribution. The relation between the temperature T of preheated rod and the distance x from the solid/liquid interface under the transference velocity v can be expressed by applying an equation of redistribution of solute in material solidified in the zone melting at constant velocity to a heat conduction.[12]

$$\frac{d}{dx}\left(\lambda\frac{dT}{dx}\right) + \rho c v\frac{dT}{dx} = 0 \qquad [2]$$

where ρ, c, and λ are the density of iron, the specific heat of iron,[13] and the thermal conductivity of iron,[14] respectively. Since the thermal conductivity is almost constant in the temperature lower than 1000 K,

an analytical solution from Eq. [2] can be derived so that the temperature of rod T can be expressed as

$$T = (T_m - T_r) \exp\left(-\frac{\rho c v}{\lambda} x\right) + T_r \qquad [3]$$

where T_m and T_r are the melting temperature of iron and the room temperature, respectively. Figure 5 shows the temperature and the heating rate as a function of the distance from the interface between liquid and solid at different transference velocities. Both the temperature gradient and heating rate increase with increasing transference velocity. Therefore, it is considered that the position in the rod where the gas is released from chromium nitride varies with the transference velocity.

Figure 6 shows measured DTG curves of $Cr_{1.18}N$ at different heating rate. The starting temperature and peak temperature of the gas release are shifted to higher temperature with increasing heating rate.[11] According to Kissinger,[15] the heating rate β is related to the peak temperature T_p for gas release by the following equation:

$$\frac{d\ln\left(\frac{\beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} = -\frac{E_a}{R} \qquad [4]$$

where E_a is an activation energy of reaction and R is the gas constant. The Kissinger plot of the peak temperature obtained from the measured DTG curves is shown in Figure 7. The result obtained at different heating rates is well fitted to the Kissinger Eq. [4]. It is predicted from the plots that the heating rates with which the peak temperature for the gas release is equal to the melting temperature (1809 K) of iron are 3.58×10^4 K min^{-1} (H.R$_1$) for CrN and 5.70×10^2 K min^{-1} (H.R$_2$) for Cr_2N.

In order to have decomposition of the nitrides into the melt, the transference velocity has to be such that the heating rate in the rod exceeds the predicted value, while there is an optimal heating rate. Figure 8 shows the relation between the temperature of the rod and heating rate, which is obtained from the results of Figures 5(a)
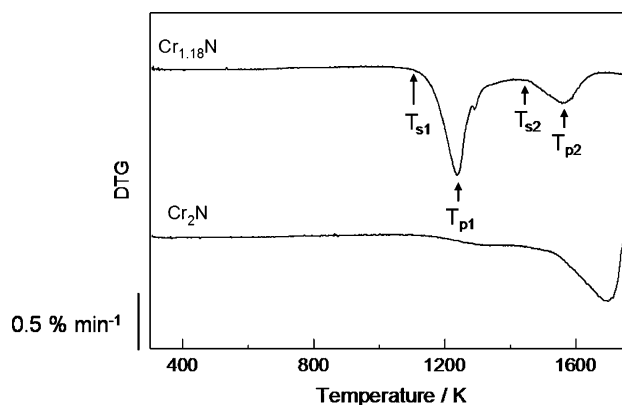
and (b). Since the predicted H.R$_1$ is higher than the heating rates at all transference velocity, gas from CrN contained in $Cr_{1.18}N$ is released before melting and does not contribute to pore evolution. On the other hand, H.R$_2$ in higher temperature than the starting temperature (about 1450 K slightly depending on the heating rates) for gas release is slower than the heating rates in the transference velocity more than 250 μm s^{-1}. Therefore, it is surmised that no pore formation at lower transference velocity of 80 μm s^{-1} is attributed to insufficient nitrogen release into the molten iron, because most of nitrogen gas released from the nitride escapes to the atmosphere: the rod is heated at high temperature by heat conduction from the melt part for a
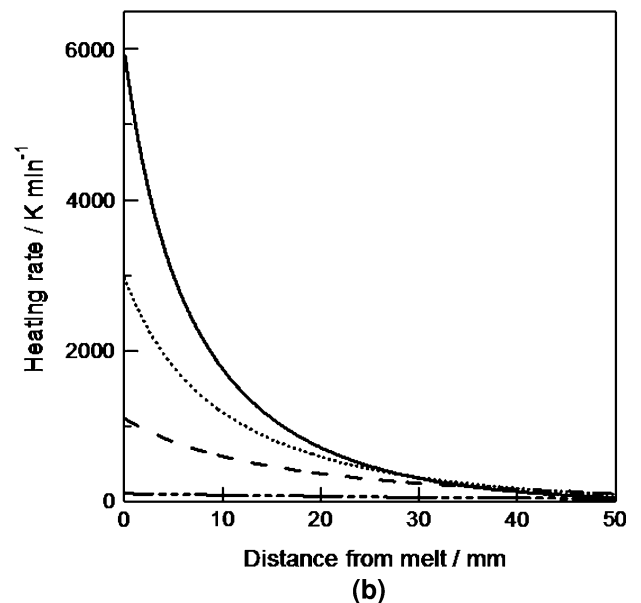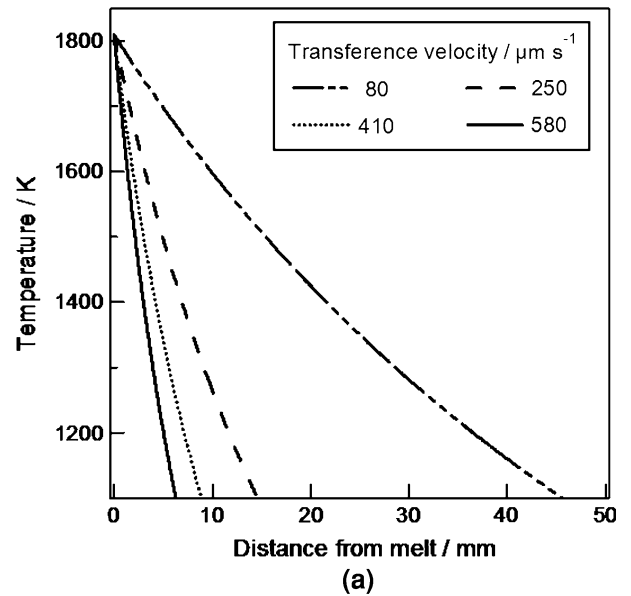

(a)

(b)

Fig. 5—Changes in temperature and heating rate as a function of the distance from the interface between liquid and solid at different transference velocities.
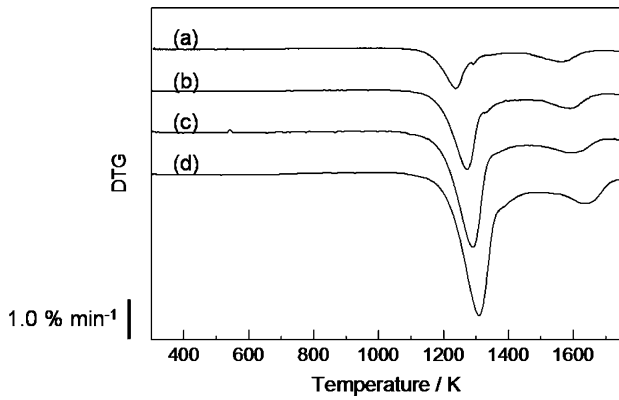

Fig. 4—DTG curves measured by the DTG with the heating rate of 10 K min^{-1} for $Cr_{1.18}N$ and Cr_2N powders. The T_s and T_p are the starting temperature and peak temperature of the gas release, respectively.

Fig. 6—DTG curves of $Cr_{1.18}N$ at different heating rates: (a) 10 K min^{-1}, (b) 20 K min^{-1}, (c) 30 K min^{-1}, and (d) 40 K min^{-1}.
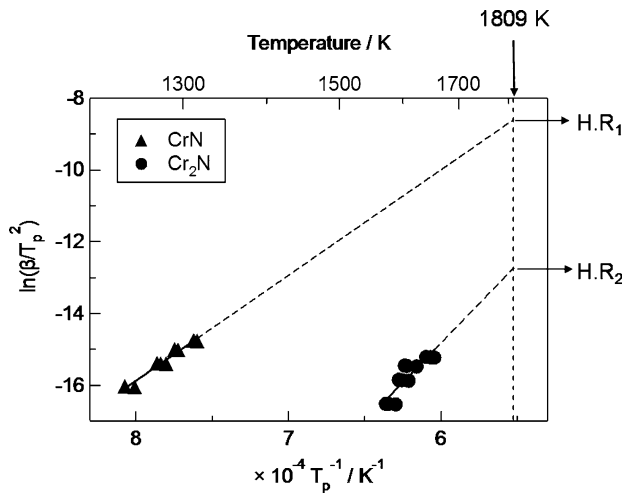

Fig. 7—Kissinger plots of the peak temperatures for decomposition of the nitrides obtained from the measured DTG curves.

Fig. 8—Relation between heating rate and temperature of the rod at different transference velocities.

longer time. It is considered that gas from Cr_2N contained in $Cr_{1.18}N$ cannot be released until part of the rod melts and is used effectively to evolve the pores. Thus, for transference velocity such that the decomposition peak temperature lies just above the melting point, decomposition of the nitrides in the melt is optimal (*i.e.*, optimal pore formation occurs).

Different from PGM, a gas equilibrium between the atmosphere (nitrogen partial pressure ~ 0) and the melt is not maintained in TDM.[7] During melting, nitrogen escapes from the melt to the atmosphere. Since the holding time of the melting condition decreases with increasing transference velocity, the amount of escaped nitrogen may decrease; thus, the porosity increases with increasing transference velocity, as shown in Figure 3(a).

Finally, a material balance of nitrogen shows that the nitrogen content in the CrN compound is much larger than the total nitrogen content in the pores and dissolved in the melt. It is surmised that nitrogen gas must evaporate during the experiments either through
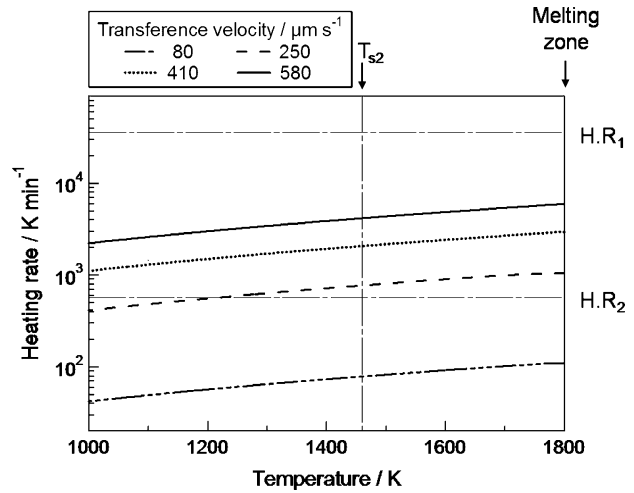
the drilled hole in the prepared sample or by bubbles formed in the melted zone.

V. CONCLUSIONS

Lotus iron was fabricated by the continuous zone melting technique through thermal decomposition of chromium nitride $Cr_{1.18}N$ in a helium atmosphere of 0.5 MPa. The results are summarized as follows.

The porosity increases with increasing transference velocity, while the pore diameter is independent of the velocity. The porosity change is due to the different decomposition rate of chromium nitride, which was affected by the heating rate of iron rod.

The pores are evolved through thermal decomposition of Cr_2N, not CrN.

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