

SHINAGAWA TECHNICAL REPORT

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要 旨

ポーラスレンガの気孔構造は、通気率、耐浸潤性を決定する重要な要素である。これは通常、BET法、水銀圧入法、X線CT等により評価されるが、気孔径が大きく、気孔構造が三次元的に複雑な場合には、X線CTによる評価が適切である。本調査では、通気率の異なるポーラスレンガのX線CT像を撮影し、それぞれの気孔構造について画像解析による評価を行った。その結果、異なる材料間の気孔構造の違いを定量的に示すことができた。

Abstract

The pore structure in porous brick is an important factor in determining its permeability and molten steel infiltration resistance. Pore structure, more exactly, the pore size in the pore structure, is usually evaluated by BET method, mercury penetration method or X-ray CT method. The X-ray CT method is appropriate for measuring an object which is characterized by complex pore structure with relatively large pore size. The differences in the pore structure in porous bricks were quantitatively evaluated by analyzing photographed X-ray CT images of porous bricks with different permeabilities.

1. 緒言

ポーラスレンガは、溶鋼の攪拌を目的に製鋼設備に設置されるポーラスプラグのコア部分として主に使用され、その気孔部分を介して溶鋼へのガス吹込みが行われる。ガス吹き込みの主な目的として、冶金反応の促進、成分・温度の均一化、非金属介在物の浮上分離があり、これらの目的を達成する上でレンガの通気率が重要なパラメーターとなる。ポーラスレンガの構造をFig.1のような粉体充填層と仮定すると、その通気率は式(1)のKozeny-Carman式^{1,2)}により表され、気孔率、気孔径、気孔の複雑さの影響を受ける。

$$K_p = \frac{\varepsilon D^2}{16k} \dots\dots\dots (1)$$

K_p : 通気率 (m^2)

ε : 見掛け気孔率

D : 気孔径 (m)

k : 気孔の複雑さを表す係数 (Kozeny係数)

1. Introduction

Porous brick is used majorly as the core part of the porous plug which is situated in bottom of molten steel vessels, such as teeming ladles and tundishes. Its function is stirring molten steel by inert gas blown through pores in the porous bricks. Promotion of metallurgical reactions, uniformization of chemical compositions and temperature of molten steel and floatation of nonmetallic inclusions are cited as major purposes of inert gas blowing from porous plugs. Porous brick permeability is a key factor in achieving such major functions in the steelmaking operation. Fig.1 shows inert gas bubbles blown from a porous plug in a water model experiment (top) and the microstructure of the packed particles in a porous brick (bottom left) and a conceptual diagram (bottom right). The permeability of the

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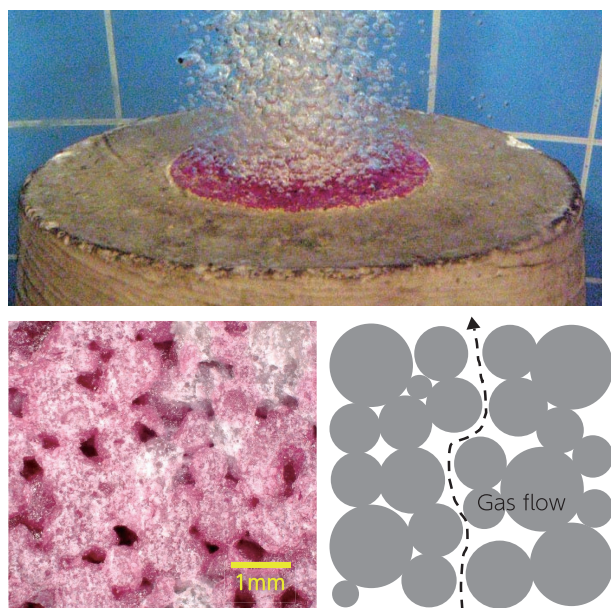


Fig. 1 Appearance of gas blowing from porous plug and microstructure of porous brick.

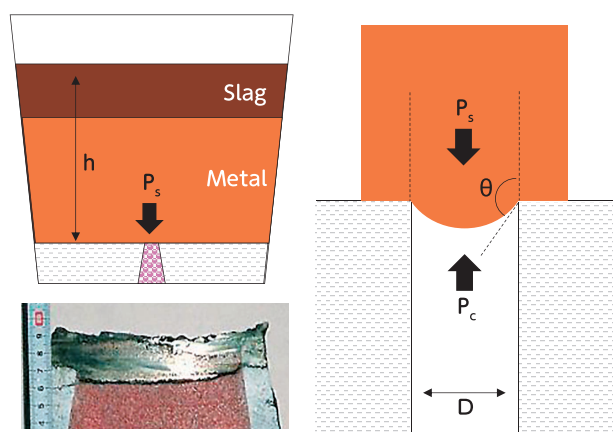


Fig. 2 Steel infiltrated porous plug (left) and schematic illustration of pore outlet in porous brick (right).

一方で、ポーラスプラグにおいては溶鋼の浸潤が大きな課題となる。Fig.2にポーラスレンガの気孔の入り口付近の模式図と、溶鋼浸潤後のポーラスプラグの様子を示す。浸潤は溶鋼の重さによる圧力と毛細管による排出力の差分により進行し、式(2)と式(3)に示すように気孔径が影響する。このように、通気率と溶鋼の浸潤には、気孔構造の特徴を表す各種パラメーターが重要となる。

$$P_s = \rho gh \quad \dots\dots\dots (2)$$

$$P_c = \frac{4\sigma_s \cos \theta}{D} \quad \dots\dots\dots (3)$$

hypothesized microstructure of the porous brick represented by the conceptual diagram in Fig. 1 is expressed with Kozeny-Carman equation^{1,2)}, namely, equation (1). As indicated by equation (1), permeability is influenced by porosity, pore size and complexity of pore structure.

$$K_p = \frac{\varepsilon D^2}{16k} \quad \dots\dots\dots (1)$$

where,

K_p : Permeability [m^2]

ε : Apparent porosity [-]

D : Pore diameter [m]

k : Constant for complexity of pore structure (Kozeny constant)

Infiltration of molten steel into porous brick is another important issue. Fig.2 shows a steel infiltrated porous plug which was retrieved from a teeming ladle (left) and a schematic illustration of an inert gas outlet of one pore in a porous brick (right). The infiltration of molten steel into porous brick takes place because of the difference between the static pressure of molten steel expressed with equation (2) and the capillary repulsion of a pore, expressed with equation (3). That is, the pore size of a porous brick influences molten steel infiltration. In short, permeability and molten steel infiltration resistance of a porous brick are influenced by several parameters relating to the pore structure of a porous brick.

$$P_s = \rho gh \quad \dots\dots\dots (2)$$

$$P_c = \frac{4\sigma_s \cos \theta}{D} \quad \dots\dots\dots (3)$$

where,

P_s : Static pressure of molten steel [N/m^2]

ρ : Density of molten steel [kg/cm^3]

g : Acceleration of gravity [m/s^2]

h : Height of molten steel [m]

P_c : Capillary repulsion [N/m^2]

σ_s : Surface tension of molten steel [N/m]

θ : Wet angle between refractory and molten steel [deg]

D : Pore diameter [m]

2. Evaluation Methods for Pore Structure

As evaluation methods for pore structure of

P_s : 溶鋼静圧 (N/m²)
 ρ : 溶鋼密度 (kg/cm³)
 g : 重力加速度 (m/s²)
 h : 溶鋼高さ (m)
 P_c : 毛細管力 (N/m²)
 σ_s : 溶鋼の表面張力 (N/m)
 θ : 溶鋼と耐火物の濡れ角度 (deg)
 D : 気孔径 (m)

2. 気孔構造の評価方法

セラミックスの気孔構造の評価方法にはBET法、水銀圧入法、X線CT等がある。Fig.3にそれぞれの評価方法の比較を示す。耐火物の気孔径は数百nmから数百 μ mまで幅広く、直線的な形状であるものや、複雑に屈曲した形状であるもの等、様々な形態をとるため、材質毎に適切な評価方法が選択される。これらの内、水銀圧入法はJIS R 1655に定められている通り一般的な評価方法である。水銀圧入法概念図をFig.4に示す。気孔径は、式(4)に示す毛細管に

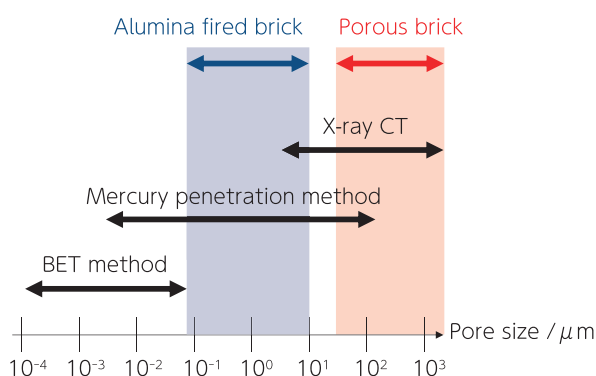


Fig. 3 Appropriate evaluation method according to pore size of ceramic.

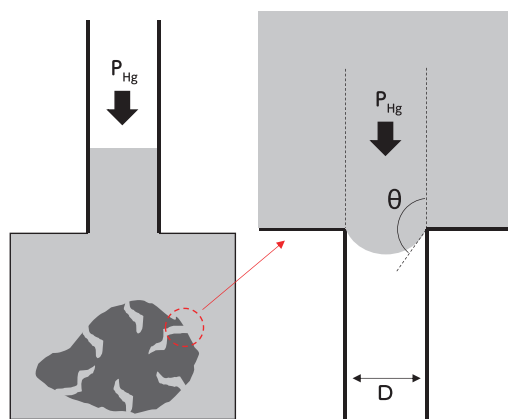


Fig. 4 Schematic image of mercury penetration method.

ceramics, The BET method, mercury penetration method (mercury porosimetry) and X-ray CT method are cited. As shown in Fig. 3, in accordance with the pore size in a ceramic body, which ranges from several-hundred nanometers to several-hundred micrometers, in a variety of configurations, such as simple linear figuration or complicatedly inflected figuration, the evaluation methods differ. Among the three evaluation methods, the mercury penetration method stipulated in JIS R 1655 (Test methods for pore size distribution of fine ceramic green body by mercury porosimetry) is generally used for evaluating pore structure, namely, pore size distribution. A schematic image of the mercury penetration method is shown in Fig. 4. Pore diameter can be calculated by equation (4) which expresses the balance between the penetration pressure of mercury and capillary repulsion of pore.

$$D = \frac{-4 \sigma_{Hg} \cos \theta}{P_{Hg}} \dots\dots\dots (4)$$

where,

D : Pore diameter [m]
 σ_{Hg} : Surface tension of mercury [N/m]
 θ : Wet angle between refractory and mercury [deg]
 P_{Hg} : Penetration pressure of mercury [N/m²]

When complex shaped pores are contained in an object being measured, the measurement result by mercury penetration method can deviate from the actual pore structure. The pore size distribution of porous brick measured by mercury penetration method is shown in Fig. 5. In comparison with the microstructure photograph in Fig. 5, the pore size distribution is apparently shifted to a smaller value. Assuming the case of the ink bottle shaped pore illustrated in Fig. 6, the pore with a large D_2 diameter is filled with mercury at higher mercury pressure at which mercury penetrates into pores with a smaller diameter of D_1 . That is, an ink bottle shaped pore with a large D_2 diameter is inaccurately measured as a pore with a smaller D_1 diameter, resulting in a shift of pore size distribution to a smaller value, i.e. deviation to smaller pore size from actual pore structure. Evaluation with X-ray CT method is useful for such situation.

Pore size measurement by X-ray CT method is

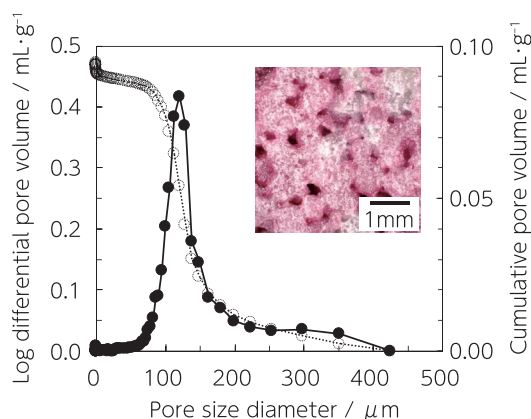


Fig. 5 Pore size distribution of porous brick measured by mercury penetration method.

よる排出力と、水銀の圧入力のつり合いの式により求められる。

$$D = \frac{-4\sigma_{Hg} \cos \theta}{P_{Hg}} \dots\dots\dots (4)$$

D : 気孔径 (m)

σ_{Hg} : 水銀の表面張力 (N/m)

θ : サンプルと水銀の接触角 (deg)

P_{Hg} : 水銀の圧入力 (N/m²)

しかし、水銀圧入法では測定対象物が複雑な気孔構造を持つ場合に問題が生じる。Fig.5に水銀圧入法で測定したポーラスレンガの気孔径分布を示す。測定された気孔径は微構造写真と比較して明確に小さい値であった。これは、例えばFig.6のようなインクボトル型の気孔を想定すると、水銀は気孔の入り口側からしか入れないため、気孔径 D_1 に相当する圧力で気孔径 D_2 の気孔にも同時に水銀が圧入されてしまい、圧入曲線が気孔径の小さい側へシフトし、本来の分布曲線との間に差異が生じることが原因である。このような場合、X線CTを利用した評価が有用である。

Fig.7にX線CT測定の模式図を示す。まず、測定対象物にX線が照射され、透過X線強度の違いが検出される。次に、試料ステージを回転させ、対象物の透過X線像を360°方向で撮影し、それらを重ね合わせて3次元像をコンピュータ上に作製する。これにより物体の気孔構造を直接的に評価できるため、複雑な気孔構造を有する耐火物の評価に有効であると言える。今回は通気率の異なるポーラスレンガについて、それぞれの気孔構造の違いをX線CTにより評価した。

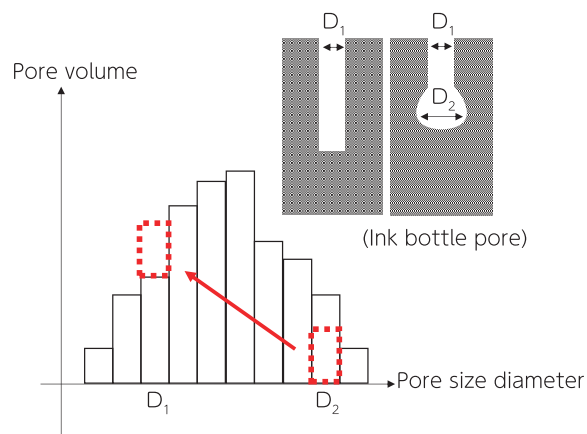


Fig. 6 Shift of pore size distribution to smaller value by ink bottle pore.

schematically shown in Fig. 7. By radiating X-ray towards the object being measured, the X-ray transmission intensity is recorded as a transmission X-ray image on a flat panel detector. The object being measured is rotated so that transmission X-ray images from all (360°) circumferential directions can be photographed. By superpositioning these transmission X-ray images, a three-dimensional image can be displayed on the computer screen. Since the pore structure of the measured object can be visually observed as a 3D image, the X-ray CT method is thought to be useful for evaluating complex pore structures in refractories. The difference in pore structure of porous bricks with different permeabilities was evaluated by X-ray CT method.

3. Experiment

The characteristics of three porous bricks used for the experiment are shown in Table 1, along with X-ray CT measuring conditions. The three porous bricks, each of which was labeled as A, B and C, were made of alumina-silica. Porous brick B and C respectively exhibit the highest and the lowest permeability. As for X-ray CT measuring conditions, unified X-ray voltage and X-ray current were adopted for all the porous bricks. The image size and voxel size were adjusted so that image resolution was nearly equalized.

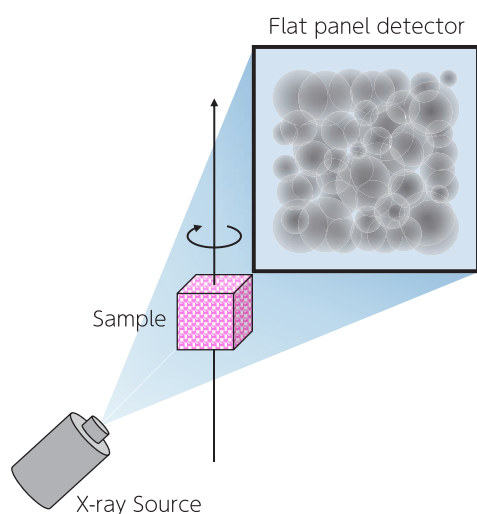


Fig. 7 Schematic illustration of pore size measurement by X-ray CT method.

3. 試験方法

Table 1に評価を行ったサンプルとX線CTの測定条件を示す。サンプルA, B, Cは全てアルミナ・シリカ質であり、通気率はサンプルBが最も高く、サンプルCが最も低い。X線CTの測定条件については、X線の管電圧、管電流を統一し、視野サイズとボクセルサイズは像の粗さが同程度となるよう調整した。

4. 結果

4. 1 各サンプルのX線CT像

Table 2にX線CTにより測定した各サンプルの立体像と、Z軸に沿って切断した断面像を示す。全てのサンプルで気孔が3次元的に繋がった網目状の構造であることが確認できた。

4. 2 X線CT像の評価方法

X線CT像の評価方法は過去の報告³⁾を参考にした。この文献は、シンターケーキと呼ばれる焼結鉱、石灰、コークスを含むベルト状の焼結体の一部分に対し、X線CT像の撮影と画像解析による気孔構造の定量的な評価を行ったものである。

今回は上記文献の方法をポーラスレンガに適用し、X線CTの断面像の気孔形状について、ブランチ幅とブランチ密度の2つのパラメーターにより評価した。それぞれのパラメーターについて、ブランチ幅は気孔径、ブランチ密度は気孔の複雑さを表す指標であると考えられる。各パラメーター

Table 1 Characteristics of porous bricks and X-ray CT measuring conditions

	A	B	C
Composition	Alumina・Silica		
Permeability / m ²	17.4×10 ⁻¹¹	20.5×10 ⁻¹¹	5.2×10 ⁻¹¹
X-ray voltage / kV	200		
X-ray current / μA	40		
Image size / mm	φ10×h18		φ7×h20
Voxel size / μm	20		15

Table 2 Three-dimensional image and vertically cut cross section image of each porous brick measured by X-ray CT method

	A	B	C
3D			
Cross section			

4. Results

4. 1 X-ray CT image of each porous brick

Table 2 shows a three-dimensional image and a vertically cut cross section image of each porous brick. It was clarified that the pores in porous bricks are three-dimensionally connected to build a network structure.

4. 2 Evaluation on X-ray CT image

An X-ray CT image of the porous bricks was quantitatively evaluated while referring to a precedent report³⁾ in which the pore structure in a belt-type sintered body composed of sintered ore, lime and cokes, so called sinter cake, was evaluated by X-ray CT image analysis. More specifically, while referring to the analysis technique described in the

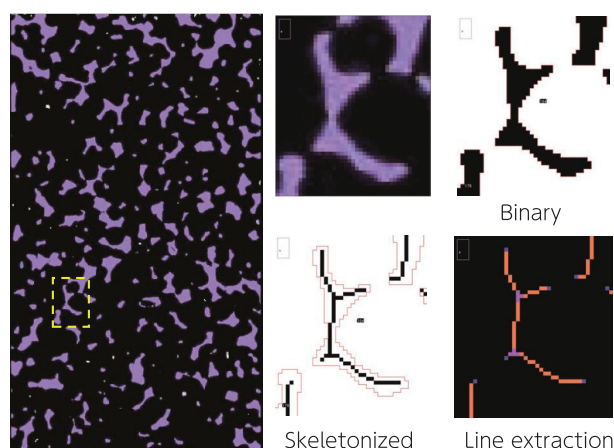


Fig. 8 Calculation procedure for branch width and branch density.

の算出方法をFig.8に示す。まず、グレースケール画像で適切な閾値を設定して気孔部分の識別を行い、1画素分の幅となるよう気孔の細線化処理を行う。その後、気孔を構成する各画素について、隣接画素数による分類を行い、気孔を構成する線分の抽出を行う。そして、ブランチ幅は式(5)、ブランチ密度は式(6)により算出した。また、それぞれのパラメーターを算出する際に必要なピクセルサイズは、画像中の既知の長さより設定した。

$$W_b = \frac{S_p}{L_b} \quad \dots\dots\dots (5)$$

$$D_b = \frac{N_b}{S_f} \quad \dots\dots\dots (6)$$

W_b : ブランチ幅 (μm)

S_p : 気孔の面積 (μm^2)

L_b : 線分の長さ (μm)

D_b : ブランチ密度 (μm^{-2})

N_b : 線分の本数

S_f : 視野面積 (μm^2)

4. 3 評価結果と考察

Fig.9に各サンプルのブランチ幅とブランチ密度を示す。サンプルA, B, Cの順にブランチ幅が小さく、即ち気孔径が小さくなることが分かった。一方で、サンプルA, B, Cの順にブランチ密度が大きくなり、即ち気孔の複雑さが大きくなることが分かった。Table 3に各サンプルのそれぞれのパラメーターの値を示す。サンプルCの通気率が最も低いのは、気孔径が小さく且つ気孔の複雑さが大きいと考えられる。また、サンプルAよりもサンプルBの通気率が高いのは、気孔率の違いが影響したためであると考えられる。

precedent report, the pore shape observed in the X-ray CT cross section images was evaluated for branch width and branch density, which is thought to correspond to pore size and is an indicator representing the complexity of pore structure, respectively. The calculation procedure used for branch width and branch density is shown in Fig. 8. Firstly, the pore region was recognized in a grey scale image as a binarized image by applying adequate threshold value. A thinning processing was applied on the extracted binary image in order to obtain a skeletonized image of one pixel width. Each picture element composing of a skeletonized image of a pore was sorted out to be extracted as a pore consisting line segment for the examination of neighboring picture elements. Afterwards, the branch width and branch density was calculated by equation (5) and equation (6), respectively. It should be noted that the pixel size necessary for calculating two parameters was set up referring to a known length in the analysis image.

$$W_b = \frac{S_p}{L_b} \quad \dots\dots\dots (5)$$

$$D_b = \frac{N_b}{S_f} \quad \dots\dots\dots (6)$$

where,

W_b : Branch width [μm]

S_p : Area of pore [μm^2]

L_b : Length of line segment [μm]

D_b : Branch density [μm^{-2}]

N_b : Number of line segment [-]

S_f : Area of visual field [μm^2]

4. 3 Evaluation results and discussion

The calculated values of the branch width and branch density of the three (3) porous bricks are compared in Fig. 9. It was clarified with calculated value of branch width which decrease in the order of $A > B > C$ that pore size in porous bricks becomes smaller with similar order. The calculated value of the branch density increased in the order of $A < B < C$. This indicates that the complexity of pore structure in porous bricks is heightened with similar order. When the pore related physical properties are jointly considered, namely, the permeability and porosity, and the two calculated parameters which

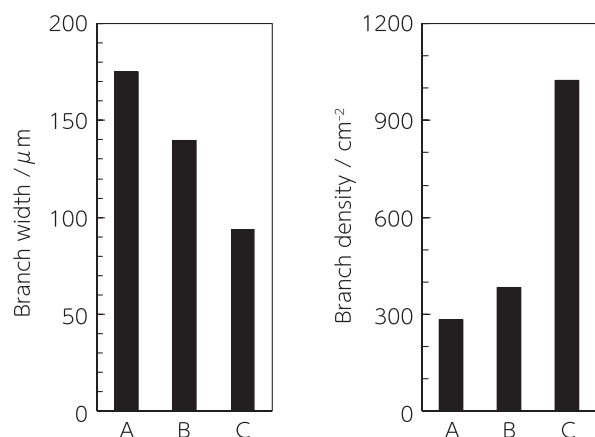


Fig. 9 Calculated values of branch width and branch density of porous bricks.

Table 3 Permeability, porosity and calculated two parameters of porous bricks

	A	B	C
Permeability / $\times 10^{-11}\text{m}^2$	17.4	20.5	5.2
Porosity / %	16.7	19.6	19.1
Branch width / μm	175.0	139.8	93.7
Branch density / cm^{-2}	281.3	383.2	1023.0

5. 水銀圧入法とX線CTの比較

まず分解能を比較すると、水銀圧入法は最大で数nm程度まで測定可能であるのに対し、X線CTは最大で数 μm 程度となる。また、気孔径の評価について比較すると、水銀圧入法ではインクボトル型細孔等、複雑な形状の気孔の場合、圧入曲線のシフトにより正確な気孔径の測定が困難である一方で、X線CTでは撮影像から直接的に気孔径を測定するため、気孔径を正確に測定することが可能である。また、気孔の複雑さの評価について比較すると、水銀圧入法では圧入曲線のヒステリシスにより評価することが可能であるが、複雑な気孔の場合、先述のように圧入曲線がシフトするため正しい評価が困難である一方で、X線CTでは同様に撮影像から直接的に評価を行うため、正しい評価が可能である。これらの特徴を考慮し、気孔構造が単純で気孔径が小さい場合は水銀圧入法を利用し、気孔構造が複雑で気孔径が大きい場合はX線CTを利用する等、測定対象物により適切な評価方法を選択することが重要である。

are summarized in Table 3, it is inferred that the smallest permeability of porous brick C is caused by small pore size (branch width) and high complexity of pore structure (branch density). It is also inferred that the higher permeability of porous brick B than that of porous brick A is derived from difference in porosity between these two porous bricks.

5. Comparison Between Mercury Penetration Method and X-ray CT Method

It was concluded that minimum pore size measurable by mercury penetration method is nm (nanometer) level and that by X-ray CT method is μm (micrometer) level when the resolution of the two methods was compared. As for the accuracy of measured pore size, the measurement value by mercury penetration method can deviate to a smaller value from that of the actual pore structure, especially when complex shaped pores, such as ink bottle shaped pores, are contained in the measured object. Since the pore size is directly measured from the photographed image in the X-ray CT method, the accuracy of the measured value is better. Next, evaluation of complexity of pore structure was compared between the two methods. The complexity of pore structure in a measured object can be evaluated to some extent by mercury penetration method by referring to hysteresis in mercury penetration curve. When complex shaped pores are contained in a measured object, however, evaluation accuracy is lowered because of the deviation of mercury penetration curve to smaller value. Since visual information on the complexity of pore structure is provided by X-ray CT images, better evaluation of the complexity of pore structures is attained by the X-ray CT method. Taking into account the characteristics of the two methods, it can be concluded that mercury penetration method is appropriate for measuring objects which are characterized by relatively simple pore structure with small pore size, and the X-ray CT method is appropriate for measuring objects with complex pore structures and relatively large pore size.

6. 結言

X線CTによりポーラスレンガの気孔構造の評価を行った。その結果、異なる通気率を持つポーラスレンガの気孔構造の違いを詳細に評価することができた。このように気孔構造の評価を行う際は、測定対象物の特徴を考慮して適切な方法を選択することが重要である。

6. Conclusion

Several types of porous bricks were evaluated by X-ray CT method. As a result, the differences in pore structure of porous bricks with different permeabilities was properly evaluated. When the pore structure in refractory products is evaluated, an adequate evaluation method needs to be selected in accordance with the characteristics of pore structure of the measured object, namely, pore size and complexity of pore structure.

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