Effects of the Pore Size of Graphite on the Mechanical Properties and Permeability of a Porous Nozzle for Continuous Casting Process

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Abstract: To analyze the effect of the pore size of graphite in a pore-forming agent, graphite was added to porous ceramics of Al₂O₃-SiO₂-ZrO₂ systems. The graphite had 45~75, 100~125, 150~180, and 75~180 μm dimensions. The properties of the ceramics, such as apparent porosity, density, dynamic elastic modulus, mechanical strength, and permeability, were investigated. The average pore size increased from 15.35 μm to 22.32 μm with the increase of the graphite size. The sample with the largest average pore size showed the highest mechanical strength and gas permeability. This was due to the sample with the largest pore size at the same porosity having fewer pores and larger distance between the pores than the sample with the smallest pore size, making cracks less likely to propagate. In addition, the large pore size reduced the repulsive power originating from the drag force between the gas and internal pore walls.

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1. INTRODUCTION

Porous ceramics have received noticeable interests due to their excellent mechanical properties, high thermal characteristic, and chemical stability. They also have been widely used in various industries such as catalyst, separation, lightweight structural materials, biomaterials, refractory, and so on [1-5]. In particular application of porous materials such as refractory industry, continuous casting of steel has achieved widespread popularity because it is capable of extracting heat at a remarkable rate with the combination of mold, sprays, and radiant cooling [6,7]. Porous nozzles are used for continuous casting process of steel in various ways, for example, upper nozzle, submerged entry nozzle, shroud nozzle, and etc [6]. In this process, an inert gas, typically Ar, is injected through a porous nozzle into the system to assist the prevention of clogging in the flow delivery system and promote the collection of inclusions such as Al₂O₃, which are responsible for loss of product quality [8]. When nozzle has heterogeneous pore size distribution, infiltrations of molten steel into the nozzles and creations of unwanted agitation are expected. Thus, proper fluid permeability is required and that is closely related to the porosity and pore size [8-10].

In our previous study, porous nozzle samples with controlled porosity were produced by adding graphite and their thermal and mechanical properties were characterized [11]. According to the relationship between mechanical strength and porosity, Rice et al reported [12], porous ceramics having the same porosity are supposed to have nearly similar strength [13]. However, the difference was founded in the strength for the porous ceramics, therefore, could be explained in terms of pore size [5,14].

In this study, the influence of pore size on mechanical properties and permeability of porous nozzle was investigated. Samples were fabricated through replica technique with using graphite as a pore-forming agent. The pore size of samples could be controlled by different size of graphite sieved into four groups dimension of 45~75, 100~125, 150~180, and 75~180 μm. Basic properties such as apparent porosity, average pore size, and bulk density were measured. In order to confirm the relation between pore size and mechanical properties, flexural strength and the dynamic elastic modulus were measured. Additionally, gas permeability, one of the most important performances in porous ceramics, was observed through
pressure drop. All results were compared and analyzed in terms of average pore size and pore size distribution.

2. EXPERIMENTAL PROCEDURE

The porous ceramic samples were produced using Al$_2$O$_3$ (AES-11, SUMITOMO, Japan) 92 wt%, SiO$_2$ (SIGMA-ALDRICH, USA) 4.5 wt%, and ZrO$_2$ (ZRO02PB, Kojundo Chemical Lab. Co., Ltd, Japan) 3.5 wt%. Graphite (KANTO Chemical, Japan) was used as a pore-forming agent. In order to control the pore size, different size of graphite were prepared and mixed with the starting powders. For the classifying graphite, they were sieved by 45~75, 100~125, and 150~180 $\mu$m. In order to make a fair comparison, a sample, added as-received graphite which is dimension of 75~180 $\mu$m, was also prepared. Powders with graphite of 20 wt% were ball milled for 24 h and dried. After drying, they were mixed with binder (Methyle Cellulose, Japan) 5 wt%, lubricant (Lu-6418, Korea) 3 wt%, and plasticizer (Glycerin, Japan) 2 wt% and aged in Const. Temp. & Humid. Chamber (TATC-150, Aero Tech, Korea) for 24 h at temperature of 60$^\circ$C and humidity of 60%. Aged powders were formed into disk type (diameter of 25 mm) and bar type (dimension of 50.24 mm $\times$ 4.20 mm $\times$ 7.35 mm) under the uniaxial pressure of 20 MPa. The green bodies were aged at room temperature for 48 h, and then all samples were heated at 800$^\circ$C for 2 h to burn out the graphite and sintered at 1550$^\circ$C in E/V furnace.

In order to avoid interference between mechanical properties and various factors such as crack behavior and stress field, the samples were prepared by same powder processing and analyzed at least five times to get the repeatability. For determination of average pore size, image analysis method was applied [15,16]. The Images were then taken of each slice using scanning electron microscopy (HITACH S4800, Japan). The bulk density and the apparent porosity of samples were measured by water immersion based on Archimedes’ principle and calculated according to the following equations [9]:

\[
\text{Bulk density (g/cm}^3\text{)} = \frac{(m_1-d)(m_3-m_2)}{m_3-m_1}\quad(1)
\]

\[
\text{Apparent porosity (%) = } \left(\frac{m_1-m_3}{m_1-m_2}\right) \times 100\%\quad(2)
\]

where $m_1$ is the mass of a dried sample in air (g), $m_2$ the mass of the sample in kerosene (g), $m_3$ the mass of the sample with free bubbles on the surface (g), and $d$ is the density of kerosene (g/cm$^3$). Mechanical properties were studied by measuring the elastic modulus of the composites and the bending strength through 3-point bending test (Universal Testing Machine, DUT-3000CM, KOREA). The bending strength was defined by the standard equation [17],

\[
\sigma_f = \frac{3PL}{2bh^2}\quad(3)
\]

, where $P$ is the fracture load, $L$ the length of support span, $b$ the sample width, and $h$ is the sample thickness. The permeability with pore size variation was studied via the pressure drop method to determine the performance of porous ceramics.

3. RESULTS & DISCUSSION

3.1. Microstructure Analysis

Fig. 1 shows microstructures of fabricated porous nozzle samples. As a function of the graphite which had graded sizes of 45~75, 100~125, and 150~180 $\mu$m added into the sample A, B, and C, respectively, and as-received graphite (size of 75~180 $\mu$m) was added for the sample D. The diameter of pores and pore size distribution was studied by the image analysis method and observed average pore sizes of each sample were 15.35, 19.42, 22.32, and 20.09 $\mu$m as shown in Fig. 2. Among the samples, the sample C (graphite of 150~180 $\mu$m was added) showed the largest average pore size of 22.32 $\mu$m and relatively homogeneous pore size distribution in the SEM micrograph. The sample D (graphite of 75~200 $\mu$m was added) showed the largest average pore size of 22.32 $\mu$m and relatively homogeneous pore size distribution in the SEM micrograph. The sample D (graphite of 75~200 $\mu$m was added) had an average pore size of 20.09 $\mu$m, however, it contained some large pores over 43 $\mu$m, indicating heterogeneous pore size distribution because of the as-received graphite which had various and heterogeneous particle sizes. In Figs. 1 and 2, the pore diameter of samples A, B, and C was increased in response to the increase of graphite size. It could be observed that the pore size was relatively smaller than the graphite size. It was contributed that the graphite particles were crushed and pressed during ball milling, shaping, and densification.