Effect of Silica Additive on the Formation of Lotus-Type Porous Alumina under Unidirectional Solidification

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Effect of silica additive on the formation of lotus-type porous alumina on the unidirectional solidification was examined. Lotus-type porous alumina with 44% porosity was formed by unidirectional solidification using the optical floating zone method under a hydrogen atmosphere when low purity alumina was used as the feed rod. However, non-porous alumina was prepared in argon atmosphere. The formed pores possessed a drop-like shape and were elongated along the solidification direction in porous alumina. Gas bubbles evolved in the molten zone and was trapped by the solid/liquid interface during the unidirectional solidification. On the other hand, lotus-type porous alumina could not be obtained when high purity alumina was used as the feed rod. The porosity of the solidified porous alumina increased with increasing silica contents in the feed rods. [doi:10.2320/matertrans.47.2167]

(Received February 28, 2006; Accepted July 19, 2006; Published September 15, 2006)

Keywords: lotus-type porous alumina, solidification, floating zone method

1. Introduction

Recently, a new type of porous metals so-called lotus-type porous metals have been prepared by unidirectional solidification under hydrogen and/or nitrogen.\(^1\)\(^-\)\(^3\) The lotus-type porous metals possess a unique structure, where long cylindrical pores are aligned in solidification direction.\(^1\)\(^-\)\(^3\) The specific strength of lotus-type porous iron whose pores oriented to the loading direction is unchanged with the porosity, and hence, lotus-type porous metals are expected to be attractive structural materials for various applications. Since superior mechanical strength, sound absorption, damping effect, permeability etc. were found, the applications for sound-absorption and heat exchanger\(^1\)\(^-\)\(^3\) are expected.

To extend the applications of lotus-type porous metals, a great interest had been focused on the preparation of new lotus-type porous materials such as lotus-type porous semiconductor and/or lotus-type porous oxides. Fabrication of the lotus-type porous silicon by mold casting was for the first time reported as a micro-porous silicon by Nakahata and Nakajima.\(^4\) On the other hand, to our knowledge, no investigations were carried out for the preparation of lotus-type porous oxides.

In general, the corrosion resistance and thermal stability of oxides are better than those of metals. Thus lotus-type porous oxides will be able to perform as high-corrosion resistance materials at elevated temperatures such as ceramic tubes.

Many basic data for the solubility of hydrogen into solid and liquid metals had been established in the field of hydrogen absorbing alloys.\(^5\) However, no data of hydrogen solubility in oxides are available.

In this study, the fabrication of lotus-type porous alumina was conducted by unidirectional solidification with an optical floating zone (OFZ) furnace. Then the formation mechanism of lotus-type porous alumina was discussed including the effect of silica additive.

2. Experimental Procedure

A sintered alumina bulk with \(\phi 6 \text{mm} \times 150 \text{mm}\) in length (ALSINT99.7 W. Haldenwanger Co. Ltd.) was used as feed rods. The compositions of the sintered alumina are given in Table 1. Since this bulk contains a small amount of impurity phases as shown in Table, to examine the effect of impurity phase on the formation of porous structure, high purity alumina bulk was prepared. Furthermore, to examine the effect of silica additive which is a component of the impurity phase, alumina feed rods with 0, 10 and 20 mol% silica contents were prepared by the sintering. High purity alumina and silica (99.99% for alumina and 99.9% for silica, Kojundo Chemical Lab. Co., Ltd.) powders were used as the starting materials. These powders were mixed in agate mortar and the pressed into rod shape by cold isostatic pressing (CIP). Then the rods were sintered at 1273 K for 43.2 ks in air. The nominal composition of the sintered alumina bulk with silica additive was summarized in Table 2. The composition of the silica powder used in this experiment was summarized in Table 3.

The sintered alumina was used as a seed rod and as a feed rod. The rods were rotated during solidification to make the
molten zone homogeneous. The solidification was conducted
under flowing hydrogen gas at atmospheric pressure. The
solidification conditions were as follows; solidification rate:
200 mm/h, sample rotation rate: 20 rpm, hydrogen gas flow
rate: 300 mL/min under normal pressure. To compare the
microstructure of porous alumina with that of non-porous
alumina, solidification was also performed in argon atmo-
sphere under the same experimental conditions. The sche-
matic view of the optical floating zone furnace is shown in
Fig. 1.

The microstructure of the solidified porous alumina was
observed on vertical cross and longitudinal sections, which
were cut by a diamond saw.

3. Results

Figure 2 shows an external view of the solidified sample
using low purity sintered alumina as shown in Table 1, where
the solidification was carried out in hydrogen gas flow under
atmospheric pressure. It can be confirmed that some pores
included in the solidified sample.

Figure 3(a) and (b) show the micro-structure of the sample
vertical cross and longitudinal sections for the sample of
Fig. 2. Many pores were formed in the solidified bulk during
solidification. In the cross section (a), it can be seen that the
size of the pores inhomogeneous. The pore size distributed
from sub-millimeter to millimeter as shown in Fig. 3(a). The
average pore diameter is \( d = 1.0 \text{ mm} \) and a large pore up to
\( d = 4.0 \text{ mm} \) exists in the solidified bulk. On the other hand, in
the longitudinal section Fig. 3(b), each pore possesses a drop-
like shape. These drop-like pores are elongated along the
solidification direction. Thus, a wide range distribution of
pore size appeared in a vertical cross section. The aspect ratio
estimated from Fig. 3(b) is about 2, which is defined as the
ratio of the longitudinal length against the diameter.

On the other hand, non-porous solidified bulk alumina was
obtained by unidirectional solidification in argon under
normal pressure. Figure 4 shows the longitudinal section
for the sample. In contrast with the porosity of Fig. 3, no
pores can be seen in the sample solidified in argon.

Figures 5(a) and (b) show the EPMA profiles for the
scaffolding powder that was collected from inner wall of
quartz tube after solidification and low purity sintered
alumina rod, respectively.

Figure 6 shows the longitudinal section of the solidified
sample using high purity sintered alumina rod without silica
additive as shown in Table 2. Although some pores are
formed in the sample the porosity is smaller than that of
Fig. 3(b), where purity sintered alumina bulk low was used as
feed rod. Figure 7 shows the porosity of the samples using
high purity sintered alumina rods with silica component. The
porosity increased with increasing the silica content.

4. Discussion

A stable molten zone was maintained during the solid-
ification by controlling the light power. Thus it is considered
that the thermal gradient at the solid-liquid interface was
constant during solidification, such that the solidification was
performed at steady state. The porosity of this solidified bulk
was 44%, calculated from the X-ray density of corundum
phase (JCPDS card No. 10-0173) and the bulk density. The
bulk density was calculated from weight and volume which
of the sample. The volume was calculated from the length
and diameter of the sample, where iterative determination of
the measurement was performed 10 times. However, the size
of the pores is inhomogeneous as shown in Fig. 3(a) and in
the longitudinal section Fig. 3(b), each pore possesses a drop-
like shape.

Since the non-porous solidified bulk was obtained by the
solidification under argon atmosphere as shown in Fig. 4.
Thus, the pore formation in the lotus-type porous alumina is
attributed to hydrogen gas. It can be assumed that the pore
formation mechanism of lotus-type alumina is similar to that
of lotus-type porous metals, namely, there is a gap in the
solubility of hydrogen gas between solid and liquid alumina
and excess hydrogen gas is released during solidification.
Pores formation in lotus-type porous metals can be explained
using the solubility gap, i.e. the excess hydrogen gas that
dissolved in the liquid phase is released upon solidification
according to the solubility gap. However, no reference for
the hydrogen solubility in liquid and solid alumina could be
obtained.
In this study, the evolution of the gas bubbles in the molten zone and the trapping of bubbles by the solid were directly observed by a CCD camera as shown in Fig. 1 during the solidification. These results suggested that the pores formation mechanism in this case includes (1) pore formation due to hydrogen gas solubility gap between liquid and solid phases and (2) gas evolution in the liquid phase and trapping the bubbles by the solid phase. Commonly, in the zone melting process, a thermal gradient might occur in the liquid phase. Thus, it can be considered that the gas evolution in the liquid phase is induced by the thermal gradient $\Delta T$. Sometimes, it was observed that the gas bubbles were released from the molten zone to the surrounding atmosphere. The released gas agglutinates on inner wall of the quartz tube. Triantafyllidis et al. discussed a formation mechanism of porous alumina by trapping of bubbles that were formed in molten alumina pool. When the velocity of bubble along the convection flow is lower than the solidification rate, the bubble was trapped by the solid phase and porous alumina was formed. In this study, it can be considered that a continual trapping of bubbles occurred by unidirectional solidification.

The silicon component as much as 0.08 mol% that...
included in the low purity sintered bulk can be detected cloudy peak in EPMA analysis. However, silicon component is clearly detected in the scaffolding powder as shown in Fig. 5. These results suggested that the major component of the scaffolding powder consisted with alumina and silica component that included in the sintered bulk as an impurity phase preferentially gasified in the molten zone.

Hence, it can be assumed that the porosity of the solidified alumina under hydrogen atmosphere is controlled by the hydrogen solubility and the mount of silica impurity phase in the liquid phase. To clear this issue, high purity sintered alumina bulk with and without silica additive was prepared as shown in Table 2 and the solidification was conducted using these bulk as the feed rod under hydrogen atmosphere. Although some pores are formed in the sample used high

Fig. 5 EPMA profiles for (a) the scaffolding powder and (b) sintered alumina rod, respectively.

Fig. 6 Longitudinal section of the solidified sample using high purity sintered alumina rod.

Fig. 7 The porosity of the samples using high purity sintered alumina rods with silica component.
purity alumina without silica additive as shown in Fig. 6, the porosity is smaller than that of Fig. 3(b). However, the porosity increased with increase of silica content as shown in Fig. 7. These results suggested that the pore formation on the unidirectional solidification of alumina was enhanced by the amount of silica component in the feed rod.

5. Conclusions

Lotus-type porous alumina was prepared by unidirectional solidification method in hydrogen atmosphere. The pores are formed in the sample by two different kinds of mechanisms during the unidirectional solidification, namely, (1) gas solubility gap between liquid and solid phases and (2) gas bubble evolution in the liquid phase and the trapping the bubbles by the solid phase. Silica component that included in the sintered bulk as an impurity phase preferentially gasified in the molten zone and enhanced the pore formation.

REFERENCES

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