

Pores Formation in Al₂O₃ Crystal during Rapid Solidification under Pressurized Hydrogen Atmosphere

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Abstract: Rapid solidification of Al₂O₃ was performed under pressurized hydrogen atmosphere. Many cylindrical pores that arranged in the direction of solidification was formed in the solidified film. The porosity remained constant and was independent of the hydrogen partial pressure. Even at a hydrogen partial pressure of 50%, the amount of hydrogen was sufficient for pore formation. The porosity of the samples prepared in this study was 35% at 0.1 MPa and 30% at 0.6 MPa. The porosity was higher than that of samples prepared by the unidirectional solidification method. The porosity did not depend on the total pressure either. The porosity decreased as the total pressure increased. Pressure is transmitted to the solid-liquid interface via the liquid phase, causing the pressure inside the pores to increase, which results in a decrease in pore size. As the hydrogen partial pressure increased, the thickness of the non-porous layer formed during the early stages of solidification increased slightly. The time required to reach a hydrogen concentration sufficient for pore formation at the solid-liquid interface increases as the hydrogen partial pressure decreases.

Keywords: Rapid Solidification, Cylindrical Pores, Pressurized Hydrogen Atmosphere.

1. INTRODUCTION

Shrinkage cavity formed during the casting of molten metal directly affect the quality of the casting [1]. In metal cavity technology, the formation of shrinkage cavities is a major problem. The formation of shrinkage cavity occurs not only in metals but also during the solidification of oxides such as fused alumina [2]. It has long been known that shrinkage cavities are formed by the volume reduction of metal during solidification, as well as by the release of gases entrapped in the molten metal or precipitated during solidification [3]. Similarly, it has been reported that shrinkage cavity form during the production of fused alumina due to volume reduction and the release of gaseous components, particularly water vapor, dissolved in the melt as it solidifies [4]. To elucidate the mechanism of shrinkage cavity formation during the solidification of oxides, it is useful to investigate the formation of pores caused by each type of dissolved gas.

Nakajima performed unidirectional solidification of various metals in a pressurized hydrogen gas environment and elucidated the mechanism by which numerous fine cylindrical pores form during the solidification [5]. When fine and uniform size pores with directionally align in one direction, they can form a porous material that does not exhibit a decrease in specific strength. In the field of metallurgy, the formation of shrinkage cavities is a major issue. Therefore, the solubility of hydrogen gas in both solid and molten metals has been compiled into a fundamental database [6]. The dissolution of hydrogen

gas in solid metal phase and molten metal phase follows the Sieverts' law. Since the solubility of hydrogen in the liquid phase is more than 100 times greater than that in the solid phase, excess hydrogen gas is released during solidification at the melting point. In general, oxide ceramics are manufactured using sintering process rather than casting. To date, very little research has been conducted on the dissolution of hydrogen gas in molten oxides. Ueno *et al.* conducted unidirectional solidification experiments on several oxides under pressurized hydrogen gas and suggested that oxides also form numerous fine cylindrical pores as same as metals [7]. In the unidirectional solidification experiments, the solidification rate is maintained at a constant rate of approximately 100 mm/h. The pores form during solidification in oxides through the same mechanism as in metals.

The mechanism of pore formation under steady-state conditions at a constant solidification rate has now been clarified. In the case of metals, shrinkage cavities formed during the casting process can cause irregularities on the surface of the casting. On the other hand, even when shrinkage cavities form, the surface of the casting may remain smooth. If shrinkage cavities form very close to the surface, it is likely that the cast surface will become uneven. In other words, it can be inferred that the location where shrinkage cavities begin to form varies depending on the casting conditions. To clarify the relationship between the formation of shrinkage cavities and solidification conditions. In this study, rapid solidification experiments for alumina in pressurized hydrogen gas was conducted and the mechanisms of pore formation and pore growth during the early stages of solidification was discussed.

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2. EXPERIMENTAND METHODS

Sintered alumina rod with a diameter of 6 mm (commercially available alumina rod with 99.7% purity) were used as feed rod. The samples were melted using a light focusing floating-zone apparatus. A xenon lamp was positioned at one of the two focal points within the elliptical mirror and the sample was melted at the other focal point. The feed rod was heated and melted by light focusing. Once the alumina sample began to melt, the rod slowly lowered to let the droplet fall. The droplets were dropped onto a copper dish positioned 23 cm below to produce rapidly solidified sample. The solidification experiments were conducted in 100% H₂ gas and 50% H₂-Ar gas. The total pressure was set between 0.1 and 0.6 MPa. The porosity and pore size of the solidified samples were calculated from SEM images. Porosity and relative pore diameter were measured at a position 100 μm above the bottom of the sample (the contact surface in contact with the copper dish). Assuming that the pores at this location are cylindrical in shape and uniformly distributed, the relative pore diameter was calculated using the following equation.

$$d=(4/\pi)\mu \tag{1}$$

Here, μ represents the average pore diameter derived from the image.

3. RESULTS AND DISCUSSION

Figure 1 shows the external view of the rapidly solidified sample produced under a pressurized hydrogen atmosphere. As an example, a sample rapidly solidified under a 0.4 MPa 100% H₂ atmosphere was presented. In all samples, a splash-shaped solidified sample was obtained. As indicated by the arrow, sand-like wrinkles were observed at a location away from the center of the sample.

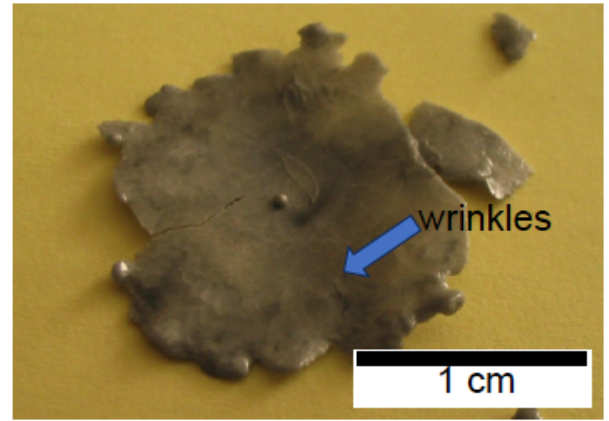


Figure 1: External view of the rapidly solidified sample.

Nagashio *et al.* conducted rapid solidification experiments on the YAG phase using an electromagnetic levitation device [8]. It has been observed that when molten YAG lands on a copper dish, it initially spreads out into a film-like layer but then, due to surface tension, flows back toward the center. Since the solidification of the molten oxide, which has been drawn toward the center by surface tension, occurs sequentially, it is believed that the solidification proceeds in several stages. It is believed that the sand-like wrinkles observed in areas distant from the center of the film were caused by solidification proceeding in several stages.

Figure 2 shows a cross-section view of the rapidly solidified sample obtained under a pressurized 100% hydrogen atmosphere. The figure shows samples 0.1 and 0.4 MPa. A non-porous layer formed on all samples up to a height of approximately 50 μm from the contact surface. As the total pressure increased, it was observed that the thickness of the non-porous layer decreased slightly and the number of nucleation sites for pore formation increased. It is believed that the non-porous layer forms because there are insufficient

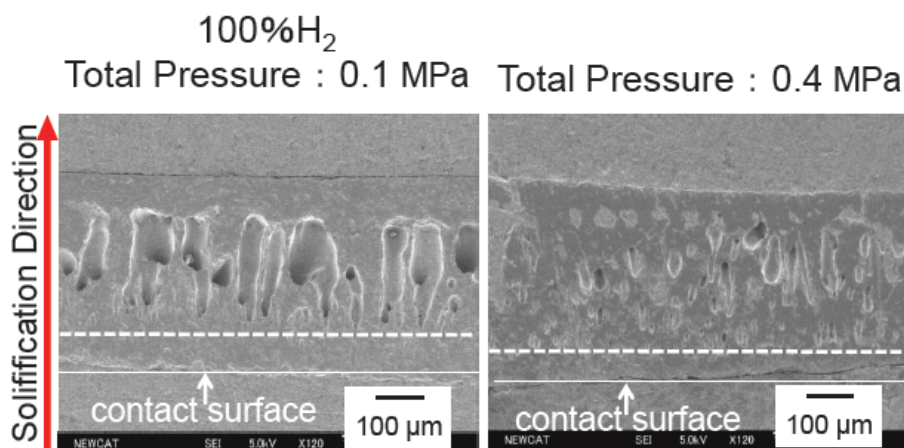


Figure 2: Cross-section image of the solidified samples prepared in 100%H₂.

hydrogen atoms on the solid phase at solid-liquid interface to initiate pore nucleation. For comparison, Figure 3 shows a cross-section of a sample rapidly solidified in argon atmosphere. When solidified in argon, no pores formed. Therefore, it can be seen that the pores shown in Figure 2 are formed by solidification in pressurized hydrogen gas. When alumina is solidified unidirectionally in pressurized hydrogen atmosphere, cylindrical pores are formed [7]. Hydrogen gas dissolves in the molten alumina and the excess hydrogen that does not dissolve in the solid phase is released during solidification. It is believed that much of the hydrogen is released into the liquid phase as a gas [5]. At the solid-liquid interface, the temperature of the solid phase is higher than that of the liquid phase. It is believed that the small amount of hydrogen atoms that can dissolve in the solid phase diffuse through the solid phase during the solidification process, forming cylindrical pores [5]. Since the pores shown in Figure 2 also extend in the solidification direction, it is reasonable to apply a model in which hydrogen atoms incorporated into the solid phase just below the melting point aggregate through diffusion to form pores.

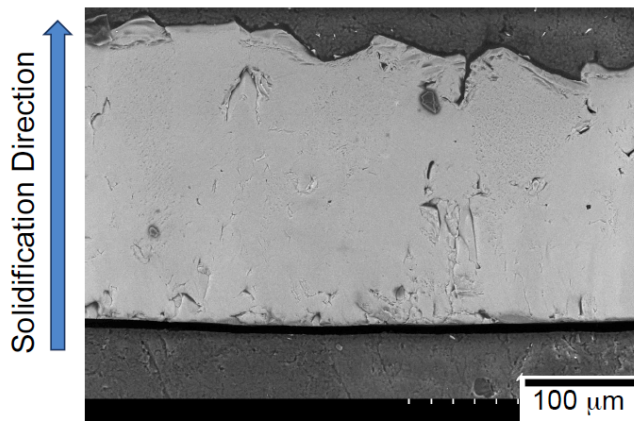


Figure 3: Cross-section image of the solidified samples prepared in Ar atmosphere.

Figure 4 shows a cross-section of the area where sand-like wrinkles were observed. It was observed that oxide melt pulled back by surface tension covered the film that had solidified under rapid solidification condition. The oxide melts subsequently solidified. No pores formed in the solidified film that solidified in the second stage. It has been reported that when a molten metal containing dissolved hydrogen gas is solidified at a slow rate, the excess hydrogen gas is released from the molten metal in the form of bubbles, thereby preventing the formation of porosity. Because alumina has low thermal conductivity, the solidification rate during the second stage was slower than during the first stage and it is believed that no pores were formed.

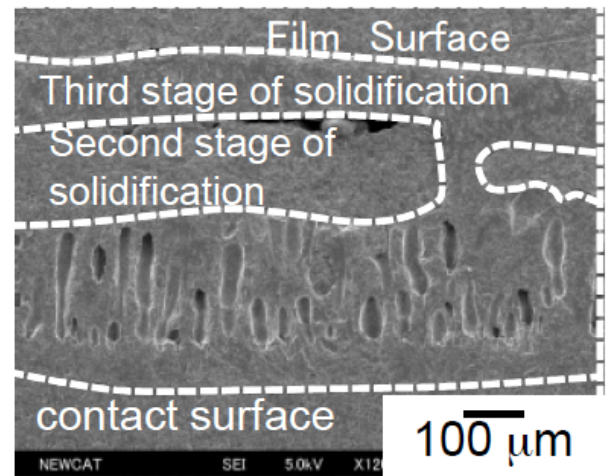


Figure 4: Cross-section view of the area where sand-like wrinkle.

Samples rapidly solidified in a 50% hydrogen-argon gas atmosphere also produced a splash-like solidified film. Figure 5 shows an SEM image of the cross-section of the solidified film. A non-porous layer approximately 100 μm thick was formed. The non-porous layer became thicker than when solidified in a 100% hydrogen atmosphere. It is believed that the non-porous layer became thicker because it took time to reach a sufficient amount of hydrogen to form pores.

Figure 6 shows porosity of the solidified sample. The porosity was determined 100 μm above the contact surface. In this position, the pores extending in one direction are uniformly distributed. The porosity of samples prepared in 100% H_2 decreased in inverse proportion to the total pressure. It has been reported that the porosity of porous alumina prepared by the unidirectional solidification method in pressurized hydrogen gas is 35% at a total pressure of 0.1 MPa and 30% at 0.8 MPa [7]. The porosity of the samples prepared in this study was 35% at 0.1 MPa and 30% at 0.6 MPa. The porosity was higher than that of samples prepared using the unidirectional solidification method. In rapid solidification, it is believed that the porosity increased because gases that would normally be released into the liquid phase were instead incorporated into the solid phase. However, much of the excess hydrogen gas which corresponds to the difference in gas solubility between the solid and liquid phases at melting point is released as gas at the melting point. Thereby pores are formed during the solidification process. Figure 7 shows a schematic diagram of the pore formation mechanism. External total pressure is transmitted to the pores through the liquid phase. It is believed that porosity decreases as total pressure increases, in accordance with Boyle's law. In contrast, the porosity of the samples prepared in 50% H_2 remained unchanged with respect to total pressure. This is believed to be due to the decrease in

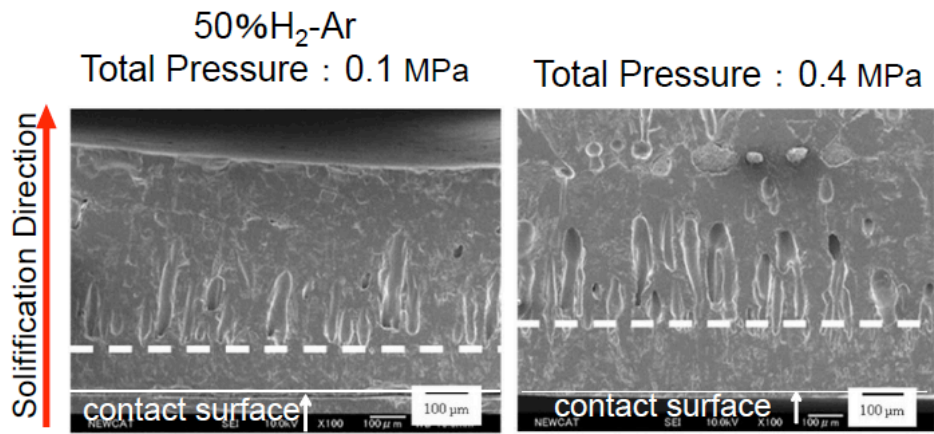


Figure 5: Cross-section image of the solidified samples prepared in 50%H₂-Ar.

porosity when the total pressure is low. When the total pressure is low, the internal pressure of the pores formed at the solid-liquid interface also decreases and causing the pores to become larger. As the pore diameter increases, the radius of curvature of the pore at the gas-liquid interface decreases and making it easier for the gas to be released into the liquid phase as a bubble, as shown in Figure 7.

It is believed that the low porosity of the samples prepared at 0.1 MPa in 50% H₂ environment is due to the gas being released as bubbles due to buoyancy. The relative pore sizes of the solidified samples calculated by equation (1) are shown in Figure 8. As total pressure increases, the pressure inside the pores also increases and causing the pore diameter to decrease. Whether the hydrogen partial pressure is 100% or 50%, it can be said that there was a sufficient amount of hydrogen to form pores. In the rapid solidification process, some of the hydrogen gas released into the liquid phase is incorporated into the solid phase, resulting in higher porosity and greater variation in pore size. The following points have been noted regarding metal casting. When the concentration of certain components reaches a certain level during the early stages of solidification [9]. In unidirectional solidification under pressurized hydrogen, cylindrical pores form at steady state [5]. Applying the theory of

micro-structure formation during the early stages of the solidification leads to the following interpretation. It is believed that hydrogen atoms left behind into the solid phase diffuse through the solid phase at the solid-liquid interface and aggregate. Once a certain concentration is reached, pores are formed. Since the temperature of the solid phase is always higher the liquid phase at the solid-liquid interface, this reasoning is valid. In this rapid solidification study, it is believed that the porosity increased because a portion of the large amount of hydrogen gas released into the liquid phase remained in the solid phase.

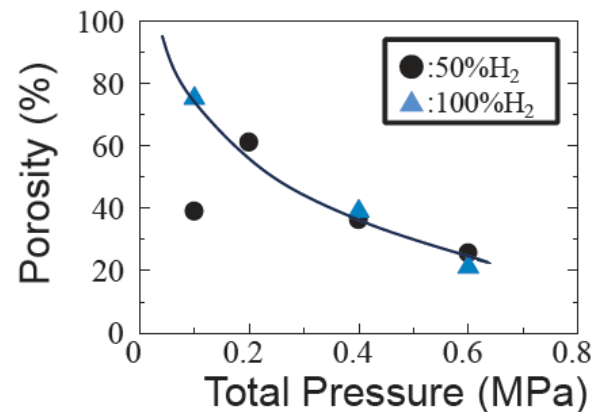


Figure 6: Porosity of the samples.

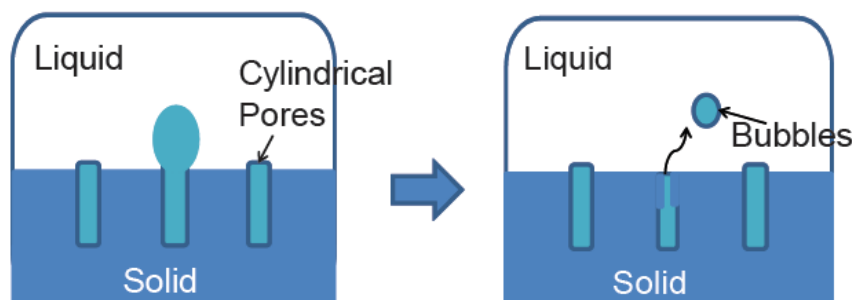


Figure 7: A schematic diagram of the pore formation mechanism.

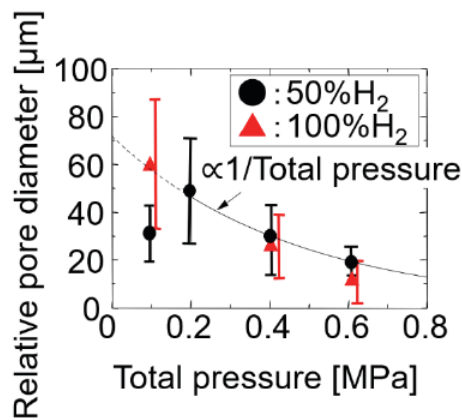


Figure 8: Average pore size of the samples.

4. CONCLUSION

The rapid solidification was performed for alumina under pressurized hydrogen atmosphere. The following has been identified as the mechanism of pore formation during the early stages of solidification. Under rapid solidification conditions, the porosity was higher than that of the porous material prepared by unidirectional solidification. The results suggest that some of the bubbles that should be released into the liquid phase remain in the solid phase. A non-porous layer forms until pore nuclei are established. When the hydrogen atom concentration C_H on the solid phase side of the solid-liquid interface exceeds a certain value C_H pores form. The thickness of the non-porous layer decreases as the partial pressure of hydrogen decreases. As the partial pressure of hydrogen increases, the concentration of hydrogen atoms quickly reaches C_H causing the non-porous layer to become thinner. Total pressure is transmitted to the pores through the liquid phase. As total pressure increases, it was concluded that the pore diameter decreased in accordance with Boyle's law.

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CONFLICTS OF INTEREST

The author declared no conflicts of interest.

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