Journal of Ceramic Processing Research. Vol. 6, No. 2, pp. 129~133 (2005)

J O U R N A L O F
Ceramic Processing Research

Floating zone growth of calcium aluminate ($Ca_{12}Al_{14}O_{33}$)

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Abundance of oxygen radicals residing in the cage-like lattice framework of calcium aluminate makes the growth of good quality single crystal difficult. Oxygen bubbles easily get trapped inside the crystal making the optical properties of the crystal inferior. In this study, we have investigated the behavior of oxygen bubbles inside the molten-zone during a conventional floating-zone growth. We have investigated the effect of different feed preparation process on the quality of the grown crystals and found that subsequent quenching of the feed from 900 °C after calcination at 1200 °C significantly reduces the bubbles in the crystal. Secondly we have performed floating-zone growth of C12A7 under a high magnetic field (up to 8T). We think that each of the bubbles become a small piece of magnet under the magnetic effect and repel each other in the molten zone. As a result we observed significant stabilization of the molten zone through early removal, and a reduction of accumulation of the bubbles.

Key words: Calcium aluminate, Superconducting magnet, Magnetic field, Floating zone technique.

Introduction

The recent discoveries of technologically important phenomena such as a persistent electronic conduction by light illumination, emission of high-density O^- ions by applying a dc-voltage, behavior as a thermally and chemically stable electride, etc., have drawn significant interest to the material of calcium aluminate ($Ca_{12}Al_{14}O_{33}$; 12CaO7Al_2O_3; C12A7) [1, 2]. Stoichiometric C12A7 consists of positive-charged $[Ca_{24}Al_{28}O_{64}]^{4+}$ and two O^{2-} ions. The cation part is a network of 12 cages each having a free-space ~0.04 nm in diameter whereas the O^{2-} anions are accommodated in the cages and bound loosely in a way that they can move freely through the channels [3]. This characteristic makes it easy to replace the incumbent oxygen and is the main reason for the discovery of the above phenomena. A large amount of active oxygen species such as O^- and O^{2-}, hydride ions (H^-) and electron anions (e^-) can be trapped stably inside the cages by annealing in oxygen gas, in hydrogen gas and in a vacuum, respectively [4]. O^-- and O_2^--entrapped C12A7 has unique characteristics, such as antibacterial effects and a strong oxidation effect on hydrocarbons [5]. H^--entrapped C12A7 is converted from an insulator to an electrical conductor by illuminating with ultraviolet light and is expected to be applicable in direct optical writing of conducting wires and formation of high-density optical memories [1]. On the other hand, e^--entrapped C12A7 where electrons are substituted for all of the anion sites is called an "electride", and is expected to be used as electrical conductors and injectors [3]. High quality single crystals of C12A7 would be a primary requirement for realization of these kinds of applications.

C12A7 melts congruently at 1415 °C in wet-air or oxygen and it is possible to grow single crystals from the melt. However, since C12A7 is highly reactive and often oxidizes the crucible materials such as Pt or Ir, single crystals of C12A7 grown by the Czochralski method turned to a pale yellow color using an iridium crucible [6]. Crystal growth has also been tried by zone-melting using electronic bombardment and by a floating-zone method using an infrared heating furnace [7, 8]. For the electronic bombardment method, there were depositions of $CaAl_2O_4$ inclusions. Furthermore, there was a volume expansion in the material when crystallizing from the melt, which would lead to cracks in the crystal if grown in a crucible. Therefore, as one of the crucible-free processes, infrared-heating FZ growth would be suitable to grow high quality C12A7 although a lot of gas bubbles were left trapped in the grown crystal which severely affected the quality of the crystal according to our previous report [8].

It turned out that the loose binding of the O^{2-} ions, that was favorable for important innovations, is actually the main obstacle when it comes to FZ growth of single crystal of the material itself. So to begin with, we tried to understand the behavior of the oxygen bubbles in the molten-zone during FZ growth. Two different processes to reduce or completely remove oxygen bubbles from the crystal were investigated. Since the removal of highly reactive oxygen radicals

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Table 1. Various conditions of feed preparation

Run Number	1	2	3	4	5	6
1st Calcination (°C)/atmosphere	1000/O_2	1200/O_2	1000/O_2	1000/O_2	1000/O_2	1000/O_2
2nd Calcination (°C)/atmosphere	1000/O_2	1250/Ar	1000/O_2	1200O_2	1200O_2	1200O_2
Quenching (°C)	-	-	-	-	900	900
Sintering/atmosphere	1250/O_2	1250/Ar	-	-	-	-
Growth atmosphere (MPa)	O_2/0.1	O_2/0.1	O_2/0.1	O_2/0.1	O_2/0.1	N_2/0.1

from the feed powder could help to reduce oxygen bubbles during crystal growth, we systematically investigated the optimum conditions for feed powder preparation, which might help reduce excess oxygen radicals, and observed the effect in the grown crystal. Secondly, we have also studied the effect of a magnetic field up to 8T during FZ growth.

Experimental Procedure

$CaCO_3$ and γ-Al_2O_3 powders were mixed in the stoichiometric ratio and calcined twice for 5 hours, systematically varying the calcination temperatures and atmospheres each time. The conditions of the two calcinations for each material synthesis are given in Table 1. Apart from the different calcination temperatures the main difference is some nutrient C12A7 powder was quenched from 900 °C to room temperature during furnace cooling of the second calcination. The C12A7 powder was then well-pulverized, put in a rubber tube and pressed under a hydrostatic pressure of 300 MPa to give the shape of a rod. The pressed rod was sintered at 1200 °C, under oxygen, argon or nitrogen atmospheres depending on the situation.

A four-ellipsoidal-mirror-type infrared heating furnace with 1.5 kW halogen lamps (Crystal Systems Inc, model FZ-T-10000-H-TY-1) was used for the crystal growth. The growth rate was 3 mm/h and the atmosphere was varied from flowing 0.8 l/minute of oxygen to argon or nitrogen.

For FZ growth of crystals under a high magnetic field, we have designed a prototype infrared heating furnace with a helium-free superconducting magnet with a maximum magnetic field of 10 T. The absolute values of the magnetic force are a maximum at the high (A) and the low (C) positions in Fig. 1, which are 150 mm apart from the center of the magnet-bore. At the high position (A) in Fig. 1, the direction of the magnetic force for paramagnetic materials, such as oxygen gas, is downward. On the other hand, the direction is upward at the low position ((C) in Fig. 1). As it is expected that the lower position growth is more favorable for removing oxygen bubbles, C12A7 crystals were grown mainly at the low (C) position. For comparison, crystals were also grown at the center (B) and high (A) positions. For all experiments growth conditions were fixed at a growth rate of 3 mm/h, 0.8 l/minute of oxygen flow, and no rotation of the lower shaft in order to suppress the forced convection. The feed rods which hung from the upper shaft were rotated less than 10 rpm during the crystal growth. The applied magnetic fields were varied from 1 to 8 Tesla.

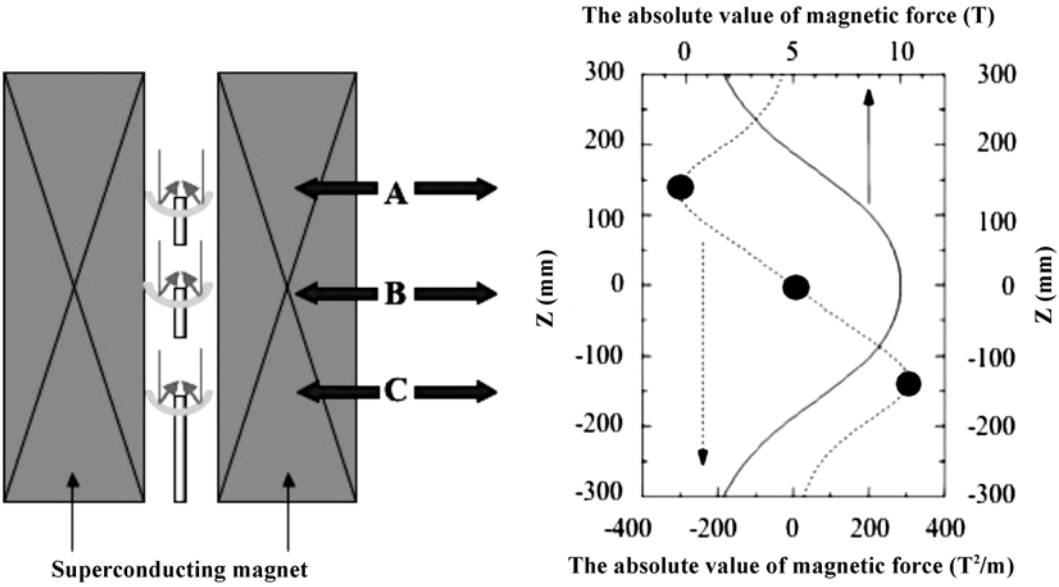

Fig. 1. Schematic of growth stage along direction of magnetic force; (A) high position, downward magnetic force is a maximum on an oxygen bubble(B) center of superconducting magnet, (C) low position, upward magnetic force is a maximum.

Results and Discussion

It was observed that C12A7 entraps O^- and O_2^- from the atmosphere below about 700 °C [4]. The oxygen radicals entrapped during the calcinations make the powder oxygen-excess, which in turn leads to plenty of oxygen bubbles trapped in the grown crystals. The objective of trying different calcination conditions were to keep the entrapment of oxygen radicals limited during the powder-preparation process. We observed that, when the nutrient powder which was quenched from about 900 °C after calcination at 1200 °C was used for feed-rod formations, gas bubbles decreased remarkably in the growth crystals. Crystals grown using feed with and without quenching after the second calcinations are shown in Fig. 2. They are generally opaque and whitened because of bubbles trapped inside of the crystal. Un-sintered feed rods were used for the crystal growth since sintering leads to cracks and distortion in the shape due to rapid absorption of O^- and O^{2-} around 700 °C. However, the diameter of the grown crystal became non-uniform periodically, because of the bubbles naturally generated inside the molten solution. These bubbles accumulate to a bigger bubble and burst out of the melt, which made the zone unstable. According to the growth experiments in different atmospheres, we believe that the atmosphere during the FZ growth also plays a role in removing the oxygen bubble from the melt (Fig. 2(b), (c)). The oxygen coming from the melt was not so reactive under a low oxygen partial pressure (N_2 atmosphere, Fig. 2(c)); they remained tiny and easily got trapped while the bubbles generated inside the melt accumulated and got big enough to burst out

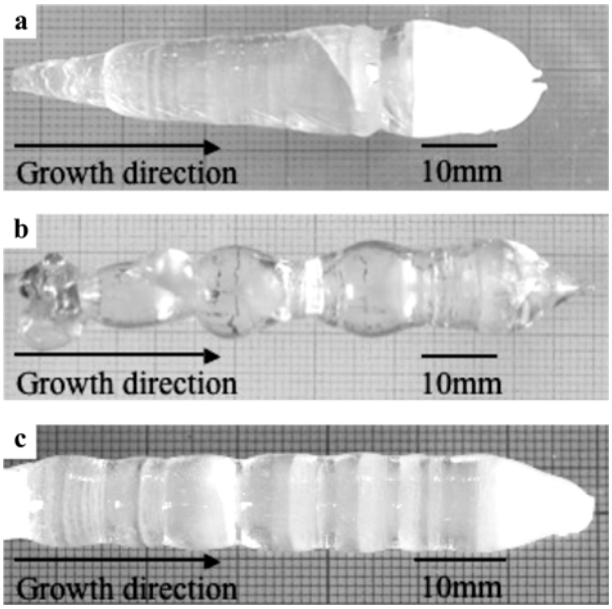

Fig. 2. Single crystals grown under various conditions; (a) sintered feed rod and an oxygen atmosphere, (b) unsintered feed rod and an oxygen atmosphere, (c) unsintered feed rod and a nitrogen atmosphere.

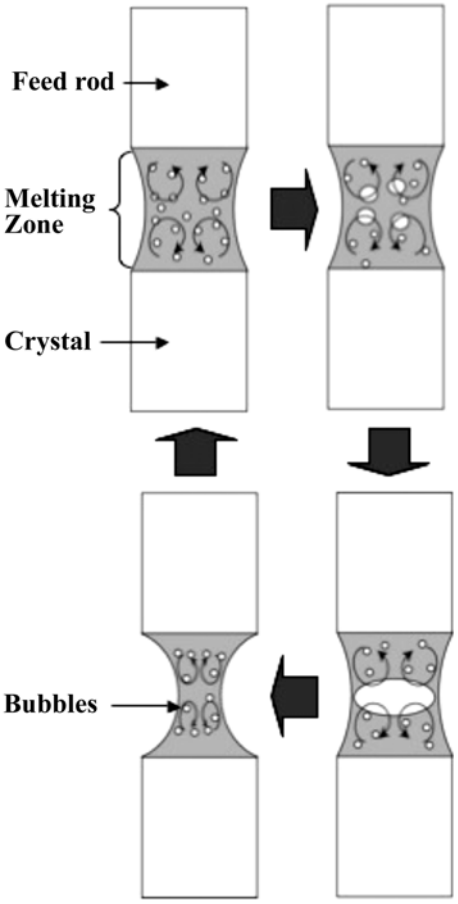

Fig. 3. Schematic illustration of the behavior of oxygen bubbles in the melt during conventional FZ growth.

of the side of the melt under an oxygen atmosphere (Fig. 2(b)). Figure 3 shows an illustration of the bubble behavior inside the melt during growth under oxygen flow. We think that the oxygen atmosphere actually enhanced the reaction with oxygen radicals in the cage and helped them accumulate.

Figure 4 shows C12A7 single crystals grown by the FZ method under high magnetic field. We observed that the accumulation of the bubbles was suppressed, and the molten-zone was stable during growth. When the magnetic field was increased, the growth stage became more stabilized by limiting the size of the bubbles. This phenomenon can be explained as the effect of act as a strong magnetic field, which induced each of the paramagnetic oxygen bubbles to small piece of magnet that repelled each other and suppressed accumulation. Figure 5 shows an illustration of the behavior of bubbles grown in different positions. We observed that the crystals grown in the upper position (Fig. 4(A)) has dense cracks near the surface. It is possible that the magnetic field attracted the bubbles downwards and the bubbles occasionally trapped at the periphery of the crystals causing cracks. For growth in the center position, although the molten-zone remained stable throughout, fine bubbles remained un-

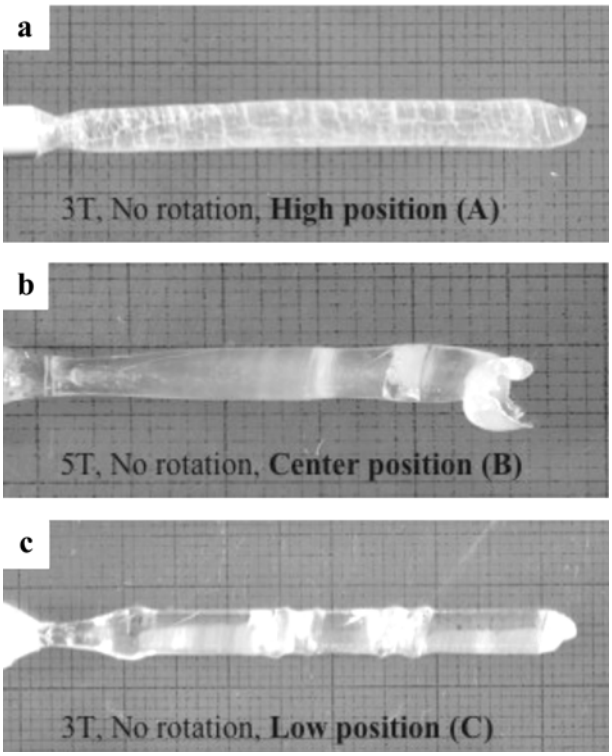

Fig. 4. Single crystals grown under magnetic field; (a) 3 T at the high position, and (b) 5 T at the center position, and (c) 3 T at the low position.

accumulated and distributed almost uniformly in the crystal as shown in Fig. 4(B). During FZ growth in the lower (C) position, bubbles moved upwards and accumulated up to a critical diameter of about 100 μm and floated out of the melt, whereas oxygen bubbles of a smaller size of a few to 40 μm in diameter behaved in a different way. These smaller bubbles were segregated in the melt and made the grown crystals half transparent and half opaque as shown in Fig. 4(C). Figure 6 shows cross-sections of crystals grown in the lower position under different magnetic fields. We observe that a higher magnetic field reduces the bubble

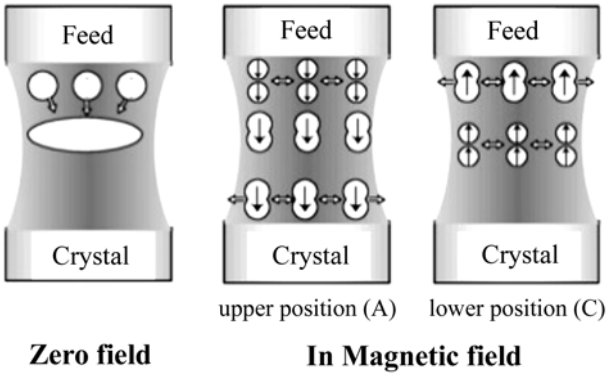

Fig. 5. Schematic illustration of behavior of bubbles in the melt without magnetic field (left), and under a magnetic field; high position (middle) and low position (right).

concentration in the non-transparent part of the crystal significantly; in addition, the transparent part of the crystal was almost free of defects.

Summary

We have optimized the feed preparation process and found that quenching of powder from 900 °C after calcination in order to prevent oxygen radicals from trapping in the nutrient powder and making it oxygen excessive is advantageous. We also observed that in an oxygen atmosphere during FZ growth bubbles generated in the melt accumulate and burst out of it. Although gas bubbles are mostly removed from the melt by this process, it also makes the molten-zone unstable and crystal non-uniform in shape. In FZ growth under a high magnetic field, we observed that the size of the bubbles remained limited due to suppression of accumulation were and retained in a stable state in the molten zone. We believe that paramagnetic oxygen bubbles in melts under strong magnetic fields act like small pieces of magnet and repel each other and give rise to different interesting phenomena.

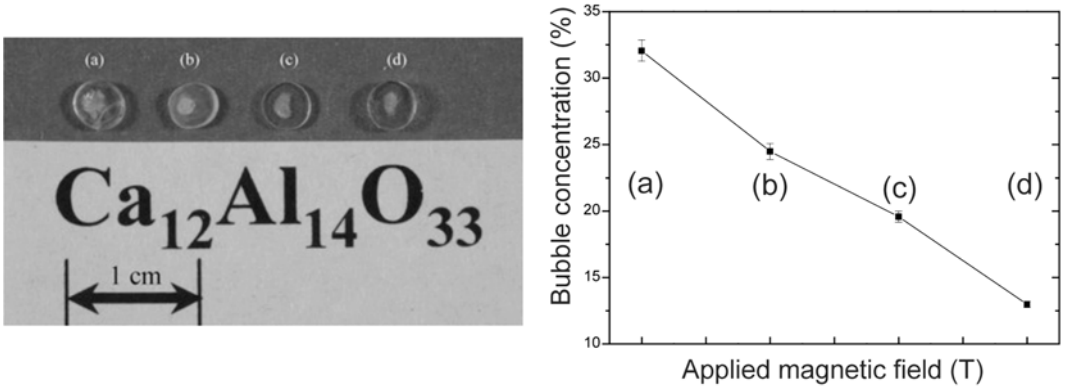

Fig. 6. Cross-section images of crystals grown at the low position under (a) 1 T, (b) 3 T, (c) 5 T, and (d) 8 T (left). This shows a reduction of bubble density with increasing magnetic fields (right).

Acknowledgements

This work was supported in part by the Grant-in-Aid for Creative Scientific Research (No.16GS0205) from the Japanese Ministry of Education, Culture, Sports, Science and Technology, and the Grant-in-Aid for Scientific Research (A) of Japan Society for the Promotion of Science. IT was supported by Sumitomo Foundation and Asahi Glass Foundation.

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