The behaviour of the internal gas-bubbles during the annealing process of the CaF_2 crystals

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1. Introduction

In the single crystal growth from the melts, if the growth process starts before the stabilization of the melts and/or the growth rate is faster than the optimum condition, the growing crystal tends to become a polycrystal. This failure to single crystals would be involved more or less in the internal impurities or the gaseous phases, which have no enough time to escape from the growing interface, present in the melts. This paper presents the behaviour of the internal gas-bubbles in the CaF_2 crystal during the annealing process.

2. Experimental process

The experimental specimen was the CaF_2 crystal, which were grown by the non-seeded Bridgman technique, with three differently oriented grains. The growth direction of a centered grain was the <553> orientation. As-grown CaF_2 crystal was annealed at 800℃ for 10 hours using a graphite felt. After the annealing process the CaF_2 crystal revealed the internal scattering defects, which was not observed before the annealing process, on the grain boundary planes. Figure 1 shows the schematic diagram of the sliced section of the grown CaF_2 crystal with three grain boundary(GB) planes(A, B and C).

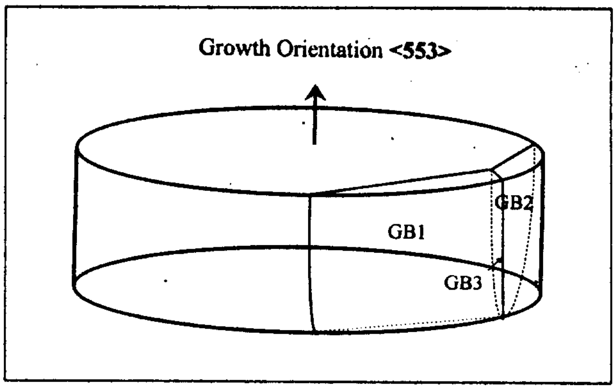

Fig. 1 The sliced section of the CaF_2 crystal grown.

3. Experimental results

Figure 2 is a optical micrograph (using a reflection and transmission mode) of the polished surface of the crystal, which was taken by the succession of the in-focus and out-focus technique. The internally scattering defects are seen to be arranged with the needle-shape along the GB planes from the GB triple junction. The density of the defects decreased with the distance from the GB planes. Figure 3 shows the internal features observed in the right direction of the GB plane.

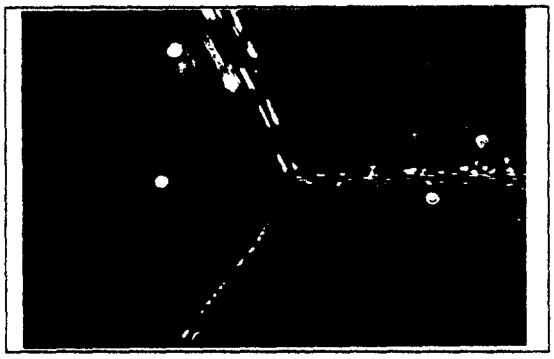

Fig. 2 Optical micrograph of the needle-shaped internal scattering defects (on the growth direction).

Fig. 3 Optical micrograph of the V-shaped scattering defects (on the GB planes).

The major features of the defects revealed are as follows;

i) The scattering defects are V-shaped and about 50μm in size.
ii) The corner of the V-shaped are head on to the opposite direction of the GB triple junction.
iii) The inner angles of the V-shaped are about 120 ° with a particular orientation.

A SEM image of the cleaved surface along the GB plane revealed the detailed structure of the defects (see Figure 4). These V-shaped hollow defects are seen to be arranged to the particular orientation on the particular plane (near to the GB plane). The EDS analysis on the region of the inner wall of the hollow defects did not show any other peak than Ca element, indicating that these defects would be the voids rather than the precipitates involved with impurities.

In order to examine the microstructure of the inner wall the AFM (Atomic Force Microscopy) was employed. Figure 5 shows that the inner wall of these defects composes of the directionally wrinkled and concave lines. This analytical results support to the expectation by the SEM analysis that the defects would be voids rather than any precipitated phases. It also is possible the explanation that the movement of the defects was not proceeded smoothly because of the collision between the driving force and the activation energy for escape from the melts. This explanation would be possible on the basis of the negative grain growth mechanism induced by the S-surface.

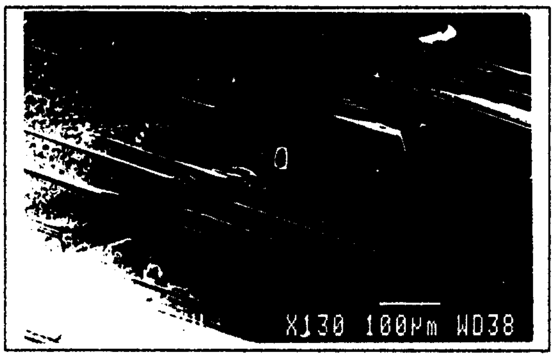

***Fig. 4** SEM of the scattering defects showing the V-shaped hollow feature.*

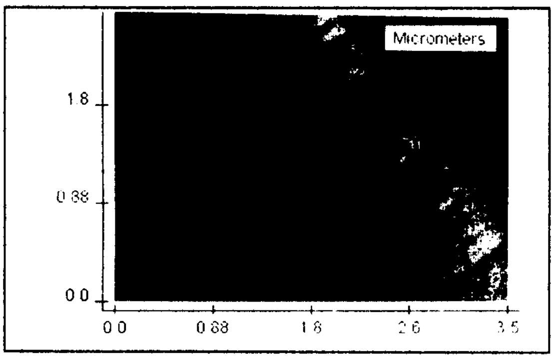

***Fig. 5** AFM of the scattering defects showing the feature of the directionally wrinkled and concave lines.*

The exact orientations determined by back-reflection X-ray Laue method confirmed that the GB plane is parallel to the {111} plane and the tips of the V-shaped defects head along toward the <110> direction with the inner angle of 120°. This results make the explanation possible that the defects were accumulated on the closed packed {111} plane during the crystal growth and their movements tend to be on the <110> direction during the annealing process. This phenomena is very similar to the behaviour of the dislocation during the slip process because the combination {111}<110> is the most common slip system of the cubic structure like CaF_2 crystal.

4. Conclusions

The gas-bubbles present in the CaF_2 crystal accumulates on the close-packed {111} planes during the growth process and tend to be oriented to the easy moving direction <110> on the plane during the annealing process and therefore it could be concluded that the behaviour of the impurities or voids present in crystals depends on the crystallographic orientation of the material like a slip process.