

Marangoni Convection Effects on Crystal Growth

S. M. Kang, J. K. Choi* and K. K. Orr

Department of Inorganic Materials Engineering,
Hanyang University, Seoul, 133-791, KOREA

*Bokwang Co. Ltd., 130 Gongdan-dong,
Kumi, Kyeong-Buk, 730-030, KOREA

결정 성장에서 Marangoni 대류의 영향

강승민, 최종건*, 오근호

한양대학교 무기재료공학과, 서울, 133-791

*(주) 보광, 경북, 730-030

ABSTRACT

When a crystal is grown by FZ process, the melt zone is located at between the solid of upper and lower side and is kept by the solid-liquid interface tension. On the surface of the melt zone, a surface tension gradient is occurred by the difference of temperature and solute concentration, it is the driving force of marangoni flow. The crystal even in the steady state growth can become imperfect for the dislocation distribution and the solute concentration in the peripheral region of the crystal are higher than those in the inner part and the probability of the formation of the defects such as voids, bubble penetration, secondary phase creation and crack is high near the solid-liquid interface. This is because the solid-liquid interface becomes irregular because of the local variation of temperature in that region due to marangoni convection.

요 약

FZ법에 의한 결정성장에 있어서 용융대는 고액 계면의 장력에 의해 유지되고 상·하부의 고체분 사이에 위치하고 있다. 따라서, 용융대의 표면에서는 온도와 농도 차이에 의해 표면장력의 구배가 발생하고 이는 marangoni 대류의 구동력으로 작용한다.

본 연구에서 정상상태의 결정성장시는 결정의 가장자리 영역에서의 Solute 농도는 결정내부 보다도 높아지게 되고 전위의 분포도 불규칙하여지며, void나 기포 침투, Secondary phase의 생성 및 미소균열등의 결함 발생 확률이 계면부근에서 높아지는 결과를 알 수 있었다. 이는 고액성장 계면

이 marangoni 대류에 의하여 이 영역에서 온도의 국부적인 변동에 의해 불규칙하여 지게 되기 때문이라 사료된다.

Since marangoni flow was reported by C. Marangoni in 1865, detail researches have been done by Chang and Wilcox and some reports about melt behavior in the melt growth process have been reported with using the computer simulation[1-8]. The fact that surface tension gradient on the free melt surface give rise to form a marangoni flow is a starting point and surface tension forces can vary locally and can have tangential component in free liquid-gas interface due to temperature or concentrational gradient along this interfaces. The surface tension gradient forces the free interface to move and are a source of convection[9-11]. Then, in the Floating Zone process, since there is the free melt-gas interface and the temperature gradient of the order of 10 to 100 Kcm^{-1} along the interface which are maintained during the growth[12], we have to take account of the behavior of the melt in the liquid zone in which complex pattern of various convections such a thermal, centrifugal and marangoni convection exist.

The reason is that the marangoni flow affects the as-grown crystals' quality.

Marangoni flow, especially, is located at the peripheral region because the marangoni shear stress act as a driving force of that flow in the free melt surface. Fig. 1 shows the presentation of that situation. Marangoni shear stress is the function of surface tension and temperature gradient at the melt surface. Marangoni flow caused by this force has the motion of vortex shape near the growth interface and this is shown in Fig. 2 of the schemetic diagram of some flows in the melt zone. In Fig. 2, if the ro-

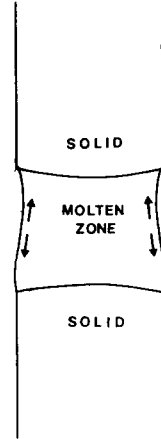


Fig. 1. The arrows represents the marangoni shear stress to which is caused in the free melt surface.

$$\tau_m = - \frac{d\delta(T)}{dT} \frac{dT(x)}{dx}$$

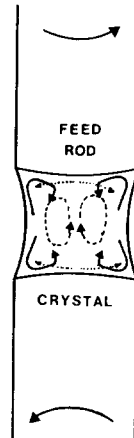


Fig. 2. Convections in the melt zone.

- > Marangoni convection
--> Forced convection
- - - -> Thermal convection

tation rate becomes high enough to keep the stability of the molten zone, marangoni vortex will be push out to the periphery[13].

The marangoni number is described as below.

$$Ma(T) = - \frac{\partial \delta}{\partial T} \frac{\Delta T_s L}{\eta D_T}$$

$$Ma(C) = - \frac{\partial \delta}{\partial T} \frac{\Delta T_s L}{\eta D_T}$$

They are dimensionless parameters to measure the dergee of marangoni convection, where D_T and D_C are thermal and solute diffusivities, $\partial \delta / \partial T$ is the temperature coefficient, L is a half zone length, η is dynamic viscosity, T_s is the gradient of temperature in the free surface of the melt. $Ma(T)$ and $Ma(C)$ notations are thermal and concentrational marangoni number respectively. In the above equation, it is understood that the temperature gradient at the melt surface and concentrational gradient in the melt are the factors to cause the marangoni flow.

In these flow affect the growing interface, heat and mass transfer across the boundary layer of the interface can be influenced due to the oscillation of the convections. Therefore if there is no fluid motion, heat and solute flow are occured by conduction and diffusion[14]. The equations are represented as follow.

$$D_T \nabla^2 T = \frac{\delta T}{\delta t} \quad D_C \nabla^2 C = \frac{\delta C}{\delta t}$$

where D_T and D_C are thermal and solute diffusivities in the relevant phases respectively and t is the time in second. These factors are all the function of temperature so in the practical growing situation, provided the local temperature gradient along the radial direction of the crystal, then heat and solute flow can be varied due to the thermal and concentrational

diffusivity variation. Through the YIG crystal growth, the solute concentration is increased with the radial direction and the peripheral region of the crystal has more high contents of the Al solute[15]. Fig. 3 represents the above mention and you can see the solute content fluctuated region. This is considered because the marangoni flow and forced convection is merging into a turbulent flow in that region. It is considered that these phenomena influence the gradient of the temperature and the concentration at the growth interface locally.

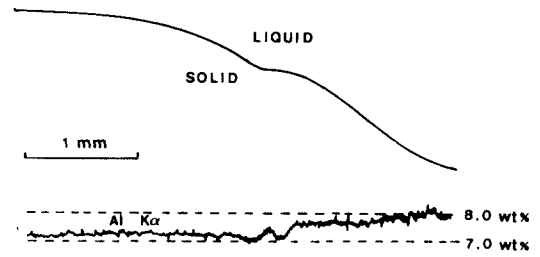


Fig. 3. Relationship between the shape of the interface due to the various convections in the melt zone and horizontal change of Al content in YIG.

In the steady state of the crystal growth, the heat transferred in a state of equilibrium from the melt across the interface is radiated from the crystal. In order to have the lowest energy state in the crystal-liquid interface, solute have a tendency to be caught in the site having lower energy state. This situation is shown at the region of periphery in the crystal as in Fig. 3.

In the present work, with the $YbFeCoO_4$ single crystal, the etching experiment was carried out and the etch pits distribution of the central and peripheral region of the crystal was investigated. The crystal was grown by FZ process

with the growth rate of 1 mm/hr and rotation rate of 30rpm with counter-rotation constantly.

As in Fig. 4, you can see the differences of the etch pits distribution in those parts. The reason of that is considered because the thermal fluctuation due to temperature variation caused by the marangoni flow is locally occurred in the peripheral region. So, the solid-liquid interface will be remelted repeatedly by it. A fact that the striations are observed with the irregular wave shape, also reflects the marangoni effect and can be shown in the case of YIG crystal experimented by Kimura et. al[16].

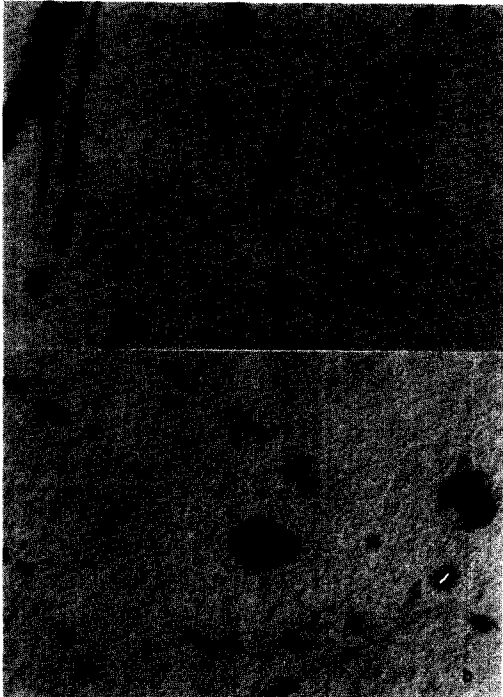


Fig. 4. The difference of the etch pits distribution between the peripheral region (marked as **a**) and inner region (marked as **b**) and in the YbFeCoO₄ single crystal.

Also, the growth rate is the function of growth temperature and K_{eff} , effective segregation coefficient. That is, the change of the growth rate influence the change of the degree of K_{eff} . When the growth rate is increased, K_{eff} is more than 1, then we can get the result as Fig. 3. K_{eff} can be defined as follows when the solute is a minor component,

$$K_{eff} = C_s / C_l$$

where C_s is the concentration of solute in a crystal and C_l is that in a melt. If the crystal have local difference of the growth temperature, then growth rate is varied with the temperature gradient in the radial direction. K_{eff} of a crystal growing at a steady state is given as a solution of the one-dimensional diffusion equation by

$$K_{eff} = k [k + (1 - k) \exp(-V\delta/D_l)]$$

where k is the interface segregation coefficient, V is the growth rate perpendicular to the interface, δ is the thickness of the diffusion boundary layer, and D_l is the diffusion coefficient of the solute in the melt[17]. As the above, in the peripheral region, the growth rate is more rapid and irregular than that in the central region and the atoms have a tendency to move to the fixed site having lower free energy. But, if the melt motion give an action of obstacles against the solute attitude, no solute has a steady state movement to their sites. Therefore, the irregular form of the growth interface shape can be appeared in the periphery region because of the remelting of the solute at the interface due to the various convections as in Fig. 5 and can provide the opportunity to create the secondary phase formation as in Fig. 6[18]. This problem is severe in obtaining the defect-free

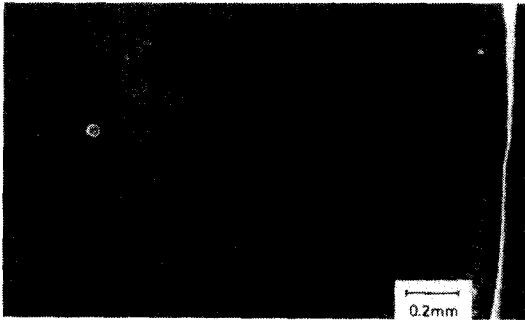


Fig. 5. Irregular interface shape viewed in the YIG crystal.

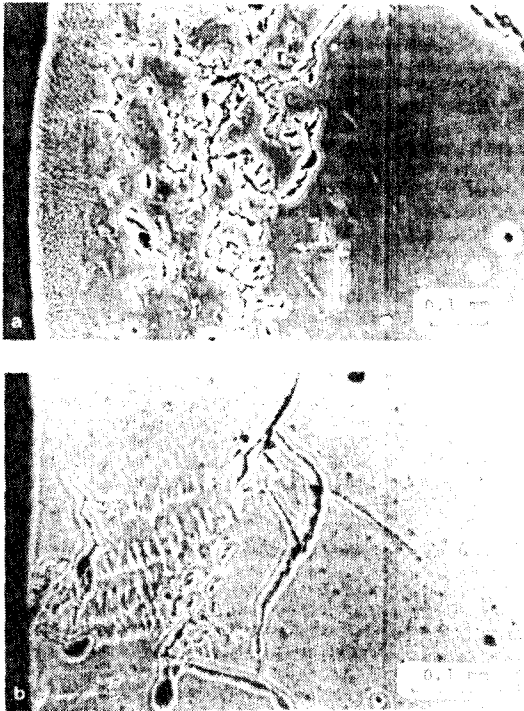


Fig. 6. Typical occurrence of secondary phases in YIG crystal

- (a) Cross section perpendicular to the growth direction,
- (b) Cross section parallel to the growth direction.

crystals of homogeneous composition, because the solute concentration is varied with the radial direction as mentioned before.

Consequently, it is realised that the crystal quality is depend on the interface morphology, the behavior of the atoms depended on the heat and mass transfer and the growth parameters such as growth rate, temperature gradient, rotation speed and etc. However these factors are so closed not only to the state of the melt zone stability but resulting temperature fluctuation in the FZ process that the variation of the surface tension force due to that influence the marangoni convection near the interface formation in the peripheral region. On the conclusion, due to the existance of the marangoni flow, it can influence the physical state of the growth interface and the quality of as-grown boules.

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