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# Tuning the sapphire EFG process to the growth of $Al_2O_3$/YAG/$ZrO_2$:Y eutectic

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ABSTRACT

In this work, a model is proposed, in order to analytically study the working point of the Edge defined Film-fed Growth (EFG) pulling of crystal plates. The model takes into account the heat equilibrium at the interface and the pressure equilibrium across the meniscus. It is validated on an industrial device dedicated to the pulling of sapphire ribbons. Then, the model is applied to pulling ceramic alloy plates, of the ternary eutectic $Al_2O_3$/YAG/$ZrO_2$:Y. This allowed understanding the experimental difficulties of pulling this new material and suggested improvements of the control software. From these results, pulling net shaped ceramic alloy plates was successful in the same industrial equipment as used for sapphire.


## 1. Introduction

The Edge-defined Film-fed Growth (EFG) technique allows growing shaped crystals directly from the melt, then avoiding post-machining operations that are costly and often generate defects in the crystal, including cracks. It has been applied to the massive production of silicon sheets for photovoltaic cells, ceramic eutectic rods and, above all, massive production of various sapphire shaped objects [1,2].

The $Al_2O_3$/YAG/$ZrO_2$:Y eutectic material is the object of active research as it has been shown to present a high toughness at temperatures close to the melting point, provided it is produced by solidification techniques. This is due to the specific eutectic structure of entangled $Al_2O_3$ and YAG single crystals, called “Chinese script”, with the additional constraining effect of the zirconia minority phase on the alumina phase, which prevents crack propagation [3,4]. Therefore, it is a very good candidate for application in equipment working at high temperature under severe mechanical constraints. The molar composition of this eutectic is 56% $Al_2O_3$/16% YAG/28% $ZrO_2$:Y and its melting point is 1720 °C.

With respect to its very high hardness, harder than sapphire, and comparable chemical composition, it has been tempting to grow this ceramic eutectic by the EFG process. Unfortunately, attempts to pull 3 mm thick plates directly from sapphire pulling equipment, crucibles and dies, have quickly shown that this material is much difficult to grow by this technique than sapphire. Several experiments evidenced that the operator is trapped between freezing the solid on the die and loss of sample cross section. However, direct use of sapphire pulling tools to ceramic pulling would be of great commercial interest for the production of these two materials in the same industrial plant. With such an objective, the working point of the EFG process should be specifically adapted to the ceramic eutectic case.

In practice, there are only two control parameters in the process:

- The pulling rate, usually imposed by a motor through a pulling shaft. It is kept as constant as possible, in agreement with the well-known crystal growth rule, that a constant growth rate gives better crystals, whatever “better” means for a particular material.
- The die top temperature usually measured by a pyrometer and controlled by adjusting the electrical power that heats the crucible. An important aspect is that, in practice, this temperature controls the height of liquid meniscus that separates the solid-liquid interface from the die top.

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**Nomenclature**

| | |
|---|---|
| $a$ | capillary constant |
| $\Delta h$ | distance between the crucible melt and the die top |
| $\Delta P$ | depression at the interface |
| $\Delta T$ | working overheating |
| $g$ | gravity acceleration |
| $grad_l T$ | temperature gradient in the liquid |
| $grad_s T$ | temperature gradient in the solid |
| $h$ | linear radiative transfer coefficient |
| $h_m$ | meniscus height |
| $k^2$ | ratio between the capillary canal section and the crystal section |
| $K_l$ | thermal conductivity in the liquid |
| $K_s$ | thermal conductivity in the solid |
| $l_f$ | capillary canal length |
| $L$ | crystal length |
| $L_s$ | latent heat of solidification |
| $e_c$ | crystal thickness |
| $e_d$ | die thickness |
| $e_f$ | capillary canal thickness |
| $r_c$ | meniscus horizontal radius of curvature |
| $r_m$ | meniscus vertical radius of curvature |
| $T$ | working temperature (temperature at the top of the die) |
| $T_0$ | shield temperature |
| $T_m$ | melting temperature |
| $U_{moy}$ | average Poiseuille flow velocity |
| $U_{max}$ | maximal Poiseuille flow velocity |
| $V$ | growth rate |

*Greek symbols*

| | |
|---|---|
| $\gamma$ | surface tension |
| $\varepsilon$ | emissivity |
| $\mu$ | viscosity |
| $\rho_l$ | density of the liquid |
| $\rho_s$ | density of the solid |
| $\sigma$ | Stefan Boltzmann constant |
| $\varphi_L$ | heat flux due to the latent heat release |
| $\varphi^l_{cond}$ | conductive heat flux in the meniscus |
| $\varphi^l_{rad}$ | heat flux radiated by the meniscus |
| $\varphi^s_{cond}$ | conductive heat flux in the crystal |
| $\psi$ | growth angle |

In a recent paper [5], we derived the equations linking these two experimental controlling parameters in order to study the process working point in the case of EFG growth of sapphire rods. The study was inspired by the seminal Chalmers's study [6] and its development by Théodore [7]. However, it was limited to cylindrical circular rods with the further hypothesis that the temperature was constant in the crystal cross section. Practically this corresponds to Biot numbers lower than 0.1, i.e., in the case of sapphire rods, a diameter smaller than 2.5 mm. The study was also lacking experimental validation.

In the present paper, the previous analysis is modified in order to study the case of thick plates pulled by the EFG process, without hypothesis on the temperature field in the crystal. Then the model results are compared to experimental data largely available from the industrial production of sapphire plates. Eventually, it is applied to the growth of the ternary ceramic eutectic plates.

## 2. Analytical model of the EFG working point for plate pulling

The objective is to derive a set of equations linking the pulling rate and the die temperature, for an expected plate thickness and given die dimensions. A first step is to relate the crystal thickness to the meniscus height. A second step is to relate the meniscus height to the die temperature and to the temperature gradient in the crystal, then to estimate this gradient. The nomenclature at the beginning of the paper gives a list of the used symbols.

The main hypotheses of the model are:

- An infinitely wide plate: end effects at the plate borders are neglected.
- The plate surface is vertical: growth occurs under stable conditions.
- An opaque solid. This is certainly true in the case of the eutectic ceramic but questionable in the case of sapphire, as it has been shown that crystal transparency should be taken into account for a correct simulation of Kyropoulos sapphire growth [8]. Surprisingly, it will be shown that the model agrees well with the experimental results, possibly, because the plate aspect ratio limits the effect of transparency on the heat transfer.
- Meniscus radius of curvature is constant. This is justified by the small meniscus height (less than 1 mm, see below) compared to the capillary length of sapphire (4.2 mm [9]).
- The growth rate is equal to the pulling rate, so that the solid-liquid interface remains at a constant distance from the die top.
- The meniscus is anchored on the external edge of the die ($k^2 < 1$).
- Physical properties do not depend on temperature: the model is restricted to the liquid meniscus and solid close to the interface, i.e. in a restricted temperature range.
- Cooling from the plate faces is mainly radiative, which is certainly the case for sapphire ($T_m$ = 2050 °C) and for the eutectic ceramic ($T_m$ = 1720 °C).

### 2.1. Meniscus shape and crystal dimensions

As the die temperature is externally controlled and the melting point constant, the meniscus height, $h_m$, depends only on the heat transfer in the liquid and solid around the interface, it will be studied in Section 2.2. The thickness of the pulled crystal depends on the die dimension, through a purely geometrical relationship. The parameters of importance are (Fig. 1):

- The growth angle ψ, between the plate and the liquid surfaces at the solid-liquid-gas triple line. It is a thermodynamic constant linked to the surface energies at the triple line (17° for sapphire [9]).
- The meniscus radius of curvature. A free liquid surface usually has two radii of curvature. However, because the plate is flat and supposed infinite, the radius of curvature in the lateral direction (along the triple line) is infinite. Only the vertical radius of curvature, $r_m$, exists in this case. The meniscus is approximated by a circular arc, then this radius is constant on the whole liquid meniscus surface.

Taking into account that the meniscus is anchored on the die edge ($e_d/2$) and on the crystal edge ($e_c/2$) the equation of the arc circle gives [5]:

$$r_m = \frac{\left(\frac{e_d}{2} - \frac{e_c}{2}\right)^2 + h_m^2}{(e_d - e_c)\cos\Psi - 2h_m \sin\Psi}. \quad (1)$$