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Transient mode features at sapphire growing by horizontal directional crystallization

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The behavior of the crystal/alumina melt boundary has been studied at the start and final stages of sapphire growing by horizontal directional crystallization. At a constant pulling speed of the crystal into the cold zone, the time dependence of the melt crystallization rate may behave nonmonotonically. The crystallization front oscillations in the initial transient process that was predicted by numerical simulation has been confirmed experimentally.

Изучено поведение границы кристалл-расплав оксида алюминия в начале и конце выращивания сапфира методом горизонтально-направленной кристаллизации. Показано, что при постоянной скорости вытягивания кристалла в холодную зону зависимость скорости кристаллизации расплава от времени может вести себя немонотонно. Получено экспериментальное подтверждение явления колебаний фронта кристаллизации в начальном переходном процессе, ранее предсказанного численным моделированием.

Sapphire occupies a leading position among modern functional materials due to its unique properties [1]. The development of novel sapphire growing technologies ryquires novel approaches to the problem of the alumina melt crystallization. This work is aimed at one such approach, namely, the monitoring of the solid/liquid alumina interface in the transient mode when the sapphire is grown by horizontal directional crystallization. The facts mentioned bylow illustrate the actuality of such studies.

It is well known that strips being the accumulations of small bubbles may arise in the sapphire during its growing. The bubbles are nucleated in the hollows of cells arising on the phase interface at the concentration overcooling (COC) of the alumina melt [2]. The transition from the smooth phase interface to the cellular one occurs in stepwise manner and is accompanied by a sharp increases of the crystallization rate [3]. When a crystal is pulled out of a binary melt being in the COC state, the crystallization rate behaves nonmonotonously, in particular, it may exhibit damping variations [4]. Such variations are due to considerable concentration overcoolings [4] that must cause instability of the smooth phase interface. However, up to now, there are only scant data on the melt COC values as well as on the residence duration of the crystal-melt system with a smooth crystallization front under the COC conditions.

In this work, the sapphire crystal of $100\times40\times15$ mm^3 size was grown [5] in about 0.1 Torr vacuum from pre-melted alumina of G-00 grade. Judging from the pink sapphire color, the initial blend contained about 10^{-3} % of titanium.

To monitor the crystallization front (CF), a Sensicam qe CCD camera was used. The shot spacing was 0.5 s, the exposure 6 ms. The data coming from the CCD camera were processed using a special software providing the CF position coordinate x_f counted from the heat screen edge overhanging the melt. The CCD matrix pixel corresponded to the

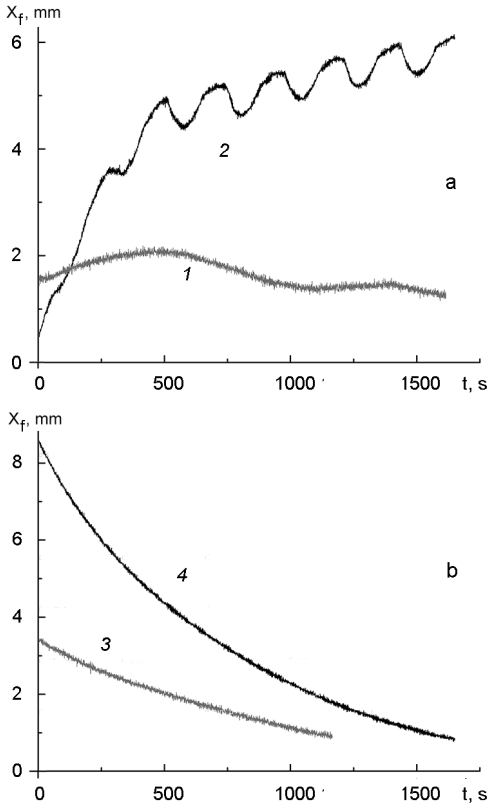

Fig. 1. Time dependencei of the crystallization front coordinate x_f after the crystal pulling device switching on (a) and switching off (b) at the pulling speed of 8 mm/h (*1*, *3*) and 43 mm/h (*2*, *4*).

0.25 mm area on the sample surface. The CF position was determined to within 0.1 mm. The CF behavior was studied in two transient processes, at the crystal pulling at the rate $W = const$ and after the pulling device was switched out ($W = 0$). The supply power of the furnace heater was constant.

Fig. 1a presents the time dependences of the x_f coordinate for the initial transient mode at two typical crystal pulling speeds, $W = 8$ mm/h and $W = 43$ mm/h. The sapphire was free of the bubble strips in the first case and contained those in the second one. The nonmonotonic character of both curves in Fig. 1a is to be noted. Since the $x_f(t)$ dependence becomes monotonic after the pulling is over (Fig. 1b), the CF speed coordinate variations observed in the initial transient regime are not connected with the possible variations of the power being supplied to the growth furnace. It was found in special experiments that the crucible placed on the pulling device sweep is displaced within the furnace without any appreciable

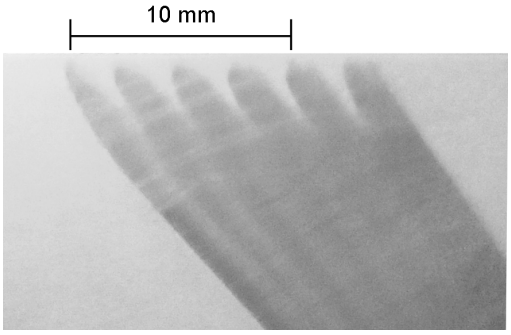

Fig. 2. Porosity in sapphire formed at the crystal pulling speed 43 mm/h. The 1.4 mm thick plate is cut out along the crystal growth axis and perpendicular to its near-bottom surface.

vibrations. Thus, the CF behavior features presented in Fig. 1a are due to redistribution of the impurities in the alumina melt.

According to calculations [4], the nonmonotonic trend of the $x_f(t)$ dependence observed in the case $W = 8$ mm/h (curve *1* in Fig. 1a) is due to the melt concentration overcooling. As the above-mentioned strips were not observed when the crystal was pulled at that speed, the phase interface can be assumed to remain smooth [2]. Thus, under the conditions being under consideration, the value $W = 8$ mm/h is most likely within the pulling speed range where the melt is concentration-overcooled and crystallizes at the same time with a smooth front.

The CF behavior at the sapphire pulling speed of 43 mm/h is found to be unusual (curve *2*, Fig. 1a). About 500 s after the pulling device start, the CF began vary vibrationally along the growth axis. A those moments, the crystallization rate was estimated to exceed 100 mm/h. As is seen in Fig. 1a, curve *2*, the variations are clearly periodic (at a period of about 230 s) and show an asymmetric trend, the gradual deceleration of the CF speed (the left peak edge) is alternated with its sharp increase (the right peak edge). The observed behavior of the phase interface can be explained by a relatively slow impurity accumulation in front of the CF followed by its fast capturing by the solid phase. As a result, the melt becomes depleted of the impurity in front of the CF, and the cycle is repeated when it is accumulated again. The variations in the crystal-melt system show all the features of so-called temporal dissipative structure [6].

An important feature of that phenomenon consists in that the variations are "synchronized" with the formation of the above-

mentioned strips in the sapphire (Fig. 2) that are manifested still at the sapphire growth stage as the characteristis knees in the time dependence of the CF coordinate.

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Особливості перехідного режиму при вирощуванні сапфіру методом горизонтальної направленої кристалізації

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Вивчено поведінку межі кристал-розплав оксиду алюмінію на початку та в кінці вирощування сапфіру методом горизонтальної направленої кристалізації. Показано, що при постійній швидкості витягування кристала у холодну зону залежність швидкості кристалізації розплаву від часу може бути немонотонною. Одержано експериментальне підтвердження явища коливань фронту кристалізації у початковому перехідному процесі, раніше передбаченого чисельним моделюванням.