

## SIMULTANEOUS CRYSTALLIZATION TESTING IN A CRUCIBLE FURNACE

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**ABSTRACT.** An air-cooled test tube, with a series of modular and movable rings (cylindrical-multilateral, folding-matryoshka “crystallization comb-key”), installed in a laboratory crucible furnace is presented. The setup allows easy regulation simultaneous crystallization tests of a series of different crystallization parameters in several columns of test tubes, enabling fast studies of obtaining crystals. This device (air body with more simple control options) can also be applied in a chamber and tube furnaces. The relations between the crystallization rate and parameters of air-cooled test tube are given and numerically analyzed.

### INTRODUCTION

The preparation of crystal in principle can be achieved in three ways: by crystallization from the solid, liquid or gas phases. Within these three possibilities, a number of methods have been developed to grow crystals [1-3]. The choice of the most suitable method for the preparation of crystals of a particular substance depends not only on its nature and physicochemical properties, but also on the intended application of the crystal, on the quality desired and the available laboratory possibilities.

The preparation of crystals from a melt, *i.e.* mono-component (pure) liquid phase, is carried out by controlled freezing. In comparison to the other techniques, it is a simple and easily controlled process. In addition, the rate of crystal growth from a melt can be much larger than in the case of the other techniques. It is also easier to control the purity of the crystals using this method. There are many crystals that can be grown from a melt, while the method may not be applicable to a material which decomposes before it melts, or its vapor pressure is too high at the melting point.

## APPARATUS

In a previous papers [4, 5] we have described models of air-cooled tubes (bilateral “crystallization combs”), installed in a laboratory crucible furnace, with the aim of regulating the crystallization fronts and rates in a columns of Tamman test tubes. In this paper, we describe the development and improvement of the interior and exterior of the cooler, i.e. modular air-cooled test tube (multilateral “crystallization comb”) (Fig. 1)] and a numerical study control options of crystallization rates in each test tube (Figs. 2 and 3). The improved cooler is simpler to build and handle, features easy regulation of different paths and rates of air flow [with the help of movable rings – see (4) in Fig. 1], i.e. crystallization rate interval, and different crystallization fronts [with the help of mounting rings – see (7) in Fig. 1b] in several columns of (Tamman) test tubes. This stationary and adaptive device (with operating body air) allows easy regulation simultaneous crystallization tests of different crystallization parameters and substances, enabling fast studies of obtaining single crystal from a family of layered materials with unknown crystallization rates (see e.g. Cabric in Tables 3.1-5 and 3.1-8 in [3]) using a laboratory furnaces.

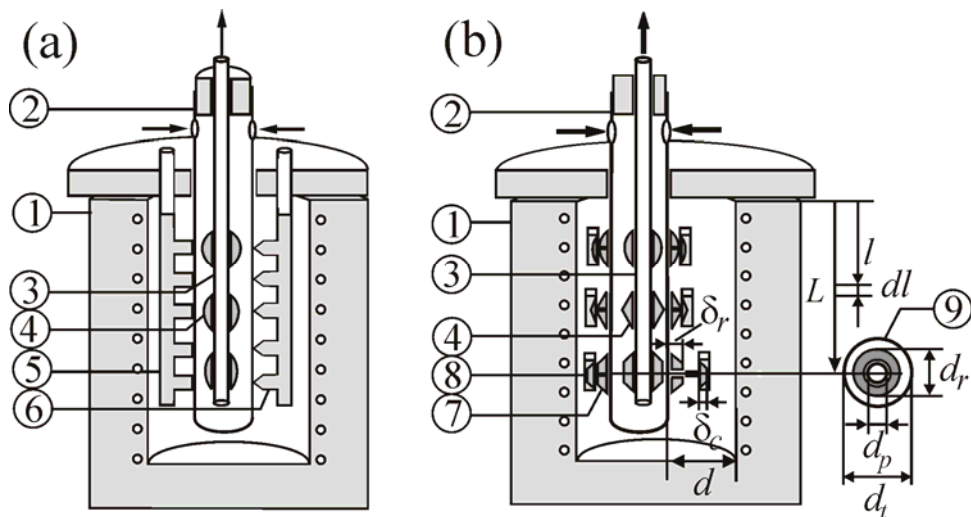


Fig. 1. - A modular air-cooled test tube [multilateral “crystallization comb-key”] in a crucible furnace: (1) laboratory crucible furnace, (2) air-cooled test tube, (3) pipe (4) modular and movable rings, (5) branched (toothy or notched) test tube, (6) branched Tamman test tube (Fig. 3.1.-8 in [2]; Fig. 3.1-2. in [3]) (“crystallization tests combs”), (7) rings with radial mounting holes (“junction rings”), (8) test tubes, and (9) cross section of the air-cooled test tube.

Rings and branched test tubes of various numbers, shapes and dimensions can be mounted and thus simultaneously tested (fineness of the comb-key). By varying the internal and external shapes and dimensions of the cooler, a set of “crystallization keys” can be modeled for tests in a various shapes of crystallization fronts and rate intervals. The air-cooled test tube can easy be modified into the tube (test tube without bottom) and installed into a tube furnace in a horizontal position (“crystallization tests bench”), or vertical position (“grafted crystallization tree”) [6]. Several different air-cooled test tubes (a family group of “crystallization fingers”) can be installed in the chamber furnace. This increases the number of simultaneous crystallization tests of different crystallization parameters, using a low-budget, air body with more simple control options, i.e. modular, adaptable, folding, easy to install and remove, portable (“pocket”) device, for fast studies of obtaining single crystals from substances with unknown crystallization parameters, and the economic expansion application (engagement) of laboratory furnaces.

## THEORY AND NUMERICAL ANALYSIS

By the assumption that the liberated latent heat of solidification is equal to the heat removed by the air stream through the test tube wall, the following expression for the crystallization rate  $R$  is derived [7]:

$$R = \frac{\Delta T_L}{\lambda \rho (1/\alpha_r + \delta_r/k_r + \delta_c/k_c)} \quad (1)$$

where  $\Delta T_L$  denotes the difference between the temperature of the melt and that of the air stream at the point  $L$  (Fig. 1b),  $\lambda$  is the latent heat of solidification,  $\rho$  designates the crystal density,  $\alpha_r$  is the coefficient of heat transfer from the cooler wall to the air stream next to the ring,  $k_r$  and  $k_c$  designates the heat conductivity of the ring and crystal respectively.

Based on the fact that the heat removed from the test tube wall is equal to the heat accepted by the air stream, we have derived the following expression (integral equation) for the difference between the temperature of the melt and that of the air stream at the point  $L$  -  $\Delta T_L$ :

$$\Delta T_L = \Delta T_0 - \frac{4}{d_t w_t} \int_0^L \frac{\alpha_t \Delta T_l}{\rho_a c_a} dl \quad (2)$$

where  $\Delta T_0$  is the difference between the temperature of the melt and that of the air stream at the point  $L=0$  (Fig. 1b),  $d_t$  is diameter of the test tube,  $w_t$  is an average velocity of the air stream in the test tube (without ring),  $\alpha_t$  is the coefficient of heat transfer from the test tube (without ring) to the airstream,  $\Delta T_l$  is the difference between the temperature of the melt and that of the air stream at the point  $l$ ,  $\rho_a$  and  $c_a$  designates density and heat capacity of the air stream, respectively.

The coefficient of heat transfer from the test tube wall to the air stream can be calculated using the following expression (p. 152 in [8]):

$$\alpha_r = \left[ 4,13 + 0,23 \frac{t}{100} - 0,0077 \left( \frac{t}{100} \right)^2 \right] \frac{w_{r0}^{0,75}}{d_t^{0,25}} \quad (3)$$

where  $t$  is average temperature of the airstream in  $^{\circ}\text{C}$  (up to  $1000^{\circ}\text{C}$ ),  $w_{r0} = w_r \left( \frac{273}{273+t} \right)$ ,  $w_r$  is average velocity of the airstream next to the ring ( $0^{\circ}\text{C}$ , 1.013 bar) in m/s.

On the basis of the continuity and the cross section of the airstream, the following expression for the velocity of the airstream next to the ring  $w_r$ , we obtain:

$$w_r = w_t \frac{d_t^2 - d_p^2}{d_t^2 - d_r^2} \quad (4)$$

where  $d_p$  is the diameter of the pipe, and  $d_r$  is diameter of the ring – see (9) in Figure 1b.

In accordance with equations (1), (2), (3) and (4), the authors obtained the numerical values of crystallization rate,  $R$ , as function of  $\Delta T_0$  and  $w_t$  (Figure 2), and,  $d_r$  and  $L$  (Figure 3) in the case of bismuth:  $T_{melt} = 271^{\circ}\text{C}$ ,  $\lambda = 52300 \text{ J/kg}$ ,  $\rho = 9800 \text{ kg/m}^3$ , and  $k_c = 7.2 \text{ W/mK}$ , In

all numerical calculation is was taken that:  $d_p = 1$  cm,  $d_t = 3$  cm,  $\delta_r = 0.5$  cm,  $k_r = 0.756$  W/mK (pyrex *i.e* borosilicate glass, softening point  $\approx 600$  °C),  $\delta_c = 0$  cm, (Figure 1b),  $\rho_a = 0.682$  kg/m<sup>3</sup>, and  $c_a = 1.035$  kJ/kgK. As can be seen from Fig. 2(a) the crystallization rate  $R$  increases with increasing the difference between the temperature of the melt and that of the air stream at the point  $L = 0$ ,  $\Delta T_0$ . The crystallization rate  $R$  increases with increasing the velocity of the air stream in the test tube  $w_t$  Fig. 2(b) which is consequence of the fact that with the increasing the  $w_t$  increases the  $\alpha_r$  - Eq. (3) and consequently increases the  $R$  - Eq. (1). As can be seen from Fig. 3(a) if  $d_r$  is larger then crystallization rate  $R$  is larger, which is consequence of the fact that if  $d_r$  is larger then  $w_r$  is larger - Eq. (4), and consequently  $\alpha_r$  and  $R$  are larger - Eqs. (3) and (1). Figure 3b shows that the crystallization rate decreases with increasing  $L$  which is the consequence of the fact that  $\Delta T_L$  decreases with the increasing of the  $L$  - Eq. (2).

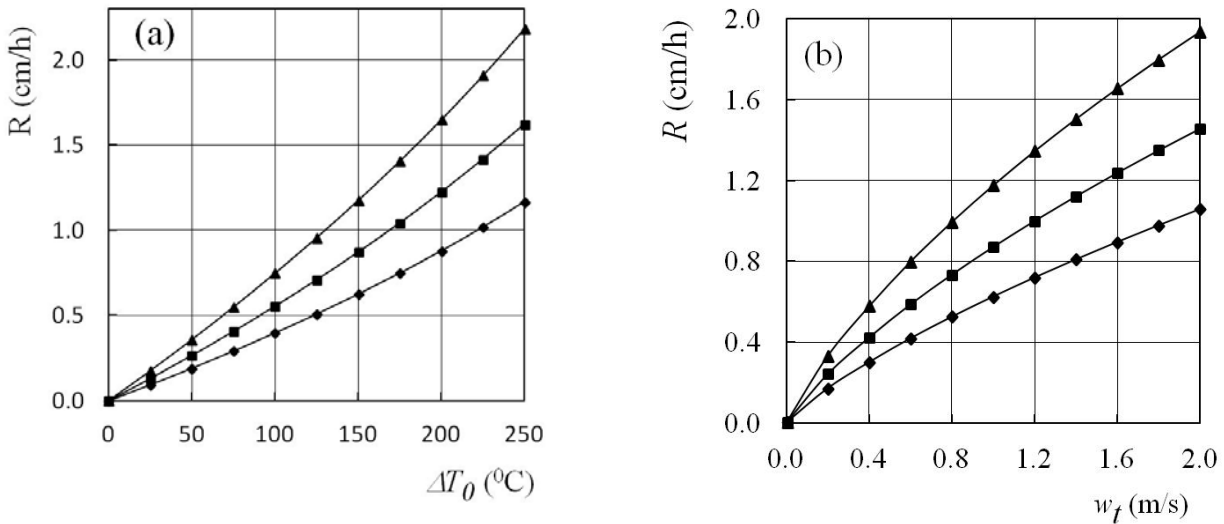


Fig. 2. - Crystallization rate  $R$  as a function of the difference between the temperature of the melt and that of the air stream at the point  $L=0$  —  $\Delta T_0$ , and velocity of the airstream in the test tube  $w_t$ , respectively, when  $L = 10$  cm :  $\blacklozenge$ —  $d_r = 1$  cm,  $\blacksquare$ —  $d_r = 2$  cm,  $\blacktriangle$ —  $d_r = 2.4$  cm; (a)  $w_t = 1$  m/s; (b)  $\Delta T_0 = 150$  °C.

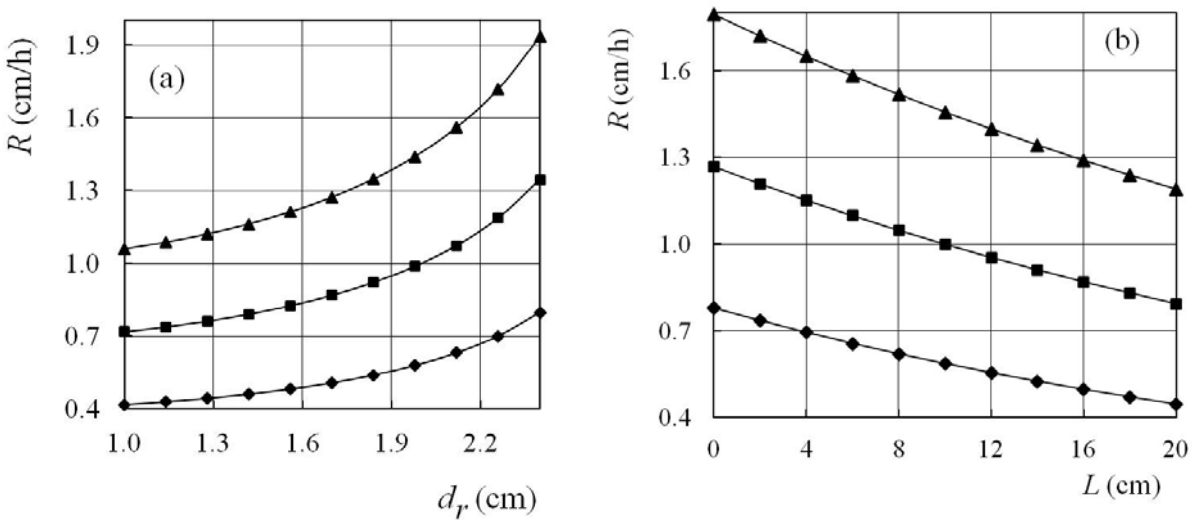


Fig. 3. - Crystallization rate  $R$  as a function of the diameter of the ring  $d_r$ , and the position of the ring along the test tube,  $L$ , respectively, when  $\Delta T_0 = 150$  °C :  $\blacklozenge$ —  $w_t = 0.6$  m/s,  $\blacksquare$ —  $w_t = 1.2$  m/s,  $\blacktriangle$ —  $w_t = 2$  m/s; (a)  $L = 10$  cm; (b)  $d_r = 2$  cm.

## CONCLUSION

The shapes of crystallization fronts in test tubes columns are regulated by the ring fronts. The crystallization rate in each test tube can be regulated by the difference between the temperature of the melt and that of the air stream, and the velocity of the air stream; and/or by the diameter of the ring and the position of the ring along the test tube. The crystallization rate in the tests tubes can also be regulated by the thickness of the ring  $\delta_r$ . Different crystallization rates in the test tubes in one ring (“wreath”) can be simultaneously tested using pipe dislocation to the axis of the air-cooled test tube, *i.e.* asymmetric key. The temperature gradient is regulated by the distance air-cooled test tube from the furnace wall  $d$ . Different temperature gradients in the test tubes in one ring can be simultaneously tested using air-cooled test tube dislocation to the axis of the furnace, *i.e.* asymmetric or inclined position of the air-cooled test tube (“crystallization key”).

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