

CRYSTALLIZATION COLUMNS IN A CHAMBER FURNACE

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ABSTRACT. Design of modular, and simple to build and handle air cooler (“crystallization comb”) installed in a laboratory chamber furnace is presented. The setup allows easy regulation and simultaneous crystallization tests of different temperature gradients, shapes of crystallization fronts and rate intervals in crucible columns, enabling fast studies of obtaining crystals. The relationship between the crystallization parameters has been derived and numerically analysed. This method can also be applied in crucible or tube furnaces.

INTRODUCTION

In principle, monocrystals can be obtained by crystallization from solid, liquid or gas phases. Within these possibilities a number of methods have been developed [1, 2]. Selection of the proper method for growing monocrystals of a given substance depends upon many factors, primarily on the nature of the substance and its physicochemical properties, quality desired and intended application of crystals as well as on available laboratory possibilities.

In many cases, monocrystals are obtained by growing from the melt, which is in essence a controlled cooling growth; in comparison with other methods for monocrystal preparation this method is simpler and easier to control. When crystals are growing from the melt a higher crystallization rate than by other methods can be achieved, the same being true for the purity of crystals obtained. With the exception of crystal growth from water solutions this process has been most thoroughly investigated from the technical standpoint. Crystal growth from the melt is widely applicable but there are limitations for non-melt-stable materials.

APPARATUS

In a previous papers [3, 4], models of air coolers in a laboratory chamber furnace, for regulating the crystallization fronts and rates in a several crucibles are shown. In this paper, we show the development and improvement of the interior and exterior of the cooler, i.e. tubes with modular and movable plugs - “crystallization combs” (Fig. 1). The improved coolers are simple to build and handle, and enable mounting different number of crucibles. In other words, this enables easy regulation and simultaneous crystallization tests (“comb”) of different number of crystallization parameters, with the purpose of obtaining single crystals from a family of newly synthesized compounds with a layered crystal structure [1] in a laboratory chamber furnace.

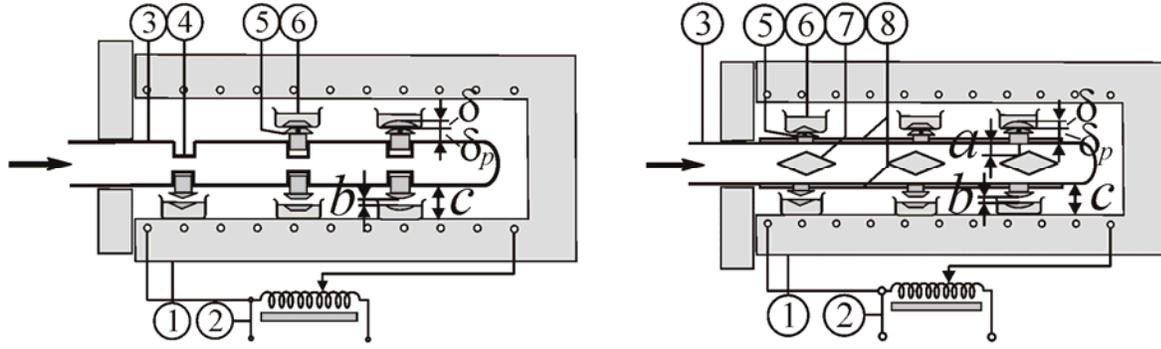


Fig. 1. Crystallization columns in a chamber furnace: (1) laboratory chamber furnace, (2) continuously changeable transformer, (3) part (fragment) of air-cooled tube in the shape of letter “U” in a horizontal plane, (4) mounting holes, (5) movable cold plugs (“crystallization comb”), (6) columns of crucibles, (7) radial holes (“cold thresholds”), and (8) slide bars.

The shapes and dimensions of the crystallization fronts in each crucible are regulated by the plug front, i.e. screw head (“crystallization seals”). The crystallization rate interval in each crucible is regulated by the cross section of the airflow a , and by the plug height δ_p . The crystallization rate in the crucibles below the cooler can also be regulated by the distance of the plug head from the surface of the melt b . The temperature gradient is regulated by the distance c , i.e. by translation movement of the cooler. Different temperature gradients in the crucibles can be simultaneously tested using an inclined cooler.

THEORY AND COMPUTATIONS

The rate of melt solidification depends upon extracting the latent heat of solidification. For a time interval t a crystal layer of thickness δ is formed (Fig.1). During the formation of an elementary crystal layer of thickness $d\delta$, the amount of heat released is $L\rho d\delta$ (L denotes the latent heat of solidification and ρ the crystal density); the latter is being extracted through the cooler for a time interval dt . On this basis the following equation may be written [5]:

$$L\rho d\delta = \frac{\Delta T}{1/\alpha + \delta_p/k_p + \delta/k} dt \quad (1)$$

where ΔT denotes the difference between the temperature of the melt and that of the air stream, α is the coefficient of heat transfer from the cooler wall to the air stream, δ_p denotes the plug height, k_p designates the heat conductivity of the plug and k is the heat conductivity of the crystal. Introducing the parameter $a = 1/\alpha + \delta_p/k_p$ and transforming equation (1), we obtain:

$$R = \frac{d\delta}{dt} = \frac{\Delta T}{aL\rho(\delta/ak + 1)} \quad (2)$$

The quotient $d\delta/dt$ denotes the rate of crystal layer growth which is usually represented by the symbol R ; it is greatest at the beginning ($\delta = 0$) and decreases with increasing thickness of the solidified layer. Since the growth of large and perfect crystals requires a smaller crystallization rate, such crystals are obtained at those parts of the melt which are most distant from the cooler [6].

Every crystallizing substance has a characteristic maximum linear rate of monocrystal growth, R_c . A monocrystal is growing on solidification provided $R \leq R_c$. From equation (2) it follows that this requirement is fulfilled from the beginning of the solidification ($\delta = 0$) if $\Delta T \leq aL\rho R_c$.

Integration of equation (2) gives the relation:

$$\delta = ak \left[\left(1 + \frac{2\Delta T}{a^2 L \rho k} t \right)^{1/2} - 1 \right] \quad (3)$$

by means of which one can calculate also the time needed for the solidification front to reach the surface or bottom of the melt. The magnitude of the heat resistance a is obtained also from the relation (3) by replacing the experimentally obtained values for δ and t .

The preparation of crystals of good quality (containing a small concentration of impurities and defects) requires crystallising substances of a high purity, vacuum or an inert atmosphere (vacuum is not suitable if the substance has a high vapour pressure at the melting temperature), crucibles made of materials which do not react chemically with the melt, a high temperature stabilization in the furnace and the absence of mechanical shocks [2].

In accordance with equation (2), we obtained numerical values of crystallization rate R as a function of thickness of crystal layer δ and the height of the plug δ_p , respectively (Fig. 2). Also, in accordance with equation (3), we obtained numerical values of thickness of crystal layer δ as a function of the height of the plug δ_p and time of crystallization t respectively, in the case of tin (Sn) (Fig. 3).

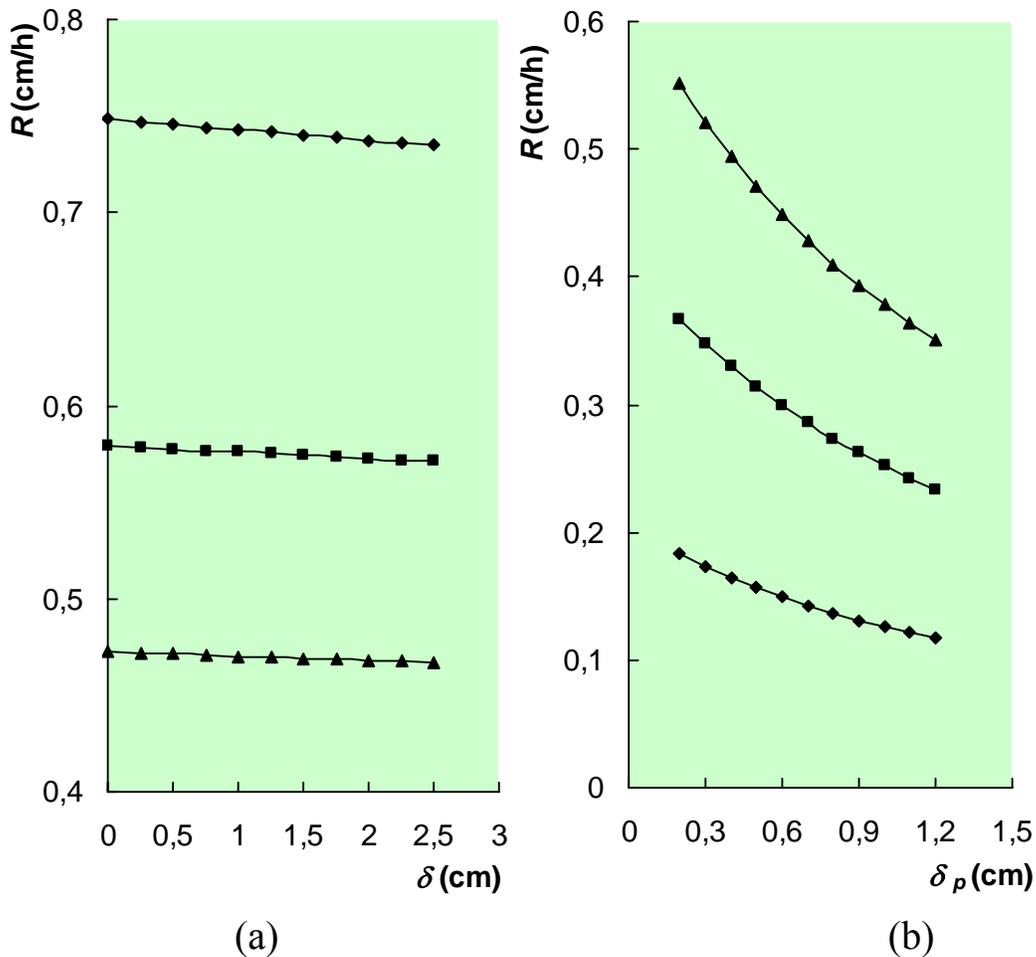


Fig. 2. Crystallization rate as a function of thickness of crystal layer δ and the height of the plug δ_p , in the case of tin (Sn): $L = 58200$ J/kg, $\rho = 7300$ kg/m³, $\alpha = 50$ W/m²K, $k_p = 0,756$ W/mK, $k = 59,8$ W/mK.
 (a) $\Delta T = 20$ K, \blacklozenge $\delta_p = 2$ mm, \blacksquare $\delta_p = 7$ mm, \blacktriangle $\delta_p = 12$ mm;
 (b) $\delta = 2,5$ cm, \blacklozenge $\Delta T = 5$ K, \blacksquare $\Delta T = 10$ K, \blacktriangle $\Delta T = 15$ K.

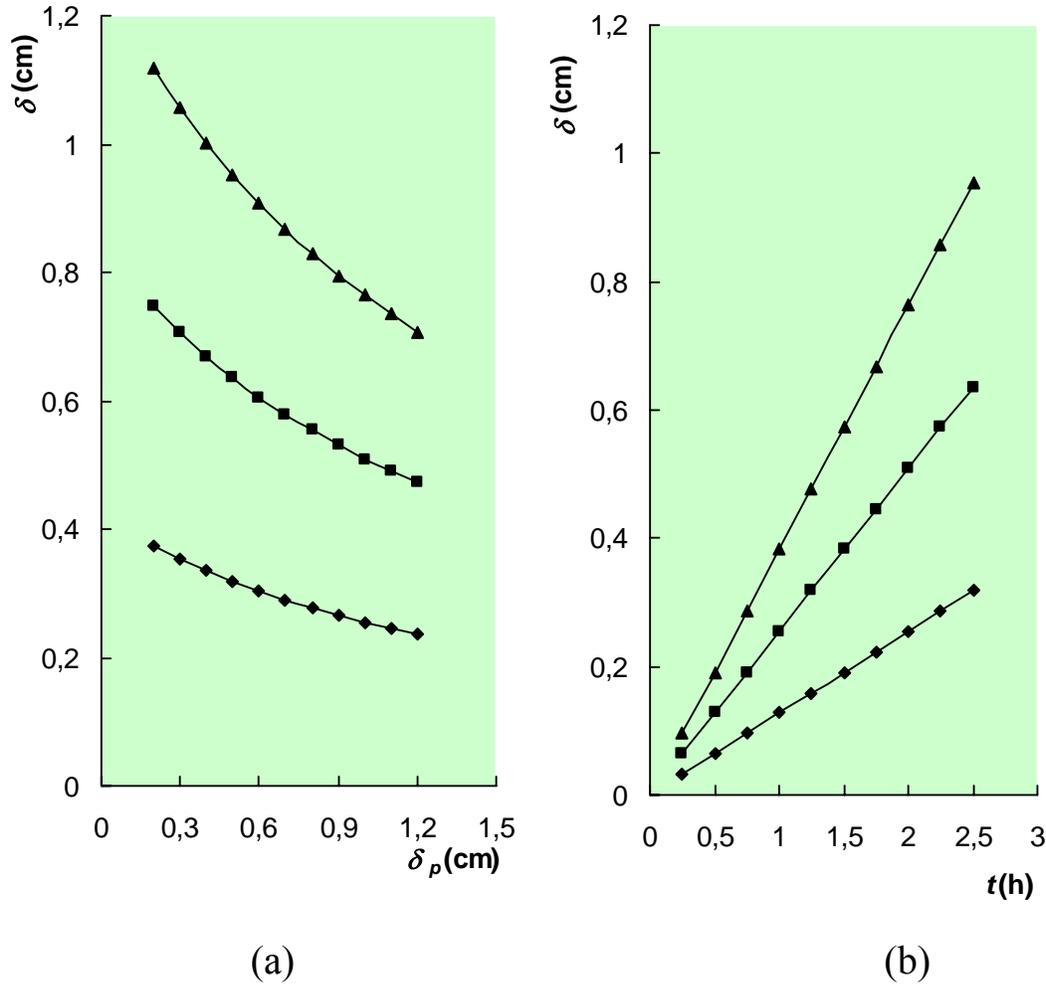


Fig. 3. Thickness of crystal layer as a function of the height of the plug δ_p and time of crystallization t , in the case of tin (Sn): $L = 58200 \text{ J/kg}$, $\rho = 7300 \text{ kg/m}^3$, $\alpha = 50 \text{ W/m}^2\text{K}$, $k_p = 0,756 \text{ W/mK}$, $k = 59,8 \text{ W/mK}$.
 (a) $\Delta T = 20 \text{ K}$, \blacklozenge $t = 0,5 \text{ h}$, \blacksquare $t = 1 \text{ h}$, \blacktriangle $t = 1,5 \text{ h}$;
 (b) $\delta_p = 1 \text{ cm}$, \blacklozenge $\Delta T = 5 \text{ K}$, \blacksquare $\Delta T = 10 \text{ K}$, \blacktriangle $\Delta T = 15 \text{ K}$.

DISCUSSION

Plugs of various shapes and dimensions can be mounted on the air-cooled tube and thus simultaneously tested (Fig. 1). By varying the internal and external shapes and dimensions of the cooler, i.e. number, shapes and dimensions of the thresholds and plugs, a set of “crystallization tubes-combs” can be modeled for tests in a wider range of crystallization parameters and substances. The cooler can be modified into a rectilinear shape and installed into a tube furnace. Also, the coolers can be applied in a crucible furnace. Several different coolers (several cold tubes in the form of horseshoes) or a planar air cooler (cold board) with several columns of plugs (“crystallization plug-board”) can be installed in a chamber furnace for the matrix: different gradients, crystallization fronts, rate intervals and substances. This increases the number of simultaneous crystallization tests (“comb”) of different crystallization parameters, enabling fast studies of obtaining single crystals, using a low-budget, and simple to regulate, portable (“pocket”) device, i.e. “crystallization keys” for laboratory furnaces and substances.

References:

- [1] WILKE, K.-Th. and BOHM, J.: *Kristallzüchtung*. Deutsch. Thun.: pp. 591-647 (1988).
- [2] TARJAN, I. and MATRAI, M.: *Laboratory Manual on Crystal Growth*, Akademiai Kiado, Budapest: pp. 221-238(1972).
- [3] ČABRIĆ, B., DANILOVIĆ, N. and ŽIŽIĆ, B.: A crystallization cooler in a chamber furnace. *J. Cryst. Growth*, **169**, 199-200 (1996).
- [4] ČABRIĆ, B., DANILOVIĆ, N. and PAVLOVIĆ, T.: Regulation of the crystallization of $\text{BaNi}_2(\text{PO}_4)_2$ in a chamber furnace. *Cryst. Res. Technol*, 31, No. **5**, K58-K59(1996).
- [5] ČABRIĆ, B., ŽIŽIĆ, B. and NAPIJALO, M.Lj.: An apparatus for crystal growth in the undergraduate laboratory. *Eur. J. Phys.* **11**, 233-235(1990).
- [6] ČABRIĆ, B., PAVLOVIĆ, T. and ŽIŽIĆ, B.: Crystallization of $\text{BaM}_2(\text{PO}_4)_2$, where M = Mg, Co or Ni. *Collection of Scientific Papers of the Faculty of Science Kragujevac*, **15**, 91-95(1994).