Kokh A.E. Hydrothermal emerald crystal syntesis under heat field rotation conditions

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keywords: [hydrothermal crystal growth; heat field rotation; heat transfer; convection; emerald]

A method for crystal growth in rotating heat fields (HFRM – Heat Field Rotation Method) was proposed and justified in [1-4]. The principle of the method is creation of a rotating heat front (a running heat wave) at the outer walls of a crucible. The HFRM is an innovative method providing a possibility for a contact-free action on heat-mass transfer processes in the medium of crystallization. The use of this method for the hydrothermal crystal growth is of special interest for it excludes an active and/or contact control over heat-mass transfer.

It is obvious that at present there is no any substantiated and/or proved idea about the processes of heat-mass transfer in a hydrothermal medium of crystallization. Tomas et al. [5] showed a pulsational character of hydrothermal processes under stable (±0.1°C) stationary outside heat field conditions in the emerald crystal growth. The authors believe that hydrothermal pulsation consists in sporadic formation of overheated and overcooled flows in the autoclave. The pulsation results in a turbulent convection and is followed by ±0.7°C temperature fluctuations, which are responsible for the formation of rhythmically-striped emerald crystals.

The idea of hydrothermal crystal growth in a rotating heat field implies the creation of a regular convection. This could provide a possibility for performing the control over the process and, therefore, its optimization for growing more homogeneous and structurally perfect crystals. Intuition suggests that there are two agents of influence of a rotating heat field on the processes inside an autoclave: 1) the vigorous dissolution in the porous lower zone due to the enforced convective regime, and 2) the ordering (regularization) of the flow pattern in the zone of crystallization and, as a result, the formation of structurally more perfect crystals. Obviously, each agent can have an essential influence on the development of the hydrothermal method for the growth of different crystals.

By now we have obtained first results of experimental studies for the first case, i.e. the rotation of the heat field within the lower zone – the zone of blend dissolution. Fig. 1 shows the experimental setup. The main element of the device is a two-zone heating furnace with vertically placed 15 heaters (in this case) in each zone. A thermal control scheme was described in details in [2]. A signal of negative feedback is emf (electromotive force) of the differential Pt-Pt/10%Rh thermocouple, which consists of 15 working junctions placed between the heaters (the figure shows one junction only). Such a construction of the regulating thermocouple provides a stable control over the mean temperature under the dynamic regime of the switching on of the heaters.

Five triplets of heaters – 1-2-9, 3-10-11 and so on (Fig. 1b) - provide an asymmetric regime of heat field rotation (rotated quazi L_2 (rotqL_2) heat field symmetry). So, a heat wave which consists of two peaks of different amplitude with a 180° discharge would move cyclically around the outer wall of the autoclave. On each switching the amplitudes of the peaks change places resulting in a five-end star trajectory of the movement of a “cold point” in the horizontal plane (in the center of Fig. 1b). A $\Delta\tau$ periodicity of switching of N groups (fife triplets in this case) of heaters defines the angular velocity of heat field rotation. The upper heating zone serves for the creation of a necessary temperature difference between the zones of dissolution and the zone of crystal growth (crystallization) inside the autoclave.

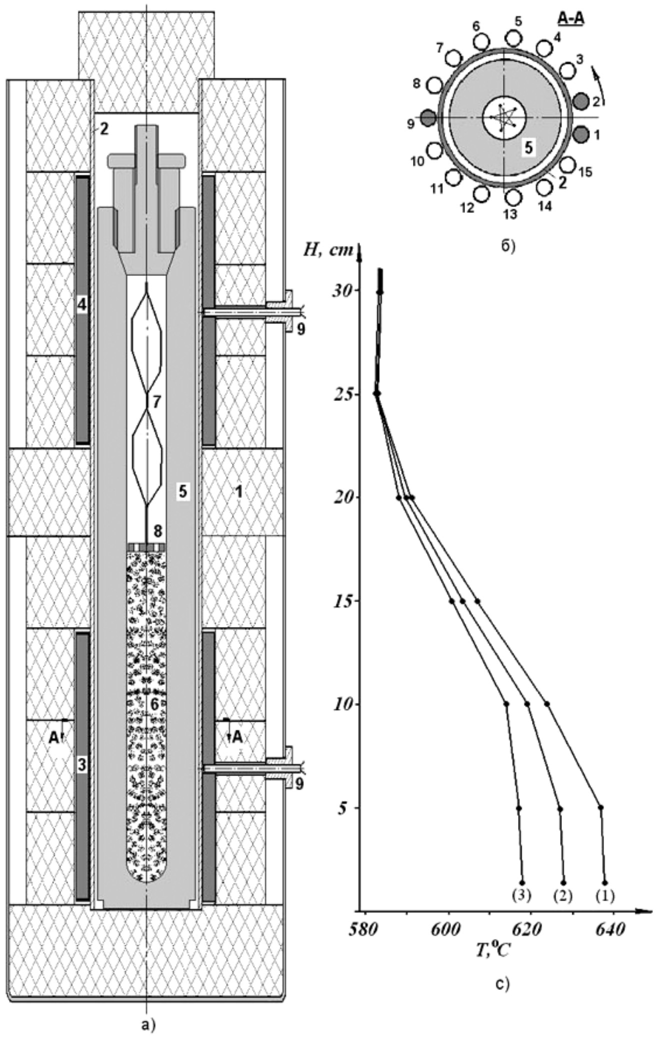

Fig. 1. Vertical (a) and horizontal (b) sections of the growth setup: (1) heat-isolating frame, (2) quartz muffle, (3) the lower heating zone, (4) the upper heating zone, (5) autoclave, (6) the zone of dissolution, (7) the zone of crystallization, (8) diaphragm, (9) regulating thermo-couple. In the center of Fig. 1b – the trajectory of a “cold point” movement under rotqL_2 symmetry of the rotating heat field; (c) temperature distribution along the autoclave axis in three experimental runs (see Table 1).

First we had to find out if a cyclic heat wave moving around the autoclave can penetrate through (strike through) its thick walls. Fig. 2 shows curves of the temperature distribution in the horizontal cross section A-A of the autoclave close to its inner wall (1) and in the center (2) depending on the period of heat field rotation. The temperature curves indicate a heat transfer from a heater to the autoclave in relation to the period of rotation. We shall restrict it to the fact that at a short period of rotation the heat field is nearly stationary having a cylindrical symmetry L_∞. At a $\Delta\tau$=25 s period of switching the temperature fluctuations appear inside the autoclave. As the period of rotation increases, so does the amplitude of temperature fluctuations at inner autoclave walls and along autoclave axis. As a result the symmetry of the heat field transforms into $rotqL_2$.

We completed experiments on hydrothermal synthesis of single emerald crystals via the recrystallization of the blend of natural beryl from the Izumrudnyje Kopi deposit (the Urals). These were grown in composite water solutions containing chlorides (halides) and fluorides at temperatures of 640-650°C and pressures of 1,200-1,500 atmospheres. The autoclave was filled with a calculated amount of water defining the above pressure. Both synthetic and natural beryl seed plates were used being oriented parallel to (5.5.-10.6) [6]. The zone of dissolution was separated from the zone of crystallization by a metallic diaphragm with two holes. The diaphragm was for more contrast temperature difference between those zones.

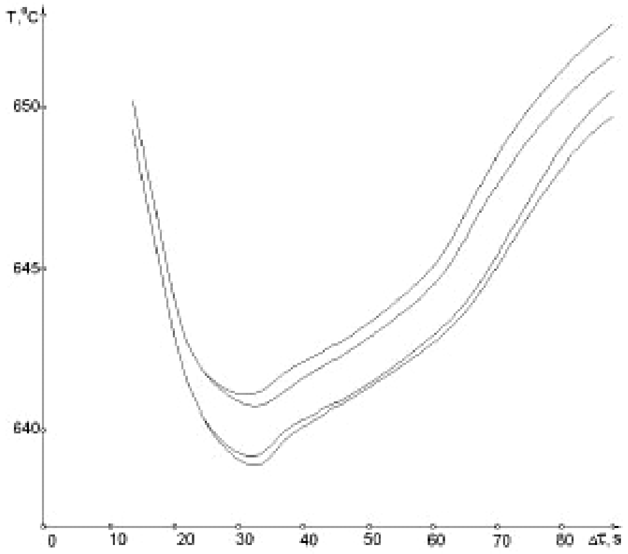

Fig.2. Temperature regime inside the empty autoclave in A-A section depending on the period of switching (Δτ) of heaters: (1) close to the inner wall of the autoclave, (2) along the autoclave axis.

These synthetic emeralds were grown in a stationary heat field at a temperature of 645±5°C in the zone of dissolution and 580±10°C in the zone of crystallization. The length of a growth cycle is about 45±5 days depending on the temperature difference between two zones. Such a time period provides a complete mass transfer of the blend material and its recrystallization to the seeds.

Three experiments have been performed in the $rotqL_2$ symmetry heat field rotating around the zone of dissolution with a period of T=5x32 s. According to the plot in Fig. 2 at that period of heat field rotation the amplitude of temperature fluctuations inside the autoclave should be 0.4°C at the inner wall and 0.25°C in the center. It is obvious that under experimental hydrothermal crystal growth conditions these values would be different. In three experiments the mean temperature in the zone of crystallization was constant - 580°C and the maximum temperature in the zone of dissolution was 638, 628, and 618°C, correspondingly (Table 1). Fig.1 shows the curves of mean temperature distributed along the axis of the empty autoclave corresponding to three experimental runs. The duration of each experiment was 32 days.

In the first experiment the emeralds were of low quality (3^{rd} category) with visually observed defects: fractures, swirl-like graining, and color zoning parallel to the seed plate. The presence of parasitic crystals indicates a supersaturated hydrothermal solution. The emeralds grown in the second and third experiments are of higher quality (2^{nd} category). They show more faces and, if examined with the unaided eye, all the samples have defect-free areas up to several cubic centimeters in volume.

Thus, the tentative experiments using the HFRM for hydrothermal crystal growth showed that the dissolution and mass transfer of the blend proceed much more actively. At equal average temperatures in the zones of dissolution and crystallization and under the action of a rotating heat field the mass transfer proceeds at least 1.5 times faster than in stationary and stable heat fields. Although the reduction of the mean temperature in the zone of dissolution results in the slower mass-transfer, the quality of crystals gets higher. So, this provides a possibility for growing crystals at lower temperatures, which could be favorable for making autoclaves live longer.

Table 1. Experimental results of emerald hydrothermal crystal growth with the method of heat field rotation around the zone of dissolution with a period of 160 sec.

Run	Maximal temperature in the zone of dissolution, T°C	Temperature difference between the zones of dissolution and crystallization, T°C	Crystal weight, g	Mass transfer, %
1	638	54	71.2	99
2	628	44	65.6	96
3	618	34	61.5	90

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