Solidification of subcooled gallium poured into a vertical cylindrical mold

Itay Harary[a], Vadim Dubovsky[b], Eli Assis[c], Gennady Ziskind[d] and Ruth Letan[e]

[a] *Ben-Gurion University of the Negev, Beer-Sheva, Israel, itay.harary@gmail.com*

[b] *Ben-Gurion University of the Negev, Beer-Sheva, Israel, vadimd@bgu.ac.il CA*

[c] *Ben-Gurion University of the Negev, Beer-Sheva, Israel, assise@netvision.net.il*

[d] *Ben-Gurion University of the Negev, Beer-Sheva, Israel gziskind@bgu.ac.il*

[e] *Ben-Gurion University of the Negev, Beer-Sheva, Israel, ruthlet@bgu.ac.il*

Abstract:

The present investigation is aimed at the solidification of subcooled liquid gallium. The gallium, in its liquid state, is contained in a cylindrical shell of copper or polypropylene, and poured into the shell, which is immersed in a cold bath. The experimental degree of subcooling varied between 5°C and 45°C. The phenomena empirically observed have been simulated in four stages: subcooling of the liquid gallium down to its nucleation temperature, a rapid transfer from nucleation to the stable solidification temperature, stable solidification up to its completion and finally cooling down of the solid gallium. The conductivity of the sample shell affects the length of each stage. In the copper shell the sample loses up to 5% of its released heat along the second stage. In the polypropylene shell, the sample does not lose any heat in that stage. The entire process for initially contained liquid gallium is analyzed by formulation of heat transfer rates at each stage. The only empirical figure used in the analysis is the nucleation temperature. Matlab software is used to solve the formulations. The model presents time-dependent temperatures and melt fraction. The model agrees well with the experiments.

For the flowing liquid gallium, the rate was 0.12 - 0.3 ml/s. The numerical study explored solidification of the flow of liquid gallium by a two-dimensional (axially symmetric) model, using Fluent 6.2 software. Previous investigations in our laboratory, using other flowing phase-change materials, have demonstrated that the solidified phase at the cooled boundaries adheres to the walls with irregular cavities. In the present study the flowing and solidifying gallium has formed an irregular boundary at the walls, too. However, the numerical model has closely predicted the entire process of solidification and cooling of the solid. At higher flow rates the solidification approached the behavior of a static liquid gallium.

Keywords:

Solidification, Subcooling, Gallium, Transient, Experimental, Simulation.

1. Introduction

Phase-change materials, metals or salt hydrates, are supposed to solidify at the stable liquid-solid temperature. However, in many cases the nucleation and solidification are inhibited, and are taking place at a lower temperature [1, 2].The phenomenon is referred to in the literature as subcooling [3, 4], supercooling [5, 6], or undercooling [7, 8].

The subcooled liquid is subjected to a metastable state till the nucleation temperature is reached. As the nuclei grow into crystals, their latent heat is released and it may be, entirely or partly, consumed by the emulsion of solid-in-liquid, depending on the rate of heat removal.

Günther et al. [3] studied subcooled solidification in hydrates. They simulated the stages of subcooling, nucleation and solidification. They validated the applicability of their simulations with experimental data, pointing out that the nucleation temperature has to be determined experimentally in a setup similar to its application. Le Bot and Delaunay [4] studied pure indium at different cooling rates. They analyzed a temperature-dependent function related to nucleation rate at subcooling.

Chen et al. [5] experimentally investigated the nucleation probability of subcooled water in cylindrical containers. They showed that the lower is the coolant temperature the higher is the nucleation probability. Their results also showed that the larger the volume of water, the higher the nucleation temperature. Yoshika et al. [7] presented a model and its numerical simulation of the solidification of undercooled alloy melts. Their model related to the microscopic phenomena, which dominate the transfer from the metastable state of undercooled liquid to the stable state of solidification. It consists of three processes: free growth, crystal expansion with relaxation, and solidification at the temperature of equilibrium. The numerical simulation links between the macroscopic heat transfer and the microscopic solidification.

Bigg [6] studied nucleation in subcooled water droplets. His conclusions were that the larger the droplet volume, or the lower the cooling rate, the higher the nucleation temperature. Herlach [8] studied the phase transformation in droplets of pure metals. This way he completely eliminated the dominant heterogeneous nucleation on the container walls. Chang and Chen [9] revisited the analysis of metal droplets solidification, by relating to the two major mechanisms, which control the process, namely the rate of latent heat release and the rate of heat removal by convection and radiation.

The effects of the container walls on the heterogeneous nucleation in subcooled liquid were studied by many researchers. Saito et al. [10] experimentally investigated the effects of surface characteristics and cooling rate on the temperature of subcooled water contained in a cylinder. Arnold [11] conducted research on subcooled water contained in spherical capsules. He concluded that the nucleation temperature is determined by the rate of cooling. Vail and Stansbury [12] conducted research on the heterogeneous nucleation of ice.

In our previous works, solidification of paraffins was conducted in spherical shells [13] and in vertical cylindrical shells [14, 15]. Of special interest are cases in which the material flows into the shell, and the flow and solidification occur simultaneously. Such cases with flowing paraffin were analyzed numerically [15, 16] and experimentally [16].

Our present study is aimed at the solidification of subcooled gallium, contained in a vertical cylindrical shell, immersed in a coolant of constant temperature in each experiment. The investigation is focused, both experimentally and analytically, on the heat transfer processes at all the stages. The path of the overall process, and in particular the prediction of the solidification completion are sought-after.

2. Experimental

The experimental apparatus consists of two thermostatic baths (Neslab RTE-7), filled with 50% polypropylene glycol and 50% distilled water. Each bath is continuously circulated at a velocity, which varies with the thermal load of the immersed sample, as to preserve a constant temperature of the bath within 0.5°C. In the present study, one bath was used to heat the sample up to 50°C, while the other one was used to subcool the sample.

The sample was commercial gallium contained in a cylindrical shell of flat bottom, and exposed to air at its top. The experiments were performed in two kinds of shells: one was made of copper, and the other one of polypropylene. The gallium properties were: latent heat L=80300 J/kg, thermal conductivity k=40.6 W/mK, density ρ=6095 kg/m^3, specific heat c_p=366 J/kgK. The inside diameter of the copper cylinder was 50.5 mm, with a wall thickness of 2.0 mm, and height of 15 cm. The copper properties were: k=380 W/mK, ρ=8954 kg/m^3, c_p=383 J/kgK. The mass of the gallium sample in the copper cylinder was always the same: M=0.55 kg, rising to a height of 45 mm. The inside diameter of the polypropylene cylinder was 50.0 mm, with a wall thickness of 2.25 mm, and height of 30 cm. Its other properties were: k=0.17 W/mK, ρ=855 kg/m^3, c_p=1900 J/kgK. The mass of gallium sample in the polypropylene cylinder was always the same: M=0.54 kg, rising to the same height as in the copper cylinder, namely 45 mm.

Temperatures were measured by thermocouples of K-type, in the bath and in the samples with an accuracy of 0.1°C. The thermocouples in the sample, referred to as TC, were installed at four heights above the cylinder bottom, and at four radial positions in the cross-section: TC1: r=3 mm, H=35 mm; TC2: r=10 mm, H=25 mm; TC3: r=17 mm, H=15 mm; TC4: r=22 mm, H=5 mm (Fig. 1). All the thermocouples were connected to a data acquisitor (Agilent 34970 A) and a PC for monitoring and data storage. The samples were vertically immersed in the bath: at first, in the heating bath being heated well above the stable temperature of solidification, which is T_m=29.8-30.0°C. Then, the sample in its shell was transferred into the cooling bath, where the coolant temperature was maintained below the stable temperature of solidification, in the range from 15°C to -20°C. In each experiment the coolant temperature was maintained constant, irrespective of the rate of heat released in the process of subcooling or solidification of the gallium. The circulation of the coolant was intensified or slowed down, to cope with the heat absorbed.
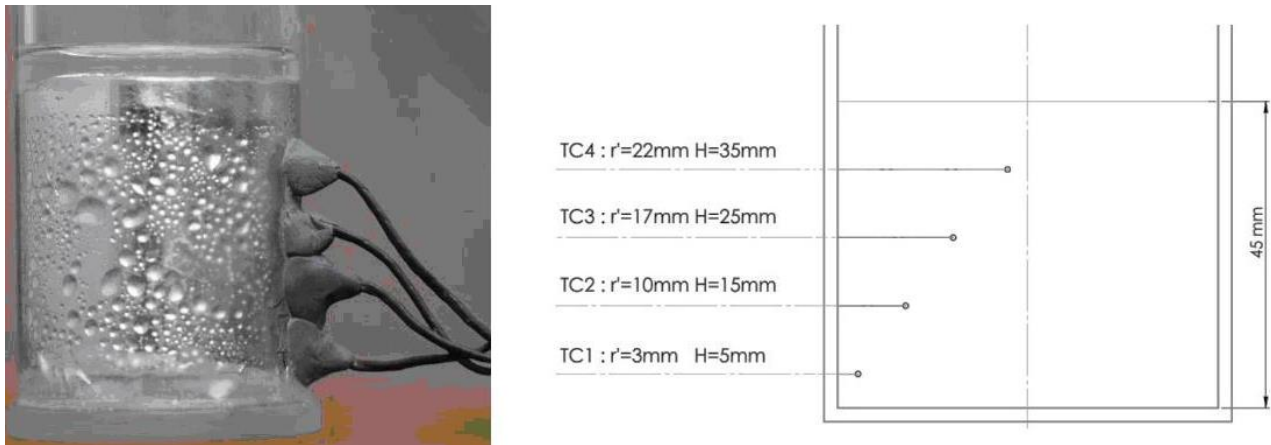

Fig. 1. Experimental cylindrical shell.

With the circulation velocity varied also the forced convection around the immersed sample, yielding a convection heat transfer coefficient of h=240 W/m²K in the zone of gallium subcooling, and h=370 W/m²K in the zone of solidification. The overall heat transfer coefficient, U, between the gallium and the coolant was obtained as follows: for the copper cylinder $U \cong h$, namely U_c=240 W/m²K in the cooling zone, and U_s=370 W/m²K in the zone of solidification. For the polypropylene cylinder the coefficient was U_c=57 W/m²K in the zone of subcooling, and U_s=63 W/m²K in the zone of solidification.

3. Heat transfer processes

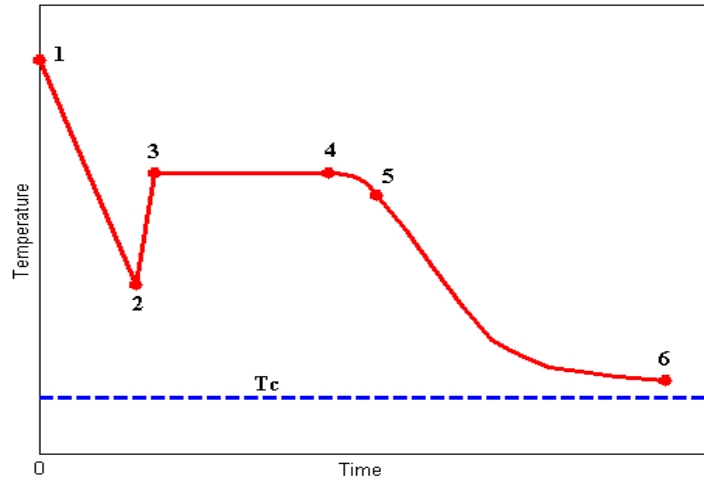The path of subcooled solidification is illustrated in Fig 2.

Fig. 2. Path of subcooled solidification.

The path consists of four stages (a)–(d):

(a) Subcooling of the liquid gallium from its initial temperature, T_i, at point (1), to its nucleation temperature, T_N, at point (2), while the coolant is at temperature, T_c,

$$\left[\left(M c_p \right)_{gal} + \left(M c_p \right)_{cyl} \right] dT \Big/ dt = -U_c A (T - T_c) \tag{1}$$

where at point (1) $t=0$, $T=T_i$; at (2) $t=t_2$, $T=T_N$, $f_m=1$. M represents the total mass, A is the wall surface around the sample, and f_m is the melt fraction, defined as the ratio of the liquid mass to the total mass of the sample, namely the gallium. The nucleation temperature, T_N, has to be specified, being obtained empirically in a heterogeneous process [3]. It varies with the surface characteristics of the walls [10, 12], and with the rate of subcooling [3, 5, 6].

(b) Nucleation at the walls of the cylinder is initiated at point (2). A layer adjacent to the wall solidifies along the path (2)-(3). The released latent heat is absorbed within the whole mass of the gallium and the cylinder, raising the temperature to T_m at (3). The process along this path is rapidly completed, without heat removal to the coolant.

$$\left(M_{23} \right)_{gal} L = \left[\left(M c_p \right)_{gal} + \left(M c_p \right)_{cyl} \right] (T_m - T_N) \tag{2}$$

where at point (3) $t_3=t_2$, $T_3=T_m$, $f_m=1-(M_{23}/M)_{gal}$. M_{23} stands for the solidified gallium. The remaining liquid gallium is,

$$M_3 = M - M_{23} \tag{3}$$

(c) Solidification of the sample core is performed along the path (3)-(4). The solid layer around the central core thickens, and with it, the thermal resistance increases. Along the path (4)-(5), the average temperature falls below the stable temperature of solidification. At point (5) the solidification is completed, $f_m=0$.

$$\left(dM \Big/ dt \right)_{liqgal} L = -U_s A (T - T_c) \tag{4}$$

(d) Cooling liquid gallium along the path (5)-(6) is performed down to an arbitrarily chosen temperature,

$$\left[\left(M c_p \right)_{gal} + \left(M c_p \right)_{cyl} \right] dT \Big/ dt = -U_c A (T - T_c) \tag{5}$$

where at (6) $t=t_6$, $T=T_6$ as chosen.

For the solution of the above equations Matlab software has been used. The modeled curves of temperature and melt fraction are further shown for comparison with the measured temperatures.

4. Results and analysis

In our previous works [13-16] we have studied the solidification of paraffin, which has a very low thermal conductivity. The thermal conductivity of the coolant, aqueous or air, was usually of the same order or lower [14, 15]. In such process the latent heat released in nucleation is either entirely or partly consumed in the solid-liquid mixture of the subcooled substance, or partly rejected into the coolant.

In our present study, the substance chosen, gallium, has a high thermal conductivity (k=40.6 W/m K), as compared to the coolant, which is an aqueous solution. The external thermal resistance between gallium and the coolant was contributed by the shell made of copper or of polypropylene, and the coolant convective layer adjacent to the shell.

In the process illustrated along the path (2)-(3) in Fig. 2, the external overall heat transfer coefficient, U, was 370 W/m^{2}K, for the copper shell, and 63 W/m^{2}K for the polypropylene shell. The thermal external resistance, expressed as $1/U$, is most significant in our case.

The simulations and the experimental measurements have demonstrated that the latent heat released in nucleation is fully absorbed in the highly conductive gallium, contained in the polypropylene shell, whereas over 95% of that heat is absorbed in the gallium when contained in the copper shell. Our analytical formulation of the heat transfer processes is based on that phenomenon. Thus, the process from nucleation up to stable solidification is instantaneous, and is presented as a vertical path.

In the literature cited, there are always two figures unknown beforehand: the nucleation temperature and the velocity of temperature change. In our case, only a single figure is unknown, namely the nucleation temperature, which has to be obtained empirically. The velocity along the nucleation path depends on the ratio of the thermal resistances, of the solidifying substance itself and the external shell and coolant.

4.1. Static gallium

The present study of subcooled solidification of gallium, contained in cylindrical shells of copper or polypropylene, relates to heterogeneous processes, in which the container walls affect the nucleation temperature and patterns of crystal growth.

Our experimental research was performed at a degree of subcooling from 5°C to 45°C. Some of the experiments were repeated to assess the reproducibility of the nucleation temperature. Chen et al. [5] have repeated 24 times each experiment in their research on freezing of water, and defined a nucleation probability function.

In our work, for each experiment and its simulation, three temperatures were specified: the initial temperature, the coolant temperature, and the stable solidification temperature. The experimental nucleation temperature has been adopted in our analysis, as a specified datum. The final temperature of the cooled solid may be chosen arbitrarily, above or close to the coolant temperature.

Figs 3 to 8 present a comparison between the experimental and simulated curves of the averaged time-dependent temperatures of the sample. The simulated melt fraction in those figures shows the gradual disappearance of the liquid, and the completion of solidification. Figs 3 to 5 illustrate the process of subcooled gallium solidification in a copper shell, at coolant temperatures of -15°C, -12°C, and -5°C, respectively. The experimental solidification curves appear 1°C - 3°C below the stable temperature, while the modeling is formulated for solidification at the stable temperature. Thus, in Fig. 3, the experimental curve reaches the stable temperature, and then gradually decreases. Finally, solidification is completed at about 10°C. The simulated curve reaches earlier the stable temperature of 30°C, but once there it closely follows the experimental path. Figs 4 to 5 exhibit similar performance.

The appearance of the experimental averaged temperature of solidification below the stable temperature is affected by two competing rates: the rate of latent heat release and the rate of heat

removal by the coolant. A lower temperature indicates that the rate of removal was too high at the stable temperature.

Figs 6 to 8 illustrate the experimental and simulated curves obtained in the polypropylene shell, at coolant temperatures of 10°C, -10°C, and -18°C, respectively.

It is obvious that the large thermal resistance of the polypropylene wall slows down the rates of heat removal. The temperature rise from the nucleation temperature to the stable solidification temperature is vertical, demonstrating that there is no removal of heat from the sample. The solidification process, in this case, is conducted at the stable temperature. The solidification lasts for 1500-3500 s, while in the copper shell it lasts only about 300 s.

Figs 6 to 8 present an excellent agreement, almost a "curve fitting", between experiment and simulation. The instantaneous (vertical) transition from nucleation to stable solidification is due to the high conductivity of gallium and the low conductivity of the polypropylene shell. In the copper shell, about 5% of the released heat is lost to the coolant. Thus, only the nucleation temperature is to be achieved experimentally. All the other temperatures are either specified or analytically obtained.
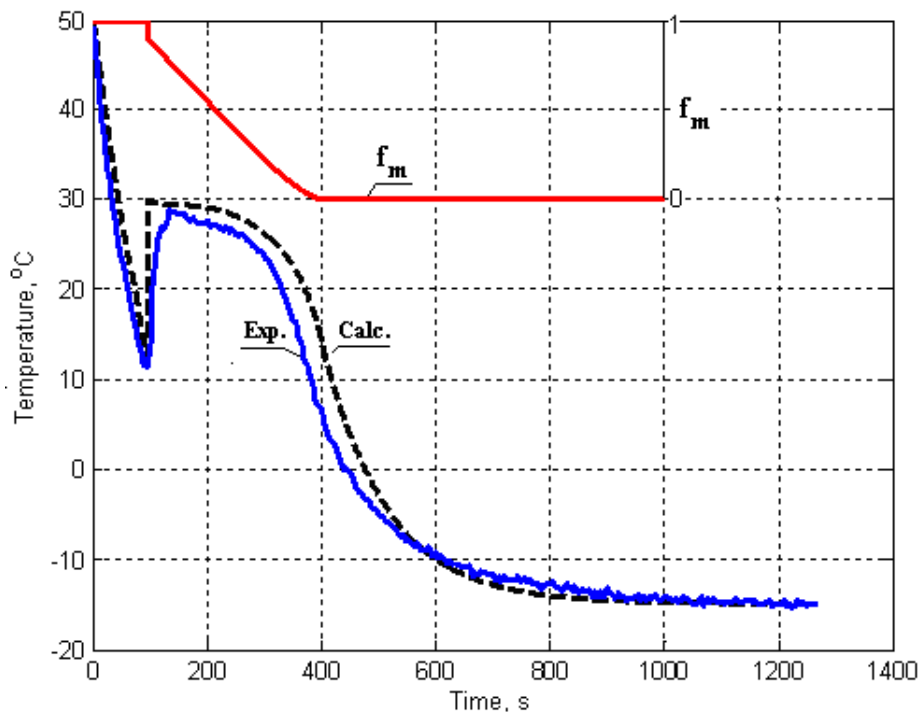

Fig. 3. Experimental and simulated time dependent temperatures and melt fraction of gallium in copper shell, in coolant at -15°C.
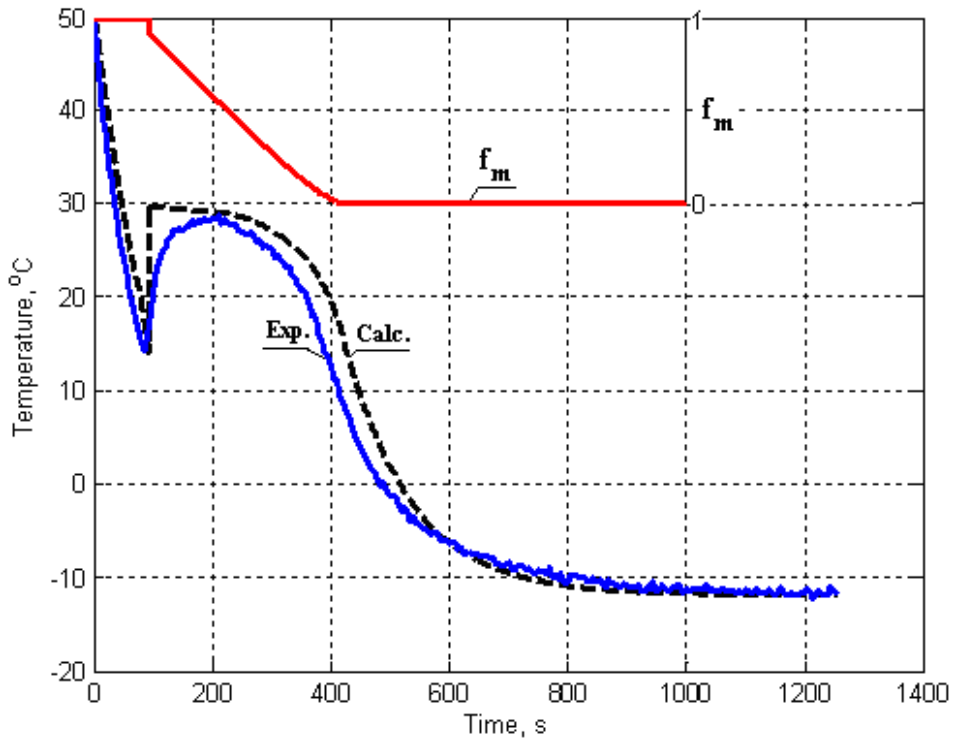
Fig. 4. *Experimental and simulated time dependent temperatures and melt fraction of gallium in copper shell, in coolant at -12°C.*
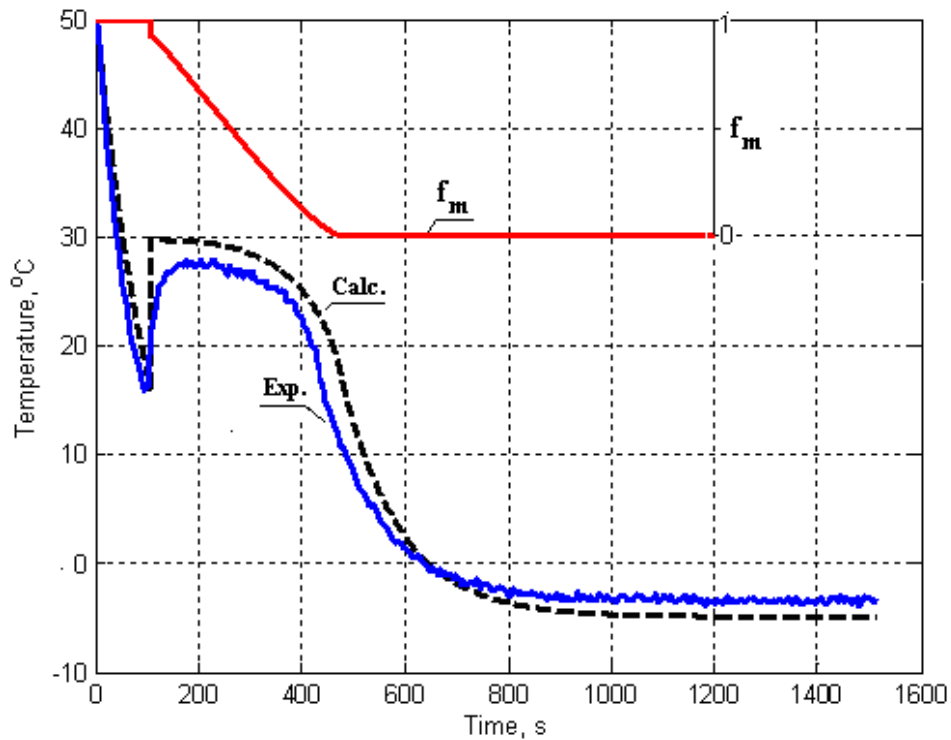

Fig. 5. *Experimental and simulated time dependent temperatures and melt fraction of gallium in copper shell, in coolant at -5°C.*
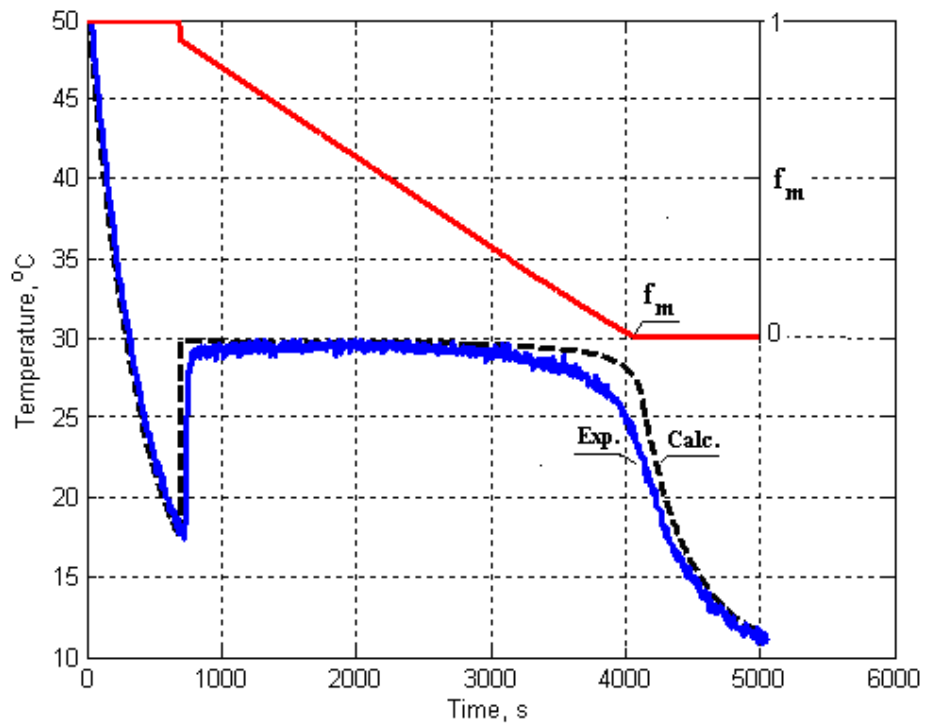
Fig. 6. Experimental and simulated time dependent temperatures and melt fraction of gallium in polypropylene shell, in coolant at 10°C.
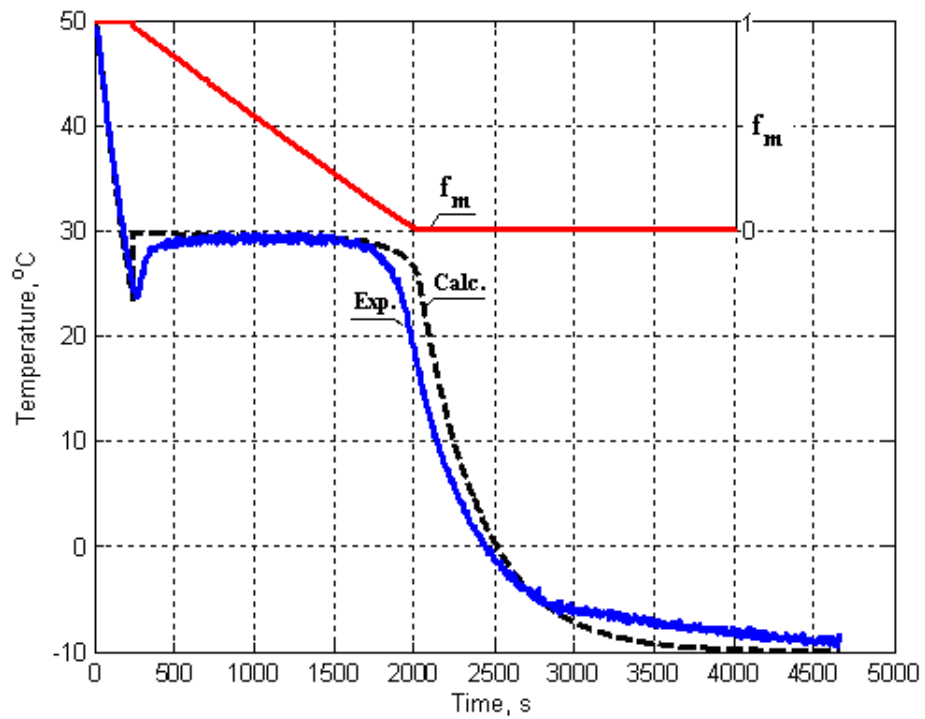

Fig. 7. Experimental and simulated time dependent temperatures and melt fraction of gallium in polypropylene shell, in coolant at -10°C.
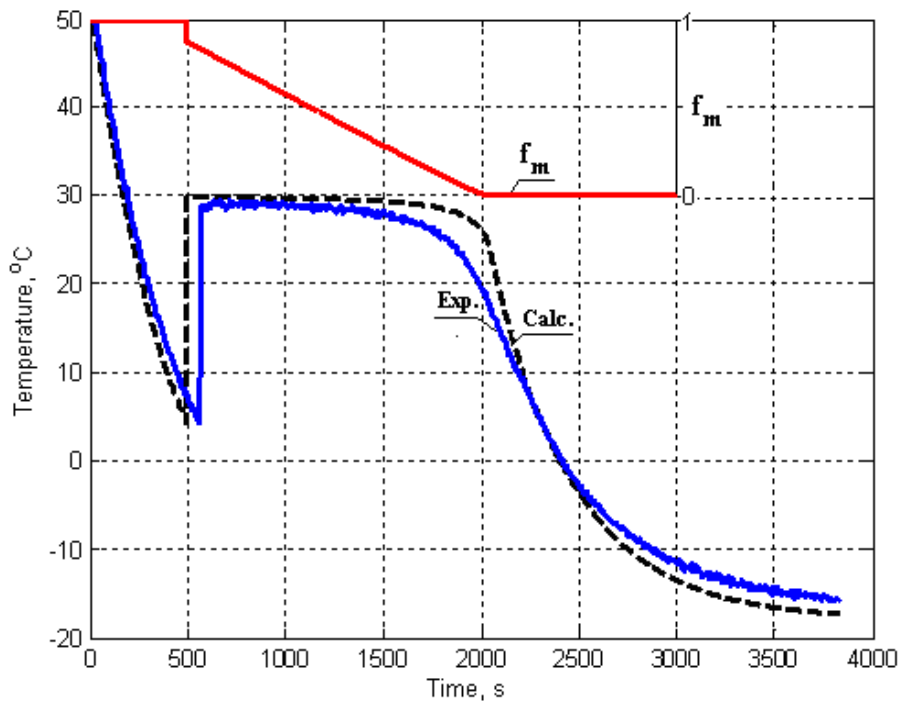
Fig. 8. Experimental and simulated time dependent temperatures and melt fraction of gallium in polypropylene shell, in coolant at -18°C.

The heat transfer experimentation and analysis have been concerned with heterogeneous subcooled solidification of gallium, contained in copper and polypropylene shells. Therefore the wall characteristics and operating conditions are expected to dominate nucleation and initial solidification. We assume that if the same conditions are preserved in applications of the process, then the path and the length of each stage, as well as the solidification completion, can be reproduced. In such case the heat transfer analysis provides a good prediction of the process.

4.2. Flow of liquid gallium

Previous investigations in our laboratory, using other phase-change materials, have demonstrated that the solidified phase at the cooled boundaries adheres to the walls without cavities for the case of the initially filled shell, and with irregular cavities for the case of poured material (Fig. 9). In this case flow and solidification occur simultaneously. The numerical study explored solidification of the flowing liquid material by a two-dimensional (axially symmetric) model, using Fluent 6.2 software. The numerical approach has been extensively described in [14, 15, 16] including a careful verification of the numerical model, in the course of which the effects of time step and grid size and structure had been examined. Also, as can be seen in Fig. 9, the numerical model has predicted an irregular boundary.
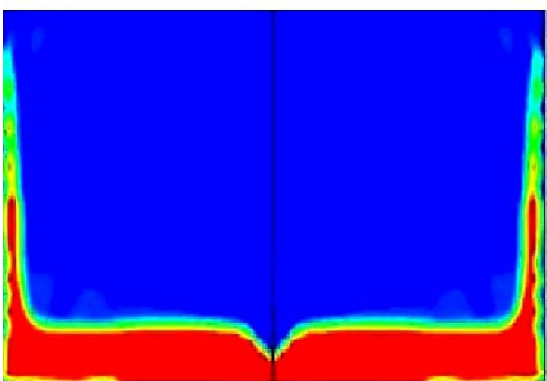
In the present study of the flowing liquid gallium, its rate was 0.12 - 0.3 ml/s. At higher flow rates the solidification approached the behaviour of an initially filled shell. The primary experimental results are presented in Fig. 10.
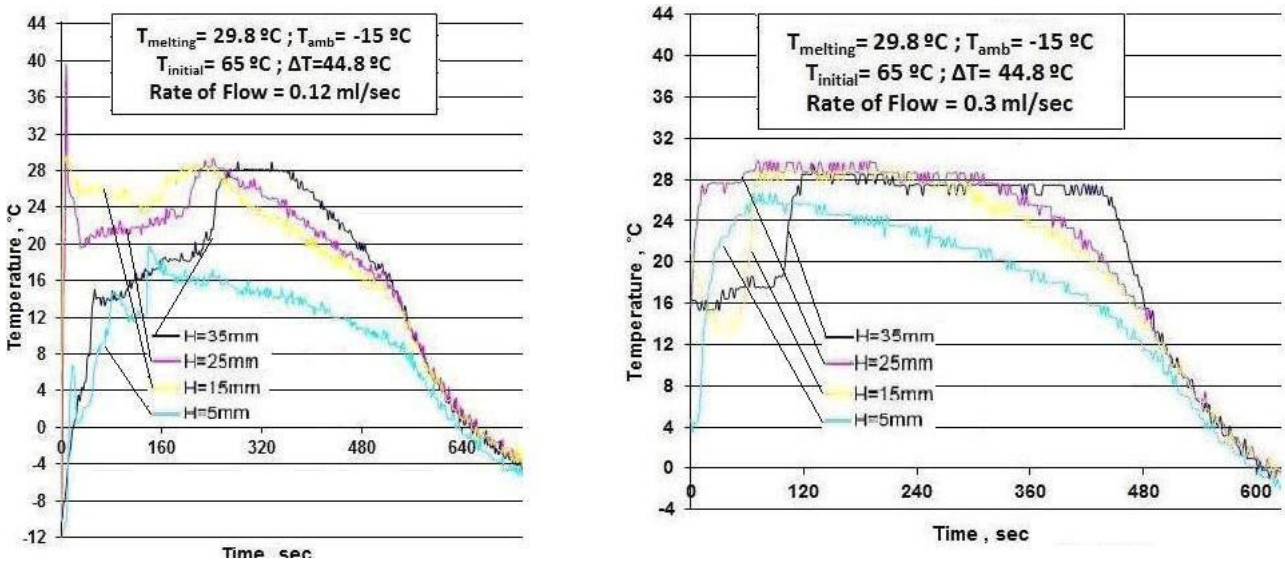

Fig. 10. Experimental results for flowing liquid gallium. Flowrate 0.12 (left) and 0.3 (right) ml/s.

Results of numerical calculations were obtained for flowrate of 0.3 ml/s. The flowing and solidifying gallium has formed an irregular boundary at the walls (Fig. 11), with cavities of sizes relatively larger than in previous investigation of flowing liquid paraffin.
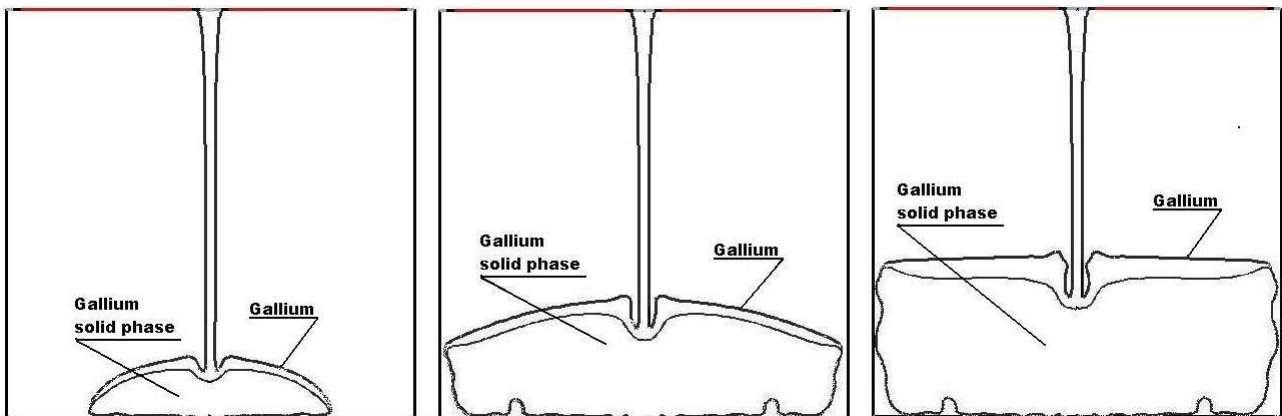

Fig. 11. Irregular boundary of flowing gallium at the rate of 0.3 ml/s. From left to right: 5, 20 and 50s.

The comparison between the flowing paraffin solidification and the flowing gallium solidification just, demonstrates the microscale phenomenon, without formulation or generalization.

5 Conclusions

Experimental and simulated time-dependent temperatures were obtained in the process of subcooled solidification of gallium, contained in copper and polypropylene cylindrical shells, immersed in a coolant of constant temperature.

The conductivity of the shell material affected the length of each stage, and of the overall process. In the conductive copper, the sample could lose up to 5% of its latent heat along the stage from its

nucleation up to its stable solidification. In the polypropylene shell of low conductivity, heat was not transferred from the sample to the coolant along this stage.

The calculated temperature curves simulate well the experimental measurements. The higher thermal resistance of the polypropylene shell has made the simulations to fully fit the experimental curves.

The high conductivity of gallium provides a very rapid change of temperature from nucleation up to stable solidification. Thus, only one empirical temperature has to be achieved in the process, namely the nucleation temperature. All other temperatures are either specified or analytically obtained.

The predictions of the process path, length of each stage, and completion of solidification are of practical significance.

For the case of flowing liquid gallium an irregular boundary at the walls is formed similarly as for previously studied flowing liquid paraffin.

Nomenclature

A wall surface, m^2

c_p specific heat, J/(kg K)

h heat transfer coefficient, W/(m^2 K)

H height, m, mm

f_m melt fraction

k thermal conductivity, W/(m K)

M mass, kg

r radial position, m, mm

t time, s

T temperature, °C, K

T_m solidification temperature, °C

U overall heat transfer coefficient, W/(m^2 K)

Greek symbols

ρ density, kg/m^3

Subscripts

1,2,3,4,5,6   number of point

c   cooling

cyl   cylinder

gal   gallium

i   initial

liq   liquid

N   nucleation

s   solidification

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