

A THEORY OF SHAPEFORMING PROCESSES BY DIRECTIONAL SOLIDIFICATION UNDER MICROGRAVITY CONDITIONS. PART I. BASIC PRINCIPLES - PLANAR SOLID/LIQUID INTERFACE

G. Kaptay

University of Miskolc, Inst. of Chemistry, Dept. of Physical Chemistry
3515 Miskolc, Hungary

ABSTRACT

The exact mathematical description of the processes accompanying the feeding (shapeforming) of castings in directional solidification experiments performed under microgravity conditions has been done. That gives a theoretical basis for planning further solidification experiments in space both by 'skin'- and 'shell'-technologies. If the initial parameters (ie the material and the final shape of the crystal, and the rate of solidification) are given, our theory of shapeforming allows us to select optimal technological parameters (eg the material of the solidification reservoir/shell/skin, the material and shape of the feeding reservoir/shell/skin) to ensure shapeforming. In fact, our theory of shapeforming involves calculation of the energy of processes, which would take place during solidification without shapeforming (W_1 = the energy of shrinkage formation) and with shapeforming (W_2 = energy of developing a lack of melt in the feeding reservoir + energy required for moving the given amount of melt with a given rate from the feeding reservoir to the solid/liquid interface). If $W_2 < W_1$ at any moment of time during solidification, the shapeforming process will take place. Equations have been evaluated for directional solidification by planar solid/liquid interface of crystals of cylindrical shape, and of any material with positive ΔV of melting.

1. Introduction

Molar volume of most materials decreases during their solidification (for details see Chapter 2), thus their solidification is accompanied by shrinkage formation. To avoid that some 'feeding' melt is usually used, which is expected to flow during solidification from the 'feeding reservoir' to the solid/liquid interface. Under earth conditions gravity can act as a driving force of such a feeding (shapeforming) process.

Under microgravity conditions some other forces should be used for ensuring the shapeforming process during solidification. Forces, generally used for this purpose can be divided into 'outer' and 'inner' ones. 'Outer' forces, ensured for example by a spring [1], seem to be a general solution to shapeforming problems. However, a whole 'volume compensation device', used in space experiment [1] occupied as much volume (length) as a specimen itself. The better utilization of space devices can be achieved by using 'inner' forces, eg interfacial forces for ensuring shapeforming. Both the 'skin'- and 'shell'- technologies are based on this principle. In skin-technology the surface of a specimen is covered by a thin ceramic layer acting as specimen chamber, while in shell-technology the independent specimen chamber is used. Some examples of a successful application of these technologies can be found in the literature [2-11]. However, the exact mathematical description of the processes taking place during shapeforming by skin- or shell- technologies has not been done yet. In the present paper the author has made an attempt to fulfill this gap and to give a theoretical basis for planning further solidification experiments in space.

The theory to be described will allow optimal technological parameters to be selected for crystallization, which will ensure shapeforming for the given initial parameters. The initial parameters are, as follows :

- i. material of the crystal to be solidified ;
- ii. final shape of the crystal to be solidified ;
- iii. rate of solidification.

'Free' technological parameters, which can be chosen for ensuring shapeforming, are as follows :

- i. material of the solidification reservoir/shell/skin (SR) and feeding reservoir/shell/skin (FR) ;
- ii. shape of the FR, etc.

Choosing these 'free' parameters, however, there are some limitations, namely :

- i. neither the solidification, nor the feeding reservoir should cause any contamination of the melt ;

ii. the shape of the feeding reservoir should be chosen in such a way that it would ensure the maximal utilization of the crystallizing space device.

The present paper deals with directional solidification of the following materials :

- i. materials with positive volume change of melting ;
- ii. materials with planar solid/liquid interface ;
- iii. materials of cylindrical shape ;
- iv. melts of clean surface, which are in direct contact with the wall/shell/skin.

2. The relative molar volume change, accompanying the crystallization process

The relative molar volume change, accompanying the crystallization of materials (ΔV_r°) can be defined as follows :

$$\Delta V_r^\circ = \frac{V_m(\text{solid}, T_{s01}) - V_m(\text{liquid}, T_{l1q})}{V_m(\text{liquid}, T_{l1q})} \quad (1)$$

where V_m - molar volume ;
 T_{s01} , T_{l1q} - solidus- and liquidus temperatures.

The theory given in the present paper is valid for materials with negative ΔV_r° , only. Hence, let us introduce the quantity ΔV° for convenience, which can be defined by the equation :

$$\Delta V^\circ = - \Delta V_r^\circ \quad (2)$$

Values of $100 \Delta V^\circ$ (%) are given in Table 1 for some elements of the Periodical Table. Data have been calculated on the basis of density and thermal expansion data of solid [12], and density data of liquid [13] elements.

Table 1. Values of $100 \Delta V^\circ$ (%) of some elements [12,13]

Li 3.5	Be* 1.7											B# 13	C ----	N ----	O --
Na 2.9	Mg 3.1											Al 7.3	Si -6.4	P ----	S --
K 3.8	Ca ---	Sc ---	Ti 2.7	V 5.3	Cr 5.3	Mn 5.8	Fe* 3.7	Co 5.5	Ni 4.2	Cu 4.4	Zn 4.6	Ga -2.9	Ge -6.5	As ----	Se 15
Rb# 3	Sr ---	Y ---	Zr 2.9	Nb 5.6	Mo 4.8	Tc ---	Ru ---	Rh ---	Pd 6.0	Ag 5.2	Cd 4.6	In 2.3	Sn 2.9	Sb 0.8	Te 6
Cs 1.4	Ba# 0.3	La* 2.5	Hf* 4.8	Ta 6.0	W 7.1	Re 5.7	Os ---	Ir ---	Pt 6.3	Au 2.9	Hg 3.5	Tl# 1.5	Pb 2.9	Bi -3.5	Po --

* - data extrapolated over a phase transition
 # - data extrapolated over a wide temperature range
 --- - data were not found in literature

The sign of ΔV° values given in Table 1 shows a good agreement with the relative coordination number change accompanying a melting process (Δn_m), which can be defined as follows :

$$\Delta n_m = \frac{n(\text{solid}, T_{s01}) - n(\text{liquid}, T_{l1q})}{n(\text{solid}, T_{s01})} \quad (3)$$

Examples of materials with different types of solid-->liquid chemical bond change and the corresponding range of Δn_m and ΔV° are given in Table 2 [12-16]. It can be seen, that the sign of ΔV° (which is the same as the sign of ΔV of melting) will be negative, if the sign of Δn_m is positive, ie if the melting process is accompanied by the increase of coordination number. That is the case for covalent--->metallic (and probably for covalent--->ionic) type of change in chemical bond accompanying melting. If $\Delta n_m \leq 0$, ΔV° will be positive, hence our theory of shapeforming will be valid for this type of material.

Table 2. Parameters of melting for different materials [12-16]

solid ---> liquid chemical bond change	100 Δn_m %	100 ΔV° %	Examples
covalent ---> covalent	± 0	+ (2...30)	N ₂ , PH ₃ , Ga ₂ Te ₃
metallic ---> metallic	- (5...10)	+ (1...8)	Na, Cu, Al
ionic ---> ionic	- (20...30)	+ (10...20)	NaCl, KBr
ionic ---> covalent	- ≈ 100	+ ≈ 50	AlCl ₃
covalent ---> metallic	+ ≈ 100	- (5...15)	Ge, GaAs, Mg ₂ Pb

The value of ΔV° for solutions (alloys), and mixtures can be calculated, assuming their ideal behavior :

$$\Delta V^\circ = \sum_{i=1}^n x_i \Delta V_i^\circ \quad (4)$$

where n - number of components ;
 x_i - molar ratio of component i ;
 ΔV_i° - ΔV° of component i .

If there is a strong chemical interaction between the components of a given solution, leading to formation of complexes or associates, these 'components' should be taken into consideration, too. Using thermodynamic properties of such associates and molar ratio of initial components, molar ratio of 'equilibrium components' (initial components + associates) can be calculated (for metallic systems see [17,18]). In order to use Eq. (4) for this case, values of ΔV° for associates, as individual compounds, must be known. It should be noted, that values of ΔV° for associates generally will not be equal to the average of ΔV° values of initial components. For example, in Mg-Pb system, which is constructed from two metallic components, melting by metallic--->metallic mechanism ($\Delta V^\circ = +0.031$ and $+0.029$, accordingly), the Mg₂Pb associate/compound will be formed, which melts by covalent--->metallic mechanism, giving $\Delta V^\circ = -0.040$ [15].

3. Feeding factor

Let us introduce a 'feeding factor' (f), a volume of a melt at liquidus temperature, which is necessary to transport from the feeding reservoir (FR) to the solid/liquid interface in order to get a unit volume of crystal of perfect shape (without any shrinkages) at solidus temperature, ie :

$$f = dV_F/dV_s \quad (5)$$

where V_s - volume of a crystal at solidus temperature ;
 V_F - volume of feeding melt at liquidus temperature, which is necessary for shapeforming of the crystal of final volume V_s at solidus temperature.

Let us consider a solidification process of the melt of volume dV_s , accompanied by feeding/shapeforming from the thermodynamical point of view, regardless of the real (kinetical) way the feeding process is taking place.

Step 1a : melt of volume dV_s is solidified, and a primary shrinkage of volume $\Delta V^\circ dV_s$ is formed ;

Step 1b : primary feeding takes place, ie some melt of volume $\Delta V^\circ dV_s$ is transported into the primary shrinkage ;

Step 2a : melt of volume $\Delta V^\circ dV_s$ is solidified, and a secondary shrinkage of volume $\Delta V^\circ (\Delta V^\circ dV_s)$ is formed ;

Step 2b : secondary feeding takes place, ie some melt of volume $(\Delta V^\circ)^2 dV_s$ is transported into the secondary shrinkage ;

Step na : melt of volume $(\Delta V^\circ)^{n-1} dV_s$ is solidified, and an n-order shrinkage of volume $(\Delta V^\circ)^n dV_s$ is formed ;

Step nb : n-order feeding takes place, ie melt of volume $(\Delta V^\circ)^n dV_s$ is transported into the n-order shrinkage.

Consequently, the total volume of the melt necessary for the given process can be described, as follows :

$$dV_F = dV_s \Delta V^\circ [1 + \Delta V^\circ + (\Delta V^\circ)^2 + \dots + (\Delta V^\circ)^{n-1}] \quad (6)$$

There is an infinite geometrical row in the brackets of Eq.(6), which can be summarized as $0 < \Delta V^\circ < 1$. Finally from Eq.(6) :

$$dV_F = dV_s \frac{\Delta V^\circ}{1 - \Delta V^\circ} \quad (7)$$

Substituting Eq.(7) into Eq.(5) one can get an expression for the feeding factor :

$$f = \frac{\Delta V^\circ}{1 - \Delta V^\circ} \quad (8)$$

4. The driving force of shapeforming

Definition : A shapeforming process by solidification under microgravity conditions is called a process, which ensures an appearance of a lack of a material in the feeding reservoir instead of a formation of shrinkage along the crystal in the solidification reservoir due to the melt transport drawn from the feeding reservoir to the solid/liquid interface.

From the thermodynamical point of view the energy-change, related to the shapeforming process equals to the energy-difference between the states 'crystal, solidified by shapeforming' (State II, W_{II}), and 'crystal, solidified without shapeforming' (State I, W_I). As real processes take place with a certain rate, the energy term, related to the transport of feeding melt (W_{tr}) should be taken into consideration, too. Hence, the total energy-change during the shapeforming process (ΔW_{SHF}) can be described, as follows :

$$\Delta W_{SHF} = (W_{II} + W_{tr}) - W_I \quad (9)$$

Definition : Driving force of the shapeforming process is equal to the energy-change during shapeforming per a unit volume of a solidifying melt, taken with an opposite sign :

$$DF = - \frac{d(\Delta W_{SHF})}{dV_s} \quad (10)$$

The value of driving force generally depends on the coordinate of solid/liquid interface, x_s . The shapeforming process will be successful, if $DF > 0$ for any value of $0 \leq x_s \leq L_s$ (where L_s is the length of the solidification reservoir).

States I and II are illustrated in Fig.1. From the thermodynamical point of view the energy terms, related to States I and II, can be divided into three parts, as follows :

$$\left. \begin{aligned} W_I &= W_{I(S)} + W_{I(F)} + W^\circ \\ W_{II} &= W_{II(S)} + W_{II(F)} + W^\circ \end{aligned} \right\} \quad (11)$$

where $W_{I(S)}$ and $W_{II(S)}$ are energy-terms related to the solidification reservoir (SR), which undergo some change during shapeforming ;
 $W_{I(F)}$ and $W_{II(F)}$ the same, related to the FR ;
 W° - does not change during the shapeforming process.

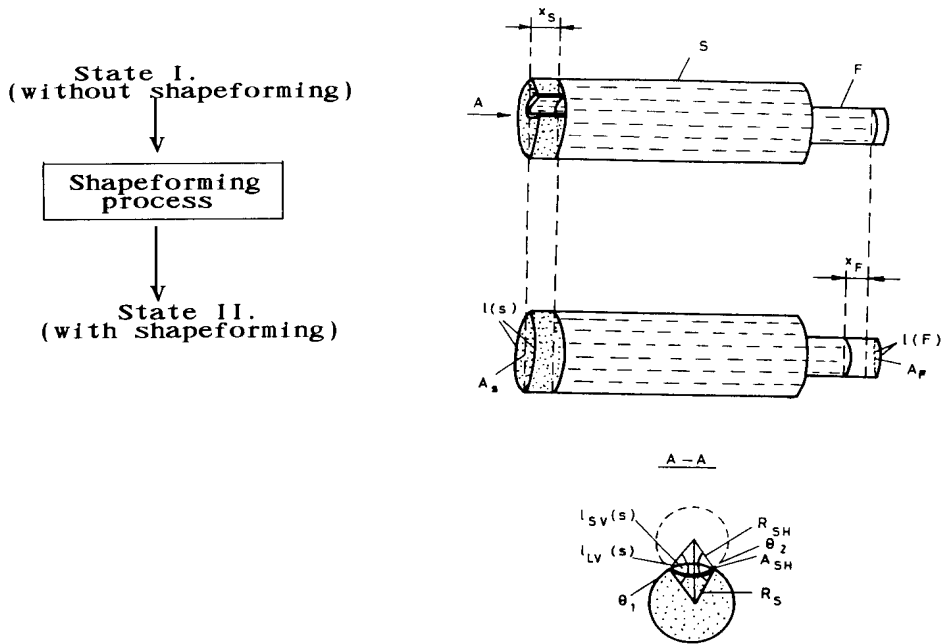


Fig.1. State I. and state II of a shapeforming process.

Substituting Eq.(9) and (11) into Eq.(10), and introducing functions $F(s)$ and $F(F)$ the following expression has been obtained

$$DF = \sigma[F(s) - F(F)] - F(tr) \tag{12}$$

where σ - surface tension of a melt - the same as σ_{lv} (see Eq.(14)) ;

A_s - cross section area of SR ;

$F(s)$, $F(F)$, and $F(tr)$ are functions, related to SR and FR, and to the transport process, consequently :

$$\left. \begin{aligned} F(s) &= \frac{1}{A_s \sigma} \frac{d[W_I(s) - W_{II}(s)]}{dx_s} \\ F(F) &= \frac{1}{A_s \sigma} \frac{d[W_I(F) - W_{II}(F)]}{dx_s} \\ F(tr) &= \frac{dW_{tr}}{A_s dx_s} \end{aligned} \right\} \tag{13}$$

- As it can be seen, in order to ensure a positive and large DF :
- i. $F(s)$ should be positive and as large as possible ;
 - ii. $F(r)$ should be small (if positive), or it should be negative, and as large as possible ;
 - iii. $F(tr)$ should be as small as possible.

In forthcoming chapters the detailed description of DF-terms will be done. Before going into details, let us make one point clear. Chapters 5 & 6 will deal with interfacial energies between the melt and the material of solidification and feeding reservoirs. Thus, thermodynamical quantities are used for description of processes taking place with a finite rate. Isn't there any contradiction in this method ? Indeed, a realization of an equilibrium value of interfacial energy between any solid and liquid phases takes some time. This interval of time can be especially long (more than a minute, but probably less than an hour), if there is a chemical interaction between the phases. However, in shapeforming processes taking place with a finite rate, we deal with processes of 'tearing' a melt from the surface. Thus, if an equilibrium had been achieved between the phases before the beginning of solidification (shapeforming) processes, the energy of 'tearing off' will be equal to the equilibrium interfacial energy taken with an opposite sign, regardless of the rate of the solidification/shapeforming/'tearing off' process. Experiments on directional solidification generally consist of three parts : melting, stabilization of the temperature field, and solidification. As a rule, time required for the stabilization of the temperature field is enough for reaching the equilibrium values of interfacial energies. Consequently, if at least half an hour has gone between melting and the beginning of solidification, equilibrium values of contact angle (θ_s and θ_r - see Chapters 5 & 6) can be used in calculations, even if the solidification process takes place with a 'high' rate.

5. Determination of function $F(s)$

The following expressions can be given for States I and II (see Fig.1) :

$$W_I(s) = X_s [l_{sv}(S) \sigma_{sv}(S) + l_{lv}(S) \sigma_{lv}] + A_s \Delta V^0 [\sigma_{sv}(S) + \sigma_{lv}] \quad (14)$$

$$W_{II}(s) = X_s l_{sv}(S) \sigma_{sl}(S) + A_s \Delta V^0 \sigma_{sl}(S)$$

where σ is the interfacial energy of the corresponding two phases (s -solid, l -liquid, g -gas). The three σ are related by Young equation :

$$\sigma_{sv} - \sigma_{sl} = \sigma_{lv} \cos \theta \quad (15)$$

where θ is a contact angle between liquid and solid phases.

Substituting Eq.(15) into Eq.(14) one can get the energy-difference $\Delta W(s) = W_I(s) - W_{II}(s)$:

$$\Delta W(s) = \sigma_{1v} x_s [l_{sv}(s) \cos \theta_s - l_{lv}(s)] + A_s \Delta V^\circ \sigma_{1v} (1 + \cos \theta_s) \quad (16)$$

where θ_s - contact angle between the melt and the wall of SR.

The second term of Eq.(16) seems to be independent of x_s . In reality this energy term equals zero at $x_s=0$, and it equals the value described by the second term of Eq.(16) at $x_s=1$ unit of crystal, ie 1 diameter of crystalizing atoms or molecules (about 10^{-10} m). Consequently, the value of $F(s)$ is very large at $x_s \rightarrow 0$. That is a reason for the fact that in our pre-experiments [11] shrinkages were never found at the very beginning of the crystal. At $x_s > 1$ unit of crystal the function $F(s) = \phi(x_s)$ becomes a horizontal line (see Fig.2). Let us mark this value of $F(s)$ as $F(s)^\circ$. Using Eq.-s (13) and (16) the following expression for $F(s)^\circ$ can be obtained :

$$F(s)^\circ = \frac{l_{sv}(s) \cos \theta_s + l_{lv}(s)}{A_s} \quad (17)$$

As follows from Eq.(17), for obtaining value $F(s)^\circ$ values of $l_{sv}(s)$ and $l_{lv}(s)$, ie the geometry of the shrinkage, should be first calculated. The geometry of the shrinkage will be determined by values ΔV° and θ_s , and by the principle of minimal energy of the system. Thus, the required values can be calculated solving the following system of equations (for symbols see Fig.1.) :

$$\left. \begin{aligned} A_{SH} &= A_s \Delta V^\circ \\ \theta_1 &= \theta_2 = \theta_s \\ \{ l_{sv}(s) \sigma_{sv}(s) + l_{lv}(s) \sigma_{lv} + [l(s) - l_{sv}(s)] \sigma_{sl}(s) \} &\rightarrow \min \end{aligned} \right\} \quad (18)$$

where A_{SH} - area of the cross-section of the shrinkage.

As follows from Eq.(18), for solidification reservoir of cylindrical shape the geometry of the shrinkage will be determined by two arcs. One of these arcs (of length $l_{sv}(s)$) is formed by the wall of SR of radius R_s , while the other one (of length $l_{lv}(s)$) is

a part of an imaginary circle of radius R_{SH} . If the temperature field inside the sample is homogeneous or at least symmetrical around the longitudinal axis of the sample, the path of the shrinkage will be parallel with the longitudinal axis. In the major part of the sample the shrinkage of the same cross-section will appear (with an area of ΔV°). However, at the very beginning, and at the very end of the sample, the shrinkage will be appearing and disappearing gradually, ie its cross section will be increasing gradually from zero to ΔV° at the beginning, and vice versa, at the end of the sample (transitional section). The typical shrinkage, obtained in our pre-experiments [11] is shown in Fig. 3.

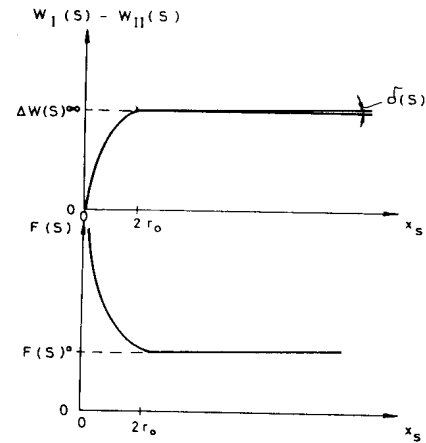


Fig.2. $F(s)$ and $\Delta W(s)$, as a function of x_s . r_0 - radius of a unit of crystal (atom, molecule)

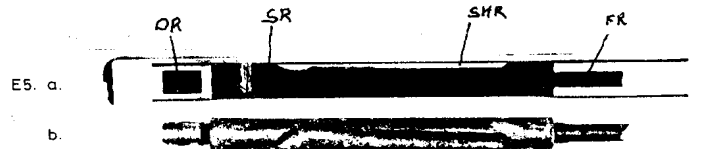


Fig.3. Illustration of a 'natural shrinkage', obtained in ground-based, horizontal experiment. X-ray image of ampoule (a.) and image of sample (b.) after the experiment [11] (directional solidification of Al-Ni eutectic alloy). OR:overflow reservoir; SR:solidification reservoir; FR:feeding reservoir; SHR:shrinkage. (___ 30 mm ___)

First, let us determine function $F(s)^\circ$ for the shrinkage with the constant cross section of ΔV° . The analytical expression for $F(s)^\circ$ cannot be delivered from Eq.(17-18) even in this simple case. That is why values of $F(s)^\circ$ have been obtained by iteration method using a computer, as a function of R_s , ΔV° , and θ_s . Functions $F(s)^\circ$ R_s are given in Fig.4a, as a function of θ_s , for

the given ΔV° values. The functions can be described with a good accuracy by the following semi-empirical equation :

$$F(s)^\circ R_s = (1 + \cos\theta_s)(\Delta V^\circ)^{1/2} + (1 - \cos\theta_s)[(1 - \Delta V^\circ)^{1/2} - 1] + K_s \sin\theta_s \quad (19)$$

where values of K_s can be taken from Fig.4b, or for $\Delta V^\circ < 0.2$ (which is most important for the practise - see Table 2) can be calculated from the empirical equation : $K_s = 0.390(\Delta V^\circ)^{0.481}$. The geometry of the cross section of the shrinkage and the values of $F(s)^\circ$ function in the transitional section can be calculated in the same way, but using instead of ΔV° the given $0 < \Delta V < \Delta V^\circ$ value, characterizing the given cross section.

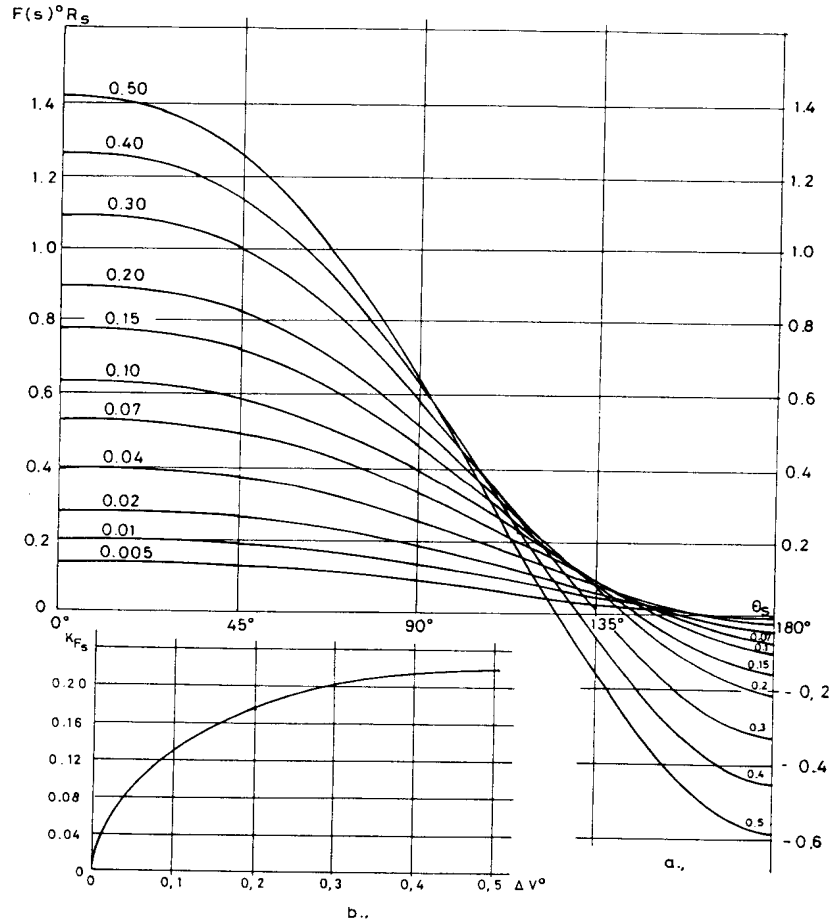


Fig.4. a. Values of $F(s)^\circ R_s$ as a function of θ_s at different values of ΔV° (figures on graphs).
 b. Values of constant K_s , as a function of ΔV° (Eq.(19))

Finally, the following conclusion can be drawn from Chapter 5. In order to increase the driving force of shapeforming of a crystal of given geometry and material (ie R_s , ΔV° , and σ are given as initial parameters), the material of the wall/shell/skin of the solidification reservoir should be chosen in such a way that as high as possible interfacial energy between the melt and the wall would appear to give minimal θ_s , and maximal $F(s)^\circ$.

6. Determination of function $F(F)$

First, let us consider some feeding melt, which is in contact with the side-walls, but not with the end-wall of a feeding reservoir. Quantities corresponding to this case are marked, as $W(F)^\circ$, and $F(F)^\circ$. Then, using symbols in Fig.1 we obtain :

$$\left. \begin{aligned} W_{I(F)}^\circ &= x_f l(F) \sigma_{sl}(F) \\ W_{II(F)}^\circ &= x_f l(F) \sigma_{sv}(F) \end{aligned} \right\} \quad (20)$$

where $\sigma(F)$ - interfacial energies corresponding to the interface between the melt and the wall of the feeding reservoir.

Before substituting these expressions into Eq.(13) the relationship between x_s and x_f is required. This expression can be obtained from the fact that a volume of feeding melt is obviously equal to a volume of a crystal multiplied by a feeding factor, ie :

$$x_f A_F = f x_s A_s \quad (21)$$

where A_F - cross section of a feeding reservoir.

From Eq.s(13, 20, 21) the following expression has been obtained :

$$F(F)^\circ = f \lambda_F \cos \theta_F \quad (22)$$

where θ_F - contact angle between the melt and the wall of the feeding reservoir ;

λ_F - specific arc (arc over area of cross section), or specific superficies (superficies over volume) of FR

$$\lambda_F = \frac{l_f}{A_F} = \frac{l_f}{A_F} \frac{dx_f}{dx_f} = \frac{S_F}{V_F} \quad (23)$$

For FR of cylindrical shape one can get from Eq.(22-23) :

$$F(F)^\circ = f \frac{2}{R_F} \cos \theta_F \quad (24)$$

where R_F - radius of the FR.

As it can be seen from Eq.s(22-24), in order to increase driving force, the material of the wall/shell/skin of the feeding reservoir should be chosen in such a way, that as low as possible interfacial energy between the melt and the wall would appear to give maximal θ_s , and to make the value of $F(F)^\circ$ as negative as possible. Principally, however, as value of θ_F may vary from 0° to 180° , function of $F(F)^\circ$ can be both positive and negative, according to Eq.s(22-24). Then, the following two cases should be considered :

i. the melt does not wet the wall of the FR ($\theta_F > 90^\circ$)

In this case $F(F)^\circ$ is negative, and so, in order to increase the driving force (see Eq.(12)), the value of λ_F should be as high, as possible. That can be achieved by using FR with cross section of irregular shape. However, there is no sense in using a 'zigzagged' shape, as the wall in the zigzags will not be in contact with a non-wettable melt. If FR of cylindrical shape is used, R_F should be as small as possible (see eq.(24)). However, decreasing R_F the length of FR must be increased. That would decrease the utilization of the space device on the one hand, and increase W_{tr} (see Chapter 7) on the other. For increasing utilization of the space furnace, a feeding device, containing a large amount of capillaries of small radius, can be used. That, again, would lead to the certain increase of W_{tr} . However, the optimal radius, and number of capillaries can be calculated, at which the value of driving force is maximal at a given value of $F(s)^\circ$ function (in details, see Chapter 7.1). Finally, it should be mentioned, that even if FR and SR of the same material and same radius are used at infinitely low rate of crystallization (W_{tr} is negligible), the shapeforming will be positive.

ii. the melt wets the wall of the FR ($\theta_F < 90^\circ$)

This case is quite undesirable, but possible, especially for melts with low surface tension, and high chemical activity. In this case $F(F)^\circ$ is positive, and so, in order to increase the driving force (see Eq.(12)), its value should be as low as possible. Hence, value of λ_F should be minimal. Among all planar geometrical forms the circle has the least value of specific arc, hence the feeding reservoir in this case must be cylindrical. As it follows from Eq.(24), the radius of the FR should be maximal. From the point of view of utilization of the cross section of the space-furnace, the optimal value for R_F is : $R_F = R_s$. If FR and SR of the same material and same radius are used at infinitely low rate of crystallization (W_{tr} is negligible), the shapeforming will be ensured, if the following inequality is valid : $(\Delta V^\circ)^{1/2} > f$ (compare Eq.s(12,19,24)). Substituting Eq.(8), the solution of this inequality can be obtained : $\Delta V^\circ < 0.38$. Consequently, for most materials (see Tables 1. and 2.) the driving force will be positive even if the solidification and feeding reservoirs are made of the same material, and are of the same radius.

Finally, at any value of contact angle, the positive driving force can be achieved even in the simplest case, ie when SR and FR of the same material and radius are used if the following conditions are fulfilled :

i. W_{tr} is negligible (see Chapter 7) ;
 ii. the melt in feeding reservoir is not in contact with the end-wall of FR before the beginning of the solidification process.
 Now, let us consider the case when the melt in the feeding reservoir is in contact with the end-wall of FR before the beginning of the solidification process. In this case the value of $F(F)$ function will differ from the value of $F(F)^{\circ}$ function at the beginning of the feeding/shapeforming process (transitional state). The first steps of the feeding process are illustrated in Fig. 5a.

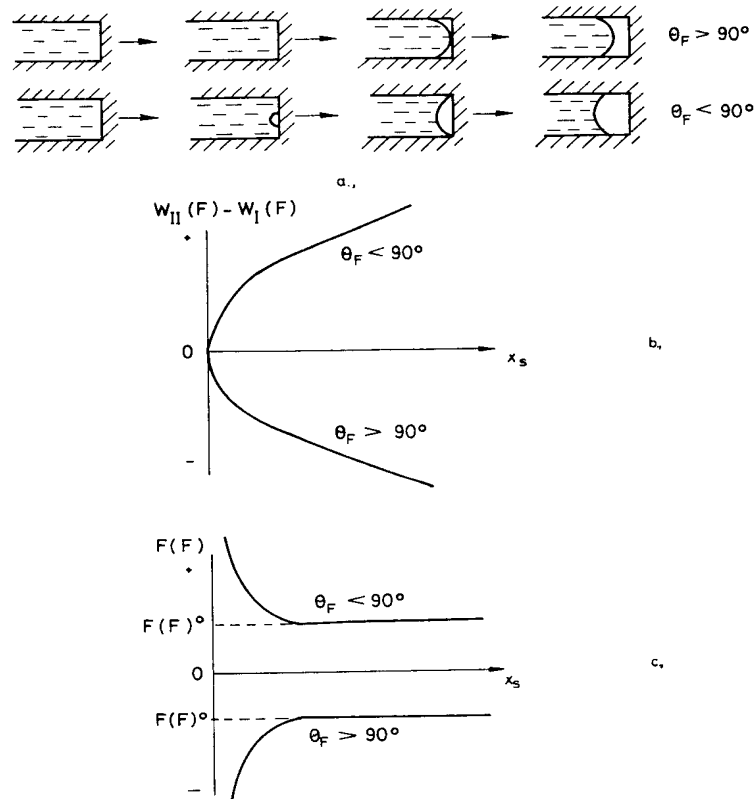


Fig. 5 Illustration of transitional state if the melt is in contact with the end-wall of FR before the beginning of solidification.
 a. the melt in the feeding reservoir during the first steps of feeding process ;
 b. $\Delta W(F)$, as a function of x_s ;
 c. $F(F)$, as a function of x_s .

The following expression can be obtained for $F(F)$ in transitional state :

$$F(F) = K_F x_s^{-1/3} \quad (25)$$

where K_F is a constant, depending on θ_F , R_s , R_f , f ;
 if $\theta_F < 90^\circ$, $K_F > 0$;
 if $\theta_F > 90^\circ$, $K_F < 0$.

Graphs of $\Delta W(F)$ and $F(F)$ for transitional state are given in Fig.5b and 5c, as functions of x_s . As can be seen, if $x_s \rightarrow 0$, $|F(F)| \rightarrow \infty$. Eq.(25) is taking place, while at least a part of a melt is in contact with the end-wall of the feeding reservoir. If R_s and R_f are values of the same order of magnitude, Eq.(25) will take place at $x_s \gg 10^{-10}$ m. On the other hand, as was mentioned in the previous Chapter, the value $F(s) \gg F(s)^\circ$ takes place at $x_s \leq 10^{-10}$, only. Consequently, for any parameters (θ_F , R_s , R_f , f) the certain range of x_s exists, where $|F(F)| > F(s)$. As K_F may have different signs, two cases should be considered :

i. if the melt does not wet the end-wall of FR, $F(F)$ is negative, and according to Eq.(12) that will help the shapeforming - driving force will be more positive. Actually, the end-wall of FR will push the non-wettable melt out of itself.

ii. if the melt wets the end-wall of FR, $F(F)$ is positive, and at the certain range of x_s (when $|F(F)| > F(s)$ - see above) the driving force will be negative, making impossible the beginning of the shapeforming process. So, wetting melt should not be in contact with the end-wall of FR, otherwise the shapeforming will not take place.

Finally, in order to ensure positive driving force, the following conclusions can be drawn :
 i. the material of FR should not be wetted by the melt ;

ii. if this requirement is impossible to achieve (melt of low surface tension and/or high chemical activity), the melt should not be in contact with the end-wall of FR.

In some cases the second requirement cannot be achieved, either. That is the case for such an active metal, as aluminum, which forms a stable oxide film on its surface under 'normal conditions' (for details, see [19]). Then, if the oxide film is thicker than the certain value, it will act as the end-wall of FR. As molten aluminium wets its own oxide film [19], shapeforming will not occur in this case. Shapeforming problems during solidification of melts, covered by films are considered in Part II of this paper [20].

7. Determination of function $F(t_r)$

In real processes of directional solidification the crystal grows with a finite, and more or less constant rate - v_{cr} . Consequently,

if shapeforming takes place during solidification, that will take place with a finite rate, too. Energy required for this process can be divided into two parts :

i. energy term, which is related to the melt flow at constant rate (stationary state); function $F(t_r)^{\circ}$ should be compared with functions $F(s)^{\circ}$ and $F(F)^{\circ}$ in expression for the driving force.

ii. energy term, which is related to the acceleration of the melt (transitional state).

Consequently, there are two independent criteria for v_{cr} . On the one hand, melt should be accelerated from zero rate to the stationary rate of flow at the very beginning of the shapeforming process, and on the other hand the flow with the stationary rate should be maintained during the whole process of shapeforming.

7.1. Determination of function $F(t_r)^{\circ}$ - stationary state

If the planar solid/liquid interface moves with a rate of v_{cr} , and a shapeforming process takes place, the melt should flow with the following average rates through SR (v_s) and FR (v_f) :

$$\left. \begin{aligned} v_s &= f v_{cr} \\ v_f &= f v_{cr} (A_s/A_f) \end{aligned} \right\} \quad (26)$$

where A_s and A_f are cross section areas of SR and FR.

The schematic rate distribution is given in Fig.6a. The pressure decrease (Δp), related to the melt flow can be divided into the following three parts :

$$\Delta p = \Delta p_s + \Delta p_f + \Delta p_{f-s} \quad (27)$$

where Δp_s , Δp_f , and Δp_{f-s} are pressure decrease values, related to the melt flow in SR, in FR, and at the border of FR and SR (see Fig.6a).

Energy, required for transportation of a melt for obtaining crystal of volume dV_s equals :

$$dW_{tr} = \Delta p dV_f \quad (28)$$

where values dV_s and dV_f have been defined at Eq.(5).

From Eq.s(5, 8, 13, 28) the expression for $F(t_r)^{\circ}$ can be obtained :

$$F(t_r)^{\circ} = f \Delta p \quad (29)$$

Hence, terms of Δp (see Eq.(27)) should be first determined for calculation of function $F(t_r)^{\circ}$.

A flow through a tube is laminar, if the Reynolds' number is smaller, than its critical value [21] :

$$Re = d_e v / \nu < 2320 \quad (30)$$

where ν - kinematic viscosity ;
 v - average rate of flow ;
 d_e - equivalent hydraulic diameter :

$$d_e = 4 A/L \quad (31)$$

where A and L are area and circumference of the cross section of a tube of given shape (for cylindrical tube of radius R : $d_e = 2 R$).

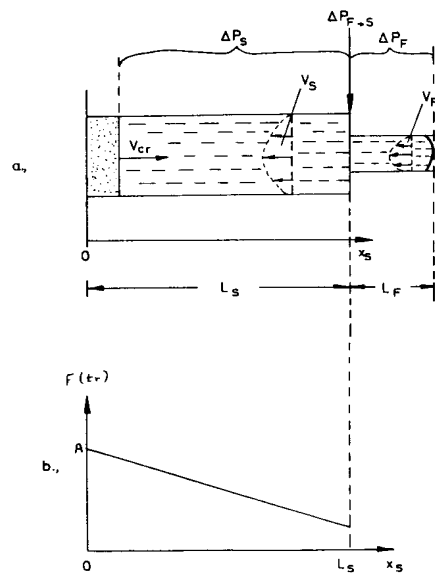


Fig.6. Rate distribution of melt flow (a) and values of $F(t_r)^{\circ}$, as a function of x_s

As kinematic viscosity of melts are not less than 10^{-6} m²/s, and diameter of crystals is not more than 10^{-1} m, for condition of laminar flow one can get (see Eq.s(26, 30, 31)) : $v_{cr} < 10^5$ mm/h. As the rate of real processes of directional solidification is much less than this value, further on the laminar flow of the melt will be taken into consideration only for determining values of Δp and, finally value of $F(t_r)^\circ$.

The pressure decrease, which takes place due to the flow of a liquid with rate v through a tube of radius R and length L , can be described as follows [21] :

$$\Delta p = 8 v \eta L R^{-2} \quad (32)$$

where η - dynamic viscosity of a melt.

If the tube is not cylindrical, Eq.(32) can be used substituting $0.5 d_e$ instead of R , and using Eq.(31). Further on only cylindrical tubes (SR and FR) will be considered.

Both in SR and FR the length of a melt is a function of a coordinate of a planar solid/liquid interface, x_s . Using symbols of Fig.6, and Eq.s(26, 32) the following expressions have been obtained :

$$\left. \begin{aligned} \Delta p_s &= 8 v_{cr} f \eta R_s^{-2} (L_s - x_s) \\ \Delta p_f &= 8 v_{cr} f (R_s/R_f)^2 \eta R_f^{-2} [L_f - x_s f (R_s/R_f)^2] \\ \Delta p_{f-s} &= 0.5 \xi f^2 v_{cr}^2 \rho \end{aligned} \right\} \quad (33)$$

where ρ - density of a melt ;

ξ - constant, depending on R_s/R_f ratio [21] :

$$\left. \begin{aligned} \xi &= 0 && \text{if } R_s/R_f = 1 \\ \xi &= [(R_s/R_f)^2 - 1]^2 && \text{if } R_s/R_f > 1 \\ \xi &= 1.1 - 0.42 (R_s/R_f)^2 && \text{if } R_s/R_f < 1 \end{aligned} \right\} \quad (34)$$

Length of melt placed into FR at initial state (L_f) is related to the length of SR (L_s) :

$$L_f = f L_s (R_s/R_f)^2 K_{LF} \quad (35)$$

where $K_{LF} \geq 1$ is a 'security factor', showing the ratio of volume of the feeding melt, placed into FR to the theoretical volume of feeding melt.

Finally, as can be seen from Eq.s(29, 33, 35) function $F(t_r)^\circ$ decreases linearly, as x_s increases :

$$F(t_r)^\circ = A^\circ - B^\circ x_s \quad (36)$$

where A° , and B° are constants :

$$\begin{aligned} A^\circ &= 0.5 \xi f^3 v_{cr}^2 \rho + 8 v_{cr} f^2 \eta L_s R_s^{-2} [1 + (R_s/R_f)^6 f K_{LF}] \\ B^\circ &= 8 v_{cr} f^2 \eta R_s^{-2} [1 + f (R_s/R_f)^8] \end{aligned}$$

Function $F(t_r)^\circ$ is given schematically in Fig.6b.

As was mentioned in Chapter 4, shapeforming will take place if DF is positive at any value of x_s . As functions $F(s)^\circ$ and $F(f)^\circ$ do not depend on x_s , constant A° can be substituted into Eq.(12) instead of $F(t_r)^\circ$, as its maximal value. That will give the first criterion for the value v_{cr} . For the simplest case, ie for the SR

and FR of the same material and the same radius, and $K_{LF}=1$, the following criterion can be obtained :

$$v_{cr} \frac{L_s}{R_s} < \frac{\sigma}{8 \eta (1+f) f^2} [F(s)^\circ R_s - 2 f \cos \theta_F] \quad (37)$$

Example 1. : $\sigma \approx 1 \text{ J/m}^2$; $\eta \approx 0.01 \text{ kg/ms}$; $\Delta V^\circ \approx 0.1$, then at any values of $\theta_s = \theta_F$ the value in brackets [] of Eq.(37) is not less, than 0.11. Consequently shapeforming will take place if rate of crystallization is less, than 100 (R_s/L_s) m/s. Then, at 'normal' ratio of $R_s/L_s \geq 0.01$, v_{cr} should be less than 1 m/s. This value is much higher, than normal rate of directional solidification.

Now, let us calculate the optimal radius of capillaries to be used in a feeding device (see text after Eq.(24), case $\theta_F > 90^\circ$). Using Eq.s(12, 24, 34, 36) radius R_F can be obtained, which will ensure maximal value of driving force at given value of $F(s)^\circ$ function. Actually, if the radius of capillaries decreases, $F(F)^\circ$ function leads to the increase (at $\theta_F > 90^\circ$), and $F(t_r)^\circ$ function leads to the decrease of the driving force. The optimal radius of capillaries can be calculated, using the following equation :

$$R_{F(opt)} = \left[\frac{3 v_{cr} f^2 (8 \eta L_s + \alpha^{-1} v_{cr} \rho R_s^2)}{-\sigma \cos \theta_F} R_s^4 \right]^{1/5} \quad (38)$$

where α - utilization of cross section area of SR by total cross-section area of capillaries ($\alpha \leq 1$).

Example 2. : $v_{cr}=0.0003 \text{ m/s}$ (1000 mm/h); $f=0.1$; $\eta=0.01 \text{ kg/ms}$; $L_s=0.1 \text{ m}$; $\alpha=0.75$; $\rho=5000 \text{ kg/m}^3$; $R_s=0.005 \text{ m}$; $\sigma=1 \text{ J/m}^2$; $\theta_F=135^\circ$. Then, from Eq.(38) : $R_{F(opt)}=0.00058 \text{ m} = 0.58 \text{ mm}$. Hence, for crystal of radius 5 mm about 50 capillaries of radius 0.6 mm should be used in a feeding device.

7.2. Determination of energy of acceleration of melt

Energy, required for acceleration of a melt from zero rate to stationary rates v_s and v_f can be described as follows :

$$\Delta W_{ac} = 0.5 \rho (A_s L_s v_s^2 + A_F L_F v_f^2) \quad (39)$$

This energy is needed during the formation of a first layer of crystal, ie during the same time as second term of Eq.(16) takes place. Hence, the shapeforming process begins if the second energy term of Eq.(16) is higher, than energy W_{ac} . Using Eq.s(16, 26, 35, 39) the second criterion for ensuring the shapeforming process has been obtained :

$$v_{cr}^2 L_s [1 + (R_s/R_F)^4 f K_{LF}] < \frac{2 \Delta V^\circ \sigma (1 + \cos \theta_s)}{\rho f f} \quad (40)$$

Example 3. : $L_s=0.1 \text{ m}$; $R_s=R_F=0.005 \text{ m}$; $K_{LF}=1$; $\Delta V^\circ=0.1$; $\rho=5000 \text{ kg/m}^3$; $\sigma=1 \text{ J/m}^2$; $\theta_s=90^\circ$. Then $v_{cr} < 0.2 \text{ m/s}$. This value is much higher, than normal rate of directional solidification.

Example 4.: the same, as Example 3., but instead of SR and FR of the same diameter, feeding device with 50 capillaries of radius 0.0006 m is used (see Example 2.). Then : $v_{cr} < 0.008 \text{ m/s} \approx 30,000 \text{ mm/h}$. That is again, much higher than normal rate of directional solidification.

From Eq.(40) it can be seen that melt should be in contact with the front-wall of the solidification reservoir. The energy, required for 'tearing off' the melt from this wall (with opposite sign) is necessary for accelerating the melt from zero rate to stationary rate of shapeforming. If the melt were not in contact with the front-wall of SR before the beginning of solidification, the shapeforming process would not start.

8. Conclusions

Equations have been evaluated for describing shapeforming processes, accompanying directional solidification by planar solid/liquid interface of crystals of cylindrical shape, and of any material with positive ΔV of melting. Finally, the following 'technological' conclusions have been achieved for melts which are not covered by any layer :

- i. solidification and feeding reservoirs of the same material and radius can be used if $\Delta V^\circ \leq 0.3$.
- ii. driving force (probability of successful shapeforming) can be increased using material of SR, which will be wetted by the melt, and material of FR, which will not be wetted by the melt.
- iii. the melt must be in contact with the front-wall of the solidification reservoir before the beginning of the solidification/shapeforming process.
- iv. if material of FR is not wetted by a melt, a feeding device containing capillaries of small diameter should be used. In this case optimal radius of capillaries should be calculated (see Eq.(38)).
- v. if material of FR is not wetted by a melt, a melt should be in contact with the end-wall of FR before the beginning of solidification/shapeforming process.
- vi. if material of FR is wetted by a melt, cylindrical FR of large diameter should be used. The melt mustn't be in contact with the end-wall of FR before the beginning of the solidification process.

Shapeforming problems during directional solidification of melts covered by any type of layers is considered in Part II. of this paper.

Acknowledgements

The author wishes to thank researchers of the University of Miskolc, involved in Project 'Material Science in Space' for their help and continuous consultations : Dr.A.Roósz, Dr. P.Bárczy, Dr. B.Tolvaj, and others. This work has been supported by the Hungarian Credit Bank Corporation (Magyar Hitelbank RT, MHB).

Literature

1. B.Billia, J.J.Favier Cellular morphology in lead-thallium alloys. In: Scientific Goals of the German Spacelab Mission D1. 1985, pp. 101-102.
2. H.Sprenger, E.Erben, H.Zeilinger Skin technology. In: Proc. of 3rd European Symp. on Material Science in Space, Grenoble, 24-27 April 1979, ESA SP-142, pp. 101-108.
3. H. Sprenger, K.Schweitzer Skin casting Experiments in Rocket Flights. In: Proc. of 5th ESA PAC Symp. on European Rocket and Balloon Programmes and Related Research, Bournemouth 14-18 April 1980, ESA-SP 152, pp. 349-356.
4. E.G.Fuchs, A.Roósz, G.Búza Method for the production of casting especially under microgravity conditions. Pat. 2251-849/82.
5. H.Sprenger Directional solidification of alloys and components in microgravity. Abstr. 2nd Coll. on Materials Technology in Space, Balatonaliga 9-13 April 1984, p. 12.
6. H.Sprenger Skin casting of alloys and composites, Results of SL-1 and TEXUS experiments. 5th European Symp. on Material Sciences under Microgravity, Schloss Elmau 5-7 November 1984, pp. 87-94.
7. H.Sprenger Skin Technology. In: Goals of the German Spacelab Mission D1. 1985, p. 147.
8. H.Sprenger, H.Nieswaag. Skin casting of grey cast-iron. Ibid., pp. 147-149.
9. E.G.Fuchs, A.Roósz, G.Búza A conception for realizing mold casting in space. Proc. 6th European Symp. on Material Science under Microgravity Conditions. Bordeaux 2-5 December 1986, pp.279-284.
10. H.Sprenger Directional solidification of an eutectic alloy. Results of the D1 Experiment. Ibid., pp. 139-140.
11. A.Roósz, G.Kaptay, I.Máté, I,Teleszky, J.Sólyom, L.L.Regel, A.M.Turchaninov The ground-based experiments of shell technology - to be published in J. Appl. Space Research in 1991.
12. Y.S.Toulonkion, R.K.Kirley, R.E.Taylor, T.Y.Lee Thermophysical properties of matter. Vol. 12-13. Thermal Expansion. N.Y., 1977.

-
13. V.I.Nizenko Density and its temperature dependence of molten metals. In: 'Metody issledovaniya i svoystva granic razdela kontaktiruyushich faz', Kiev, 1977, pp. 125-163 (in Russian).
 14. A.R.Ubbelohde Melting and crystal structure. Oxford, 1965.
 15. V.M.Glazov, S.N.Chizevskaya, H.H.Glagoleva Molten semiconductors. Moscow, 1967 (in Russian).
 16. H.Krebs Grundzüge der Anorganischen Kristallchemie. Stuttgart, 1968.
 17. F.Sommer Association model for description of thermodynamic functions of liquid alloys. Parts I-II. Z. für Metallkunde, 1982, B.73., H.2., S.72-86.
 18. K.Wasai, K.Mukai A consideration of thermodynamic properties of binary liquid alloys with negative deviation of activities from Rault's Law, based on associated solution model. J.Japan Inst. Metals, 1982., v.46., N°3., pp.226-274 (in Japanese).
 19. G.Kaptay On surface properties of molten aluminium alloys of oxidized surface. This volume.
 20. G.Kaptay, G.Lámer A theory of shapeforming processes by directional solidification under microgravity conditions. Part II. Melts covered by a deformable film. Solidification of Al-alloys. This volume.
 21. W.Bohl Technische Strömungslehre. Kamprath-Reihe : Kompaktlehrbuch-Technik. Vogel-Verlag, Würzburg, Hungarian translation, Múszaki Könyvkiadó, 1983.

