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A THEORY OF SHAPEFORMING PROCESSES BY DIRECTIONAL SOLIDIFICATION UNDER MICROGRAVITY CONDITIONS. PART II. MELTS COVERED BY FILMS - SOLIDIFICATION OF ALUMINIUM ALLOYS

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ABSTRACT

In this part of our paper the role of the film, covering the melt is taken into consideration during directional solidification by planar solid/liquid interface of crystals of cylindrical shape. The expression for the "critical thickness" δ_c of the film has been delivered (for the Al-alloys covered by Al_2O_3 the critical thickness of $\delta_c \cong 5{,}2$ μm has been found).

If $\delta > \delta_c$, the film will not be deformed during the shrinkage-formation and/or the shapeforming processes. The film simply will act as the wall of the solidification and feeding reservoirs. All the equations of Part I. are valid.

If $\delta < \delta_c$ the film will be deformed during the shrinkage-formation and/or the shapeforming processes. Energy terms, related to these processes have been calculated. The optimal technological parameters for ensuring the shapeforming process have been obtained.

1. Introduction

In Part I. of this contribution [1] a theory of shapeforming for melts, being in direct contact with the wall of the solidification and feeding reservoirs (SR and FR) have been developed. However, in some cases melts can be covered by a film. This film can be a natural one (like Al_2O_3 on Al-melt) or an artificial one (like films used in the skin technology [2]). That is why, the aim of our present contribution is to develop a theory of shapeforming during directional solidification by planar solid/liquid interface of crystals of cylindrical shape from melts, covered by films of any type and any thickness.

Basic principles and equations obtained in Part I. are valid for melts covered by a film, too. However, the presence of the film should be taken into consideration. As it is shown in Fig. 1. films can behave in the two following ways during the shrinkage--formation :

i. if the film is too thick (ie its thickness is larger than the critical thickness $\delta > \delta_c$), it will not be deformed during the shrinkage-formation, and it will act as a wall of the solidification reservoir (see Fig. 1.a.) ;

ii. if the film is thin enough ($\delta < \delta_c$), it will be deformed during the shrinkage-formation (Fig. 1.b.).

In the following chapters these two cases will be analysed, and the critical thickness of the film will be calculated.

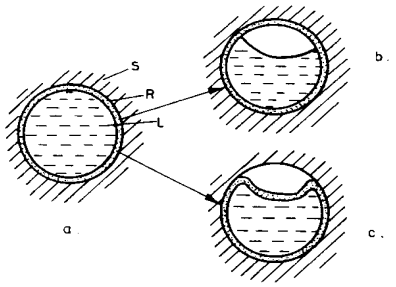

Fig. 1. Cross section of the solidification reservoir during the shrinkage-formation. Behavior of the film. S=solid (wall of the SR); R=refractory (film); L=liquid (melt)
a. $\delta > \delta_c$ - undeformable film
b. $\delta < \delta_c$ - deformable film

2. The case of undeformable films ($\delta > \delta_c$)

In this case the film will act as the wall of the SR and FR, consequently all the equations, obtained in Part I. are valid. It

should be mentioned, however, that in this case Θ_S and Θ_F are contact angles between the melt and the film. As it was pointed out at the end of Chapter 6. of Part I. [1], the shapeforming process will be possible if the 'end' of the melt in the FR will not be covered by a film. This requirement, however, is realistic for artificial films, only.

In case of natural films, like Al_2O_3 on aluminium melts, the film will cover the whole free surface of the melt (which is not in contact with any other phases, except the gasous one), including its 'end' in the FR. That will take place even in the case of a 'fresh' surface of the melt, as that is impossible to reach a partial pressure of oxygen at a level of 10^{-50} Pa, which is the thermodynamical condition of having at least half of the surface of the molten aluminium free of the oxide [8]. The behaviour of such a thin, deformable films is discussed in Chapter 3.4.2.

3. The case of deformable films ($\delta < \delta_c$)

In this case the film will move together with the surface of the melt, ie the film will be deformed during the shrinkage-formation and the shapeforming processes. Consequently the energy terms, related to the deformation of the film during the shrinkage-formation ($W_d(s)$) and the shapeforming ($W_d(F)$) processes should be taken into consideration. Then Eq.(11) of Part I. should be rewritten as follows:

$$\left.\begin{aligned} W_I &= W_I(s) + W_I(F) + W^\circ + W_d(s) \\ W_{II} &= W_{II}(s) + W_{II}(F) + W^\circ + W_d(F) \end{aligned}\right\} \quad (1)$$

Then Eq.(12) of Part I. should be rewritten, as well:

$$DF = \sigma[F(s) - F(F)] - F(tr) + F_d(s) - F_d(F) \quad (2)$$

where functions $F_d(s)$ and $F_d(F)$ are equal to :

$$\left.\begin{aligned} F_d(s) &= \frac{d[W_d(s)]}{A_S\, dx_S} \\ F_d(F) &= \frac{d[W_d(F)]}{A_S\, dx_S} \end{aligned}\right\} \quad (3)$$

In order to determine the driving force of the shapeforming process, five functions (see Eq.(2)) should be delivered. If the melt covered by a deformable film is not in any contact with any walls, functions F(s) and F(F) are equal zero. If the melt covered by a film is in contact with the walls of SR and FR, functions F(s) and F(F) can be calculated from Eq.-s(17) and (22) of Part I. [1]. In our case, as follows from the assumptions made in Chapter 3.2., the elongation of the film during its deformation

is negligible, ie $1_{sv}(s) = 1_{lv}(s)$. Substituting this equality into Eq.(17) of Part I., one can get an expression for function $F(s)^\circ$ for the case of a deformable film :

$$F(s)^\circ = \frac{1_{sv}(s)}{A_s}(1 + \cos\Theta_s) \qquad (4)$$

Function $F(tr)$ can be calculated from Eq.(36) of Part I. This expression should be slightly changed if the shape of the feeding reservoir is changed (see Chapter 3.4.), but for the first approximation Eq.(36) of Part I. can be used. Functions $F_d(s)$ and $F_d(F)$ can be calculated using the theory of elastic shells. That will be considered in following the Chapters.

3.1. On the mechanical behaviour of the deformable film

For calculating functions $W_d(s)$ and $W_d(F)$ the deformable film is considered as a rigid, perfectly and linearly elastic body during the solidification process. In addition to these ones the following assumptions are made :

i. the film is a thin shell, ie its thickness is less by lots of orders of magnitude than its curvature radius ;

ii. the thickness of the film is constant ;

iii. the strain is small (ie components of the strain tensor are much less than 1), but the displacement vector of the shell can be large [3] ;

iv. the mechanical behaviour of the film can be described by the Kirchhoff-Love hypothesis [4].

3.2. Determination of function $F_d(s)$

In addition to the assumptions made in Chapter 3.1., for calculating the deformation energy of a *cylindrical* film the following two assumptions have been made:

v. the film is in plane stress state [4] ;

vi. the film undergoes deformation by buckling [5,6] during the shrinkage-formation (that is proved by results of experiments [10], see Fig.3. in Part I.).

In Fig. 2. the solidification reservoir and its deformed state after the buckling process, as well as geometrical parameters and (the coordinate system used in following calculation are shown.

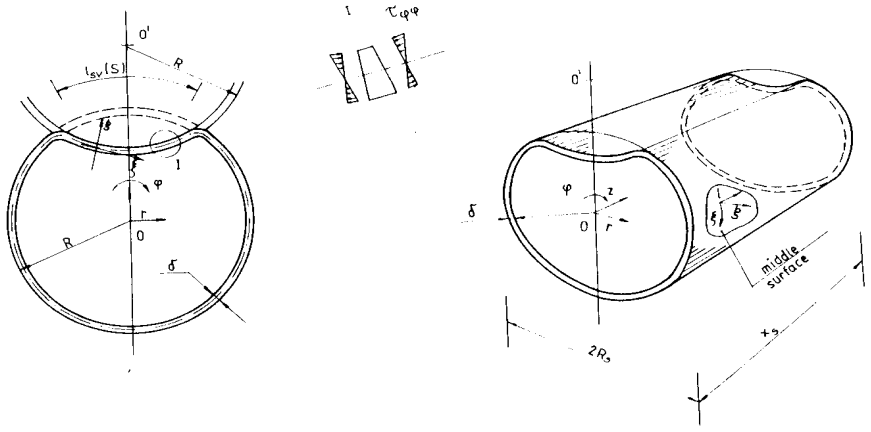

Fig.2. Shape of the shrinkage, formed in an abscence of shapeforming process

The deformation energy of the film can be calculeted as follows:

$$W_d(s) = \frac{1}{2}\int_V \tau_{ij}\varepsilon_{ij}dV \qquad (5)$$

where τ_{ij} and ε_{ij} are the components of the stress and of the strain tensors (Einstein's convention is used). On the base of the assumptions (see above) only the following component differs from zero:

$$\varepsilon_{\varphi\varphi} = \kappa_{\varphi\varphi}\zeta \qquad (6)$$

where $\kappa_{\varphi\varphi}$ is the change of the curvature tensor of middlesurface of the film during the buckling process :

$$\kappa_{\varphi\varphi} = \frac{1}{R} - \left[-\frac{1}{R}\right] = \frac{2}{R} \qquad (7)$$

On the base of the assumptions (see above), using Hooke-law:

$$\tau_{\varphi\varphi} = (\lambda + 2\mu)\varepsilon_{\varphi\varphi} \qquad (8)$$

where λ and μ are Lame moduli.
Subtituting Eq.-s(6,7,8) into Eq.(5) one can finally get the following expression:

$$W_d(s) = 2(\lambda + 2\mu)\frac{\delta^3}{12}\frac{1_{sv}(s)x_s}{R^2} \qquad (9)$$

This expression allows us to calculate the deformation energy of the cylindrical film of thickness δ, of radius R, and of length x_s if the volume between the undeformed and post-buckling states of

the shell is equal to $\Delta V^{\circ} R^2 \pi x_s$ (the value of ΔV° see in Chapter 2. of Part I. [1]). Parameter $1_{sv}(s)$ in Eq.(9) can be calculated as follows (see Fig. 2.) :

$$1_{sv}(s) = R\varphi \frac{\pi}{180} \qquad (10)$$

where angle φ can be obtained by an iteration procedure from the following equation:

$$\frac{\pi}{180}\varphi - \sin\varphi = \Delta V^{\circ}\pi \qquad (11)$$

Substituting Eq.(9) into Eq.(3), one can finally get the following expression for $F_d(s)$, if parameters $1_{sv}(s)$, δ, R, and ΔV° do not depend on the coordinate x_s :

$$F_d(s) = 2(\lambda + 2\mu)\frac{\delta^3}{12} \frac{1_{sv}(s)}{R^4\pi} \qquad (12)$$

Functions F(s) related to the energy of the shrinkage-formation are shown in Fig.3., as a function of a thickness of the film (parameters, used in calculations are given below, at Example 1.).

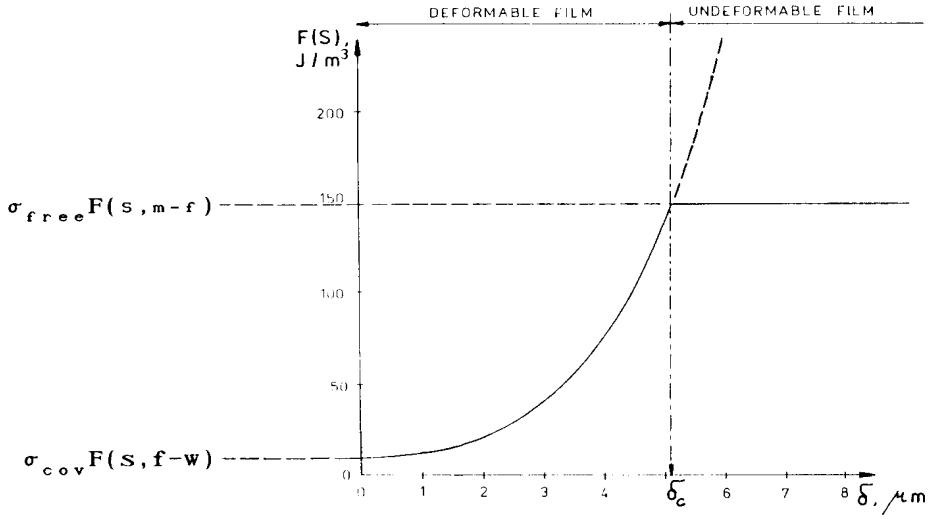

Fig.3. Functions F(s), related to the energy of the shrinkage--formation during solidification of aluminium alloys, as a function of the thickness of the Al_2O_3 film, covering the melt (parameters see at Example 1.).

As it can be seen from Eq.(12), function $F_d(s)$ increases as the thickness of the layer increases. The whole energy of the shrinkage formation process (see Eq.(2)) is related to the sum of the functions : $\sigma F(s)+F_d(s)$. For ensuring a maximal driving force, the sum of these functions should be as great as possible, hence the thickness of the film should be as high as possible. However, these functions will characterize the energy of the shrinkage--formation process if $\delta<\delta_c$. At $\delta>\delta_c$ the film will not be deformed any more during the shrinkage-formation process, and its energy will be related to $\sigma F(s)$ function, only (see Chapter 2.). The value of this function does not depend on the thickness of the film. Consequently in order to ensure the maximal driving force of the shapeforming the thickness of the film in the solidification reservoir should be higher, than the critical thickness of the film. That is why it is important to have an expression for calculating δ_c.

3.3. Determination of the critical thickness of the film

Definition: The critical thickness of the film δ_c is called a thickness, above which the deformation of the film will not take place during the shrinkage-formation, but the film will act as an undeformable wall of the solidification reservoir (see Fig. 1.).

As it can be seen from the definition the critical thickness can be calculated from the equality of the $F_d(s) + \sigma F(s)$ functions of the deformable film (see Eq.-s(4) and (12)) and of the $\sigma F(s)$ function of the undeformable film (see Fig. 4. in [1]), ie:

$$\delta_c = \left\{ [\sigma_{free} F(s,m\text{-}f) - \sigma_{cov} F(s,f\text{-}w)] \frac{6R^4\pi}{(\lambda + 2\mu) 1_{sv}(s,def)} \right\}^{1/3} \qquad (13)$$

where σ_{free} and σ_{cov} are the surface tension of the melt of free surface, and of surface covered by a film ;

$F(s,m\text{-}f)$ and $F(s,f\text{-}w)$ are the functions $F(s)$, for the melt-film (see Fig.4. of Part I.), and for the film-wall (see Eq.(4)) interfaces ;

$1_{sv}(s,def)$ - the $1_{sv}(s)$ function for the deformable film, which can be calculated by Eq.(10).

If the expression in brackets of Eq.(13) : $[\sigma_{free} F(s,m\text{-}f) - \sigma_{cov} F(s,f\text{-}w)] < 0$, then $\delta_c < 0$, which does not have any physical sense. That means, that an adhesion energy between the film and the wall is higher than between the melt and the film. While this situation obviously takes place quite rarely, in this case $\delta_c=0$ should be taken into consideration, which means, that even the first atomic/molecular layer will form the undeformable film during the shrinkage-formation process.

Example 1. Calculation of δ_c for a natural Al_2O_3 film, covering an aluminium melt.

Parameters : $\Delta V°=0.07$ [1]; $\varphi=64°$ (see Eq.(11)); $1_{sv}(s,def)=0.00447$ m (see Eq.(10)); $R_S=0.004$ m, $L_S=0.07$ m (planned Hungarian space experiment [7]); $\sigma_{free}=1.1$ J/m^2 [8]; $\Theta(melt-film)\approx 50°$ [8]; $F(s,m-f)=137.5$ J/m^3 (see Fig.4. of Part I. [1]); $\sigma_{cov}=0.86$ J/m^2 [8]; $\Theta(film-wall)\approx 150°$ [8]; $F(s,f-w)=11.9$ J/m^3 (see Eq.(4)); $\lambda=7.9\ 10^{11}$ J/m^3 [9]; $\mu=1.6\ 10^{11}$ J/m^3 [9].

Result : $\delta_c = 5.2\ 10^{-6}$ m = 5.2 μm (see Eq.(13)).

Remark : The validity of the result have been proved experimentally [11]. In the first series of experiments the oxide layer was obtained oxidizing for 3 hours at 500 °C in vacuum, with $po_2\approx 10^{-8}$ Pa. The thickness of the oxide layer was surely below 1 μm. In the solidification process of this specimen in a horizontal furnace on the Earth without shapeforming the film *was deformed* during the shrinkage-formation. In the second series of experiments the layer of 10 μm was obtained in an electrochemical way. In the solidification process of this specimen in a horizontal furnace on the Earth without shapeforming the film *was not deformed, but the shrinkage was formed 'under' the film.* Consequently the calculated value of the critical thickness of the film (5.2 μm) is inside of the experimentally proved interval [11].

3.4. Determination of function $F_d(F)$

As it can be seen from Eq.-s(2-3), in order to ensure maximal positive driving force of shapeforming the sum of functions $\sigma F(F) + F_d(F)$ should be as low as possible. Therefore the shape of the feeding reservoir should be chosen in such a way that it would ensure a minimal deformation energy of the film covering a melt in FR. In the following sub-chapters the possibility of the shapeforming process will be considered in case of different shapes of the feeding reservoir.

3.4.1. Undeformable film

If both for the solidification and for the feeding reservoirs cylindrical, undeformable film of the same radius and same material will be used, the shapeforming will be ensured (see Chapter 2. above, and [1]) if the end of the melt in the FR is not covered by a film. That is the case for the so called 'skin technology', applied in [2]. This technology can be used for melts, which are not too active towards gasous components, ie do not form natural films on their own surface. If the melt is the chemically active one (eg aluminium), a natural oxide film will be formed on its surface. This case is considered in the following sub-chapters.

3.4.2. Deformable films. The hemispherical FR

The melt inside a cylindrical wall (or undeformable film) forms a hemisphere at its end if $\Theta=0°$ or if $\Theta=180^{O}$. If $0°< \Theta < 180°$, a spherical segment will be formed. If $\Theta > 90°$, the double volume of the melt inside the spherical segment can be used for the shapeforming, as a result of the buckling of the film, covering the melt.

The average deformation energy of the buckling process of a spherical segment, ie the function $F_d(F)$ can be calculated using results of [6]:

$$F_{d(F,spher)} = \frac{2\mu(3\lambda + 2\mu)f\delta^3(1 + \beta^2)}{(\lambda + 2\mu)R^3\beta(3 + \beta^2)} \qquad (14)$$

where f - feeding factor [1] ;
β - parameter, depending on Θ (contact angle between the melt covered by a film and the wall of the FR) :

$$\beta = \frac{1 - \sin(180 - \Theta)}{\cos(180 - \Theta)} \qquad (15)$$

(expression (14) has any physical sense, if $\Theta > 90°$).

Using parameters of Example 1., one can get : $F_{d(F,spher)}=6\ 10^{17}\delta^3$ Comparing this result with $\sigma_{free}F(s,m-f)=151$ J/m^3 (see Example 1), one can get : $\delta_F \leq 6$ μm, which is the condition for the positive driving force of the shapeforming (this comparison can be done, because function $F(F)=0$, as the melt covered by a film is not in contact with the wall of the FR at initial the state). Obviously, the thickness of the natural oxide film on aluminium alloys will be much less than this value [8], and so the shapeforming will be ensured. However, that is true only for the volume of the melt, stressed out of the FR by the buckling process. That is enough for the solidification accompanied with the shapeforming of the crystal of limited length, namely :

$$L_{S,max} = \frac{R_F^3\ \beta(3 + \beta^2)}{3\ f\ R_S^2} \qquad (16)$$

Using parameters of Example 1. : $L_{S\,max}$=35 mm, while in our planned space experiment L_S=70 mm [7]. After buckling of the spherical segment, the shapeforming process could be ensured by creasing of the film only. That would request too much energy even in the case $\delta < 1\mu$m. Consequently the semi-spherical shape of the feeding reservoir can be used for shapeforming of a crystal of a limited length. In the following chapter a conodical feeding reservoir is suggested in order to avoid such a limitations.

3.4.3. Deformable films. The conodical FR

As it follows from the theory of small strain with large displacement [3], in order to achieve minimal deformation energy of a film of given thickness, the change in Gauss-curvature of the middlesurface of the film should be zero. That is the case for instance for rolling surfaces, eg. for a cylinder, a cone, a conoid, etc. Now, we are suggesting a certain conoid, which is expected to have a small value of $F_d(F)$.

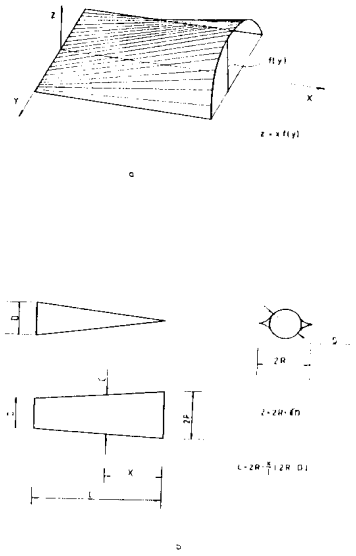

Fig.4. The normal (a) and the contracted (b) conoid

In Fig.4. a normal (Fig.4a) and a contracted (Fig.4b) conoids are shown. Parameters C and D of the conoid are given in Fig.4b. The feeding reservoir suggested by us can be designed as follows. The contracted conoid should be joint the transitional rotational surface, which is in direct contact with the solidification reservoir of cylindrical shape (Fig.5a). The contracted conoid is used (instead of the normal one) for obtaining the same *final* radius of the film as the radius of the SR after the melt has been pressed out of the FR.

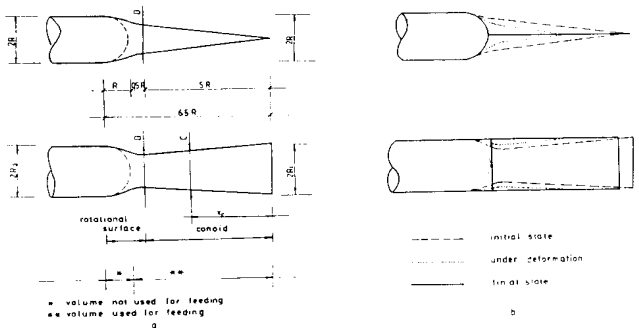

Fig.5. Shape of the feeding reservoir
a. geometrical parameters
b. deformation states of the film

The volume of the conoid (see Fig.5.), and consequently the volume of the melt pressed out of the conoid as a result of its deformation (shapeforming) can be calculated as follows :

$$V_{con} = \pi D L_F (R + D)/12 \qquad (17)$$

where L_F - the length of the conoid necessary for shapeforming can be calculated using the total volume of the melt to be solidified, and the feeding factor. From Eq.(8) [1] and Eq.(17) :

$$L_F = 12 L_S \frac{R_S^2 f}{D(D + R_F)} \qquad (18)$$

Using parameters given at Example 1., and equality $R_S = R_F$ one can finally get : $L_F = 20$ mm $\approx 5 R_S$ (see Fig.5a). Consequently FR of conodical shape has less limitations than FR of semispherical shape.

As all the parameters of the conoid vary linearly with x_F, it can be stated with a good accuracy that all the curvatures will vary linearly from zero at $x_F=0$ to 2/D at $x_F=L_F$. Then the deformation energy can be calculated in an analogous way, as it was done in Chapter 3.2. The only difference is, that parameter $\kappa_{\varphi\varphi}$ equals 2/D instead of 2/R (see Eq.(7)). Finally, the fo lowing expression has been obtained by estimating methods for $F_d(F)$:

$$F_d(F) \approx 1.1(\lambda + 2\mu) f \frac{\delta^3}{R^3} \qquad (19)$$

Using parameters of Example 1. : $F_d(F)=1.4\ 10^{18}\delta^3$. Comparing this result with $\sigma_{free}F(s,m-f)=151\ J/m^3$ (see Example 1), one can get : $\delta_F \leq 4.8\ \mu m$, which is the condition for the positive driving force of shapeforming (we can do this comparison, because function $F(F)=0$, as the melt covered by a film is not in contact with the wall of the FR at initial state). Obviously, the thickness of the natural oxide film on aluminium alloys will be much less than this value [8], and so shapeforming will be ensured.

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