Heat Flow in Solidification

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Abstract

Solidification phenomena play an important role in many of the processes used in fields ranging from production engineering to solid-state physics. For instance, a metal is usually continuously cast or ingot cast before forming it into bars or sheets.

The objective of the present work is to study the heat flow in solidification. Starting from fundamentals, the basic similarities of the widely different solidification processes become evident. The heat flow is an essential element of all solidification processes.

Key words: *heat flow in solidification, solidification of materials, casting, heat extraction.*

The Importance of Solidification

Solidification is a phase transformation which is familiar to everyone, even if the only acquaintance with it involves the making of ice cubes.

Solidificaţion is of such importance simply because one of its major practical applications, namely casting, is a very economic method of forming a component if the melting point of the metal is not too high.

Nowadays, cast metal products can be economically produced from alloys having melting points as high as 1660°C (Ti).

In the case of metals, melting is accompanied by an enormous decrease in viscosity, of some twenty orders of magnitude, as illustrated in figure 1. Thus, instead of expending energy against the typically high flow stress of a solid metal during forging or similar processes, it is only necessary to contend with the essentially zero shear stress of a liquid. If the properties of castings were easier to control, then solidification would be an even more important process. In this respect, solidification theory plays a vital role since it forms the basis for influencing the microstructure and hence improving the quality of cast products.

The effect of solidification is most evident when casting is the final operation since the resultant properties can depend markedly upon the position in the casting (fig.2).

The fundamental advantage of solidification, as a forming operation, is that it permits metal to be shaped with a minimum of effort since the liquid metal offers very little resistance to shear stresses. When the material solidifies due to a decrease in the temperature, τ, its viscosity increases continuously (glass formation) or discontinuously (crystallization), by over 20 orders

of magnitude, to yield a strong solid, the viscosity of which is defined arbitrarily to be greater than 10^{14}Pas. (The reduced temperature τ, is used here since it leads to a single curve which is applicable to many substances. The suffix, f or v, indicates the melting point or boiling point, respectively) [1].

The use of casting as a production route unfortunately poses its own problems. One of these is the local variation of the microstructure, leading to compositional variations, and this is illustrated for example by the dendrite arm spacing, λ_2, measured as a function of the distance, d, from the surface of the casting. This can lead to a resultant variation in properties such as the ultimate tensile strength and the elongation. Like the weakest link in a chain, the inferior regions of a casting may impair the integrity of the whole. Thus, it is important to understand the factors which influence the microstructure. Finer microstructures generally have superior mechanical properties and finer structures, in turn, generally result from higher solidification rates. Such rates are found at small distances from the surface of the mould, in thin sections, or at laser-remelted surfaces. [2].
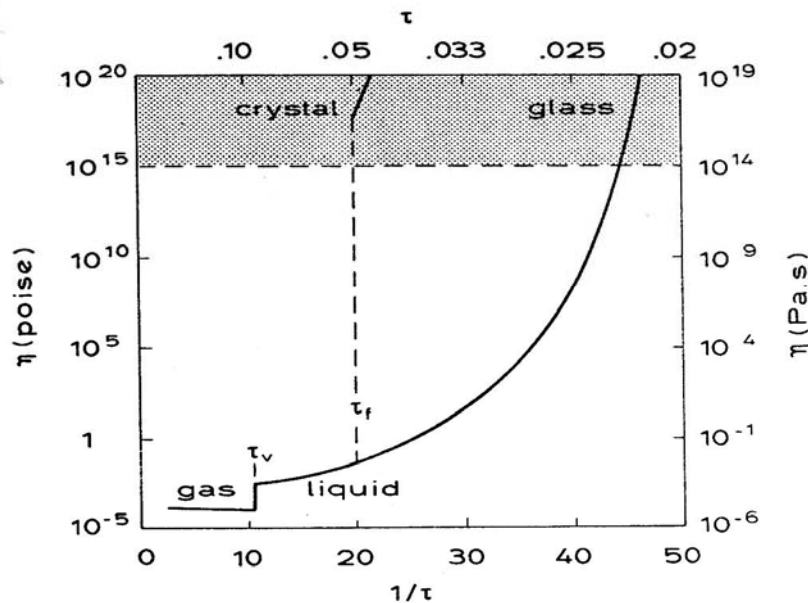

Fig. 1. Dynamic viscosity as a function of temperature
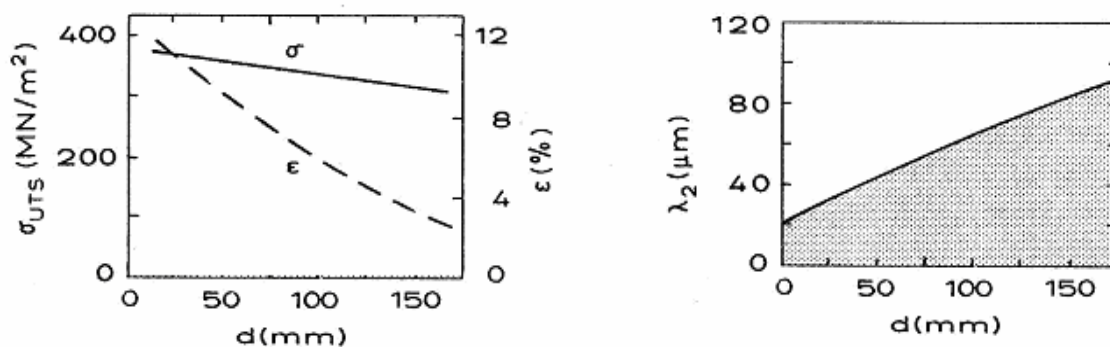

Fig. 2. Alloy properties as a function of position in a casting

Its influence is also seen in a finished product, even after heavy working, since a solidification structure and its associated defects are difficult to eliminate once they are created. Solidification defects tend to persist throughout subsequent operations.

Some important processes which involve solidification are:

° Casting: continuous, ingot, form, precision, die;
° Welding: arc, resistance, plasma, electron beam, laser, friction (including the micro-mechanisms of wear);
° Rapid Solidification Processing: melt-spinning, planar-flow casting, atomization, bulk undercooling, surface remelting;
° Directional Solidification: liquid metal cooling, Czochralski.[3].

Heat Extraction

The various solidification processes mentioned above involve extraction of heat from the melt in a more or less controlled manner. Heat extraction changes the energy of the phases (solid and liquid) in two ways:

1. There is a decrease in the enthalpy of the liquid or solid, due to cooling, which is given by:
$$\Delta H = \int c dT.$$

2. There is a decrease in enthalpy, due to the transformation from liquid to solid, which is equal to the latent heat of fusion, ΔH_f.

Heat extraction is achieved by applying a suitable means of cooling to the melt in order to create an external heat flux, q_e. The resultant cooling rate, *dT/dt,* can be deduced from a simple heat balance if the metal is isothermal (low cooling rate) and the specific heats of the liquid and the solid are the same. Using the latent heat per unit volume, $\Delta h_f = \Delta H_f / v_m$ (defined to be positive for solidification), and also the specific heat per unit volume, c, in order to conform with the dimensions of the other factors, then:

$$q_e\left(\frac{A'}{\upsilon}\right) = -c\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right) + \Delta h_f\left(\frac{\mathrm{d}f_S}{\mathrm{d}t}\right)$$

$$\text{so that} \quad \dot{T} = \frac{\mathrm{d}T}{\mathrm{d}t} = -q_e\left(\frac{A'}{\upsilon c}\right) + \left(\frac{\mathrm{d}f_S}{\mathrm{d}t}\right)\left(\frac{\Delta h_f}{c}\right) \tag{1}$$

The first term on the right-hand-side (RHS) of equation 1 reflects the effect of casting geometry (ratio of surface area of the casting, A', to its volume, v) upon the extraction of sensible heat, while the second term takes account of the continuing evolution of latent heat of fusion during solidification. It can be seen from this equation that, during solidification, heating will occur if the second term on the RHS of equation 1.1 becomes greater than the first one. This phenomenon is known as recalescence. For an alloy, where solidification occurs over a range of temperatures, the variation of the fraction of solid as a function of time must be calculated from the relationship:

$$\frac{df_S}{dt} = \left(\frac{dT}{dt}\right)\left(\frac{df_S}{dT}\right),$$ since f_s is a function of temperature. In this case;

$$\dot{T} = \frac{-q_e\left(\dfrac{\dot{A}}{\upsilon c}\right)}{1 - \left(\dfrac{\Delta h_f}{c}\right)\left(\dfrac{df_S}{dT}\right)} \qquad (2)$$

It is seen that solidification decreases the cooling rate since df_S/dT *is* negative.

Figure 3 illustrates two fundamentally different solidification processes
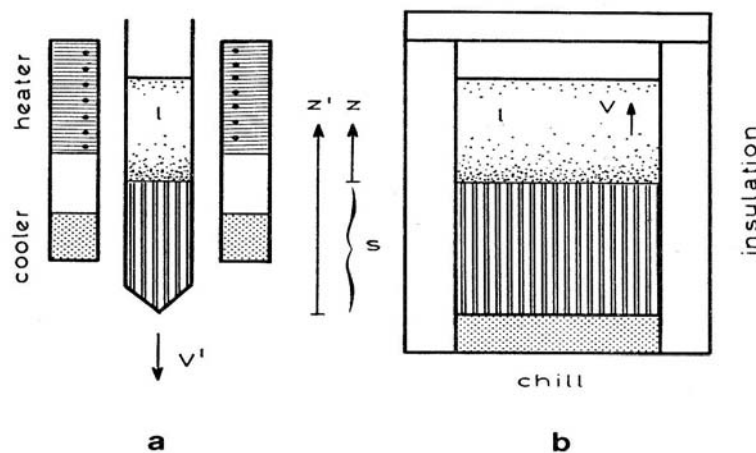

Fig. 3. Basic method of controlled solidification

Without heat extraction there is no solidification. The liquid must be cooled to the solidification temperature and then the latent heat of solidification appearing at the growing solid/liquid interface must be extracted. There are several methods of heat extraction. In directional (Bridgman-type) solidification (a): the crucible is drawn downwards through a constant temperature gradient, G, at a uniform rate, V', and therefore the microstructure is highly uniform throughout the specimen. The method is restricted to small specimen diameters and is expensive because it is slow and, paradoxically, heat must be supplied during solidification in order to maintain the imposed positive temperature gradient. In directional casting (b), the benefits of directionality, such as a better control of the properties and an absence of detrimental macro segregation, are retained but the microstructure is no longer uniform along the specimen because the growth rate, V, and the temperature gradient decrease as the distance from the chill increases. The process is cheaper than that of (a) and is used for the directional solidification of gas-turbine blades, for example. Combined with proper alloy development, these processes result in a higher efficiency and a longer life for the gas-turbines of aircraft [8].

In figure 3a, the heat is extracted in an almost steady manner by moving the crucible at a fixed rate, V', through the temperature profile imposed by the furnace. Such a process is usually used for single crystal growth or directional solidification. It permits the growth rate of the solid, V, and the temperature gradient, G, to be separately controlled. If V' is not too high, both the heat flux and the solidification are unidirectional. The cooling rate at a given location and time is given by:

$$\dot{T}_{S+\varepsilon} = \left(\frac{\partial T}{\partial t}\right)_{S+\varepsilon} = \left(\frac{\partial T}{\partial z'}\frac{\partial z'}{\partial t}\right)_{S+\varepsilon} = G \bullet V\big|_{S+\varepsilon} \quad , \qquad (3)$$

where the time - dependent position of the solid/liquid interface is s = *z'- z*, and *z'* is the coordinate with respect to the system (the crucible), while z is the coordinate with respect to the moving *s/l* interface and ε is a small quantity with respect to *s*. Here, V is the rate of movement of the *s/l* interface and *G* is the thermal gradient in the liquid when *z'=s+ε* (also called *G1)* or the thermal gradient in the solid when *z'=z-ε* (called G_s). Due to differences in the conductivity of solid and liquid and due to the evolution of latent heat at a moving interface, $G_l \neq G_S$ .For reasons of simplicity, the temperature gradient in the liquid will be mostly used in this book and written as $G \equiv G_l$.

Another directional casting process is illustrated by figure 3b. Here, heat is extracted via a chill and, as in figure 3a, growth occurs in a direction which is parallel, and opposite, of the heat-flux direction. In this situation, the heat-flux decreases with time as do the coupled parameters, *G* and *V*. Thus *T* also varies. Heat flow in the mould/metal system leads to an expression for the position, s, of the solid/liquid interface, which is of the type:

$$s = Kt^{\frac{1}{2}} , \qquad (4)$$

This equation is exact only if the melt is not superheated, if the solid/liquid interface is planar, and if the surface temperature of the casting at the chill drops immediately, at *t* = 0, to a constant value. [5]

Growth of Single Crystals

The growth of single crystal is an application of the heat flow in solidification.

A variety of different techniques are employed to produce single crystals from melts. These can be grouped in three categories as those in which the entire charge is melted and then solidified from one end, a large charge is melted and a small crystal withdrawn sloth from it and only a small zone of the crystal is melted at any one time.

The first category of crystal-growing techniques is termed normal freezing. A commonly used normal freezing method for low-melting-point metals is growth in a horizontal boat. Here, a charge of metal is contained within a long crucible of small cross section open at the top. A seed crystal may be placed at one end of the boat to obtain a crystal of predetermined orientation. The charge and part of the seed are first melted in a suitable furnace. Next, the furnace is withdrawn slowly from the boat so that growth proceeds from the seed: alternatively, the boat is withdrawn slowly from the furnace and the solid-liquid interface moves until the whole charge is solid. In a similar crystal-growing method, the crucible is vertical and open at the top: this is often termed the Bridgeman method. In a minor modification of these techniques, neither the furnace nor the crucible moves [6].

The basic heat-flow objectives of all crystal-growing techniques are to obtain a thermal gradient across a liquid-solid interface which can be held at equilibrium and subsequently to alter or move this gradient in such a way that the liquid-solid interface moves at a controlled rate. A heat balance at a planar liquid-solid interface in crystal growth from the melt is written

$$K_S G_S - K_L G_L = \rho_S \cdot H \cdot R \quad , \qquad (5)$$

where K_s is the thermal conductivity of solid metal, K_L − thermal conductivity of liquid metal, G_S − temperature gradient in solid at the liquid-solid interface, G_L − temperature gradient in liquid at the liquid-solid interface, R − growth velocity, ρ_S − density of solid metal, H − heat of fusion.

Note from equation (5), that growth velocity R is dependent, not on absolute thermal gradient, but on the difference between $K_S G_S$ and $K_L G_L$. Hence, thermal gradients can be controlled independently of growth velocity. This is an important attribute of single crystal-growing furnaces since growing good crystals of alloys requires that the temperature gradients be high and growth rate be low. K_S, K_L, H, and ρ_S, are constants of the materials being solidified: G_L is directly proportional to the heat flux in the liquid at the liquid –solid interface.

Growth velocity would be at a maximum when G_L becomes negative (undercooled melt); however, good crystals cannot be grown in undercooled liquids, and so the practical maximum growth velocity occurs when $G_L \rightarrow 0$, or from equation (5),

$$R_{\max} = \frac{K_S G_S}{\rho_S H} \quad , \tag{6}$$

 G_S, thermal gradient in the solid at the interface, is evaluated by experiment or heat flow calculations.

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Fluxul de căldură la solidificare

Rezumat

Fenomenul solidificării joacă un rol important în multe dintre procesele utilizate în domenii cuprinse între ingineria tehnologică şi fizica solidului. De exemplu, un material metalic este în mod normal turnat continuu sau în lingouri înainte de a fi deformat plastic pentru a se obţine bare sau table.

Obiectivul prezentei lucrări este studiul fluxului de căldură la solidificare. Pornind de la fundamentele solidificării, principalele similitudini ale diferitelor procese de solidificare devin evidente.. Fluxul de căldură este în concluzie, un element esenţial al proceselor de solidificare.