

Modelling Micropore Formation during Directional Solidification

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In this work we have developed two criteria which can characterize the susceptibility to microporosities formation of alloys. These defects are influential in determining mechanical properties of materials. The first criterion is used when the fraction eutectic is important : then the porosity formation is essentially caused by dissolved gases or formed during chemical reactions. The second is employed when the alloy possesses low fraction eutectic. In that case, because of the pressure drop, the liquid is unable to feed through interdendritic spaces to accommodate solidification shrinkage. The pressure drop is composed of two terms which influence in contrary direction : the first is due to solidification shrinkage and the second to gravity. This term is the most important except for low fraction eutectic. The fraction liquid (or the fraction eutectic) is an important factor. It depends on the alloy composition and on solidification conditions. In fact, we have showed that, depending on initial alloy concentration, the solidification conditions have opposite effects on the fraction liquid : if $C_0 > KC_E$, the fraction liquid decreases if the ratio $\frac{G}{R}$ decreases and if $C_0 < KC_E$ it increases if the ratio $\frac{G}{R}$ decreases.

Die Erstellung von Modellen für die Bildung der Mikroporosität bei der gerichteten Erstarrung. Bei dieser Untersuchung wurden 2 Kriterien entwickelt, die die Neigung einer Legierung zur Bildung von Mikroporosität, gefolgt von einer Herabsetzung der mechanischen Eigenschaftswerte, kennzeichnen. Das erste ist bei wichtiger Fraktion Eutektikum anwendbar : hierbei ist die Porenbildung im wesentlichen auf gelöstes Gas oder auf durch chemische Reaktionen mit einer Gasphase gebildetes Gas bedingt. Das zweite gilt für Legierungen mit nur einer geringen Fraktion Eutektikum, wobei der Einfluß der Erstarrungsschrumpfung durch den Druckabfall vorherrscht. Tatsächlich hindert der Druckabfall daß die interdendritischen, durch die Erstarrungsschrumpfung erzeugten Spalten durch die flüssige Phase gut gefüllt werden. Der für den Druckabfall anzusetzende Ausdruck besteht aus zwei Termen, die sich einander entgegengesetzt auswirken : der eine Term berücksichtigt die Erstarrungsschrumpfung, während der andere Term der Schwerkraftwirkung Rechnung trägt. Dieser letzte Term ist, ausgenommen bei geringer Fraktion Eutektikum, überwiegend. Die Fraktion Flüssigkeit (oder die demgemäße Fraktion Eutektikum) ist von erheblichem Einfluß. Sie hängt gleichzeitig von der Art der Legierung und von den Erstarrungsbedingungen ab. Es konnte tatsächlich aufgezeigt werden, daß infolge der Ausgangskonzentration der Legierung die Erstarrungsparameter von unterschiedlichem Einfluß auf die Entwicklung der Fraktion Flüssigkeit sind : für $C_0 > KC_E$ verringert sich die Fraktion Flüssigkeit mit Abnahme des Verhältnisses $\frac{G}{R}$ während demgegenüber für $C_0 < KC_E$ sich dieselbe mit kleiner werdendem

$\frac{G}{R}$ erhöht.

Modélisation de la formation de microporosités en solidification dirigée. Dans ce travail, nous avons développé deux critères permettant de caractériser la tendance d'un alliage à la

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formation de microporosités, cause de dégradation des propriétés mécaniques. Le premier s'emploie lorsque la fraction eutectique est importante : alors la formation des pores est principalement due au gaz dissous ou formé par réactions chimiques en phase gazeuse. Le second s'applique lorsque les alliages sont pauvres en fraction eutectique, dans ce cas l'influence du retrait de solidification par le biais de la perte de charge est prédominante. En effet, la perte de charge gêne le bon remplissage par le liquide, des espaces interdendritiques créés par le retrait de solidification. L'expression de la perte de charge est composée de deux termes qui l'influencent en sens contraire : l'un reflète l'effet du retrait de solidification et l'autre l'effet de la gravité; ce dernier terme est prédominant sauf pour une faible fraction eutectique. La fraction liquide (ou la fraction eutectique à laquelle elle est liée) est un facteur important. Elle dépend à la fois de la nature de l'alliage et des conditions de solidification. En fait, nous avons montré que suivant la concentration initiale de l'alliage, les paramètres de solidification ont des effets différents sur l'évolution de la fraction liquide : pour $C_0 > KC_E$ la fraction liquide diminue si le rapport $\frac{G}{R}$ diminue par contre pour $C_0 < KC_E$ elle augmente si $\frac{G}{R}$ diminue.

Opstelling van een wiskundig model van de vorming van microporositeiten bij gerichte stolling. In dit onderzoek hebben we twee criteria ontwikkeld, ter kenschetsing van de neiging van een legering tot de vorming van microporositeiten, die de oorzaak zijn van het afnemen van de mechanische eigenschappen. Het eerste criterium wordt bij grote fractie eutectiek toegepast : dan is de porievorming voornamelijk te wijten aan het opgeloste of door chemische reacties in de gasfase gevormde gas. Het tweede geldt wanneer de legeringen arm zijn aan fractie eutectiek; dan is de invloed van de stollingskrimp, d.m.v. het drukverlies, overwegend. Het drukverlies verhindert dat de door het stollingskrimpen gevormde interdendritische ruimten gevuld worden door het vloeibare metaal : het drukverlies wordt door een vergelijking gegeven, die twee tegenwerkende termen bevat : de eerste spiegelt de invloed van de stollingskrimp weer, en de andere de invloed van de zwaartekracht; behalve bij lage fractie eutectiek is deze laatste overwegend. De fractie vloeistof (of de fractie eutectiek waaraan zij gebonden is) is een belangrijke faktor. Zij hangt tevens af van de legeringsaard en van de stollingsvoorwaarden. We hebben getoond dat, in afhankelijkheid van de aanvangssamenstelling van de legering, de stollingsparameters werken verschillend in op de evolutie van de fractie vloeistof : bij $C_0 > KC_E$ neemt de fractie vloeistof af wanneer de verhouding $\frac{G}{R}$ afneemt, daarentegen

bij $C_0 < KC_E$ neemt zij toe als $\frac{G}{R}$ afneemt.

INTRODUCTION

The problem of micropores in cast alloys is always a matter of concern to investigators working on the theories of metal-casting; the mechanical properties of alloys are seriously affected by the presence of these defects.

The origin of micropore formation during directional solidification, as in ordinary castings, is attributed to the gas dissolved contained in the alloy and shrinkage during solidification.

To facilitate the study of these defects we have tried to define a criterion making it possible to characterise the susceptibility of an alloy to micropore formation as a function of solidification parameters and the nature of the alloy.

We have developed two criteria characterising susceptibility to micropore formation. The first applies when alloys have a very small fraction eutectic, and the second when the fraction eutectic is large. When the fraction eutectic is large the origin of micropores is mainly the dissolved gas but, in the contrary case, the influence of solidi-

fication shrinkage arising from the pressure drop is predominant : the fraction eutectic (or the fraction liquid to which it is connected) is therefore an important factor in a study of pore formation. It depends simultaneously on the nature of the alloy and solidification parameters.

We have shown that, depending on the initial alloy concentration, solidification parameters have a varying effect on changes in the fraction liquid : for $C_0 < KC_E$, the fraction liquid increases when the ratio $\frac{G}{R}$ decreases (G being the thermal gradient and R the solidification rate) (Fig. 1 A); and :

for $C_0 > KC_E$, the fraction liquid decreases when the ratio $\frac{G}{R}$ decreases (Fig. 1 B).

I. — PORE FORMATION

In the interdendritic space, in the "mushy" zone, a pore forms when the local pressure of the interdendritic liquid p_L is :

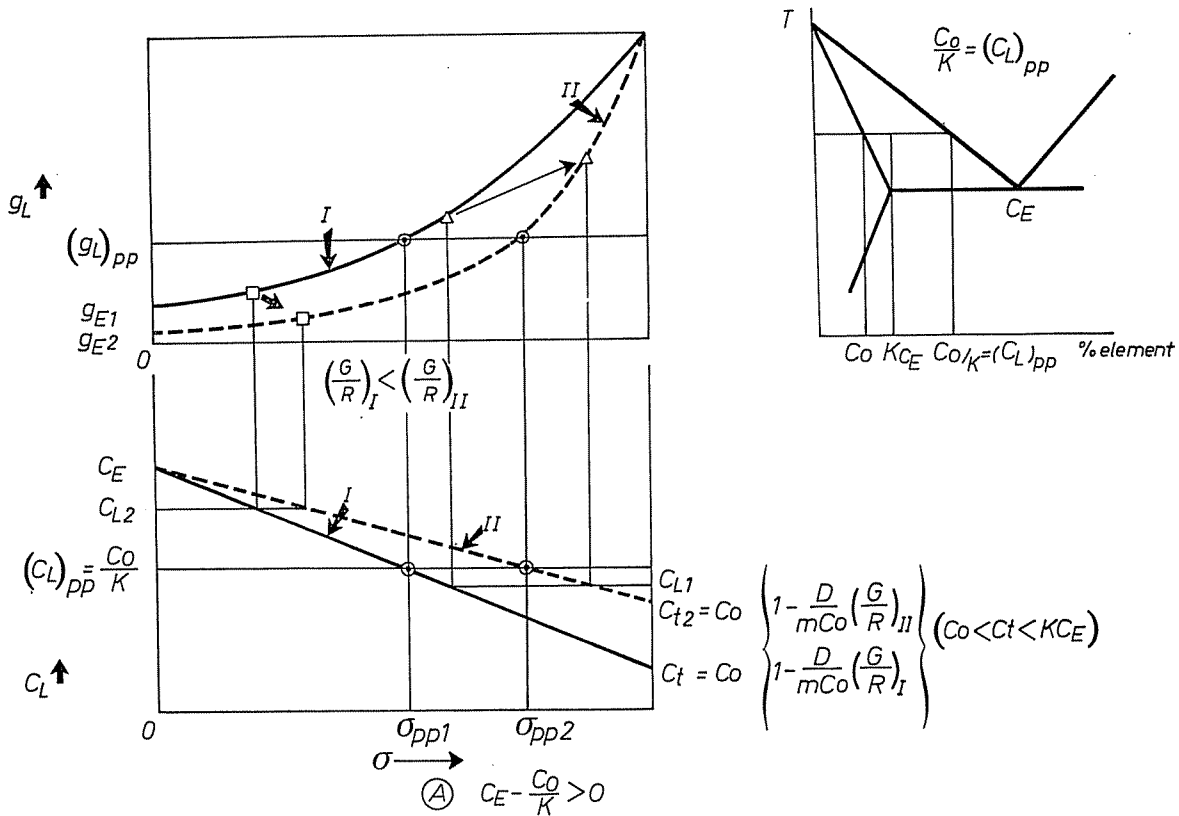


FIG. 1A.

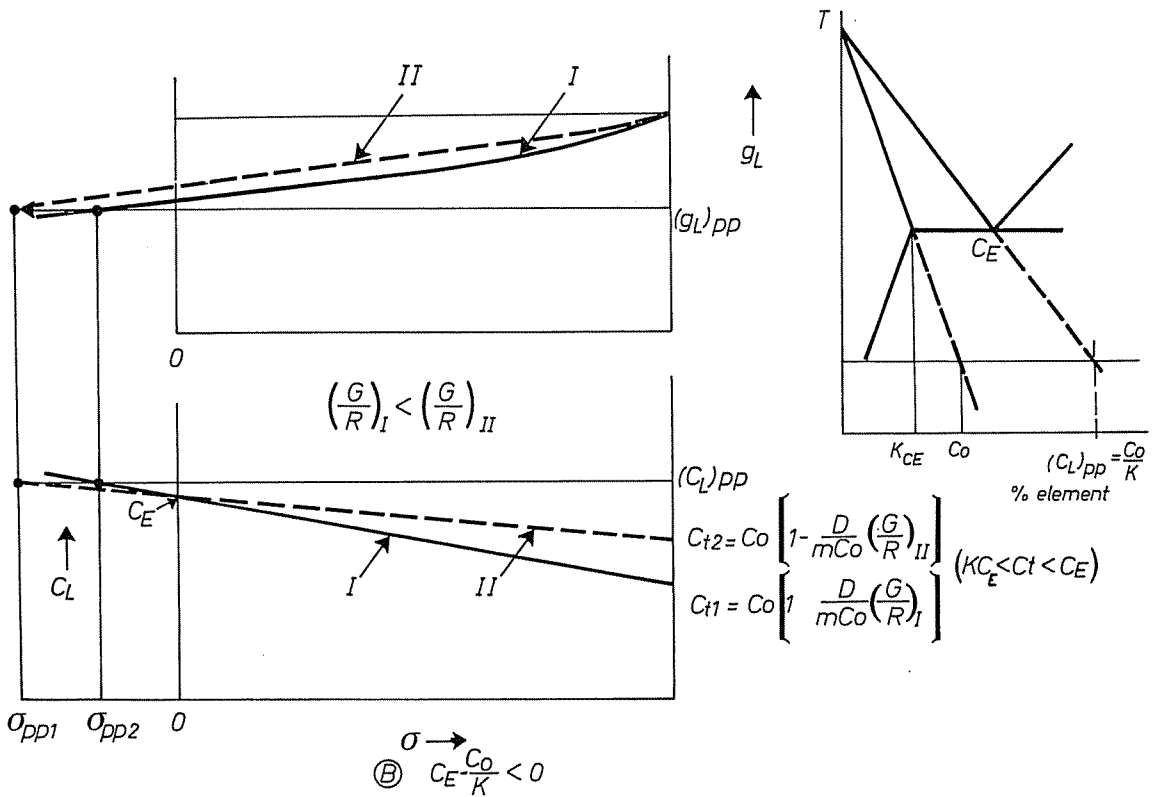


FIG. 1B.

FIG. 1, A et B. Influence of the solidification conditions on the fraction liquid g_L and on the position of the permanent point σ_{pp} .

$$p_L \leq p_g - p_\sigma \quad (1)$$

where :

p_g : equilibrium partial pressure of the dissolved gas;

p_σ : pressure due to the tension at the liquid metal/gas interface.

Now :

$$p_L = p_a + p_h - \Delta p \quad (2)$$

where :

p_a : atmospheric pressure in the furnace chamber;
 p_h : static pressure of the liquid alloy, applied to the solidification front;

Δp : pressure drop [1, 2, 3, 7, 9, 10].

This pressure drop represents the energy lost by friction from the interdendritic liquid flowing along the dendrite surface. Local pressure is mainly a function of the pressure drop.

Using the expression for the pressure drop which will be introduced in Section V we have shown that, for directional solidification under vacuum conditions, if the height of the liquid alloy above the tips of the primary dendrites is sufficient compared with that of the mushy zone (L), there then exist two factors which have a crucial effect on local pressure p_L : these are the static pressure of the liquid alloy p_h and the pressure drop Δp . The static pressure is initially important and then it is the turn of the pressure drop Δp .

Over a large distance, from the start of solidification up to the end, local pressure in the mushy zone does not vary much, because of the static pressure. At the end of solidification, because of the sudden increase in the pressure drop, local pressure drops rapidly and becomes lower than the equilibrium partial pressure at this location. The dissolved gas and solidification shrinkage thus jointly contribute to micropore formation. If the pressure drop Δp is small, the dissolved gas could never have any effect on micropore formation. Atmospheric pressure (or the vacuum in the chamber) p_a and the static pressure of the alloy p_h can be artificially controlled. The pressure drop Δp , however, is simultaneously dependent on the nature of the alloy and solidification parameters. When the solidification parameters are fixed the pressure drop depends only on the nature of the alloy.

The pressure drop Δp thus satisfactorily represents the inherent susceptibility of the alloy to micropore formation.

A large pressure drop indicates susceptibility to pore formation but this is also the case with an increase in the partial pressure of the dissolved gas. The important factor (gas or shrinkage) in solidification depends on the alloy and the solidification parameters.

We have tried to clarify this question by a mathematical treatment of some known formulae

but first we examined the influence of solidification parameters on the fraction liquid.

II. — FRACTION LIQUID

Let us consider a binary alloy which is subjected to directional solidification in a stable state. Assuming [7] that :

- the isotherms are flat and perpendicular to the direction of solidification;
- solidification reaches equilibrium at the solid/liquid interface i.e. $C_s = KC_L$, where C_s and C_L are the respective solid and liquid concentrations at the interface and K is the partition ratio (less than 1 in the case considered);
- the primary dendrite spacings are such that there is no constitutional supercooling in the mushy zone;
- dendrite size is sufficient for their radius of curvature not to have any effect on the melting point;
- there is no diffusion into the solid; the fraction liquid is expressed as under :

$$g_L = \left[\frac{C_L - \frac{a}{K-1}}{C_0 - \frac{a}{K-1}} \right] \frac{1}{K-1} \quad (3)$$

where :

- g_L : the fraction liquid by volume; if the difference in density between solid and liquid is neglected;
- C_L : the concentration of interdendritic liquid;
- C_0 : the initial concentration of the alloy;
- with :

$$a = \frac{DG}{mR C_0}$$

where :

- D : coefficient of diffusion of the solute in the alloy;
- G : the temperature gradient in the mushy zone;
- m : equilibrium liquidus slope in relation to the concentration of interdendritic liquid, negative when $K < 1$; $C_L - C_0 = m(T - T_{LO})$;
- R : solidification rate;
- T_{LO} : temperature of liquidus corresponding to C_0 .

III. — INFLUENCE OF SOLIDIFICATION PARAMETERS ON THE INTERDENDRITIC FRACTION LIQUID

Equation (3) can be rewritten as under :

$$g_L = \left[\frac{C_L - \frac{D}{mC_0(K-1)} \frac{G}{R}}{C_0 - \frac{D}{mC_0(K-1)} \frac{G}{R}} \right] \frac{1}{K-1} \quad (4)$$

By differentiating equation (4) with respect to $\left(\frac{G}{R}\right)$ we get :

$$\frac{\delta g_L}{\delta \left(\frac{G}{R}\right)} = \frac{1}{K-1} g_L (2-K) \frac{D}{m C_0 (K-1)} \left(\frac{K C_L}{C_0} - 1\right) \left[1 - \frac{K D G}{m C_0 (K-1)}\right]^{-2} \quad (5)$$

that is :

$$\frac{\delta g_L}{\delta \left(\frac{G}{R}\right)} > 0, \text{ for } \frac{K C_L}{C_0} - 1 < 0 \quad (6)$$

$$\frac{\delta g_L}{\delta \left(\frac{G}{R}\right)} = 0, \text{ for } \frac{K C_L}{C_0} - 1 = 0 \quad (7)$$

$$\frac{\delta g_L}{\delta \left(\frac{G}{R}\right)} < 0, \text{ for } \frac{K C_L}{C_0} - 1 > 0 \quad (8)$$

where :

C_L : concentration of interdendritic liquid, which varies between C_t and C_E ;

C_t : concentration of liquid at dendrite tips;

C_E : eutectic concentration.

According to equation (7) when $C_L = \frac{C_0}{K}$, the solidification parameters have no effect on the fraction liquid; then the fraction liquid at this point will be determined by equation (4), by inserting equation (7) :

$$(g_L)_{pp} = \left(\frac{1}{K}\right)^{\frac{1}{K-1}} \quad (9)$$

where :

$(g_L)_{pp}$: interdendritic fraction liquid for which the corresponding concentration of interdendritic liquid has a value of $\left(\frac{C_0}{K}\right)$.

In the remainder of this discussion we shall term $(g_L)_{pp}$ the "permanent point". On both sides of this "permanent point" the solidification variables present a contrary aspect as regards influence on the fraction liquid : the fraction liquid increases

with increasing $\left(\frac{G}{R}\right)$ when : $\frac{K C_L}{C_0} - 1 < 0$;

it decreases with increasing $\left(\frac{G}{R}\right)$ when :

$$\frac{K C_L}{C_0} - 1 > 0.$$

Any binary alloy system has a "permanent point" which is solely a function of its partition ratio.

Obviously, if $(g_L)_{pp}$ is less than the fraction eutectic the "permanent point" will be outside the mushy zone. The so-called "permanent point" designates a point where the fraction liquid is independent of solidification parameters and remains constant; as regards its position relative to the mushy zone, it is not permanent, as we shall see later in this report.

IV. — DISTRIBUTION OF FRACTION LIQUID ACCORDING TO DIRECTION OF SOLIDIFICATION

Assuming that the temperature distribution in the mushy zone is linear the interdendritic liquid concentration can be expressed as under :

$$\text{or : } \left. \begin{aligned} C_L &= C_E - \frac{C_E - C_t}{L} x \\ C_L &= C_E - (C_E - C_t) \sigma \end{aligned} \right\} \quad (10)$$

where :

C_L : concentration of the interdendritic liquid;

C_t : concentration of liquid at the tips of the primary dendrites;

L : length of mushy zone;

x : distance from the bottom of primary dendrites :

$$\sigma = \frac{x}{L}$$

Taking into account that :

$$C_t = C_0 \left(1 - \frac{D G}{m C_0 R}\right) \quad [7] \quad (11)$$

equation (10) assumes the following form :

$$C_L = C_E - \left[C_E - C_0 \left(1 - \frac{D G}{m C_0 R}\right) \right] \sigma \quad (12)$$

Introducing equation (12) into equation (4) we have :

$$g_L = \left\{ \frac{C_E}{C_0} - \frac{D G}{m C_0 (K-1) R} \right. \\ \left. 1 - \frac{K D G}{m C_0 (K-1) R} \right. \\ \left. - \frac{\left[\frac{C_E}{C_0} - \left(1 - \frac{D G}{m C_0 R}\right) \right] \sigma}{1 - \frac{K D G}{m C_0 (K-1) R}} \right\}^{\frac{1}{K-1}} \quad (13)$$

As :

$$\frac{\frac{C_E}{C_0} - \frac{D G}{m C_0 (K-1) R}}{1 - \frac{K D G}{m C_0 (K-1) R}} = g_E K - 1,$$

if we put :

$$\frac{\frac{C_E}{C_0} - \left(1 - \frac{D G}{m C_0 R}\right)}{1 - \frac{K D G}{m C_0 (K-1) R}} = A,$$

equation (13) is simplified as under :

$$g_L = \left(g_E K - 1 - A \sigma \right) \frac{1}{K-1} \quad (14)$$

Let us examine the effect of the solidification parameters on distribution of the fraction liquid along the direction of solidification. Differentiating equation (13) with respect to $\left(\frac{G}{R}\right)$ we get :

$$\frac{\delta g_L}{\delta \left(\frac{G}{R}\right)} = \frac{1}{K-1} g_L (2-K) \frac{D}{m C_0 (K-1)} (1-\sigma) \left(\frac{K C_E}{C_0} - 1 \right) \frac{1}{\left(1 - \frac{K D G}{m C_0 (K-1) R}\right)^2} \quad (15)$$

and for :

$$\frac{K C_E}{C_0} - 1 < 0, \quad \frac{\delta g_L}{\delta \left(\frac{G}{R}\right)} > 0 \quad (16)$$

for :

$$\frac{K C_E}{C_0} - 1 > 0, \quad \frac{\delta g_L}{\delta \left(\frac{G}{R}\right)} < 0 \quad (17)$$

It is clear that the influence of the solidification parameters on the fraction liquid depends on the initial concentration of the alloy. Equations (16) and (17) show that when the concentration of the alloy exceeds the limit of solubility the increase in $\left(\frac{G}{R}\right)$ also increases the fraction liquid but it reduces the fraction liquid if the concentration of the alloy is less than the limit of solubility.

By definition, the interdendritic liquid concentration corresponding to the "permanent point" is expressed by equation (9) : the position of the "permanent point" relative to the length of the mushy zone can easily be determined from equation (12) :

$$\sigma_{pp} = \frac{C_E - \frac{C_0}{K}}{C_E - C_0 \left(1 - \frac{D G}{m C_0 R}\right)} \quad (18)$$

where :

σ_{pp} position of the "permanent point" relative to the mushy length.

Since the liquidus could never be less than the solidus and when $C_E - \frac{C_0}{K} > 0$ the maximum liquid concentration at the tips of the primary dendrites, C_t , must be $\frac{C_0}{K}$ and for $C_E - \frac{C_0}{K} < 0$ this maximum is C_E , the denominator of the expression on the right side of equation (18), $C_E - C_0 \left(1 - \frac{D G}{m C_0 R}\right)$ is therefore always positive. It goes without saying that the sign for σ_{pp} will only depend on the sign of the numerator, $C_E - \frac{C_0}{K}$. In other words, for $C_E - \frac{C_0}{K} > 0$, σ_{pp} is positive and for $C_E - \frac{C_0}{K} < 0$, σ_{pp} is negative.

Since :

$$\frac{\delta \sigma_{pp}}{\delta \left(\frac{G}{R}\right)} = - \frac{\frac{D}{m} \left(C_E - \frac{C_0}{K}\right)}{\left[C_E - C_0 \left(1 - \frac{D G}{m C_0 R}\right) \right]^2} \quad (19)$$

it follows that σ_{pp} increases when $\left(\frac{G}{R}\right)$ increases if $C_E - \frac{C_0}{K} > 0$, and if $C_E - \frac{C_0}{K} < 0$, σ_{pp} decreases with increasing $\left(\frac{G}{R}\right)$.

Summing up, when considering the influence of solidification parameters on the fraction liquid and the distribution of the latter in the direction of solidification, a distinction should be made between two cases : when $C_E - \frac{C_0}{K} > 0$ and when $C_E - \frac{C_0}{K} < 0$.

In the first case, the fraction which is liquid over the entire length of the mushy zone decreases with $\left(\frac{G}{R}\right)$ and, in this case, the "permanent point" is located inside the mushy zone; in the second case, however, the fraction liquid increases with $\left(\frac{G}{R}\right)$ and in this case the "permanent point" is outside the mushy zone. All these conclusions are illustrated in schematic representation in Figures 1A and 1B.

V. — PRESSURE DROP
IN THE DIRECTION OF SOLIDIFICATION

According to Flemings [7] the mushy zone can be compared with a porous medium and Darcy's law applies i.e.

$$V = - \frac{\alpha}{\mu g_L} \left(\frac{\delta p}{\delta x} + \rho_L g_r \right) \quad (21)$$

where :

- V : interdendritic flow rate
- α : constant, permeability
- μ : viscosity of the interdendritic liquid
- g_L : fraction liquid
- $\frac{\delta p}{\delta x}$: pressure gradient in the direction of solidification x
- ρ_L : density of the liquid
- g_r : acceleration due to gravity.

Still according to Flemings and Pivonka [1, 7] we get :

$$V = - \beta' R, \beta' = \frac{\beta}{1 - \beta}, \beta = \frac{\rho_s - \rho_L}{\rho_s} \quad (22)$$

$$\alpha = \gamma g_L^2 \quad (23)$$

$$\gamma = \frac{1}{8 \pi n t} \quad (24)$$

where :

- R : solidification rate;
- ρ_s : density of the solid
- ρ_L : density of the liquid
- n : number of primary dendrites per unit surface area
- t : "tortuosity", constant.

If the relative position is defined as :

$$\sigma = \frac{x}{L} \quad (25)$$

introducing equations (22) to (25) into equation (21) we get :

$$\frac{dp}{d\sigma} = \frac{\mu \beta' R L}{\gamma g_L} - \rho_L g_r L \quad (26)$$

differentiating equation (14) we get :

$$d\sigma = - \frac{K-1}{A} g_L^{K-2} dg_L \quad (27)$$

Combining equations (26) and (27) we find :

$$dp = - \frac{(K-1) \mu \beta' R L}{A \gamma} g_L^{K-3} dg_L + \frac{(K-1) \rho_L g_r L}{A} g_L^{K-1} dg_L \quad (28)$$

Integrating equation (28) with the boundary conditions :

for $p = p_a + p_h, g_L = 1$
for $p = p_L, g_L = g_L$

we arrive at the pressure drop as a function of the fraction liquid, as under :

$$\begin{aligned} \Delta p &= \int_{p_L}^{p_a + p_h} dp = \\ &= - \frac{(K-1) \mu \beta' R L}{A \gamma} \int_{g_L}^1 g_L^{K-3} dg_L + \\ &\quad \frac{(K-1) \rho_L g_r L}{A} \int_{g_L}^1 g_L^{K-2} dg_L \\ &= \frac{(K-1) \mu \beta' R L}{(K-2) A \gamma} (g_L^{K-2} - 1) - \\ &\quad \frac{\rho_L g_r L}{A} (g_L^{K-1} - 1) \end{aligned} \quad (29)$$

where

p_a : atmospheric pressure acting on the solidification front

p_h : static pressure of the liquid alloy acting on the solidification front.

If equation (14) is introduced into equation (29) the pressure drop will be expressed as a function of the relative position, by means of the equation :

$$\begin{aligned} \Delta p &= \frac{(K-1) \mu \beta' R L}{(K-2) A \gamma} \\ &\quad \left[\left(g_E^{K-1} - A \sigma \right)^{\frac{K-2}{K-1}} - 1 \right] - \\ &\quad \rho_L g_r L [(g_E^{K-1} - A \sigma) - 1] \end{aligned} \quad (30)$$

On the right-hand side of equation (29) or equation (30), the first term represents the influence of the interdendritic flow or solidification shrinkage on the pressure drop while the second term shows the influence of gravity on pressure drop. When the liquid fraction is small, the first term occupies the dominant position but, because of the low coefficient :

$$\left[\frac{(K-1) \mu \beta' R L}{(K-2) A \gamma} \right]$$

of the first term, it is the second term which plays an important part when the liquid fraction is large.

VI. — INFLUENCE OF GAS DISSOLVED
IN THE ALLOY ON MICROPORE FORMATION

The solubility of the gas at a given temperature is higher in the liquid than in the solid; consequently when the alloy solidifies, the gas rejected by the solid passes into the liquid and the liquid therefore becomes gradually enriched in gas in proportion as solidification proceeds. For an alloy which has a certain solidification range, this gas transfer process takes place in the mushy zone.

When the equilibrium partial pressure of the gas dissolved in the interdendritic liquid reaches and

even exceeds the local pressure it might be thought that micropores will form but this would be in ignorance of the kinetics of micropore formation.

According to Sievert's law (for diatomic gas) :

$$V_s = K_s \sqrt{p_g} \quad (31)$$

$$V_L = K_L \sqrt{p_g} \quad (32)$$

where :

V_s, V_L : the quantities of gas dissolved in the solid and in the liquid respectively, for a certain weight of alloy;

K_s, K_L : solubility constants of the gas in the solid and liquid respectively;

p_g : partial pressure of the dissolved gas, common to the solid and liquid.

Since the solid and liquid constituents in the mushy zone are alternately side by side and the primary dendrite spacing is generally very small it is reasonable to consider that the gas rejected by the solid diffuses and penetrates fully into the interdendritic liquid before the micropores form. Assuming that the quantity of gas dissolved in the alloy to be solidified is V_i , the quantity of gas dissolved must still be conserved, namely :

$$V_i = V_s (1 - g_L) + V_L g_L \quad (33)$$

where :

g_L : the fraction liquid;

V_i : the initial quantity of dissolved gas.

Combining equations (31), (32) and (33) above we get :

$$p_g = \left[\frac{V_i}{K_s (1 - g_L) + K_L g_L} \right]^2 \quad (34)$$

or :

$$p_g = \left\{ \frac{V_i}{K_L [g_L (1 - K') + K']} \right\}^2 \quad (35)$$

with $K' = \frac{K_s}{K_L}$; K' is generally of the order of $10^{-1} \sim 10^{-2}$.

The partial pressure of gas dissolved in the mushy zone rises in proportion as solidification progresses. When solidification is nearly complete, for example $g_L = 0.01$, p_g reaches its maximum, (p_g) max, which only depends on V_i , K_L and K' . More simply, (p_g) max is expressed as under :

$$(p_g) = \left[\frac{V_i}{K_L (K' + g_L)} \right]^2 \quad (36)$$

Equation (36) helps to clarify why, during directional solidification in an argon atmosphere, micropores begin to appear very close to the tips of the primary dendrites. The fraction liquid suddenly drops, when moving away from the tips of the primary dendrites, which causes p_g to reach its

maximum value and exceed the local pressure, resulting in micropore formation.

VII. — CRITERIA CHARACTERISING THE SUSCEPTIBILITY OF ALLOYS TO MICROPORE FORMATION

Let us take equation (21) again, introducing equation (22) :

$$\frac{dp}{dx} = \frac{\mu \beta' R \sigma g_L}{x} - \rho_L g_r \sigma$$

and we obtain the pressure drop in the form of a sum :

$$\Delta p = \mu \beta' R (\Delta x) \sum \frac{g_L}{g_L x} - \rho_L g_r (L - x) \quad (37)$$

where Δx = the length of the differential segments dividing L .

If there are n segments in the mushy zone, Δx is expressed by :

$$\Delta x = \frac{L}{n} \quad (38)$$

and $L = \frac{\Delta T}{G}$ where ΔT is the solidification range.

Then equation (37) assumes the following form :

$$\Delta p = \mu \beta' \frac{\Delta T R}{n G} \sum \frac{g_L}{g_L x} - \rho_L g_r (L - x) \quad (39)$$

For a small fraction liquid, g_L less than 10^{-4} for example, the effect of gravity can be neglected. Also, for the points which will be close to the end of solidification the pressure drop Δp is determined

by the sum of the ratios $\sum \frac{g_L}{x}$.

If the mushy zone is compared with a set of cylindrical pipes the fraction liquid can be expressed as :

$$S_L = g_L = n \pi r^2 \quad (40)$$

$$P_e = 2 n \pi r t \quad (41)$$

where :

n : the number of channels (or primary dendrites) per unit of surface area perpendicular to the direction of solidification;

r : mean radius of channels at a given point;

P_e : perimeter of channels per unit surface area (depending on t);

t : tortuosity of the channels, with an approximate value of 2;

S_L : surface area of liquid per unit of surface area perpendicular to the direction of solidification.

Combining equations (23), (24), (37), (39), (40) and (41) we get :

$$\Delta p \simeq \mu \beta' \frac{\Delta T R}{n G} \sum_{g_L}^1 \left(\frac{P_e}{S_L} \right)^2 \quad (42)$$

At the limit :

$$(S_L)_{\min} = S_E, (P_e)_{\min} = P_{eE} \quad (43)$$

where :

S_E : the surface area of the eutectic per unit surface area;

P_{eE} : perimeter of the channels per unit surface area at the end of solidification.

It is therefore possible to express the pressure drop at the end of solidification $(\Delta p)_E$ as under :

$$\begin{aligned} (\Delta p)_E &\simeq \mu \beta' \frac{\Delta T R}{n G} \sum_{g_E}^1 \left(\frac{P_e}{S_L} \right)^2 \\ &= \mu \beta' \frac{\Delta T R}{n G} \left[\left(\frac{P_{eE}}{S_E} \right)^2 + \dots + \left(\frac{P_{e2}}{S_{L2}} \right)^2 + \left(\frac{P_{e1}}{S_{L1}} \right)^2 \right] \end{aligned} \quad (44)$$

Due to the fact that the coefficients β' and μ do not vary much for different alloys and the ratio $\frac{(P_{eE})^2}{S_E}$ is much more important than others in the

sum, the term $\Delta T \frac{R}{G} \left(\frac{P_{eE}}{S_E} \right)^2$ can therefore represent the extent of the pressure drop in an alloy at the end of solidification. Let us define the ratio $\frac{P_{eE}}{S_E}$ as the specific perimeter of the eutectic, $(PS)_E$. We then have criterion 1 :

$$\Delta T \frac{R}{G} (PS)_E^2 = (\Delta p) \text{ characteristic} \quad (45)$$

to characterise susceptibility to micropore formation for a small fraction eutectic. The higher criterion 1, the greater the microporosity. When the solidification parameters are fixed, criterion 1 represents the inherent susceptibility of an alloy to a micropore formation; on the other hand, once the alloy is selected, it represents the effect of the solidification parameters on the susceptibility of the alloy to micropore formation.

For alloys rich in eutectic where the fraction eutectic is greater than 10^{-3} , the pressure drop at the end of solidification can no longer be represented by equation (45).

It is of the same order of magnitude as the partial pressure drop due to gravity. At this point in time, micropore formation can be attributed to the gas dissolved in the alloy.

Taking equation (36) again for a given quantity of dissolved gas we then have criterion 2 :

$$(p_g)_{\max} = \frac{(p_g)_0}{(K' + g_E)^2} \quad (46)$$

to characterise the susceptibility to micropore formation for a large fraction eutectic : the higher criterion 2, the greater the microporosity. Like equation (45), equation (46) simultaneously represents the effects of the nature of the alloy and solidification parameters on susceptibility to micropore formation. Summing up, we have two criteria characterising susceptibility to micropore formation : criterion 1 and criterion 2, the first applying to alloys with little eutectic and the second applying to alloys which are rich in eutectics. The specific perimeter and fraction eutectic can both be measured by an image analyser.

VIII. — CONCLUSIONS

(1) Micropore formation is attributed to the gas dissolved in the alloy and solidification shrinkage. When the fraction eutectic is large, the gas dissolved in the alloy is undoubtedly the main cause of micropore formation. On the other hand, when the fraction is small, it would appear that the main cause is solidification shrinkage arising from the pressure drop.

(2) Since the limit reached by the equilibrium partial pressure of dissolved gas and the maximum pressure drop both depend on the fraction eutectic, the eutectic fraction is a critical factor in the two cases mentioned above. The fraction eutectic depends on the nature of the alloy and solidification parameters. The fraction eutectic is the minimum for the fraction liquid which varies as a power as a function of the relative position with respect to the length of the mushy zone.

(3) The solidification parameters have a varying effect on the fraction liquid or eutectic according to circumstances : for $C_0 < KC_E$ the fraction liquid or eutectic increases when the ratio $\frac{G}{R}$ decreases, and for $C_0 > KC_E$ it is the opposite.

(4) The partial pressure of the dissolved gas varies as a function of the fraction liquid. When the alloy solidifies under vacuum conditions this pressure is too low at the end of solidification since the initial quantity of dissolved gas is small. During solidification in a gas medium it is very high at the end of or even during solidification.

(5) The pressure drop consists of two terms, one of which reflects the effect of gravity B and the other the effect of solidification shrinkage A. $\Delta p = A - B$. From the beginning to the end of solidification, over quite a long distance, gravity remains dominant : only for a small fraction liquid, for example 10^{-4} , the term representing

solidification shrinkage suddenly increases and surpasses the term for gravity. At this time the pressure drop could make a contribution to the micropore formation. A negative pressure drop retards micropore formation whereas a positive pressure drop has the effect of extending micropore formation. Since a positive pressure drop is only found for a small fraction liquid it can be considered that the pressure drop only acts on micropore formation, individually or together with the dissolved gas, when the alloy only has a small fraction eutectic. The pressure drop is equally determined by the nature of the alloy and solidification parameters.

(6) We have introduced two criteria characterising the susceptibility of the alloy to micropore formation: criterion 1 and criterion 2. The first is valid when the fraction eutectic is small and the second when the fraction eutectic is large. They are a function of solidification conditions and the nature of the alloy, through the intermediary of the specific perimeter and the fraction eutectic which can both be calculated in the case of primary alloys or measured.

(7) As regards the gas contained in the alloy we have only spoken of the dissolved gas. There may be other sources of gas: chemical reactions in gaseous phases and vaporisation of certain

volatile alloy elements, for example. Other sources of gas must therefore not be omitted when studying micropore formation.

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