

Review

Pore formation in cast metals and alloys

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Porosity occurs in cast solidifying metals and alloys due to negative pressures generated during solidification contraction, and pressure developed by gases dissolved in the molten metal. Both the above processes may act either together or separately to produce such shrinkage or gas defects (collectively termed pores). They are generally unwanted and constitute a major industrial problem. This paper is an attempt to review up-to-date knowledge of the conditions of pore formation in cast metals and alloys. Various mechanisms responsible for pore nucleation and growth are summarized, and experimentally evaluated using an unfed type of mould with aluminium alloy castings. The observations are in support of a non-nucleation mechanism of pore formation playing a major role in the occurrence of such defects in cast metals. Further, in gas-containing alloy melts the critical amounts of gas required for single and multiple pore nucleation have been determined quantitatively and are listed in the text. The gas contents of the melts were measured using an apparatus based on the "first bubble technique". It is also experimentally observed that under poor feeding conditions more than one of the non-classical nucleation mechanisms may be functional at the same time for the formation of such defects.

Nomenclature

P_e	Sum of external forces which tend to collapse a pore	f_L	Fraction of liquid left in the casting of mushy freezing alloys, $\pi r^2 nt / \pi R^2$
P_h	Hydrostatic pressure	B	$K_L \pi n t (1 - K')$
P_g	Internal gas pressure in liquid metal	nb_i^2	B^2 (approximately)
P_a	Atmospheric pressure applied during solidification	r^*	Critical radius for pore nucleation (pore below r^* size cannot exist)
P_s	Shrinkage pressure	σ	Surface tension of liquid
γ	Surface tension at gas-metal interface	N	Avogadro's number
P_f	Fracture pressure of liquid metal	k	Boltzmann constant
$2\gamma/r$	Surface tension resistance	h	Planck's constant
V_i	Volume of initial gas content of liquid metal	T	Temperature (K)
P_i	Total internal pressure due to gas and/or shrinkage	a, b	Inner and outer radii of solidified shell
K_s, K_L	Gas solubility constants of solid and liquid metal, respectively	Y	Uniaxial yield stress
K'	K_s/K_L	η, η_s	Energy per unit area of solid-liquid and solid-vapour interface, respectively
r	Radius of liquid channel	λ	Thermal diffusivity of solid metal
R	Radius of cylindrical casting	C_p	Specific heat of solid metal
L	Length of liquid channel	m, K_1, K_2	Constants
L_c	Length of cylindrical casting	α	Fractional contraction of liquid phase on solidification [(solid density - liquid density)/solid density]
f_i	Fraction of liquid left in the casting of pure and short freezing-range alloy, $\pi r^2 L / \pi R^2 L_c$	α'	$\alpha / (1 - \alpha)$
V_i^*	Critical gas content	Γ	Vortex circulation factor
t	Tortuosity of channel	d	Density of liquid
n	Number of channels (approximately number of dendrite arms per unit area)	μ	Metal viscosity
		h_1	Thermal conductivity of mould
		H	Heat of fusion of metal

2.3. Fracture pressure of liquid metal, P_f

Fisher's analysis [7] on homogeneous nucleation of a pore leads to a fracture pressure in a liquid as follows:

$$P_f = - \left(\frac{16\pi\sigma^3}{3kTLn(NkT/h)} \right)^{1/2} \quad (8)$$

where σ is the surface tension of the liquid; N , k and h are the Avogadro, Boltzmann and Planck constants, respectively. Equation 4 assumes that both the gas pressure built up due to gas precipitation and tensional forces produced by solidification shrinkage contribute together to the nucleation of the bubble. The term fracture pressure (tensile strength) of liquid is included in the equation, since the first bubble that forms fractures the liquid metal and its value will change depending upon many factors, particularly the nucleation mechanism. In the deduction of this equation, Fisher has, however, neglected the forces of atmospheric pressure and hydrostatic pressure due to the head of liquid metal above the site of nucleation, both tending to collapse the bubble. Since the shrinkage pressure is usually negative, the effect of gas precipitation and shrinkage are therefore additive and encourage nucleation. The cooperative action of gas and shrinkage may be viewed as the gas pressure pushing the pore from the inside, and shrinkage pressure pulling from the outside. In a gas-free melt P_f equals the negative pressure; P_s equals the internal equilibrium gas pressure, P_g , required for gas bubble nucleation.

Nussey has theoretically calculated the liquid fracture pressure in an isolated body of liquid in a solidifying metal sphere, assuming that the solidifying shell is perfectly rigid. However, the fracture pressure of liquid calculated was very high.

About two decades ago, Campbell [18] critically assessed and practically formulated the process of computation of the liquid fracture pressure in an isolated liquid body of various metals and alloys employing spherical and later cylindrical symmetry, which appears to be closer to a real casting system. Campbell [18] made an attempt to evaluate the fracture pressure P_f on a spherical casting by considering an elastic model with elastic-plastic collapse of the outer solidified shell of the casting. A relation was established for fracture pressure as follows:

$$P_f = P_a + \frac{2\eta}{a} + \frac{2\eta_s}{b} - 2Y \ln(b/a) \quad (9)$$

2.4. Viscous flow of liquid

Volumetric contraction in a cylindrical casting of length L_c of a pure metal or narrow freezing-range alloy and/or with a high temperature gradient occurs during solidification in the form of central line shrinkage (pipe formation), and to feed this cavity liquid must flow from the riser down to the liquid channel; the pressure difference between the two ends ΔP (the pressure shrinkage P_s) is expressed as follows [19]:

$$\Delta P = \frac{32\mu\alpha'\lambda^2 L_c^2}{r^4} \quad (10)$$

In the case of mushy-freezing alloys, there is viscous flow of residual liquid through interdendritic channels and the pressure differential along the length of the casting L_c is

$$\Delta P = \frac{32\mu\alpha'\lambda^2 L_c^2 t^2}{r^4 \pi R^2 \eta} \quad (11)$$

However, the elastic-plastic model analysis was based on the analogous assumption that yield stress is independent of strain rate, whereas in the actual solidification process the cast metals and alloys are at their melting points and the yield stress is strongly dependent upon strain rate. The inadequacy of previously-proposed elastic-plastic and rigid-shell models were therefore reviewed and compared with more reliable results of analysis for creep and viscous flow of liquid.

2.5. Creep model

Assuming that deformation of solid metal at its melting point is best described by a creep mechanism [20] for long freezing-ranging alloys and/or with a low temperature gradient

$$\Delta P = \frac{\eta}{a} - \frac{m}{2K_2} \left(\frac{4\alpha\lambda^2}{K_1} \right)^{1/m} \times \left(1 - \frac{a^2}{b^2} \right)^{-1/m} \left(1 - \frac{a^{2/m}}{b_1^{2/m}} \right) a^{-2/m} \quad (12)$$

and for pure metal and short freezing-range alloys or with a high temperature gradient

$$\Delta P = \frac{\eta}{a} - \frac{m}{2K_2} \left(\frac{2.5\alpha h c_p \Delta T}{K_1 b H} \right)^{1/m} \times \left(1 - \frac{a^{2/m}}{b_1^{2/m}} \right) a^{-1/m} \quad (13)$$

where b_1 is radius of liquid core.

Hence, for the flow of liquid through interdendritic channels there is a critical radius between 10^{-3} and 10^{-4} cm. Below this size, although channels are still interconnected yet the viscous resistance to flow of liquid becomes extremely high; at this stage creep flow of solid occurs preferentially. The maximum hydrostatic tension is limited by collapse of the casting. The negative pressure developed due to hydrostatic tension of the casting was calculated and found to be in the range -1500 to -4200 atm pressure for nickel, aluminium, copper and iron.

3. Mechanisms of pore nucleation

A number of possible theories of nucleation of pores in solidifying metals are now available and experimental evidence has also been produced for them. These may be briefly described under the following headings.

3.1. Homogeneous nucleation

Formation of pores occurs without being influenced by impurities and/or external surfaces. For many years the possibility of pore nucleation in a homogeneous liquid phase has been conceived and examined

TABLE II Fracture pressure calculated from Fisher's equation

Liquid	Surface tension (erg cm ⁻¹) ^a	Melting temperature (K)	Fracture pressure, P _f (atm)
Aluminium	850	933	30 500
Mercury	490	300	23 100
Copper	1300	1356	48 000
Iron	1850	1800	70 800
Rhenium	2700	3430	90 500
Water	72	300	1 380

^a1 erg = 10⁻⁷ J.

and it has been recognized that this would require very high pressure. The latter will be of the order of the fracture pressure of the liquid for initiating an infinitely small size of bubble, which for iron is of the order of 70 000 atm [13]. In reality such pressures are not attainable in the melts (Table II). Making a reasonable assumption (described in detail elsewhere) of maximum concentration of solid at a solidification front, Campbell [13] has calculated the maximum equilibrium gas pressure attainable in liquid iron to be of the order of 2000 atm. He has also estimated [18–20] the maximum possible values of the shrinkage pressure in the castings of various metals and has set the arbitrary limit at – 2000 atmospheres. As is obvious from Table II, he has thus concluded that not only in iron castings, but in practically all types of metal casting, neither gas nor shrinkage acting alone or in combination can meet the very stringent conditions defined by Equation 4.

Homogeneous nucleation does not therefore seem to be a feasible mechanism for pore creation. Thus heterogeneous nucleation by gas impurities or external surfaces (mould wall, crevices etc.) or some non-nucleation mechanism operates to create the pores normally observed in thin fed regions of the casting. So in principle, in the absence of suitable nuclei present in the liquid metal no pores will form and the casting will freeze perfectly sound. Similar conclusions have also been drawn by some other investigators [21, 22]. Against these, however, Fredriksson and Svensson [23] have demonstrated that micropores can be homogeneously nucleated in an interdendritic area according to the pressure drop caused by solidification shrinkage. The work of Hirschfeld and Weinberg [24] also provides similar support for the feasibility of homogeneous nucleation of pores.

3.2. Heterogeneous nucleation

Pore nucleation is influenced by some impurities present in the melts and/or by external surfaces such as gas bubble surfaces, inclusions, the mould wall and crevices. In the literature [25–29] from time to time, the presence of certain oxides and various types of inclusion in the melt has been correlated with the nucleation of gas bubbles, although the mechanism by which such particles operate has not been explained. Campbell [13] has predicted that certain solid non-metallic inclusions and complex inclusions containing poorly-wetting solid and liquid phases may act as

potential sites for pore nucleation under extreme conditions of shrinkage and gas cooperation. For heterogeneous nucleation of a bubble at a solid–liquid interface (Fig. 2a), Equation 8 for the fracture pressure for decohesion at the interface is modified as

$$P_f = - \left[\left(\frac{16\pi}{3kT} \right) \frac{\gamma_{LV}\phi}{Ln(6N^{2/3}kT/h)} \right]^{1/2} \quad (14)$$

and

$$\phi = (2 - \cos\theta)(1 + \cos\theta)^2/4$$

where θ is the angle of contact and γ_{LV} is the liquid–vapour surface tension. Using the maximum possible value of the contact angle of 160° for any liquid–solid combination, Campbell [13] found that the value of P_f cannot be reduced by more than a factor of 16 by even the most efficient solid. He thus concluded that although this makes heterogeneous nucleation more favourable than the homogeneous kind in terms of pressure requirement, it does not make the former definitely feasible. A number of authors are of the opinion [9, 13, 30] that the solid–liquid interface of a growing crystal can be also a site for heterogeneous nucleation of pores, but a plane solidification front is not suitable for the same since it is completely wetted by the liquid. However, it is considered [7] that the work of formation of an embryonic bubble is reduced on a concave substrate (Fig. 2b) and becomes zero for perfectly sharp notches (Fig. 2c). Chalmers [9] therefore considers that a cellular–dendritic or dendritic solidification interface is a much more favourable nucleation site, partly because of the presence of grooves such as cell walls (Fig. 3) and partly due to the higher local gas concentration. It is envisaged that the liquid at position A has

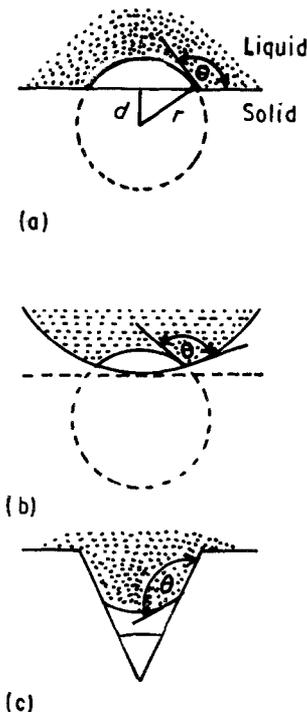


Figure 2 Heterogeneous nucleation of a gas bubble at various interfaces [13]: (a) nucleation on a plane surface, (b) nucleation on a concave substrate, (c) extreme form of (b).

with gas-hole formation. Tiwari and Beech [37] have provided an example of a porous oxide inclusion containing trapped gases in its capillary crevices. Such inclusions were formed as dross during melting and casting, entered the casting during pouring and got uniformly distributed to act as effective nuclei for gas holes. The authors of the present paper [46] have also experimentally demonstrated evidence for suitable nucleating sites of gas-filled crevices for pore nucleation in Al alloy castings. A piece of porous refractory brick was introduced intentionally into the mould cavity before pouring the characteristic alloy. Drastic changes in the occurrence of various shrinkage defects were observed (Fig. 5) and can be explained. The negative pressure generated due to volumetric contraction of the metal is relieved by the presence of gas-filled crevices in the porous refractory brick surface.

In all the above examples of gas-filled crevices, any number of geometries can be envisaged and hence the stringent conditions of classical pore nucleation can easily be avoided in many cases [13]. When a bubble is nucleated and its radius at the entrance to the crevice exceeds the critical size for mechanical stability, then the pore expands unstably and at a critical size detaches itself and floats off, allowing this process to be repeated in the remaining gas in the crevice. Hence, one such nucleus is able to produce many bubbles before it is exhausted.

To summarize, it may be said that although several mechanisms are possible in which a pore may be nucleated, there are greater chances that one of the non-classical or non-nucleation processes may be operating, which provides a means of avoiding the stringent conditions required for classical nucleation. They permit pore formation at internal pressures of only a few atmospheres [10, 38] as opposed to the several hundred atmospheres required by homogeneous or heterogeneous nucleation processes. Pores occur re-

adily in castings, indicating that the barrier for nucleation is easily surmounted. It is also quite likely that under normal casting conditions, more than one of these processes may be operating together at a time. Further, it is apparent from the discussion of the nucleation problem that two criteria for avoiding casting porosity can be postulated. Either the solidifying liquid metal should be free from suitable nuclei or other such sources of nucleation, or the internal pressure in the liquid must be prevented from reaching levels at which existing nucleation gives rise to void formation. However, the first alternative is little more than an academic possibility and therefore the second one should be explored.

4. Growth of pores

The growth of shrinkage pores or gas bubbles has not been analysed as extensively as their nucleation mechanisms. There are a few mathematical treatments of bubble growth [23, 47–54] which assume different models to correlate bubble size or bubble growth rate with the gas concentration, solidification rate and other parameters. However, the qualitative treatments of this problem by Whittenberger and Rhines [3] and later by Chalmers [9] throw a quite sufficient light on the modes of pore growth under different solidification conditions.

4.1. Modes of pore growth

Generally, two modes of growth have been distinguished depending on whether or not liquid feeding occurs between the cavity and the exterior of the casting.

1. Where feeding exists between the cavity and the exterior of the casting, the pore adjusts to the volume of its gas content under the combined pressure of atmosphere, hydrostatic head and surface tension and its rate of growth is controlled by the rate of gas deposition alone.

2. Where feeding from the exterior does not exist, the total volume of the void space that will develop must be exactly equal to the shrinkage of the body of the isolated liquid. This volume will be shared by all the cavities in such a way that the gas pressures are equalized among all cavities that are in hydrostatic communication. Thus the average growth rate is determined by the shrinkage rate, but the growth rate of individual cavities will be modified by any differences that exist in the localized rates of gas rejection.

The growth by gas precipitation is a diffusion process and, as such, its rate must depend either upon the rate of movement of gas atoms through the condensed phases, or on their rates of passage into the vapour phase at the surface of the cavity, whichever may be slower. The growth will proceed at a declining rate until stopped by the local completion of freezing. It will never be stopped by the completion of gas precipitation, since in a diffusion process, infinite time is required to attain complete equilibrium at a fixed temperature. It is thus expected that the pores will be larger, the longer is their period of growth. In other

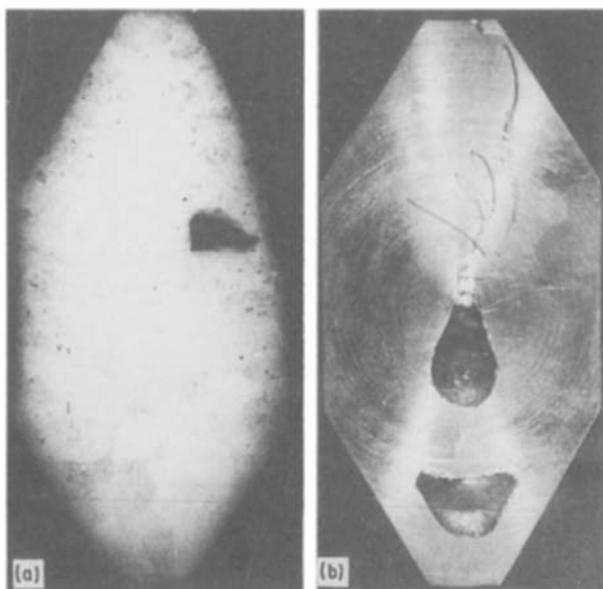


Figure 5 Al-40 wt % Cu alloy casting poured under non-feeding conditions into cast-iron moulds preheated to 500 °C [46]. $\times 0.75$. (a) Etched section showing general surface puncturing; (b) polished section showing elimination of surface sinking as in (a).

words, the total volume of gas porosity should increase as the cooling rate decreases. However, as the gas may be rejected through the external surface of the casting during cooling, this loss with extremely slow cooling may reduce, to some extent, the amount of gas available for bubble growth. Further, the time available for growth will depend on the rate of heat extraction from the casting and also on the temperature interval through which the alloy will cool to complete solidification. Hence, long freezing-range alloys should develop a larger volume of porosity for a given initial gas content than pure metals or short freezing-range alloys.

In the case of shrinkage-controlled cavity growth, the latter will proceed in direct proportion to the quantity of heat extracted from the body of the confined liquid. Where a single nucleation is followed by multiple nucleation, the original single cavity has a growth advantage over the gas cavities that start their growth later. Thus, the single nucleation is expected to result in the formation of one cavity that is much larger than any of its neighbours. However, the relative size of the neighbouring pores will be greater, the earlier their nucleation starts, i.e. the higher is the gas content of the metal. Further, where a melt contains enough gas so that only multiple nucleation occurs, no major cavity (pipe) will form in the body of the isolated liquid. The microporosity in this region will equal the total volume of the shrinkage and the individual pores are likely to be larger in size than those occurring in the regions where feeding was maintained. However, with very high gas content, the order of pore sizes may be reversed. Those which grow in fed regions may attain a size equal to or larger than those in unfed regions, where the ultimate size is limited by the shrinkage.

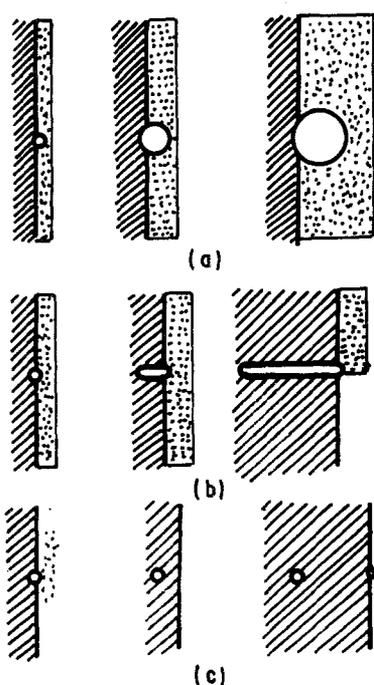


Figure 6 Effect of growth rate on the interaction between a bubble and the solid-liquid interface [9]: (a) slow growth rate (type (ii) behaviour), (b) intermediate growth rate (type (iii) behaviour), (c) fast growth rate (type (iv) behaviour).

It has been described above how an advancing solid-liquid interface may be a favourable site for gas bubble nucleation. Chalmers [9] and others [23, 55] have discussed the growth of such a bubble in relation to the advance of the solidification interface and have explored the possibility of four types of behaviour:

(i) the bubble may grow by diffusion of gas into it from the surrounding liquid to such an extent that it floats away from the interface and escapes from the liquid at the free surface;

(ii) it may move with the interface, growing at the same time to become entrapped in due course;

(iii) it may grow at a speed equal to that of the advancing interface so that it becomes incorporated into the interface to grow as an elongated (cylindrical) blow-hole;

(iv) it may be rapidly overgrown by the interface and become entrapped.

The occurrence of the last three types of behaviour is shown in Fig. 6 and the experimental evidence for the same has also been produced [9, 23, 56].

Besides the relative growth rates of the bubble and the interface, the stage at which the pore is nucleated in a solidifying metal is also quite an important factor in deciding the form and position of the gas holes formed [10]. It is possible that pores arising early in the solidification process will have a high probability of nearly or completely disappearing, so that little or no trace of them can be found in the finished casting. Pores forming at some intermediate stage may be frozen into the casting in a form and position possibly quite different from those in which they originated. For example, pores formed initially as rather rounded bubbles at the base of the casting may be finally discovered as rather flattened shapes with irregular dendritic intrusions under the top surface of the casting. However, when the solidification is more than about 90% complete, pores formed at this stage would be expected to grow and be frozen into the casting in an almost unaltered form.

5. Conclusion

In metal-casting practice, the important factor is to achieve a sound casting and so it is always desirable to control and eliminate shrinkage or gas-hole defects entirely. Pores are generally formed by one of the non-nucleation mechanisms and hence avoid the stringent conditions required for a classical nucleation mechanism. Further, it is experimentally seen and concluded that non-nucleation mechanisms play a major role in the formation of pores in aluminium alloy casting. Single-pore nucleation of a major shrinkage cavity is seen at nil or lowest gas content when it is nucleated on an oxide inclusion (already present in the alloy melt). However, in gas-contaminated melts the major shrinkage cavity slowly vanishes with increase in gas content and is substituted by complete gas-hole porosity dispersed throughout the casting, i.e. multiple nucleation at transition gas content. The alloy freezes in a skin-forming manner or freezes at a higher thermal gradient, frequently showing pore nucleation by a