On the Removal of Pores from Castings by Sintering

ROBERT L. COBLE AND MERTON C. FLEMINGS

The causes, sizes, and distribution of porosity in castings have been reviewed and quantitatively evaluated for several important modes of alloy solidification. In general, gas exsolution is found to be the most probable cause of porosity in castings which solidify in either a cellular or dendritic fashion. On the other hand, solidification alone may cause porosity creation if the interdendritic liquid metal cannot feed the solidification shrinkage. This effect may be enhanced by gas exsolution.

Removal of porosity by "sintering" after solidification requires that the grain size be of the order of, or smaller than, the pore spacing, and that the pores be small ($\sim 1 \mu$) for removal within reasonable times (tens of hours). When gas exsolution is the cause of pore creation, the gas must be diffused out of the sample to permit pore shrinkage. Small ingot sizes ($\sim 10 \text{ cm}$) and rapidly diffusible gases (H₂) are required for pore elimination within reasonable times (tens of hours).

The application of low pressure (~20 atm) during sintering increases the rate, or the size (to ~10 m μ) of the pores which can be eliminated within ~20 hr.

THERE is a considerable body of foundry literature on pore formation during solidification and on foundry techniques for its reduction or elimination.¹⁻⁷ The pores are caused by shrinkage occuring during solidification, by exsolution of dissolved gases, or by a combination of both. Thus, the methods of minimizing the porosity include reducing the content of dissolved gases, assuring an adequate supply of liquid feed metal during solidification, and making solidification more "directional". The importance of achieving low porosity in cast metals is that even in very small amounts it can markedly reduce mechanical properties. In large amounts porosity causes pressure castings to leak, results in a poor surface finish, or causes cracking during use.

In this paper we describe current work on formation of microporosity in solidification of alloys. We show that gas is likely to be a contributing factor, if not the major factor, leading to the microporosity observed in most cases in practice. We summarize our understanding of the morphology of microporosity in typical cases, and of its relation to grain size and grain boundaries. Finally, the kinetics for the removal of microporosity by sintering are considered quantitatively.

PORE FORMATION IN CASTINGS

The origin of microporosity during solidification is generally attributed to gas exsolution and/or the inability of liquid to feed through interdendritic spaces to accommodate the volume contraction accompanying the phase change. Piwonka and Flemings² and Campbell^{3,4} have estimated the pressures for different solidification conditions and the probability of pore nucleation with various necessary assumptions. However, the complexity of the flow field and the necessity for assumptions regarding pore nucleation make precise prediction difficult.

The important variables which may affect pore creation are: gas content, solidification shrinkage, surface tensions, distribution coefficient, alloy content, freezing rate, casting shape, and heat extraction (unidirectional or isotropic). To illustrate the effects of these variables on pore formation, we consider the formation of pores in the three different cases illustrated in Fig. 1. The first is for pore formation in single crystal growth, when growth is cellular; the second for unidirectional dendritic solidification; and the third for solidification of a "mushy" alloy in a relatively in-



Fig. 1—Three modes of solidification: (a) cellular solidification, (b) collumnar dendritic solidification, and (c) "mushy" solidification in a sand cast plate.

ROBERT L. COBLE and MERTON C. FLEMINGS are Professor of Ceramics and Professor of Metallurgy, respectively, Department of Metallurgy and Materials Science, M.I.T., Cambridge, Mass.

This paper is based on an invited talk presented at a symposium on Homogenization of Alloys, sponsored by the IMD Heat Treatment Committee, and held on May 11, 1970, at the spring meeting of The Metallurgical Society of AIME, in Las Vegas, Nev.

sulating mold material (such as sand). It will be seen, on the basis of best available data, that in the first two examples, shrinkage alone is unlikely to cause the porosity observed in practice. In the last case, porosity observed may be caused by shrinkage, gas, or a combination of both. All of these cases have been treated previously;² in the latter two cases, pressure drops have been recalculated using a refined procedure described by Mehrabian, Keane, and Flemings.⁸

In each case, fluid must flow between "cells" or dendrite arms to feed solidification shrinkage. The frictional resistance to this flow lowers the absolute pressure, P_M , at points within the casting. Also, during solidification, dissolved gases may be rejected into the liquid. A void of radius, r, will then form when the equilibrium partial pressure of dissolved gas, P_g , is just equal to the local absolute pressure P_M , plus the pressure change due to the curved pore surface and the influence of surface tension:

$$P_g = P_M + \frac{2\gamma}{r} \tag{1}$$

where γ = vapor-liquid surface energy, and r = pore radius. Eq. [1] assumes no barrier to pore nucleation and that equilibrium is maintained between the gas in solution locally with that in the pores. P_g increases during solidification because the solubility of the gas is lower in the solid than in the liquid. If the equilibria for incorporation of a diatomic gas in the liquid and solid are $Q_l = k_l P_g^{-1/2}$ and $Q_s = k_s P_g^{-1/2}$, and after partial solidification the volume fraction liquid is g_e , the initial quantity of gas (Q_0) will then be distributed in both phases, but in different concentration. Assuming locally complete diffusion of the gas within liquid and solid, but that no gas escapes to the surroundings $Q_0 = Q_s + Q_l$, and the gas pressure as function of g_l is:

$$P_g = \left[\frac{Q_0}{g_l(k_l - k_s) + k_s}\right]$$
[2]

Pore nucleation during solidification can be predicted from Eqs. [1] and [2] provided the local pressure, P_M at the point of interest becomes less than P_g . P_M is the sum of ambient pressure, P_a , metallostatic pressure P_h , and of the pressure drop due to frictional resistance to fluid flow. It is calculated below for the examples of interest.

CELLULAR GROWTH

Consider first the example in Fig. 1(*a*). This is an idealized example of liquid "grooves" which may exist between cells in single crystal growth; the microstructure for an actual casting is shown in Fig. 2.¹ For purposes of calculation, the groove is assumed to be cylindrical, of radius r. Then the pressure drop along the length of groove is that for the pressure drop in laminar flow along a pipe. The absolute pressure at a distance (L) from the entrance is:

$$P_{M,L} = P_a + P_h + \frac{8\mu Lv}{\gamma^2}$$
[3]

where v = metal flow velocity (negative for flow into grooves), $\mu = \text{viscosity of liquid metal}$, L = length of groove, and r = groove radius. Relating the fluid flow

Fig. 2—Decanted solid:liquid interface of an aluminum crystal exhibiting cellular growth, showing pores in cell walls. After electroplating. Magnification 272 times.

velocity (v) to interface velocity V,

$$v = -\frac{\beta}{1-\beta} V$$
 [4]

where β = solidification shrinkage. Note that the interface velocity is defined as being positive for solidification. Combining Eqs. [3] and [4] yields:

$$P_{M,L} = P_a + P_h - \left(\frac{\beta}{1-\beta}\right) \frac{8\mu L V}{r^2}$$
[5]

It has been shown,² upon combining expressions [1], [2], and [5] for assessment of the probability of pore formation in cell boundaries and applying the result to the growth of a single crystal of aluminum, that the solidification rates at which pore formation is observed are 3 to 4 order of magnitude lower than the limiting values calculated from the flow models. This leads to the conclusion that pore formation in unidirectionally solidified single crystals undergoing cellular growth is probably due to gas exsolution.

UNIDIRECTIONAL DENDRITIC SOLIDIFICATION

Fine microporosity can often, if not always, be observed in unidirectionally solidified dendritic alloys. Examples are shown in Figs. 3 and 4 for commercial steel and aluminum alloys. The porosity is generally extremely small in size and is only observed by metallography or microradiography. The contribution of



Fig. 3—Porosity formed during solidification of low alloy steel castings: (a) directionally solidified, (b) equiaxed. Magnification 14 times.

(b)

solidification shrinkage to this porosity is determined by calculating the pressure drop due to interdendritic flow to feed the shrinkage, as for the case in Fig. 1(b). The result obtained by Mehrabian, Keane, and Flemings⁸ includes the more general volume fraction eutectic g_E as a variable, and the minimum pressure, located at the solidus isotherm as:

$$P_{M} = P_{a} + P_{h} + \frac{\beta}{1-\beta} \frac{\mu VL}{\gamma'(1-g_{E})} \ln [g_{E}]$$
 [6]

 γ' is a measure of the resistance of the dendrites to fluid flow.

The pressure can be related to channel radius by assuming a linear variation of the volume fraction liquid (g_l) in the liquid-solid zone (L) and from the geometric requirement that

$$g_l = n\pi r^2$$
 [7]

where n = number of flow channels per unit area, and r = equivalent channel radius.

For calculations, we require a numerical value for the resistance of the 'bed'' to fluid flow, γ' . There is one direct measurement of this resistance,² and an indirect measurement of Mehrabian, Keane, and Flem ings,⁸ which indicate that a reasonable value for γ' is 6×10^{-7} sq cm for Al-4.5 pct Cu with a solidification velocity of 0.02 cm per sec. For this system, $g_E = 0.09$, (and other proper numerical constants) the calculated pressure drop due to fluid flow for a mushy zone length of 5 cm is approx. 0.3×10^{-4} atm, which is a negligibly small pressure drop. Thus, shrinkage is unlikely to be



Fig. 4-Porosity formed in a sand casting of Al 4.5 pct Cu.

METALLURGICAL TRANSACTIONS

a significant factor causing pore formation in unidirectionally solidified aluminum alloys.

To illustrate the effects of gas, we first consider equilibrium of gas with respect to the liquid. Suppose hydrogen is initially present in the liquid alloy at 30 pct of its solubility limit at 1 atm pressure (*i.e.*, Q = 0.21 cu cm stp per 100 g). With a dendrite arm spacing (d) of 100 μ , and 1 channel per dendrite arm: $n \simeq 1/d^2 = 10^4$ per sq cm. Then solving Eqs. [1] and [2] yields a pore size of ~25 μ . The pores begin to form when ~20 pct of the liquid remains. Pores observed are frequently in this size range, and are generally found to begin at some distance from the chill in qualitative accordance with this calculation. Thus, gas exsolution is concluded on these direct grounds, and on the indirect basis above, to be the dominant source of pores in unidirectionally solidified ingots.

SAND CASTINGS

Fig. 1(c) shows an example of pore formation in a sand casting of a "mushy" freezing alloy. Here, temperature differences throughout the casting are small compared with the freezing range of the alloy, and so fraction solid is nearly uniform throughout the casting at any time during solidification. Sand castings of commercial aluminum and magnesium alloys typically freeze in this way and always exhibit microporosity, if sufficiently carefully examined. Fig. 4 is an example.

The pressure within a long casting of uniform cross section (such as a cylinder or bar) with a riser at one end has been calculated previously² and recently recalculated.⁸ The pressure, P, at location, L, from the riser is related to fraction liquid by the expression:

$$P_{M,L} = P_a + P_h - \left(\frac{\beta}{1-\beta}\right) \frac{\mu B^2 L^2}{4\gamma' g_l}$$
[8]

in which the interface velocity from Eq. [4] has been related to the rate of heat transfer:

$$B = \frac{A}{V} \frac{2K(T_M - T_0)}{\rho_m H \sqrt{\pi \alpha}}$$

A = surface area of the casting, V = volume of the casting, K = mold thermal conductivity, T_M = mean solidification temperature of the alloy, T_0 = mold temperature, ρ_m = metal density, \dot{H} = heat of fusion, and α = mold thermal diffusivity.

The example considered was for a plate 2 cm thick and 45 cm long, with n and γ' as in the previous example. Solution of the equations yields a pore size of approximately 25 μ , or about that which would have resulted in the absence of shrinkage from a gas content of 0.21 cu cm stp per 100 g. Thus, it is clear that microporosity can result in sand castings from shrinkage alone. However, the absolute pressures from the shrinkage effect are of the same order as the partial pressures of dissolved gases which therefore approximates the condition for pore formation due to gas exsolution. Thus, either shrinkage, gas exsolution or both, are potential causes of the porosity observed in such castings.

Further qualitative support of the importance of flow resistance through a mushy zone on pore creation may be taken from the influence of varying alloying additions on the residual porosity formed in several systems.¹⁴ The alloy content affects the length (L) of the

mushy zone through its control of the solidification range (ΔT_f) . These are related to the average temperature gradient (G):

$$L = \frac{\Delta T_f}{G}$$
[9]

In eutectic systems, the "equilibrium" solidification range represents the temperature interval between the liquidus and solidus for a composition, it is zero for pure metals, increases as the alloying addition increases, reaches a maximum value at the composition corresponding to the maximum solid solubility of the second component in the primary phase, and then decreases to zero at the eutectic composition. Campbell⁴ has shown that the nonequilibrium solidification range similarly exhibits a maximum as a function of alloying addition. Campbell's experimental investigations of Fe-C and Al-Cu alloys showed cusped maxima in residual porosity with alloying additions. Further support was taken from previously cited literature:" increases in residual porosity at low alloy additions have been reported for various systems, and in others, decreases in residual porosity were observed as the eutectic composition was approached.

Qualitatively, these variations can be considered in relationship to the flow resistance $(\Delta P = P_a + P_h - P_{M,L})$ from Eq. [8] by substituting for L from Eq. [9], and for g_L using Eq. [7]:

$$P \propto \frac{A \Delta T f^2}{n^2 \pi r^4 G^2}$$

where *n* is the channel density and *r* is the effective radius. With the dendrite side-arm spacing proportional to $G^{-1/2}$; we get $r^4 \propto (G^{-1/2})^4$, and obtain therefore:

$$\Delta P \propto A' \Delta T_f^2$$
 [10]

This relation shows that the pressure drops and hence the probability of pore formation is related to the solidification range of the alloy. The changes in porosity with alloying addition cited above are qualitatively in agreement with this model. Thus, pore creation in "mushy" alloys is attributable to the difficulty of feeding liquid to accomodate the solidification shrinkage, although gas exsolution may also be a factor.

PORE STRUCTURE

Figs. 3 and 4 show typical examples of microporosity in unidirectionally solidified casting, and in sand castings. Pore sizes shown are typical and are in the order of 5 to 10 μ for the unidirectional solidified castings and 25 μ for the sand casting. Observed pore sizes range from larger than this for slowly solidified castings with high gas contents, to smaller sizes for rapidly solidified, well-fed castings of low gas content.

The amount of porosity is generally less than 1 pct for well-fed castings, as shown by the data of Fig. 5, for two steel castings. Porosity increases with increasing distance from the casting end, is decreased by vacuum melting, and is less for the unidirectionally solidified casting than for the sand casting.

In many castings, the distance between pores is much less than the grain size; in stainless steels and nongrain refined light alloys, the pore spacing is of the order of the dendrite arm spacing (typically ~ 200 to 500μ) while



Fig. 5—Volume fraction porosity (V) vs distance from ingot base for unidirectional and equiaxed ingots of low alloy steel.

the grain size may be a centimeter or more. In other materials, as in well grain-refined aluminum and magnesium alloys, the grain size is much smaller and the order of the pore spacing. In materials such as plain carbon and low alloy steels that undergo a solid state phase transformation, the final grain size may be much less than pore spacing.

Types of porosity other than the fine microporosity discussed herein are amply described in the literature. These include centerline shrinkage, "piping", in "layer porosity", and others. These types of porosity are, in general, sufficiently coarse so that they cannot be removed in any reasonable time by sintering (without working) and are therefore not considered here.

REMOVAL OF POROSITY BY SINTERING; INFLUENCE OF GAS

There are two observations on the behavior of powder compacts during sintering which are pertinent for considering the possibility of pore elimination from castings:

1) If sintering is conducted in 1 atm of ambient gas pressure, the gas must be either diffusible and/or soluble in the solid to permit the solid to be sintered to theoretical density. In most cases, sintering in a vacuum is an acceptable alternative.⁹

2) The occurrence of discontinuous grain growth during sintering, which normally encloses numerous pores within large grains, is generally responsible for the cessation of shrinkage.^{10,11} At high temperatures, where sintering is normally conducted, these results are interpretable based on the assumption that grain boundaries provide internal defect sources or sinks in polycrystalline solids, which are important for maintaining near-equilibrium concentrations of defects at one of the boundaries of the diffusion field. For rapid diffusive transport of atoms to fill the pores, either for sintering powder compacts or castings, the grain size must be of the order of, or smaller than, the interpore spacing. This restriction may be relaxed under special circumstances: when the pore content and size is small and inhomogeneously distributed. The information required to apply the general diffusion model presented below to a specific case is that discussed in the previous section: amount of porosity, pore size and distribution, and grain size. In most cases, all of this information is not available; when this is the case, one may only estimate the annealing times which will be required. When gas exsolution controls or contributes to pore formation during solidification, the gas must be removed during annealing in an appropriate atmosphere if pore elimination is to be achieved by sintering. For gas removal by diffusion, another important parameter is the minimum dimension of the ingot.

Annealing might also be conducted under an applied mechanical pressure, which provides a contribution additional to the surface energy as the driving force for pore elimination. The diffusion model developed below includes both driving forces, from which the pressure which will significantly decrease the required annealing times can be calculated for specific, observed, pore sizes. When a gas is present, it should be noted than an applied mechanical pressure may only reduce the equilibrium pore size, without permitting complete elimination of porosity, unless 1) the gas is permitted to diffuse out of the sample or 2) the pressure is raised to a level allowing incorporation of the gas into solution.⁶ Sound castings produced in this manner however, may "blister" upon exposure to high temperature at ambient pressure.

The total quantity of gas in the sample (Q_T) is distributed in solution $k_s P_g^{1/2}$ and in the pores (nP_gV/RT) . If the quantity in solution is in equilibrium with the pressure inside the pores the pressure is $P_g = P_a + 2\gamma/r_e$ and the total quantity in the sample is $k_s P_g^{1/2} + nP_gV/RT$, or by expanding the pressure terms:

$$Q_T = k_s \left(P_a + \frac{2\gamma}{r_e} \right)^{1/2} + \frac{n}{RT} \frac{4}{3} \pi r_e^3 \left(P_a + \frac{2\gamma}{r_e} \right) \quad [11]$$

where r_e is the equilibrium pore size, and n is the number of pores per cu cm solid. If the quantity in the sample is in equilibrium with P_a , the solution to Eq. [11] would give negative values for r_e , which means that the gas could simply enter solution as the pores shrink to zero size.¹² A (meta) stable equilibrium pore content only exists when $Q_T > k_s P_a$. However, we take as a criterion for sinterability that $Q_{T_0} < k_s P_a$ in order to facilitate pore removal and to avoid pore formation upon cooling from the sintering temperature.

Let us now examine the times which would be required for gas elimination from castings for typical gas diffusivities and ingot sizes.

Analytic expressions for diffusive homogenization for various initial and boundary conditions show that equilibrium is approached when $D_t/l^2 \simeq 2.0$. Accepting this for gas elimination to permit pore removal the time required is dependent upon the gas diffusivity D and the half-thickness (l) of the casting. Essentially, only those gases which diffuse interstitially will be removed within sufficiently short times to be of interest for this assessment. Thus, hydrogen diffusion in iron, with a value for D of 10^{-3} sq cm per sec at 1450° C is of interest for cases when excess hydrogen is present in steel castings.¹³ Similarly, the diffusion of carbon and oxygen would be of interest for semikilled steels. The available data for carbon gives a diffusivity in the range

METALLURGICAL TRANSACTIONS

Table I. Times Required for Reduction in Gas Concentration to 1 Pct of the Initial Value for Ingots of Selected Sizes

	Half Thickness	
	1 cm	10 cm
$D_H = 10^{-3} \text{ cm}^2/\text{sec}$	~30 min	~2.5 days
$D_c = 10^{-5} \text{ cm}^2/\text{sec}$	2.5 days	8 months

of 10⁻⁵ sq cm per sec at 1450°C.¹⁴ Because of the lack of availability of oxygen diffusion data, we may assume that carbon monoxide decomposes on entering solution and that the net transport is governed by the diffusivity of carbon. It is recognized that if the diffusivity of oxygen is lower than carbon, longer times will be required for homogenization. The time intervals required for annealing ingots of different sizes are shown in Table I. It is seen that for anything over modest-sized specimens, the required annealing times are extensive, being longer than the times utilized for solution annealing. However, the extended anneals required for hydrogen elimination to avoid the embrittlement of large forgings are already appreciated. The general result is that when gases are present initially, the extended times required for gas elimination to permit pore removal would probably preclude annealing as a mechanism of casting homogenization for anything other than small sized castings.

Although the necessity of gas entering solution or being eliminated by diffusion to the surface of the sample is a necessary criterion for densification by diffusion, it is not a sufficient one. We also require an atom source for diffusion to fill the space occupied initially by the pore. This is provided by the grain boundaries where the defects may equilibrate.^{10,11} It should be noted that *only* the grain boundaries are effective; cell walls, the boundaries formed around inclusions totally within crystals, and the boundaries between dendrites belonging to a grain are inadequate for the purpose. Our second general requirement is that the grain size should not be larger than the interpore spacing.

THE SINTERING MODEL

The basic information needed for formulating a diffusion sintering model is the pore shape and the locations of grain boundaries. The concentrations of defects at the pore surface and on the grain boundaries are then related to the pore surface curvature and the applied pressure, respectively, using the Gibbs-Thompson equation (for low stresses):

$$C_d = C_0 + \frac{C_0 \sigma \Omega}{kT}$$
[12]

where C_d is the local concentration of defects in equilibrium with the local normal stress on the surface (σ) , C_0 is the equilibrium concentration when $\sigma = 0$, Ω is the volume contributed to the crystal lattice per defect, k is Boltzman's constant, and T is temperature. This expression is valid only at small stresses, with C_d $- C_0/C_0 \ll 1$. For the curved (spherical) pore surface the normal stress is: $2\gamma/r$ where γ is the surface energy and r is the radius. With these equilibrium values for the defect concentrations on the respective surfaces, steady-state diffusive transport will take

r	1 μm	10 µm	100 µm
G.S.	$10\mu m$	100 µm	1000 µm
Time for p	ressure free sintering – Eq.	[16]	
Δt	10^3 sec	\sim 15 days	~30 years
Pressure sin	tering - Eq. [19]; time for	size reduction to $1 \mu m$ w	ith σ = 300 psi
Δt_1		∼14 hr	\sim 2 months

place between them which can be evaluated for a solution to $D\nabla^2 C = 0$, and which also satisfies the geometric boundary conditions. It has been shown for the intermediate stage of sintering that steady-state flow equations for different geometric relations between the pores and grain boundaries give nearly identical total flows of material.^{11,15} From familiarity with those solutions, the flow equation adopted here for modeling the typical pore structures in castings is that for flow between concentric spherical shells, radii, r_1 and r_2 , with defect concentrations C_1 and C_2 :

$$\frac{dV}{dt} = J\Omega = \frac{4\pi D_v \Delta C r_1 r_2}{r_2 - r_1} \Omega$$
[13]

where J is the total flow, and D_v is the defect diffusion coefficient. For the pressure-free case, the concentration difference arises totally from the pore surface curvature; assuming spherical pores of radius r_1 :

$$\Delta C = \frac{C_0 \Omega}{kT} \left(\frac{2\gamma}{r_1} \right)$$
[14]

In this case the volumetric flow into the pore may be expressed as $4\pi r_1^2 dr_1/dt$, which is substituted for dV/dt. With the lattice diffusion coefficient (D_L) defined by: $D_L = D_v C_0 \Omega$, we obtain, following substitution into Eq. [13]:

$$r_{1}^{2} \frac{dr_{1}}{dt} = \frac{2D_{L}\gamma\Omega}{kT} \frac{1}{r_{1}} \left(\frac{r_{1}r_{2}}{r_{2}-r_{1}}\right)$$
[15]

When the grain size is approximately equal to the interpore spacing, and the porosity is small, $(r_2 > r_1 \text{ when}$ the porosity is less than 1 pct), then $r_2 - r_1 \simeq r_2$ and all r's on the right hand side may be cancelled. Then, upon integration between limits $r_0 \rightarrow 0$ the time interval needed (Δt) for pore removal is:

$$\Delta t = \frac{r_0^3 k T}{(6D_L \chi \Omega)}$$
[16]

For close-packed metals annealed just below their melting points: $D_L \simeq 10^{-8}$ sq cm per sec, $\Omega \simeq 10^{-23}$ cu cm, $\gamma \simeq 10^3$ erg per sq cm, and $kT \simeq 10^{-13}$ erg per atom, Eq. [16] yields:

 $\Delta t = r_0^3 \ 10^{15} (\text{sec}/\text{cm}^3)$

The time intervals required for elimination of pores covering the range of sizes observed are given in Table II. The grain sizes necessary for conformance to the model are also given.

ANNEALING UNDER PRESSURE

If annealing is to be conducted under an applied pressure (σ) , the sintering model may be modified by eval-

uating the defect concentration difference between the pores and grain boundaries in relationship to the pore curvature and applied pressure independently, using Eq. [12]. The net concentration difference obtained in this case is:¹⁶

$$\Delta C = \frac{C_0 \Omega}{kT} \left(\frac{2\gamma}{r_1} + \frac{\sigma}{\rho} \right)$$
 [17]

where ρ is the relative density. For castings with 1 pct porosity, the maximum variation in ρ is $0.99 \rightarrow 1.0$; hence, this term may be neglected. Substitution of Eq. [17] into [13], and proceeding as above yields:

$$r_1 \frac{dr_1}{dt} = \frac{D_L \Omega}{kT} \left(\frac{2\gamma}{r_1} + \sigma \right)$$
 [18]

When the pores are large, $\sigma \gg 2\gamma/r_1$, we obtain:

$$\Delta t_1 = -\left[\frac{kT}{2D_L\Omega\sigma}r^2\right]_{r_0}^{2\gamma/\sigma}$$
[19]

Selecting $\sigma = 2\gamma/(r = 1 \ \mu m)$, the time interval may be calculated which is required to reduce larger initial sizes to 1 μ m, in which range Eq. [18], and subsequently Eq. [16], becomes pertinent. For the initial pore sizes for which the time intervals for removal by sintering were evaluated in Table II, the time intervals for size reduction 1 μ m, under a pressure of 300 psi are also given. These intervals were evaluated in Eq. [16] for pressure free sintering. The reduction in time with modest applied pressure is significant; it is noteworthy that the intervals now used for "solution annealing" copper alloys are in the range of 15 hr, which is that found here for pressure sintering 20 μ m (diam) pores with 20 atm applied pressure. Thus with modest pressure, the porosity present in some castings might be eliminated during a solution anneal.

CONCLUDING REMARKS

In the first section of this paper, the causes of the porosity formed in several modes of solidification, the sizes of pores formed, and the locations of pores with respect to grain boundaries, have been reviewed. In the second section, the criteria for pore elimination from castings by annealing are stated and then developed quantitatively. It has been tacitly assumed that annealing will be conducted at high temperatures to hasten pore removal. Therefore, lattice diffusion has been considered as the mechanism of material transport. Analogous models have already been developed for lower temperature annealing, at which grain boundary diffusion may be predominant. Large pores require extended time intervals for removal; hence, pipes, layer porosity, and pores due to center-line shrinkage, would require unreasonably long times for elimination by sintering.

Pores formed during cellular solidification and unidirectional dendritic growth probably result from gas exsolution during solidification. For these cases, sintering (for porosity elimination after solidification) requires gas elimination; the times required are unreasonably long except for small castings (<10 cm) and rapidly diffusible gases (H₂).

In the solidification of mushy alloys, the porosity may result from (solidification) shrinkage alone, without being influenced by gas exsolution. In those instances, the sintering times required for pore elimination depend on the solid diffusivity, the pore size, and pore spacing relative to the grain size in the ingot. Time intervals of the order of 10 to 20 hr were found to be adequate for some specific, observed structures.

The application of pressure reduces significantly the required time intervals for pore elimination when no gas is trapped, and makes feasible the elimination of larger pores than in the pressure-free case. When gas is present, the application of pressure reduces the residual porosity.

REFERENCES

- 1. P. E. Doherty: Ph.D. Thesis, Harvard University, May, 1961.
- T. S. Piwonka and M. C. Flemings: Trans. TMS-AIME, 1968, vol. 242, pp. 50-55.
- 3. J. Campbell: Trans. AIME, 1968, vol. 242, pp. 264, 268.
- 4. J. Campbell: Trans. TMS-AIME, 1967, vol. 245, p. 2325.
- A. Tsavaros and M. C. Flemings: *Trans. TMS-AIME*, 1965, vol. 233, pp. 355-59.
- 6. J. Campbell: Trans. TMS-AIME, 1968, vol. 242, p. 1464.
- 7a. E. J. Wittenberger and R. N. Rhines: AIME Trans., 1952, vol. 194, pp. 409-20.
- b. J. Czikel: Freiberger Forschungsh., 1960, vol. B45, pp. 7-20; Brit. Steel Castings Res. Ass'n, Trans., no. 202/CMH, 1961.
- c. R. A. Flinn and H. G. Kunsmann: Trans. Am. Foundry Soc., 1961, vol. 69, pp. 208-20; 1961, vol. 70, pp. 1295-1309.
- d. R. Jan and A. Cibula: Foundry Trade J., 1956, vol. 101, p. 131.
- R. Mehrabian, M. Keane, and M. C. Flemings: *Met. Trans.*, 1970, vol. 1, pp. 1209-20.
- 9. R. L. Coble: Ceram. Soc., 1962, vol. 45, pp. 123-27.
- J. E. Burke: Grain Growth in Ceramics, in *Kinetics of High Temp. Proc's*, Ch. 16, W. D. Kingery, Tech Press and John Wiley & Sons, New York, 1959.
- 11. R. L. Coble: J. Appl. Phys., 1961, vol. 32, pp. 787, 793.
- 12. R. L. Coble: Phys. Sintering, Boris Kidric Inst., Belgrade, 1967, vol. 1, no. 6.
- L. Darken and R. W. Gurry: *Physical Chemistry of Metals*, McGraw Hill Book Co., New York, 1953.
- 14. P. Shewmon: Diffusion in Solids, McGraw-Hill Book Co., New York, 1963.
- R. L. Coble and T. K. Gupta: in *Sintering and Related Phenomena*, p. 423, Gordon and Breach, New York, 1967.
- 16. R. L. Coble: J. Appl. Phys., vol. 41, pp. 4798-4807, 1970.