

Introduction.

There has been extensive commercial interest and considerable activity in recent years on removing undesirable impurities from liquid aluminium. For this reason a review of important engineering principles is given.

The impurities of interest are dissolved hydrogen, dissolved magnesium, sodium and lithium and other alkaline earth elements, and non-metallic inclusions. Nitrogen and argon are commonly used purge gases. Chlorine and chlorine- (or fluorine-) containing freons are also used alone or together with inert gas in a variety of industrial processes. Powdered salts may be injected with the purge gas; and salts are also added to the surface of the melt. It is possible to use vacuum treatment in combination with the others listed above. A variety of filtering schemes are in use to remove inclusions. Also impurities may be separated out by electrolysis (Hoopes cell); by partial solidification and washing away of interdendritic liquid. Finally intermetallics such as Al-Fe, Ni, Ti, B may be separated out.

Removal of hydrogen from the melt as a two-atomic gas has been treated in detail in a separate paper (1). The chemistry involved in the use of reactive gases, such as chlorine, fluorine or oxygen containing gases is studied in a second paper (2).

Here we consider kinetic and chemical factors which describe the removal of dissolved impurities in molten aluminium using purge gas, vacuum treatment and reactive gases. The model employs the engineering concepts of mass transfer coefficient, k , interfacial contact area A , total pressure, P , and vapor pressure, p_c (1, 3). The treatment is similar to that applied for the removal of hydrogen (1). To some extent the hydrogen model has been verified by comparison with experimental results.

Various models of gas purging and vacuum treatment have been presented previously in the literature (4). This work mainly differs from these previous studies in that combined gas purging and vacuum systems are described in terms of rather simple, analytical solutions.

Model of bubbles, assumptions, equations.

The pressure and mass balance equations for the bubbles are derived. In the following section they are solved to relate the pressure of the dissolved element, C , or of the reactive gas in the exiting bubbles, p_c or p_r , with bath concentration, $[\% C]$.

The impurity, C , is transferred out of the melt by a series of steps which, for the sake of the discussion, are outlined below. We consider

- (1) Transport in the melt to the vicinity of an inertgas bubble by a combination of convection and diffusion.
- (2) Diffusive transport through a thin stagnant layer of fluid called a boundary layer, surrounding the bubble.
- (3) The chemical adsorption onto and subsequent desorption from the bubble surface, and
- (4) Diffusion as a gaseous species inside the bubble of purge gas.

MOLTEN ALUMINIUM PURIFICATION

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Summary.

Engineering principles important for the purification of liquid aluminium have been reviewed. Kinetic and chemical factors are given which describe the removal of dissolved impurities using purge gas, vacuum, or reactive gases. The model employs the engineering concepts of mass transfer coefficient, interfacial contact area, total pressure and vapor pressure. It is shown that - except for hydrogen - gas purging and vacuum treatment are rate limited by the equilibrium (the vapor pressure of the dissolved species). With reactive gases removal is limited by liquid-film mass transfer. A relation is given for the maximum concentration of reactive component in the purge gases that can be absorbed and utilised.

In addition to these steps, we may also consider

- (5) Removal at the melt surface or at the refractory walls.

The first step will occur quickly in a well-stirred system, which any effectively designed process should be. The third step represents the chemical reaction. This is assumed to proceed quickly, so the equilibrium constant may be used to give the ratio between p_c and $[\% C]$ at the bubble surface. This assumption seems to be valid for hydrogen (1), so it is probably valid for monatomic species. (The chemical reaction is simpler in this case, and should proceed more rapidly). Gas diffusion, step 4, is much more rapid than diffusion in the liquid metal (1), so the second step is seen to be the slowest, or rate-limiting. Moreover, we shall assume that removal at the walls is unimportant.

The following assumptions are made in the model equations and in the solution.

- (A) The metal bath is well stirred, and the resulting mixing of metal causes the concentration in the melt to be essentially uniform.
- (B) The gas bubble surface area is a function only of height in the bath and not of the horizontal position. This is tantamount to assuming that all bubbles irrespective of location in horizontal direction have the same behaviour as they rise up.
- (C) Bubbles are spherical.
- (D) Coalescence of bubbles is neglected.
- (E) Impurity element gas or reactive gas pressure is much less than inert gas pressure.

Thermal expansion of the gas due to the high bath temperatures can be taken into account by treating three extreme cases:

- a) The gas is preheated to bath temperature before and during formation of the bubble.
- b) Bubbles are heated up immediately after formation.
- c) Bubbles remain "cold".

The error involved in assumption C) is probably small, since changes in mass transfer coefficient k , contact area A and bubble velocity U can be related to bubble volume, V . Therefore in this paper an equivalent diameter d given by $V = \pi d^3/6$ is used.

Neglecting viscous forces, the total pressure in the bubble is:

$$p_{tot} = p_s + \rho g (h_s - h) + 4 \sigma / d \quad (1)$$

The first term on the right hand side is the pressure of the evacuated system; the second is the ferrostatic head of aluminum; the third is the pressure caused by surface tension forces. For a bubble one centimeter in diameter, $4 \sigma / d$ is equal to about 0.017 atmospheres. The ρg term is 0.227 atm/m at 1000°K, so the surfaces tension forces can be seen to be negligible at depths below the surface more than a few centimeters.

It therefore is important mainly in placing a lower limit on bubble pressure near the surface. Szekely (4, 5) has considered viscous forces in some detail. His results show that they are important in the top two or three centimeters of the bath when the total surface pressure is less than about 0.01 atmospheres. Also, bubbles are not points, but occupy some finite volume. When the top surface of the bubble first breaks through the surface, part of the bubble is still below the surface, and at higher pressure. This would account for the commonly observed violent "explosion" of bubbles. The surface and viscous terms are combined to "an effective pressure p_{tot}^* at the surface" so that

$$p_{tot} = p_{tot}^* + \rho g (h_s - h) \quad (2)$$

where $p_{tot}^* = p_s + 4 \sigma / d +$ pressure due to viscous forces. p_{tot}^* should be of the order of magnitude 0.01 atm in evacuated systems.

p_{tot} is also equal to the sum of the partial pressures:

$$p_{tot} = p_c + p_{inert} \quad (3)$$

or for a reactive gas where the reaction product is molten or solid:

$$p_{tot} = p_r + p_{inert} \quad (3a)$$

Coalescence (collision) of bubbles rising up through the bath is not included in the mathematical treatment. This may give a serious error when removal is mass transfer limited. The assumption (E) that the amounts of impurity gas removed or of reactive gas employed are small compared to the inert gas used, seems to be fulfilled in practice.

The mass transfer coefficient for "large bubbles" is a function of bubble size, d , and bubble velocity U (1, 7):

$$k = 2 \sqrt{\frac{D U}{\pi d}} \quad (4)$$

For bubble velocity the following relation valid for "large bubbles" is employed:

$$U = \sqrt{\frac{g d}{2}} \quad (5)$$

Inserted in eq. (4) this gives

$$k = 2 \sqrt{\frac{D}{\pi}} \cdot \left(\frac{g}{2 d}\right)^{1/4} \quad (6)$$

Equations (4) - (6) are used in this model even though they are only rough approximations for bubbles that are not "large".

We now consider the ascent of gas bubbles through a small control volume of thickness Δh in our reactor. (See Figure 1). A mass balance for C gives:

C that leaves the bath control volume = Increase of C in the bubbles during their travel through this control volume

or

$$\frac{k_c \rho \Delta A}{100} ([\% C] - [\% C]_e) = \dot{G} \left(\frac{p_c}{p_{inert}} \right) m_c \quad (7)$$

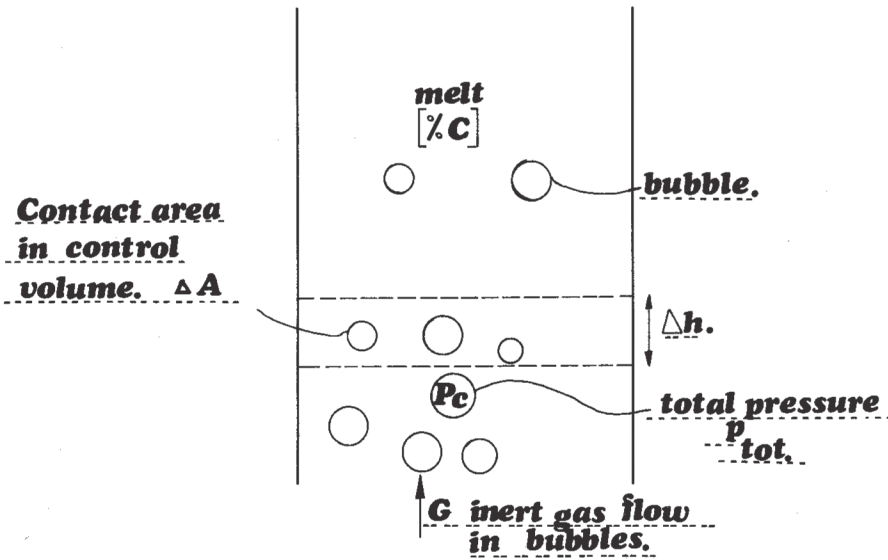


Fig. 1 - Control volume of a gas purging reactor.

An empirically determined mass transfer coefficient, k , and the surface area of bubbles in our control volume, ΔA , are the only unknown variables. ρ is the density of liquid aluminium; G is the molar flow rate of inert gas in the bubbles; m_C is the molecular weight of C; P_{tot} is the total pressure in the bubble, P_C is the partial pressure of C, and p_{inert} is the pressure of inert gas. The equilibrium concentration of C in the metal at the bubble surface, $[\% C]_e$, is given by the relation:

$$[\% C]_e = \frac{P_C \cdot K_C}{f_C} \quad (8)$$

so eq. (7) may be rewritten

$$\frac{k_C \rho \Delta A}{100 m_C G} \left([\% C] - \frac{P_C K_C}{f_C} \right) = \Delta \left(\frac{P_C}{P_{inert}} \right) \quad (9)$$

or

$$\frac{k_C \rho [\% C] \cdot \Delta A}{100 m_C \cdot G} \left(1 - \frac{P_C K_C}{f_C [\% C]} \right) = \Delta \left(\frac{P_C}{P_{inert}} \right) \quad (10)$$

For practical reasons a vapor pressure \hat{p}_C at one percent standard solution, $f_C = 1$ has been introduced in the following, $\hat{p}_C = \frac{1}{K_C}$.

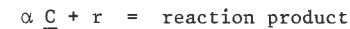
If a reactive gas is utilized, the mass balance eq (7) must be changed. The right side is then given in terms of the reactive gas component. Thus we write instead of eq (7):

C that leaves the bath control volume = Decrease of r in the bubbles during their travel through this volume

or

$$\frac{k_C \rho \Delta A}{100 \cdot m_C} ([\% C] - [\% C]_e) = - \alpha G \Delta \left(\frac{p_r}{P_{inert}} \right) \quad (7a)$$

α is a stoichiometric coefficient given by the total reaction between the dissolved component, C, and the reactive gas, r:



The reaction product is usually a molten or solid separate phase. This is the case studied here. Details are given in (2). In the present work it is assumed that $[\% C]_e$ is so small with a reactive gas that

$$[\% C]_e = 0 \quad (8a)$$

Eq (10) is then replaced by

$$\frac{k_C \rho [\% C] \Delta A}{100 \cdot m_C \cdot \alpha \cdot G} = - \Delta \left(\frac{p_r}{P_{inert}} \right) \quad (10a)$$

Solution of equations for bubbles.

The mathematical treatment is simplified by considering dimensionless pressures:

$$\eta = P_{tot} / P_{tot}^{\circ} \quad (11)$$

$$Y = P_C / P_{tot}^{\circ} \quad (12)$$

or for a reactive gas

$$Y_r = P_r / P_{tot}^{\circ} \quad (12a)$$

where P_{tot}° is the total pressure at the bottom of the melt, or at the height that bubbles are introduced to the melt.

It will be found practical to relate all quantities to the inlet conditions for the gas.

Differentiation of eqs (2) and (11) gives:

$$d\eta = -\rho g dh/p_{tot}^o \quad (13)$$

The number of moles of gas in a bubble increase during rise by the factor $\eta/(\eta-Y)$. Therefore according to the ideal gas law the volume at any height in the bath, V , is related to the original bubble volume, V_o , (at $h = 0$), by the equation

$$\frac{V}{V_o} = \frac{d^3}{d_o^3} = \frac{p_{tot}^o}{p_{tot}} \frac{\eta}{(\eta-Y)} = \frac{1}{\eta-Y} \quad (14)$$

When a reactive gas is employed the moles of gas in a bubble decrease during ascent by the factor $\eta(1-Y_r^o)/(\eta-Y_r)$ where Y_r^o is the ratio between the pressure of reactive gas, p_r^o , and the total pressure p_{tot}^o at the inlet, $Y_r = p_r/p_{tot}$. Eq (14) is then replaced by

$$\frac{V}{V_o} = \frac{1 - Y_r^o}{\eta - Y_r} \quad (14a)$$

The number of bubbles found per unit height of reactor N is

$$N = \frac{\dot{N}}{U} = \frac{\dot{N}}{U_o} \sqrt{\frac{d_o}{d}} \quad (15)$$

where \dot{N} is the number of bubbles that enter the bath per unit time.

$$U_o = \sqrt{\frac{g d_o}{2}}$$

The contact area ΔA in eq (9) is given by

$$\Delta A = \pi d^2 \cdot N \cdot \Delta h \cdot e \quad (16)$$

where e is a factor that takes the deviation from spherical form into account. Strictly it depends on bubble size d .

Equation (15) inserted into eq (16) gives

$$\Delta A = \frac{\pi \dot{N} \cdot d_o^2 \cdot e}{U_o} \cdot \left(\frac{d}{d_o}\right)^{3/2} \cdot \Delta h \quad (17)$$

Finally insertion of eqs (3), (6), (11), (12), (13), (14) and (17) into eq (10) presents the following equation

$$\frac{k_o \cdot \rho [\% C] \pi \cdot \dot{N} \cdot d_o^2 \cdot e \cdot p_{tot}^o}{100 \cdot m_C \cdot G \cdot U_o (\eta-Y)^{5/12} \cdot \rho \cdot g} \left(1 - \frac{K_C p_{tot}^o \cdot Y}{f_C [\% C]}\right) = -d \frac{dY}{\eta-Y} \quad (18)$$

This equation is simplified if the following dimensionless groups are introduced:

"Inverse dimensionless equilibrium pressure of the dissolved component"

$$b = \frac{K_C p_{tot}^o}{f_C [\% C]} = \frac{p_{tot}^o}{\tilde{p}_C f_C [\% C]} \quad (19)$$

"Capacity of the melt for mass transfer divided by the mass flow of gas"

$$a = \frac{k_o \cdot \rho [\% C] \pi \cdot \dot{N} \cdot d_o^2 \cdot e \cdot p_{tot}^o}{100 \cdot m_C \cdot G \cdot U_o \cdot \rho \cdot g} \quad (20)$$

k_o is obtained by inserting d_o for d in eq (5). The following equation is found:

$$a \cdot (\eta-Y)^{-5/12} (1-bY) d\eta = -d \frac{dY}{\eta-Y} \quad (21)$$

For the reactive gas eq (21) becomes

$$a_r (\eta-Y_r)^{-5/12} d\eta = +d \frac{dY_r}{\eta-Y_r} \quad (21a)$$

where

$$a_r = \frac{a}{\alpha} (1-Y_r^o)^{5/12} \quad (20a)$$

This means that in the following the case where reactive gas is used may be derived from the differential equations for removal of C in the gaseous form by setting $b = 0$ and replacing a by $-a_r$.

Differentiation of the right hand side of eq (21), gives

$$\frac{dY}{d\eta} = \frac{Y}{\eta} - \frac{a (\eta-Y)^{19/12}}{\eta} (1-bY) \quad (22)$$

In order to set up a mass balance for the refining reactor the exit concentration of the bubbles, p_c , must be known.

$$\frac{p_c}{p_{inert}} = \frac{Y}{\eta-Y} = \frac{v}{1-v}$$

When $v = Y/\eta$ is introduced in eq (22), one obtains:

$$\eta \frac{dv}{d\eta} = -a \eta^{7/12} (1-v)^{19/12} (1-bv\eta) \quad (23)$$

Finally the independent variable $x = \eta^{7/12}$ and the dependent variable $Z = 1/(1-v)^{7/12}$ are introduced so that eq (23) transforms to

$$\frac{dZ}{dx} = -a (1-b (1-Z^{-12/7}) x^{12/7}) \quad (24)$$

At $x = 1, Z = 1$. One wishes to determine p_c and v when the gas leaves the melt. For vacuum systems exit of the gas is at x (or η) ≈ 0 .

It is seen that Z is a function of a and of ab :

$$\frac{k_o \pi \cdot N \cdot d_o^2 \cdot e \cdot p_{tot}^o}{100 \cdot m_c \cdot G \cdot U_o \cdot g \cdot f_c \cdot p_c} = N \quad (25)$$

This quantity may be termed the "Capacity of the melt for mass transfer divided by the capacity of the gas for removal". It is seen that ab , in the following called N , is proportional to the square of the total pressure, and inversely proportional to the vapor pressure, p_c^o .

If the partial pressure of the component removed is much less than the pressure of the inert gas so that $\frac{p_c}{p_{inert}} = \frac{v}{1-v} < 0.25$, it is possible to find an approximate analytical solution to eq (24). For $v < 0.2$ a Taylor expansion then gives that

$$1 - Z^{-12/7} \approx \frac{12}{7} (Z-1)$$

This inserted in eq (24) results in:

$$\frac{dZ}{dx} = -a + \frac{12}{7} N (Z-1) x^{12/7} \quad (26)$$

The integral of this equation is

$$Z - 1 = a \cdot e^{19} \int_x^{19/7} \frac{12 N \cdot x^{19/7}}{e^{19}} - \frac{12 N s^{19/7}}{19} ds$$

or

$$\frac{1}{(1-v)^{7/12}} = 1 + a \cdot e^{19} \int_x^{19/7} \frac{12 N x^{19/7}}{e^{19}} - \frac{12 N s^{19/7}}{19} ds$$

and employing a Taylor expansion for the left-hand side:

$$v \approx \frac{12}{7} \frac{N x^{19/7}}{e^{19}} \int_x^{19/7} \frac{12 N s^{19/7}}{e^{19}} - \frac{12 N s^{19/7}}{19} ds \quad (27)$$

For the mass transfer limited case when $N < 1$ eq (27) may be approximated by

$$v \approx \frac{12}{7} a e^{19} \left(x^{19/7} - \frac{(1+x)^{19/7}}{2} \right) (1-x) \quad (28)$$

where $x = \eta^{7/12}$

For the case with reactive gas eq (28) becomes at the exit:

$$v_r^s = Y_r^o - \frac{12}{7} a_r (1-\eta_s^{7/12}) \quad (28a)$$

The factor $\frac{12}{7}$ takes into account the change of contact area and mass transfer coefficient due to the expansion of the bubbles caused by the decrease in pressure during ascent.

For the equilibrium limited case when $N x_s^{19/7} > 1$ eq (27) may be approximated by the first terms in an asymptotic expansion

$$v \approx \frac{a}{N x^{12/7}} (1 - e^{-\frac{12 N (1-x)^{19/7}}{19}})$$

or at the exit, inserting $N = ab$ and $x = \eta_s^{7/12}$.

$$v_s \approx \frac{1}{b \eta_s} (1 - e^{-\frac{12 N (1-\eta_s^{19/12})}{19}}) \quad (29)$$

Here $\frac{1}{b \eta_s}$ is the value given by the equilibrium.

$$- \frac{12 N (1-\eta_s^{19/12})}{19}$$

The factor $(1 - e^{-\frac{12 N (1-\eta_s^{19/12})}{19}})$ takes the deviation from equilibrium into account.

Model of refining reactor.

In a reactor in addition to the refining effect of the bubbles removal also takes place at the top surface of the melt. This surface is partly in contact with atmosphere, partly covered by oxides or salts. This combination of purification mechanisms is illustrated in Fig. 2. A mass transfer coefficient k_s and contact area A_s has been introduced to describe the properties of this top surface. A_s is the geometric contact area, while relations for k_s are given in (1).

The total removal is then:

$$\frac{G \cdot p_c}{p_{inert}} m_c + k_s \cdot A_s \cdot \rho [\% C] / 100$$

For the case with reactive gas one obtains, similarly:

$$\frac{G \alpha (p_r^o - p_r^s) m_c}{p_{inert}} + k_s \cdot A_s \cdot \rho [\% C] / 100$$

In this paper we assume that reactive gas consumption is set so low that it reacts quantitatively (stoichiometrically). The case where no reactive gas is employed is more complex and is treated in the following. It may be mentioned that removal by reactive gas (with no gaseous reaction product) and by inert gas purging is additive.

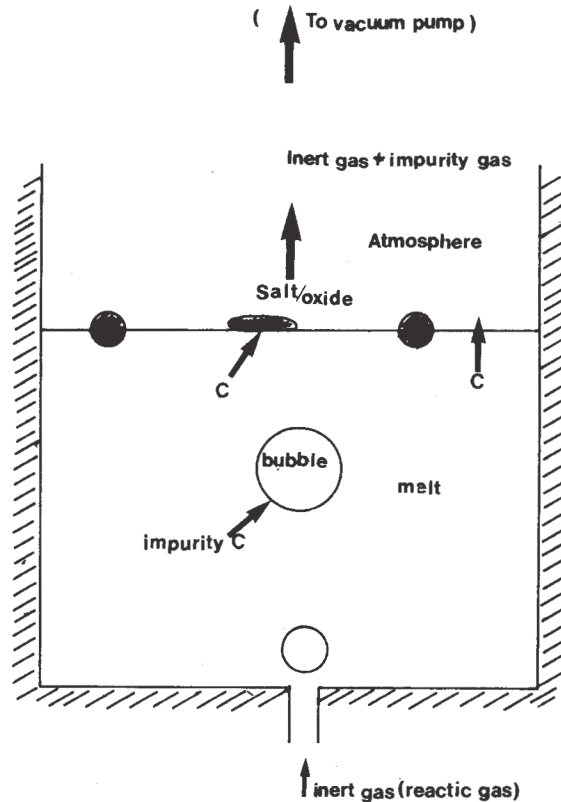


Fig. 2 - Illustration of various paths for removal of impurity component C.

$$\frac{p_C}{p_{inert}} = \frac{v}{1-v} \approx v \text{ for } v \ll 1. \text{ It is seen from equations (20) and (23) that } v \text{ for the exiting bubbles, } v_s, \text{ is proportional to } [\% C]. \quad (30)$$

Thus for the mass transfer control case eqs (28) and (20) give that

$$v_s = [\% C] B_m \quad (31)$$

where

$$B_m = \frac{k_o \pi N d_o^2 e p_{tot} o 12 e^{-\frac{12}{19} N (x_s^{19/7} - (\frac{1+x_s}{2})^{19/7})}}{100 m_C G U_o g 7} (1-x_s) \quad (32)$$

For equilibrium control eqs (29) and (19) give:

$$v_s = [\% C] B_e \quad (33)$$

where

$$B_e = \frac{f_C \cdot p_C (1 - e^{-\frac{12}{19} N (1-\eta)^{19/12}})}{p_{tot} \cdot \eta_s} \quad (34)$$

For the batch reactor one obtains from a mass balance

$$\frac{[\% C]}{[\% C]_o} = \exp \left[- \frac{(G \cdot B \cdot m_C \cdot 100 + k_s \cdot A_s \cdot \rho) t}{M} \right] \quad (35)$$

where M is the metal mass in the reactor. B = B_m or B = B_e for the mass transfer and equilibrium cases, respectively.

Similarly for a continuous reactor one obtains

$$\frac{[\% C]}{[\% C]_o} = \left(1 + \frac{G \cdot B \cdot m_C \cdot 100 + k_s \cdot A_s \cdot \rho}{M} \right)^{-1} \quad (36)$$

where M now is the mass throughput.

Discussion of numerical values, application of equations.

The various quantities that enter into eqs (35) and (36) for batch reactors and continuous reactors can be divided into three groups:

- 1) Fundamental quantities - that often are known - such as the vapor pressure p_C, activity coefficient, f_C, and molar weight of the dissolved component, m_C. Fig. 3 gives the vapor pressure, p_C, in atmospheres of selected elements in aluminium (2). For dilute solutions usually f_C ~ 1.
- 2) Quantities known from operating conditions or reactor design. These are: G, the input of inert gas, the bottom pressure p_o ≈ p_{surface} + ρg h_o and the top pressure, p_{surface}, the top surface contact area A_s, the mass of the melt M or the throughput flow M.

3) Quantities determined by operating conditions or reactor design but which cannot be measured directly; they must be calculated or estimated from theory or measured indirectly. These factors are the mass transfer coefficient k_o , the number of bubbles generated per unit time \dot{N} , bubble size d_o and bubble velocity U_o (all at the inlet point) and the top surface mass transfer coefficient, k_s .

In the following some of these type 3 quantities are evaluated. As seen from eq (6) k_o is proportional to the square root of the diffusivity D and inversely proportional to the 1/4 power of the bubble diameter. It is found that $D \approx 10^{-8} \text{ m}^2/\text{s}$ (8) as may be expected (9); this is approximately the same value as for the self-diffusion coefficient of aluminium.

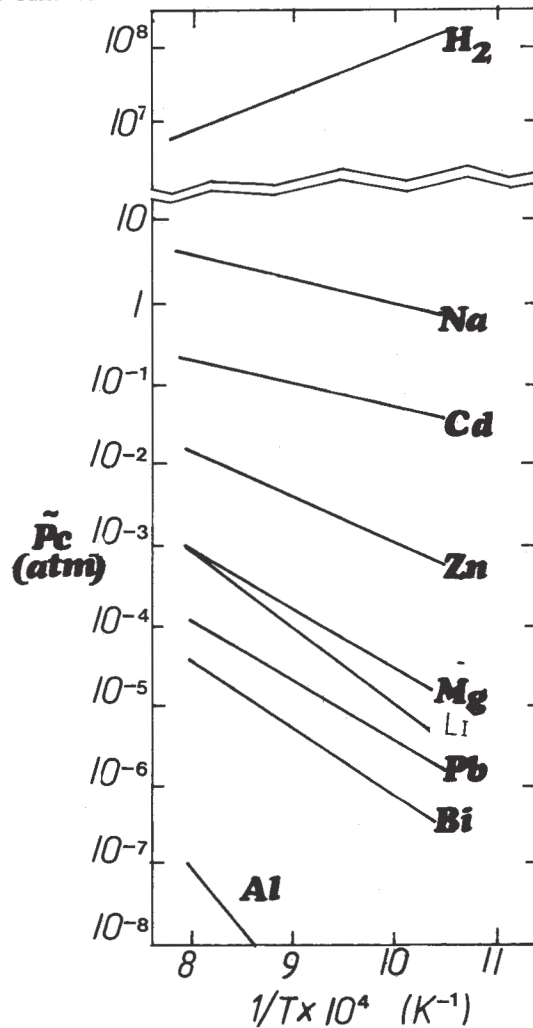


Fig. 3 - Calculated Vapor Pressures of Selected Elements Dissolved, C, in Aluminium at the "Hypothetical" One Weight Percent Standard Solution. The Vapor Pressure of Pure Al is Shown at the Bottom for Comparison.

Relations are not given for bubble diameter, d , except by reference to the literature (10, 11). d may be determined from the contact area A between melt and bubbles, measured in model experiments (11). In a numerical example in the following d_o for the SNIF (12) is taken as 0.004 m . (A bubble greater than about 0.001 m can be considered as "large.")

\dot{N} may be measured in model experiments (11) or calculated from the molar gas flow rate \dot{G} and bubble volume $\pi d_o^3/6$:

$$\dot{N} = \frac{\dot{G} \cdot 22.4 \cdot 1}{P_{tot} \cdot \pi d_o^3/6} \quad (37)$$

where 22.4 is molar volume in m^3/N . The factor 1 is included to symbolize the dimensions of atm.

If eq (37) is inserted in eq (25), the dimensionless group for N reduces to

$$N = \frac{k_o \cdot e \cdot P_{tot} \cdot 6 \cdot 22.4 \cdot 1 \cdot 0.1013 \cdot 10^5}{100 \cdot m_C \cdot \tilde{P}_C \cdot U_o \cdot d_o \cdot g \cdot f_C} \quad (38)$$

The factor $1.013 \cdot 10^5$ gives the conversion from atm to S.I. units. Since the product P_{tot}/\tilde{P}_C is dimensionless, one may employ units of atm for P_{tot} and \tilde{P}_C . N increases with increasing mass transfer coefficient, k_o , and total pressure P_{tot} and with decreasing bubble size d_o , velocity U_o and vapor pressure \tilde{P}_C .

To illustrate what numerical values of N are obtained in practice when bubbles are small, a gas purging reactor operating at atmospheric pressure is studied: Removal of Na in SNIF. Bubble size is small; we take

$$\begin{aligned} d_o &= 0.004 \text{ m}, \tilde{P}_C = 1 \text{ atm}, \\ f_C &= 1, m_C = 23 \\ P_{tot} &= 1.15 \text{ atm}, U_o = 0.14 \text{ m/s}, k_o = 6.68 \cdot 10^{-4} \text{ m/s}. \end{aligned}$$

This gives $N = 830$. Clearly removal in this example is equilibrium controlled. This is the case to an even greater degree for other components in aluminium with lower vapor pressures, \tilde{P}_C , than Na.

Thus for these eq (34) applies. However, using reasonable values for inert gas consumption per kg aluminium, it is found that only Na is substantially removed in SNIF.

If vacuum is used so that $P_{tot} \approx 0.01 \text{ atm}$ and bubble size d_o is greater than in SNIF, for instance $d_o = 0.04 \text{ m}$, N for Na would become approximately one, so that we are in the transition from equilibrium to mass transfer control. However, for components with lower vapor pressures than Na, equilibrium control would still apply. In this case for $N \gg 1$, inserting eq (11) and eq (34), eq (33) simplifies to

$$v_S \approx \frac{f_C \cdot \tilde{P}_C [Z \text{ C}]}{P_{tot}} \quad (39)$$

Discussion and conclusion.

where $p_{tot}^* \approx 0.01$ atm for vacuum systems. v_s is proportional to the vapor pressure of the dissolved component, p_c , and inversely proportional to the "effective pressure at the surface" p_{tot}^* .

Practical values for gas consumption per kg Al $\frac{G \cdot 22.4}{M}$ or $\frac{G \cdot 22.4 \cdot t}{M}$ are around $1 \text{ m}^3/\text{ton Al}$. For these values it is seen that from eqs (40), (35) and (36) that only elements Na, Cd and Zn can be removed by inert gas bubbles in vacuum to any noticeable extent.

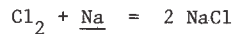
The equilibrium limitation can be removed by the use of reactive gases. In this case eq (28a) applies. It is especially interesting to choose the operating conditions so that no reactive gas escapes. This condition can be determined by setting $v_r = 0$ in the equation. This gives:

$$Y_r^o = \frac{12}{7} a_r (1 - \eta_s)^{7/12}$$

or inserting for a_r

$$\frac{Y_r^i}{(1 - Y_r^o)^{5/12}} = \frac{12 a}{7 \cdot \alpha} (1 - \eta_s)^{7/12} \quad (40)$$

As an example Y_r^o for $[\% \text{ Na}] = 0.002$ is determined in a SNIF-unit using the same values as previously. The reactive gas used is Cl_2 . The total reaction is



This gives for the stoichiometric coefficient $\alpha = 2$. From eq (20) and (37) one obtains:

$$a = \frac{k_o [\% \text{ C}] \cdot 22.4 \cdot 6 \cdot e \cdot 1.013 \cdot 10^5}{100 \cdot m_c \cdot U_o \cdot g \cdot d_o} \quad (41)$$

and:

$$a = \frac{6.68 \cdot 10^{-4} \cdot 0.002 \cdot 22.4 \cdot 6 \cdot 1 \cdot 1.013 \cdot 10^5}{100 \cdot 23 \cdot 0.14 \cdot 9.81 \cdot 0.004} = 1.4.$$

The right-hand side of eq (40) becomes $\frac{12 \cdot 1.4}{7 \cdot 2} \left(1 - \frac{1}{1.15}\right)^{7/12} = 0.094$.

This gives $Y_r^o = 0.09$. The purge gas can contain up to 9 % Cl_2 .

It is seen using of the order of 1 m^3 inert gas per ton Al that only Na (and H) can be removed by gas purging. If vacuum is applied also Cd and Zn content is reduced. Removal is governed by the equilibrium vapor pressure, eq (39), if bubbles are small (as in a correctly operated SNIF unit) and if coalescence and "flooding" (3) of bubbles is not too serious. These two phenomena are not discussed here. However, work is proceeding in this area at the institute in Trondheim. If coalescence and flooding (3) take place conditions can be displaced from equilibrium to mass transfer control. Eq (15) then no longer applies.

If a reactive gas is employed, the equilibrium limitation no longer applies. A number of elements may then be removed (2). Mass transfer is rate controlling. The content of reactive gases remaining in the exiting bubbles is given by eq (28a) and eq (41). These depend on mass transfer k , bubble velocity U and bubble size, d . We are attempting to determine numerical values for the physical quantities that influence k , U and d , for instance surface tension for the system Al - inert gas/ Cl_2 and wetting properties in the system nozzle - Al inert gas/ Cl_2 .

Once the content of reactive gases (preferably zero) in the exiting bubbles is known, removal of an impurity can be determined from the mass balance. However, for the removal of several impurities simultaneously, the relative mass transfer coefficients must be known.

In a future revised model eqs (4) - (6) will be modified when applied to "small bubbles". Also it will be attempted to deal with thermal expansion in a more satisfactory manner.

List of Symbols used.

- a - dimensionless constant, eq (20)
- a_r - " " " " , eq (20a)
- A - contact area of bubbles in melt
- A_s - melt surface area
- b = $\frac{K_C P_t^0}{f_C [\% C]}$
- B - proportionality constant
- $[\% C]$ - weight percent of element C
- D - diffusivity in molten M (m^2/s)
- D_C - diffusivity of element C in aluminium (m^2/sec)
- d - equivalent diameter of bubble (m)
- d_o - equivalent diameter of bubble at inlet (m)
- d_s - " " " " at surface (m)
- e - factor for deviation from spherical form of bubble
- f_C - Henrian activity coefficient of element C
- \dot{G} - flowrate of inert gas (kg mole/sec)
- g - gravitational constant
- h - distance travelled by bubble from the bottom
- h_s - height of aluminium bath (m)
- k - mass transfer coefficient (m/s)
- k_C - mass transfer coefficient for element C (m/s)
- k_o - " " " " " C at bottom of melt (m/s)
- K_C - equilibrium constant for element C
- \dot{M} - flowrate of aluminium in a continuous reactor (kg/sec)
- M - weight of aluminium bath (kg)
- N - dimensionless group eq (38)
- \dot{N} - number of bubbles generated per unit time (s^{-1})
- m_C - molecular weight of element C

- P_C - pressure of C (atm.)
 - P_{inert} - pressure of inert gas (atm)
 - P_r - pressure of reactive component r (atm.)
 - P_r^o - " " " " at bottom of the melt (gas inlet) (atm.)
 - P_{tot} - total pressure (atm.)
 - P_{tot}^o - total pressure at the bottom of the melt (gas inlet) (atm.)
 - P_{tot}^* - effective total pressure at bath surface (atm.)
 - \hat{P}_C - vapor pressure in equilibrium with "hypothetical" one weight percent standard solution (atm.)
 - r - reactive gas
 - t - time from start of degassing (sec.)
 - T - absolute temperature (K)
 - U - rise velocity of bubbles (m/s)
 - U_o - rise velocity of bubbles at inlet ($\frac{m}{s}$)
 - v - mol fraction of component C in bubbles (m^3)
 - v_r - " " " reactive component r in bubbles
 - V - bubble volume (m^3)
 - Y - P_r/P_{tot}
 - Y_r - P_r/P_{tot}^o
 - Y_r^o = P_r^o/P_{tot}^o
 - x - integration variable $x = \eta^{7/12}$
 - Z - " " " "
 - α - stoichiometric coefficient
 - η = P_{tot}/P_{tot}^o
 - ρ - density of liquid aluminium (kg/m^3)
 - σ - surface tension (N/m)
- Indices:
- e indicates equilibrium
 - inert -" - inert gas
 - m -" - mass transfer
 - o -" - input conditions (bottom of melt)
 - r -" - reactive gas
 - s -" - bath surface conditions
 - tot -" - total pressure in bubbles

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