Homogeneous Nucleation of CO Bubbles in Fe-C-O Melts

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The formation of CO(*g*) bubbles in Fe-C alloy droplets during spray-decarburization operations is described in terms of a homogeneous nucleation process enabled by the surface active properties of oxygen. An expression is obtained for the reversible work to form a vapor nucleus that includes electrostatic terms involved in forming a layer of chemisorbed oxygen ions. These additional terms make the critical nucleation conditions a sensitive function mainly of the oxygen content of the melt. The critical oxygen activity is found to be in the 0.001 to 0.003 wt pct range at 1823 K.

THE formation of carbon monoxide bubbles in liquid iron alloys is often observed as a carbon boil or droplet explosion during spray-decarburization operations in oxygen. Although this interesting phenomenon is of practical interest in other industrial processes,[1,2] and has been the subject of extensive research,[3-10] no satisfactory theoretical explanation of the bubble formation process had been developed until recently.[11,12] In particular, classical nucleation theories have been unable to reconcile the formation of critical vapor embryos in these metallic systems with the high surface or interfacial tensions and the relatively low vapor pressures involved.[9,12] Moreover, the nature of the alternative process that has been modeled to rationalize bubble formation, vortex nucleation,[10,13] is unclear.

While other possibilities, such as heterogeneous nucleation, are not excluded, it seems most probable that bubble formation occurs in this iron alloy system by a homogeneous nucleation process in spite of the high surface tension, low vapor pressure paradox. This strong inference comes from the explosion and sac formation studies in the zirconium system[14-16] where the very high temperatures involved, the reactivity of the system, and the expected wide homogeneity range of the Zr-O-N melt appear to deny the existence of heterogeneous processes. Moreover, the systematic changes in the sac formation behavior with droplet size and nitrogen content is suggestive of a homogeneous nucleation process. This inference implies that the classical theories that have been used are oversimplified and are not applicable to these multicomponent systems without some modification. In particular, a more complete description of the surface layer is required in order to account for the effects of chemisorbed ions[11,12] since the thermodynamic properties of the system will depend strongly on the presence of electrical charges in the surface layer.

In this report, we neglect many features of the decarburization process, which have been investigated and treated elsewhere,[3-10] and concentrate on the bubble nucleation process. For simplicity, it is assumed that the spray-refining operation has reached a stage where oxygen diffuses into the iron carbon alloy from the outer surface region. A small volume element of the resulting ternary alloy is considered further in detail. For such a ternary system, the probability[17,18] of a fluctuation producing a critical vapor embryo is proportional to exp $(-\Delta F^*/kT)$ where ΔF^* is the reversible work done by the system to form the metastable nucleus from the melt. The kinetics of nucleation is sensitive to the magnitude of ΔF^* so that care is required in formulating a model for the system. In the following, a Gibbs model for the interface between embryo and melt is used to describe the adsorption of oxygen and carbon. This formulation leads without difficulty to an expression for ΔF^* which includes electrostatic terms involved in establishing the chemisorbed layer. These latter terms, not considered in prior nucleation theories, modify the Laplace equation for mechanical equilibrium as well as the magnitude of ΔF^*. The results for the reversible work are incorporated into the nucleation process and then related to the decarburization operation.

SYSTEM MODEL

Consider an isolated spherical embryo of CO(*g*) within a ternary Fe-C-O melt as illustrated in Fig. 1. Since oxygen is surface active,[19-21] it is shown schematically in the figure as a doubly charged chemisorbed ion in the surface layer even though this is an oversimplified representation. Let the system consist of a fixed in-

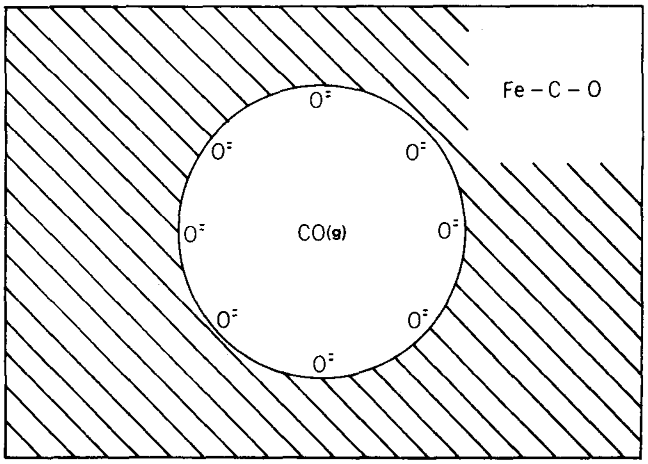

Fig. 1—Bubble nucleation model for the Fe-C-O system.

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ventory of each component, N_C, N_O, and N_{Fe}, with the entire mass occupying a constant unit total volume. The temperature, T, is constant and uniform throughout.

The volume of the melt and embryo are V_1 and V_2, respectively. Let n_{10}, n_{11}, and n_{12} be the number of C, O, and Fe atoms in the melt and n_2 the number of $CO(g)$ molecules in the embryo. It is assumed that other vapor species are present in the embryo at such a low concentration that they can be ignored. Note that the subscripts 1 and 2 refer to the bulk melt and vapor regions, respectively, and that a second subscript is used to identify a component in the melt. The subscript 3 will be used in the following to refer to the surface region.

The surface concentration of each component as well as the volume and atom content of each phase depend on the location of the Gibbs dividing interface. By convention, we choose the location that makes the adsorption of iron zero. This choice also makes the experimentally significant relative adsorption[22] of carbon or oxygen with respect to iron equal to the surface concentration at this particular location.

While carbon is not surface active in the binary Fe-C system,[19-21] no systematic measurements have been made in the ternary Fe-C-O system. It is known, however, that an activated complex, CO†, and other intermediate adsorbed species[21,23] are involved in the desorption of $CO(g)$ from the surface and should also be involved in the equilibrium between $CO(g)$ and the Fe-C-O melt. As a first approximation, however, it will be assumed that the concentration of adsorbed CO species is small and can be ignored.

Using this assumption, a mass balance for the system then requires that

$$N_C = n_{10} + n_2 \qquad [1]$$

$$N_O = n_{11} + n_2 + n_3 \qquad [2]$$

$$N_{Fe} = n_{12} \qquad [3]$$

where n_3 is the number of chemisorbed oxygen ions. These three constraints together with the fact that $V_1 + V_2 = 1$ are used in deriving the reversible work done by the system to form a vapor embryo from the melt.

THE REVERSIBLE WORK

The Helmholtz free energy change to form a vapor embryo that does not differ greatly in size from the critical embryo is given by[12]

$$\Delta F = -(p_2 - p_1)\, V_2 + \sigma A + n_2(\bar{\mu}_2 - \bar{\mu}_{10} - \bar{\mu}_{11}) + n_3(\bar{\mu}_3 - \bar{\mu}_{11}) \qquad [4]$$

where it is assumed that the surface tension, σ, is the same as the equilibrium value for the critical embryo and that p_2, the pressure in the embryo, is the same as the equilibrium value corresponding to size r. In Eq. [4], p_1 is the constant liquid pressure and the $\bar{\mu}$'s are all molecular electrochemical potentials for the appropriate components. In the bulk phases, however, each unit volume element is neutral and there is no electric field so that the electrochemical potential can be identified[24] with the ordinary chemical potential, μ. Because of the large electric field at the interface, $\bar{\mu}_3$ must include some electrostatic energy terms and therefore differs from the ordinary chemical potential.

Eq. [4] has a simple interpretation. It is the sum of different types of reversible work done by the system in forming the vapor embryo from the melt. The first term on the right is the net volume work done in forming the cavity against the liquid pressure p_1 and filling it with vapor at pressure p_2. The second term is the reversible work done against surface tension forces. The third is the chemical work done in forming n_2 molecules of $CO(g)$ from its components in the melt. Finally the last term is the chemical and electrostatic work done in forming n_3 chemisorbed oxygen ions on the surface from its component in the melt.

According to Parsons,[25] Tompkins,[26] Boudart,[27] and Higuchi, *et al.*,[28]

$$\bar{\mu}_3 = \mu_3 + ze\chi \qquad [5]$$

where ze is the charge on the chemisorbed ion and χ is the surface or contact potential. If the dipoles formed by the oxygen ions are radially oriented, uniformly distributed, and have their negative ends directed into the embryo then [ignoring the small contribution from the activated complex involved in the desorption of $CO(g)$ from the surface]

$$\chi = -4\pi\Gamma_3 zel \qquad [6]$$

where l is the dipole length (assumed to be the radius of the oxygen ion), $\Gamma_3 \equiv n_3/A$, and A is the surface area. Then

$$\sigma_0 = -ze\Gamma_3\chi \qquad [7]$$

or

$$\sigma_0 = 4\pi\Gamma_3^2 z^2 e^2 l \qquad [8]$$

is the electrostatic energy density of the surface region so that

$$n_3(\bar{\mu}_3 - \mu_{11}) = n_3(\mu_3 - \mu_{11}) - \sigma_0 A \qquad [9]$$

Thus, the last term in Eq. [4] is a function of both n_3 and r, the radius of the embryo.

Providing that σ_0 and σ are not a function of r (see Appendix), the extremum condition $\delta(\Delta F) = 0$ results in

$$\mu_2^* = \mu_{10} + \mu_{11} \qquad [10]$$

$$\bar{\mu}_3^* = \mu_{11} \qquad [11]$$

$$(p_2^* - p_1) = 2(\sigma - \sigma_0)/r^* \qquad [12]$$

which are three conditions that must be met simultaneously for the embryo and melt to coexist in an unstable equilibrium. The first two are requirements for chemical and chemisorptive equilibrium. The last is a Laplace equation for mechanical equilibrium that is modified by the electrostatic energy density. Eq. [4] then becomes

$$\Delta F = -(p_2 - p_1)V_2 + \sigma A + n_2(\mu_2 - \mu_2^*) + n_3(\bar{\mu}_3 - \bar{\mu}_3^*) \qquad [4a]$$

by use of Eqs. [10] and [11] so that at the extremal point,

$$\Delta F^* = -(p_2^* - p_1)\, V_2^* + \sigma A^* \qquad [13]$$

which is the same result as that obtained by others[29,30] for ΔF^*. Thus, while ΔF *is* a function of the oxygen and carbon potential in the melt, ΔF^* *is not* because of the extremum conditions in Eqs. [10] and [11].

Eq. [13] simplifies to either

$$\Delta F^* = (\sigma + 2\sigma_0)A^*/3 \qquad [14]$$

by use of Eq. [12] for $(p_2^* - p_1)$, or equivalently, after simplification, to

$$\Delta F^* = (16\pi/3)\sigma^3\Psi/(p_2^* - p_1)^2 \qquad [15]$$

by use of Eq. [12] for r^* where Ψ, the surface tension function, is

$$\Psi = (1 - \sigma_0/\sigma)^2(1 + 2\sigma_0/\sigma) = 1 - 3(\sigma_0/\sigma)^2 + 2(\sigma_0/\sigma)^3 \qquad [16]$$

The corresponding results obtained by others[29,30] are

$$\Delta F^* = \sigma A^*/3 \qquad [17]$$

$$\Delta F^* = (16\pi/3)\sigma^3/(p_2^* - p_1)^2 \qquad [18]$$

so that the dipole layer formed by the chemisorbed oxygen ions has a significant effect on the reversible work to form a vapor embryo as well as on the condition for mechanical equilibrium.

THE ELECTROSTATIC ENERGY DENSITY

The parameter σ_0 is the energy stored (per unit area) in the electric field of the chemisorbed oxygen ions and their image charges in the conducting melt. Since σ_0 is a function of Γ_3, it depends mainly on the oxygen activity in the liquid phase and is not limited by surface tension or ambient pressure. Accordingly, both positive and negative values of $(\sigma - \sigma_0)$ could occur during the decarburization operation. If σ_0 exceeds σ, then $\delta(\Delta F) = 0$ only if p_1 exceeds p_2^* at $r = r^*$ in accord with Eq. [12]. Near r^*, the free energy behaves as[12]

$$\Delta F \simeq \Delta F^* - 4\pi(\sigma - \sigma_0)(r - r^*)^2 \qquad [4b]$$

where both ΔF^* and r^* are positive. Thus, ΔF will have a maximum at r^* only for positive $(\sigma - \sigma_0)$ whereas it will be a minimum if σ_0 exceeds σ. In the latter case, spontaneous growth or dissolution of the bubble would not occur and only stable vapor nuclei of size r^* would form if they form at all. It is concluded that homogeneous nucleation and spontaneous growth of CO bubbles are possible only for $(\sigma - \sigma_0) \geq 0$ whereas the system is inherently stable for $(\sigma - \sigma_0) < 0$.

It is reassuring to find in the limit of small σ_0 relative to σ (say due to the absence of a chemisorbed layer) that the modified Laplace equation simplifies to its more familiar form

$$(p_2^* - p_1) = 2\sigma/r^* \qquad [12a]$$

and that ΔF^* in Eqs. [14] and [15] reduces to the classical results in Eqs. [17] and [18].

THE SURFACE TENSION FUNCTION

The free energy change to form a small vapor embryo from the melt involves a positive contribution from the work done against surface tension forces whereas all other work terms, including electrostatic, are negative. The excess of this positive work over the negative terms for the critical embryo represents a barrier to phase change which is proportional to $\sigma^3\Psi$. In the absence of any electrostatic work (say due to no chemisorption) the barrier is proportional to σ^3. Thus, the surface tension function, Ψ, modifies the classical barrier for the work recovered by setting up the chemisorbed dipole layer.

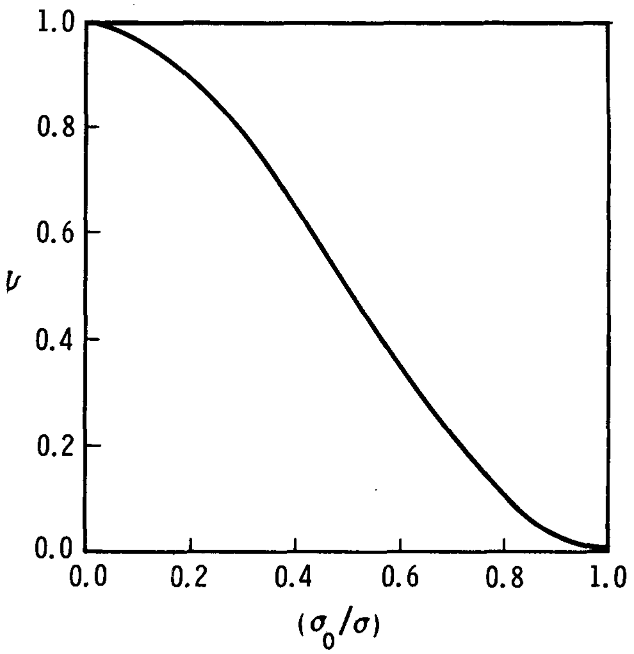

Fig. 2—The effect of electrostatic energy density changes on the surface tension function.

The dependence of Ψ on the magnitude of σ_0 (in multiples of the more familiar σ) is illustrated in Fig. 2. If the electrostatic work, σ_0, is small (relative to the surface tension work σ) then Ψ approaches unity and the barrier to phase change is essentially unaltered from the usual σ^3 term. If the electrostatic work increases, then Ψ decreases from unity and the barrier is proportional to $\sigma^3\Psi$. Finally if the electrostatic work approaches the surface tension work, then both Ψ and the barrier to phase change approach zero. Since the system is stable for $(\sigma_0/\sigma) > 1$, then Ψ exists only in the $0 \leq (\sigma_0/\sigma) \leq 1$ domain.

NUCLEATION KINETICS

The classical theory of nucleation leads directly to the following expression[12]

$$J = Z\beta^* A^* N \exp(-\Delta F^*/kT) \qquad [19]$$

for the steady rate of nuclei formation per unit volume where

$$N \cong N_C + N_O + N_{Fe} \qquad [20]$$

is the total atom inventory per unit volume, β^* is the rate of molecular gain by the critical embryo per unit area of surface [the desorption of CO(g) from iron melts has been investigated by others[21,23]], and

$$Z = [4kT(\sigma - \sigma_0)]^{1/2}/A^* p_2^* \qquad [21]$$

is the nonequilibrium factor.[12]

It is assumed that the nucleation process terminates when a single critical vapor embryo forms. The subsequent nonequilibrium vapor expansion has been considered by others.[31-33]

DISCUSSION AND CONCLUSIONS

Swisher and Turkdogan[21] reported on the surface tension and the oxygen adsorption isotherm of the binary Fe-O system at 1823 K as a function of the oxy-

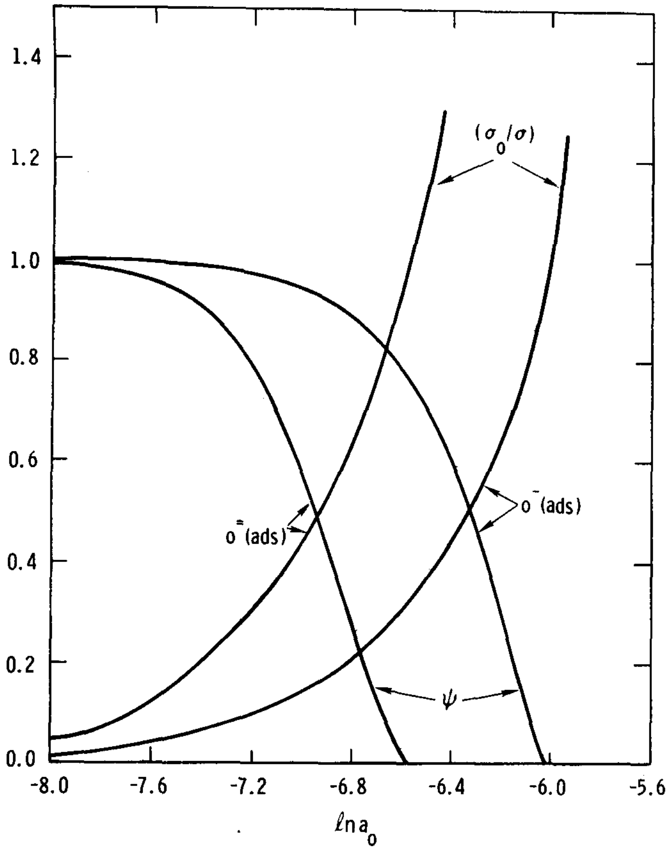

Fig. 3—The effect of oxygen concentration changes in the Fe-C-O system on (σ_0/σ) and Ψ based on the surface tension and oxygen adsorption isotherm reported by Swisher and Turkdogan.[21]

Table I. System Parameters at $\Psi = 0$

	$O^=$(ads)	O^-(ads)
a_0*, wt pct	0.0014	0.0025
σ, dynes/cm	1680	1700
θ*	0.10	0.15
T, K	1823	1823
p_1, bars	1	1

gen activity of the melt. They found, based on an average of surface tension measurements made by others,[19,20] an asymptotic adsorption limit, Γ_0, of 1.05×10^{15} atom/cm^2. This result corresponds to an area/adsorbed atom of 9.52Å^2 which is close to the area that would be occupied by an O^- ion with a Pauling radius of 1.76Å.[34] (The empirical Pauling radius may not apply in the surface region.) However, oxygen may be adsorbed as an $O^=$ ion with a Pauling radius of 1.40Å[34] at the low end of the adsorption isotherm, where the carbon boil and explosions most likely occur,[12] although no evidence was found to support this belief. It is assumed that these results also apply to the ternary system.

Calculations of (σ_0/σ) and Ψ were made, from Eqs. [8] and [16], as a function of oxygen activity, a_0, in the melt using the surface tension and adsorption isotherm reported by Swisher and Turkdogan.[21] The results are displayed in Fig. 3 for the two adsorbed oxygen ion configurations. The approximate values of a_0, σ and $\theta(\equiv\Gamma_3/\Gamma_0)$ corresponding to $\Psi = 0$ are summarized in Table I.

It appears, from inspection of Fig. 3, that nucleation of CO(g) bubbles must occur in the vicinity of $\Psi = 0$ for at any other oxygen concentration the barrier to phase change within the melt, represented by $\sigma^3\Psi$, greatly exceeds the equilibrium vapor pressure of CO(g) because of the precipitous increase of Ψ with small decrease in oxygen activity. Moreover, bubble formation at other melt compositions due only to moderate temperature increases is not expected because the surface tension would still be quite large and the CO(g) vapor pressure relatively low. The values of a_0 and θ at $\Psi = 0$ must therefore be approximately equal to the critical values and are so designated in Table I. This behavior of the Fe-C-O melt is different from that of simpler systems in which moderate superheating is used to adjust the vapor pressure and the surface tension to achieve critical conditions. This conclusion emphasizes the fact that critical bubble nucleation conditions in the Fe-C-O system are determined almost entirely by the oxygen content of the melt and that, approximately, a_0^* is a critical concentration. In addition, since the oxygen adsorption isotherm undoubtedly changes with temperature, then a_0^* will surely vary with temperature also. Stated differently: the reversible work to form the vapor embryo is excessive (and J therefore vanishingly small) everywhere except in the vicinity of $\Psi = 0$.

Conditions at the surface of the Fe-C alloy droplet become more oxidizing at some late stage of the spray-decarburization process.[9] When this occurs, the oxygen activity of the melt at the outer surface increases and an oxygen concentration profile is established in the interior by normal diffusion and convection processes providing that the oxygen activity is less than a_0^*. Further oxygen content increases to a_0^* and higher are possible and do occur at the outer surface of the droplet where nucleation is not involved. When this does occur, the natural flow of oxygen from its high value (greater than a_0^*) at the outer surface of the droplet toward lower values in the interior is interrupted by CO gas bubble formation at $R(a_0^*)$, the position in the melt at which $a_0 = a_0^*$. Note that CO bubble formation removes both oxygen and carbon from the melt. This phase change process should eliminate or reduce the inward flow of oxygen beyond $R(a_0^*)$—at least until the local equilibrium vapor pressure of CO is greatly reduced by carbon depletion. Sharp changes or discontinuities in both oxygen and carbon activity should then occur at $R(a_0^*)$ because of the relative ease of bubble formation at this point.

If the reaction is spherically symmetric, then a shrinking shell of small bubbles forming in the interior of the iron droplet is visualized separating the droplet into two distinct regions. The outer region $[R > R(a_0^*)]$ should be characterized by an oxygen activity in excess of a_0^*, an inward flow of oxygen, and a negligable concentration of carbon, whereas the inner region $[R < R(a_0^*)]$ would have a low oxygen activity (less than a_0^*), a high carbon activity and an outward flow of carbon. The mixing and turbulence caused by bubble formation and expansion, however, would blunt or blur some of these effects as well as the sharp concentration changes at $R(a_0^*)$.

These results and conclusions are a departure from other studies[3-10] of the carbon boil phenomena that searched for and depended on a high oxygen activity in the melt mainly to increase the CO(g) vapor pressure for bubble nucleation. As illustrated in Table I, the magnitude of a_0^* is quite small. Perhaps control or adjustment of the electrostatic energy density in the surface region might be feasible and beneficial in future industrial operations.

It should be pointed out that the contact or surface potential change due to adsorption is equal in magnitude but opposite in sign to the change in the work function.[26] It is the potential or work function change that has significance whereas the relationship in Eq. [6] is a derived quantity usually used in the reverse manner to estimate the dipole moment per atom from adsorption and potential changes. The use of measured work function changes caused by oxygen chemisorption at a liquid Fe-C alloy surface would be a desirable future refinement to establish the value of σ_0 more accurately. In the meantime, the approach and results presented here should have at least semiquantitative validity.

ACKNOWLEDGMENT

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NOMENCLATURE

A	surface area
a_0	oxygen activity in melt (weight percent)
e	electronic charge
ΔF	Helmholtz free energy change
J	nucleation frequency per unit volume
k	Boltzmann constant
l	dipole length
N	atom inventory
n	number of atoms
n_2	number of CO(g) molecules
n_3	number of chemisorbed oxygen ions
p	pressure
R	radial position in droplet
$R(a_0^*)$	radial position in droplet at which $a_0 = a_0^*$
r	radius of embryo
T	absolute temperature
V	volume
Z	nonequilibrium factor
z	number of charges

<u>Greek</u>:

β	desorption frequency per unit area
γ	net surface energy density $(\sigma - \sigma_0)$
Γ_0	asymptotic adsorption limit of oxygen
Γ_3	n_3/A
θ	fraction of a monolayer coverage (Γ_3/Γ_0)
$\bar{\mu}$	electrochemical potential
μ	chemical potential
σ	surface tension
σ_0	electrostatic energy density
χ	contact or surface potential
Ψ	surface tension function

<u>Subscripts and Superscripts</u>:

*	critical conditions
O	oxygen
C	carbon
Fe	iron
1	melt
2	embryo
10	carbon component of melt
11	oxygen component of melt
12	iron component of melt

APPENDIX

The Gibbs dividing surface is located in the interface at the position that makes the adsorption of iron zero. This position may differ from the surface of tension and because of this σ may be a function of curvature.[35-37] It seems most likely, however, that the departure from the surface of tension would be less than a molecular diameter, δ. Since σ varies as $(1 + \delta/r)$, the effect of curvature on σ is negligible for the very large nuclei formed during bubble formation.[12]

The electrostatic energy density, σ_0, is a function of the relative adsorption, Γ_3. If it is assumed that Γ_3 is <u>only</u> a function of the oxygen activity of the melt, then the modified Laplace equation, Eq. [12], is obtained since the variation of σ with r for large embryos is negligible. If, however, the relative adsorption of oxygen is influenced by the mechanism of vaporization of CO(g) or by other components of the vapor phase, then Γ_3 and σ_0 would vary with embryo size. We wish to examine the effect of this curvature dependence on the reversible work to form a critical vapor embryo.

If both σ and σ_0 vary with r, then the extremum condition results in

$$(p_2^* - p_1) = 2\gamma^*/r^* + (\partial\sigma/\partial r)_{r^*} - (\partial\sigma_0/\partial r)_{r^*} \qquad [\text{A1}]$$

where $\gamma \equiv (\sigma - \sigma_0)$ is the net surface energy density. Eq. [A1] becomes

$$(p_2^* - p_1) = (1/A^*)(\partial A\gamma/\partial r)_{r^*} \qquad [\text{A2}]$$

Thus wherever γ is a function of curvature, mainly due to $\sigma_0(r)$ here, the Laplace equation becomes [A2] and its effects on the reversible work and the kinetics of nucleation will be similar to that found by others[35,36] for a one-component system with a curvature dependent surface tension. The form of $\sigma_0(r)$ would have to be known.

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