COMMENTARY

Evaporation Processes in Vacuum Metallurgy

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Born of necessity in the metallurgy of the reactive metals, vacuum technology is now being applied to the steel-making resulting in excellent quality control and properties not otherwise realizable. To provide an insight into the selection and evaluation of the experimental data, the authors have considered it advisable to present a systematic review of the principles and theories on evaporation phenomena. This article contains the basic aspect of the free evaporation under perfect vacuum, the vapor transfer through the thermal boundary layer under poor vacuum, the enhancement of evaporation, the restriction evaporation and the selective evaporation from multi-component bulk.

1. Introduction

Vacuum metallurgy may be said to include the purifying, shaping, and treating of metals and alloys under vacuum or reduced pressures. Obviously, successful application of vacuum technology to metallurgical processes has so far been made to produce high-purity or clean metals and alloys owing to high-performance vacuum pumping system. Like many new technological developments, the basic ways of thinking on vacuum metallurgy are quite old. Even though application range has been extended and quality control became excellent, the fundamental theory on vacuum metallurgy rests limited. Therefore, most part of this article only treats the basic aspect of evaporation phenomena common to the individual vacuum-metallurgical processes.

2. Equilibrium Basis

In the thermodynamic term, the driving force for evaporation is escaping tendency and its index is called fugacity, f . It is related to the molar Gibbs free energy, G , by the relation:

$$G = RT \ln f + B, \quad (1)$$

where B is the constant depending only on temperature, T . So, the chemical potential is also an index for driving force of evaporation. Usual convention is that, when a pure substance is in equilibrium with its vapor in the state of ideal gas, the fugacity of the substance is equal to the pressure of the vapor, P . Therefore, when the vapor is completely swept away in an instant, the substance tends to vaporize with a tension, P .

In general, the density of a gas decreases with increase in temperature. On the contrary, the density of the equilibrated vapor over a substance increases with increase in temperature as indicated as follows. Change in molar volume of the vapor over a substance, V_g , with regard to temperature is given by:

$$\frac{dV_g}{dT} = \frac{V_g}{T} \cdot \left(1 - \frac{\Delta H}{RT}\right), \quad (2)$$

where ΔH is the heat of evaporation. Equation (2)

shows that because $\Delta H \gg RT$ and $dV_g/dT < 0$, V_g decreases as temperature increases, or the density of the vapor increases with increase in temperature. As an illustrative example, melting of high-melting point metals may result in evaporation loss as high as that for low-melting-point metals.

3. Free Evaporation

Theoretical expression describing the rate of evaporation of a substance most frequently referred to in the study of practical vacuum evaporation is the Langmuir free evaporation equation. It may be, then, essential to be fully informed of its background and restriction for its utilization by deriving the equation from the starting point. Here, we will consider the free evaporation in vacuum from a liquid metal surface.

The rate of evaporation in this theory means the number of particles issued from the unit area of the metal surface per unit time into a perfect vacuum surrounding the metal. An assumption is posed on that the number of particles leaving the metal surface is equal to the number of particles initially existing in the vapor phase equilibrated with the metal at a given temperature and striking the unit area of the metal surface per unit time. It is assumed that, in equilibrium, the number of particles escaping from the metal surface must be equal to the number of particles condensing on the metal, and that when the vapor is completely swept away at a given instant, the metal must issue the particles with the same rate as in the metal-vapor equilibrated state. Therefore, it is reduced to the problem of calculating the number of gas molecules striking a wall of unit area per unit time.

Figure 1 is a velocity-space diagram demonstrating the distribution of gas molecules moving toward the metal surface. Consider a small circle part of area dS on the metal surface. The molecules of a gas are moving at random. The molecules which come from the direction v and strike the surface dS are obviously those having the velocity v and being contained in an oblique cylinder with the bottom area dS and generatrix $v dt$. Here, it is assumed that dt is so short that these molecules do not undergo any collision with each other, or that the mean free paths of the molecules are sufficiently long. The total number of particles strik-

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Fig. 1. The solid angle subtended by dS at a point O in the spherical coordinate system.

ing dS is then given by summing up all the velocity vectors. Such a summation can be conducted by integration with respect to the velocity and the incident angle θ .

Now, the number of molecules dn per cubic centimeter having velocities between v and $v+dv$ and having all the moving directions within $d\omega$ may be expressed using Maxwell-Boltzmann distribution function $f(v)$ as:

$$dn = n \cdot f(v) dv \cdot \frac{d\omega}{4\pi}, \quad (3)$$

whence, total number dN of such molecules being contained in the oblique cylinder that has the volume $dS \cdot v \cos \theta \cdot dt$ (see in Fig. 1) is:

$$dN = n \cdot f(v) dv \cdot \frac{d\omega}{4\pi} \cdot dS \cdot v \cdot \cos \theta \cdot dt. \quad (4)$$

On the other hand, change in ω with respect to change in θ can be written by the well-known relationship which can be derived from solid angle analysis:

$$d\omega = 2\pi \sin \theta \cdot d\theta. \quad (5)$$

Then, by integrating Eq. (4) with respect to the velocity and the incident angle, and by utilizing Eq. (5), the total number of molecules striking the metal surface is given by:

$$N = \left[\int_0^\infty \int_0^{\pi/2} n \cdot f(v) dv \cdot \frac{2\pi \sin \theta \cdot d\theta}{4\pi} \cdot v \cos \theta \right] dS \cdot dt, \quad (6)$$

here, the integration is made for the ranges:

$$\begin{aligned} 0 \leq \theta \leq \pi/2, \\ 0 \leq v \leq \infty. \end{aligned} \quad (7)$$

Thus, the number of molecules Γ striking unit area per unit time can be obtained by dividing N by $dS \cdot dt$:

$$\begin{aligned} \Gamma &= n \cdot \int_0^\infty v \cdot f(v) dv \cdot \left(\frac{1}{2} \right) \cdot \int_0^{\pi/2} \sin \theta \cdot \cos \theta \cdot d\theta \\ &= \left(\frac{1}{4} \right) \cdot n \cdot \langle v \rangle, \end{aligned} \quad (8)$$

here, $\langle v \rangle$ is the mean velocity of molecules and given by the kinetic theory of gases as:

$$\langle v \rangle = \int_0^\infty v \cdot f(v) dv = \frac{2}{\sqrt{\pi}} \cdot \left(\frac{2kT}{m} \right)^{1/2}, \quad (9)$$

where k is Boltzmann constant and m the mass of a particle. Now, in the background of the present kinetic approach the magnitude Γ is prescribed to be equal to the rate of free evaporation ($d\omega/dT$), so that the final expression may be written, by combining Eq. (8) with Eq. (9) and by using the relation, $p = nkT$, as:

$$\frac{d\omega}{dt} = p \cdot \left(\frac{1}{2\pi mkT} \right)^{1/2}, \quad (10)$$

where the pressure p is the saturated vapor pressure of

Fig. 2. Schematic illustration showing the model of mass transfer through the boundary diffusion layer.

the liquid metal.

It must be noted that in the free evaporation processes Eq. (10) can be true only if no collision occurs among gaseous particles in the gas phase. If the particles undergo many collisions, some particles will be reflected and return to the condensed phase, and the net rate of evaporation will be smaller than the rate given by Eq. (10). Therefore, the rate calculated from Eq. (10) may be referred to the maximum rate of evaporation. The maximum evaporation rate would be obtained if a perfect vacuum could be maintained over the liquid. Therefore, Eq. (10) may only be accurately applicable to an evaporation process that is conducted under high vacuum on materials with very low vapor pressure.

4. Transport Phenomena in Gas Phase

Vacuum is a relative term. Evaporation in ordinary vacuum metallurgy is a complex process, general formulation of which has not so far been done to evaluate rate of evaporation solely on theoretical basis. A common feature of most of these systems is that there exist foreign gas particles with relatively high density in the vicinity of the surface of condensed phase.

In this regard, a model proposed for evaporation suggests the existence of a boundary diffusion layer in the gas space in the immediate vicinity of the vaporizing surface.¹⁾ The image of mass transfer through this layer is illustrated in Fig. 2. Here, the attempt will be made to formulate qualitatively the transport phenomena.

Atoms diffused from the interior of the metal to its surface leave the metal lattice and pass into the state of adsorption at the surface. Atoms leaving the surface repeat collisions with molecules of a foreign gas, and gradually lose kinetic energy as metal atoms diffuse through the residual gas molecules. At some distance these atoms begin to combine each other to form a sort of condensed clusters. The region with this distance is called the boundary diffusion layer,²⁾ and the rate of evaporation may be predominantly determined by the rate of diffusion through this layer.

Let x the distance in a direction perpendicular to the metal surface and toward the region of vapor transport. In the region of the boundary diffusion layer, initial flux J_0 of the vapor atoms liberated from the metal surface attenuates as caused by collisions and reflections with an attenuation coefficient μ . This gives rise to resident vapors in this region, then the flux J_c may be expressed by one-dimensional expression as:

$$J_c = J_0 \cdot e^{-\mu x} \quad (11)$$

The resident vapors cause in their turn a gradient of concentration. Putting $\rho(x)$ as the density of the residual vapor, the flux of the vapor J_d driven by this concentration gradient is given by:

$$J_d = -D \cdot \frac{\partial \rho(x)}{\partial x}, \quad (12)$$

where D is the diffusion coefficient of the atom of the vapor and depends on the pressure of the foreign gas. Thus, total flux $J(x)$ of the vapor is:

$$J(x) = J_0 \cdot e^{-\mu x} + \left(-D \cdot \frac{\partial \rho(x)}{\partial x} \right). \quad (13)$$

By the law of continuity of fluid,

$$\frac{\partial J(x)}{\partial x} = -\frac{\partial \rho'(x)}{\partial x}, \quad (14)$$

where $\rho'(x)$ is the density of the vapor. Substituting Eq. (13) in Eq. (14), one obtains the following formula:

$$D \cdot \frac{\partial^2 \rho(x)}{\partial x^2} + J_0 \cdot \mu \cdot e^{-\mu x} = \frac{\partial \rho'(x)}{\partial x}. \quad (15)$$

Since the density of the vapor does not vary with time everywhere in the steady-state such as,

$$\frac{\partial \rho(x)}{\partial x} = 0. \quad (16)$$

Equation (15) is reduced to the expression for the density of vapor:

$$\frac{\partial^2 \rho(x)}{\partial x^2} + \left(\frac{J_0 \cdot \mu}{D} \right) \cdot e^{-\mu x} = 0. \quad (17)$$

By inspection of the differential equation (17), the distribution of vapor density may be qualitatively sketched as seen in Fig. 2. Obviously, the maximum in the density appears near the vaporizing surface, and for the sake of this maximum there occurs the counter diffusion toward the metal-gas interface.

5. Enhancement of Evaporation

Enhanced evaporation could be brought about by two types of effect: (1) effect of cooling, and (2) effect of reactive gases.

When the vapor from the metal surface is cooled by an inert gas with temperature lower than that of the vaporizing vapor, there will be homogeneous nucleation of droplets from vapor, giving rise to decrease in the vapor pressure in the gas phase and to increase in the vapor pressure gradient. Then, mass transfer in the gas phase will be promoted. This phenomenon will be formulated as follows. Blowing of an inert gas onto the liquid metal surface under continuous evacuation is a way to cool the vapor. Integrating Eq. (17),

$$\frac{\partial \rho(x)}{\partial x} = -\left(\frac{J_0 \cdot \mu}{D} \right) \cdot \int e^{-\mu x} dx + C. \quad (18)$$

Then, the flux J_c at the condensing surface x_c in Fig. 2 is expressed as:

$$J_c = \left(1 + \frac{1}{D} \right) \cdot J_0 \cdot \mu \cdot e^{-\mu x_c} + C, \quad (19)$$

where C is the integration constant. Since cooling of

the vapor makes the boundary diffusion layer thinner, that is to make x_c smaller, according to Eq. (19) the magnitude of J_c becomes larger. The fact that when argon gas is blown over the liquid iron under vacuum, one observes fumes standing upward may be the consequence of cooling the vapor of iron.

As an illustrative example of the enhanced evaporation by reacting gas, when an oxidizing gas like argon+oxygen mixture is blown over liquid iron under vacuum, the iron vapor is oxidized to form iron oxide particles. As a result of this reaction, the partial pressure of oxygen influences the rate of vaporization of the iron. As the partial pressure of oxygen in the gas stream increases, the thickness of the boundary diffusion layer for metal vapor increases, resulting in an increased rate of vaporization. When molten silicon is attacked by a stream of argon+nitrogen mixture under vacuum, there is a marked increase in the vaporization rate with increasing nitrogen partial pressure. The accelerated vaporization in this case was attributed to the formation of silicon nitride, Si_3N_4 .³⁾ The top-blowing of ammonia gas onto liquid pure copper under atmospheric pressure also accelerates the vaporization of copper.⁴⁾ The same phenomena are observed when the urea (NH_2CONH_2) is blown onto liquid pure copper and iron.⁵⁾ The marked increase in the rate of vaporization in these cases is caused by direct formation of gaseous nitrides.

6. Restriction of Evaporation

In order to account for the probability that some of the vaporized atoms collide with foreign gas molecules and are reflected during passing through the boundary diffusion layer, Knudsen⁶⁾ has inserted α , evaporation coefficient, into Eq. (10) describing the maximum rate of evaporation. The inert gas effect on the rate of evaporation has been well recognized. In the presence of argon or helium, the diffusivity of the metal vapor in Eq. (19) becomes smaller than in perfect vacuum.

Evaporation is essentially endothermic process, and the heat of evaporation must be fixed. However, that in many cases observed activation energies for evaporation differ from that heat can be justified as the contamination of the evaporation surface by oxide film and the presence of absorbed residual gas on the liquid surface. In some gases, particularly hydrogen and helium, the amount of heat given up to the gas by the solid and liquid is only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with it before leaving. This fraction is called the accommodation coefficient.⁷⁾ Changes in the accommodation coefficients of the residual gases will affect the rate of evaporation.

When oxygen is dissolved in liquid iron and copper, the rate of evaporation decreases with increase in oxygen concentration.⁸⁾ It is thought that oxygen dissolved in liquid metals behaves as a surface active element and oxygen atoms occupy the active sites on the surface of liquid metals, so the base metals vaporize through available oxygen free sites.

7. Selective Evaporation

Selective evaporation is concerned with the predom-

inant vaporization of particular substances from the solid and liquid of multi-component system. Because escaping tendency of a component from the condensed phase is related to the fugacity which is defined as its equilibrium partial pressure over this phase, the selective evaporation is conducted more effectively in vacuum at high temperatures because the fugacity is larger in such conditions like purification of metals.

Selective evaporation via chemical reaction may be also a key to the vacuum refining of metals. For example, carbon and oxygen dissolved in liquid iron can easily eliminated to a very low level of concentration by vaporizing as CO gas molecule under vacuum. Oxygen in niobium can be removed by vaporization of volatile suboxide of base metal, NbO, under vacuum at high temperatures. Selective vaporization of copper dissolved in liquid iron can be made by blowing the ammonia and urea gas under reduced pressure maintained by continuous evacuation.^{9), 10)} The ammonia and urea gases undergo cracking on the metal surface to produce hydrogen and nitrogen in nascent state, which will react with copper atoms revealed on the active sites of the metal surface to form the gaseous copper hydride and nitride.

8. Conclusion

Three key factors, the evaporation under high vacuum or under poor vacuum, the enhancement and the restriction of vaporization, are all important processes involved in vacuum metallurgical operations. Langmuir equation is often employed to evaluate the rate of actual vaporization under reduced pressure.

However, it must be noted that this equation is based on the kinetic theory only applicable to the evaporation under perfect vacuum, so that one must take into account of some error in his evaluation. Regarding to the enhanced or selective vaporization, they are in some cases achieved by making use of chemical reactions.

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