

Mole fraction modification of binary alloys during thermal evaporation

A. Ramírez*

Benemérita Universidad Autónoma de Puebla
 Instituto de Ciencias, 17 Oriente # 1603, Puebla, Pue., México

A. Zehe

Facultad de Ciencias Físico-Matemáticas,
 Apdo. Post. # 1505, 72000 Puebla, Pue., México.

Thermal evaporation of binary alloys occurs in a number of practical applications, as e.g. in the fabrication of electrical resistors by use of a Cr-Ni alloy. The chemical composition of the alloy determines the physical properties of the deposited film. During the evaporation process the number of atoms of both species and thus source, vapor and thin film compositions are continuously changed, with possible adverse effects on the film properties. In order to maintain high quality features in mass production of devices and components, it is important to know the mass fraction that may be evaporated without modifying too much the intended composition of the thin film of the binary alloy. The present paper describes a theoretical analysis of the evaporation behavior of a molten binary alloy through changes in the chemical composition of the source, the vapor, and the thin film during the process. We employed Rault's law to described the relation between partial vapor pressure and composition for an ideal alloy and for the evaporation of pure metals the Hertz-Knudsen equation.

Keywords: binary alloys, thin film, mole fraction, vapor pressure.

1. Introduction

The manufacture and the technological use of thin films are well established, but still are subject of dynamic development. Diverse processes for producing thin films have made it possible to manufacture a wide variety of products [1, 2]. In the area of magnetic data recording, ferromagnetic films made of CoFe and NiCr alloys are used. Optical data storage, based on the Kerr effect, is realized employing Co/Pt and CoNi films. Even simple electrical resistors are fabricated by thermal evaporation of CrNi alloys [3].

The underlying technological problem in all these cases is to translate the chemical composition of an alloy A_xB_y in the evaporation source (with $x+y = 1$), to the thin film on the substrate.

Given a certain difference in the partial vapor pressures of the components of the alloy, as the evaporation proceeds, the concentration of the involved components in the crucible, and thus on the substrate, will continuously change. As consequence the physical properties of the deposited films will change. It is the aim of this paper, to study the evaporation process of a binary alloy through the evolution of the chemical composition of the alloy A_xB_y and its transformation to $A_{x_f}B_{y_f}$ in the thin film (f) on the substrate.

1. Definitions and calculations

We consider a common evaporation process [4] as shown in figure 1. The crucible is filled with a binary alloy A_xB_y , with n_0 being the initial number of gram-Moles. The molar fractions of the A and B components are represented by x and y respectively. The subscripts s , v and f represent the molar fractions of the each component in the crucible, the

vapor and the film respectively. For instance, the amount of component A present in the crucible at the beginning of evaporation is $n_0 \times x_s$.

We suppose that the A component has a higher vapor pressure than B, as commonly happens in most of the alloys. After a time interval Dt of the evaporation process a number of Dn mols is evaporated.

The vapor space contains both species A, B in an initial relation $x_v \times Dn$ and $y_v \times Dn$, respectively. Obviously the initial number of atoms A in the crucible minus the number of atoms A in the vapor space is the same as the missing number of atoms A in the crucible:

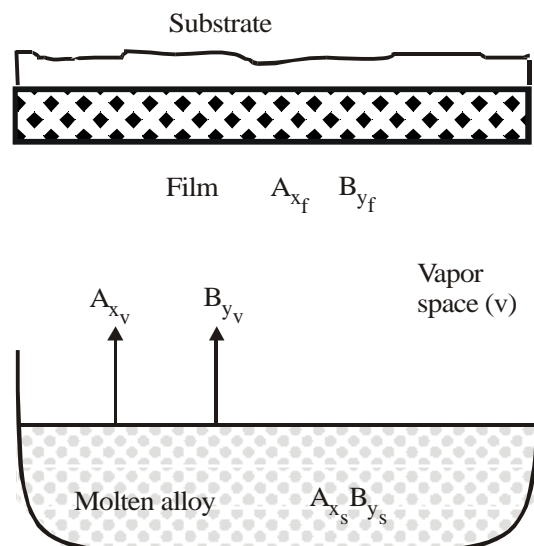


Fig. 1: Vacuum chamber with evaporation source at temperature T containing a binary alloy $A_x B_y$. The film deposited on the substrate will be formed of a composition $A_{x_f} B_{y_f}$ different from the original alloy.

$$x_v dn - x_s dn = n dx_s \tag{1}$$

$$\frac{dn}{n} = \frac{dx_s}{x_v - x_s} \tag{2}$$

After integration from n_0 to n and x_{s0} to x_s we obtain:

$$\ln\left(\frac{n}{n_0}\right) = \int_{x_{s0}}^{x_s} \frac{dx_s}{x_v - x_s} \tag{3}$$

We define the range of evaporation Z as the interval $\langle x_{s0}, x_s \rangle$, which in a certain sense can be understood as the difference in the level of the filling prior and after the evaporation in the crucible:

$$Z = Z \Big|_{x_{s0}}^{x_s} = \frac{\Delta n}{n_0} = 1 - \frac{n_A}{n_0} \tag{4}$$

Combining eq. (3) and (4) results in:

$$Z = 1 - \exp\left[\int_{x_{s0}}^{x_s} \frac{dx_s}{x_v - x_s}\right]. \tag{5}$$

Then, for a given evaporation range Z at any time, the mole fraction x_v of the A component in the vapor space takes a mean value \bar{x}_v :

$$\bar{x}_v \Big|_{x_{s0}}^{x_s} = x_s + \frac{(x_{s0} - x_s)}{\left\{1 - \exp\left[\int_{x_{s0}}^{x_s} \frac{dx_s}{x_v - x_s}\right]\right\}} \tag{6}$$

Supposing a sticking coefficient on the substrate equal to 1 for all the atoms in the vapor space, we can obtain from eq. (6) the mole fraction of the component A in the film.

In order to resolve the integral in eq. (6) it is necessary to find a relation between x_v and x_s , which is particular for any

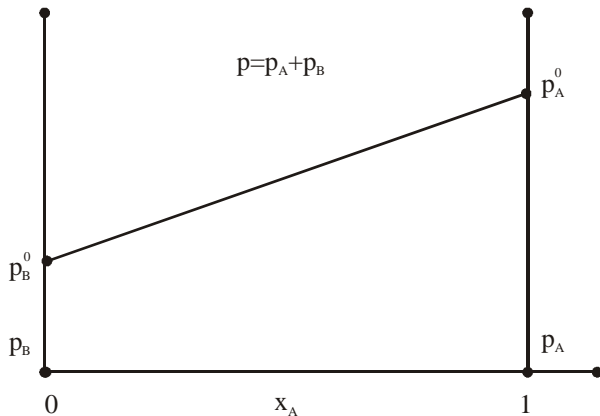


Fig. 2: Representation of the Raoult's law: The vapor pressure p of an ideal solution (binary alloy) depends only on the mole fraction x_A (concentration) of component A dissolved in B .

alloy. In a first approach we consider alloys obeying Raoult's law (see fig. 2), where the vapor pressure p of the component A dissolved in a solution of the component B depends only on the concentration of that component [5],

$$p_A(T) = p_A^0(T) \cdot x \tag{7}$$

$$p_B(T) = p_B^0(T) \cdot (1 - x) \tag{8}$$

Where p_A and p_B are the partial vapor pressures of the components A and B respectively, in the molten binary alloy. p_A^0 and p_B^0 are the vapor pressures of the pure metals composing the alloy.

The evaporation of a pure metal in vacuum obeys the Hertz-Knudsen equation [6]:

$$J = \frac{\alpha p(T)}{\sqrt{2\pi MRT}}, \tag{9}$$

where:

α - dimensionless evaporation coefficient,

M - molecular weight [$g \cdot mol^{-1}$]

R - universal gas constant ($8.315 \times 10^7 \text{ erg} \cdot K^{-1}$)

J - number of molecules leaving the source per cm^2 per s.

The composition of the vapor with respect to x_v is described by:

$$x_v = \frac{J_A}{J_A + J_B} = \frac{p_A(T) / \sqrt{M_A}}{p_A(T) / \sqrt{M_A} + p_B(T) / \sqrt{M_B}}. \tag{10}$$

By using of eq. (7, 8), we get from eq. (10):

$$\frac{x_v}{1 - x_v} = \frac{p_A^0(T) \sqrt{M_B} x_s}{p_B^0(T) \sqrt{M_A} (1 - x_s)} = b \frac{x_s}{1 - x_s}. \tag{11}$$

where b is defined as a number which depends on the physical properties of the components forming the alloy.

The relation between x_v and x_s is now:

$$x_v = \frac{b x_s}{1 + (b - 1) x_s} \tag{12}$$

and can be used in order to resolve the integral of eq. (5):

$$\int_{x_{s0}}^{x_s} \frac{dx_s}{x_v - x_s} = \frac{1}{b - 1} \left(\ln \frac{x_s}{x_{s0}} - b \ln \frac{1 - x_s}{1 - x_{s0}} \right) \tag{13}$$

The evaporation range Z and the mole fraction x_f of the component A in the deposited film are given by:

$$Z = 1 - \exp \left[\frac{1}{b-1} \left(\ln \frac{x_s}{x_{s0}} - b \ln \frac{1-x_s}{1-x_{s0}} \right) \right] \quad (14)$$

$$x_f \Big|_{x_{s0}}^{x_s} = x_s + \frac{(x_{s0} - x_s)}{1 - \exp \left[\frac{1}{b-1} \left(\ln \frac{x_s}{x_{s0}} - b \ln \frac{1-x_s}{1-x_{s0}} \right) \right]} \quad (15)$$

2. Results

The expressions from eqs. (12), (14) and (15) are graphically represented in figs. 3 and 4 as:

$$\begin{aligned} x_s &= x_s(Z) \text{ from eq. (14),} \\ x_v &= x_v(Z) \text{ from eq. (12),} \\ x_f &= x_f(Z) \text{ from eq. (15),} \end{aligned}$$

with **b** taken as a parameter.

The results were obtained considering the binary alloy A_xB_y with the mole fractions of $x_{s0}=0.5$ and $x_{s0}=0.8$. The specific nature of the *A* and *B* components (as e.g. size and shape of the molecule) is included in the **b** parameter. At the beginning of the evaporation process ($Z=0$, eq. 4) the mole fraction *x* corresponds to the initial value x_{s0} of the molten alloy. As the evaporation time increases, all mole fractions of the *A* component, x_s , x_v and x_f suffer a continuous change with a relatively steep fall close to $Z=1$ (empty crucible with respect to n_A). At the start (crucible almost full) and the end of the evaporation process (crucible almost empty) changes in the film composition are emphasized and as a consequence the physical properties of the films grown at the beginning and at the end of the evaporation process are quite different. In fig. 3, the behavior of x_s , x_v and x_f is presented for three values of the **b** parameter: 2, 6, and 10. The initial composition of the component *A* in the crucible was $x_{s0}=0.5$. It is seen in fig. 3b that the composition of the vapor has strongly changed as the evaporation process of the ideal alloy evolves (from $Z=0$ to 1). As the **b** value increases, the change in the composition of the vapor is larger. Fig. 3c allows us to stimate the *Z* value of the alloy in order to obtain the desired composition of the film. Fig. 4 presents the results for x_s , x_v and x_f when the initial composition of the alloy is $x_{s0}=0.8$. Here, the composition of the vapor is more or less constant up to a certain evaporation level, but suffers a rapid change beyond this value (at about $Z=0.6$).

3. Discussion

The composition of the vapor is drastically changed during the evaporation process of a binary alloy as shown in figs. 3 and 4. This effect is more pronounced for an alloy with large β -values, i.e. when either the molecular weights or the vapor pressure properties of the alloy-forming species, or both are very different.

From these graphics, the ideal evaporation range *Z* can be chosen to produce a thin film with a specific composition,

as well as when the evaporation process is interrupted in order to recharge the crucible.

An additional aspect must be mentioned. As it is seen in figs. 3a, 3b and 4a, 4b, the composition of the condensing film changes more rapidly than the average composition \bar{x}_f of the whole film. If the diffusion processes during the

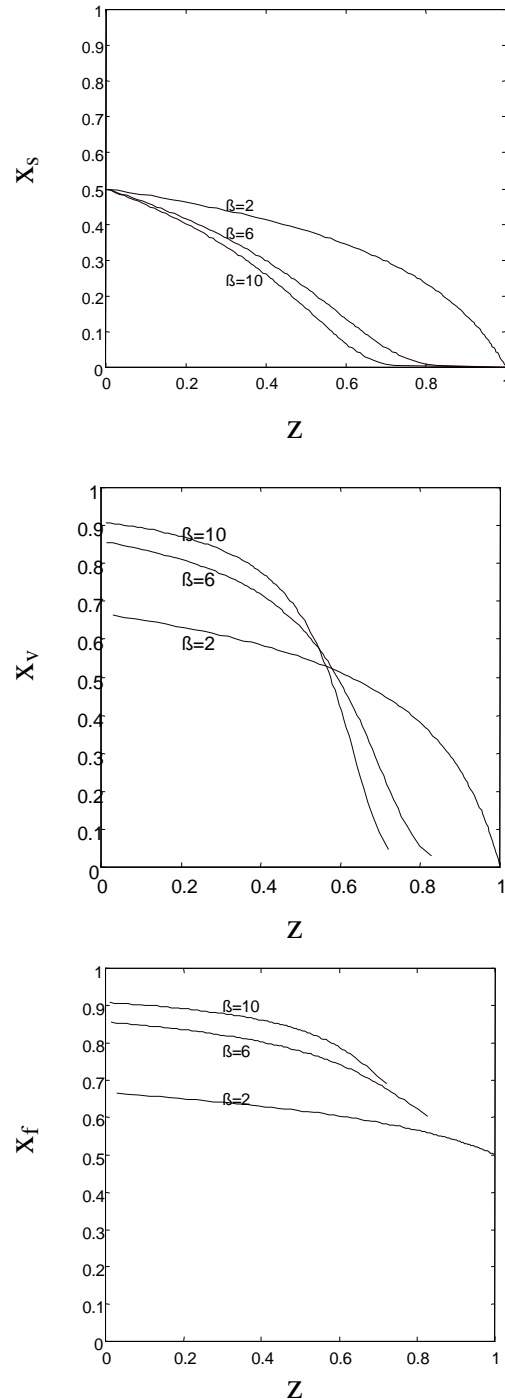


Fig. 3: Mole fraction of the volatile component of an ideal alloy A_xB_y as a function of the evaporating range *Z*, with an initial value $x_{s0}=0.5$; (a) mole fraction x_s in the crucible; (b) x_v in the vapor space; (c) x_f in the deposited film.

deposition are slow, the composition of the alloy close to the substrate–film interface will be different from that close to the surface of the film. Then, the utilization of such a thin film as an electrical conductor could provoke additional diffusion processes during its operation with a number of undesired effects, as e.g. a slow change of the electrical conductivity.

Acknowledgements

The authors are grateful to CONACyT for financial support, and to L. Alonso, Facultad de Cómputo de la BUAP, for computational assistance.

References

- [1] G. Kienel (ed.), “Vakuumbeschichtung”, ed. VDI Verlag, Dusseldorf 1994.
- [2] F. F. Y. Wang, “Materials Processing: Theory and Practices” ed. North Holland, Amsterdam 1980.
- [3] A. Zehe, “Tecnologías y Sistemas en Alto Vacío”, ed. TECNOPLUS, México 1996.
- [4] J. F. O’Hanlon, “A users guide to vacuum technology” Intersci. Publ. J. Wiley & Sons, N.Y. 1980
- [5] P. W. Atkins, “Physical Chemistry”, ed. W. H. Freeman & Sons, San Feor 1978.
- [6] M. Knudsen, Annalen der Physik (Leipzig), **47**, 697 (1915).

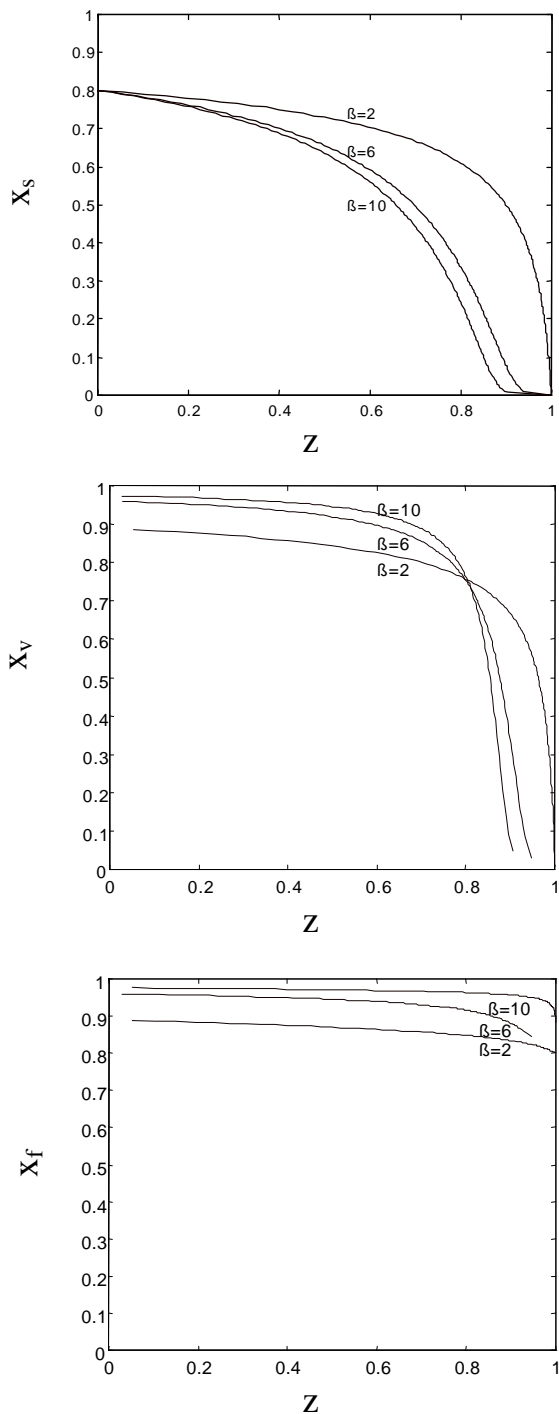


Fig. 4: Mole fraction of the volatile component of an ideal alloy A_xB_y , as a function of the evaporating range Z , with an initial value $x_0 = 0.8$; (a) mole fraction x_s in the crucible; (b) x_v in the vapor space; (c) x_f in the deposited film.