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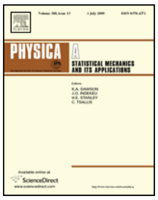

Phase transitions in solid–liquid–gas systems with applications to alkali metal generators

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ABSTRACT

Motivated by physical applications we consider a mathematical model describing the evaporation process in solid–liquid–gas systems with two moving boundaries of the phase transition. An alkali metal generator with a working substance in the form of an intermetallic compound and the evaporation of a volatile component into a vacuum is considered. Explicit analytical solutions of the problem under consideration are constructed in three different geometries of the process. We demonstrate that the evaporation boundary moves much more slowly than the dissolution boundary and the liquid layer thickness increases with time. The role of the evaporation coefficient on the evaporation stream and the nonlinear dynamics of the process is studied. An approach developed in the present study can be used for solutions of mathematical models describing similar Stefan-type processes met in other areas of applied physics.

1. Introduction

The seemingly trivial problem of the time evolution of a phase transition boundary comes under the rubric of the so-called Stefan problems. Stefan published theoretical and experimental papers on the theory of heat and mass transfer in fluids [1,2], on the growth of sea ice [3], and on evaporation processes [4]. In these works Stefan describes mathematical models for physical problems, containing an unknown time-dependent interface position. Since Stefan gives the first detailed analysis of these problems, moving boundary problems are called Stefan-type problems. Therefore, their rich nonlinear behavior, has attracted a substantial research interest in the field of transport phenomena (e.g. Refs. [5–7]), and their ubiquity in fields ranging from geophysics to material physics has stimulated a continual rediscovery of Stefans work. Generally speaking, explicit analytical solutions of the Stefan-type problems on evaporation are unknown due to the fact of nonlinearities in the boundary conditions imposed at the time-dependent phase transition interfaces (see, among others, steady-state approximations [8] or numerical schemes developed for unsteady-state conditions [9]). The present paper develops analytical approaches for the solution of Stefan-type evaporation problems met in different areas of applied physics.

Solid–gas phase transitions in the presence of a thin liquid layer produced by a melting process occur in many engineering, environmental, and technological systems, including metallurgy, geophysics, crystal growth, electronics, applied physics, etc. In many applications, the evaporation processes from alloys containing a volatile component form the basis of a large number of technological processes such as the deposition of metallic films [10] or the refining of metals [11]. In many cases, the evaporation and deposition procedures in alloys are complicated by the diffusion mechanism: the decrease of the concentration of the volatile component leads to phase changes, which modifies the evaporation and melting rates. This situation is typical, e.g., for intermetallic generators of the alkali metals. These metals are widely used in the deposition

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of the photocathode materials (Cs_3Sb, Na_2KSb, etc.) and in the treatment of the ready metal (W, Ni, etc.) or semiconductor (Si, GaAs, etc.) surfaces by vapour [12]. The thermal disintegration in a vacuum of a solid or melted intermetallics containing alkali components has been cited as an example of the alkali metal vapour production [12]

$$\mathrm{A}_n\mathrm{Me}_m \to \mathrm{A}_x + \mathrm{A}_{n-x}\mathrm{Me}_m - \Delta H,$$

where $0 < x \le n$, A is an alkali metal, Me is an element, the vapour pressure of which under the deposition temperature is many times lower than the vapour pressure of the component A, and ΔH is the thermal effect of the reaction. The intermetallic compound $\mathrm{A}_n\mathrm{Me}_m$ (e.g., synthesised by the ampoule-vacuum method [13]) can be prepared as a compact ingot, and the second component, Me, can be selected so that partial pressures of vapour of the components P_A and P_Me would satisfy the condition $P_\mathrm{Me}/P_\mathrm{A} \sim \varepsilon$ ($\varepsilon \sim 10^{-8}$ according to the estimates given by Chuntonov and Mansurov [12,14] and $\varepsilon \sim 10^{-6}$ according to the experiments discussed by Chuntonov and Setina [15]). The aim of the present paper is to develop the theory of phase transitions for these materials when they are heated up to the temperatures of deposition.

2. The model

Let us consider the model of a direct-fired generator, the working substance of which represents a wire [16] or spherical granules [12] of the composition $\mathrm{A}_n\mathrm{Me}_m$ covered by a thin shell of the second component Me. For the sake of simplicity, the one-dimensional model of the process under consideration related to Cartesian coordinates will be our initial concern. The main principles of the problem in the given case remain the same and the theoretical analysis becomes easier.

The generator, the scheme of which is demonstrated in Fig. 1, is filled with an intermetallic compound $\mathrm{A}_n\mathrm{Me}_m$. This compound is isolated by a thin layer of the Me component from the outer atmosphere. This layer is firmly kept on the surface by adhesion forces of the solid phase $\mathrm{A}_n\mathrm{Me}_m$ for the phase diagram of system A − Me shown in Fig. 1. The thin layer in thermodynamic equilibrium with the $\mathrm{A}_n\mathrm{Me}_m$ crystals protects atoms of A from evaporation in the stage of storage at the temperature preventing heating (T_h in Fig. 1). Increasing the temperature up to the working temperature $T \ge T_w$ increases the value $C \ge C_0$ and, as a result, a stream of evaporation of J arises. This process leads to a concentration gradient in the liquid layer which reaches the liquid–solid boundary (the surface of $\mathrm{A}_n\mathrm{Me}_m$ crystals). As a result, a decrease in the concentration causes a dissolution of the liquid–solid boundary. Thus, the process under consideration is divided into three regions (solid, liquid and gas layers) by two moving phase transition boundaries, the evaporation boundary gas–liquid and the dissolution boundary, liquid–solid. The mathematical models of such processes originating from the frontal formulation of the Stefan problem [6] represent nonstationary sets on nonlinear equations and boundary conditions in partial derivatives with moving boundaries of the phase-transition regions. As is known, there are no general methods of solving such problems. This work is devoted to the the derivation of explicit solutions of the process of isothermal evaporation in the system under consideration under the assumption that the transfer of the volatile component is carried out by way of molecular diffusion.

Initially, at time $t = 0$, the region $-R_{GL}(0) < r < 0$ is filled with the liquid at a concentration of C_S/k ($k \gg 1$ is the equilibrium partition coefficient determined from the phase diagram; see, among others, [17]), whereas the region $r > 0$ is occupied by the solid material at a concentration of C_S (Fig. 2). At $t > 0$, the evaporation process of the component A into the gas phase begins from the gas–liquid boundary $r = R_{GL}(t)$. We shall now consider the case $P_\mathrm{Me} \ll P_\mathrm{A}$ (or $P_\mathrm{Me} \to 0$) so that the evaporation stream J can be treated as a linear function of the concentration of the A component on the phase transition boundary $r = R_{GL}(t)$ in the form $J = \alpha C$, where $\alpha = aKM_B/\rho(2\pi M_\mathrm{A}RT)^{1/2}$ is the reduced evaporation coefficient [14] (a is the evaporation coefficient, K is the Henry constant, ρ is the mean density of the liquid layer, R is the gas constant, M_A and M_B are the molecular weights of the components A and Me). This quantity is weakly dependent on the concentration [12], which we shall first consider to be constant.

The mass balance conditions at the moving evaporation and dissolution boundaries can be written in a standard form by analogy with the Stefan problem of binary melt solidification (see, among others, [18])

$$\frac{C_S}{k}\frac{\mathrm{d}R_{LS}}{\mathrm{d}t} + D\frac{\partial C}{\partial r} = C_S\frac{\mathrm{d}R_{LS}}{\mathrm{d}t}, \quad r = R_{LS}(t), \tag{1}$$

$$J = \alpha C = \rho\frac{\mathrm{d}R_{GL}}{\mathrm{d}t}, \quad r = R_{GL}(t), \tag{2}$$

$$C\frac{\mathrm{d}R_{GL}}{\mathrm{d}t} + D\frac{\partial C}{\partial r} = \alpha C, \quad r = R_{GL}(t), \tag{3}$$

where D is the coefficient of diffusion of the component A in the liquid layer.

We consider the phase transition interface $r = R_{LS}$ at equilibrium. In this case, we have the following condition at the boundary of dissolution

$$C = C_S/k, \qquad r = R_{LS}(t). \tag{4}$$

It is of interest to estimate the concentration relaxation time t_C and the characteristic time t_{LS} of the movement of the liquid–solid boundary (e.g., asymptotic solutions obtained by Chuntonov and Mansurov [12,14] show that the evaporation boundary moves much more slowly than the dissolution boundary). These times can be written in the form

$$t_C \sim R_{LS}^2/D, \qquad t_{LS} \sim R_{LS}/(\mathrm{d}R_{LS}/\mathrm{d}t).$$