

PHASE TRANSITION IN METAL OXIDES UNDER IRRADIATION

V. A. VOLPERT*, L. D. MARKS and R. AI

*Center for Surface Radiation Damage Studies,
Department of Materials Sciences and Engineering, Northwestern University,
Evanston, IL 60208*

(Received 16 September 1992)

A model to describe experimental results on phase transitions in vanadium oxides was suggested recently by Marks, Volpert and Ai (1992). This work is devoted to a more detailed analysis of the model. An analytical approach to the problem based on a quasistationary approximation is used to find the distribution of the concentration and the interface velocity. A multiplicity of modes of the interface propagation is shown to be possible depending on the kinetics of the phase transformation. The stability of the interface to small perturbations is studied. Two-interface propagation is also considered.

KEY WORDS: Electromicroscopy, irradiation, metal oxides, interface propagation.

1 INTRODUCTION

There are many experimental results which show that surface radiation damage can lead to a transformation of maximal valence transition metal oxides into lower oxides or metals (DIET I, 1983). A special experimental method involving high resolution electron microscopy provides the possibility of studying the kinetics of the process (Marks, 1983; Marks and Smith, 1984; Singh and Marks, 1989; Ai, Fan, Stair and Marks, 1990). In some cases, phase transition routes are rather complicated and depend on the intensity of the electron flux (Ai, Fan and Marks, 1992). In particular, more than one interface can propagate into a sample from the surface. Phase separation in the bulk due to precipitation was also observed.

A theoretical description of the process was given recently (Marks, Volpert and Ai, 1992). Comparison with experimental data showed that the model, though rather simplified, reflected the main features of the experiments. In this paper we continue the theoretical investigation. We begin with a brief description of the process and recap the model and results of the previous study. Then we apply an analytical approach to the problem based on a quasistationary approximation (Section 2). Section 3 is devoted to an analysis of the interface stability. Finally, two-interface propagation is considered in Section 4.

Schematically, phase transitions in metal oxides under irradiation can be represented in the following way. There is an electron flux which is perpendicular to

* Current address: Department of Mathematics, University Lyon I, 69622 Villeurbanne Cedex, France.

the surface of a sample. It leads to a loss of oxygen from the material, probably oxygen ions due to a process such as interatomic Auger decay (see Knotek and Feibelman, 1978a, 1978b). The oxygen loss occurs only from the profile edge (side surface). (Experimentally, if new phases were formed at the top and bottom surfaces, this would have been readily visible.) The exact reason why the loss occurs primarily from the side surface is still unclear, but is probably due to the dipole polarization normal to the electron beam of energy losses with high energy electrons. The loss of oxygen in effect creates oxygen vacancies at the surface which can diffuse into the material. At some level of oxygen deficiency a phase transformation to a lower oxide takes place at the side surface, and the interface appears near it and propagates into the sample. This first phase transition can be followed by others.

To describe the process, we consider a simplified model which includes diffusion of oxygen in the bulk and movement of the interface. The interface movement can be determined by the balance of mass on the interface and by two additional relations connected with the kinetics and thermodynamics of the phase transition. The values of the concentration on the interface and the interface velocity can then be obtained.

Thus we consider the free boundary problem

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2}, \quad 0 < x < y(t), \quad y(t) < x < L \quad (1.1)$$

$$x = 0: \frac{\partial u}{\partial x} = hu, \quad x = L: \frac{\partial u}{\partial x} = 0 \quad (1.2)$$

$$x = y: D \left(\frac{\partial u}{\partial x} \Big|_{y-0} - \frac{\partial u}{\partial x} \Big|_{y+0} \right) = y'(u_+ - u_-) \quad (1.3)$$

$$g \left(u|_{y \pm 0}, \frac{\partial u}{\partial x} \Big|_{y \pm 0}, y' \right) = 0 \quad (1.4)$$

$$y' = f(u_+, u_-) \quad (1.5)$$

$$t = 0: u = u_0. \quad (1.6)$$

Here u is the concentration of oxygen, D the diffusion coefficient, h a constant which characterizes the loss of oxygen through the side surface and which is supposed to be proportional to the value of the electron flux, u_0 an initial concentration of oxygen,

$$u_{\pm} = u(y(t) \pm 0, t), \quad \frac{\partial u}{\partial x} \Big|_{y \pm 0} = \frac{\partial u(y(t) \pm 0, t)}{\partial x},$$

and $y' = dy/dt$. The notation $y(t) \pm 0$ means that the limit is taken, as x tends to $y(t)$ from the right or the left. Condition (1.3) gives the balance of mass on the interface. (1.5) is a kinetic equation. Condition (1.4), which is necessary to have a well-posed problem, is given here in a general form. We specify the functions f and g below. We note that the conditions on the interface we consider here is close to those considered by Gurtin and Voorhees (1992).

To complete the formulation of the problem we should put a condition on the interface appearance. We denote by y_0 the critical nucleus size and suppose that the interface appears for $t = t_0$ if $u(y_0, t_0) = u_e$. We have

$$y(t_0) = y_0, \quad u_{\pm}(t_0) = u_e.$$

In two-interface propagation the conditions on the second interface and of the second interface appearance are similar.

The problem under consideration was studied numerically by Marks, Volpert and Ai (1992) for linear kinetics and an impenetrable interface (see Section 2). It was shown that one interface propagation occurred for high values of the electron beam intensity (large h). For low values of the electron flux the appearance of the first interface accelerated the appearance of the second. Then the presence of the second interface led to a decrease of the first interface velocity, they merged and the intermediate phase disappeared. These results were in accordance with the experimental data (Ai, Fan and Marks, 1992).

We begin the analytical investigation of the problem with one-interface propagation.

2 ONE-INTERFACE PROPAGATION

Conditions on the interface

Consider the diffusion equation written in the moving frame such that the interface is located at the origin:

$$\frac{\partial v}{\partial t} = D \frac{\partial^2 v}{\partial x^2} + c \frac{\partial v}{\partial x}, \quad -y(t) < x. \quad (2.1)$$

Here $c = y'(t)$. The boundary conditions have the form

$$x = -y(t): \frac{\partial v}{\partial x} = hv \quad (2.2)$$

$$x = 0: D \left(\frac{\partial v}{\partial x} \Big|_{-0} - \frac{\partial v}{\partial x} \Big|_{+0} \right) = c(v_+ - v_-). \quad (2.3)$$

To specify (1.4), we consider the interface with a non-zero width located in the interval $l < x < 0$. Diffusion of oxygen inside the interface is described by the boundary value problem

$$\frac{\partial v}{\partial t} = D_i \frac{\partial^2 v}{\partial x^2} + c \frac{\partial v}{\partial x}, \quad -l < x < 0$$

$$v(-l, t) = v_-(t), \quad v(0, t) = v_+(t).$$

Here D_i is the value of the diffusion coefficient inside the interface. Using a quasistationary approximation we can find the concentration profile

$$v_i(x, t) = v_+ - \frac{v_+ - v_-}{e^{cx/D_i} - 1} (e^{-cx/D_i} - 1).$$

From the matching conditions at $x = 0$

$$D \frac{\partial v}{\partial x} \Big|_{+0} = D_i \frac{\partial v}{\partial x} \Big|_{-0} \quad (2.4)$$

we have

$$\frac{\partial v}{\partial x} \Big|_{+0} = \frac{c}{D} \frac{v_+ - v_-}{e^{cx/D_i} - 1}. \quad (2.5)$$

This equality determines the function g in (1.4). For the limiting case of small D_i (2.5) has the form

$$\frac{\partial v}{\partial x} \Big|_{+0} = 0. \quad (2.6)$$

This is the case of an impenetrable interface. Another possible limiting case is that of a small interface velocity. In this case we have

$$\frac{\partial v}{\partial x} \Big|_{+0} = d(v_+ - v_-) \quad (2.7)$$

where d is a constant.

We proceed now to the kinetic equation (1.5). Since we do not consider vacancies and interstitials in the model, as well as specific features of the original and the new crystal structures, the kinetics of the transition from the higher oxides to the lower oxides should be determined by the function f only. We assume that the reduction rate is a function of the concentration of oxygen on the interface, or, more precisely, of the deviation of the concentration from some equilibrium value $q = u_e - v_s$. Here u_e is the equilibrium concentration and v_s the mean value of the concentration on the interface. We take for simplicity $v_s = 0.5(v_+ + v_-)$. The rate of the reduction is supposed to be zero when the oxygen concentration on the interface is rather high, and the two phases are in equilibrium, and it increases with decreasing oxygen concentration. An example is linear kinetics when $f(q) = kq$. The second possible assumption about the kinetics is that the reduction rate can be decelerated by the products of the reduction. This is a well known effect for heterogeneous reactions and, in particular, for phase transformations in metal oxides (King, 1989). In our model we can take this effect into account assuming that the reduction rate is small for small values of the oxygen concentration on the interface (for large deviations from the equilibrium value). We consider a model function f of the form

$$f(q) = kq^n e^{-mq}$$

which reflects the specific features of the kinetics described above. Obviously, we have linear kinetics when $n = 1$, $m = 0$.

Linear Kinetics

We consider the problem (2.1)–(2.3), (2.5), (1.5), (2.6) with a linear function f . To find the solution analytically we apply a quasistationary approximation. We suppose that the concentration $v(x, t)$ to the right of the interface is equal to the initial value of the concentration

$$u(x, t) \equiv u_0, \quad 0 \leq x \leq L - y(t), \quad t \geq 0.$$

This is the case for an exact solution of the problem if the critical nucleus size y_0 is zero.

We assume that the interface location and its velocity change slowly, so that the concentration profile can be found as a stationary solution of (2.1)–(2.3). This approximation can be used if the characteristic diffusion time y^2/D is much less than the characteristic times of the changing of the interface location and the interface velocity:

$$\frac{y^2}{D} \ll \frac{y}{y'}, \quad \frac{y^2}{D} \ll \frac{y'}{y''}. \tag{2.8}$$

In this case we have from (2.1)–(2.3)

$$v(x, t) = u_0 \left(1 - \frac{\exp\left(-\frac{c}{D}(x + y)\right)}{1 + c/Dh} \right). \tag{2.9}$$

For linear kinetics ($n = 1, m = 0$)

$$y' = k \left(u_e - u_0 + \frac{u_0}{2} * \frac{\exp\left(-\frac{yy'}{D}\right)}{1 + y'/Dh} \right). \tag{2.10}$$

A simple analysis of (2.10) shows that if $u_e > u_0$ then $y' \sim k(u_e - u_0)$ and condition (2.8) is not satisfied. If $u_0 > 2u_e$ then there are no solutions with positive velocities. We consider now the case when $u_e < u_0 < 2u_e$. Then the interface velocity tends to zero as time increases and

$$y(t) \sim \left(2Dt \ln \frac{u_0}{2(u_0 - u_e)} \right)^{1/2}. \tag{2.11}$$

Condition (2.8) is satisfied if

$$\ln \frac{u_0}{2(u_0 - u_e)} \ll 1, \tag{2.12}$$

or u_0 is close to $2u_e$.

Condition (2.12) provides the applicability of the quasistationary approximation for large time. We can consider another case when (2.8) is also satisfied. This is the case of small y . Replacing (2.10) by

$$y' = k \left(u_e - u_0 + \frac{u_0}{2} * \frac{1}{1 + y'/Dh} \right). \tag{2.13}$$

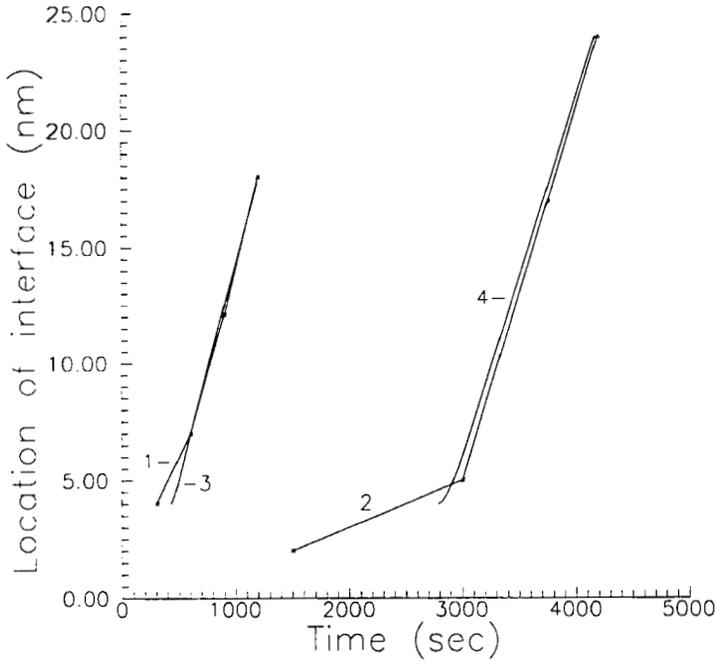


Figure 1 Location of the interface versus time: 1, 2—experimental results, 3, 4—numerical simulations; 1—flux 5.5 A/cm², 2—2.0 A/cm² (from [1]).

we can find the interface velocity explicitly as

$$\tilde{c} = -1 + \sqrt{1 + a}.$$

Here

$$\tilde{c} = \frac{c}{Dh + k(u_0 - u_e)}, \quad a = \frac{Dhk(2u_e - u_0)}{(Dh + k(u_e - u_e))^2}.$$

If $a \ll 1$ then we have approximately

$$y' \approx \frac{k(2u_e - u_0)}{2\left(1 + \frac{k}{Dh}(u_0 - u_e)\right)}.$$

We see that if $k(u_0 - u_e)/Dh \ll 1$ then the interface velocity depends on h (or the value of the electron beam intensity) weakly, and this is the case for the experimental results (see Figure 1).

The approximation of a constant interface velocity, developed above, is an intermediate asymptotic, when the velocity does not depend on the initial conditions, but the velocity decrease is still negligible. This approximation reflects the specific behavior of the experimental curves and of the numerical solution of the whole problem (Figure 1).

We note that the approximation gives a good description only for the second part of the experimental curve. The same is true for simulations of the whole problem (see Marks, Volpert and Ai, 1992). We recall that all the analysis above is fulfilled for linear kinetics. To give a better description of the experimental results we proceed now to more general kinetics where m and n are arbitrary.

Nonlinear kinetics

The applicability of the approximation of a constant velocity is determined only by the condition (2.8), and it does not depend on the kinetics of the phase transformation. Thus we can apply it not only to linear kinetics but to any other kinetic function. We have

$$c = f(u_e - \frac{1}{2}(u_0 + u_-)). \tag{2.14}$$

Here c is the interface velocity, $u_- = v(0, t)$ and can be found from (2.9)

$$u_- = u_0 \left(1 - \frac{1}{1 + c/Dh} \right). \tag{2.15}$$

Thus (2.14), (2.15) give an equation for c . Denoting

$$q = u_e - \frac{1}{2}(u_0 + u_-),$$

we have

$$Dh \left(\frac{u_0}{2(q + u_0 - u_e)} - 1 \right) = f(q). \tag{2.16}$$

This equation can have one or more solutions depending on the value of the parameters. We now find the conditions for non-uniqueness of the solutions. Equation (2.16) can be rewritten in the form

$$b \left(\frac{1}{w + a} - 1 \right) = w^n e^{-pw}, \tag{2.17}$$

where a, b, p, w are dimensionless parameters

$$a = 2 \frac{u_0 - u_e}{u_0}, b = \frac{Dh}{k} \left(\frac{2}{u_0} \right)^n, p = \frac{mu_0}{2}, w = \frac{2q}{u_0}.$$

There are 4 parameters in Eq. (2.17). In the corresponding 4-dimensional space there are different regions which correspond to different numbers of solutions of (2.13). These regions are separated by surfaces which are determined by two equations. One of them is (2.17), and the other one we obtain as an equality between the derivatives of the left-hand side and the right-hand side of (2.17) with respect to w :

$$-b \frac{1}{(w + a)^2} = w^{n-1} e^{-pw} (n - pw). \tag{2.18}$$

From (2.17), (2.18) we have

$$-w = (w + a)(1 - a - w)(n - pw). \quad (2.19)$$

We now look for solutions of (2.13) in the interval $0 < w < 1 - a$. If (2.19) does not have a solution in this interval, then (2.17) has only one solution for all b . If there are two solutions of (2.19) for some values of a, n, p then on increasing b , we intersect the surface which separates the regions with one solution and the region with three solutions twice. This means that, if for small b , (2.17) has one solution, then for b in some interval this equation has three solutions, and it has again only one solution for large b . Figure 2 shows a graphical solution of (2.17) for different values of the parameters.

Thus a non-uniqueness of solutions of (2.17) occurs if (2.19) has solutions in the interval $0 < w < 1 - a$. There are three parameters in this equation and, as above, there are different regions in the 3-dimensional space with a different number of solutions. In this case these regions can be found explicitly. To do this along with (2.19) we should consider again the equation which is obtained by differentiation of (2.19). Excluding w from them, we have an equation which determines the boundary of the regions. However, this equation is too awkward. Thus we consider here some limiting cases. We note that $0 < a < 1$, $n > 0$, $p > 0$, and $n/p < 1 - a$. This last inequality implies $w < 1 - a$.

The first limiting case we consider is $a = 0$. In this case (2.19) has two solutions if

$$n > p + 2\sqrt{p} \quad \text{or} \quad n < p - 2\sqrt{p}$$

Only the second solution satisfies the condition on the parameters presented above.

The second limiting case is when $a = 1$. Then $n = 0$ and p is arbitrary. Finally, if $n = 0$ then again from (2.19) we find that this equation has two solutions for $p > 4$.

Thus we can describe now the domain in (n, p, a) space where (2.19) has two solutions in the interval $0 < w < 1 - a$, or, the same, (2.17) has three solutions for some values of b . First of all it is located in the region

$$0 < a < 1, p \geq 4, 0 < n < p - 2\sqrt{p}.$$

Furthermore, for any positive n and a between 0 and 1 the multiplicity of solutions of (2.17) can occur for all p large enough.

Thus we can make the following conclusions. The asymptotic behavior of the solutions of (1.1)–(1.6) for large time does not depend on the kinetics of the phase transformation, and is unique. The behavior of the solutions for finite time can be described by the approximation of a constant velocity of the interface, and is determined by the kinetic function. In particular, there can exist one, two, or three modes of interface propagation with different velocities for the same values of the parameters. The multiplicity of solutions takes place in the case of strong deceleration of the reaction rate by the products of the reaction. If the kinetic parameters are taken in such a way that the multiplicity can occur, the number of solutions is determined by the value of the product Dh of the diffusion coefficient and the constant which characterizes the intensity of the electron flux. If it is large there is only one

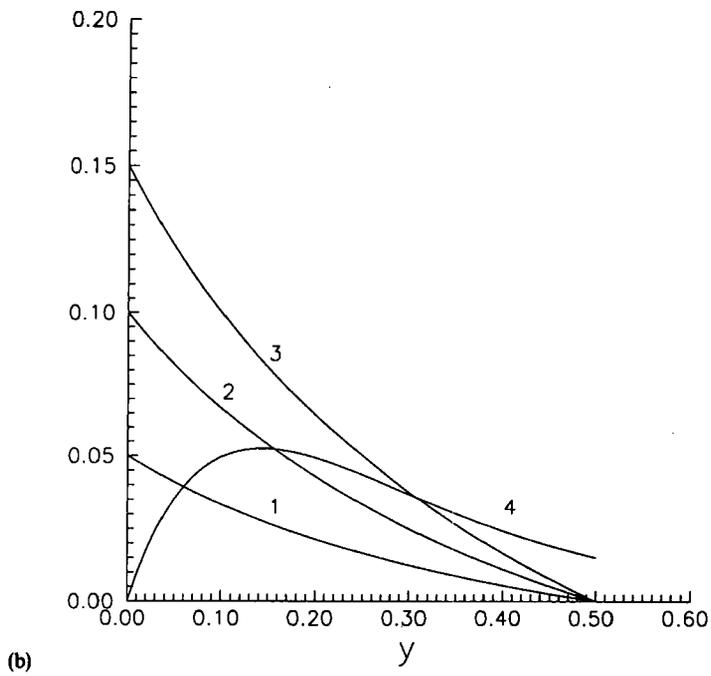
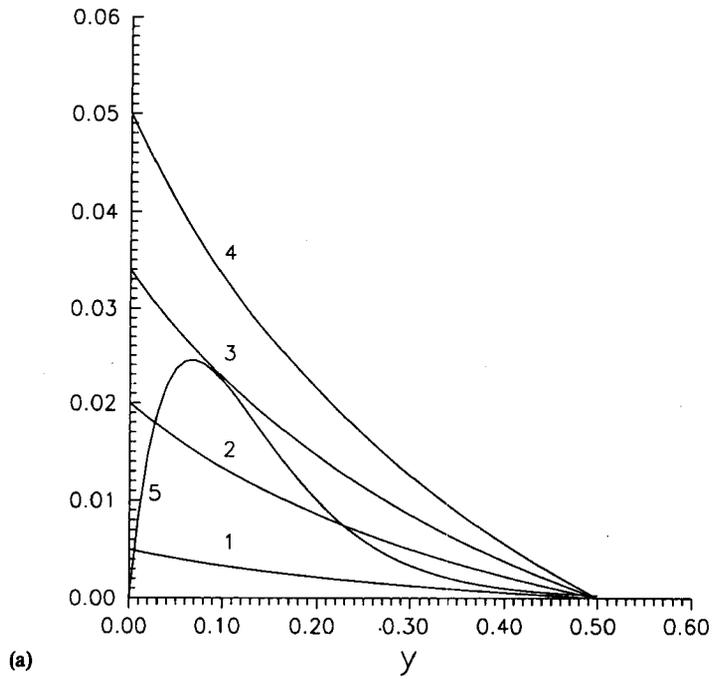


Figure 2 Graphical solution of (2.17), $a = 0.5$, $n = 1$. (a) $p = 15$, 1. $b = 0.005$, 2. 0.02, 3. 0.034, 4. 0.05; (b) $p = 7$, 1. $b = 0.05$, 2. 0.1, 3. 0.15.

solution with a small velocity (see Figure 2a). Decreasing Dh leads to a velocity increase. Then for a critical value of this quantity two more solutions appear. They coincide if the values of the parameters are equal to the critical ones, and they are different for the smaller values. Further decrease of Dh causes the disappearance of the solutions with small and intermediate velocities.

We return now to a comparison of the experimental and theoretical results. The experimental curves have two parts. On each of them the interface velocity is close to a constant, but first its value is small and then increases. The model (1.1)–(1.6) with linear kinetics gives an interface velocity close to a constant. This is a good approximation to the second part of the experimental curves, but does not describe the first one. If we consider now non-linear kinetics with deceleration of the reaction rate by the products, then a multiplicity of the modes of the interface propagation can occur. If this is the case and there are three modes for the same value of the parameters then the two with the largest and smallest velocities are stable, and the intermediate node is unstable (see the next section). This unstable solution has stable and unstable manifolds. Solutions approach the quasistationary solution along the stable manifold and move away from it along the unstable one. Therefore, if at some time a solution is close to the stable manifold, it will approach the unstable quasistationary solution, and the interface velocity will be close to the velocity of the interface for the intermediate solution. Then after some time the transition to the stable solution will occur, and the interface velocity will change. This behavior is similar to what was observed experimentally.

One more experimental result which confirms the explanation above is connected with the dependence of the interface velocity on the parameters. Increasing of the value of Dh leads to an increase of the interface velocity for the unstable intermediate solution. If we compare now the experimental curves which correspond to the values of the electron flux 2.0 A/cm^2 and 5.5 A/c^2 (Figure 1), we see that the interface velocity on the first part of the curve is greater in the second case when the values of the diffusion coefficient and constant h are greater (see Marks, Volpert and Ai, 1992).

We note that the multiplicity of stationary modes is well-known for chemical reactors and combustion processes (see Zeldovich, Barenblatt, Librovich and Makhviladze, 1985; Khaikin and Khudyaev, 1979) where it is caused also by an interaction of reaction and diffusion processes.

3 LINEAR STABILITY ANALYSIS

Stability of an interface to small perturbations can be studied by linearization of the problem on a stationary solution and investigation of the location of the eigenvalues. Such analysis has been performed for different phase transition problems (see, for example, Christian, 1981; Weeks, Saarloos and Grant, 1991). Phase transitions in metal oxides under irradiation have some specific features connected with the type of boundary conditions and the conditions on the interface. Moreover there is no stationary solution for the problem under consideration, and we will instead linearize it on the quasistationary solution which was found in Section 2.

Consider a two-dimensional formulation of the problem

$$\frac{\partial v}{\partial t} = D \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2} \right) + c \frac{\partial v}{\partial x} \tag{3.1}$$

$$x = -y: \frac{\partial v}{\partial x} = hv, \quad x = L - y: \frac{\partial v}{\partial x} = 0 \tag{3.2}$$

$$D \left(\frac{\partial v}{\partial x} \Big|_{\xi-0} - \frac{\partial v}{\partial x} \Big|_{\xi+0} \right) = (c + \xi'_t)(v_+ - v_-) \tag{3.3}$$

$$c + \xi'_t = f(v_+(\xi, t), v_-(\xi, t)) \tag{3.4}$$

$$\frac{\partial v}{\partial x} \Big|_{\xi+0} = 0 \tag{3.5}$$

Here z is the second spatial variable, $\xi(z, t)$ the location of the interface. We suppose that the function f depends on the difference $v_+ - v_-$, where v_+ is an equilibrium value of the concentration.

We can write a solution of (3.1)–(3.5) in the form

$$\xi = \varepsilon \exp(\omega t + ikz), \quad v = v_s + \tilde{v} \exp(\omega t + ikz), \tag{3.6}$$

where ω is an eigenvalue, k the wave number, v_s the quasistationary solution, \tilde{v} a small perturbation, ε a small parameter. Substituting the expression for v from (3.6) into (3.1), we have

$$D\tilde{v} + c\tilde{v}' - (\omega + Dk^2)\tilde{v} = 0.$$

Thus

$$\tilde{v}(x) = c_1 \exp(\mu_1 x) + c_2 \exp(\mu_2 x), \quad -y < x < \xi,$$

$$\tilde{v}(x) = c_3 \exp(\mu_1 x) + c_4 \exp(\mu_2 x), \quad \xi < x < L,$$

where

$$\mu_{1,2} = -\frac{c}{2D} \pm \left(\frac{c^2}{4D} + k^2 + \frac{\omega}{D} \right)^{1/2},$$

From the boundary conditions (3.2)–(3.5) we conclude that $c_3 = c_4 = 0$ and $v \equiv u_0$ for $x \geq \xi$.

We obtain from (3.2)–(3.4)

$$\tilde{v}'(-y) = h\tilde{v}(-y)$$

$$D\tilde{v}'(0) = -c\tilde{v}(0) + \varepsilon\omega(u_0 - v_s(0))$$

$$\varepsilon\omega = f'(v_s(0))(\varepsilon v'_s(0) + \tilde{v}(0))$$

We note that this system of equations is not solvable in the case $f'(v_s(0)) = 0$. This means that there are no eigenvalues with a positive real part in this case and the

solution is stable. If $f'(v_s(0)) \neq 0$ then the system can be written in the form

$$\tilde{c}_1 + \tilde{c}_2 = \varepsilon(\sigma\Omega - 1) \quad (3.7)$$

$$\frac{1}{2}\tilde{c}_1(d-1) - \frac{1}{2}\tilde{c}_2(1+d) = -(\tilde{c}_1 + \tilde{c}_2) + \varepsilon\Omega \quad (3.8)$$

$$\tilde{c}_1(d-1-\tilde{h})\exp((1-d)s) - \tilde{c}_2(1+d+\tilde{h})\exp((1+d)s) = 0 \quad (3.9)$$

Here

$$\tilde{c}_i = c_i \frac{D}{c(u_0 - v_s(0))}, \quad i = 1, 2, \quad d = (1 + \tilde{k}^2 + 4\Omega)^{1/2}, \quad \tilde{k}^2 = 4\left(\frac{kD}{c}\right)^2, \quad \Omega = D \frac{\omega}{c^2}$$

$$\sigma = \frac{c}{f'(v_s(0))(u_0 - v_s(0))}, \quad \tilde{h} = 2 \frac{Dh}{c}, \quad s = \frac{cy}{2D}.$$

The condition of nontrivial solvability of (3.7)–(3.9) with respect to c_1, c_2, ε gives an equation for Ω

$$(d-1-\tilde{h})[(d-1)\Delta + 2\Omega] = (d+1+\tilde{h})[(d+1)\Delta - 2\Omega] * \exp(2ds), \quad (3.10)$$

Here $\Delta = \sigma\Omega - 1$. The interface is stable if the real part of Ω is negative for all k , and it is unstable if Ω lies in the right half plane of the complex plane for some k . If Ω has zero real part then (3.10) gives the stability boundary. It corresponds to cellular instability if $\Omega = 0, \tilde{k} \neq 0$, and to oscillatory instability if $\Omega = i\phi, \phi \neq 0$.

We recap that (3.10) is obtained by linearizing the problem on a quasistationary solution which is obtained under the assumption $cy/D \ll 1$. To have the stability analysis consistent with the quasistationary analysis we should put in (3.10) $s = 0$. In this case equation (3.10) can be solved explicitly as

$$\Omega = \frac{\tilde{h} + 2}{\sigma(\tilde{h} + 2) - 2}. \quad (3.11)$$

It follows from (3.11) that the interface is stable for $f' < 0$. In particular, this is the case for linear kinetics. The condition for instability of the interface is

$$\sigma > \sigma_c = \frac{2}{\tilde{h} + 2} \quad (3.12)$$

It was shown in the previous section that a multiplicity of solutions can occur, and for some critical values of the parameters two solutions appear or disappear. The usual situation is that for critical parameters the linearized system of equations has zero eigenvalue. But we see from (3.11) that there are no zero eigenvalues for any values of the parameters. Formally there is one for $f'(v_s(0)) = 0$ but (3.10) is obtained when this derivative is not equal to zero. When it equals zero all the eigenvalues are negative (see above). In our case the solutions bifurcate not for zero for for an infinite eigenvalue. To show this we should differentiate (2.14) with respect to c (u is given by (2.15)). This equation defines the parameters when two solutions merge, and it coincides with (3.12). From this we can conclude that the solution with a large interface velocity is stable, and an intermediate one unstable. Indeed, we know that

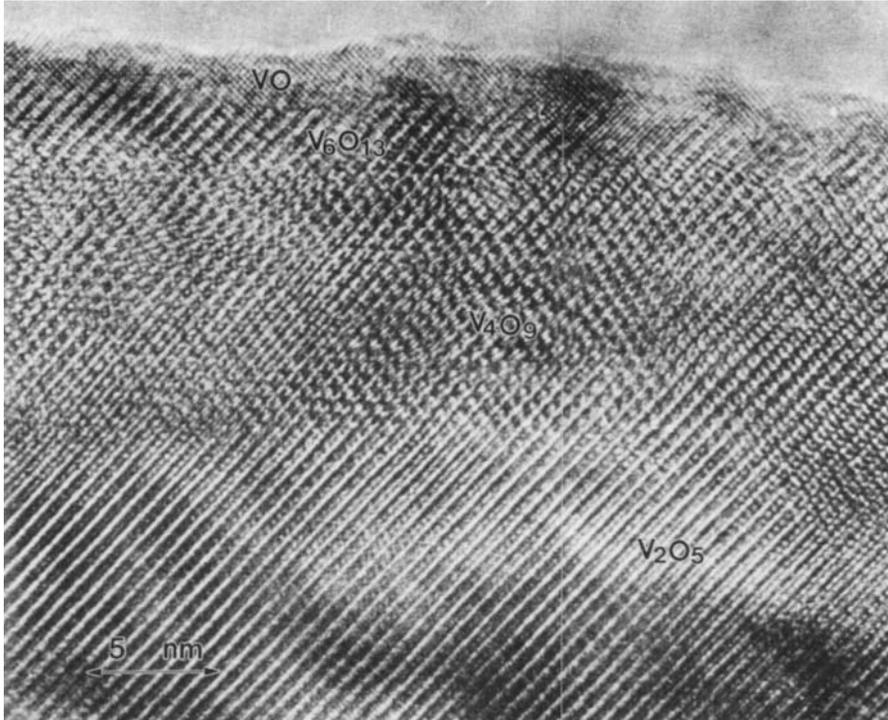


Figure 3 High-resolution image showing the roughness of the V_2O_5/V_4O_9 interface. The image was taken along the $[001]$ zone axis after about 15 min electron irradiation at a beam flux $< 1.5 \text{ A/cm}^2$.

the solutions with $f'(v_s(0)) \leq 0$ are stable, and they change their stability when the denominator in (3.11) changes sign.

Thus if an initial condition is close to a mode with an intermediate velocity, then the solution can stay close to it for some time, and then a transition to a stable quasistationary solution occurs. Such behavior is in accordance with the experimental data (see Section 2). We note also that the positive eigenvalue does not depend on the wave number. If we consider a sample bounded in the z direction, then a discrete set of wavenumbers is determined by the boundary conditions. This means that a cellular instability, when the interface is curved and its shape and velocity are constant, can also take place. The experimental results show that such phenomena can occur for a phase transformation in metal oxides under irradiation (Figure 3).

4 TWO-INTERFACE PROPAGATION

We have considered above the case of one-interface propagation. However, the experimental results show that two and three interfaces can propagate into a sample

one after another (Ai, Fan and Marks, 1992). This section is devoted to two-interface propagation. We consider the diffusion equation written in the moving frame, such that the second interface is located at $x = 0$, and denote by s the distance between the interfaces. Thus we have the following formulation of a free boundary problem

$$\frac{\partial v}{\partial t} = D \frac{\partial^2 v}{\partial x^2} + c_2 \frac{\partial v}{\partial x}, \quad y(t) < -x \quad (4.1)$$

$$x = -y(t): \frac{\partial v}{\partial x} = hv \quad (4.2)$$

$$x = 0, s: D \left(\frac{\partial v}{\partial x} \Big|_{-}^{(i)} - \frac{\partial v}{\partial x} \Big|_{+}^{(i)} \right) = c_i (v_{+}^{(i)} - v_{-}^{(i)}) \quad (4.3)$$

$$\frac{\partial v}{\partial x} \Big|_{+}^{(i)} = 0 \quad (4.4)$$

$$c_i = f_i(v_{+}^{(i)}, v_{-}^{(i)}) \quad (4.5)$$

$$\frac{dy}{dt} = c_2 \quad (4.6)$$

$$\frac{ds}{dt} = c_1 - c_2 \quad (4.7)$$

Here $i = 1, 2$ and index 1 corresponds to the first interface, index 2 the second, + and - mean that the value of the quantity from the right or from the left of the interface are taken.

We obtain from (4.1), (4.3), (4.4)

$$\int_0^s \frac{\partial v}{\partial t} dx = c_1 (v_{+}^{(1)} - v_{-}^{(1)}) + c_2 (v_{-}^{(1)} - v_{+}^{(2)}) \quad (4.8)$$

$$\int_{-y}^0 \frac{\partial v}{\partial t} dx = c_2 (v_{+}^{(2)} - v_{-}^{(2)}) - Dhv|_{-y} + c_2 (v_{-}^{(2)} - v|_{-y}) \quad (4.9)$$

This is a more general form of mass balance. If (4.3) gives the balance of mass on the interface, then (4.8)—between the interfaces, (4.9)—on the interval to the left of the second interface. If we consider an exact solution then the problems (4.1)–(4.7) and (4.1), (4.2), (4.4)–(4.9) are equivalent. But for approximate solutions they can give different results.

We proceed now to the construction of an approximate analytical solution. The main assumption here is that

$$\frac{c_2 y}{D} \ll 1, \quad \frac{(c_2 - c_1)s}{D} \ll 1. \quad (4.10)$$

We note that it is in accordance with the real values of the parameters (Marks, Volpert and Ai, 1992). (4.10) means that the characteristic diffusion time is much less

than the characteristic time of variation of the interval length. This allows us to apply a quasistationary approximation but, contrary to (2.4), does not imply constant interface velocity. The approximation of a constant interface velocity was used in Section 2 for the case of one-interface propagation. We know from the experimental results and numerical analysis that the interface velocities are not constant particularly for two-interface propagation. In particular, the first interface decelerates, the distance between the interfaces decreases, and they merge. The purpose of this section is to give a simple analytical description of the process. Therefore, we cannot use the approximation of constant velocities here.

Using the quasistationary approximation we obtain from (4.1), (4.2), (4.4):

$$v = v_2 \left(1 - \frac{e^{-c_2(x+y)/D}}{1 + c_2/Dh} \right), \quad -y < x < 0$$

$$v(x, t) = v_1, \quad 0 < x < s, \quad v(x, t) = v_0, \quad s < x$$

where v_0 is an initial value of the concentration, v_1 and v_2 are to be found from the other equations of the system. From (4.10) we conclude that v depends weakly on x in the interval $y < x < 0$, and we can approximately equate

$$v = v_2 \left(1 - \frac{1}{1 + c_2/Dh} \right), \quad -y < x < 0. \tag{4.11}$$

Thus we approximate the solution of the problem by a piecewise constant function. This is in accordance with the results of numerical analysis.

If we use now the balance of mass on the interface (4.3) we obtain formally $c_1 = c_2 = 0$. This shows that we should use here the integral form of the mass balance (4.8), (4.9) rather than the local one. Indeed the approximation of the solution by a piecewise constant function means actually that we consider the limit of infinite diffusion coefficient. In this case the balance of mass gives

$$\left. \frac{\partial v}{\partial x} \right|_{\pm}^{(i)} = 0, \quad i = 1, 2$$

(see (2.4)).

One more assumption we make to simplify the problem is that $c_2/Dh \ll 1$. In this case we have from (4.11) $v = 0$, $-y < x < 0$. Thus we have the system of equations (4.5), (4.7), (4.8) to find v_1 , s , c_1 , c_2 . We can rewrite it in the form

$$\frac{dv_1}{dt} = \frac{(v_0 - v_1)f_1(v_1)}{s} \tag{4.12}$$

$$\frac{ds}{dt} = f_1(v_1) - f_2(v_1) \tag{4.13}$$

$$t = 0: s = s_0, v_1 = v_{10}$$

We keep here the same notations for the kinetic functions as functions of one variable v_1 . Obviously, (4.12), (4.13) can be reduced to the equation

$$\frac{dv_1}{ds} = \frac{(v_0 - v_1)f_1(v_1)}{s(f_1(v_1) - f_2(v_1))}$$

from which we find

$$s = c \exp \int \frac{f_1(v_1) - f_2(v_1)}{(v_0 - v_1)f_1(v_1)} dv_1.$$

Here c is an arbitrary constant which is to be found from the initial conditions. To have an explicit answer we consider the linear kinetics

$$f_1(v_1) = k_1(u_{e1} - 0.5(v_0 + v_1)), \quad f_2(v_1) = k_2(u_{e2} - 0.5v_1).$$

In this case

$$s = c(v_0 - v_1)^{a_1}(2u_{e1} - v_0 - v_1)^{a_2},$$

where

$$a_1 = \frac{k_2}{k_1} \frac{2u_e - v_0}{2(u_{e1} - v_0)} - 1, \quad a_2 = \frac{k_2}{k_1} \frac{u_{e1} - 0.5v_0 - u_{e2}}{u_{e1} - v_0}.$$

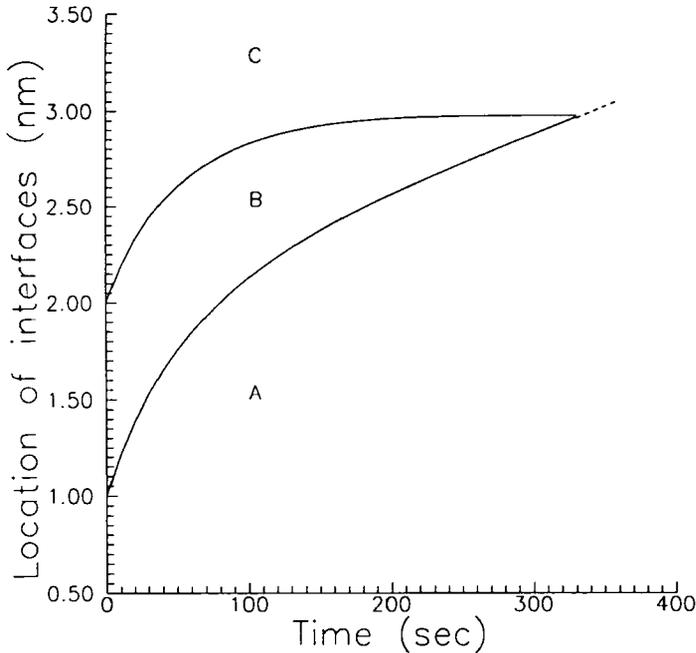


Figure 4 Location of the interfaces versus time in the case of two-interface propagation. A—final phase, B—intermediate phase, C—original phase.

We make a natural assumption that $u_{e2} < u_{e1} < v_0$. We conclude from (4.12) that v_1 increases. There are two basic cases. If $a_2 < 0$ then $c_2 = 0$ at $t = t_0$, where

$$t_0 = \frac{2c}{k_1} \int_{v_{10}}^{u_{e2}} (v_0 - v_1)^{a_1-1} (2u_{e1} - v_0 - v_1)^{a_2-1} dv_1,$$

$$c = s_0(v_0 - v_1)^{-a_1} (2u_{e1} - v_0 - v_1)^{-a_2},$$

Thus in the first case the second interface stops while the first one continues to move.

If $a_2 > 0$ then $c_1 = 0$ and $s = 0$ at $t = t_1$,

$$t_1 = \frac{2c}{k_1} \int_{v_{10}}^{2u_{e1} - v_0} (v_0 - v_1)^{a_1-1} (2u_{e1} - v_0 - v_1)^{a_2-1} dv_1.$$

This means that the distance between the interfaces decreases and they merge. Such behavior was observed experimentally (Ai, Fan and Marks, 1992) and in numerical simulations (Marks, Volpert and Ai, 1992). Figure 4 shows a numerical solution of (4.12), (4.13). First there are two interfaces, then they merge and the intermediate phase disappears. For $t > t_1$ we have one-interface propagation (see Section 2).

5 CONCLUSION

This paper completes a cycle of experimental and theoretical work devoted to phase transitions in metal oxides under irradiation (see references above). The purpose of the theoretical analysis is to suggest a mathematical model which describes the experimental results and, at the same time, is not too complicated to allow us to form a simple understanding of the process. This is the reason why we consider only one substance, oxygen, in the model although the real process is more complicated and involves vacancies and interstitials as well. Accepting this simplification, we have a diffusion equation in the bulk, a radiative boundary condition on the external surface of the sample, and an interface (one or more) which propagates the sample.

An important point here is to choose appropriate conditions on the interface. There are two well-known limiting cases: diffusion control and interface control (see, for example, Christian, 1981). But the physical idea of the process under consideration is that the concentration step on the interfaces is equal to zero at the moment the interface appears, and then the step increases. This means that we should consider mixed control rather than one of the limiting cases above. There are some works which consider mixed control for solidification problems (see Aziz and Kaplan, 1988; Coriell and Sekerta, 1983; Merchant and Davis, 1990; Spencer, Voorhees, Davis and McFadden, 1992) and in a general thermodynamic formulation (Davi and Gurtin, 1990; Gurtin and Voorhees, 1992). We cannot apply these models directly, but we also use the balance of mass, kinetics of the phase transformation, and one more relation describing an interaction of the bulk and the interface to determine the conditions on the interface. The balance of mass has a conventional form. The kinetics

of the phase transformation is discussed above in this paper, and one more condition on the interface is derived under the assumption that we can use a quasistationary approximation to find the distribution of the concentration inside the interface. This condition has a rather general form, and, as a particular case, it includes the case of an impenetrable interface which we consider in this paper. The physical explanation of the impenetrability of the interface for the diffusive flux is as follows. The transition from higher oxides to lower oxides leads to the appearance of extra oxygen atoms and, in the limiting case, the concentration of the vacancies on the interface is zero, while the concentration of the interstitials is maximal. This means that the oxygen atoms cannot diffuse through the interface. The more general case of a partially penetrable interface is also described by our model and is a subject for further analysis. Here we note only that in the limiting case of large penetrability there is no concentration step on the interface, and the free boundary problem becomes degenerate: the diffusion equation can be solved independently of the interface location.

One of the important conclusions of the theoretical analysis is that, after an induction period connected with the initial conditions, the interface velocity is close to constant. This was first found experimentally, then in the numerical simulations. Now we understand that it is connected with the presence of the small parameter cy/D in the system. This means that in a real time scale the velocity increase is not observed, though it tends to zero as time tends to infinity. In other words we have here an intermediate asymptotic when the system forgets about the initial conditions and is still 'far' from infinity. We emphasize again that, though the interface velocity is close to constant, it is not an interface controlled process.

The presence of the small parameter allows us also to apply a quasistationary approximation, which makes it possible to find the interface velocity explicitly. We note that experimentally the interface velocity depends on the value of the electron flux only weakly. The analytical approach gives the same result.

The approximation of a constant velocity is applicable for any kinetics. If we take into account a deceleration of the rate of the reduction by the products then a multiplicity of solutions can occur depending on the values of the parameters. This means that the interface can propagate with different velocities, and the choice of the velocity is determined by the initial distribution of oxygen concentration. The non-uniqueness of the modes of the interface propagation can take place only for a finite time. The asymptotic behavior of the interface velocity, as time tends to infinity, is unique.

When the multiplicity occurs one of the solutions, as usual, is unstable. Since we consider only a leading term of the expansion with respect to small parameters, linear stability analysis shows that the positive eigenvalue does not depend on the wave number. This means that one-dimensional perturbations, which correspond to zero wavenumber, grow with the same rate as two-dimensional perturbations which lead to the appearance of non-flat interfaces. Non-flat interfaces were observed in some of the experiments.

One of the interesting experimental results is that more than one interface can propagate into the sample depending on the value of the electron flux. In some cases the interfaces merge and the intermediate phase disappears. In our previous work

we showed numerically that the model describes these effects. For high values of the flux the time difference between the appearance of the first and second interfaces is too small, the distance between them is also small, and the intermediate phase cannot exist if we assume that the critical nucleus size is positive. For small values of the flux the time difference is large, and the first interface is rather far from the side surface of the sample when the second interface appears near it. In this case these interfaces coexist for some time. However, the experiments and the numerical computations show that the appearance of the second interface decelerates the first one. The reason is that the second interface is impenetrable for oxygen (or partially impenetrable) and the oxygen concentration between the interfaces grows. This leads to a decrease of the first interface velocity, while for the second one this effect is compensated by oxygen loss through the side surface. As a result the interfaces can merge. In this paper we give an analytical description of these phenomena. This analysis is based on the assumption, confirmed numerically, that the oxygen concentration between the interfaces depends on the spatial variable only weakly.

We note that in the limiting case of diffusion control, when the values of the concentration on the interface are given and constant, the interfaces cannot merge: when the distance between them decreases the flux from the first interface increases and it accelerates.

Acknowledgements

The authors would like to thank Peter Voorhees for useful discussions. This work was supported by the Air Force Office of Scientific Research on grant number AFOSR-90-0045/B.

References

- Ai, R., H.-J. Fan and L. D. Marks (1992). Phase transition in DIET of vanadium pentoxide. I. Experimental results, *Surf. Sci.*, to be published.
- Ai, R., H.-J. Fan, P. C. Stair and L. D. Marks (1990). In-situ study of radiation damage in V_2O_5 induced by low energy electrons, *Mat. Res. Soc. Symp. Proc.*, **157**, pp. 599–604.
- Aziz, M. J. and T. Kaplan (1988). Continuous growth model for interface motion during alloy solidification, *Acta Metall.*, **36**, No. 8, pp. 2335–2347.
- Christian, J. W. (1981). *The Theory of Transformation In Metals and Alloys*, 2nd ed, Pergamon Press, New York.
- Coriell, S. R. and R. F. Sekerka (1983). Oscillatory morphological instabilities due to non-equilibrium segregation, *J. Crystal Growth*, **61**, pp. 499–508.
- Davi, F. and M. E. Gurtin (1990). On the motion of a phase interface by surface diffusion, *J. Applied Math. and Physics (ZAMP)*, **41**, pp. 782–811.
- DIET I. Desorption induced by electronic transition. Eds: N. H. Tolk, M. M. Traum, J. C. Tully, T. E. Madey, *Springer Series in Chemical Physics*, Vol. 24, Springer-Verlag, New York.
- Gurtin, M. E. and P. W. Voorhees (1992). On the thermodynamics of rapidly evolving two-phase systems driven by mass transport. To be published.
- Khaikin, B. I. and S. I. Khudyaev (1979). Non-uniqueness of combustion temperature and rate when competing reactions take place, *Dokl. Phys. Chem.*, **245**, No. 1–3, pp. 225–228.
- Knotek, M. L. and P. J. Feibelman (1978a). Ion desorption by core-hole Auger decay, *Phys. Rev. Letters*, **40**, No. 14, pp. 964–967.
- Knotek, M. L. and P. J. Feibelman (1978b). Reinterpretation of electron-stimulated desorption data from chemisorption systems, *Phys. Rev. B*, **18**, No. 12, pp. 6531–6539.
- Kung, H. H. (1989). Transition metal oxides: surface chemistry and catalysis. *Studies in Surface Science and Catalysis*, V. 45, Elsevier, New York.

- Marks, L. D. (1983). Direct imaging of carbon-covered and clean gold (110) surfaces, *Phys. Rev. Lett.*, **51**, No. 11, pp. 1000–1002.
- Marks, L. D. and D. J. Smith (1984). Direct atomic imaging of solid surfaces, II. gold (111) surface during and after in-situ carbon etching, *Surf. Sci.*, **143**, pp. 495–508.
- Marks, L. D., V. A. Volpert and R. Ai (1992). Phase transition kinetics of vanadium pentoxide. II. Theoretical results, *Surf. Sci.*, to be published.
- Merchant, G. J. and S. H. Davis (1990). Morphological instability in rapid directional solidification. *Acta Metall. Mater.*, **38**, No. 12, pp. 2683–2693.
- Singh, S. R. and L. D. Marks (1989). Diffusion during electron-beam-induced reduction of tungsten trioxide, *Phil. Mag. Letters*, **60**, No. 1, pp. 31–36.
- Spencer, B. J., P. W. Voorhees, S. H. Davis and G. B. McFadden (1992). The effect of compositionally-generated elastic stresses on morphological instability during directional solidification, *Acta Metall. Mater.*, to be published.
- Weeks, J. D., W. Saarloos and M. Grant (1991). Stability and shapes of cellular profiles in directional solidification: expansion and matching methods, *J. Crystal Growth*, **112**, pp. 244–282.
- Zeldovich, Ya. B., G. I. Barenblatt, V. B. Librovich and G. M. Makhviladze (1985). The mathematical theory of combustion and explosion, *Consultants Bureau, New York*.