POSSIBLE INFLUENCE OF THE SELF DIFFUSION OF THE ATOMS ON MASS DISPLACEMENT IN A SOLID UNDERGOING A SURFACE REACTION

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UDC 532.72

The possible influence of a diffusive flow of atoms (vacancies) on mass displacement in a solid undergoing a surface reaction is examined analytically.

In two earlier papers [1, 2] devoted to experimental investigations into the high-temperature reactions of carbon, changes observed in the densities of the samples were attributed to the occurrence of a substantial solid-phase diffusion of atoms from the interior of the solid to its surface. The atoms in the solid tended to occupy lattice vacancies at the surface formed as a result of the reaction, while the vacancies themselves diffused into the interior.

In this paper we shall use a mathematical model in order to elucidate the conditions under which the diffusive flow of atoms or vacancies may make a substantial contribution to the loosening of a solid in the presence of a surface reaction.

It is well known [3] that in real crystals at high temperatures the ideal crystal structure is inevitably distorted by defects such as vacancies or interstitial atoms (the probability that the latter will occur in close-packed structures formed by atoms of a single type is practically zero). Sources (or sinks) of vacancies may be provided either by the external surfaces of the sample or by defects of various kinds in the interior (dislocations, pores, etc.). The equilibrium vacancy concentration c_0 is given by the equation

$$c_0 = \exp\left\{-\frac{U}{kT}\right\}. \tag{1}$$

In the absence of equilibrium, the changes taking place in the vacancy concentration with time are due to diffusion, together with vacancy sources and sinks. Subsequently we shall consider the diffusion equation in the quasi-steady-state approximation* ($\partial c/\partial f \approx 0$), assuming that the characteristic time of the process, i.e., the time required for an appreciable loosening of the material, is considerably greater than τ_s (the x axis is directed toward the interior of the solid):

$$D_v \frac{d^2c}{dx^2} = \frac{c - c_0}{\tau_s}, \tag{2}$$

where D_v is the self-diffusion coefficient of the vacancies

$$D_v = \frac{1}{6}\frac{\delta^2}{\tau_s} = \frac{1}{6}\frac{\delta^2}{\tau_0}\exp\left\{-\frac{\Delta U}{kT}\right\}, \tag{3}$$

while the relaxation time τ_s may vary over a wide range according to the degree of defectiveness of the crystal. Thus if the vacancy sinks are pores of radius r uniformly distributed throughout the volume and lying an average distance l apart, we have [4]

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*If we put $t_1 \sim 1/mv_0$ and $D_v m > w_0$, in accordance with (29) and (18) respectively, by using (9) and (19) we obtain $\tau_s/t_1 < v_0/w_0 \ll 1$.

Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussion SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 26, No. 2, pp. 332-338, February, 1974. Original article submitted April 26, 1973.

$$\tau_s \approx \frac{l^3}{\pi^2 r D_V}. \tag{4}$$

The boundary condition on the surface x = 0 may be obtained in the form

$$w_0(c - c_0) - v_0 = D_V \frac{dc}{dx} \tag{5}$$

by generalizing the corresponding condition in [3] if we put

$$w_0 \approx \frac{1}{6} a \exp\left\{-\frac{\Delta U}{kT}\right\}. \tag{6}$$

As indicated by Ya. I. Frenkel' [3], in addition to ordinary evaporation, which corresponds to the complete removal of a surface atom from the crystal, we also have to consider processes of incomplete evaporation. One of these processes lies in the transition of surface atoms from the regularly-constructed surface layer to the top of that layer; this corresponds to the formation of a new outer layer and the development of vacancies, with the subsequent diffusion of these into the interior. Condition (5) describes the balance of vacancies at the crystal boundary in the absence of equilibrium; here v_0 is the rate of vacancy formation by the surface reaction.

As we shall later be using the resultant equations for approximate calculations, let us write down an approximate solution to Eq. (2) with the boundary condition (5), subject to the condition at infinity $c = c_0 = \text{const}$ (regarding the diffusion coefficient as constant):

$$c \approx c_0 + A \exp\{-mx\}, \tag{7}$$

where

$$A = \frac{\dfrac{dc_0}{dx} + \dfrac{v_0}{D_V}}{\dfrac{w_0}{D_V} + m}, \tag{8}$$

$$m = 1/\sqrt{D_V \tau_s}. \tag{9}$$

Before studying the resultant solution we make the following comments.

For ideal crystals the ratio w_0/D_V is quite large (order of $1/\delta \approx 10^8$ cm^{-1}). We may therefore consider $w_0/D_V \gg m$. However, in solids with macroscopic crystal lattice defects the experimentally-measured values of the diffusion coefficient are much greater than the values of the diffusion coefficient corresponding to single crystals. This is due to the existence of easy diffusion paths in real crystals (paths associated with the development of a network of boundaries between structural elements, microcracks, and pores, possibly connected to the outer surface by microcapillaries [2, 4]). The coefficients of surface and boundary diffusion at a temperature close to the melting point exceed the coefficient of three-dimensional diffusion in a single crystal by four or five orders of magnitude.

For example, let us suppose that microcapillaries of radius r_1 pass out to the outer surface. Let us calculate the flow of adsorbed atoms through unit length of such a capillary. The adsorbed atoms diffusing along the surface will be absorbed by vacancies emerging at the surface of the capillary. The flow of these vacancies through unit surface area equals $w_0 c$. We shall now consider that, as for an infinite cylinder, the number of adsorbed atoms absorbed by the solid is in local equilibrium with the flow of vacancies from the solid. This means that the whole of the diffusion flow of adsorbed atoms through unit length may be expressed in terms of the concentration gradient of the vacancies in the interior of the solid:

$$j_1 = D_1 \frac{d}{dx}(w_0 c \tau_1) = D_1 w_0 \tau_1 \frac{dc}{dx}, \tag{10}$$

where τ_1 is the lifetime of an adsorbed atom, D_1 is the coefficient of surface diffusion. The total surface flow of adsorbed atoms through unit surface area of the solid at x = 0 (ε is the surface porosity) equals

$$\bar{j}_1 = D_1 w_0 \tau_1 \frac{dc}{dx} 2\pi r_1 \frac{\varepsilon}{\pi r_1^2} = \varepsilon \frac{2D_1 w_0 \tau_1}{r_1} \frac{dc}{dx}. \tag{11}$$

Then the effective diffusion coefficient which is to be used in the expressions just given takes the form

$$D_{V\,\mathrm{eff}} = D_V(1 - \varepsilon) + \frac{2D_1 w_0 \tau_1}{r_1} \varepsilon, \tag{12}$$

As already noted, $D_1 >> D_V$. Hence the ratio $w_0/D_{V.\mathrm{eff}}$ may be several orders of magnitude smaller than the corresponding value for the single crystal. In this case we may have the inequality $w_0/D_{V.\mathrm{eff}} < m$.

However, if we take account of the finite length of the microcapillarities emerging on the surface of the solid, the foregoing local equilibrium between the diffusing adsorbed atoms and vacancies in the interior of the solid will not take place. In this case, strictly speaking, we should carry out a simultaneous solution of the equation for surface diffusion, with the corresponding boundary condition at $x = 0$ [5], and the equation for the three-dimensional diffusion of the vacancies. Then in addition to the effective diffusive flow of atoms through each unit of surface area some of the adsorbed atoms will pass directly from the surface of the capillary to the surface of the solid and there enter into the reaction. This surface flow of adsorbed atoms is not associated with the vacancy mechanism of diffusion, and it is difficult to incorporate it into the boundary condition (5) and correspondingly into Eq. (8). We can only note that the surface flow in question will also reduce the rate of forward motion of the reaction front, at the same time tending to loosen the material internally.

Let us now turn to the foregoing solution (7)-(9). Let us consider two limiting cases (subsequently we shall understand D_V to mean the effective diffusion coefficient:

I. $w_0/D_V >> m$.

Then the relative supersaturation of the vacancies for $x = 0$ is

$$\frac{c - c_0}{c_0} = \frac{\Delta c}{c_0} = \frac{1}{w_0 c_0}\left(D_V \frac{dc_0}{dx} + v_0\right)\left(1 - \frac{mD_V}{w_0}\right). \tag{13}$$

As already indicated, the atoms diffusing from the inside of the solid replace the vacancies formed at the boundary $x = 0$. In this way the forward velocity of the reaction front v is reduced, i.e.,

$$\begin{aligned} v - v_0 = \Delta v = D_{\text{в}} \frac{dc}{dx}\Big|_{x=0} &= D_V \frac{dc_0}{dx}\Big|_{x=0} \\ &- \frac{mD_V}{w_0}\left(v_0 + D_V \frac{dc_0}{dx}\Big|_{x=0}\right). \end{aligned} \tag{14}$$

If in addition to this $v_0 \gg D_V\, dc_0/dx$ (we shall consider in future for simplicity that the temperature gradients in the solid are small), we have

$$\frac{\Delta c}{c_0} = \frac{v_0}{w_0 c_0}\left(1 - \frac{mD_V}{w_0}\right), \tag{15}$$

$$\frac{\Delta v}{v_0} = -\frac{mD_V}{w_0}. \tag{16}$$

We see from Eq. (16) that in the case $w_0/D_V >> m$ the relative change in velocity $\Delta v/v_0$ tends to zero and loss of material takes place from the surface.

II. $w_0/D_V << m$,

$$\frac{\Delta c}{c_0} = \frac{v_0}{D_V m c_0}\left(1 - \frac{w_0}{D_V m}\right), \tag{17}$$

$$\frac{\Delta v}{v_0} = -1 + \frac{w_0}{D_V m}. \tag{18}$$

It follows from (18) that in the case $w_0/D_V << m$ the rate of progress of the reaction front v will tend to zero and the loss of mass will take place from the interior by virtue of the diffusion of the atoms composing the solid to the surface.

Let us now consider the problem of the loosening of the material, i.e., the change taking place in its density with time. We know [3] that the mobility and diffusion coefficient of the atoms respectively equal:

$$w_a = w_0 c, \; D_a = D_V c. \tag{19}$$

Hence the expression for the density of the diffusive flow of atoms may be written in the form [6]

$$j_a(x) = n(x) w_a(x + \delta) - n(x + \delta) w_a(x) = -D_a \frac{dn}{dx} + nD_V \frac{dc}{dx}. \tag{20}$$

Substituting (20) into the equation

$$\frac{\partial n}{\partial t} - v\frac{\partial n}{\partial x} = -\frac{\partial j_a}{\partial x}, \tag{21}$$

we obtain

$$\frac{\partial n}{\partial t} - v\frac{\partial n}{\partial x} = D_a\frac{\partial^2 n}{\partial x^2} - nD_{\mathrm{V}}\frac{d^2 c}{dx^2}. \tag{22}$$

Using (7) we have (for case II in which $v \to 0$)

$$\frac{\partial n}{\partial t} = D_a\frac{\partial^2 n}{\partial x^2} - n(x,\, t)\,D_{\mathrm{V}} m^2 A \exp\{-mx\}. \tag{23}$$

For the boundary condition $x = 0$ we have

$$-D_a\frac{\partial n}{\partial x} + nD_{\mathrm{V}}\frac{dc}{dx} = nD_{\mathrm{V}}\frac{dc}{dx},$$

i.e.

$$D_a\frac{\partial n}{\partial x} = 0. \tag{24}$$

For large m the source in Eq. (23) may be replaced by an equivalent surface source, by incorporating this into the boundary condition. Then (23) and (24) take the form

$$\frac{\partial n}{\partial t} = D_a\frac{\partial^2 n}{\partial x^2}. \tag{25}$$

$$D_a\frac{\partial n}{\partial x} = nv_0. \tag{26}$$

The solution to the problem (25)-(26) ($n\,|_{t=0} = n_0$) is quite well known [7]. In particular the value of n at the surface $x = 0$ equals

$$\frac{n_s}{n_0} = \exp\left\{\frac{v_0^2}{D_a}t\right\}\Phi^*\left(v_0\sqrt{\frac{t}{D_a}}\right). \tag{27}$$

For short times ($t \ll D_a/v_0^2$)

$$\frac{n_s}{n_0} \approx 1 - \frac{2}{\sqrt{\pi}}v_0\sqrt{\frac{t}{D_a}}. \tag{28}$$

At the same time it follows [7] from the solution to the problem (23)-(24) for short times $t \ll 1/mv_0$ (for which we may consider $n(x, t) = n_0$ on the right-hand side of (23)) that

$$\frac{n_s}{n_0} \approx 1 - mv_0 t. \tag{29}$$

Comparison of (28) and (29) shows that for $t \ll 1/mv_0$ the state of distribution of the source in (23) is very important.

The equation of energy for the solid may be written [8]:

$$\rho\frac{\partial h}{\partial t} - \rho v\frac{\partial h}{\partial x} = \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x} + \rho D_{\mathrm{V}}\sum_{i=1}^{2} h_i\frac{dc_i}{dx}\right), \tag{30}$$

where

$$h = \sum_{i=1}^{2} c_i h_i;\ h_1 = c_p T + \bar{U};\ h_2 = c_p T. \tag{31}$$

In case II by using (7) and (27) we obtain

$$\rho c_p\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right) + \bar{U}\rho D_{\mathrm{V}} m^2 A \exp\{-mx\}. \tag{32}$$

The plus sign of the right-hand side of (32) is due to the recombination of the excess vacancies inside the solid, as a result of which energy is evolved.

The boundary condition for Eq. (32) when $x = 0$ takes the form

$$g + \lambda \frac{\partial T}{\partial x} = -\rho D_V \frac{dc}{dx}(L - \bar{U}) = \rho v_0 (L - \bar{U}). \tag{33}$$

As in (23) the source on the right-hand side of (32) may be replaced (for large m) by an equivalent surface source by incorporating it into the boundary condition. Then Eq. (33) takes the form

$$g = -\lambda \frac{\partial T}{\partial x} + \rho v_0 L. \tag{34}$$

For $t = 150$ sec and a 15% mass loss the value of $n_s/n_0 \approx 0.5$, was obtained experimentally [1]; this was maintained for a fairly long reaction period. The problem of the loosening of carbon was therefore formulated in the following way in [1]:

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x}\left(D_a \frac{\partial n}{\partial x}\right),$$
$$n = 0 \quad \text{for} \quad x < 0,\ t = 0,$$
$$n = n_0 \quad \text{for} \quad x > 0,\ t = 0.$$

If we calculate n_s/n_0 from Eq. (27) using the following values of the original data: $t = 150$ sec, $v_0 = 0.24 \cdot 10^{-3}$ cm/sec (which corresponds to a mass loss of 15%), $D_a \approx 1.4 \cdot 10^{-5}$ cm^2/sec [1], we also obtain $n_s/n_0 \approx 0.5$. Owing to the slow fall in the function (27), the change in n_s/n_0 is only very slight as the argument increases further (for $t = 300$ sec, $n_s/n_0 \approx 0.43$). We thus obtain qualitative agreement between the calculated data for n_s/n_0 and existing experimental results [1]. In addition to this, a consideration of the kinetic characteristics of the vacancies within the framework of the model here proposed enables us to formulate the boundary problem correctly both for the diffusion equation and for the energy equation in the solid in the presence of a surface reaction.

NOTATION

c	is the vacancy concentration;
U	is the energy of vacancy formation;
ΔU	is the energy required for the motion of the vacancies;
n	is the number of particles in unit volume of the solid;
k	is the Boltzmann's constant;
T	is the absolute temperature;
δ	is the interatomic distance;
τ_0	is the period of the vibrations of the atoms around the equilibrium position ;
τ_V	is the sessile lifetime of a vacancy;
a	is the velocity of sound;
D_V	is the vacancy diffusion coefficient;
D_a	is the atomic diffusion coefficient;
v	is the velocity of the reaction front;
ρ	is the density of the solid;
c_p	is the specific heat of the solid;
h	is the enthalpy of the solid;
L	is the heat of the reaction;
g	is the density of the external thermal flux;

$\Phi^*(z) = 2/\sqrt{\pi} \int_z^\infty \exp(-y^2)dy.$

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