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The effect of combined diffusion and kinetic transport barriers on multi-phase solid state reactions with a vapour reactant

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Analytical models are presented for the rates of layer thickness growth of $MoSi_2$ and of Mo_5Si_3 that form by reaction of vapour-supplied Si with Mo or with partially silicided Mo. The models are applicable to other systems. Coupling of the diffusive flux of the reactive species Si with the rate of the chemical reactions determines the growth kinetics. The rate of chemical reaction is assumed to be proportional to the magnitude of a discontinuity in the Si activity at the physical boundary where the silicide reaction is occurring. Various combinations of diffusive versus chemical-kinetics-dominated transport in the two phases which grow in tandem are found to affect the functional dependence of the growth kinetics on time. Models include cases in which the host solid is heterogeneous, as occurs when the average composition of the host lies in a poly-phase region of the phase diagram.

Nomenclature

The highest relative Si-content phase $MoSi_2$, the Mo_5Si_3 phase, and the unreacted "core" material will be abbreviated as materials 1, 2, and 3, respectively. The subscripts 0, 1, 2 and 3 refer to Si, $MoSi_2$, Mo_5Si_3, and Mo species and/or layer phases, respectively.

The following symbols are defined as:

p = porosity, (For example p_1 is the porosity of the $MoSi_2$ layer.)
q = $1 - p$
v_i = volume fraction of i in the unsilicided compact.
V_i = theoretical molar volume of i
ω_i = theoretical volume per gram atom of Si in i
β_i = $(1 - p_i)/\omega_i$ in g atoms of Si per unit volume in i
D_i = Diffusion coefficient of Si in i.
K_i = Kinetic rate constant for conversion of phase i to phase $i + 1$ in g.At $cm^{-2} s^{-1}$ per ΔC.
J_i = Flux of Si through phase i in g.At $cm^{-2} s^{-1}$.
The following are concentrations of Si expressed as gram atoms per cm^3:
C_0—in $MoSi_2$ at outer surface in equilibrium with Si vapour.
C_1—in $MoSi_2$ at boundary in equilibrium with Mo_5Si_3
C_2—in Mo_5Si_3 at boundary in equilibrium with $MoSi_2$
C_3—in Mo_5Si_3 at boundary in equilibrium with Mo
C_4—in Mo at boundary in equilibrium with Mo_5Si_3
C'_1—in $MoSi_2$ at boundary with Mo_5Si_3, but at a higher Si activity than the equilibrium value
C'_3—in Mo_5Si_3 at boundary with Mo, but at a higher Si activity than equilibrium value
ΔC_{ij} = $C_i - C_j$
$A(Si)$ = Atomic weight of Si
t = elapsed time since start of siliciding in seconds.
X, Y = thicknesses of $MoSi_2$, Mo_5Si_3 layers in cm.

1. Introduction

This paper models the evolution and the kinetics of the progressive inward chemical transformation of one solid into another from exposure to a vapour-supplied reactive species. Specifically, the present model was motivated by a process [1, 2] for producing $MoSi_2$ by exposing to silicon vapour either pure or partially silicided molybdenum in the form of a porous or fully dense starting material. We have previously reported [3, 4] a computer model of the geometric and time-dependant evolution of silicide phase growth. That model included cases in which the starting material was initially an heterogeneous, equilibrated, but incompletely silicided solid, i.e., in which the starting solid was a two phase material having an average Si concentration less than that of the fully silicided phase $MoSi_2$.

The present paper offers analytical solutions of the growth process to allow easy interpretation of experimental kinetic data with respect to the transport and reaction processes involved in the growth. Both the growth kinetics for the intermediate Mo_5Si_3 which precedes the final conversion to $MoSi_2$, and that of the $MoSi_2$ phase are examined. The paper also offers a partial explanation for the unexpected observed dependence [2] of the layer growth rate constants on the Si content of the starting material. As is shown in Fig. 1, the parabolic growth rate constant for the advance of the $MoSi_2$ layer appears to be unaffected by the addition of Si to the initial solid until a threshold Si concentration is reached. The rate constants then increase linearly with increasing Si concentration. This increase appears to approach saturation when the Si content becomes sufficiently large.

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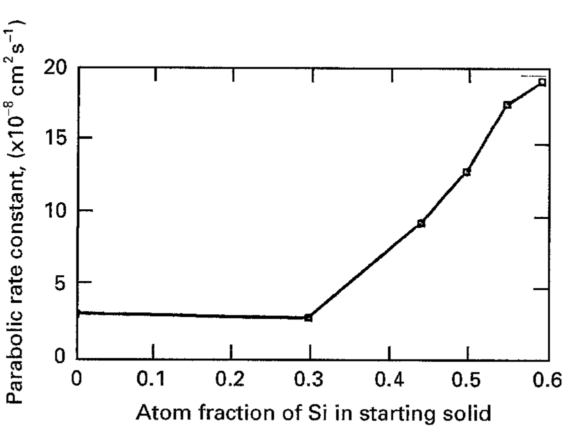

Figure 1 Dependence of the parabolic growth rate constants for the siliciding of an equilibrated Mo + Si solid compact.

Analyses of the growth kinetics of the solid reaction product have been reported in the literature [5, 6] that further refine the analysis for the cases where one[5] and two[6] solid compound phases separate the reactants, assumed to be elements. The effect of a chemical reaction at the boundary between adjoining phases that controlled the flux across that boundary was considered in addition to the usual assumption of diffusion controlled flux. The contacting phases are assumed to be compositionally related in accordance with the phase diagrams.

The present analysis differs from the above [5, 6] in various respects. In particular (a) the rate of the chemical reaction is assumed to be proportional (as a first approximation) to an excess Si activity at the phase boundary where the siliciding reaction is occurring and not just to be a fixed value (b) the large volumetric change that accompanies the compound formation and its effect on the porosity of the solids is incorporated into the present modelling (c) the diffusive transport is limited to Si which has been shown [7] to be the dominant mobile species and (d) cases are included in which the starting solid is a heterogeneous, partially converted polyphase material consisting of islands of Mo_5Si_3 embedded in Mo, or of $MoSi_2$ embedded in Mo_5Si_3. The model is developed in sufficiently general terms to allow its extension to analogous solid state reactions in which the progression of phases from the richest to the leanest with respect to the concentration of the invading species is maintained as the reaction front propagates into the interior of the starting material.

2. Modelling of the phenomena

2.1. Assumptions

Quasi-equilibrium is assumed to be established as Si, supplied as a vapour at the outer surface of the reactable Mo-containing solid, diffuses into the sample. Thus (1) transient effects can be neglected allowing Fick's first law for diffusion to be adequate for modelling Si transport; (2) the concentration varies linearly across a given phase and the diffusion coefficients do not vary within a given phase; (3) phases in direct contact must be compatible with equilibrium phase diagrams; and (4) there can be a step in the Si activities of adjoining phases to drive the chemical reaction that occurs at the phase boundary. The exception to (3) is the failure to detect the phase Mo_3Si separating Mo_5Si_3 from Mo, i.e., direct contact between Mo_5Si_3 and Mo is allowed.

Thermodynamic calculation shows that solid Si can deposit from the experimental gas mixture in the vapour phase. Thus, the Si activity in the gas and in the $MoSi_2$ at the external surface which is in contact with the vapour is taken to be unity. The Si concentration in any given compound is assumed to vary over the stoichiometry range for that compound. The concentration of Si in the $MoSi_2$ phase is theoretically lowest at the $MoSi_2/Mo_5Si_3$ boundary, and where it is also the highest in the Mo_5Si_3 phase. Similar conditions apply to the Mo_5Si_3/Mo boundary. There the Mo is saturated with Si, fixing the Si concentration.

The partially silicided solid was prepared by mixing and compressing the blended Mo and $MoSi_2$ powders. This mixture equilibrated quickly by diffusion to form a mixture of (a) Mo_5Si_3 + Mo particulates or of (b) $MoSi_2$ + Mo_5Si_3 particulates. In case (a) the Si activity is uniformly that for the Mo/Mo_5Si_3 equilibrium throughout the solid; in case (b) it is that for the $Mo_5Si_3/MoSi_2$ equilibrium. This equilibration occurred before the onset of significant siliciding from the vapour-supplied Si.

2.2. Model for the conversion of Mo_5Si_3 to $MoSi_2$

In this case only two phases are involved. Assume that the starting phase has already been converted to the homogeneous phase, Mo_5Si_3, which on the arrival of the diffusing Si is converted directly to homogeneous $MoSi_2$. We defer the more complicated case in which a phase intermediate in composition separates the starting material from the outer richest phase. This occurs when Mo is first converted to Mo_5Si_3 which in turn is converted to $MoSi_2$.

The reaction requires the diffusive transport of the reactive species through the outer layer, but may also encounter a reaction kinetic barrier at the boundary between the phases.

The thickness of the outer layer is measured along an axis x normal to the outer surface which defined the origin. At this surface $x = x_0 = 0$. At the boundary between; (1) the outer $MoSi_2$ phase and (2) the inner Mo_5Si_3 phase, $x = x_1$. Thus, the thickness $X = x_1 - x_0 = x_1$.

2.2.1. Case 1. No reaction barrier to trans-boundary transport

Let J_1(diff) be the flux of Si atoms through $MoSi_2$:

$$J_1(\text{diff}) = -D_1(C_0 - C_1)(1 - p_1)/X \qquad (1)$$

$$= -D_1(\Delta C_{01}/X)q_1$$

This flux represents the Si supply to Mo_5Si_3 needed to convert it to $MoSi_2$, $(\Delta C_{01}/X)$ being the concentration gradient. Let an incremental advance in the boundary δx_1 occur during a time increment δt. Then the g atoms per unit area of Si contained in the incremental addition to 1 is $\delta x_1\, \beta_1$, but a quantity of Si g atoms equal to $\delta x_1\, \beta_2$ was already in that space per unit area. Thus, the net required flux for the advance is:

$$J_1(\text{mass}) \;=\; \delta x_1(\beta_1\text{-}\beta_2)/\delta t. \tag{2}$$

Equating Equations 1 and 2 and integrating leads to

$$x_1 = (2D_1\Delta C_{01}q_1/B_1)^{1/2}(t)^{1/2} \;=\; 2a_1(t)^{1/2} \tag{3}$$

where $a_1 \;=\; (D_1\Delta C_{01}q_1/2B_1)^{1/2}, B_1 \;=\; \beta_1 - \beta_2$ and

$$\mathrm{d}x_1/\mathrm{d}t \;=\; a_1/(t)^{1/2} \tag{4}$$

2.2.2. *Case 2. Reaction barrier to interphase transport*

In addition to the above, the kinetics of conversion require a difference in the Si activity at the phase boundary that is proportional to $C_1' - C_1$. The kinetically defined rate of conversion or flux is J_1(kin) given by

$$J_1(\text{kin}) \;=\; K_1(C_1' - C_1) \tag{5}$$

The fluxes given by Equations 1, 2 and 5 must be equal. Equating Equations 1 and 5 allows C_1' to be eliminated. Upon setting this result equal to Equation 2, one obtains

$$\mathrm{d}x_1/\mathrm{d}t = (K_1D_1q_1\Delta C_{01})/[B_1(D_1q_1\text{-}K_1x_1)]. \tag{6}$$

Upon integrating, the boundary position as a function of time is:

$$x_1(t) \;=\; [D_1q_1/K_1][(1 + Wt)^{1/2} - 1] = X(t) \tag{7}$$

and

$$\mathrm{d}x_1/\mathrm{d}t = 1/(g_1^2 + h_1\mathrm{t})^{1/2} \tag{8}$$

in which in the above $W = 2\;\mathrm{K}_1^2\;\Delta C_{01}\;/(B_1\;D_1\;q_1)$, $g_1 = B_1/(\Delta C_{01}K_1)$, and $h_1 = 2B_1/(D_1\Delta C_{01}\,q_1)$. At short times Equation 7 reduces to the linear law

$$x_1 \;\approx\; K_1(\Delta C_{01}/B_1)t. \tag{9}$$

As can be seen from Equation 5 the magnitude of $C_1' - C_1$ decreases inversely proportionally to $1/K_1$. Thus, as the value of the kinetic constant increases, its effect on the growth rate decreases. At the limit $K_1 = \infty$ or at long times, the growth law reduces to Equation 3.

Instead of following the advance of x_1, the conversion process can be monitored by measuring m, the increase in mass per unit area, which is given by:

$$m = x_1B_1A(\text{Si}) \tag{10}$$

and which on substitution into Equation 3 gives the related parabolic law

$$m = B_1A(\text{Si})(2D_1\Delta C_{01}q_1/B_1)^{1/2}(t)^{1/2}. \tag{11}$$

2.3. Model for the conversion of homogeneous Mo to $MoSi_2$

In this situation a Mo_5Si_3 layer forms between the $MoSi_2$ and the Mo phases. At time t the interface between $MoSi_2$ and Mo_5Si_3 is at $x_1(t)$, and that between Mo_5Si_3 and Mo is at $x_2(t)$. As before the thickness of; (1) the $MoSi_2$ layer is given by $X = x_1(t) - x_0 = x_1(t)$, and the thickness of (2) the Mo_5Si_3 layer is $Y = x_2(t) - x_1(t)$. This is shown schematically in Fig. 2.

An intermediate layer is observed which is calculated below to be much thinner than the $MoSi_2$ layer. Thus, most of the flux passing out of layer 1 passes through layer 2 into layer 3. Although the absolute values of D_1 and of D_2 [7] are somewhat uncertain, the D_2/D_1 ratio is broadly accepted to be of the order of 1:50.

The Si flux through the $MoSi_2$ layer was given above by Equation 2. The flux through Mo_5Si_3 is given similarly by

$$J_2(\text{diff}) \;=\; -D_2\nabla Cq_2 \;=\; -D_2(C_2 - C_3')q_2/Y \tag{12}$$

where ∇C is the concentration gradient. Let the boundary between 1 and 2 advance a distance δx_1 that is small in comparison with the thickness of layer 2. At the same time the interface between 2 and 3 advances δx_2 which is defined by the incremental increase in the thicknesses of 1 and 2. In terms of the time rates

$$\mathrm{d}x_2/\mathrm{d}t \;=\; \mathrm{d}x_1/\mathrm{d}t + \mathrm{d}Y/\mathrm{d}t. \tag{13}$$

or

$$\mathrm{d}Y/\mathrm{d}t \;=\; \mathrm{d}x_2/\mathrm{d}t - \mathrm{d}X/\mathrm{d}t. \tag{14}$$

The equivalent expression to Equation 2 for the flux through 2 is

$$J_2(\text{mass}) \;=\; \mathrm{d}x_2(\beta_2 - C_4q_3)/\mathrm{d}t \tag{15}$$

The continuing existence of 2 requires that $\mathrm{d}x_2/\mathrm{d}t \geqslant \mathrm{d}x_1/\mathrm{d}t$, or that the ratio $(\mathrm{d}x_2/\mathrm{d}t)$: $(\mathrm{d}x_1/\mathrm{d}t) \geqslant 1$. Expressions for the rates are obtained by setting Equation 1 equal to Equation 2 and Equation 12 equal to Equation 15. Inserting these values into the inequality gives

$$X/Y \;>=\; (D_1/D_2)\phi \tag{16}$$

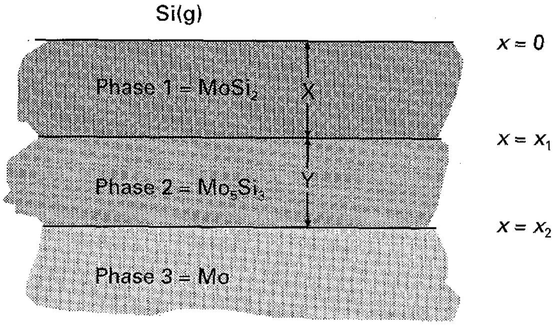

Figure 2 Schematic representation of phases present in siliciding of Mo.

where the factor ϕ, which is independent of time, is expected to be of the order of unity or even greater, and is given by

$$\phi = \frac{q_1}{q_2}\frac{V_2}{V_1}\frac{(\beta_2 - C_4 q_3)}{B_1}\frac{C_0 - C'_0}{C_2 - C'_3} \tag{17}$$

indicating that theoretically the $MoSi_2$ layer should be much thicker than the Mo_5Si_3 layer, as was indeed observed.

The kinetics for the growth of the outer layer 1 were presented by Equations 1–11. The equations are applicable to three phase growth since none of the parameters involve the Mo phase and there is only a minor dependence on the Mo_5Si_3 phase through K_1 and β_2. However, the variables x_2 and Y reflect the time dependence for the growth of the outer layer as shown by Equations 13 and 14. Hence, the possible presence of kinetic barriers presents four possible situations: the presence or absence of a kinetic barrier in converting phase 2 to phase 1; similarly but independently, the presence or absence of a kinetic barrier in converting phase 3 to phase 2. These possibilities are presented next in which we make extensive use of Equation 14.

2.3.1 Case 3. No kinetic barriers at (1)|(2) or (2)|(3) interfaces.

The rate of thickening dY/dt of layer 2 is given by equating Equations 12 and 15 to give

$$dx_2/dt = [D_2 \Delta C_{23} q_2/B_2]/Y = b/Y, \tag{18}$$

in which $b = D_2 \Delta C_{23} q_2/B_2$. Introducing this result into Equation 14 and using Equation 4 gives

$$dY/dt = b/Y - a_1/(t)^{1/2}. \tag{19}$$

By defining $\tau = 2(t)^{1/2}$, and $Z = Y/\tau$, upon rearrangement Equation 18 becomes

$$Z\, dY/d\tau = b/2 - a_1 Z, \tag{20}$$

where Z can be expressed as a power series $Z_0 + Z_1\tau + Z_2\tau^2 + \ldots$ It can be readily shown that all terms except Z_0 vanish, and that Z_0 must satisfy $Z_0{}^2 = b/2 - a_1 Z_0$, or

$$Z_0 = (1 + 2b/a_1^2)^{1/2} - 1, \tag{21}$$

from which

$$Y = 2Z_0(t)^{1/2} \tag{22}$$

Recalling from Equation 3 that $X = 2a_1(t)^{1/2}$, we can write

$$Y/X = Z_0/a_1 \tag{23}$$

and

$$x_2 = X + Y \tag{24}$$

showing that the thickness of layer 2 remains proportional to that of layer 1, and the advance of the siliciding front x_2 is a parabolic function of time.

2.3.2 Case 4. Kinetic barrier at (1)|(2), no barrier at (2)|(3) interface

The rate of thickening of layer 2 is determined by Equation 14. The term dx_2/dt is given by Equation 16, but dx_1/dt is now given by Equation 8, leading to

$$dY/dt = b/Y - 1/(g_1^2 + h_1 t)^{1/2}. \tag{25}$$

$$\approx b/Y - 1/g_1 \quad \text{for } t \ll g_1^2/\mathrm{h}_1. \tag{26}$$

Integration results in

$$Y = (2bt)^{1/2}. \tag{27}$$

At $t \gg g_1^2/h_1$

$$dY/dt \approx b/Y - 1/(h_1 t)^{1/2}. \tag{28}$$

This expression is the analogue of Equation 19 in which a_1 is replaced by $1/(h_1)^{1/2}$. Introducing this substitution into Equation 21 gives

$$Z_0 = [(1 + 2bh_1)^{1/2} - 1] \tag{29}$$

and

$$Y = Z_0(t)^{1/2}. \tag{30}$$

Although this has the same form as Equation 27 for short times, the expression for the proportionality constant Z_0 changes with time and its magnitude decreases with increasing time. Thus, there is a transition region at $t \approx g_1^2/h_1$ over which the growth slows.

2.3.3 Case 5. No kinetic barrier at (1)|(2), barrier at (2)|(3)

This case can be shown to be physically impossible. Equation 14 serves again as the starting point for this derivation; dx_2/dt is now given by the analogue to Equation 6 for layer 1, namely

$$dx_2/dt = [K_2 D_2 q_2 \Delta C_{23}]/[B_2(D_2 q_2\text{-}K_2 Y) \tag{31}$$

$$= 1/[g_2 + h_2 Y] \tag{32}$$

where $g_2 = B_2/(K_2 \Delta C_{23})$ and $h_2 = B_2/(D_2\, q_2\, \Delta C_{23})$. The term dx_1/dt is obtained from Equation 8, so that dY/dt is

$$dY/dt = 1/[g_2 + h_2 Y] - a_1/(t)^{1/2} \tag{33}$$

The usual substitutions are introduced, namely, $\tau = 2(t)^{1/2}$, $Z = Y/\tau$, resulting in

$$(g_2 + h_2\tau Z)(dY/d\tau) = \tau/2 - a_1(g_2 + h_2\tau Z) \tag{34}$$

When $t = 0$, $\tau = 0$, and the equation reduces to

$$(dY/d\tau) = -a_1 \tag{35}$$

This result in combination with the condition that $Y = 0$ when $t = 0$ leads to a clearly non-physical solution which can only be resolved if g_2 vanishes, i.e., if there is no kinetic barrier between 2 and 3. That is layer 2 could disappear if there were a kinetic barrier between 2 and 3, but none between 1 and 2.

2.3.4 Case 6. Kinetic barrier at (1)|(2) and (2)|(3)

This case is treated in a similar manner to the above except that the term dx_1/dt is given instead by Equation 8 to give;

$$dY/dt = 1/[g_2 + h_2 Y] - 1/(g_1^2 + h_1 t)^{1/2}. \quad (36)$$

For times $t \ll g_1^2/h_1$ the dx_1/dt term is approximately constant with a value of $1/g_1$. Introducing this approximation allows the above expression to be integrated to yield;

$$[g_1 g_2/(g_1\text{-}g_2)]Y + [g_1 h_2/(g_1\text{-}g_2)]Y^2/2 = t. \quad (37)$$

This is only physically possible if $g_1/g_2 > 1$, that is if

$$(B_1/B_2)(K_2/K_1)(\Delta C_{23}/\Delta C_{12}) > 1$$

i.e., if the kinetic barrier between 1 and 2 is much greater than between 2 and 3.

2.4 Models of initial solid a heterogeneous multiphase material

The initial solid need not be homogeneous. When the starting material was prepared from admixtures of $MoSi_2$ and Mo powders, upon annealing a heterogeneous mixture resulted of Mo plus Mo_5Si_3 granules, or of Mo_5Si_3 plus $MoSi_2$ granules, depending on the composition of the initial mixture.

2.4.1 Case 7. Initial solid a mixture of phase 2 and phase 3

2.4.1.1 Effect on the growth kinetics of phase 1. Phases 2 and 3 being initially in equilibrium and in intimate contact, each have uniform compositions corresponding to Mo_5Si_3 saturated with Mo and to Mo saturated with Si. Upon exposure to Si(g), a $MoSi_2$ layer (phase 1) forms and advances inward from the outer surface preceded by a Mo_5Si_3 layer (phase 2). This is similar to the situation if the starting material had been pure homogeneous Mo. The main difference is that some of phase 2 was already present before the exposure to Si vapour. With the possible exception of some minor transient effect in establishing "equilibrium" at the interface between phase 1 and those initial Mo_5Si_3 regions, the presence of those regions has no effect on the activity gradient conditions in phase 1. Thus, the advance of phase 1 at $x = x_1$ should be given by Equations 3 or 7. The only parameter in these equations that might be influenced by the initial heterogeneity is $B_1 = \beta_1 - \beta_2$, and of these only the latter term is likely to be affected. That is, the porosity of the region occupied by phase 2, could differ from that resulting entirely from the siliciding of phase 3. A revised value for β_2 would have to be determined experimentally.

2.4.1.2 Effect on the kinetics for the advance of boundary between phase 2 (Mo_5Si_3) and the unreacted heterophase region. Experimentally the boundary between phase 2 and 3 is not unambiguously definable because of involutions apparently stemming from mergers of the advancing Mo_5Si_3 layer with the Mo_5Si_3 regions initially present. For simplicity an approximate one-dimensional model is proposed based on the following assumptions: (1) the Mo_5Si_3 phase initially present in the starting solid occurs as uniformly sized particulates, having a circular cross-section of diameter $2r$; (2) the particulates are spatially distributed at random; (3) the volume fraction of the particulates is v_2, where $v_2 \ll 1$, and is calculable from the original admixture composition; (4) the advance of the $MoSi_2$ phase into those regions of the starting solid not converted to Mo_5Si_3 is substantially given by Equations 3 or 7; (5) the composition gradient in any given particulate is uniform and is determined by the distance between where it emerges from the $MoSi_2$ growth front and its furthest extension into the unreacted solid. For the purposes of this model we focus on those particulates for which some portion lies in the Mo_5Si_3 band of width Y, given by Equations 22, 27, 30 or 37 for the case of advance into a *homogeneous* solid as illustrated in Fig. 3.

Let w be a coordinate normal to the plane of the advancing $MoSi_2$ front that increases in value with increasing distance into the sample interior and let w locate the position of the centre of a given particulate. The value of w for that particle (a) that is about to be completely converted to $MoSi_2$ and to be swept out of the Mo_5Si_3 band is defined as zero. Another particle (b) is about to be covered by that band, so that it no longer extends into the unreacted starting solid has a value $w = Y$. This is shown in Fig. 3. At the other extreme a particle (c) that is about to make contact with the band has $w = 2r + Y$. By assumption, particulates over the range $0 < w < (2r + Y)$ are equally probable. However, for particulates in the range $0 < w < Y$, the concentration gradient ∇C is the same as for a homogeneous solid, i.e., $\nabla C = \Delta C/Y$; outside of that range $\nabla = \Delta C/w$. The gradient averaged over the initial $MoSi_2$ and Mo_5Si_3 regions is given by

$$\langle \nabla C \rangle_{\text{Ave}}$$

$$= \Delta C \left[V_2 \left\{ \frac{\int_Y^{2r+Y} \frac{dW}{W}}{2r+Y} + \frac{Y}{2r+Y}\frac{1}{Y} \right\} + \frac{1-V_2}{Y} \right]$$

$$= \Delta C \left[V_2 \left\{ \frac{1 + \ln\frac{2r+Y}{Y}}{2r+Y} - \frac{1}{Y} \right\} + \frac{1}{Y} \right]$$

$$= \left\langle \frac{\Delta C}{Y} \right\rangle_{\text{Ave}} \quad (38)$$

Thus, the average value of the gradient is less than for the case of the homogeneous solid. Thus, in order to satisfy the concentration gradient requirement of Equation 12, theoretically the layer thickness of

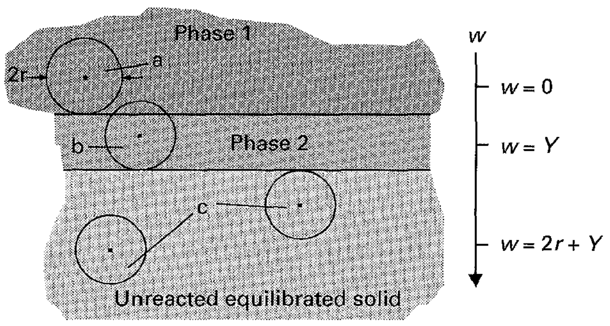

Figure 3 Schematic representation of distribution of Mo_5Si_3 regions in equilibrated solid undergoing siliciding.

phase 2 would be actually reduced. However, experimentally this would be difficult to verify because of the irregularity of the front between phases 2 and 3. Note also that when $v_2 \approx 1$ the structure is expected to consist of isolated regions of Mo embedded in a matrix of Mo_5Si_3 so that Equation 38 is no longer applicable.

2.4.2 *Case 8. Initial solid a mixture of $MoSi_2$ and Mo_5Si_3; effect on the growth kinetics of phase 1*

As in the above case, phases 1 and 2, being initially in equilibrium, will each be free of compositional gradients. Upon exposure to Si(g), the Mo_5Si_3 regions begin to convert to $MoSi_2$, the activity of Si becomes unity across the surface, but elsewhere the Si activity is expected to remain defined by the equilibrium between phase 1 and phase 2. During the early stages of the siliciding when the thickness of the $MoSi_2$ growth layer is small compared to the size of the initial $MoSi_2$ regions, the growth into the Mo_5Si_3 regions will be given by Equations 3 or 7.

The initial $MoSi_2$ regions cannot be significant sinks for Si. Due to the relatively high mobility of Si in $MoSi_2$, this phase can act like a 'short circuit" conduit for the lateral transport of Si to the sinks where the Mo_5Si_3 + Si reaction is occurring. Such lateral transport is increasingly enhanced as the thickness of the growth layer increases relative to the mean size of the initial $MoSi_2$ regions. An analysis of the intermediate stages of this process would be extremely complicated. Fortunately, the essential features of this process can be revealed by a time-incremented finite element computer simulation [4]. Qualitatively, the situation in which the $MoSi_2$ layer is thick relative to the size of the initial $MoSi_2$ regions can be treated as a modification of the two phase system discussed above. The Si flux entering from the outer surface is now funneled to the Mo_5Si_3 regions by the "short circuiting" initial $MoSi_2$ regions that statistically intercept the growth front. This locally enhances the concentration gradient in the Mo_5Si_3 region.

2.4.2.1 Model for the Growth Kinetics. For simplicity we consider that the mean gradient in the Mo_5Si_3 region at the growth front remains normal to the outer surface. We also assume that the gradient in the $MoSi_2$ layer at the outer surface is laterally uniform. That is the diffusion of Si through the $MoSi_2$ is independent of whether the latter was initially present or was produced by reaction with Mo_5Si_3. Then the Si flux entering the solid from the vapour can again be expressed as J_1(diff) given by Equation 1.

$$J_1(\text{diff}) = -D_1(\Delta C_{01}/X)q_1 \qquad (1)$$

At the growth front that flux is directed to the Si sink regions which is where the reaction is occurring and is limited to an area fraction v_2. Thus the flux at the growth sites is

$$J_1(\text{diff}) = -D_1(\Delta C_{01}/X)q_1/v_2 \qquad (39)$$

Since at the growth front Si only needs to be supplied to the Mo_5Si_3 regions instead of Equation 2, the net required flux for the advance is:

$$J_1(\text{mass}) = \delta x_1(\beta_1\text{-}\beta_2)v_2/\delta t. \qquad (40)$$

Equating Equations 39 and 40 and integrating leads to

$$x_1 = 2[a_1/v_2](t)^{1/2} \qquad (41)$$

where x_1 is the thickness of the $MoSi_2$ layer and a_1 is a constant defined in Equation 3, showing that after a sufficient time the growth of the $MoSi_2$ layer is strongly dependent on v_2 the volume fraction of Mo_5Si_3 in the equilibrated starting solid.

By analogy to Equations 10 and 11, the effect of the heterogeneous structure on the mass of Si the mass gain per unit area of starting solid, corresponding to the formation of the $MoSi_2$ layer of thickness x_1 is given by:

$$m(Si)/\text{area} = [x_1 \text{ area } v_2 B_1 A(\text{Si})]/\text{area}$$
$$= 2a_1 B_1 A(\text{Si})(t)^{1/2} \qquad (42)$$

showing that no significant dependence of the mass gain on v_2 is expected.

The presence of a kinetic barrier to the conversion of Mo_5Si_3 to $MoSi_2$ leads to similar predictions to those given above.

3. Discussion

3.1 A discussion of Cases 7 and 8 and a comparison with experiment

The general model is one-dimensional that considers the layer thickness to be uniform over the entire sample. If the starting solid is already a partly reacted, random polyphase material then the transformation process becomes more complex and the boundaries of the layers less well defined. This situation, considered in Cases 7 and 8, offers a partial interpretation of the kinetic behaviour of partially pre-reacted materials shown in Fig. 1. The discussion in sections 2.4.1.1 and 2.4.1.2 indicates that the presence of islands of Mo_5Si_3 have little effect on the growth rate provided that some Mo remains initially unreacted,

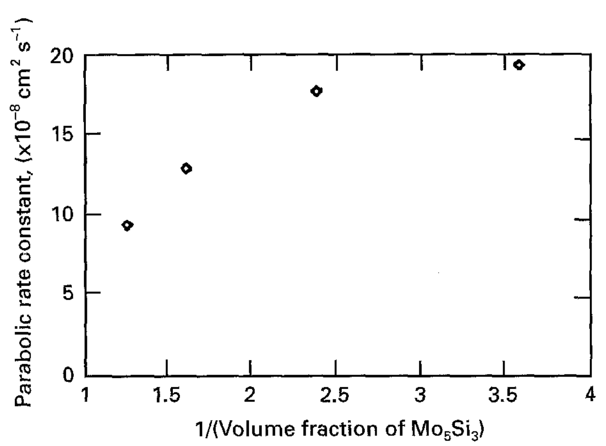

Figure 4 Dependence of the parabolic growth rate constants for the siliciding of an equilibrated Mo + Si solid compact on 1/(volume fraction of Mo_5Si_3) of heterogeneous solid consisting of $MoSi_2$ and Mo_5Si_3 phases.

i.e., for atomic fractions of Si less than 0.3. This expectation is consistent with Fig. 1. At higher initial Si concentrations islands of $MoSi_2$ appear. These islands are no longer sinks for Si. The enhancement of the growth rate from these effects was modelled in Equation 41, which indicates that the parabolic rate constant should increase linearly with $1/v_2$. The limited available quantitative data is plotted this way in Fig. 4 and is qualitatively consistent with the model over experimental Mo_5Si_3 volume fractions ranging from 0.79–0.42.

As discussed above, the increase in the kinetic rate constants is expected to saturate at a sufficiently low volume fraction, where the structure is expected to change from that of $MoSi_2$ islands dispersed in a matrix of Mo_5Si_3 to the inverse structure. This may account for the substantially smaller value of the rate constant when the volume fraction is 0.28 ($1/v_2 = 3.6$), or the model may be too simple. Microstructural analysis would be useful in resolving this issue.

4. Conclusions

Providing that adequate data is available for the time dependent growth of the various layers, the above analyses provide a basis for detecting the presence and characterizing the magnitude of possible kinetic barriers to the processes of siliciding Mo to Mo_5Si_3 or of Mo_5Si_3 to $MoSi_2$. The model concludes that a large kinetic barrier to the former process but not to the latter is incompatible with the assumption of local quasi-thermodynamic equilibrium and the fact of much greater Si mobility in $MoSi_2$ compared to Mo_5Si_3. The models are presented in sufficiently general terms to be translatable to other analogous systems.

The present "semi-microscopic" model offers a qualitative interpretation of; (1) the observed insensitivity of the layer growth rate to the addition of Si at concentrations in which unreacted Mo remains present, and (2) the increase in that rate when the initial Si concentration is great enough to ensure that no unreacted Mo is present in the equilibrated solid. Experimentation is needed to determine how well the model corresponds to the actual growth processes.

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