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Acta Materialia 51 (2003) 959–974



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## Stresses induced in alloys by selective oxidation

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Received 9 August 2002; accepted 19 October 2002

### Abstract

Consider a substitutional solution of two metallic elements A and B. When the alloy is exposed to air at an elevated temperature, A oxidizes, but B does not. In the alloy, the two elements diffuse in opposite directions, but usually at different rates; the nonreciprocal diffusion is known as the Kirkendall effect. At the oxide-alloy interface, metallic atoms may either emit from or inject into the interior of the alloy. Both the nonreciprocal diffusion and the interfacial process generate stress in the alloy, while creep relaxes the stress. If tensile, this stress could generate voids. This paper formulates governing equations both in the alloy and at the interface. Numerical examples are given for nickel-aluminum alloys. The stress in the alloy near the interface can be either tensile or compressive, depending on the oxidation mechanism, as well as on the relative diffusion rates of Ni and Al.

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*Keywords:* Oxidation; Diffusion; Nickel-aluminide; Stress generation; Voids

### 1. Introduction

Stress generation and voiding in alloys upon selective oxidation is a long-standing problem in materials science. In some binary alloys (NiAl being the most intensively studied), pronounced interdiffusion occurs. In Ni-rich compositions, cavities form at the oxide/alloy interface, but are rarely observed in the Al-rich compositions [1]. Oxidation-induced voiding can also occur in multi-component alloys, exemplified by a PtNiAl alloy containing Cr and Co (Fig. 1) after long exposures.

A more contemporary example of interdiffusion driven by selective oxidation occurs in thermal barrier coated superalloys used in gas turbines. Such systems comprise a layer of Al-rich Ni based alloy, known as the bond coat, and a superposed layer of zirconia, which provides thermal insulation. Oxidation of the bond coat creates a thin intervening layer of  $\text{Al}_2\text{O}_3$ . As the  $\text{Al}_2\text{O}_3$  grows, Al depletes near the surface of the bond coat, motivating Al in the interior to diffuse out, and Ni near the surface to diffuse in. Interdiffusion between the bond coat and the superalloy also depletes Al and enriches Ni in the bond coat. The durability of thermal barrier coated systems has been related to a variety of processes linked to interdiffusion [2–5].

To prepare for the modeling of these phenom-

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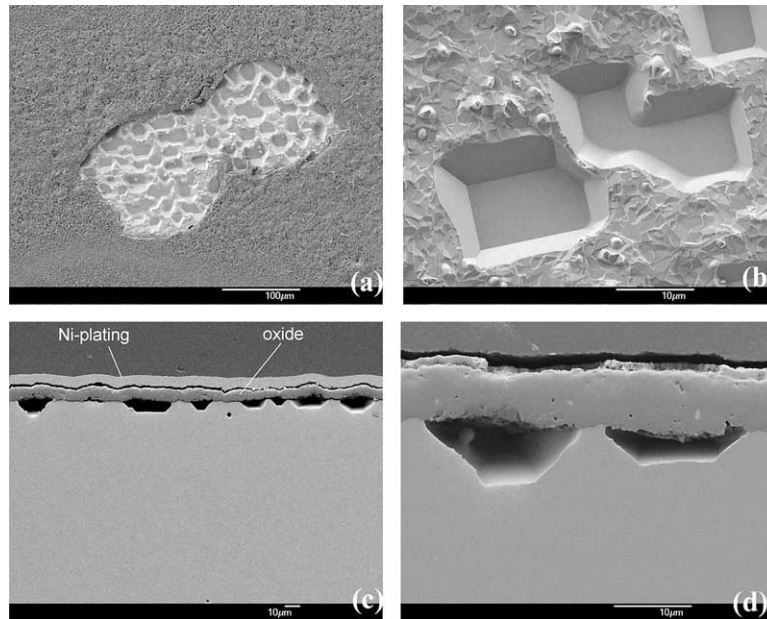


Fig. 1. Micrographs of a bulk sample of Pt-modified NiAl after oxidation at 1150 °C for 300 h. (a) A piece of oxide has spalled off, exposing metal surface with voids. (b) Higher magnification image of the voids. (c) The cross-section shows the voids in the metal, under the oxide. The bright layer on top of the oxide is Ni plated to preserve the oxide upon polishing. (d) Higher magnification image of the cross section.

ena, this paper examines a simpler phenomenon, having many of the same physical features, but not the extreme mathematical complexity. Fig. 2 illustrates a substitutional solid solution, of metallic elements A and B, exposed to air at an elevated temperature. The alloy is semi-infinite and has no voids. The element A preferentially oxidizes, and the element B remains in the alloy. At time  $t$ , the

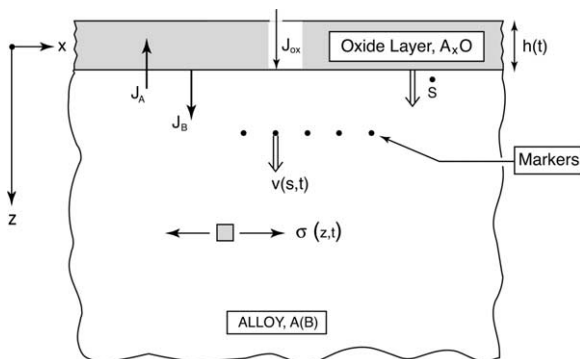


Fig. 2. A schematic of the selective oxidation of a binary alloy.

oxide thickness is  $h(t)$ , and the oxide-alloy interface is at position  $z = S(t)$  and moves at velocity  $\dot{S}$ . The composition in the alloy is uniform in the  $x$  and  $y$  directions, but nonuniform in the  $z$  direction, so that diffusion fluxes are along  $z$ , causing a marker velocity field  $v(z,t)$  and a biaxial stress field,  $\sigma(z,t)$  in the alloy.

While aspects of this problem have been investigated, beginning with nonreciprocal diffusion [6], and selective oxidation [7], the generation of stress and its relaxation by creep have never been addressed with the rigor needed to perform numerical calculations. This is the goal of the present article. We specify how diffusion and oxidation remove or insert atoms and, thereby, generate a stress field, which is simultaneously relaxed by creep. A moving boundary problem is formulated, and applied to Ni-Al alloys. Compositions, fluxes, and stresses are calculated.

## 2. Synopsis

Selective oxidation induces stress in the alloy by two processes: nonreciprocal diffusion inside the alloy, and injection or emission at the oxide-alloy interface. Before formulating the theory, we outline the main physical considerations. Nonreciprocal diffusion was first appreciated upon observing that molybdenum wires sandwiched between  $\alpha(\text{Zn,Cu})$  solid solution and pure Cu, upon annealing, move toward the Zn-rich region [8]. The marker motion demonstrated that Zn diffuses faster than Cu and that, to fill the space, atoms enter the region by convection. In his original analysis, Darken [6] asserted that contributions to the volume change other than convection could be neglected: that is, the elastic strains are negligible, as well as the lattice volume changes dictated by the composition. Also, he tacitly assumed that enough dislocations climb to maintain vacancy concentrations close to equilibrium [9], in accordance with several experimental findings; for example, voids in Ni-Cu diffusion couples (wherein Cu diffuses faster than Ni) can be suppressed by imposing small pressures [10]. *The same assertions are made in this article.*

As illustrated in Fig. 3a, nonreciprocal diffusion causes a mass gain or loss inside the alloy, generating a dilatational strain-rate field [11–14]. In the direction of the diffusion flux, the material is free to move, so that no stress is generated. In the directions transverse to the diffusion flux, however, material is constrained, so that a biaxial stress field arises to drive creep (Fig. 3b). The creep strain-

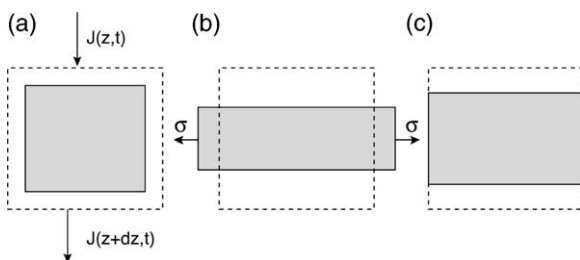


Fig. 3. (a) Nonreciprocal diffusion has a flux divergence, causing dilatational strain-rate. (b) Stresses in transverse directions drive creep. (c) Diffusion and creep combined to satisfy the constraint in the transverse directions. The net strain-rate in the longitudinal direction gives rise to the marker velocity.

rates change the shape of the material element, but conserve its volume. Creep and nonreciprocal diffusion, in combination, meet the constraint (Fig. 3c).

The processes at the oxide-alloy interface dictate the sign and magnitude of a second source of stress. Analogous effects occur in thin film deposition [15]. Three cases are assessed, designated in terms of the  $\alpha$  parameter. This parameter is a non-dimensional measure of the ratio of the atom flux at the oxide-alloy interface to the interface velocity, formally defined in Section 4.

1. *The  $\alpha$  zero case* (Fig. 4a). The substrate atoms removed from interface ledges are replenished by atoms emitted from dislocations, located near (or at) the interface, that climb parallel to the surface. This situation does not introduce stress in the substrate [16]. To accommodate the vertical displacements, the oxide moves by a rigid body displacement relative to the substrate.
2. *The  $\alpha$  positive case* (Fig. 4b). The substrate atoms removed from interface ledges are replenished by atoms emitted from substrate dislocations that climb normal to the surface. This process is equivalent to the injection of vacancies into the substrate from the interface (typically associated with observations of vacancy loops). The climb of the substrate dislocations causes a contraction transverse to the flux, and the constraint induces a biaxial tensile stress. Note that, when all ledge atoms removed from the substrate to form the oxide are replaced, the new oxide is accommodated at the free surface.
3. *The  $\alpha$  negative case* (Fig. 4c). When all of the new oxide forms at the interface, some substrate atoms removed from interface ledges can form interstitials (typically associated with observations of interstitial loops) that attach to dislocations in the substrate, causing climb normal to the surface. This process may also occur by means of a vacancy flux from the substrate. The climb of the substrate dislocations causes an expansion transverse to the flux, and the constraint induces a biaxial compressive stress.

These processes are illustrated by the oxidation

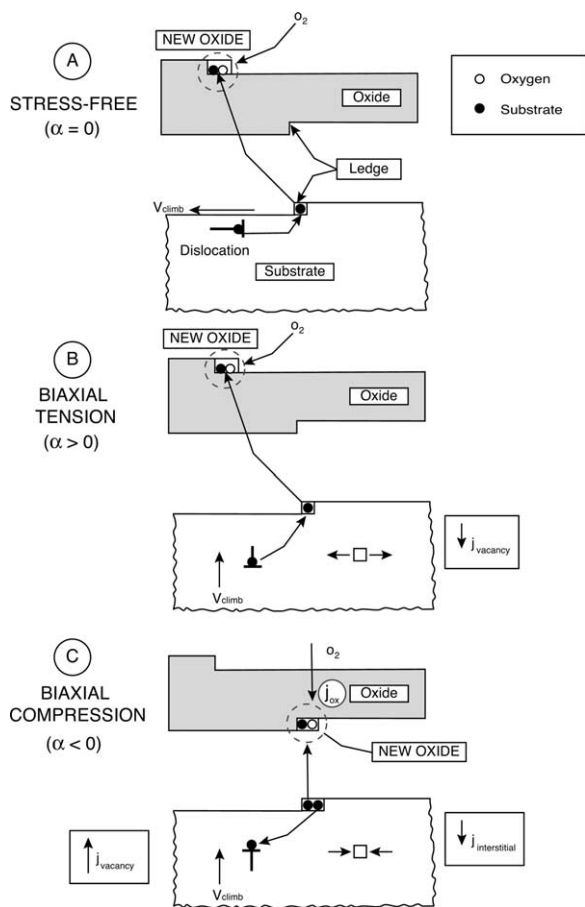


Fig. 4. The interfacial processes (substrate atom removal or new oxide formation) are accompanied by the movements of the dislocations in the substrate, located near (or at) the interface, climbing (a) parallel to the surface, or (b) normal to the surface equivalent to vacancy injection, or (c) normal to the surface equivalent to interstitial injection or vacancy emission. In (b) and (c), biaxial stresses are generated, which may motivate other dislocation activities, such as creep.

of elemental substrates. In one limit, when Ni oxidizes, the new oxide forms at the oxide-air interface, causing a mass loss at the oxide-substrate interface. This results in a vacancy flux into the substrate, causing biaxial tension [17–20]. The oxidation of Si illustrates another limit. New oxide forms at the oxide-substrate interface, leading to a mass gain that causes Si interstitials to inject into the substrate, forming interstitial loops and extrinsic stacking faults, which cause biaxial compression in the Si [21–24].

For a binary alloy, in addition to the interfacial mass change, the relative diffusivity of the two elements in the alloy determines whether there is a volume loss or a volume gain at the oxide-alloy interface. A microscopic theory of the interface mass exchange based on Fig. 4 is beyond the scope of this paper. Instead, we assume that the injection or emission flux is proportional to the interface velocity, through the (phenomenological)  $\alpha$  parameter.

Based on these considerations, the ensuing analysis has the following steps.

1. The marker velocity in a binary alloy is related to the diffusion flux.
2. The material strain rates in the alloy are derived in terms of the marker velocity.
3. Two atom placement rules in the alloy are contrasted: one in which atoms are removed/inserted only on planes normal to the flux (all-or-nothing rule), and the other in which atoms are removed/inserted equally on all planes (isotropic rule). The latter is compatible with experimental evidence, and is used for all subsequent assessments.
4. Conditions operative at the interface between the oxide and the binary alloy are examined and an expression presented that relates the flux in the alloy near the interface to the interface velocity. The sign of the flux is specified through a parameter  $\alpha$  governed by mechanisms operative in the oxide and at the interface.
5. The diffusion and creep laws applicable to a binary alloy are used to set up a differential equation for the stress, the flux and the concentration gradient, as well as the boundary conditions.
6. Non-dimensional groups representing the stress, the flux and the concentration gradient are derived.
7. Results are calculated for the oxidation of NiAl.
8. Oxidation-induced stress in an elemental substrate is analyzed in the Appendix, which may be read before the body of the text.

### 3. Kinematics in the alloy

#### 3.1. Nonreciprocal diffusion and marker movement

Following Darken [6], we assume that the alloy has a constant volume per atom, denoted by  $\Omega$ . Let  $C^A$  and  $C^B$  be the numbers of atom A and atom B per unit volume. Specify the composition of the alloy by the number fraction of A, namely,  $c = C^A / (C^A + C^B)$ . Thus, the number fraction of B is  $1 - c$ ,  $C^A = c / \Omega$  and  $C^B = (1 - c) / \Omega$ .

Imagine a plane normal to  $z$  and stationary in a fixed space (Fig. 5). Let  $N^A$  be the net flux of A: the number of A atoms crossing the plane per area per time. Similarly, denote the net flux of B by  $N^B$ . Imagine a box, volume  $V_0$ , also stationary in space. When all strains other than convection are negligible, no matter how erratically atoms move, the box must contain  $V_0 / \Omega$  atoms at all time. Consequently, the net flux of the two elements combined,  $N^A + N^B$ , is independent of the position of the stationary plane,  $z$ . The alloy is sufficiently thick that diffusion remote from the oxide-alloy interface is negligible. We choose the fixed space such that the alloy far from the interface is stationary. In this space, the sum of the net fluxes of the two elements vanishes:

$$N^A + N^B = 0. \tag{1}$$

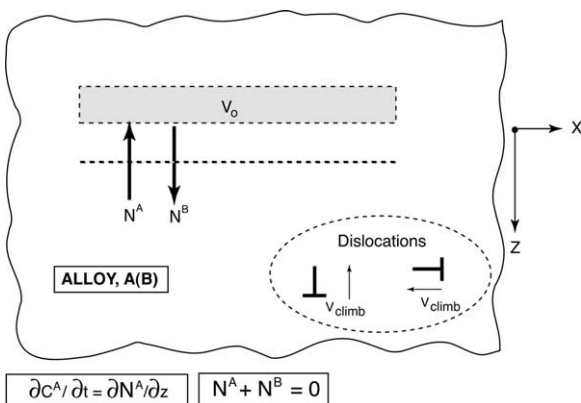


Fig. 5. The net flux  $N^A$  is the number of A atoms per time per area crossing a plane stationary in space. In an imaginary box fixed in space, the total number of atoms is constant, but the composition can change with time. Atoms are inserted and removed by dislocation climb on planes of various orientations.

At any time, relative to any plane stationary in this space, the number of A crossing in one direction equals the number of B crossing in the opposite direction.

In the imaginary box, although the total number of atoms is constant, the composition can change with time. The number density of A changes at a rate governed by the divergence of its net flux, namely,

$$\frac{\partial C^A}{\partial t} = -\frac{\partial N^A}{\partial z}. \tag{2}$$

A similar relation applies to B, but is redundant, because the total number of atoms in the box is constant.

The net flux  $N^A$  counts the number of A atoms crossing the stationary plane, regardless of the cause. For example, should the entire sample move by a rigid-body translation, speed  $v_{\text{rigid}}$  relative to the fixed space, the net flux of A would be  $N^A = C^A v_{\text{rigid}}$ . Rigid body motion is a special case of convection. Imagine that inert markers are placed at various locations along the  $z$ -axis, and move at different velocities. Let  $v(z, t)$  be the velocity of the marker at position  $z$  and time  $t$ . Convection carries a number,  $C^A v$  of A atoms across the stationary plane per area per time. Define the diffusion flux  $J^A$  as the number of the A atoms crossing the stationary plane per area per time in excess of that carried by the convection, namely,

$$N^A = J^A + C^A v. \tag{3a}$$

The net flux  $N^A$  is partitioned into two contributions: that due to diffusion  $J^A$ , and that due to convection  $C^A v$ . The flux of B can be similarly partitioned, namely,

$$N^B = J^B + C^B v. \tag{3b}$$

The net flux for each element is well-defined; in principle, it can be counted experimentally. The partition into diffusion and convection, however, is by convention. In fluid mechanics, the common practice is to specify the convection velocity by the net fluxes themselves: for example, by the mass-average net flux, or by the number-average net flux, or by the volume-average net flux [25]. The diffusion fluxes,  $J^A$  and  $J^B$ , depend on how one specifies the convection velocity. In this paper, we

follow Darken [6] and specify the convection velocity by the marker movement.

In a substitutional metallic solution, diffusion occurs by individual atoms jumping into nearby vacancies. Typically, the jump frequency of one element differs from that of the other, so that the two elements diffuse in the opposite directions, but at different rates. The diffusion is nonreciprocal, namely, the sum of the *diffusion fluxes* does not vanish,  $J \equiv J^A + J^B \neq 0$ . However, as discussed above, the sum of the *net fluxes* of the two elements vanishes,  $N^A + N^B = 0$ . Adding (3a) and (3b), one relates the marker velocity to the diffusion flux:

$$v = -\Omega J. \quad (4)$$

To fill the space, the markers must move in the direction opposite to  $J$ . Eq. (4) is a main result of Darken's analysis.

### 3.2. Marker velocity and strain-rates

To reconcile the marker movement and the zero net atomic flux, Darken [6] only needed to declare that the two elements had unequal diffusion fluxes, and then compensate for the difference by convection. He did not need to specify how convection occurred. However, to calculate the stress induced, we must specify the means. Such a specification cannot be deduced from Darken's theory; additional premises must be made.

To proceed we examine the physical significance of the marker velocity field,  $v(z,t)$ . Imagine two markers at different positions along  $z$ , moving at different velocities. When the two markers move apart, layers of atoms have to be inserted into the intervening space. When the two markers approach, layers of atoms have to be removed. This effect is dramatically demonstrated in a recent experiment [26], wherein markers originally placed on one plane (nominally the same  $z$ , but different  $x$  and  $y$ ) sometimes separate into multiple planes.

At time  $t$ , one marker is at  $z$ , and the other at  $z + dz$ . Their velocities are, respectively,  $v(z,t)$  and  $v(z + dz,t)$ . The second marker moves relative to the first at velocity  $v(z + dz,t) - v(z,t)$ . The velocity gradient is  $\partial v / \partial z = [v(z + dz,t) - v(z,t)] / dz$ . When  $\partial v / \partial z > 0$ , the two markers move apart, and  $(\partial v / \partial z)(dz / \Omega)$  atoms need to be inserted into

the intervening space per area per time. The velocity gradient defines the strain-rate:

$$d_z = \partial v / \partial z. \quad (5)$$

We assume that the thickness of the diffusion zone is small compared to the overall sample dimensions, to exclude transverse velocities in the diffusion zone. Consequently, the strain-rates in the two transverse directions vanish,  $d_x = d_y = 0$ .

The cause of the marker motion has yet to be specified. Once again imagine the box stationary in space (Fig. 5). The divergence of the diffusion flux is  $\partial J / \partial z$ . Nonreciprocal diffusion removes atoms from the box when  $\partial J / \partial z > 0$ , and inserts them when  $\partial J / \partial z < 0$ , as implied by Darken's theory. However, to determine the planes on which the atoms are removed or inserted, we must specify *the placement rule*. Two rules are envisaged.

### 3.3. All-or-nothing placement rule

Insert and remove atoms only on the planes normal to the flux direction, so that the diffusion induces strain-rates

$$d_z^D = -\Omega \frac{\partial J}{\partial z}, \quad d_x^D = d_y^D = 0 \quad (6)$$

(All – or – nothing rule).

The material is free to move in the flux direction, so that no stress will be generated. The diffusion-induced strain-rate  $d_z^D$  is responsible for the convection. Integrating (6), we recover the marker velocity field (4) obtained by Darken. This rule, however, is inconsistent with at least three experimental observations.

1. Upon the selective evaporation of Zn from thin foils of  $\alpha$ -(Zn,Cu), thinning, voiding and lateral shrinkage occur, each with comparable contributions to the solid volume reduction [27]. The lateral shrinkage and thinning indicate that lattice planes are removed throughout the crystal in all directions.
2. Thin foil diffusion couples bend upon nonreciprocal diffusion, indicating differential lateral shrinkage [13].
3. Massive dislocation activities accompany such

diffusion [28], whereas the all-or-nothing rule permits only dislocations with the Burgers vectors in the flux direction to climb, and absorb or inject vacancies (Fig. 5).

### 3.4. Isotropic placement rule

Atoms can only be added and removed from within the alloy grains where edge dislocations exist, by means of a climb mechanism. Since dislocations have Burgers vectors in multiple directions, the atoms removed and inserted can lie on planes other than those normal to the diffusion flux (Fig. 5). If the Burgers vectors are taken to be equally likely in all three orientations, the divergence of the diffusion flux causes isotropic strain-rates:

$$d_x^D = d_y^D = d_z^D = -\frac{\Omega \partial J}{3 \partial z} \quad (\text{Isotropic rule}). \quad (7)$$

This rule has been invoked in several previous studies [11–14], and will be adopted in this article.

The isotropic placement rule requires that diffusion generate an incompatible strain-rate field: it does not correspond to the unidirectional marker velocity (Fig. 3). To compensate, processes other than nonreciprocal diffusion, such as creep, must cooperate. Creep conserves volume, but changes shape. The net strain-rate in every direction,  $d_i$ , is the sum of that due to creep  $d_i^C$ , and that due to diffusion  $d_i^D$ , namely

$$d_x = d_x^C + d_x^D, \quad (8a)$$

$$d_y = d_y^C + d_y^D, \quad (8b)$$

$$d_z = d_z^C + d_z^D. \quad (8c)$$

In the two transverse directions,  $x$  and  $y$ , the rule (9) specifies  $d_x^D = d_y^D = -\frac{\Omega \partial J}{3 \partial z}$ , but the net strain rates vanish,  $d_x = d_y = 0$ . Consequently, the creep strain-rates in the transverse directions are  $d_x^C = d_y^C = +\frac{\Omega \partial J}{3 \partial z}$ . Since creep conserves volume,  $d_x^C + d_y^C + d_z^C = 0$ , the creep strain-rate in the  $z$ -direction must be

$$d_z^C = -\frac{2\Omega \partial J}{3 \partial z}. \quad (9)$$

The net strain-rate is the sum of that due to diffusion (7) and that due to creep (9),

$$d_z = -\Omega \frac{\partial J}{\partial z}. \quad (10)$$

This net strain-rate is responsible for the convection. Integrating (10), once again we recover the marker velocity field (4) obtained by Darken.

The isotropic placement rule is consistent with the observations of lateral shrinkage of thin foils during selective evaporation, and also predicts the bending of a thin foil diffusion couple. However, it is not a consequence of any fundamental principle, and should be modified if, for any reason, atoms are placed preferentially on certain crystal planes.

## 4. Boundary conditions at the oxide-alloy interface

The oxide thickness changes with time,  $h(t)$ . Let  $\Omega_{\text{ox}}$  be the volume of the oxide per metal ion. The growth of the oxide consumes  $\dot{h}/\Omega_{\text{ox}}$  number of A atoms per area per time. The interface moves at velocity  $\dot{S}$ , such that the alloy loses  $\dot{S}/\Omega$  number of A atoms per area per time. The number of A consumed by oxidation equals that lost by the alloy, so that

$$\frac{\dot{h}}{\Omega_{\text{ox}}} = \frac{\dot{S}}{\Omega}. \quad (11)$$

For present purposes, the interface velocity,  $\dot{S}$ , is prescribed and treated as a boundary condition on diffusion and stress development in the alloy.

Element B remains in the alloy and does not enter the oxide, causing a net flux of B into the alloy from the oxide-alloy interface. Again imagine a box stationary in fixed space, with one face in the oxide, and another in the alloy (Fig. 6). The area of the two faces is unity, and the thickness of the box is infinitesimal. Atoms of B do not enter or leave the box from the face in the oxide. But  $N^B(S,t)$  atoms of B leave the box from the face within the alloy per unit time. Let  $c_s$  be the number fraction of A atoms within the alloy at the interface. As the interface moves at velocity  $\dot{S}$ , the box

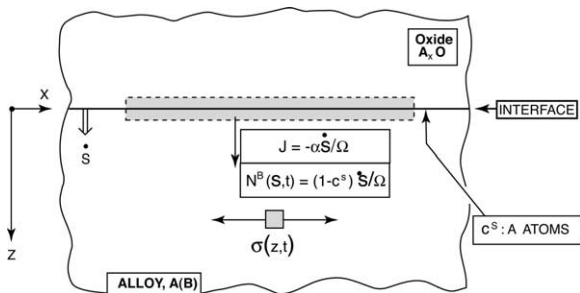


Fig. 6. The boundary conditions at the oxide-alloy interface. B atoms does not oxidize, so that its net flux at the interface,  $N^B(S, t)$ , is due to the motion of the interface. Oxidation may remove atoms from the alloy beneath the interface, or inject atoms into it, causing a diffusion flux. We assume that the diffusion flux in the alloy at the interface,  $J(S, t)$ , is proportional to the interface velocity.

loses  $(1 - c_s)\dot{S}/\Omega$  atoms of B per unit time. Equating the two numbers, we obtain the boundary condition for the net flux of B atoms:

$$N^B(S, t) = (1 - c_s) \frac{\dot{S}}{\Omega}. \quad (12)$$

The placement rule must be revisited in the presence of an oxide-alloy interface. The movements of interfacial ledges accommodate the removal of metal atoms on the interface, and dislocation climb accommodates the removal of metal atoms inside the alloy. If the interface ledge sites have a high mobility, relative to the lattice sites, the alloy would lose atoms primarily on the interface. To adjust the volume change, the oxide would displace relative to the substrate by a rigid-body translation. Then, oxidation would not induce stress in the alloy. This situation is analogous to the “all-or-nothing” placement rule. Conversely, if the interface ledge sites are relatively immobile, the oxide consumes the A atoms partly on the interface, and partly from the interior of the alloy. Then, the interface velocity  $\dot{S}$  is partitioned into two contributions: that due to the removal of metal atoms on the interface, and that due to the removal of metal atoms inside the alloy. As discussed in Section 2, the latter process corresponds to a diffusion flux  $J$  from the interior of the alloy to the interface.

Imagine that a marker is placed in the alloy at  $z = S^+$ , very close to the interface. Both the interface velocity  $\dot{S}$  and the marker velocity  $v$  are rela-

tive to a stationary site in the alloy well beneath the interface. Focus on the layer of alloy between the interface  $z = S$  and the marker  $z = S^+$ . If  $\dot{S} = v$ , no atoms are added to or removed from the layer. If  $\dot{S} > v$ , atoms must be removed from the layer. If  $\dot{S} < v$ , atoms must be added to the layer. The alloy loses  $\dot{S}/\Omega$  atoms per area per time. Of these,  $(\dot{S} < v)/\Omega$  atoms come from substrate dislocations climbing parallel to the surface, and  $-J$  atoms from substrate dislocations climbing normal to the surface. The partition is governed by the relative density and mobility of these dislocations. Here, we assume that  $J$  in the alloy near the interface is proportional to the interface velocity  $\dot{S}$ , namely,

$$J(S, t) = -\alpha \dot{S} / \Omega, \quad (13)$$

with  $\alpha$  a dimensionless constant. Because the marker velocity,  $v$ , relates to the sum of the diffusion fluxes of the two elements,  $J$ , according to (4), placement rule (13) is equivalent to  $v(S, t) = \alpha \dot{S}$ . That is, the marker velocity near the interface is proportional to the interface velocity. As discussed in Section 2, the interfacial process can generate stress even in the substrate of a single element, where nonreciprocal diffusion is absent. This case is treated in the Appendix.

It is possible to envisage an experiment to determine  $\alpha$ , wherein rows of small insoluble cylinders or particles are embedded in the alloy, close to the original surface [29]. Determination of their displacement relative to a fixed reference site in the substrate, for various  $h$ , as well as of the position of the interface with the oxide, yields  $\alpha$ . Note that markers close to the surface will be consumed by the moving oxide interface. The authors are unaware of experiments of this type for  $\beta$ -NiAl alloys, although voids and vacancy dislocation loops have been observed in such alloys during oxidation [1,30]. We will prescribe several values of  $\alpha$  in the calculation.

## 5. Kinetics

### 5.1. The diffusion law

Darken assigned unequal intrinsic diffusivities,  $D^A$  and  $D^B$ , to the two elements, but neglected the



effect of stress on the diffusion. Following Stephenson [12], we assume that the diffusion fluxes are driven by both the composition and stress gradients:

$$J^A = -D^A \frac{\partial C^A}{\partial z} + \frac{cD^A \partial \sigma_m}{\phi kT \partial z}, \quad (14a)$$

$$J^B = -D^B \frac{\partial C^B}{\partial z} + \frac{(1-c)D^B \partial \sigma_m}{\phi kT \partial z}. \quad (14b)$$

The dimensionless number  $\phi = d(\ln a)/d(\ln c)$  is Darken's thermodynamic factor, which he introduced to relate mobility and diffusivity. Here  $a$  is the activity of element A in the solution. We have adopted the isotropic placement rule. Consequently, when an atom is relocated from a stress-free position to a stressed position, the reduction in the free energy caused by the stress is  $\Omega \sigma_m$ , where  $\sigma_m$  is the mean stress.

We will use several combinations of the intrinsic diffusivities: the interdiffusion coefficient  $D = (1-c)D^A + cD^B$ , the average diffusivity  $\bar{D} = cD^A + (1-c)D^B$ , and the differential diffusivity  $\Delta = D^A - D^B$ . The first two are always positive, but the third can have either sign.

The sum of the diffusion fluxes of the two elements is

$$J = -\frac{\Delta \partial c}{\Omega \partial z} + \frac{\bar{D} \partial \sigma_m}{\phi kT \partial z}. \quad (15)$$

The contribution due to composition gradient is proportional to the differential diffusivity. When  $D^A > D^B$ , the composition gradient drives the flux  $J$  to the B-rich region. The appropriate diffusivity for the contribution due to the stress gradient is the average diffusivity of the two elements, as expected. The stress gradient drives the flux  $J$  to the region of large mean stress.

It is evident from (15) that the sign of the stress gradient at the interface depends on two processes: the nonreciprocal diffusion ( $\Delta = D^A - D^B$ ), and the oxidation process ( $\alpha$ ). The latter determines the sign of  $J$  at the interface according to (13). The consequences can be appreciated by examining two special cases.

1. When  $\Delta = 0$  and  $\alpha > 0$ , the composition gradient does not contribute to the diffusion flux  $J$ ,

but the stress gradient does. The positive  $\alpha$  dictates that atoms emit from the alloy, so that the stress gradient is negative, whereupon *the stress at the interface must be tensile*.

2. When  $\Delta > 0$  and  $\alpha = 0$ , the composition gradient causes a diffusion flux toward the interface. However, since  $\alpha = 0$ , at the interface  $J = 0$ , whereupon the stress gradient causes the diffusion flux to be directed away from the interface, and *the stress at the interface is compressive*.

A combination of (4) and (15) expresses the marker velocity in terms of the composition and stress gradients:

$$v = \Delta \frac{\partial c}{\partial z} - \frac{\bar{D} \Omega \partial \sigma_m}{\phi kT \partial z}. \quad (16)$$

Substituting (14a) and (16) into (3a), we can express the net flux of A in terms of the composition and stress gradients, namely,

$$N^A = -\frac{D \partial c}{\Omega \partial z} + \frac{c(1-c) \Delta \partial \sigma_m}{\phi kT \partial z}. \quad (17)$$

The net flux of B is  $N^B = -N^A$ .

Substituting (17) into the matter conservation Eq. (2), we obtain that

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left[ D \frac{\partial c}{\partial z} - \frac{\Omega c(1-c) \Delta \partial \sigma_m}{\phi kT \partial z} \right]. \quad (18)$$

This is a generalized diffusion equation.

The boundary conditions (12) and (13) become

$$\frac{D \partial c}{\Omega \partial z} - \frac{c_s(1-c_s) \Delta \partial \sigma_m}{\phi kT \partial z} = (1-c_s) \frac{\dot{S}}{\Omega}, \quad (19)$$

and

$$\frac{\Delta \partial c}{\Omega \partial z} - \frac{2\bar{D} \partial \sigma}{3\phi kT \partial z} = \alpha \frac{\dot{S}}{\Omega}. \quad (20)$$

The composition gradient and the stress gradient in (19) and (20) are evaluated at the oxide-alloy interface.

## 5.2. The creep law

Under uniaxial stress  $\sigma$ , power law creep is expressed as

$$d^C = d_0(\sigma/\sigma_0)^n, \quad (21)$$

where  $d^C$  is the creep strain-rate in the loading direction,  $n$  is the stress exponent (in the range 3–5),  $\sigma_0$  is the reference stress, and  $d_0$  is a strain-rate coefficient. The uniaxial stress also causes strain-rates  $-d^C/2$  in the two transverse directions, as required by volume conservation. In the diffusion couple, each material element is subject to an equal biaxial stress state in the  $x$  and  $y$  directions. Denote this stress field by  $\sigma(z,t)$ . Creep strain-rates are unchanged if a hydrostatic stress is superimposed. In particular, we can superpose a hydrostatic state of magnitude  $-\sigma(z,t)$  to material at  $(z,t)$ , so that the stress state becomes uniaxial. The creep law (21) gives the transverse strain-rate under the biaxial stress state:

$$d_x^C = d_y^C = (d_0/2)(\sigma/\sigma_0)^n. \quad (22)$$

The above is valid when the stress is tensile. An expression correct for both tension and compression is  $d_x^C = d_y^C = (d_0/2)(\sigma/\sigma_0)(|\sigma|/\sigma_0)^{n-1}$ .

In the direction  $x$ , diffusion induces a strain-rate,  $d_x^D = -\frac{\Omega \partial J}{3 \partial z}$ , where  $J$  is given by (15), and the net strain-rate vanishes, so that

$$\frac{d_0}{2} \left( \frac{\sigma}{\sigma_0} \right) \left( \frac{|\sigma|}{\sigma_0} \right)^{n-1} = \frac{1}{3} \frac{\partial}{\partial z} \left[ -\Delta \frac{\partial c}{\partial z} + \frac{\Omega \bar{D} \partial \sigma_m}{\phi k T \partial z} \right]. \quad (23)$$

In the biaxial stress field, the mean stress (defined as 1/3 the sum of the principal stresses) is  $\sigma_m = 2\sigma/3$ .

## 6. Non-dimensional groups and calculation procedures

Alloys that form alumina are rate-limited by diffusion in the oxide, such that the interface position at time  $t$  is

$$S = \sqrt{Kt}. \quad (24)$$

The parabolic rate constant  $K$  is known from experiment and becomes an input for determination of the fluxes and the stresses.

A dimensionless ratio can be formed between  $K$  and the diffusivity. Since the intrinsic diffusivities

are functions of composition,  $D^A(c)$  and  $D^B(c)$ , it is more convenient to express the response in terms of  $D_0$ , the interdiffusion coefficient at composition  $c_0$ . The dimensionless ratio

$$\gamma = \sqrt{\frac{K}{D_0}}, \quad (25)$$

designates the rate of diffusion of oxygen in alumina relative to that in the alloy.

The stress scales with the thermal energy per unit volume:

$$\Sigma = \frac{3\phi k T}{2\Omega}, \quad (26)$$

whereupon Eq. (23) sets a length:

$$\Lambda = \sqrt{\frac{2D_0(\sigma_0)^n}{3d_0(\Sigma)^n}}. \quad (27)$$

We scale the coordinate  $z$  and the interface position  $S$  by  $\Lambda$ . The diffusion Eq. (18) sets a time:

$$\tau = \frac{\Lambda^2}{D_0} = \frac{2}{3d_0} \left( \frac{\sigma_0}{\Sigma} \right)^n, \quad (28)$$

which depends only on the creep of the alloy. We scale the time  $t$  by  $\tau$ .

In terms of the scaled quantities, the diffusion Eq. (18) becomes

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left[ D \frac{\partial c}{\partial z} - c(1-c)\Delta \frac{\partial \sigma}{\partial z} \right], \quad (29)$$

and Eq. (23) becomes

$$\sigma |\sigma|^{n-1} = \frac{\partial}{\partial z} \left[ -\Delta \frac{\partial c}{\partial z} + \bar{D} \frac{\partial \sigma}{\partial z} \right]. \quad (30)$$

The two boundary conditions (19) and (20) set the gradients of the composition and the stress at the oxide-alloy interface. In terms of the scaled quantities, the boundary conditions become

$$\frac{\partial c}{\partial z} = \frac{(1-c_s)\bar{D} - \alpha c_s(1-c_s)\Delta}{D^A D^B} \frac{\gamma}{2\sqrt{t}}, \quad (31)$$

$$\frac{\partial \sigma}{\partial z} = \frac{(1-c_s)\Delta - \alpha D}{D^A D^B} \frac{\gamma}{2\sqrt{t}}. \quad (32)$$

The following calculations begin with no stress

in the alloy, and uniform composition  $c(z,0) = c_0$ . The composition is fixed at infinity at all time,  $c(\infty,t) = c_0$ . At time  $t$ , the position of the oxide-alloy interface moves to,  $z = \gamma\sqrt{t}$ . We evolve the composition field, the stress field, and the interface position simultaneously as follows. Based on the known stress and the composition field at time  $t$ , during a small time step,  $dt$ , we update the composition field according to the diffusion Eq. (29), the boundary condition (31), and the boundary condition  $c(\infty,t) = c_0$ . The composition at the interface,  $c_s$ , must also be updated, as well as the position of the interface. The updated composition field then is used to update the stress field by solving the second order ordinary differential Eq. (30), subject to the boundary condition (32) and vanishing stress at infinity.

## 7. Oxidation of $\beta$ -NiAl

Figs. 7–10 present the results of numerical computation for the oxidation of  $\beta$ -NiAl. To perform the second order ordinary differential Eq. (30), been chosen. The parabolic rate constant and the interdiffusion coefficient for  $\beta$ -NiAl at 1100 C suggest a representative value,  $\gamma \approx 0.01$  [1,31]. We use the intrinsic diffusivities,  $D^{\text{Ni}}$  and  $D^{\text{Al}}$ , in  $\beta$ -NiAl measured at 1100 C [31]. The initial Al composition is set at  $c_0 = 0.48$ , well within the  $\beta$ -phase field [32]. For such a Ni-rich composition, Ni diffuses faster than Al,  $D^{\text{Ni}} \approx 3D^{\text{Al}}$ . The creep exponent,  $n = 4$ , is representative of that for power law creep in  $\beta$ -NiAl at 1100 C [33–35]. To embrace the full range of possibilities, we consider several cases  $\alpha = 2/3, 0, -2/3$ .

The singularity in (31) and (32) at  $t = 0$  leads to numerical difficulties. Accordingly, we start the calculation at  $t = 1.0\tau$ . Fig. 7 plots composition profiles at several times for  $\alpha = +2/3$  and  $\alpha = -2/3$ . In both cases, Al depletes near the interface as oxidation proceeds, with a corresponding enrichment in Ni. The trend of the composition profile is insensitive to the choice of  $\alpha$ . The diffusion depth,  $z^*/\Lambda$ , increases with time as  $z^*/\Lambda \approx (t/\tau)$ .

Both the diffusion flux and the stress are vitally dependent on  $\alpha$ . When  $\alpha > 0$  (Fig. 8a), the com-

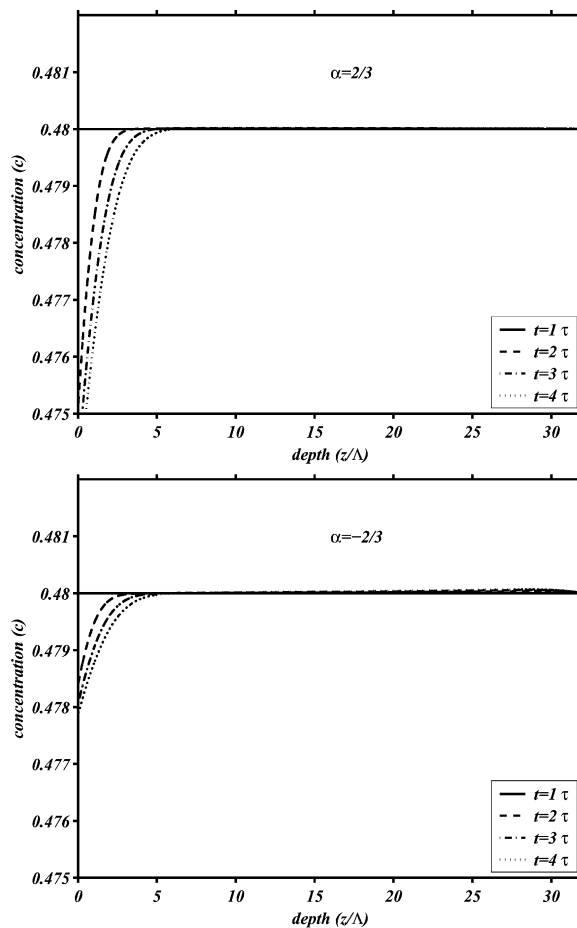


Fig. 7. Numerical results for the composition gradients at two values of  $\alpha$ .

combined diffusion flux of the two components,  $J$ , is negative, and atoms emit from the substrate. In this case, markers (velocity  $v = -\Omega J$ ) move toward the bottom of the substrate. At the interface itself, the diffusion flux is prescribed,  $J = -\alpha\dot{S}/\Omega$ . With time, as the oxidation rate decreases, the flux diminishes. By contrast, when  $\alpha < 0$  (Fig. 8b), the flux is positive, atoms inject into the substrate, and markers move toward the interface.

Since  $D^{\text{Ni}} > D^{\text{Al}}$ , the composition gradient alone would drive the combined diffusion flux into the substrate ( $J > 0$ ), in a direction opposite to that ascertained in the calculations (Fig. 8a). The paradox is associated with the induced stresses (Fig. 9). For  $\alpha > 0$  (Fig. 9a), the stress is tensile near the

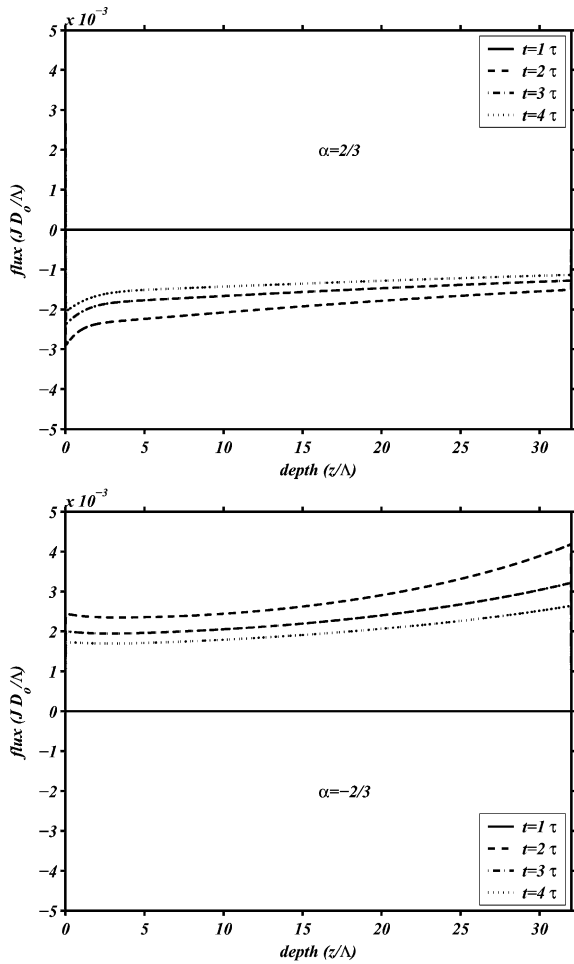


Fig. 8. Numerical results for the diffusion fluxes at two values of  $\alpha$ .

interface, and decreases with distance into the alloy. The atoms drawn into the regions of greater tension dominate the flux. The initial stress is zero. A tensile stress rises rapidly during the initial stages of oxidation. Within the time interval analyzed, the stress decreases with time, as the oxidation rate decreases. This tensile stress could be the source of voids at the interface. Conversely, when  $\alpha < 0$  (Fig. 9b), the stress is compressive and would suppress voids. Both the stress and the diffusion flux decay to zero far away from the interface. However, the rate of decay is slow, because of the relatively large creep exponent,  $n$  (Appendix A).

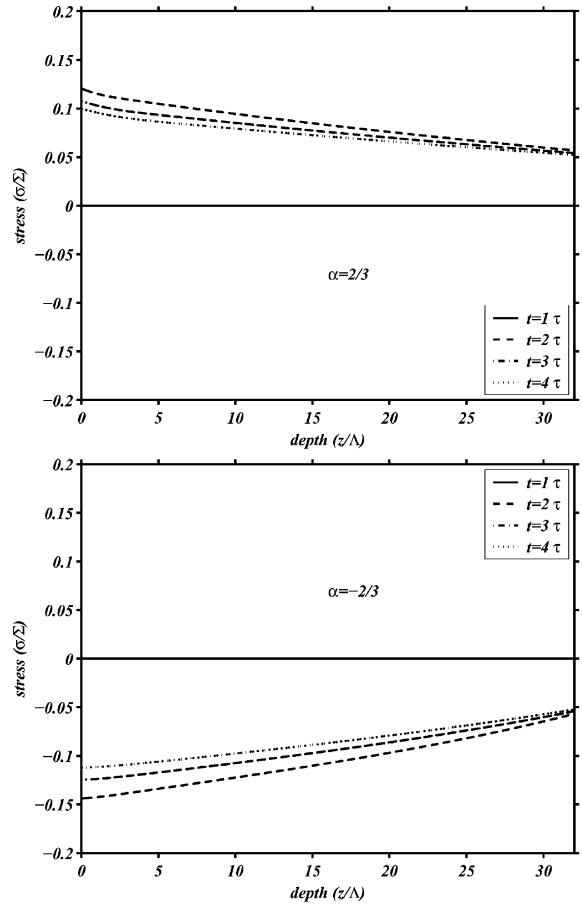


Fig. 9. Numerical results for the induced stresses at two values of  $\alpha$ .

When  $\alpha = 0$ , atoms neither inject into nor emit from the substrate, so that only the nonreciprocal diffusion inside the alloy generates stress. Because  $D^{Ni} \approx 3D^{Al}$ , the dominant Ni flux causes a mass loss at the interface, leading to a tensile stress (Fig. 10a). To illustrate the effect of the relative diffusivity, some calculations have been performed for  $D^{Ni} = D^{Al}/3$ , pertinent to Al rich NiAl, while keeping everything else unchanged. The hypothetically dominant Al flux causes a mass gain at the interface, leading to a compressive stress (Fig. 10b). Note that, for positive  $\alpha$ , while the stress would be tensile regardless of the flux divergence, the tension would be lower when  $D^{Ni} < D^{Al}$ , diminishing the tendency to form voids.

These results, in non-dimensional form, are

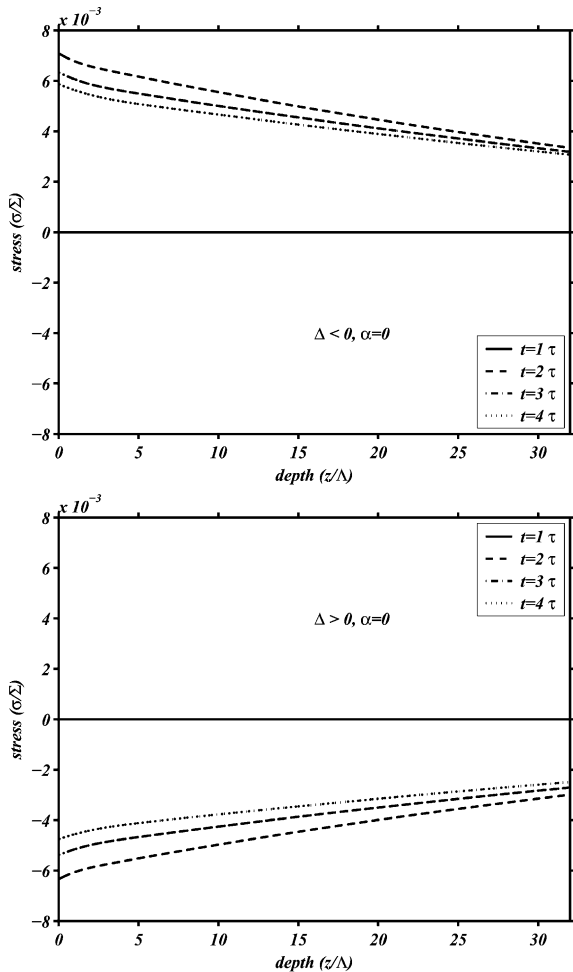


Fig. 10. Numerical results for the induced stresses for two cases: ( $\alpha = 0, \Delta < 0$ ) and ( $\alpha = 0, \Delta > 0$ ). For visual clarity, Figs. 9 and 10 plot the stresses in different scales.

insensitive to the creep exponent,  $n$ . However, the length scale,  $\Lambda$ , is strongly affected by this exponent, as well as by the diffusion and creep coefficients. For reasonable choices of these coefficients (based on the range reported in the literature),  $\Lambda$  ranges from nanometers to millimeters. Accordingly, in order to obtain meaningful comparisons between Figures 7–10, independent information is needed about creep and diffusion. The stress scale,  $\Sigma$ , defined by (26), is in the GPa range.

Note that the Al and Ni concentration profiles near the interface do not provide an indication of

the sign of the stress and hence, of void formation tendencies. In all cases, Al is depleted near the interface and Ni is enriched. The differentiation is only apparent in the direction of motion of markers in the bond coat, beneath the interface, relative to a fixed location remote from the interface. Ascertaining this direction presents the pre-eminent experimental challenge.

## 8. Comparison with observations

An assessment of the literature concerning void formation during the oxidation of  $\beta$ -NiAl type alloys [1,36–40] supports the following assertion. *To form voids, the generation of a tensile mean stress is a necessary, but not sufficient, condition. A void nucleation criterion must also be satisfied.* The situation parallels that for the widely documented void formation during creep [41] and upon electromigration [42]. The nucleation requirement is illustrated by observations that, when Pt [38], Y [39], or Hf [40] is added to alloys, the propensity for voids upon oxidation is eliminated. The role of Y and Hf is to getter impurities, especially S, that would otherwise segregate to the oxide-alloy interface and the alloy surface, enhancing void nucleation by changing the interface and surface energy. The role of Pt in suppressing voids is uncertain. Similar tendencies are manifest in the contrast between FeCrAlY and FeCrAl alloys, albeit that the observation of voids is convoluted with the occurrence of oxide wrinkling. The FeCrAl alloy wrinkles and voids form, generally at the apex of the wrinkles [37]. The S in this alloy is believed to segregate to the interface, facilitating the nucleation of voids. The Y in the FeCrAlY alloy getters the S, suppressing void formation. Moreover, the oxide remains flat. In all of the preceding cases, where voids form, it is implicit that  $\alpha$  is positive (or zero) and that  $D_{Ni} > D_{Al}$ , allowing the stress in the alloy to be tensile. That is, the atom flux should be toward the interface, with corresponding marker displacement. The marker displacement should be verified by experiment. Observations that oxidation is accompanied by the formation of vacancy loops is consistent with this assessment [30].

Other observations correlate with the magnitude of the stress. Void formation is more prevalent when transient oxides ( $\theta\text{-Al}_2\text{O}_3$ ) are being formed. In this case, oxidation occurs by the outward diffusion of Al. This would be consistent with a mass loss at the interface (large positive  $\alpha$ ) and a tensile stress. The stress is also tensile when  $\alpha\text{-Al}_2\text{O}_3$  is formed. The difference must be in the magnitude of the stress, manifest either in smaller  $\alpha$  or a different diffusivity ratio. This could be checked experimentally.

There are also apparent differences in the occurrence of voids with the Ni content in  $\beta\text{-NiAl}$  [1,36]. Since the sign of  $\alpha$  is probably unchanged, the difference is most likely related to the diffusivity differential,  $\Delta = D^{Al} - D^{Ni}$ , through its effect on the stress gradient (15). The measured diffusivity data for  $\beta\text{-NiAl}$  show that  $D^{Al} < D^{Ni}$  in the Ni-rich alloys, and  $D^{Al} > D^{Ni}$  for Al-rich alloys [31]. According to our theory, provided that  $\alpha$  is positive or zero, then when  $D^{Al} < D^{Ni}$ , the dominant Ni flux away from the interface causes tensile stress. When  $D^{Al} > D^{Ni}$ , the dominant Al flux toward the interface causes either compression or reduced tension. The observed void density in the Ni-rich alloys is markedly higher than that in the Al-rich alloys [1]. This trend is consistent with the theory.

## 9. Concluding remarks

This paper considers selective oxidation of a semi-infinite alloy and, in particular, the two processes that generate stress in the alloy. First, as oxidation depletes A in the alloy near the interface, the diffusion rates of A and B are usually unequal, leading to a flux divergence. Second, at the oxide-alloy interface, in addition to consuming metallic atoms on the interface, oxidation may also cause metallic atoms to emit from or inject into the substrate. We specify placement rules to relate the strain-rates to the divergence of the nonreciprocal diffusion flux in the interior of the alloy, and to relate the interfacial velocity to the diffusion flux at the interface. The diffusion-generated strain-rates are incompatible with the observed marker velocity field. To compensate, the alloy must creep, setting up a biaxial stress field in the directions

normal to the diffusion flux. We have formulated a theory to model concomitant oxidation, diffusion, and creep. Numerical results show that the stress generated in the alloy can be either tensile or compressive, depending on both the nonreciprocal diffusion in the alloy and the oxidation process near the interface. To focus on main ideas, we have neglected several other causes of strains, and formulated the theory for uni-directional diffusion.

## Acknowledgements

This work has been supported by ONR through MURI contract N00014-00-1-0438. The work of ZS and DVK has also been partly supported by NSF through grant CMS-9820713. Discussions with Professor G.H. Meier have been helpful.

## Appendix A. Oxidation-induced stress induced in a pure metal

When a pure metal oxidizes, voids and vacancy loops sometimes grow in the metal, indicating that the metal emits atoms, and has a *self-diffusion* atomic flux field  $J(z,t)$ . As illustrated in Fig. 3, the flux divergence,  $\partial J/\partial z$ , causes a dilatational strain-rate field, generating a biaxial tensile stress field  $\sigma(z,t)$ , and a marker velocity field  $v(z,t)$ . Both the stress and the marker velocity fields can be measured experimentally in principle. This Appendix calculates these fields, upon assuming that no voids form in the metal.

In the metal, the self-diffusion flux is driven by the stress gradient:

$$J = \frac{D \partial \sigma_m}{kT \partial z}, \quad (\text{A1})$$

where  $D$  is the self-diffusivity, and  $\sigma_m$  is the mean stress, which is related to the biaxial stress as  $\sigma_m = 2\sigma/3$ .

In the transverse direction  $x$ , self-diffusion generates strain-rate  $d_x^D = -\frac{\Omega \partial J}{3 \partial z}$ , and the biaxial stress generates the creep strain-rate  $d_x^C =$

$\frac{d_0}{2} \left( \frac{\sigma}{\sigma_0} \right)^n$ . The constraint requires that the net strain-rate vanish, so that

$$\frac{d_0}{2} \left( \frac{\sigma}{\sigma_0} \right)^n = \frac{2D\Omega \partial^2 \sigma}{9kT \partial z^2}. \quad (\text{A2})$$

This is a second order ordinary differential equation for the stress distribution in the metal.

On the interface, we require that  $J = -\alpha \dot{S}/\Omega$  at the interface. Combining with (A1), this boundary condition becomes

$$\frac{\partial \sigma}{\partial z} = -\frac{3\alpha kT \dot{S}}{2D\Omega}. \quad (\text{A3})$$

The differentiation is evaluated at the interface,  $z = S$ . The stress in the metal far from the interface vanishes, namely,  $\sigma \rightarrow 0$  as  $z \rightarrow \infty$ .

Adopt the scales for the stress and the length similar to those in the body of the paper:

$$\Sigma = \frac{3kT}{2\Omega}, \quad \Lambda = \sqrt{\frac{2D}{3d_0} \left( \frac{\sigma_0}{\Sigma} \right)^n}. \quad (\text{A4})$$

The dimensionless parameter

$$\beta = \alpha \Lambda \dot{S}/D, \quad (\text{A5})$$

measures the interface velocity relative to diffusion and creep in the metal.

Solving the differential Eq. (A2) subject to the boundary conditions, we obtain the stress distribution in the metal:

$$\sigma = \beta \Sigma \exp \left[ -\frac{z-S}{\Lambda} \right], \quad \text{for } n = 1; \quad (\text{A6})$$

$$\sigma = \Sigma \left[ \frac{n+1}{2} \beta^2 \right]^{\frac{1}{n-1}} \left[ 1 + \frac{n-1}{\sqrt{2(n+1)}} \left[ \frac{n+1}{2} \beta^2 \right]^{\frac{n-1}{2(n+1)}} \frac{z-S}{\Lambda} \right]^{\frac{2}{n-1}}, \quad \text{for } n > 1. \quad (\text{A7})$$

Eq. (A7) assumes that  $\alpha > 0$  and the stress is tensile. When  $\alpha < 0$ , the stress is compressive, and (A7) is modified with a negative sign in the front. The stress decays exponentially if the metal creeps linearly, but decays slowly if the metal creeps with a large  $n$ .

A substitution of the stress field into (A1) gives the diffusion flux  $J$  in the metal. Partition the net atomic flux  $N$  into that due to self-diffusion and that due to convection:  $N = J + v/\Omega$ . Following similar assumptions made in Section 3, the net flux

vanishes,  $N = 0$ . Consequently, the marker velocity still relates to the diffusion flux as  $v = -\Omega J$ .

## References

- [1] Brumm MW, Grabke HJ. Corros Sci 1993;34:547–61.
- [2] Evans AG, Mumm DR, Hutchinson JW, Meier GH, Pettit FS. Prog Mater Sci 2001;46:505–53.
- [3] Tolpygo VK, Clarke DR. Elevated temperature coatings: Science and technology IV. In: Dahotre NB, Hampikian JM, Morral JE, editors. Session I. Thermal barrier coatings. Warrendale, PA: TMS; 2001. p. 93–108.
- [4] Zhang Y, Haynes JA, Lee WY, Wright LG, Pint BA, Cooley KM et al. Metall Mater Trans 2001;32A:1727–41.
- [5] Padture N, Gell M, Jordan E. Science 2002;296:280–4.
- [6] Darken LS. Trans Am Inst Min Engrs 1948;175:184–201.
- [7] Wagner C. J. Electrochem Soc 1952;99:369–80.
- [8] Smigelskas AD, Kirkendall EO. Trans Am Inst Min Engrs 1947;171:130–42.
- [9] Balluffi RW. Acta Met 1954;2:194–202.
- [10] Barnes RS, Mazey DJ. Acta Met 1958;6:1–7.
- [11] Schlipf J. Acta Met 1973;21:435–40.
- [12] Stephenson GB. Acta Met 1988;36:2663–83.
- [13] Daruka I, Szabo IA, Beke DL, Cserhati CS, Kodentsov A, van Loo FJJ. Acta Mater 1996;44:4981–93.
- [14] van Dal MJH, Pleumeekers MCLP, Kodentsov AA, van Loo FJJ. Acta Mater 2000;48:385–96.
- [15] Chason E, Sheldon BW, Freund LB, Floro JA, Hearne SJ. Phys Rev Lett 2002;88:156103.
- [16] Vermilyea DA. Acta Met 1957;5:492–5.
- [17] Pieraggi B, Rapp RA. Acta Met 1988;36:1281–9.
- [18] Pieraggi B, Rapp RA, Hirth JP. Oxid Met 1995;44:63–79.
- [19] Gibbs GB, Hales R. Vacancies. Metals Society, London 1977;76:201–7.
- [20] Harris JE. Acta Met 1978;26:1033–41.
- [21] Jaccodine RJ, Drum CM. Appl Phys Lett 1966;8:29–30.
- [22] Prussin S. J Appl Phys 1972;43:2850–6.
- [23] Hsieh CM, Maher DM. J Appl Phys 1973;44:1302–6.
- [24] Leroy B. Phil Mag B 1987;55:159–99.
- [25] Cussler EL. Diffusion. Cambridge, UK: Cambridge University Press, 1997.
- [26] van Dal MJH, Gusak AM, Cserhati C, Kodentsov AA, van Loo FJJ. Phys Rev Lett 2001;86:3352–5.
- [27] Balluffi RW, Seigle LL. Acta Met 1955;3:170–7.
- [28] Doo VY, Balluffi RW. Acta Met 1958;6:428–38.
- [29] Isakov MG, Tolpygo VK. Defect and Diffusion Forum 1989;66-69:1539–46.
- [30] Hutchings R, Loretto MH, Smallman RE. Met Sci 1981;January:7–13.
- [31] Shankar S, Seigle LL. Metal Trans A 1978;9:1467–70.
- [32] Miracle DB. Acta Mater 1993;41:649–84.
- [33] Pan D, Glynn M, Chen M, Hemker KJ. In: Mishra RS, Earthman JC, Raj SV, editors. Creep deformation: fundamentals and applications. Warrendale, PA: TMS; 2002. p. 209–18.

- [34] Nathal MV. Ordered intermetallics-physical metallurgy and mechanical behavior. In: Liu CT, Cahn RW, Sauthoff G, editors. Kluwer Academic Publishers; 1992. p. 541–63.
- [35] Johnson DR, Oliver BF, Noebe RD, Whittenberger JD. *Intermetallics* 1995;3:493–503.
- [36] Zimmerman D, Tolpygo VK, Ruhle M, Clarke DR, in preparation.
- [37] Tolpygo VK, Clarke DR. *Acta Mater* 1998;46:5167–74.
- [38] Felten EJ, Pettit FS. *Oxid Met* 1976;10:189–223.
- [39] Kumar A, Nasrallah M, Douglass DL. *Oxid Met* 1974;8:227–63.
- [40] Pint BA. *Oxid Met* 1997;48:303–8.
- [41] Riedel H. *Fracture at high temperature*. Berlin: Springer, 1987.
- [42] Baker SP, Korhonen MA, Arzt E, Ho PS, editors. *Stress-induced phenomena in metallization*. AIP Conference Proceedings, vol. 612, New York, 2002.