Oxidation of Metals, Vol. 44, Nos. 1/2, 1995

Role of Interface Structure and Interfacial Defects in Oxide Scale Growth

Bernard Pieraggi,[*] Robert A. Rapp,[†] and John P. Hirth[‡]

Received December 1, 1994

Recent studies of the structure and dynamics of solid–solid interfaces have provided some understanding about the role of the scale–metal interface in the growth of reaction product scales on pure metals. The action of interfacial defects (misfit dislocations, misorientation dislocations and disconnections) in the creation and annihilation of the point defects supporting the diffusional growth of scales is considered. Anion point defects (vacancies/interstitials) supporting scale growth by anion diffusion are annihilated/created by the climb of misorientation dislocations or disconnections in the scale at the interface. For scale growth by cation diffusion, cation point defects (vacancies/interstitials) can be annihilated/created by the climb of interfacial misfit or misorientation dislocations in the metal. Because of their necessarily high density, in most cases, the dominant climb of misfit dislocations would be favored. The blocking of interfacial reaction steps can be a means to retard the scaling kinetics and to alter the fundamental scaling mode. For instance, the interfacial segregation of large reactive element ions can pin the interface dislocations, an action which poisons the usual interfacial reaction step. Such considerations are consistent with the well-known phenomena ascribed to the reactive element effect (REE).

KEY WORDS: scale growth; oxidation mechanism; kinetics; scale adherence; reactive element effect; interfacial segregation.

[*] Laboratoire des Matériaux, URA 445 CNRS, INP-ENSC, Toulouse, 31077 France.
[†] Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio 43210.
[‡] Department of Mechanical and Materials Engineering, Washington State University, Pullman, Washington 99164.

INTRODUCTION

The success of the classic theory of C. Wagner[1] in rationalizing the mechanism and rate of scale growth on pure metals has led to a general acceptance that the scale–metal and gas–scale interfaces are in local equilibrium, so that diffusional rate control leads to predictable parabolic kinetics. Within the Wagner formalism, one may discount the interfacial reaction steps, because they would not contribute to rate control. However, even for diffusion-limited reaction kinetics, the interfacial reactions must provide the means for the creation and annihilation of the point defects supporting diffusion, and for the incorporation of cations and anions into newly formed lattice sites. Indeed, if an interfacial reaction step is blocked, partially or completely, then Wagner's classic scaling theory is not valid in detail, and revisions must be introduced.

Vermilyea[2] suggested that interfacial ledges are involved in the growth of scales during metal oxidation. With the advent of line defect models to describe interfaces, explicit mechanisms for the role of interfacial dislocations as sources/sinks for point defects, together with the possibility of partial rate control of scaling kinetics by an interfacial step, have been suggested by the authors.[3] Tiller[4] described the action of interfacial misfit dislocations as a source for silicon interstitials in silicon for the specific case of silica growth on silicon. For silicon oxidation, partial interface control, as described by the linear/parabolic oxide growth model of Deal and Groves,[5] has been interpreted in terms of a constraint to the climb of misfit dislocations.[6]

For scale growth limited by cation diffusion, the climb of misfit dislocations for the annihilation of cation vacancies, or the creation of cation interstitials, has been proposed.[7] Similarly, the climb of misfit and misorientation interface dislocations serves as the source/sink for metal atoms/vacancies for the growth of phases in metallic diffusion couples.[8] More generally, line defects with both ledge and dislocation character have been suggested as sources/sinks of metal atoms.[9] For the scaling of a number of metals (Ni, Co, Fe and Cu), forming a cation-diffusing oxide scale, partial interfacial rate control was ascribed to a difficulty in vacancy annihilation arising from a blocking of the climb of interfacial misfit dislocations caused by the pinning action by segregated reactive element ions.[10,11]

In the analysis of the interfacial line defects as sources/sinks of point defects, the authors[3] have pointed out that the different line defects serve different roles depending on whether the diffusion of cation or else anion defects is dominant. Based on these mechanisms,[3] the reactive element effect (REE) can be explained by a blocking of the usual interfacial reactions for cationic growth, through the pinning of the interfacial dislocations by large reactive element ions segregated at the scale–metal interface. More recently,[12] other interfacial dislocations, namely misorientation dislocations and disconnections (a new interface defect) were introduced as potential participants in the interfacial reaction steps. The aim of the current paper is to present a more detailed description of the interface defects and their actions in scaling, and to illustrate this description by the role of the interface in the REE.

INTERFACIAL REACTIONS DURING SCALE GROWTH

In the following, the main characteristics of the interfacial reactions occurring during scale growth controlled by cationic or anionic transport are briefly presented. The notation is adapted from Kroger and Vink[13]; the underlined species belong to the metal lattice.

Cationic Diffusing Scales

The interfacial reactions involved in the growth of a $MO_{z/2}$ oxide scale on a pure metal by cation/vacancy diffusion are

Growth of the oxide lattice at the external interface:

$$\frac{z}{4}\mathrm{O_2(g)} \rightarrow \frac{z}{2}\mathrm{O_O^X} + \mathrm{V_M^{z'}} + \dot{\mathrm{h}} \qquad (1)$$

Consumption of metal lattice at the internal interface:

$$\mathrm{V_M^{z'}} + z\dot{\mathrm{h}} + \underline{\mathrm{M}}_\mathrm{M} \rightarrow \mathrm{M_M^X} \qquad (2)$$

The sum of Eqs. (1) and (2) obeys a conservation of mass, charge and sites and describes the gross scaling reaction. Thus, as shown by Eq. (2), the cation vacancies must be annihilated at the scale–metal interface. This interfacial action is often described in terms of the transfer (injection) of cation vacancies into the metal lattice, Eq. (2) is then written

$$\mathrm{V_M^{z'}} + z\dot{\mathrm{h}} + \underline{\mathrm{M}}_\mathrm{M} \rightarrow \mathrm{M_M^X} + \underline{\mathrm{V}}_\mathrm{M} \qquad (2')$$

But, in that case, the sum of Eqs. (1) and (2′) does not correspond to a conservative process, i.e., additional lattice sites are created, so that metal vacancies created by Eq. (2′) must be annihilated at the scale–metal interface or close to it. Such an annihilation process would occur at any kind of vacancy sinks S, as described by the reaction

$$\underline{\mathrm{V}}_\mathrm{M} + \mathrm{S} \rightarrow \mathrm{S} \qquad (3)$$

The annihilation of metal vacancies is equivalent to the recession of metal lattice which can occur by the displacement of the scale–metal interface, or by the translation of the metal lattice if the interface is not able to move.

Anionic Diffusing Scales

For the growth of $MO_{z/2}$ oxide by anion/vacancy diffusion, the interface reactions are

The annihilation of anion vacancies at the gas–scale interface:

$$\tfrac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e' \rightarrow O_O^X \qquad (4)$$

The growth of oxide lattice and consumption of metal lattice occurring simultaneously at the scale–metal interface:

$$\underline{M}^X \rightarrow \frac{z}{2} V_O^{\bullet\bullet} + M_M^X + ze' \qquad (5)$$

These equations show that the growth of the oxide scale occurs at the scale–metal interface by the creation of a "scale unit" consisting in one cation for each $z/2$ anions. There are two possible interpretations of the process described by Eq. (5):

The creation of the "scale unit" results from a direct displacement of the scale–metal interface and does not involve any jump of metal atoms into the oxide lattice through the scale–metal interface, or else,
The metal atoms jump from the metal lattice into the scale lattice, perhaps following some diffusion in the scale–metal interface. Then Eq. (5) must be written

$$\underline{M}^X \rightarrow \frac{z}{2} V_O^{\bullet\bullet} + M_M^X + ze' + \underline{V}_M \qquad (6)$$

Thus, as for the cationic-controlled growth, the conservation of lattice sites requires an additional reaction, again described by Eq. (3), for the annihilation of metal vacancies created by Eq. (6).

Anionic diffusion controls the scaling of the metals of Groups IV and V which dissolve large amounts of oxygen to form metallic solid solutions. The corresponding interface reaction shows that additional oxygen vacancies are then created:

$$O_O^X \rightarrow V_O^{\bullet\bullet} + 2e' + \underline{O}_i \qquad (7)$$

These vacancies also participate in the scale growth; thus, for metals or alloys able to dissolve some amounts of oxygen, no control of the anionic scale growth would be possible without the control or inhibition of Eq. (7).

INTERFACIAL LINE DEFECTS

Epitaxial relations between two lattices are not restricted to the parallel cube-on-cube orientation relationship commonly observed between two FCC latices. Indeed, more complex orientation relationships are also possible, and the interface structure between any two crystalline phases would also be described in terms of more or less complex networks of interfacial dislocations. The interface structure can be schematically described by the combination of several sets of linear defects. For a semicoherent scale–metal interface, these defects can be classified into two main categories:[12]

> Defects such as misorientation dislocations, with their extra planes in the scale or in the metal. These defects characterize the departure of the scale–metal interface from an ideal habit plane which often corresponds to the parallelism of high density lattice planes and/or lattice directions.
>
> Defects such as misfit dislocations, and ledges, whose characteristics depend strongly on the relative sizes of the lattice cells for the metal and the scale, i.e., the relative molar volumes of the scale and metal often characterized by their ratio (Pilling-Bedworth ratio).

In addition to these two categories, a specific defect (called a disconnection) participates in the lattice misorientation and depends on the cell size difference.[12] The disconnection may be seen as the combination of monoatomic ledges of the metal and of the oxide at the interface, as described later. A more detailed description of all these interfacial defects has been presented elsewhere.[12]

In the following, the schematic drawings are presented to illustrate the possible structure of the interface defects which can appear at the interface between a divalent metal M and its oxide MO. The ratio for the lattice parameters for the M and MO lattices is close to 1.2, a value representative for the Ni–NiO interface.

As illustrated by Fig. 1a, the misfit dislocations in the metal are a direct result of the inherent difference in the lattice parameters for the metal compared to the scale compound; for the usual lattices and orientation relations, these misfit dislocations are rather closely spaced, e.g., ~20 Å. Misfit edge dislocations have extra planes in the metal phase for the usual case where the lattice spacing of metal plane is less than the lattice spacing of cation planes. These misfit dislocations could have mixed edge and screw character, but only their edge components (**b** parallel to the interface plane and normal to the dislocation line) serve to relieve misfit. Crystallographically, the misfit dislocations can glide in the interface or climb into the metal (annihilating vacancies) without forming stacking faults if their

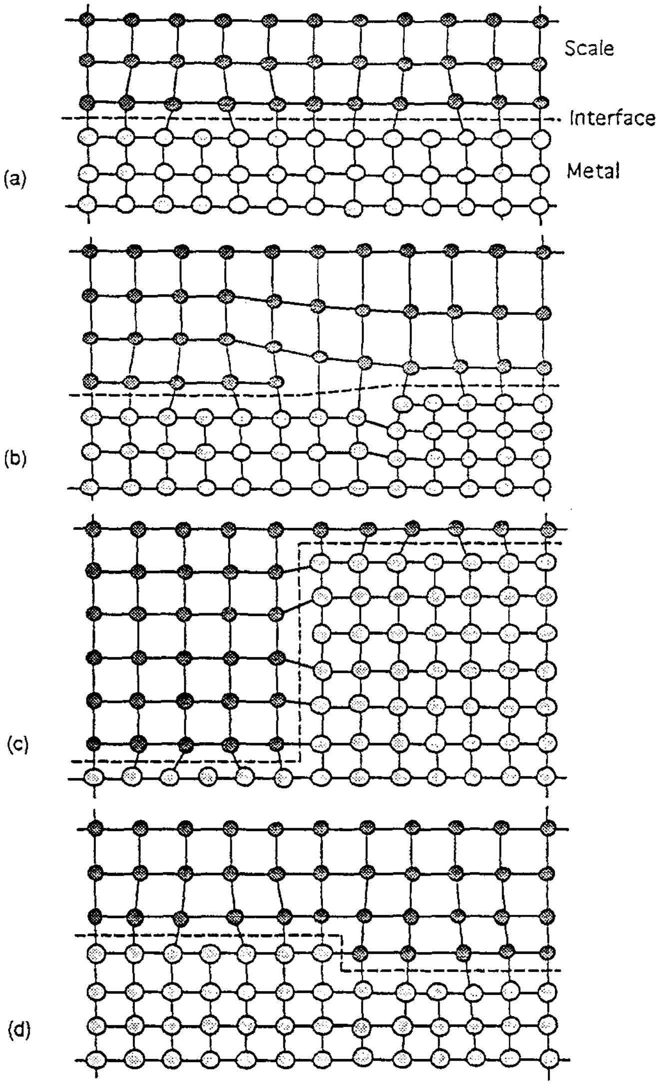

Fig. 1. Schematic drawings showing the various interfacial line defects at a metal–oxide interface: (a) misfit dislocations, (b) misorientation dislocations, (c) ledge, (d) disconnection.

Burgers vectors are perfect vectors of the metal and scale lattices, these dislocations can then climb or glide without constraint. The observation by Goulden[14] of dislocations emitted from Cu_2O nuclei during the oxidation of (111) Cu surfaces could be interpreted as the glide of interfacial dislocations along the metal interface plane.[15] Misfit dislocations of smaller Burgers vector can glide within the interface, but cannot climb away from it without fault formation in either the interface or the bulk lattices.

Figure 1b illustrates both a misorientation dislocation with its extra plane in the scale, and a misorientation dislocation with its extra plane in the metal. These misorientation dislocations, with Burgers vectors nominally normal to the interface, are not inherently present, but must be created from sources present in both the scale and metal. These defects provide a minor tilt of the interface away from the ideal epitaxial orientation, and in combination, they can exist with the same, or with opposite, signs (tilts). If their Burgers vectors are perfect lattice vectors in one lattice or the other, misorientation dislocations can climb in the interface or glide out of it, without fault formation.

Figure 1c shows a pure ledge for which the step height must correspond exactly to rational numbers of lattice planes in both the metal and in the oxide lattices to preserve the semicoherency, and Fig. 1d shows a "disconnection." A disconnection can be formed by the attractive bonding of a misorientation dislocation from the scale with one of opposite sign from the metal; it has both ledge and dislocation character since a plane of the scale joins a plane of the metal. If the metal lattice plane spacing d_M were equal to the scale lattice plane spacing d_S, the defect would have pure ledge character with no dislocation strain field.[16] But in the more general case, the disconnection has a part of dislocation character and a part of ledge character. As long as the sum of the Burgers vector of dislocation part and displacement vector of the ledge part is a perfect vector, the disconnection can move along the interface without fault formation.

As in the growth of thin films, once the scale exceeds a thickness of a few nanometers, there is a large driving force, arising from coherency strain, to cause misfit dislocation formation. As scaling proceeds, added extrinsic dislocations with misfit character can reach the interface by climb and glide, while misfit dislocations can also climb away from the interface,[7] and opposite sign dislocations can annihilate. The misfit dislocation density is expected to be large and not greatly different from the stress-free equilibrium spacing because of the large elastic strain energy penalty.

On the other hand, misorientation dislocations in the interface are formed only by their injection by climb, by the glide of extrinsic dislocations into the interface, or by the operation of an interface Bardeen–Herring source. Disconnections can be nucleated on the interface or can form by the attractive interaction of one misorientation dislocation each from the scale and the metal. Disconnection formation is statistically less likely to occur in the interface than misfit dislocation formation. Hence, the density of misfit dislocations is expected to far exceed the density of the other interface line defects for usual cases of scaling, where the volume changes attendant to oxidation typically lead to equilibrium misfit dislocation spacings of about 1 to 3 nm.

SCALE–METAL INTERFACIAL REACTIONS AND INTERFACE DEFECTS

The roles of interfacial defects in cationic scale growth have been described[7,12] both for interfacial defect creation or annihilation reactions and for lattice extension, i.e., in scale growth. Briefly, at a scale–metal interface, cation vacancies can be annihilated or interstitial cations created by the climb of misfit dislocations into the metal, or by the interfacial climb of metal lattice misorientation dislocations. These processes are discussed later in more detail, but, at this point, it must be emphasized that interfacial reactions, as for all other kinds of chemical reactions, require a contact between the reactants, i.e., that the reactants are as close as possible. Therefore, for chemical reactions between solid phases, an epitaxial relationship between the lattice is required for the mass transfer and the creation/annihilation of point defects. Mass transfer and creation/annihilation of point defects may not be possible for an incoherent interface since the two lattices would be structurally independent. Such interface reactions at incoherent interfaces would probably only result in void formation.

For scaling reactions, a few TEM examinations of the structure of the metal–oxide interface have been performed for cation and anion diffusive growth.[17–20] Simple epitaxial orientation relationships between the metal and oxide lattices and excellent contact between the phases are usually reported, even though grains farther into the scale have adapted incoherent orientations. The structure of the interface, and thus the nature and density of interfacial defects, depends on the epitaxial orientations of metal and scale lattices, and thus also depends on the initial orientation and structure of metal surfaces. The influences of surface orientation and surface treatment on scale growth kinetics are well documented, particularly for nickel oxidation,[21,22] and have been interpreted in terms of some changes in the scale microstructure. But, these effects of surface orientation and treatment can also be seen as an illustration of the importance of interface reactions.

Cationic Growing Scale

The role of interfacial reaction during the growth of a cationic scale is schematized on Fig. 2. As shown by Eq. (1), the growth of scale lattice and the formation of cation vacancies occurs at the external interface and can

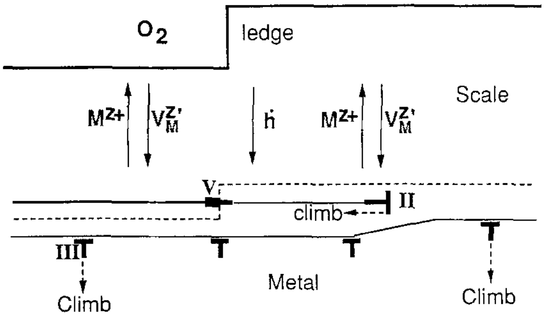

Fig. 2. Schematic illustration of scale growth by cation/vacancy diffusion and associated interfacial processes.

be schematized by the translation of a monoatomic ledge along this interface, as shown on Fig. 2.

The reaction occurring at the internal interface must permit the annihilation of the vacancy flux at this interface. Such annihilation can occur by the climb of interfacial dislocations. However, climb of misorientation dislocations on the scale side is not permitted because it necessarily involves the transport of some anions or anions vacancies, which may not occur for a cationic growing scale. A similar situation arises for the translation of disconnection along the interface, which obviously implies anion diffusion. Therefore, the only possibility to annihilate incoming vacancies is the climb of misorientation and misfit dislocations in the metal (defects II and III in Fig. 2). Equations (2′) and (3) can be combined as follows:

$$V_M^{z'} + z\dot{h} + \underline{M}_M \rightarrow M_M^X + \underline{V}_{\perp M} \qquad (8)$$

where $\underline{V}_{\perp M}$ represents a vacancy annihilated by the climb of interfacial dislocations. However, the climb of misorientation dislocations leads to their consumption and the formation of a monoatomic ledge, which is energetically unfavorable because of the large stress associated with a monoatomic ledge for systems with a large difference in lattice parameters.

Then, because of their inherent presence and close spacing, the climb of misfit dislocations to annihilate cation vacancies must be favored normally. Furthermore, the local interfacial stress resulting from the climb of these dislocations out of the interface can be minimized by an adjustment of their spacing and their resupply to the interface by return glide,[7] so that the localized climb of interfacial dislocations nucleates a kind of Bardeen–Herring mill at the scale–metal interface.

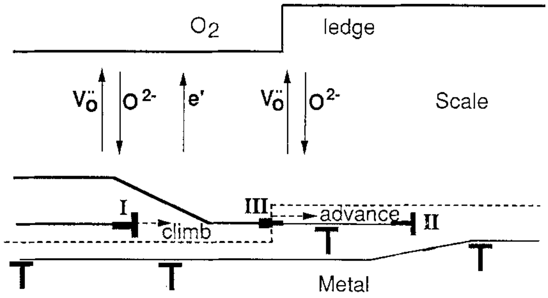

Fig. 3. Schematic illustration of scale growth by anion/vacancy diffusion and associated interfacial processes.

Anionic Growing Scale

In the growth of scales at the scale–metal interface, the attachment of the diffusing anions and the corresponding creation of anion vacancies, occur by either the climb of misorientation dislocations of the scale, or by the translation of the disconnection (defects I and III of Fig. 3), in the scale–metal interface. These two modes of growth are described, respectively, by Eqs. (6) and (5). The climb of misorientation dislocations necessarily involve the jumps of metal atoms into the scale lattice. As for the cationic growth, vacancies resulting from the jumps of metal atoms into the scale can be annihilated by the climb of metal interface dislocations (misfit or misorientation dislocations).

The direct displacement of the scale–metal interface, as represented by Eq. (5), corresponds to the translation of a disconnection along the interface. Equation (5) is conservative; therefore the displacement of a disconnection apparently does not involve any jump of vacancies or metal atoms, and permits the direct transformation of the metal lattice into the scale lattice. However, as represented schematically in Fig. 4, this process must involve some minor cation diffusion in combination with dominant anion diffusion in order to maintain the misfit dislocations at the interface between the two lattices. For example, for oxide growth at the interface by the translation (to the left) of the specific (boxed) disconnection shown in Fig. 4, one cation must diffuse away, annihilating one cation vacancy from the scale, upon the conversion of five metal atoms into cations.

If the misfit dislocations cannot be maintained at the scale–metal interface because the required cation diffusion cannot occur, or occurs too slowly, then large interfacial stresses, tensile in the metal and compressive in the oxide, could result for scales grown by anion diffusion. Large growth stresses are indeed observed for the oxidation of metals such as Ti, Zr, Hf, Nb, Ta, etc. Furthermore, the formation of layered scales during the isothermal

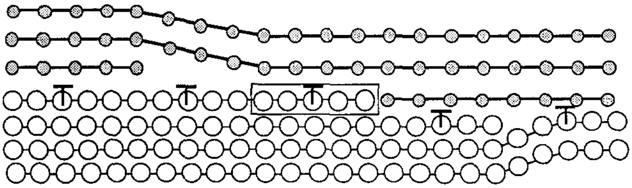

Fig. 4. Schematic drawing illustrating the necessary cation or metal diffusion required to maintain the misfit dislocation at the scale–metal interface during anionic growth.

oxidation of Ti, Nb or Ta[23] could perhaps be related to the inability of the interface to maintain the misfit dislocations at the scale–metal interface. The layered structure has not been observed during the isothermal oxidation of Zr and Hf in pure oxygen which leads to the growth of a fine-grain columnar scale.[24,25] A more detailed analysis of the metal–scale interface structure would certainly be useful for a better understanding of this different behavior.

This coordinated cationic and anionic diffusion needed for disconnection translation (scale growth) at the scale–metal interface may become important in interpreting the REE, as discussed later. As is well known for edge dislocations within a solid, they are subject to the specific adsorption of impurities with atom sizes both larger than and smaller than the solvent species, because the maintenance of such a solute atmosphere on either the tensile or compressive side of the dislocation serves to lower its elastic strain energy. The drag of such adsorbed solutes is said to pin the dislocation. Such pinning must also be expected for interface dislocations, whereby a large impurity segregant in the oxide at the interface should bond tightly especially to the misfit dislocations whose climb into the metal would require an escape from the segregant. For misorientation dislocations in the metal or in the oxide, segregant adsorption is also possible, but such solutes may be able to diffuse in the interface to retain their bond to the dislocation. Such specific adsorption of large reactive ions to the misfit dislocations has been credited with the realization of the REE, especially for the growth of chromia scales on alloys,[3] as discussed next.

THE REACTIVE ELEMENT EFFECT AND INTERFACE REACTIONS

Since its accidental observation by Pfeil,[26] the REE has received special attention by both researchers and engineers interested in scaling resistance and especially scale adherence upon temperature cycling. Whittle and

Stringer[27] reviewed the early literature on this subject, and more recent reviews are also available.[28,29]

For the growth of chromia scales on alloys of Fe–Cr, Ni–Cr and Co–Cr and for pure Cr itself, the following effects are induced by small amounts of certain reactive elements, e.g., Y, Ce, La, etc., which elements all have very large atomic and ionic sizes relative to the host alloy or oxide structures:

1. The parabolic rate constant for chromia scale growth may be greatly reduced, by more than an order of magnitude, this effect being greater at temperatures below the maximum use temperatures for the alloys.
2. The adherence of the scale is greatly improved, leading to reduced scale spallation in cyclic oxidation.
3. The concentration of chromium in the alloy required to realize the REE is reduced considerably (although extensive data are not available).
4. Most importantly for a mechanistic interpretation, the chromia scale seems to grow at the scale–metal interface, instead of at the scale–gas interface, implicitly requiring anion diffusion.

The reduction in scale growth rate can be easily explained by considering the occurrence of interfacial steps in the growth kinetics. Then, for a mixed kinetics with interfacial and diffusion steps in series, the usual question of growth rate and reaction kinetics for a single reacting species are expressed by

$$\frac{dw}{dt}=\left(\frac{1}{k_l}+\frac{2w}{k_p}\right)^{-1} \tag{9}$$

and

$$t=\frac{w^2}{k_p}+\frac{w}{k_l} \tag{10}$$

where w and t represent the weight gain per unit area and the time, while k_l and k_p are the linear and parabolic rate constants for the interfacial and diffusion steps, respectively. Figure 5 and Eq. (9) show that the initial value of dw/dt at $t=0$ is equal to k_l. This quite simple remark indicates that a decrease of the rate constant k_l would induce a decrease of the overall kinetics. Therefore, a decrease in the global oxidation rate is not necessarily related to a decrease of the parabolic rate constant, but can also occur by a decrease in k_l resulting from some modifications (inhibition) of the interfacial reactions. Furthermore, considering that anionic and cationic interfacial and

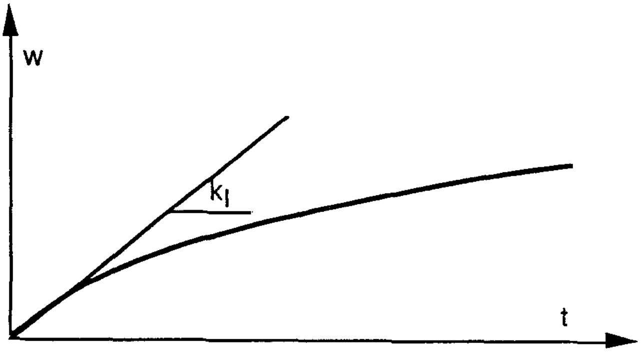

Fig. 5. Schematic illustration of the influence of interfacial kinetics on the overall kinetics.

diffusional steps occur in parallel during scale growth, the overall growth rate is then expressed as

$$\frac{dw}{dt}=\left(\frac{dw}{dt}\right)_a+\left(\frac{dw}{dt}\right)_c=\left(\frac{1}{k_{la}}+\frac{2w}{k_{pa}}\right)^{-1}+\left(\frac{1}{k_{lc}}+\frac{2w}{k_{pc}}\right)^{-1} \tag{11}$$

where the index a and c refer to anionic and cationic growth control, respectively.

Upon integration and for sufficiently small values of w, the growth kinetics are expressed in a form similar to Eq. (10) with average rate constant[3]:

$$\frac{1}{\bar{k}_l}=\frac{1}{k_{la}}+\frac{1}{k_{lc}} \tag{12a}$$

$$\frac{1}{\bar{k}_p}=\frac{1}{(k_{la}+k_{lc})^2}\left[\frac{k_{la}^2}{k_{pa}}+\frac{k_{lc}^2}{k_{pc}}\right] \tag{12b}$$

Equations (12) permit each species, the cations and the anions, to each be driven by the entire Gibbs energy of the scaling reaction. According to the classic Wagner theory, the constants k_{lc} and k_{la} are very large so that diffusional control results in an expression involving only k_{pc} and k_{pa}. Equations (12) show that the decrease in growth kinetics and the change in growth mechanism can simply result from the blocking of the cationic step. Indeed, if k_{lc} is decreased to 0, then $\bar{k}_p$ would equal k_{pa}. From this observation and the previous description of interface reactions and interface structure, the authors proposed the PIM or poisoned interface model.[3,12]

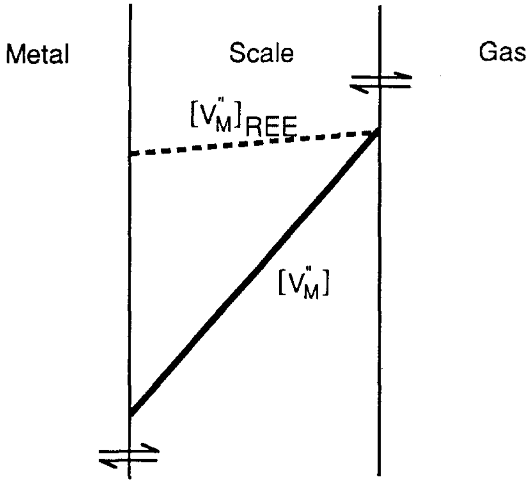

Fig. 6. Schematic plot for Wagnerian scaling (full line) and for blocked interfacial reaction (dotted line).

In this model, the blocking of the usual cationic interface reaction at the scale–metal interface results from the segregation of large and highly stable RE ions at the metal–scale interface and the pinning of interfacial dislocations by these segregated RE. Indeed, if the misfit dislocations and the misorientation dislocations of the metal are unable to climb and thereby annihilate vacancies (or create metal interstitial ions for other scale–metal systems), then the classic Wagner model with the interfacial reactions at local equilibrium is not valid. Likewise, an equilibrium within the scale for cations and anions, and their defect species, cannot be satisfied.

Furthermore, if large segregated RE ions block the annihilation of cation vacancies required to support cation transport in the scale, by pinning the interfacial dislocations and preventing their climb, then the constant k_{lc} in Eqs. (12) has a very small magnitude. Therefore, anionic scale growth would replace normal cationic scale growth, as is observed for the REE for chromia growth. Relative to the partitioning of the Gibbs energy driving the transport of cations with a blocked interface, a significant drop in Gibbs energy at the interface, corresponding to a large step in the cation vacancy concentration, must occur, as shown in Fig. 6. Consistent with a significant reduction in the cation flux, the gradient in cation vacancies through the scale is very small. However, local equilibrium at the interface is maintained for the anions, so their concentration profile is not changed by the blocking of the cation interfacial step.

If the PIM for the REE is correct, then significant applications should also be possible for the growth of scales other than chromia and alumina.

But one should not expect that the same RE (e.g., Ce and Y) would provide the same interfacial segregation for other metal–oxide systems. The pinning action of segregated RE strongly depends on their size as shown by the analysis of the force acting on the interfacial dislocations.[12] Therefore, as a first approximation, one might suppose that the ratio of ionic sizes for the RE compared to that for the host cation of the scale might need to be approximately similar to that which has demonstrated an effectiveness for chromia scales. This criterion would also insure that the RE has little solubility in the scale, so that segregation would be expected.

To provide a demonstrative test for the PIM proposed by the authors,[3] Strawbridge and Rapp[10] studied the scaling of the pure metals Fe, Ni, Co and Cu in air, each coupon being coated with only 250 Å of an evaporated alkaline earth metal: Sr, Ca or Ba. The scaling temperature for each metal was sufficiently high so that grain boundary diffusion in the scale would not contribute importantly to the diffusion process for the untreated coupons, thereby avoiding any relevance of the "grain boundary segregation/diffusion model." The alkaline earth elements were chosen for the study, because they form very stable oxides with large divalent cations (no doping effect), having a range of ionic radii relative to the base metal cations similar to that for Ce^{4+} or Y^{3+} compared to Cr^{3+}, i.e., about a 45% larger radius.

Strawbridge and Rapp[10] found that the parabolic scaling rate constant for each of the pure metals Fe, Ni, Co and Cu was reduced substantially by 250 Å-thick films of alkaline earth. The most effective individual segregant for each metal was the particular alkaline earth with an ionic radius ratio closest to 1.45, that corresponding to the radius ratios for Ce^{4+} and Y^{3+} compared to Cr^{3+}. While a superficial Ca deposit reduced the scaling rate constant for pure Ni by only 50% at 1000°C, at 850°C where the Ca solubility in NiO is lower and the scale is thinner, the rate constant was reduced by a factor of 20, and the NiO scale obviously grew by anion diffusion. Similarly, Gonzalez *et al.*[11] observed that CaO coatings formed from the decomposition of calcium nitrate deposits have a comparable effect on the oxidation of pure Ni, and decrease the oxidation rate by a factor of 4 at 900°C. In addition, significant changes in the morphologies of the scale was always observed. These studies seemed to support the PIM interpretation of the REE, and extend its application, with the exclusion of other REE interpretations. Gonzalez *et al.*[30] have studied also the effect of small superficial Ca additions on Ni oxidation at lower temperature. At 600°C, the observed reduction in parabolic scaling rate constant caused by the PIM is even larger, two orders of magnitude.

These latter studies[10,11,30] have examined the kinetics and scale growth mode resulting from the REE for pure metals, and have not been concerned with the other characteristic REE aspects, namely improved scale adherence and the reduction in solute content required to form the protective scale for an alloy. However, as discussed previously,[3] the improved adherence is a natural result of retaining a semicoherent scale–metal interface, as is inherent for scales grown by anion diffusion. Thus, the studies mentioned here[10,30] showing the reduction in scaling kinetics and the change in scale growth mode are considered to be evidence for the PIM to explain the REE.

CONCLUSIONS

The main interfacial defects and the fundamental reaction steps at the scale–metal interface for the growth of oxide lattice and the consumption of metal lattice in combination with the creation or annihilation of the point defects supporting scale growth by cation and anion diffusion have been described and discussed. For cationic growth, a significant blocking of the interfacial reaction step associated with the annihilation of cation vacancies (or the creation of interstitial cations) can be achieved by the segregation of large stable reactive element cations at the scale–metal interface. This interfacial poisoning corresponds to the pinning of the interfacial misfit and misorientation dislocations whose climb otherwise achieves the creation or annihilation of point defects. Based on this poisoned interface model, the REE has been observed for the oxidation of pure metals such as Fe, Ni, Co and Cu by superficial films of the alkaline earths. Significant reductions in the scaling rate have been observed and have been interpreted in terms of the PIM model.

REFERENCES

1. C. Wagner, in *Atom Movements* (American Society of Metals, Metals Park, 1951), p. 153.
2. D. Vermilyea, *Acta Metall.* **5**, 492 (1957).
3. B. Pieraggi and R. A. Rapp, *J. Electrochem. Soc.* **140**, 2844 (1993).
4. W. A. Tiller, *J. Electrochem. Soc.* **127**, 625 (1980); **128**, 689 (1981).
5. B. E. Deal and A. S. Groves, *J. Appl. Phys.* **36**, 3770 (1965).
6. J. P. Hirth and W. A. Tiller, *J. Appl. Phys.* **56**, 947 (1984).
7. B. Pieraggi and R. A. Rapp, *Acta Metall.* **36**, 1281 (1988).
8. B. Pieraggi, R. A. Rapp, F. J. J. VanLoo and J. P. Hirth, *Acta Metall. Mater.* **38**, 1781 (1981).
9. J. P. Hirth, *Metall. Trans.* **22A**, 1331 (1991).
10. A. Strawbridge and R. A. Rapp, *J. Electrochem. Soc.* **141**, 1905 (1994).
11. J. J Gonzales, D. Oquab and B. Pieraggi, Proc. Krakow Conf. on High Temperature Corrosion, 1994.
12. J. P. Hirth, B. Pieraggi, and R. A. Rapp, *Acta Metall. Mater.* **43**, 1065 (1995).
13. F. A. Kroger, *Chemistry of Imperfect Crystals* (North-Holland, Amsterdam, 1964).
14. D. A. Goulden, *Phil. Mag.* **33**, 393 (1976).
15. B. Pieraggi, *Advances in Ceramics*, M. F. Yan and A. H. Heuer (eds.) **6**, 117 (1983).
16. R. C. Pond and J. P. Hirth, *Solid State Phys.* **47**, 287 (1994).
17. M. Leseur and B. Pieraggi, *J. Phys.* **C4**, 135 (1983).
18. L. W. Hobbs, H. T. Sawhill, and M. T. Tinker, *Trans. Jpn. Inst. Metals* **24**, 115 (1983).
19. B. Lamine, M. Leseur, and B. Pieraggi, Mater. Sci. Mono. **28B**, 135 (1985).

20. R. Ploc, *J. Nucl. Materials* **28**, 48 (1968).
21. R. Herchel, N. N. Khoi, T. Homma, and W. W. Smeltzer, *Oxid. Met.* **4**, 35 (1972).
22. F. Czerwinski and W. W. Smeltzer, *J. Electrochem.* **140**, 1181 (1993).
23. L. Lattaud, D. Ciosmak, J. Bertrand, J. J. Heitzmann, A. Vadon, and C. Laruelle, *Reactivity of Solids* **1**, 57 (1985).
24. P. Kofstad, *High Temperature Corrosion* 307 (1988).
25. B. Pieraggi, F. Dabosi, *J. Microsc. Spectrosc. Electron.* **4**, 595 (1979).
26. L. B. Pfeil, Improvements in Heat-Resisting Alloys, U.K. Patent No. 459848 (1937).
27. D. P. Whittle and J. Stringer, *Phil. Trans. Roy. Soc.* **A295**, 309 (1980).
28. D. P. Moon, *Mater. Sci. Technol.* **5**, 754 (1989).
29. J. Stringer, *Mater. Sci. Eng.* **A120**, 129 (1989).
30. J. J. Gonzales, D. Oquab, and B. Pieraggi, unpublished data.