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The role of the metal/oxide interface in the growth of passive films in aqueous environments

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Abstract

A mechanistic methodology has been developed to understand the role of the metal/scale interface in the growth of scales at high temperatures. Specifically, cation vacancies arriving at the metal/scale interface are annihilated by the climb of misfit and misorientation interfacial dislocations. If this mechanism is blocked, e.g. by the tangling of dislocations within the metal, then cation diffusion cannot continue to support the growth of an adherent oxide. To the extent that adherent, crystalline and epitaxial passive or anodic films formed in aqueous environments also grow by cation diffusion over vacancies, the same mechanisms must apply. The segregation of large reactive element cations to the metal/scale interface and their importance in enhancing scale adherence by blocking vacancy annihilation, also constitute concepts that might find relevance for passive films in aqueous solutions.

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1. Introduction

The detailed involvement of the metal/scale interface in the growth of a thick crystalline scale on metals and alloys at high temperatures has often been neglected. For example, in his classic thermodynamic approach to describe parabolic scale growth on a pure metal, Wagner [1] in 1933 assumed local equilibrium at the metal/scale interface without any mechanistic model to suggest how that equilibrium is maintained. The growth of a crystalline (oxide or sulfide) scale on most engineering metals (Cu, Ni, Fe, Co, Mn, etc.) involves the diffusion of cations over vacancies in the lattice or grain boundaries of the adherent product scale. Therefore, some specific mechanism for the exchange of the metal atom and the cation vacancy at the metal/scale interface must operate to support continued scale growth without loss of adherence. In fact, for the growth of scales with cations of valence +4 or +5 (Ti, Zr, Nb, Ta, etc.), anion vacancy diffusion occurs in the crystalline adherent scale. In this case, a different defect reaction must occur at the metal/scale interface to create the anion vacancies necessary to maintain the growth of the adherent scale. By ignoring the necessary interfacial reactions, or assuming that they are not involved in deciding the corrosion rate, one neglects the possibility to understand the detailed mechanism, and loses the opportunity to manipulate these reactions to affect the corrosion product morphology, the stress state, and perhaps the corrosion kinetics.

Already four decades ago, the research groups of Benard [2–4] and Gwathmey [5–7] prepared carefully polished low-index surfaces for single crystals of copper, iron and nickel. Upon oxidation of these metals to form thin oxide layers, one or several epitaxial relationships between the underlying metal and the polycrystalline scale were always observed, depending upon the specific orientation, oxidation conditions, etc. “Parallel orientations”, whereby equivalent planes and directions of the metal and the scale are matched across the interface were the most commonly observed epitaxies. In fact, different faces exhibited differing scaling rates, which was not expected from Wagner’s classic theory. More recent studies of Ni single crystal oxidation by Herchel et al. [8] obtained similar results. However, the interpretation that this orientation-dependence of the kinetics arises from oxide grain growth providing time-dependent rates of grain boundary diffusion was dispelled by Larson [9] who showed that the apparent differences in kinetics are a result of different starting times for oxide growth at the same parabolic rate.

In certain instances, thorough characterizations of anodic passive films formed on metals in aqueous solutions have also found the oxide films to be both epitaxial and crystalline. MacDougall and Cohen [10,11] studied the growth and breakdown of passive films on Ni single crystals which had been electropolished, cathodically reduced, and then anodically oxidized in pH 8.4 Na_2SO_4 . These studies were extended by MacDougall et al. [12,13] to cover other pHs as well as the borate buffer solution. In general, the “air-formed” oxide film on electropolished Ni is a highly epitaxed, crystalline NiO surface film, 6–8 Å in thickness, having an average particle size of ca. 20 Å; its lattice parameter is ca. 2.5% expanded over that of pure, stoichiometric NiO. For anodized Ni, the “passive films” are highly epitaxed, crystalline NiO, 9 to 12 Å thick, with an average particle size of ca. 10 Å. With increasing time and po-

tential of anodization, the lattice parameter approaches that for pure, stoichiometric NiO to within $\pm 0.3\%$, i.e. within experimental error. This variation in lattice parameter was thought to result from changes in the concentration of cation vacancies within the oxide film, and therefore from changes in the concentration of Ni^{3+} . The more Ni^{3+} in the film (the more highly oxidized), the larger the measured lattice parameter (most probably associated with electrostatic repulsion forces). Indeed, these subtle changes in oxide film properties, such as lattice parameter, are thought to be responsible for the greater degree of film stability brought about by time and potential of anodization, as opposed to simply changes in oxide film thickness. The argument is that film stability is inversely related to the concentration of Ni^{3+} (two of these species arising for every cation vacancy that is present). Likewise, a film with lower Ni^{3+} concentration would be more tightly attached to the substrate and more highly reduced. Such epitaxial passive films with parallel orientations between the metal and the oxide are thought to grow by the migration of cations over vacancies, probably at the grain boundaries in the oxide film. Certainly, for some other metals and environments, a hydrated and/or amorphous passive film is believed to form. For example, a thick ($>1000 \text{ \AA}$) porous anodic oxide film of NiOOH is grown in a borate buffer solution pH 7.65; but beneath this outer film resides an adherent epitaxial protective NiO film of 9–12 $\text{\AA}$ thickness, which appears to control the growth kinetics of the thick, outer film [14].

The case of Fe is more complicated than that of Ni because anodizing must usually be performed in “buffered” solutions to achieve a compact passive film. The “passive” film thus formed is also epitaxed and highly crystalline; however its thickness is strongly dependent on potential, with a variation from 0.5 to 4 nm over the passive range [15]. The composition of the film is also more complex than that on Ni, with an inner layer of Fe_3O_4 -like oxide and an outer layer of gamma- Fe_2O_3 -like oxide giving rise to a bilayer-type structure [16]. The point to be made here is that for the growth of passive films in aqueous solutions, at least for certain combinations of metal, surface preparation and the environment, a compact epitaxial, crystalline oxide is thought to grow by the diffusion of cations over lattice vacancies in the oxide. The passive films on Ni and Fe were chosen here as examples both because of their structural simplicity and the significant characterization information that is available.

2. Interface dynamics for cation-diffusion grown oxides

Fifteen years ago, in interpreting scale growth by cation diffusion, the high-temperature oxidation community envisioned a simple jump (exchange) of an atom from the metal lattice into the cation vacancy of the scale. The vacancy “injected” into the metal was thought to diffuse and eventually be annihilated at some internal sink in the metal, e.g. at a dislocation or an internal interface [17]. Pieraggi and Rapp [18], however, pointed out that the interfaces of epitaxial adherent crystalline scales on metals indeed exhibit an inherent defect structure comprising misfit interfacial dislocations which necessarily arise from the differences in lattice parameters, and

structure, between the metal and the scale. For example, for an adherent scale of NiO on Ni, obeying the most commonly observed parallel epitaxial orientation: $(001)(100)_{\text{Ni}}$ parallel to $(001)(100)_{\text{NiO}}$, the 18% difference in lattice parameters leads to a square (planar) grid of interfacial misfit dislocations in the metal, having Burgers vectors parallel to the interface, with two parallel edge dislocations for every 13 atomic planes of Ni. During scale growth, it is inconceivable that cation vacancies in the scale arriving at the metal/scale interface could bypass these natural vacancy sinks to effect a simple atomic exchange with a metal atom. Rather, the cation arriving at the metal–scale interface would be annihilated by the climb of some fraction of these interfacial dislocations into the metal, forming a dislocation loop in the metal connected to the interface. The other misfits would adjust, i.e. increase, their spacing to maintain the epitaxy at the expense of introducing tensile stress in the metal and compressive stress in the scale at the interface.

A minor tilt of the metal/scale interface away from the ideal epitaxial orientation would correspond to the insertion of “misorientation” interfacial dislocations, with their Burgers vectors normal to the interface, as shown in Fig. 1a. These interfacial misorientation dislocations are equivalent to the presence of monatomic interfacial steps, and they can be created upon plastic deformation in the metal at the intersection of glide planes with the metal/scale interface, as shown in Fig. 1b. The climb of the misorientation dislocations within the interface could also annihilate cation vacancies [19]. However, the density of the extrinsic misorientation dislocations would not be so high as for the intrinsic misfit dislocations. Pieraggi et al. [20] have described the relevant interfacial structures, interfacial defects, and vacancy annihilation dynamics for metal/scale interfaces, for both cation/vacancy and anion/vacancy diffusing systems. Fig. 1b and c show schematic representations of an epitaxial metal/scale interface indicating the presence of both misfit and misorientation dislocations [21].

Fig. 2 shows a simplified “equilibrium” representation of this interface, i.e. prior to further growth of the oxide [21]. Fig. 3 presents a schematic frontal view of the metal/scale interface and the climb processes supporting vacancy annihilation during scale growth [20]. Oxide growth by cation diffusion over vacancies requires the annihilation of the vacancies by the climb of either misfit or misorientation interfacial dislocations. Fig. 4 illustrates the climb of only misfit dislocations to form a loop in the metal, and the corresponding spacing readjustment of the remaining interfacial misfits [20]. This extraction of some fraction of the misfits from the interface introduces tensile stress in the metal and compression in the oxide at the interface. These resultant stresses then serve to support the dissociation of the sessile dislocation in the metal and to permit the glide of the glissile component back to the interface (a sort of dislocation mill), as illustrated in Fig. 4b. Ultimately, excessive interfacial stress could activate the glide of edge dislocations in the oxide (Fig. 4c). According to this general mechanism, the continued growth of the adherent oxide is dependent upon maintaining this dynamic epitaxial metal/scale interface. If the cation diffusion step cannot be supported by vacancy annihilation via the climb of interfacial dislocations, then the growth of an adherent scale by cation diffusion cannot continue. If the metal lattice near the interface becomes so damaged, e.g. by

Fig. 1. Schematic illustration of interfacial misorientation dislocations: (a) atomic planes at the interface (without lattice mismatch); (b) equivalence to atomic steps or ledges (with lattice mismatch); (c) intersection of screw dislocation from the metal with the metal–scale interface, creating misorientation dislocations [21].

simultaneous mechanical deformation (SCC?) that the dislocations become entangled, then the increased interfacial stress could result in vacancy condensation in the interface, corresponding to void formation and a local loss of scale adherence. Thereafter, cation vacancies diffusing to the interfacial void can only contribute to growth of the void, and a translation of the scale toward the environment. Ultimately, variations in adherence along the interface should lead to film fractures.

Another important phenomenon in high-temperature oxidation, the Reactive Element Effect (REE), can also be rationalized in terms of a manipulation of

Fig. 2. Schematic illustration of metal/scale interface with parallel epitaxial orientation showing interfacial and misorientation dislocations [21].

Fig. 3. Schematic illustration of scale growth by cation/vacancy diffusion and associated interfacial processes [20].

the defects at the metal/scale interface. Pieraggi and Rapp [22] have proposed the “Poisoned Interface Model (PIM)”, illustrated in Fig. 5, to explain the REE in the growth of protective chromia scales on Fe–Cr, Ni–Cr and Co–Cr alloys. A fraction of a percent of one of several reactive elements (e.g. Y, Ce, La) with relatively large ionic sizes is known to improve greatly the scale adherence, to decrease greatly the scale growth kinetics, and to change the dominant scaling mechanism from outward cation diffusion to inward anion diffusion. As illustrated in Fig. 5, the large RE ions are virtually insoluble in the scale and therefore segregate to the metal/scale interface where they should reside adsorbed to interfacial dislocations. Such a pinning solute should prevent the climb of interfacial dislocations which is required to support the vacancy annihilation tied to cation diffusion. As a result, cation-diffusion-supported growth cannot occur, and the dominant scaling mechanism converts to the much slower anion diffusional growth with formation of an inward-grown, inherently adherent fine-grained scale. This PIM describes the important features of the REE in high-temperature scaling, but the fraction of a monolayer of segregated RE required to poison the metal/scale interface is difficult to confirm analytically.

Fig. 4. Climb of misfit interfacial dislocations to annihilate vacancies and glide return to the interface: (a) misfit dislocations at equilibrium spacing; (b) upon oxidation, climb of some fraction of misfit dislocations into metal and dissociation and return/glide to interface; (c) dislocation glide in the oxide; (d) two-dimensional view of metal/scale interface during scaling [18,21].

Fig. 5. Segregation of large highly charged reactive element cations to pin dislocations at the metal/scale interface [22,23].

As a further test of the PIM, which must apply generally for the growth of any cation-diffusion supported scale, Strawbridge and Rapp [23] evaporated 150–250 Å of several alkaline earth metals (Sr, Ca, Ba) onto the external surfaces of Cu, Fe, Ni and Co. Subsequent oxidation in air resulted in decreases in the scaling kinetics. For each of the four metals, that RE with an ionic misfit most closely matching the

45% ionic misfit provided by Y and Ce with chromia scales resulted in the maximum reduction in scaling rate. For the temperatures of these experiments, only the scaling of Ca-poisoned Ni led to a switch in mechanism to anion diffusion. At 700 °C, the parabolic rate constant for NiO growth on a Ca-doped initial surface was reduced (reproducibly) by a factor of 20. At excessively high temperatures, the REE becomes less effective, as the solubility of the RE is increased, and its bond to the interface is decreased. In that case, interfacial vacancy annihilation may be retarded, with a lesser reduction in scaling rate, without a switch in mechanism to anion diffusion.

Pieraggi [24] studied the oxidation of Ni at 650 °C for coupons which had their surfaces contaminated by Sr applied by immersing the coupons in a hot (80 °C) saturated aqueous solution of $\text{Sr}(\text{NO}_3)_2$ for two hours. The parabolic rate constant for Ni oxidation at 650 °C in air was reduced (reproducibly) by a factor of 20, although the cation-diffusing mechanism did not obviously change.

3. Extension of mechanisms to aqueous passive films

The purpose of this paper is to introduce to the aqueous community some of the observations and literature concerning the important mechanisms involving the metal/scale interface in high-temperature scaling. At least some metals in some aqueous environments (certainly Ni in Na_2SO_4) form adherent crystalline epitaxial anodic films which grow by cation diffusion, necessarily requiring vacancy annihilation. However, the role of the interface in film growth is not usually considered for passive film growth in aqueous solutions. A few possible applications of this interfacial picture might be suggested, requiring future critical experiments and analysis.

One often demonstrated aspect of the passive film on anodized Ni is its resistance to galvanostatic cathodic reduction, with an apparent current efficiency much lower than 2% in pH 2.8 Na_2SO_4 ; in pH 8.4 Na_2SO_4 , the passive NiO film cannot be removed at all [10]. In high temperature reducing gases, some oxide scales can be reduced using a gas atmosphere with low driving force, by reversing the oxidation mechanism, i.e. by returning the cations to the metal across the metal/scale interface, thereby reversing the dislocation climb process. At room temperature, the reversal of the film growth process may not be able to occur, such that any cathodic film removal corresponds only to film dissolution. Perhaps even the observed nominal “limiting thickness” for some passive films might be associated with an exhaustion of the interfacial vacancy annihilation mechanism resulting from dislocation tangles in the metal. (How important is the stacking fault energy in the alloy?) Finally, the elusive “defects” in the passive film, which are so important to their breakdown, might be related to (subsurface) interfacial voids resulting from vacancy condensation following failure of the dislocation climb mechanism [11].

The same element, cerium, which is so effective as the RE influencing the growth of chromia and alumina scales in high-temperature scaling, finds similar advantageous effects for the growth of passive films involving these same oxides [25,26]. Certainly, the electrochemical aspects of the oxide/environment interface are quite different for dry gaseous oxidation compared to wet aqueous corrosion. Therefore,

the consensus explanation of the “cerium effect” in aqueous solutions, blocking the kinetics of the oxygen reduction step, may well be correct. However, one might also inquire whether the cerium is otherwise involved in segregation and poisoning at the metal/scale interface. As a related question relative to inhibition, the sort of immersion/passivation of metals in hot aqueous solutions as practiced by Pieraggi [24], with the intention to poison the metal/scale interface, might find an equivalent application in improving the stability of passive films. Such a process could offer an alternative to chromate inhibition.

4. Conclusions

The mechanisms operative at the metal/scale interface to annihilate cation vacancies supporting scale growth at high temperatures should also apply for adherent crystalline epitaxial passive films in aqueous solutions. Some suggestions are made for possible applications and implications of such an interpretation. Some further experimentation and analyses are required to decide the extent to which such considerations are important.

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