

ROLE OF THE METAL/OXIDE INTERFACE IN THE  
GROWTH OF PASSIVE FILMS IN AQUEOUS  
ENVIRONMENTS

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ABSTRACT

The detailed involvement of the metal/scale interface in the growth of crystalline scale on metals and alloys has often been neglected. Upon oxidation of the metal to form a thin oxide layer, one or more epitaxial relationships between the underlying metal and the scale are always observed, depending upon the specific orientation, etc. "Parallel orientations", whereby equivalent planes and directions of the metal and the scale are matched across the interface are the most commonly observed epitaxies. 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 be operative to support continued scale growth without loss of adherence. 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.

In certain instances, thorough characterization of anodic passive films formed on metals in aqueous solutions has also found them to be both epitaxial and crystalline. MacDougall and Cohen (1,2) 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<sub>2</sub>SO<sub>4</sub>. These studies were extended by MacDougall et al. (3-5). Generally, the crystalline passive NiO film with a normal lattice parameter on such anodized Ni single crystals included a "highly epitaxed NiO surface film of 4 to 6 Å". Such epitaxial passive films with parallel orientations between the metal and the oxide are also thought to be grown by the migration of cations over vacancies probably at the grain boundaries. Certainly, for some metals and environments, a hydrated and/or amorphous passive film is believed to form. 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 be grown by the diffusion of cations over lattice vacancies. The passive film on Ni was chosen here as the example both because of its structural simplicity and the significant available characterization.

Fifteen years ago, Pieraggi and Rapp(6) pointed out that the interfaces of epitaxial adherent crystalline scales on metals 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><sub>Ni</sub> parallel to (001)<100><sub>NiO</sub>, the 18% difference in lattice parameters leads to a square (planar) grid of interfacial misfit dislocations in the metal, with two parallel edge dislocations for every 13 atomic planes of Ni. It is inconceivable that during scale growth cation vacancies in the scale arriving in the metal/scale interface could bypass these natural vacancy sinks to effect a simple atomic exchange with a metal atom. Rather, some fraction of these interfacial dislocations would climb into the metal, annihilating cation vacancies, and forming a dislocation loop in the metal connected to the interface. The other misfits would readjust/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, equivalent to the presence of monatomic interfacial steps. These interfacial misorientation dislocations can be created upon plastic deformation in the metal at the intersection of glide planes in the metal with the metal/scale interface. The climb of the misorientation dislocations within the interface could also annihilate cation vacancies.(7,8) However, the density of the extrinsic misorientation dislocations would not be so high as for the intrinsic misfit dislocations.

In this paper, a mechanist methodology to understand the role of the metal/scale interface in the growth of scales at high temperatures is reviewed. 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 grow 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 and blocking vacancy annihilation, also constitute concepts that might find relevance for passive films in aqueous solutions.

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