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A novel explanation of the “reactive element effect” in alloy oxidation (*)

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Abstract. — The precise measurements of oxidation kinetics for an undoped Fe-25Cr alloy by Hussey *et al.* [1] have been analyzed to determine values for both the parabolic rate constant for diffusion and the linear rate constant for the interfacial step. The greatly reduced scaling kinetics for Fe-25Cr in response to a CeO₂ surface doping are consistent with a blocking of the interfacial step for creation of cation interstitials at the metal/scale interface. For sufficient doping (Ce ion segregation) at the metal/scale interface, cation transport is replaced by anion diffusion over vacancies. The poisoning of the interfacial cationic reaction step results from pinning of the misfit edge dislocations whose climb action otherwise creates interstitial cations. But the creation of the anion vacancies at the metal/scale interface is not blocked by the segregated reactive element ions. This model provides a consistent interpretation for the commonly observed REE consequences in the growth of chromia scales on alloys, especially the changes in growth direction and scale growth kinetics.

1. Introduction.

The action of very small concentrations of reactive elements (Y, Ce, La, etc.) in improving the protection by chromia scales of binary alloys such as Fe-25Cr, Ni-30Cr, and Co-45Cr is a particularly interesting and popular research subject with significant engineering importance. As generally accepted, the reactive element effect (REE) results in four important changes in the growth of chromia scales on alloys: 1) scale adherence is improved greatly; 2) scaling kinetics are greatly reduced; 3) a lower Cr content in the alloy is sufficient to stabilize an exclusive chromia scale; and 4) the chromia growth mechanism is changed from outward growth by cation diffusion to inward growth by anion diffusion. According to recent reviews [2, 3], a coherent and detailed REE mechanism for chromia growth is still lacking.

The change in reaction mechanism, from cation to anion diffusion, provides the best clue to a comprehensive mechanism. Indeed, a very fine oxide grain size and excellent adherence at a clean metal/scale interface are already well known characteristics for scales grown by anion diffusion. Generally, the reaction steps required at the metal/scale interface to support either cation or anion transport through the scale are given little attention, because they are frequently sufficiently fast so that diffusion control with global parabolic kinetics is observed. The authors [4] have explained how the climb of interfacial misfit edge dislocations is responsible for cation vacancy annihilation at the metal/scale interface, and this mechanism can also apply for the creation of interstitial Cr cations for the growth of chromia. Kofstad and Lillerud [5] interpret the principal point defects in chromia at low oxygen activities to

(*) Invited paper.

be Cr interstitials. The blocking (poisoning) of an interfacial reaction step by a fraction of an adsorbed monolayer of impurity is well known for the gas/solid interface [6-7]. Likewise, the pinning of dislocations in solids by segregated impurities is also well understood [8]. In this paper, segregated RE elements are suggested to pin the misfit edge dislocations at the metal/scale interface and thereby block the creation of Cr interstitial ions required to support cation diffusion. By default, unblocked anion diffusion supports the growth of an adherent, fine-grained scale with greatly reduced kinetics.

2. Analysis of scale growth kinetics.

For the growth of a scale by the transport of one diffusing species, the kinetics can be described by the expression:

$$dw/dt = 1 / (1/k_l + 2w/k_p) \quad (1)$$

where w is the weight gain of oxidant in scale growth, k_p is the parabolic rate constant, and k_l is the sum of the linear rate constants for the reaction steps at the gas/scale and the scale/alloy interfaces. Integration of equation (1) gives an expression describing mixed kinetics:

$$t = w^2/k_p + w/k_l \quad (2)$$

with $w = 0$ at $t = 0$. Deal and Groves [9] have plotted this function as t/w vs. w to obtain values for both k_p and k_l for the oxidation of silicon. The important point to remember is that the assumption of finite interfacial rate implies that the scale, and particularly the gas/scale and alloy/scale interface, could not be considered as fully equilibrated, and furthermore that the inhibition or "poisoning" of one of the interfacial steps could lead to a complete inhibition of the overall reaction as shown by equation (1), indeed, the reaction rate decreases with the linear rate constant k_l .

In case of the simultaneous diffusion of two species, e.g. cations and anions, as treated by the classic Wagner paper [10], the rate of weight gain is described by the sum of two expressions such as equation (1). The integration for this case is known [11], but too complex for presentation here. However, as previously stated for the simple case of one diffusing species, the growth associated to the diffusion of a given species could be inhibited from the poisoning of one of the interface reactions involving the considered species.

Hussey *et al.* [1] have published precise kinetic measurements for the oxidation of an Fe-25Cr alloy in 10^{-2} to 1 torr oxygen at 1100 °C, and the effect on the kinetics of very small quantities (2-30 nm) of CeO₂ sputtered onto the external surface. Their plot of the resulting kinetics is given as figure 1. An external sputtered deposit of only 2 nm CeO₂ effected a small change in the oxidation rate by outward cation diffusion, while a deposit of 4 nm CeO₂ or more resulted in similar greatly reduced kinetics with scale growth at the alloy/scale interface.

Figure 2 is a plot of these oxidation kinetics according to the method of Deal and Groves [9], which provides the indicated individual values for the parabolic and linear rate constants. The 2 nm CeO₂ deposit reduced both rate constants by factors of about two, while the greater CeO₂ deposits reduced k_p greatly, as well as the rate constant k_l . The calculated values of k_p and k_l constants are listed in table I.

Careful characterization [1] of the scale composition indicated that some Ce was present at the metal/scale interface while the bulk of the Ce resided near the oxide/gas interface, this latter observation consistent with the behavior expected for externally applied inert markers for a scale grown by anion diffusion.

Fig. 1. — Kinetics of oxidation of Fe-25Cr alloy in $p_{O_2} = 10^{-2} - 1$ torr at 1100 °C (data from Hussey *et al.* [1]).

Fig. 2. — Plot of oxidation kinetics to determine rate constants of oxidation of undoped and doped Fe-25Cr alloys.

Table I. — Parabolic and Linear rate constants for the oxidation of Fe-25Cr alloy at 1100 °C and $p_{O_2} = 10^{-2} - 1$ torr.

	undoped	2 nm CeO ₂	4 nm CeO ₂
k_p (mg ² ·cm ⁴ ·h ⁻¹)	0.560	0.235	0.032
k_l (mg·h ⁻¹)	0.550	0.230	0.125

3. Discussion.

Our interpretation of these results is as follows. Large Ce ions ($r = 0.92 \text{ \AA}$ for Ce^{4+} and $r = 0.63 \text{ \AA}$ for Cr^{3+} , with $CN = 6$) are preferentially segregated to the misfit edge dislocations at the metal/scale interface. By locally expanding the oxide lattice at the interface, the metal is subjected to a local tensile stress, as also occurs upon the climb of misfit dislocations. Therefore the segregated RE ions act to pin the misfit dislocations and prevent their climb into the metal which would otherwise support the creation of interstitial Cr cations (or the annihilation of cation vacancies). For the smallest CeO_2 coating, the poisoning was inadequate to prevent cation diffusion dominance, although the linear rate constant for the interfacial reaction step was halved. For larger CeO_2 coatings, both the parabolic and linear rate constants were decreased greatly as the growth direction changed. In this case, the cation interstitial creation reaction was completely blocked, but the annihilation of anion vacancies at the metal/scale interface was not blocked so that anion diffusion accounted for a reduced rate of scale formation.

Figure 3 shows schematically a generalized model for the metal/scale interface comprised of misfit edge dislocations and misorientation dislocations as described earlier [12]. Similar to the mechanism proposed by the authors [4] for cation vacancy annihilation by the climb of interfacial misfit dislocations, Cr interstitial ions would also be created by such climb. In figure 3, one intersection of misfit dislocations is pictured as an active source for Cr interstitial ions, although most of the misfit dislocations are shown pinned by the segregated Ce ions. In the absence of segregated RE ions, the climb of misfit dislocations normal to the interface supports scale growth at the scale/gas interface by the creation of cation interstitials (or by the annihilation of cation vacancies), with the introduction of tensile stress into the metal [4].

Fig. 3. — Schematic illustration of alloy/scale interface showing pinned misfit dislocations and creation of Cr interstitials by climb of misfit dislocations.

Figure 4 shows schematically a set of misorientation dislocations corresponding to a minor tilt in the interface plane from the ideal epitaxial orientation. Such misorientation dislocations have Burgers vectors normal to the interface plane and can be considered as monoatomic ledges in the interfaces. Unlike the intrinsic misfit dislocations, the misorientation dislocations must be created or supplied to the interface *via* an active source in the alloy. The climb

Fig. 4. — Schematic illustration of misorientation dislocations, corresponding to monoatomic ledges at alloy/scale interface.

of misorientation dislocations in the interface results in the creation of anion vacancies at the alloy/scale interface, and such climb supports the growth of the oxide locally. Because the lateral climb of the misorientation dislocations (monoatomic ledge translation) does not introduce stress into the metal, these dislocations are not pinned tightly by the segregated RE ions.

Then the REE observed for Fe-25Cr by Hussey *et al.* [1], but also for alloys of Co-45Cr [13] and Ni-30Cr [14], etc., can be interpreted as follows. In the absence of RE additions, scale growth occurs at the scale/gas interface, as Cr interstitials are created at the alloy/scale interface by the climb of misfit dislocations. Upon the introduction of RE ions into the scale (by sputtering, ion implantation, alloying, oxide particles, etc.), some of the large RE cations segregate to the alloy/scale interface where they immobilize the climb action of the misfit dislocations. Such poisoning of this interfacial step eliminates cation transport, but does not prevent the creation of anion vacancies by the lateral climb of interfacial misorientation dislocations, which results in slower scale growth at the alloy/scale interface. In this way, the growth direction and the growth kinetics are changed, and the inward grown scale inherently results in a fine grain size with excellent adherence [15].

The fourth RE effect, that a lower Cr content is adequate for selectively forming a chromia scale can be explained by the theory of Wagner, whereby the diffusion rate in the alloy is coupled to the rate of parabolic growth of the protective scale. According to this theoretical model, the minimum required concentration for the protective component is inversely proportional to the square root of the parabolic rate constant. The much slower growth of chromia limited by anion/vacancy diffusion is consistent with the reduction in Cr concentration observed experimentally.

4. Conclusions.

The REE in chromia growth on alloys occurs because the reaction step supporting cation transport is blocked (poisoned) at the alloy/scale interface. Large RE ions segregate to the alloy/scale interface and pin the misfit edge dislocations whose climb normally creates cation interstitials (or annihilates cations vacancies). The slower growth of an adherent, fine-grained

scale at the alloy/scale interface results from anion vacancy creation supported by the lateral climb of misorientation dislocations.

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References

- [1] HUSSEY R.J., PAPAIIVOCOU P., SHEN J., MITCHELL D.F., GRAHAM M.J., Corrosion and Particles Erosion at High Temperatures, V. Srinivasa, K. Vedula Eds. (TMS publications, 1989) p. 567.
- [2] MOON D.P., *Mater. Sci. Technol.* **5** (1989) 754.
- [3] STRINGER J., *Mater. Sci. Eng.* **A120** (1989) 129.
- [4] PIERAGGI B., RAPP R.A., *Acta Metall.* **36** (1988) 1281-1289.
- [5] KOFSTAD P., LILLERUD K.P., *J. Electrochem. Soc.* **127** (1980) 2410.
- [6] TURKDOGAN E.T., GRIEVESON P.M., *J. Electrochem. Soc.* **114** (1967) 59.
- [7] GRABKE H.J., PAULITSCHKE W., TAUBER G., VIEFHAUS H., *Surf. Sci.* **63** (1977) 577.
- [8] HIRTH J.P., LOTHE J., Theory of dislocations, 2nd edition (Wiley, New York, 1982).
- [9] DEAL B.E., GROVES A.S., *J. Appl. Phys.* **36** (1965) 3770.
- [10] WAGNER C., *Z. Phys. Chem. B* **21** (1933) 25.
- [11] DYBKOV V.I., *J. Mater. Sci.* **21** (1986) 3078.
- [12] PIERAGGI B., RAPP R.A., VAN LOO F.J.J., HIRTH J.P., *Acta Metall.* **38** (1990) 1769.
- [13] PRZYBYLSKI K., GARRATT-REED A.J., YUREK G.J., *J. Electrochem. Soc.* **135** (1988) 509.
- [14] PATIBANDLA N., RAMANARAYANAN T.A., COSANDEY F., *J. Electrochem. Soc.* **138** (1991) 2176.
- [15] LEE B.S., RAPP R.A., *J. Electrochem. Soc.* **131** (1984) 2998.