Chromium-Depleted Zones and the Oxidation Process in Stainless Steels

H. E. Evans,* D. A. Hilton,* and R. A. Holm*

It is suggested that, during the oxidation of stainless steels, matter is conserved at the oxide–metal interface by the creation of a dynamic balance between the chromium diffusion fluxes in the alloy and in the oxide. It is shown that the rate of oxidation is insensitive to alloy composition so that a necessary consequence is that the rate-controlling process is always diffusion through the oxide. In addition, the interfacial concentration of chromium remains invariant with time at a value higher than that in thermodynamic equilibrium with the oxide. Some of the predictions made with regard to the depth and kinetics of growth of chromium-depleted zones within the alloy have been checked experimentally in oxidation tests in CO_2 at $1123°$ K on a 20Cr–25Ni stainless steel containing a dispersion of TiN particles. It is concluded that the matter-conservation hypothesis is valid for this material.

INTRODUCTION

Austenitic stainless steels from a particularly useful class of alloys combining good oxidation resistance with a potential for high creep strength. Even though it has been recognized for many years that the oxidation properties can be attributed to the formation of a dense, adherent chromic oxide layer, there is still debate over the nature of the rate-controlling process. The uncertainty arises over the exact roles played by the transport of chromium ions through the oxide film and their rate of supply from the metal interior.

*C.E.G.B., Berkeley Nuclear Laboratories, Berkeley, Glos., United Kingdom.

A popular view has been to consider the slower of these transport processes as rate-controlling so that in principle the oxidation process could be governed by diffusion within the alloy. This was suggested some time ago by Wagner[1] and, more recently, by Soustelle and Lalauze[2] and by Hales et al.[3] Circumstantial evidence such as extensive surface zones of chromium depletion has been used to support the thesis.

   This note presents some simple postulates of the nature of the rate-controlling process and the part played by the depleted zones. The predictions are compared with the results of experimental work on a TiN-strengthened 20 wt.% Cr–25 wt.% Ni stainless steel. This material has a very high creep strength[4] and is being considered for possible usage as fuel cladding in Civil Advanced Gas-cooled Reactors; preliminary oxidation results have been presented elsewhere.[5]

THE RATE-CONTROLLING PROCESS

   The oxide is taken to be an electronic conductor deficient in cations, so that metal ion transport occurs outward through the oxide film, reaction occurring at the oxide–gas interface. A basic tenet is that matter must be conserved at the oxide–metal interface, so that here a dynamic balance exists between the chromium flux arriving from the alloy interior and that passing through the oxide. For parabolic kinetics to obtain, it follows that the flux of ions from the metal j_I at this interface will vary with time t as

$$j_I \propto t^{-1/2}$$

and this restraint acts as a boundary condition for diffusion within the metal. Taking the latter to have an initial uniform mole fraction f_B of chromium and to have dimensions sufficiently large for it to be considered as semiinfinite gives the variation of chromium mole fraction f as a function of distance x into the alloy as

$$(f - f_{IM})/(f_B - f_{IM}) = \text{erf}\,[x/2(D_m t)^{1/2}] \tag{1}$$

where f_{IM} is the chromium fraction in the metal at the oxide–metal interface and the solution (1) applies if this is constant, invariant with time, i.e., it has a dynamic equilibrium value. D_m is the lattice diffusion coefficient of chromium in the alloy and erf is the error function. This result assumes that mass transport occurs predominantly by lattice diffusion and that the contribution of grain boundary diffusion is negligible. This is probably true for most metals at temperatures $> 0.6\,T_M$, where T_M is the melting temperature in °K, and is shown in the Appendix to be a good approximation for the alloy used in the present work.

A value of f_{IM}, and hence the depth of chromium depletion, can be obtained provided that the parabolic rate constant for oxidation k_p is known. Considering, again, only parabolic kinetics, the rate of growth of oxide thickness y per unit area of surface is related to j_I and k_p by

$$dy/dt = j_I v = k_p^{1/2} t^{-1/2}/2 \qquad (2)$$

where v is the volume of oxide produced per chromium ion. Using the equivalent of Eq. (1) and expressing concentration C in number of ions per unit volume to evaluate j_I, we get

$$f_{IM} = f_B - [(\pi k_p/D_m)^{1/2}(\rho_o W_{Cr}/\rho_m W_o)] \qquad (3)$$

where ρ_o and ρ_m are, respectively, the densities of oxide and alloy, W_{Cr} is the atomic weight of chromium, and W_o is the molecular weight of the oxide. These parameters are introduced above since $v = W_o/2\rho_o N_A$ and $f = CW_{Cr}/\rho_m N_A$, where N_A is Avogadro's number. Equation (3) is a limiting form of more general equations developed by Gibbs et al. (Gibbs, G. B., Smith, A. F., and Curtis, M. T., unpublished work).

Existing experimental data on metal systems which form a chromic oxide layer have recently[3] been used to support the view that the oxidation process in stainless steels is controlled by diffusion within the metal. Hales et al.[3] argue that the k_p values found in binary iron–chromium alloys are similar to those for pure chromium and are significantly higher than those for austenitic steels. The data available show considerable scatter and it is the present contention that this reflects systematic deviations which tend to bias the conclusions. For example, it is known[6] that at temperatures in excess of ~1273°K the parabolic oxidation of pure chromium is complicated by the occurrence of oxide blistering, leading to enhanced oxidation rates. This effect is, perhaps, responsible for the consistently high k_p values found by Mortimer and Post[7] compared with earlier work.[6,8] A comparison is made in Fig. 1 between these earlier results on chromium and published work on iron-based alloys containing significant quantities of chromium.* The references included are not exhaustive but are thought to be representative.

It is clear that although appreciable scatter still occurs, it is not possible to detect any systematic differences between the various alloy compositions. It follows, therefore, as a necessary conclusion that if chromic oxide exists as an adherent, compact layer, chromium ion diffusion through this will always control the oxidation process. It is noteworthy that the activation energy for k_p evident in Fig. 1 is very similar to that of 257 kJ/g mole found by Hagel and Seybolt[9] for chromium diffusion in chromic oxide.

---

*The k_p values shown are expressed in terms of oxide thickness and can be converted to terms of gross weight gain by multiplying by 2.706.
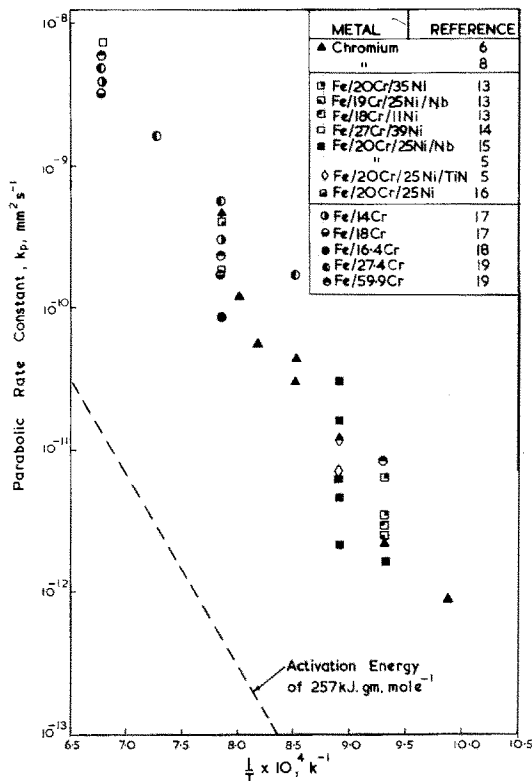
Fig. 1. Comparison of parabolic rate constants in different alloy systems.

The consequences of postulating matter conservation at the metal–oxide interface can now be seen from Eqs. (1) and (3). An immediate feature is that the "dynamic equilibrium" value f_{IM} of the interfacial chromium fraction is set by the need to balance the diffusion fluxes at that interface and is not controlled by thermodynamic equilibrium as envisaged in the Wagner treatment.[1] High values of D_m (e.g., in ferritic alloys) need small concentration gradients in the metal to achieve balance and, accordingly, the extent of chromium depletion will be limited and f_{IM} will be high; conversely, low values of D_m (e.g., in austenitic alloys) will extend the region of chromium depletion and result in low values of f_{IM}. In principle, it is possible for this dynamic equilibrium to occur, through Eq. (3), at a value of f_{IM} less than that in thermodynamic equilibrium with chromic oxide. Under such a condition, the protective oxide film will tend to dissociate in favor of other, presumably iron-based, oxides.

The conservation-of-matter hypothesis is an idealized restraint which assumes that no voidage forms at the metal–oxide interface, that the oxide remains uncracked, and that it is formed at theoretical density. It is relatively easy, however, to check the applicability of the hypothesis through the relationship of the growth kinetics of the chromium-depleted zones with k_p. Thus, from Eqs. (1) and (3)

$$\text{erf}\left[x_D/2(D_m t)^{1/2}\right] = \{1 - (f_B - f_D)/[(\pi k_p/D_m)^{1/2}(\rho_o W_{Cr}/\rho_m W_o)]\} \quad (4)$$

where f_D is the chromium mole fraction at which the depletion becomes undetectable and x_D is the distance from the metal–oxide interface at which this occurs. Experimental confirmation of this equation is presented in this paper.

EXPERIMENTAL

Techniques

The alloy used was a 20Cr–25Ni steel containing a dispersion of TiN particles with additional small quantities of chromium-rich phases, mainly nitrides. The initial alloy composition is given in Table I, and the dispersion of nitrides was produced from this by annealing 20 mm × 20 mm × 0.38 mm coupons in an atmosphere containing 95 vol.% N_2–5 vol.% H_2 at 1423°K for $1\frac{3}{4}$ hr. This treatment allowed through-penetration of the diffusion front but also left an excess of nitrogen in solution, which was largely removed by subsequent outgassing for $1\frac{1}{4}$ hr in H_2 at the same temperature. The resulting weight gain, representing nitrogen pick-up, was ~0.53%, compared with a value of 0.45% corresponding to a dispersion of stoichiometric TiN.

The oxidation tests were performed either in CO_2 containing 1 vol.% CO and 1200 vpm H_2O at 2.03 N/mm^2 (20 atm) pressure and 1123°K, or in CO_2 containing 2 vpm H_2O at 0.03 N/mm^2 (0.3 atm) pressure, also at 1123°K. In the former case, the specimens were periodically removed from the autoclave for weighing, but in the latter continuous measurements were made. In agreement with previous work[5,10] no systematic difference could be detected between the two sets of data and no differentiation of the testing procedure is made in the presentation of results. After testing,

Table I. Initial Composition of the Alloy, wt. %

Cr	Ni	Ti	Si	Nb	Mn	C	Fe
19.8	25.2	1.55	0.92	0.21	0.65	0.015	Balance

specimens were nickel-plated and sectioned transversely and parallel to the original rolling direction. The chromic oxide layer was identified using x-ray energy analysis techniques (KEVEX) coupled with a "spot" traverse on the scanning electron microscope. Measurements of the thickness of this layer were made either on the same instrument or by using optical microscopy. Compositional results using largely the same techniques have been reported previously.[5] The electron probe microanalyzer (EPMA) was also used to determine elemental distributions, although quantitative analyses were made only at positions remote from the alloy–oxide interface; such quantitative usage near the interface produced unreliable results because of beam overlap onto the oxide layer.

Results

The variation of chromic oxide thickness with time is shown in Fig. 2, together with the best-fit parabolic curve. The rate constant k_p corresponding to this is 2.32×10^{-12} mm^2/sec. The variation of gross weight gain with time is shown, similarily, in Fig. 3, where the broken line represents the weight gain due to chromic oxide, calculated from Fig. 2 with $\rho_o =$ 5.21 mg/mm^3. These gravimetric results show a clear departure from the expected rate.

The appearance of the oxide at relatively short and long times is shown in Figs. 4(a) and 4(b), respectively. The compact layer which formed initially was principally chromic oxide which had an underlying silicon-rich layer (cf.
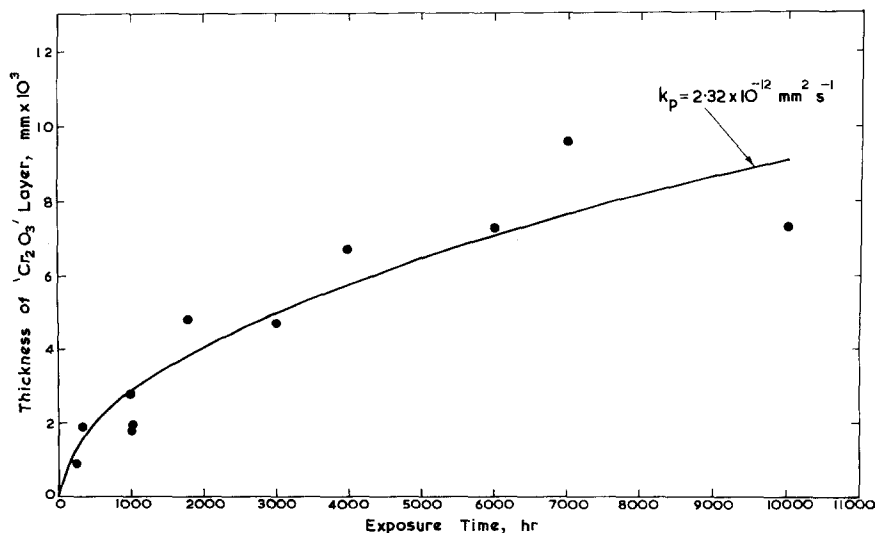

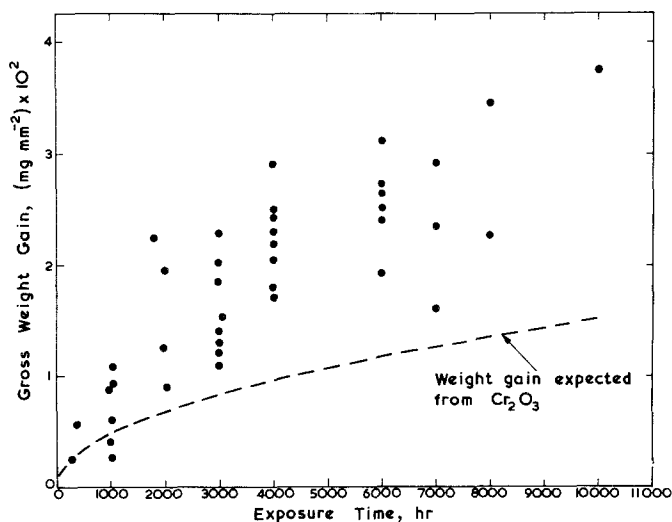**Fig. 2.** Variation of chromic oxide thickness with time for the nitrided alloy.

Fig. 3. Variation of gross weight gain with time for the nitrided alloy.

Ref. 5). Over longer periods a more porous oxide formed above the "Cr_2O_3" layer [Fig. 4(b)], rich in iron, manganese, and nickel (Fig. 5).

Significant chromium depletion existed near the oxide–metal interface and resulted in the dissociation of the chromium-rich precipitates within the alloy to a depth corresponding to a local chromium mole fraction of 0.200 ± 0.005 (18.7 ± 0.5 wt.%). This depleted zone is shown in the etched specimen of Fig. 4(b) and also in Fig. 5. It was used as a measure of the extent of chromium depletion, and the variation of its depth with time is shown in Fig. 6 together with the best-fit parabolic curve. The "rate" constant k_D in the relationship

$$x_D = (k_D t)^{1/2} \tag{5}$$

was obtained as 1.78×10^{-10} mm^2/sec. Since both the chromic oxide thickness and depletion depth have parabolic kinetics, they will be related directly as

$$x_D = (k_D / k_p)^{1/2} y \tag{6}$$

This relationship is plotted in Fig. 7 using the proportionality constant of 8.76 calculated from the data of Figs. 2 and 6.

The nature of the internal attack shown in Fig. 4(b) in which voids are formed within the chromium-depleted zone will be considered in a subsequent publication.
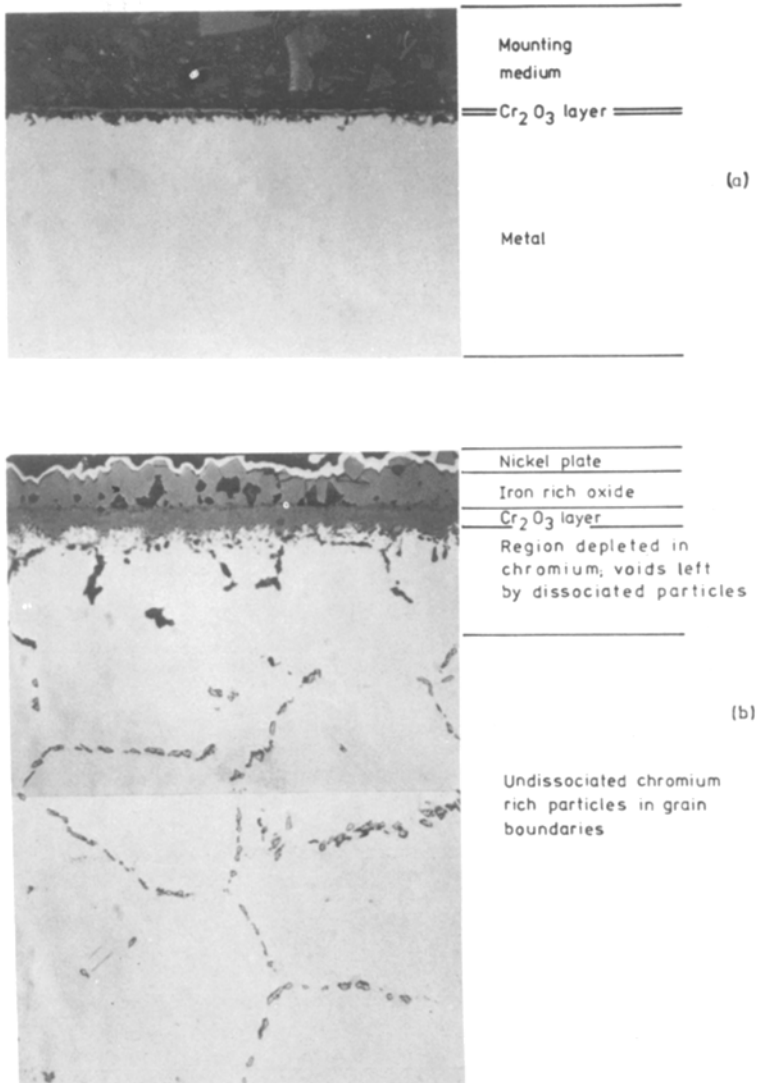
Mounting
medium

Cr$_2$O$_3$ layer

(a)

Metal

Nickel plate

Iron rich oxide

Cr$_2$O$_3$ layer

Region depleted in
chromium; voids left
by dissociated particles

(b)

Undissociated chromium
rich particles in grain
boundaries

Fig. 4. Cross section of titanium nitride strengthened 20Cr–25Ni steel. (a) After
1000-hr oxidation; (b) after 6000-hr oxidation.

Outer oxide, Cr absent
Cr$_2$O$_3$ layer
Cr depleted layer
Metal
Cr rich precipitates

(a) Chromium

Outer oxide, containing Fe
Inner oxide
Metal

(b) Iron

Outer oxide, containing Mn
Inner oxide
Metal

(c) Manganese

Ni plate to retain oxide
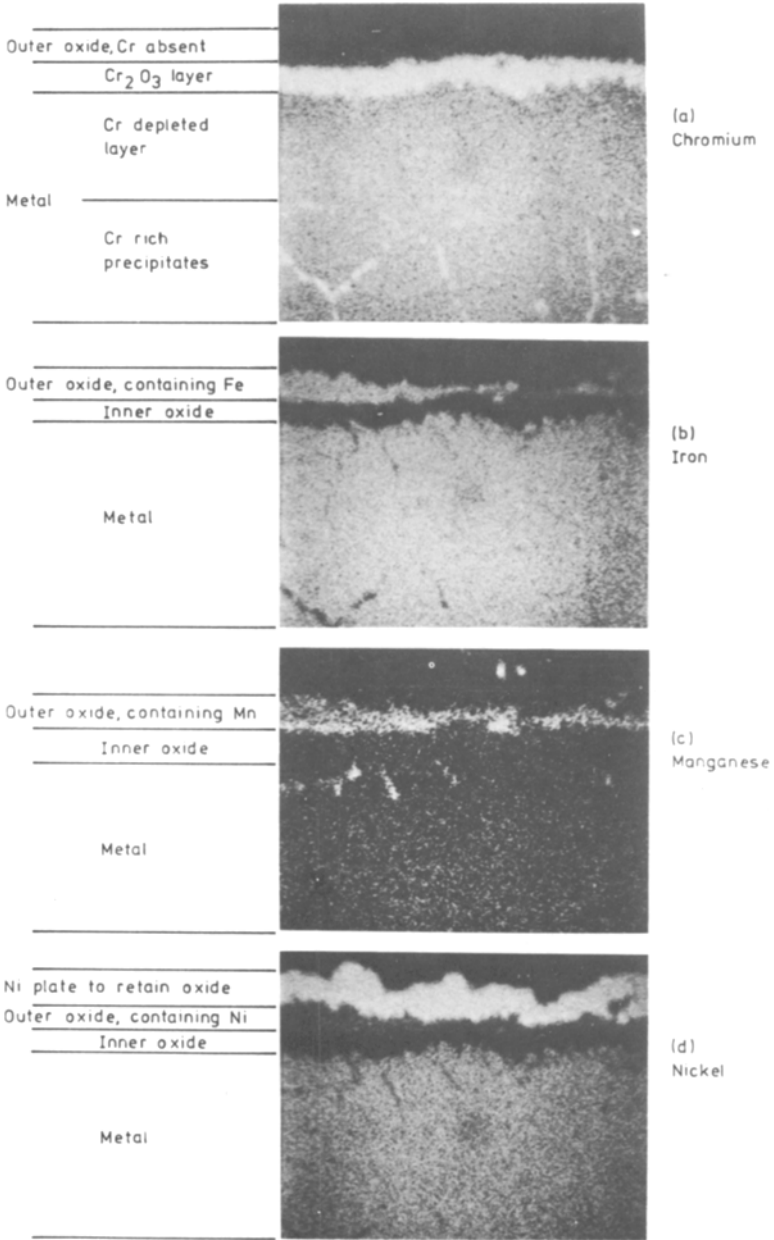Outer oxide, containing Ni
Inner oxide
Metal

(d) Nickel

Fig. 5. X-ray scanning images of the chromium, iron, manganese, and nickel distributions in nitrided 20Cr–25Ni steel oxidized for 6000 hr.
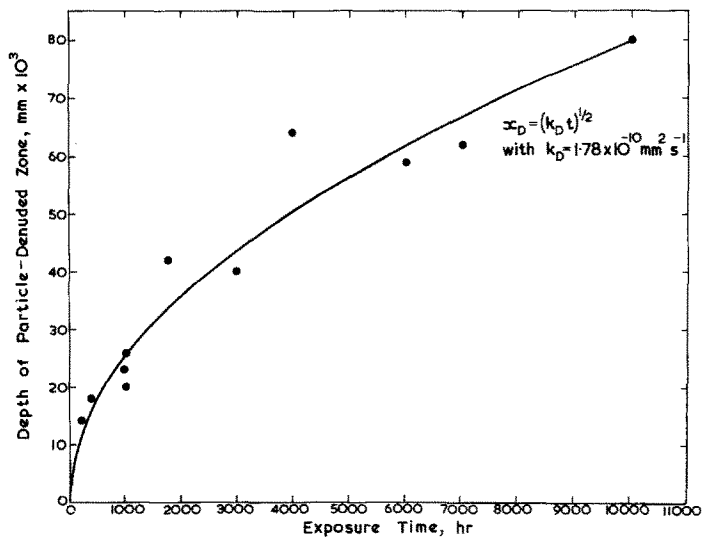
Fig. 6. Variation of the depth of particle-denuded zone with time for the nitrided alloy.
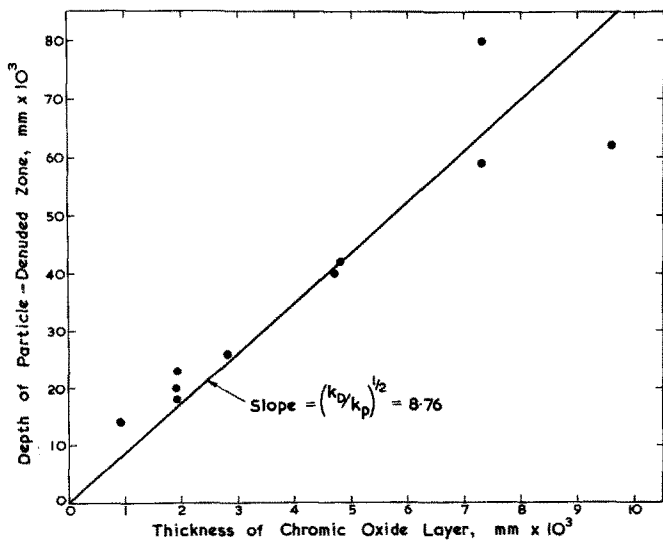

Fig. 7. Interrelationship between zone depth and chromic oxide thickness for the nitrided alloy.

DISCUSSION

The departure from the parabolic kinetics applicable to chromic oxide growth shown in Fig. 3 for measurements of gross weight gain is compatible with the observations (e.g., Ref. 10) of "paralinear" behavior in the base 20Cr–25Ni, Nb-stabilized steel. It can be explained in the present work by the gradual oxidation of other alloy constituents, mainly iron (Figs. 4 and 5), presumably by outward diffusion, and does not reflect a fundamental change in the oxidation mechanism. This is evident from the continuing parabolic growth of the chromic oxide layer (Fig. 2).

Such growth kinetics of the oxide layer allow a comparison to be made with the predictions of Section 2, based on the tenet of matter conservation at the oxide–metal interface. An important observation in this context is that the chromium-depleted zone also grows with parabolic kinetics [Fig. 6, Eq. (5)]. This would be expected only if the matter conservation hypothesis holds, so that the chromium concentration profile could be represented by the error function of Eq. (1), and this, in turn, would be a valid solution only if the mole fraction of chromium f_{IM} at the metal–oxide interface is independent of time. This contrasts with the predictions of Hales et al.[3] and Killeen et al.,[11] who envisage a decrease of f_{IM} with time, gradually approaching the value of $\sim 10^{-5}$ in thermodynamic equilibrium with chromic oxide. The dynamic equilibrium level of f_{IM} is given from Eq. (3), with[12] $D_m = 6.22 \times 10^{-11}$ mm^2/sec, $\rho_m = 7.93$ mg/mm^3, and the measured value of k_p, as 0.135 (12.6 wt.%)—very much greater than the thermodynamic value. That this result is reasonable is shown by Eq. (4), which,

with $f_D = 0.200$ (± 0.005), predicts $k_D = 2.51 \begin{pmatrix} +1.05 \\ -0.64 \end{pmatrix} \times 10^{-10}$ mm^2/sec, in

satisfactory agreement with the observed value (Fig. 6) of 1.78×10^{-10} mm^2/sec.

An implication of the dynamic balance existing at the oxide–metal interface is that the chromium concentration there f_{IM} is a function of the transport properties of the oxide and metal (Section 2) and is thus, in principle, adjustable. It has been suggested[5] that mechanical damage to the chromic oxide scale can lead to anomalously high rates of oxidation, which are especially prolonged if the rate of re-healing of the protective layer is low. This situation is likely to obtain at low values of f_{IM}. It has been shown in Section 2 that the transport properties of chromic oxide are insensitive to the exact alloy composition, so that it follows from Eq. (3) that high values of f_{IM} and, hence, high resistance to anomalous attack should be obtained with alloys having a high chromium diffusion coefficient (e.g., ferritic stainless steels) or high values of the bulk concentration f_B.

CONCLUSIONS

i. It is postulated that during the oxidation of stainless steels conservation of matter occurs at the metal–oxide interface so that a dynamic balance exists between the chromium diffusion fluxes in the alloy and oxide. The "dynamic equilibrium" value of the chromium concentration in the metal at this interface is constant, invariant with time, when parabolic kinetics pertain and will be considerably greater than that in thermodynamic equilibrium with chromic oxide.

ii. The parabolic rate constant k_p for oxidation is insensitive to alloy composition, so that the oxidation process will always be controlled by diffusion through the oxide when a dense, adherent layer of chromic oxide forms.

iii. The matter conservation hypothesis has been confirmed on a 20Cr–25Ni steel, containing a dispersion of TiN particles, during oxidation tests in CO_2 at 1123°K for periods up to 10,000 hr. It is shown that both the chromic oxide thickness and the depth of the depleted zone vary parabolically with time and are interrelated in the manner expected from theory. The dynamic equilibrium concentration of chromium in the metal at the metal–oxide interface is calculated to be 12.6 wt.%.

iv. On the same alloy, the oxidation kinetics measured gravimetrically show a significant departure with time from the rate of chromic oxide growth due to the concurrent oxidation of other alloy constituents, mainly iron.

APPENDIX

Shade and Speight (unpublished work) have considered the role of grain boundaries in enhancing the supply of chromium from the alloy to the surface oxide. They show that the diffusion situation can be treated by an effective diffusion coefficient D_c, where

$$D_c = D_m + 3wD_g/l \tag{A-1}$$

where D_m is the chromium diffusion coefficient through the grains, D_g is that along the grain boundaries, w is the grain boundary width, and l is the grain size. In the early stages of oxidation the appropriate diffusion coefficient is D_m, but with increasing time the apparent diffusion coefficient rises to the value D_c. Taking D_m and wD_g from Smith and Gibbs[12] and putting $l = 0.1$ mm in Eq. (A-1) we get, at 1123°K,

$$D_c = 1.18 \, D_m \tag{A-2}$$

From this and Eqs. (1) and (3) of the text, the maximum error in the calculated value of x_D will be ~5%, but due to the time dependence of the

effective diffusion coefficient should be ~2–3% for the present work. Both these values lie within the uncertainty associated with the experimental measurements.

ACKNOWLEDGMENTS

REFERENCES

1. C. J. Wagner, *J. Electrochem. Soc.* **99**, 369 (1952).
2. M. M. P. Soustelle and R. L. Lalauze, *Oxid. Met.* **7**, 23 (1973).
3. R. Hales, A. F. Smith, and J. C. Killeen, Proc. BNES Conf. on Corr. of Steels in CO_2, Reading (1974), p. 311.
4. H. E. Evans, D. Raynor, A. C. Roberts, and J. M. Silcock, Proc. Third Int. Conf. on Strength of Metals and Alloys, Cambridge (1973), Vol. 1, p. 190.
5. H. E. Evans, R. Hales, D. A. Hilton, R. A. Holm, G. Knowles, and R. J. Pearce, Proc. BNES Conf. on Corr. of Steels in CO_2, Reading (1974), p. 369.
6. E. A. Gulbransen and K. F. Andrew, *J. Electrochem. Soc.* **104**, 334 (1957).
7. D. Mortimer and M. L. Post, *Corros. Sci.* **8**, 499 (1968).
8. W. C. Hagel, *Trans. Am. Soc. Met.* **56**, 583 (1963).
9. W. C. Hagel and A. U. Seybolt, *J. Electrochem. Soc.* **108**, 146 (1961).
10. H. C. Cowen and S. J. Webster, Proc. BNES Int. Conf. on Nuclear Fuel Performance, London (1973), Paper 8.
11. J. C. Killeen, A. F. Smith, and R. K. Wild, *Corros. Sci.*, in press (1976).
12. A. F. Smith and G. B. Gibbs, *Met. Sci. J.* **3**, 93 (1969).
13. T. Ericsson, *Oxid. Met.* **20**, 401 (1970).
14. M. G. Hobby and G. C. Wood, *Oxid. Met.* **1**, 23 (1969).
15. J. E. Antill, C. S. Campbell, D. Goodison, W. B. Jepson, and C. G. Stevens, Proc. Third Int. Conf. on Peaceful Uses of Atomic Energy, Geneva (1964), Vol. 9, p. 523.
16. J. E. Croll and G. R. Wallwork, *Oxid. Met.* **4**, 121 (1972).
17. D. P. Whittle, D. J. Evans, D. B. Scully, and G. C. Wood, *Acta Metall.* **15**, 1421 (1967).
18. G. C. Wood and D. P. Whittle, *Corros. Sci.* **4**, 263 (1974).
19. D. P. Whittle, G. C. Wood, D. J. Evans, and D. B. Scully, *Acta Metall.* **15**, 1747 (1967).