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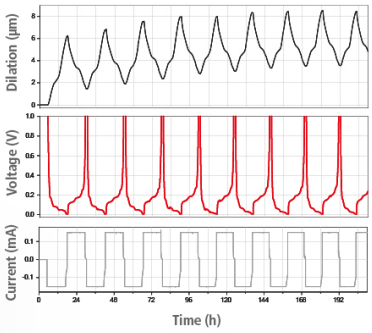

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The Effect of Oxide Volatilization on the Oxidation Kinetics of Cr and Fe-Cr Alloys

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ABSTRACT

The oxidation of Cr and Fe-Cr alloys which form Cr_2O_3 scales involves at least two processes: (*i*) the solid-state, diffusive transport of ionic species, with parabolic kinetics, and (*ii*) the oxidation of Cr_2O_3 to a volatile species, probably CrO_3, with linear kinetics. The effects of this second reaction cannot be neglected, either in interpretation of short-term oxidation results, or in predicting long-term oxidation behavior. In this paper equations are derived which describe the oxidation behavior of a system in which both diffusive and gas/oxide interface processes occur simultaneously. According to the model, the oxide scale grows to a limiting thickness which is determined by the parabolic rate constant and the surface-reaction rate constant; as the limiting thickness is approached, a transition from parabolic to linear kinetics takes place. The model is applied to the oxidation of Cr and Fe-Cr alloys, and good agreement with experimental data is found.

When Cr_2O_3 is heated to above 1000°C in an oxidizing atmosphere, it loses weight (1-6). This weight loss cannot be accounted for simply by vaporization of the oxide, since it occurs only when the specimen is exposed to an oxidizing atmosphere (3-5); furthermore, the reported values of the vapor pressure of Cr_2O_3 (4, 7) are too low to account for the observed rates of weight loss. The chemical reaction involved in the Cr_2O_3 weight loss has not been completely identified, but is probably (3, 7)

$$Cr_2O_3(s) + 3/2\ O_2(g) \rightarrow 2CrO_3(g) \qquad [1]$$

Reduction of CrO_3 back to Cr_2O_3 subsequently occurs in cooler parts of the system.

Hagel (4) measured the rate of weight loss of Cr_2O_3 samples exposed to oxygen and found that the weight loss could be expressed by

$$\frac{\Delta M}{A}\left(\frac{g}{cm^2}\right) = -k_v t \qquad [2]$$

where the "volatilization rate constant," k_v, has the temperature dependence

$$k_v = 0.214 \exp(-48{,}000 \pm 3000/RT)\ g\ cm^{-2}\ sec^{-1} \qquad [3]$$

Although Hagel (4) corrected his highest temperature (1350°C) Cr oxidation data for such weight loss, the large effect that this surface reaction has on the parabolic oxidation kinetics of Cr and alloys which form Cr_2O_3 scales has not been generally recognized. It will be seen in the following discussion that unless this surface reaction is taken into account in oxidation studies, two significant effects can appear: (*i*) short-time oxidation kinetic data may be incorrectly interpreted, and (*ii*) estimates of service life will be in error.

That a surface-controlled reaction could alter parabolic oxidation kinetics was pointed out by Loriers (8). Subsequently, Webb, Norton, and Wagner (9) derived more general equations in order to explain their tungsten oxidation data. More recently, Birchenall (10) has discussed various factors which could alter parabolic oxidation kinetics, including the effect of a gas/oxide interface reaction.

Derivation of Rate Equations

Rate of scale-growth.—Consider the case of a metal having an adherent, dense, external scale, of thickness x at some time t. The instantaneous rate of growth of the scale is given by

$$\frac{dx}{dt} = \frac{k_d}{x} \qquad [4]$$

where k_d is equal to one-half of the usual parabolic rate constant, k_p. Because of the oxide-gas interface reaction, the scale will tend to get thinner, and the kinetics for this process are described by

$$\frac{dx}{dt} = -k_s \qquad [5]$$

where k_s is proportional to k_v. Combining Eq. [4] and [5] gives

$$\frac{dx}{dt} = \frac{k_d}{x} - k_s \qquad [6]$$

Integration of Eq. [6] yields

$$\frac{-x}{k_s} - \frac{k_d}{k_s^2}\ln(k_d - k_s x) + C = t \qquad [7]$$

where C is the integration constant. The integration constant may be evaluated applying the boundary condition that $x = 0$ at $t = 0$. Solving for C and rearranging terms gives

$$t = \frac{k_d}{k_s^2}\left[-\frac{k_s}{k_d}x - \ln\left(1 - \frac{k_s}{k_d}x\right)\right] \qquad [8]$$

Since the rate of scale growth decreases with increasing thickness, eventually the rate of growth of the scale will become zero, and a limiting scale thickness is reached. For Cr oxidation, this means that the rate of supply of Cr^{+3} cations to the gas/oxide interface from diffusion through the scale is balanced by the rate of loss of Cr ions, presumably due to reaction [1] or some similar process. The limiting scale thickness may be determined by setting Eq. [6] equal to zero, yielding

$$x_f = \frac{k_d}{k_s} \quad [9]$$

If c.g.s. units are employed then the dimensions of k_d and k_s are $cm^2\ sec^{-1}$ and $cm\ sec^{-1}$, respectively. Obviously Eq. [8] is valid only for $0 \leq x < x_f$.

The logarithm term in Eq. [8] may be expanded in a Taylor series, whereby Eq. [8] becomes

$$t = \frac{1}{2}\frac{x^2}{k_d} + \frac{1}{3}\frac{k_s}{k_d{}^2}x^3 + \ldots + \frac{1}{n}\frac{k_s{}^{n-2}}{k_d{}^{n-1}}x^n + \ldots \quad [10]$$

Equation [10] is useful when either x or k_s is small. It is seen from Eq. [10] that when $k_s = 0$, parabolic kinetics obtain, and $k_d = \frac{1}{2}k_p$.

If the activation energies for the parabolic and linear reactions are Q_d and Q_s, respectively, then the limiting scale thickness x_f will be temperature dependent if $Q_d \neq Q_s$. When the limiting scale thickness is reached, the oxidation reaction is no longer diffusion-limited, and oxidation proceeds with a linear rate.

Rate of metal recession.—It is also of interest to determine the effect of a surface reaction such as that described above on the rate of metal recession, since it is this quantity that is of most interest to the corrosion engineer. Let y be the extent of metal recession at some time t ($y = 0$ is the original metal/gas interface at $t = 0$); the differential equations describing the parabolic and linear contributions to the metal recession rate are then

$$\frac{dy}{dt} = \frac{k_d'}{y} \quad [11]$$

and

$$\frac{dy}{dt} = k_s' \quad [12]$$

respectively. Combining these equations yields

$$\frac{dy}{dt} = \frac{k_d'}{y} + k_s' \quad [13]$$

which is of the same form as Eq. [6]. Integrating and solving with the boundary condition above gives

$$t = \frac{k_d'}{(k_s')^2}\left[\frac{k_s'}{k_d'}y - \ln\left(1 + \frac{k_s'}{k_d'}y\right)\right] \quad [14]$$

The logarithmic term in Eq. [14] may be expanded to give an equation analogous to [10].

Kinetic measurements.—A common method of determining the oxidation kinetics of a metal is to measure the weight-change that occurs when a sample is exposed to an oxidizing atmosphere. Clearly, if two reactions are taking place, such as described above, then the weight-change measured is the difference between the gain due to oxygen pick-up and the loss due to metal escaping in the volatile oxide. The weight change may be predicted by utilizing Eq. [5] and [8]. With Eq. [8], the weight-gain arising from oxygen in the oxide can be accounted for, since the oxide thickness at a given time can be calculated. The weight loss, due to the metal contained in the volatile oxide, can be determined as a function of time, by integration of Eq. [5]. The difference between these quantities, that is, oxygen pick-up in Cr_2O_3 and Cr loss in CrO_3, is what is actually measured in a gravimetric experiment.

Application to Cr, Fe-Cr *Alloys, and Other Alloys Which Form* Cr_2O_3 *Scales*

Since the rate of loss of Cr_2O_3 by reaction [1] ought to be essentially independent of the source of Cr_2O_3, the oxidation kinetics of any alloy which forms an adherent, protective Cr_2O_3 scale will be influenced by the loss. This would include such alloys as the ferritic stainless steels which contain more than about 13% Cr (11, 12). Since both oxidation data (4, 13) and Cr_2O_3 evaporation data (3, 4) are available, the constants k_d, k_s, k_d', and k_s' may be evaluated as a function of temperature.

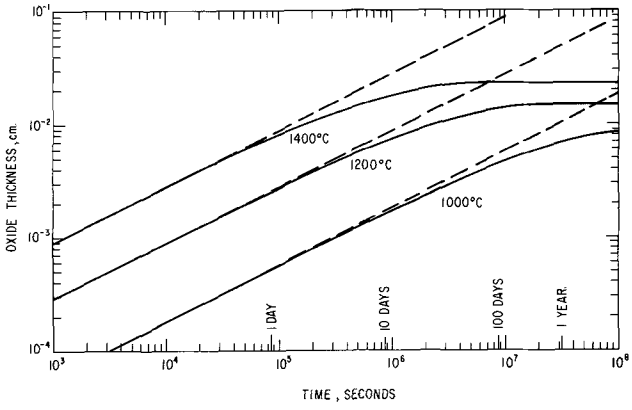

Fig. 1. Calculated oxide thickness as a function of time. The solid curves were calculated from Eq. [8]. — — — Parabolic kinetics.

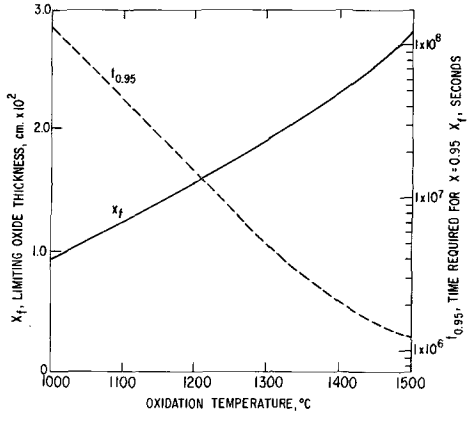

Fig. 2. Temperature dependence of the limiting oxide thickness and the time required for the scale to grow to 95% of its limiting thickness.

Rate of Growth of Cr_2O_3 *Scale.*—Using the data of Hagel (4) to determine the rate constants, Eq. [8] has been evaluated for various temperatures and is plotted in Fig. 1. The dashed lines show the expected growth assuming only parabolic kinetics. For short times, *e.g.*, $t < 10^5$ sec, the growth rate appears to be nearly parabolic. By 10^6 sec, however, significant departures from parabolic behavior are seen at all three temperatures. It is seen that the limiting oxide thickness increases with increasing temperature; however, with increasing temperature, shorter times are required to reach that limiting thickness. The temperature dependence of the limiting oxide thickness is shown in Fig. 2 which also shows the time required for the oxide scale to grow to 95% of its final value, as a function of temperature. By the time the thickness of the scale has reached this value, it is much less than the thickness expected from parabolic kinetics alone.

Metal recession rate.—Metal recession values as a function of time are presented in Fig. 3 for three temperatures. After about 10^7 sec at 1200°C, it is seen that the transformation to linear kinetics is essentially complete. Note that at 10^6 sec, or about 116 hr, the estimated metal-recession is about 20% greater than that expected from parabolic kinetics alone.

Weight-gain rate.—With Eq. [5] and [8], using the data from ref. (4), the net weight-gain (or loss) has been calculated as a function of time for a given temperature. The results of this calculation at 1200° and 1300°C are shown as solid lines in Fig. 4. The dashed curves indicate the weight gain that would be ex-

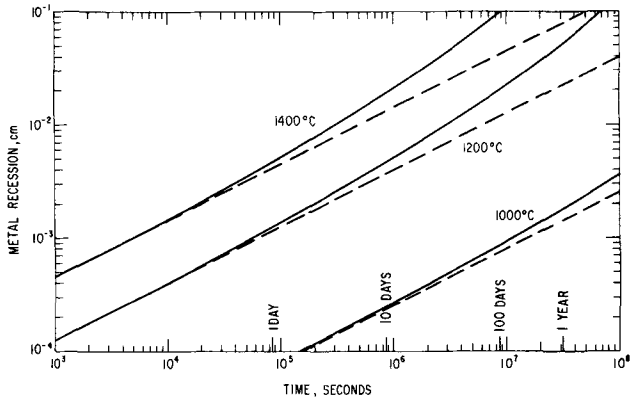

Fig. 3. Calculated metal-recession as a function of time. The solid curves were obtained from Eq. [14]. — — — Parabolic kinetics.

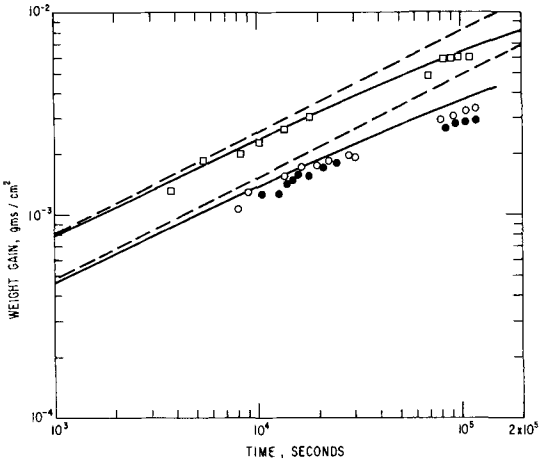

Fig. 4. Calculated and experimental values of weight-gain as a function of time, for short times. P_{O_2} = 100 Torr. □ Fe-70 w/o Cr, 1300°C; ○ Fe-45 w/o Cr, 1200°C; ● iodide Cr, 1200°C. — — — Parabolic kinetics; ——— corrected for loss.

pected from parabolic kinetics alone. Also presented in this figure are some oxidation data for three different alloys which form Cr_2O_3 scales, *viz*, Fe-70 w/o Cr, Fe-45 w/o Cr, and iodide-grade Cr. In spite of the scatter, the data are in good agreement with the calculated curves obtained from Eq. [5] and [8]. The departure from parabolic kinetics for these experiments is not large, because relatively short times are involved. If the data were interpreted in terms of parabolic behavior, the parabolic rate constants thus obtained would be essentially valid when interpreted in terms of ionic transport mechanisms (14, 15). Such data, however, are insufficient to describe the oxidation process fully, especially for extended times. This is shown in Fig. 5, which presents weight-change data for Cr which contained 0.2 w/o Y. This sample was oxidized at 1200°C for almost two weeks. The solid curve is the calculated weight-change evaluated from Eq. [5] and [8]. The dashed curve is the weight change expected from parabolic oxidation kinetics. The circles are experimental gravimetric data; the agreement between calculated values and experimental data may be considered to be quite good.

Summary

The oxidation behavior of Cr and alloys which form Cr_2O_3 scales cannot be accurately described by a parabolic rate law; the effects of a gas/oxide interface reaction, probably $Cr_2O_3(s) + 3/2\ O_2(g) \rightarrow 2CrO_3(g)$ must be recognized and taken into account.

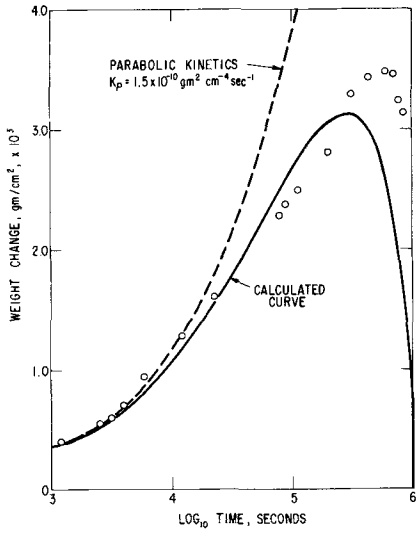

Fig. 5. Calculated and experimental values of weight-gain for extended oxidation. ○ Cr + 0.2Y alloy, 1200°C.

The effect of this surface reaction is to cause a transition from parabolic to linear oxidation kinetics. The oxide scale will grow to a limiting thickness; thereafter, metal-recession will proceed at a linear rate. Also, as the limiting value of oxide thickness is approached, gravimetric data will show departure from parabolic kinetics, and eventually weight loss will ensue at a linear rate. The interpretation of short-time oxidation data and estimated long-term oxidation performance will therefore be in error if based only on a parabolic rate law.

The equations presented herein, while applied to the specific cases of Cr and Cr-alloy oxidation, have completely general applicability to any scaling reactions involving processes possessing parabolic and linear kinetics.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1967 JOURNAL.

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