Oxidation of Metals, Vol. 5, No. 1, 1972

The Functional Form of Rate Curves for the High-Temperature Oxidation of Dispersion-Containing Alloys Forming Cr_2O_3 Scales*

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Received May 4, 1972

It has been shown recently in a number of investigations that the presence of dispersed stable oxides in chromium-containing alloys can result in the formation of protective Cr_2O_3 scales, which appear to grow considerably slower than similar scales on alloys not containing dispersoids. In addition, Cr_2O_3 is removed by further oxidation to the volatile species CrO_3, and the rate of this process is unaffected by the dispersoid. Simple kinetic models have been used to describe the results, but it is suggested, on the basis of a curve-fitting analysis, that these approaches are incorrect.

INTRODUCTION

Pure chromium, and alloys of Fe, Co, and Ni containing significant amounts of chromium form Cr_2O_3 scales on oxidation at elevated temperatures. At the lower temperatures in this range, which in practice means below 1200°C or so, the rate of thickening of the scale, or the overall weight gain of the specimen, effectively follows a parabolic rate law:

$$w^2 \text{ (or } x^2) = k_p t \tag{1}$$

However, at higher temperatures, or at very long times, deviations from this become apparent. Eventually the weight of the specimen reaches a maximum and starts to diminish, the rate of weight loss tending asymptotically to a

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*This work has been supported by the Naval Air Systems Command under Contract No. N00019-71-C-0079.

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constant value (linear rate law) and the scale thickness also approaching a constant value asymptotically.

This is due to the oxidation of the Cr_2O_3 to the volatile species CrO_3. The rate of this reaction is determined by diffusion through a gaseous boundary layer, and is independent of the thickness of the scale; it does however depend on gas pressure and velocity. The kinetics of the oxidation/volatilization have been studied by Hagel[1] and by Graham and Davis.[2]

It is a relatively simple matter to calculate the form of the kinetics for the situation where a scale is thickening by a diffusion-controlled process and thinning by an interface-controlled volatilization: Lewis[3] used a graphical method and Tedmon[4] has developed an analytical expression. Briefly, his analysis may be expressed as follows:

If the scale has thickness x at time t and is growing by a parabolic (diffusion-controlled) process, the instantaneous rate of growth is:

$$(dx/dt)_g = k_p/2x \tag{2}$$

where k_p is the parabolic rate constant. However, the scale is becoming thinner because of the (thickness-independent) linear oxidation/volatilization process:

$$(dx/dt)_v = -k_s \tag{3}$$

where k_s is proportional to the volatilization rate constant k_v. Then, the overall rate of scale growth is

$$dx/dt = (dx/dt)_g + (dx/dt)_v = k_p/2x - k_s \tag{4}$$

Integrating,

$$-(x/k_s) - (k_p/2k_s^2)\log[(k_p/2) - k_s x] + C = t \tag{5}$$

where C is a constant of integration. Substituting the boundary condition $x = 0$ when $t = 0$ and rearranging gives

$$t = (k_p/2k_s^2)\{-(2k_s/k_p)x - \log[1 - (2k_s/k_p)x]\} \tag{6}$$

This equation is in an inconvenient form for solving on a desk calculator, but it can be made more tractable. Clearly, the thickness of the scale approaches a limiting thickness, x_f, when the rate of thickening is equal to the rate of thinning:

$$x_f = k_p/2k_s \tag{7}$$

and if t_n is the time taken for the scale to grow to a thickness which is a fraction n $(0 \leq n \leq 1)$ of the limiting thickness, then eq. (6) becomes

$$t_n = (x_f/k_s)[-n - \log(1 - n)] \tag{8}$$

The expression in square brackets can then be simply tabulated, and given rate curves fitted by selecting values of x_f and k_s. Note that the thickness of the scale at time t_n is nx_f; and in this time the specimen has also lost an amount of material proportional to $k_s t_n$; the overall weight change can thus be calculated from the difference of these two quantities. Although it is simple to use a computer to fit Tedmon's equation to rate curves, it is often more revealing to have the equation in a form which allows hand fitting.

Tedmon's equation, and Lewis's equivalent treatment, fit the observed data for the oxidation of chromium quite well. However, recently several investigators[5–9] have shown that alloys of Ni–20 wt.% Cr[5–8] and Co–21 wt.% Cr[9] containing between 1 and 3 vol.% of a dispersed oxide, such as ThO_2, Y_2O_3, or CeO_2, give rate curves on oxidation for relatively short times (100 hr) at quite moderate temperatures (1000–1200°C) which show features similar to those found only for much longer times and higher temperatures in the case of chromium. It appears that the dispersoid does not affect the volatilization rate of Cr_2O_3, and thus, in terms of Tedmon's equation, the parabolic rate constant must have been reduced.

Giggins and Pettit[5] used a computer program to fit Tedmon's equation in a form in which the "parabolic rate constant" was allowed to vary with time, and found that their curves could be fitted; but k_p decreased asymptotically to a value between 10 and 15 times smaller than that for a Cr_2O_3 scale growing on an alloy without a dispersed phase. It should be noted that *any* curve can be fitted if one of the rate constants is allowed to vary, so that the fitting is not in itself very helpful; the general form of the variation of the apparent value of k_p with time or with scale thickness would be useful, but this is not stated. Davis *et al.*[6] and Lowell[7] have also used Tedmon's equation, but did not consider it gave good fit to their results. During earlier studies[8,9] qualitative analysis had suggested that (a) the maximum in the weight gain curve came too soon, and (b) the rate of weight loss approached the asymptotic constant value too rapidly for Tedmon's equation to be valid. It therefore appears that the *form* of the rate law for *either* the growth process *or* the volatilization process has been altered. Experimental evidence suggests that in fact the volatilization process is unaffected, so for the purposes of this paper it is assumed to remain constant, and an experimental rate curve is analyzed to determine the form of the growth kinetics.

ANALYSIS OF AN EXPERIMENTAL RATE CURVE

In order to analyze the rate curves, a priori it seemed best to determine the dependence of the flux of material through the scale layer, dw/dt, as a function of the scale thickness. Now, the overall rate of weight change dw'/dt in the reaction is made up of the rate of weight increase due to oxygen

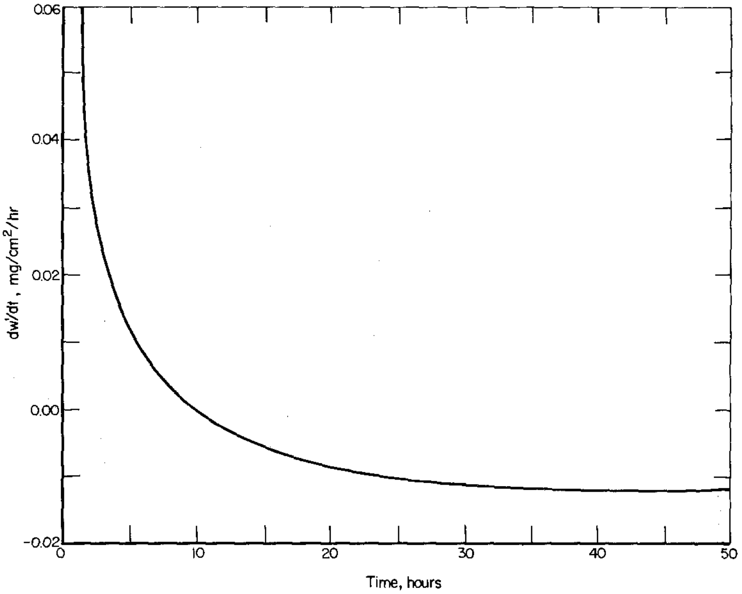

Fig. 1. The quantity dw'/dt vs t estimated graphically from a rate curve for the oxidation of Co–21 wt.% Cr–3 vol.% Y_2O_3 oxidized at 1200°C in oxygen at 100 torr[9] (specimen 593).

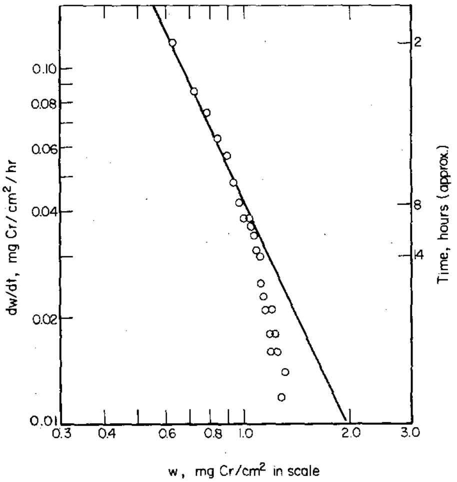

Fig. 2. The quantity dw/dt vs w from the data of Fig. 1.

present as solid Cr_2O_3 on the metal surface, dw_0/dt, and the rate of weight decrease due to chromium loss as CrO_3 vapor, dw_v/dt:

$$dw'/dt = dw_0/dt - dw_v/dt \tag{9}$$

and the flux of material through the scale layer is equal to the flux of chromium required to form solid Cr_2O_3, which is $a \times (dw_0/dt)$ where a is the weight of chromium per unit weight of oxygen in Cr_2O_3, *plus* the flux of chromium required to form the volatile CrO_3, which again is dw_v/dt:

$$dw/dt = a(dw_0/dt) + dw_v/dt \tag{10}$$

Thus,

$$dw/dt = a(dw'/dt) + (1 + a)(dw_v/dt) \tag{11}$$

In general, we expect dw/dt to approach dw_v/dt eventually, so apparently dw'/dt will approach $-dw_v/dt$, which we assume to be constant. Thus, provided the reaction has been continued for sufficiently long, all these quantities can be estimated graphically from the rate curve. Figure 1 shows dw'/dt vs t determined graphically from a typical rate curve. It approaches a limiting value of -0.012 mg/cm²/hr, so

$$dw_v/dt = +0.012\ \text{mg/cm}^2/\text{hr}$$

and

$$dw/dt = 2.1667(dw'/dt) + 0.038$$

This now must be plotted against the scale thickness, w, and in order to keep the units consistent the thickness is expressed in terms of milligrams per square centimeter of chromium present as Cr_2O_3. This is estimated from the overall weight gain, w', together with the loss due to volatilization w_v: clearly

$$w = a(w' + w_v) = 2.1667(w' + 0.012t)$$

Figure 2 shows dw/dt vs w, plotted on a logarithmic scale: for small values of w the curve is well fitted by a straight line of slope -2. The deviation at larger values of w is neither surprising nor alarming, since these points are derived from the later portions of the rate curve where the curvature is small in relation to the scatter of the data points. Furthermore, it is possible that the real asymptote of the dw'/dt vs t curve (Fig. 1) is rather lower than the value chosen, since this is a not uncommon error unless the extrapolation is done analytically. If the values of dw/dt are all increased by 0.01, all the points lie close to a line of slope -2.

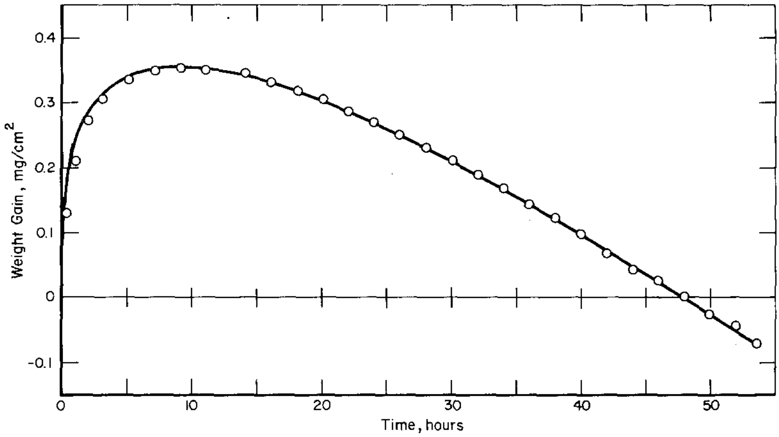

Fig. 3. Fit of eq. (14) (full line) to the experimental curve (open circles) used for plotting Figs. 1 and 2.

From this, it appears that the transport kinetics through the scale for this reaction have the form:

$$dw/dt = k_c'/w^2 \tag{12}$$

which corresponds to the cubic rate law

$$w^3 = k_c t \tag{13}$$

It is quite simple to rewrite Tedmon's analysis by replacing the parabolic growth law with a cubic rate law: using the same terminology as before,

$$t_n = (x_f/k_s)\{-n - 0.5 \log [(1 - n)/(1 + n)]\} \tag{14}$$

Figure 3 shows a curve fitted from this equation, together with the original experimental data points from which the analysis was derived, and the agreement is clearly very good. It should be noted that in the early stages Fig. 2 shows that the growth law is apparently genuinely cubic; to regard it as a changing parabolic rate constant is therefore incorrect, since this would result in the slope of the line in Fig. 2 approaching 1 at small times, and this is clearly not so.

However, in detail all the rate curves are not well fitted by eq. (14) either: a similar analysis on a curve from the work of Davis *et al.*[6] suggested a growth law of the form

$$w^4 = k_q t \tag{15}$$

leading to an overall rate law of the form

$$\begin{aligned} t_n = (x_f/k_s)[-n - \tfrac{1}{3}\{\sqrt{3}\tan^{-1}[-(2n+1)/\sqrt{3})] \\ + \log[(1-n)/(n^2+n+1)^{1/2}]\} + I] \end{aligned} \tag{16}$$

where the integration constant I is given by

$$I = \tfrac{1}{3}\{\sqrt{3}\tan^{-1}(-1/\sqrt{3})\}$$

Although this expression appears complicated, the expression in square brackets can again be tabulated, and then fitting any given rate curve is quite simple.

COMPARISON WITH DATA IN THE LITERATURE

Figure 4a–4c illustrates the fit of the three rate equations to some results from this investigation and from the literature. The maximum in the overall rate curve occurs at approximately $0.3x_f$ for the parabolic function, $0.5x_f$ for the cubic function, and $0.7x_f$ for the quartic function; the significance of this is that the rate curve becomes effectively linear when n exceeds about 0.9, so that the sooner the rate curve becomes linear after it has passed through the maximum, the higher the probable degree of the rate equation. Figure 5 shows the three equations fitted to an experimental rate curve: since there are two rate constants, x_f and k_s, it is necessary to fit two values on the curve, and for convenience it is easiest to fit the *maximum weight* and the *time at which the overall weight gain is zero*, since in general this gives a curve which has a

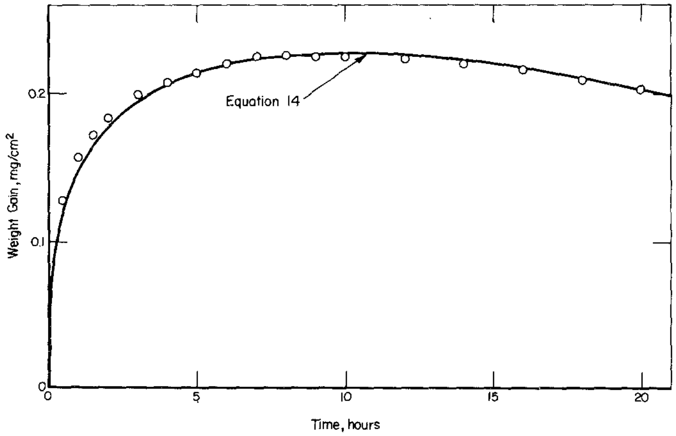

Fig. 4a. Fit of eq. (14) to the experimental data (open circles) of Giggins and Pettit[5] for the oxidation of TDNiCr at 1100°C in oxygen at 76 torr.

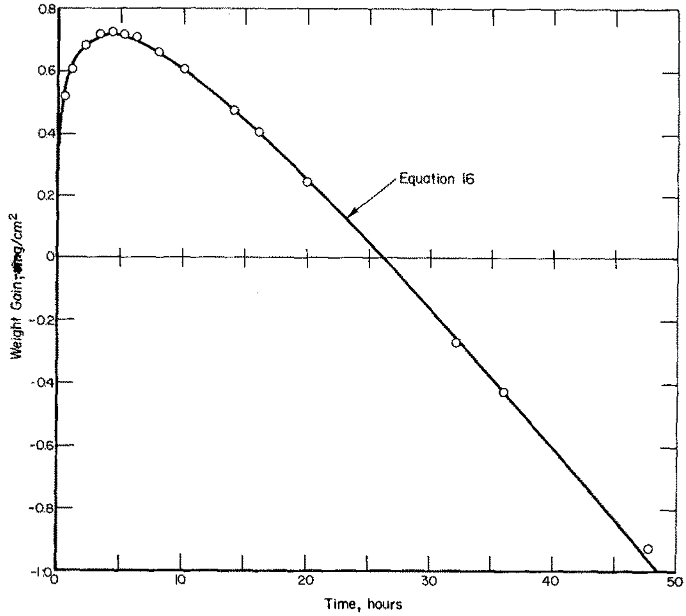

Fig. 4b. Fit of eq. (16) to the experimental data (open circles) of Davis et al.[6] for the oxidation of Ni–22.6 wt.% Cr–1 vol.% ThO_2 at 1200°C in oxygen at 150 Torr.

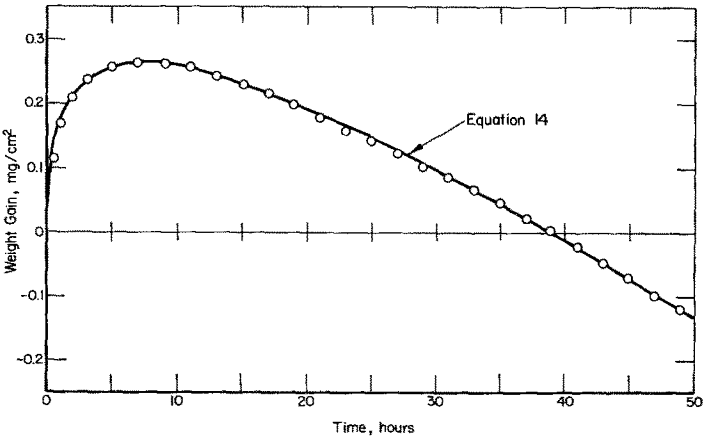

Fig. 4c. Fit of eq. (14) to the oxidation of Ni–20 wt.% Cr–3 vol.% CeO_2 at 1200°C in oxygen at 100 Torr (open circles).[8]

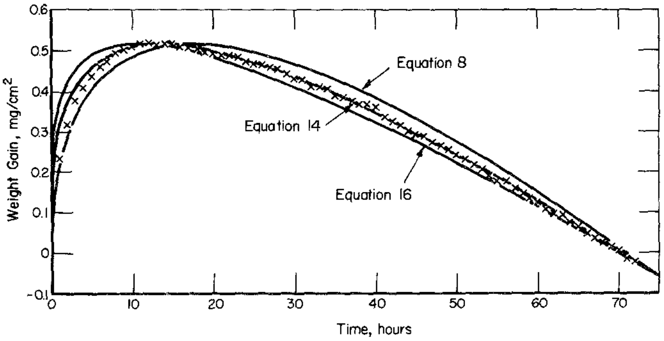

Fig. 5. A comparison of the fit of the three rate equations derived in the text with a typical rate curve curve (crosses) for the oxidation of a Ni–20 wt.% Cr–3 vol.% Y_2O_3 alloy (4/1/4 material) at 1200°C in oxygen at 100 Torr.[8]

shape most similar to the experimental rate curve; in practice a good fit can be obtained with two or three iterations, and within the limits of experimental accuracy it is not necessary to use a detailed curve-fitting procedure. The three curves in Fig. 5 indicate the general character of the rate equations: for these two boundary conditions the maximum occurs at successively earlier times as the degree of the growth equation increases, and as remarked before, the approach to rectilinearity after the maximum is more rapid. The experimental points shown are typical, in that none of the equations fit exactly: it would be relatively simple to produce an equation with a continuously variable rate index and allow a computer to fit the curve for the rate index as well, but this does not really seem to be justified by the results.

It is worth asking what the significance of this curve-fitting procedure is. In the earlier study,[8,9] the scale growth consisted of two distinct parallel processes; the growth of the relatively thick, nodular scale; and the growth of the thin scale. It is clear from the failure to fit the rate curves with an expression involving a parabolic growth step that both processes cannot be parabolic; but since they are unlikely to be described by a single rate law, the use of a single expression of whatever order in the rate equation is unlikely to accurately represent the true situation. Although in this study only very minor amounts of other oxides were observed, other investigations have reported the formation of significant amounts of $NiCr_2O_4$ in the early stages of oxidation, and again any kinetic model ignoring the presence of such phases is unlikely to be accurate.

However, it is interesting to note that Seybolt[10] has shown that the oxidation of chromium containing a Y_2O_3 dispersion under conditions where the volatilization was negligible could be described by rate laws with indices as high as 4 at 1150°C, and apparently increasing with decreasing temperature. Furthermore, Kravchenko and Zhuk[11] have reported rate indices in the range 2.4 to 3.1 for the oxidation of Ni–20 wt.% Cr containing dispersed Cr_2O_3, Al_2O_3, TiO_2, and ZrO_2 in air for times up to 500 hr at temperatures of 800 and 900°C, where the volatilization process should have been negligible. There seems good reason to believe therefore, that the effect of a dispersed oxide phase is to alter the form of the growth law of the oxide; but in the absence of models capable of interpreting higher order growth laws it is not possible to attempt a mechanistic interpretation of this result.

ACKNOWLEDGMENT

The author would like to thank Battelle Memorial Institute for the award of a Battelle Institute Fellowship.

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