A Theoretical Treatment of the Kinetics of the Oxidation of Metals

By Hiroshi YOSHISAKI and Toyojiro ISANO

(Received July 14, 1964)

It is generally believed that the progression of the isothermal oxidation of metals is governed by the so-called parabolic law which can be represented by the following equation:

$$y^2=Gt \tag{1}$$

where y represents the total quantity of oxide produced during the time lapse, t, both measured from the initiation of the progression, and where G is a constant.[1,3]

Actually, the above law holds with moderate accuracy as long as the observations are restricted within sufficiently short periods and are made after sufficiently long lapses of time from the initiations. However, when the above conditions are not satisfied we can never use Eq. 1 with success, especially for early periods. According to the parabolic law, the initial rate of oxidation should be infinite, whereas no facts have ever been found to suggest the existence of an infinite rate; moreover, such a rate is, indeed, erroneous in principle also. In fact, we can see as much when we look at the example of our recent observations, still unpublished, shown in Fig. 1. It can clearly be seen from this figure that the process begins with a finite rate, not an infinite one.

Under these circumstances, we have undertaken this investigation with the purpose of looking into the discrepancies of the parabolic law and of deduction of a more reasonable law, one which can agree with the actual functions controlling the process of the oxidation of metals.

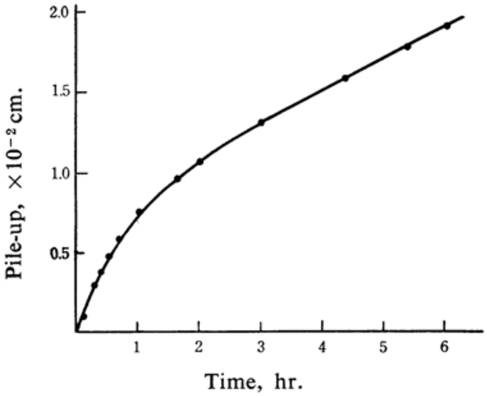

Fig. 1. Oxidation isotherm of copper in the air at 825°C.

The Mechanism of the Progression

When a metal regulus is held at a high temperature under an oxidizing atmosphere, it becomes covered by an oxide film, which gradually grows thicker and thicker as time elapses. If the coverage is assumed to be perfect, then the oxidation must continue its progression by means of one of two processes; in one, oxygen molecules from the atmosphere pass by diffusion through the oxide layer towards the oxide-metal boundary surface, where they combine with the metal atoms upon arrival; in the other, metal atoms from the regulus diffuse through the layer towards the surface exposed to the atmosphere, where they combine with oxygen upon arrival. Several papers recently published suggest that in reality the latter is

---

[1] P. V. Geld and A. K. Krasovskaya, *Zhur. Fiz. Khim.*, **34**, 1585 (1960).

the case, for in major cases the oxide scale produced shows evidence that the growth of the scale is due to the accumulation of oxide on the exposed surface.[2,3] This opinion, therefore, seems reasonable.

As to the time rate of the oxidation of metals, it is clear that it is determined by the slowest of the consecutive processes of which the whole change consists. According to our point of view, as the rate of the combination of metal with oxygen should greatly surpass that of its diffusion through the oxide layer, the rate of oxidation should be determined by the diffusion of metal.

However, there is a difficulty. If the oxidation progresses in the above-mentioned manner then the metal surface should of itself retire from the initial place into the interior of the regulus due to the surrendering of the metal material to the oxide layer, while, on the other hand, the inside surface of the oxide layer should stay unmoved, so that a vacant space or interstice grows up between them; nevertheless, in reality this is not the case. Probably this problem may be answered in terms of the heterogeneity in the structure of the scale, so as Mrowec states.[2,3]

The Deduction of an Equation Isotherm

It is well known that the parabolic law comes from the assumption that the concentration of diffusing matter is distributed at a uniform gradient all through the medium, so that;

$$\nabla c = \text{constant}$$

where c represents the concentration at any point. However, this condition can never be satisfied in reality since the medium can not be perfectly homogeneous nor can the surface of the regulus be ideally even, regardless of how it is made. Thus the diffusion must unavoidably be a turbulent one. For this reason we should refer to the general condition to begin with:

$$\nabla^2 c = k^2 c \tag{2}$$

where k represents a constant. If we now restrict ourselves to one dimention, the general solution of Eq. 2 is obtained as follows:

$$c = (K/k)\sinh(-kx+\kappa) \tag{3}$$

where x is the coordinate of the point at which the concentration, c, is measured, and K and κ are two constants. If we assume for the boundary condition that the concentration of the reactant metal on the surface of the scale in contact with the oxidizing atmosphere is zero, then Eq. 3 becoms:

$$c = (K/k)\sinh\{k(\xi - x)\} \tag{4}$$

where ξ represents the coordinate of a point on the exposed surface.

Now we will take up a small portion, σ, of the exposed surface, localized at will, so small that it can be taken as a part of a spherical surface with the center of curvature at O. Moreover, we will set up an x axis with O as the origin, and crossing σ at a point, P, in its interior, as is shown in Fig. 2. The coordinate at P is ξ, of course. The solid segment based on σ and with O as its vertex, cuts the surface elements, σ_0 and σ_1, from the initial metal surface and the oxide-metal boundary surface respectively, both of which can be taken as spherical and concentric with σ. The intersections of these surfaces with the x axis are Q and R, the coordinates at which being x_0 and x_1 respectively.

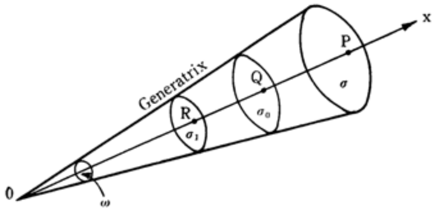

Fig. 2. Scheme of the space under consideration.

Now, if we assume, at time t, that the amount of metal which was initially contained in the disk-like space enclosed by σ_0, σ_1 and the generatrices has turned as a whole into the oxide scale contained in the disk-like space enclosed by σ, σ_1 and the generatrices, then the following equation should hold:

$$\frac{\omega}{4\pi}\cdot\frac{4}{3}\pi(x_0^3 - x_1^3)c_r = \frac{\omega}{4\pi}\cdot\frac{4}{3}\pi(\xi^3 - x_1^3)c_p \tag{5}$$

where c_r and c_p represent the total concentrations of metal in the reactant regulus and in the resultant scale respectively, and ω, the solid angle enclosed by the generatrices. Differentiating Eq. 5 with respect to ξ, we obtain:

$$\frac{\mathrm{d}x_1}{\mathrm{d}\xi} = -\frac{\xi^2}{x_1^2}\cdot\frac{c_p}{c_r - c_p} \tag{6}$$

Assuming that the rate of the loss of metal in the regulus is equal to the rate of its transfer across any fixed surface section enclosed by the generatrices, we can write:

$$\omega x^2 cu = -c_0\omega x_1^2\frac{\mathrm{d}x_1}{\mathrm{d}t} \tag{7}$$

---

[2] S. Mrowec, *Zeit. f. pfys. Chem. Neue Folge*, **29**, 48 (1961).

[3] L. Czerski, S. Mrowec and T. Werber, *J. Electrochem. Soc.*, **109**, 273 (1962).

where u represents the average value of the x-components of the atomic velocities on the surface apart from O as far as x, and c_0 represents the concentration on the boundary surface, which can be taken as a constant. Combining this relation with the fundamental equation:

$$cu = -D\frac{\mathrm{d}c}{\mathrm{d}x}$$

we obtain the following equation:

$$Dx^2\frac{\mathrm{d}c}{\mathrm{d}x} = c_0{x_1}^2\frac{\mathrm{d}x_1}{\mathrm{d}t} \tag{8}$$

where D represents the diffusion constant of the metal in the scale. Substituting $\mathrm{d}c/\mathrm{d}x$ in the left hand side according to Eq. 4, we obtain:

$$\int_{x_0}^{\xi}\frac{\xi^2\mathrm{d}\xi}{\cosh\{k(\xi-x)\}} = \frac{KD}{c_0}\left(\frac{c_r}{c_p}-1\right)\int_0^t x^2\mathrm{d}t+L \tag{9}$$

where L is the integration constant which must vanish for the initial condition, $\xi=x_0$, for $t=0$.

If we define X as $X=\xi-x_0$, where the initial surface, σ_0, on which x takes a value x_0, is prefered as a fixed reference surface, then X represents in practice the pile-up of the exposed surface of the resultant oxide scale due to the progress, and is a measurable quantity. Then Eq. 9 becomes:

$$\int_0^X\frac{(X+x_0)^2}{\cosh(kX)}\mathrm{d}X = A{x_0}^2t \tag{10}$$

where

$$A = \frac{KD}{c_0}\left(\frac{c_r}{c_p}-1\right)$$

As Eq. 10 has been derived for a convex portion of the metal surface, it can also be obtained for a concave portion with the identical terms. Thus this equation can be taken as a general equation isotherm at a point, either convex or concave, x_o being the radius of the curvature. We can reasonably assume that, if the observation is done on a well-finished sound regulus, Eq. 10 may be satisfied in a macroscopic extent by substituting a function, $\bar{x}_0$, for x_0, $\bar{x}_0$ being characteristic of the evenness of the surface in a macroscopic scale. Moreover, if we define γ as the reciprocal of $\bar{x}_0$, then Eq. 10 becomes:

$$\int_0^X\frac{\left(X+\frac{1}{\gamma}\right)^2}{\cosh(kX)}\mathrm{d}X = \frac{1}{\gamma^2}At \tag{11}$$

where γ represents a parameter indicating the coarseness of the surface. This is the general equation isotherm for the oxidation of metals holding in measurable scales.

For a small value of X, that is, unless too long a time has elapsed since the initiation, we can expand the integrand in Eq. 11 into a power series of X and integrate it, writing it as follows:

$$\begin{aligned} X + \gamma X^2 + \frac{1}{3}\left(\gamma^2-\frac{k^2}{2}\right)X^3 - \frac{1}{4}\gamma k^2X^4 \\ -\frac{1}{2}k^2\left(\frac{1}{5}\gamma^2-\frac{1}{12}k^2\right)X^5 + \frac{5}{72}\gamma k^4X^6 \\ +\cdots = At \end{aligned} \tag{12}$$

where A represents a constant proportional to the diffusion constant of the metal in the oxide layer.

Discussion

As has been established in the preceding section, the progression of isothermal oxidation is governed by a somewhat more complicated law than the parabolic law. That Eq. 12 begins with a linear term shows that, for a short initial period, the oxidation process begins with a finite velocity instead of an infinite one; a theory supported by the experimental facts.

Now, we find that the left hand side of Eq. 12 consists of three groups of terms: first, those independent of γ; second, those each containing a factor γ; and third, those each containing a factor γ^2. Thus we can rewrite Eq. 12 as follows:

$$\begin{aligned} \left[X - \frac{1}{6}k^2X^3 + \frac{1}{24}k^4X^5 - \cdots\right] \\ + \gamma\left[X^2 - \frac{1}{4}k^2X^4 + \frac{5}{72}k^4X^6 - \cdots\right] \\ + \gamma^2\left[\frac{1}{3}X^3 - \frac{1}{10}k^2X^5 + \cdots\right] = At \end{aligned} \tag{13}$$

As γ can vary from zero to infinity, it may be seen that the progression of oxidation may have considerably different aspects, even for the same reactant species, because of the fluctuation of the coarseness of the surface. If the surface is ideally flat, the progression of the oxidation will be governed by the following equation:

$$X - \frac{1}{6}k^2X^3 + \frac{1}{24}k^4X^5 - \cdots = At$$

since the second and third terms on the left hand side of Eq. 13 vanish for $\gamma\rightarrow0$. On the other hand, for very coarse surfaces, for instance, with finely pulverized metals, it will be governed by:

$$\frac{1}{3}X^3 - \frac{1}{10}k^2X^5 + \cdots = \frac{1}{\gamma^2}At$$

the third term in Eq. 13 assuming prominent values because of the large value of factor γ^2, except in the early stages. In major cases, however, all terms in Eq. 13 will contribute equally. Thus we may suggest the following equation as a rough approximation for sufficiently small values of X:

$$X + \gamma X^2 + \frac{1}{3}\left(\gamma^2 - \frac{k^2}{2}\right)X^3 = At \qquad (14)$$

Summary

We have attributed the deficiency of the parabolic law to its original assumption of a uniform gradient of the concentration of the reactant, and, beginning with a general assumption of a turbulent gradient, we have deduced an alternative equation, one somewhat more complicated than the parabolic one. In discussing the behavior of the new equation, it was found that the mode of progression largely changes its profile as a result of the fluctuation of the coarseness of the surface to be oxidized.

We are indebted to Messrs. Yutaka Sakuma and Tsutomu Itô for their honest assistance.

Department of Chemistry
Faculty of Liberal Arts and Science
Yamagata University
Koshirakawa-cho, Yamagata

Appendix

Deduction of Equation 2.—This equation was deduced as follows: Take arbitrarily, in the field of the turbulent stationary diffusion, a space element shaped like a rectangular cylinder; the axis thereof may be taken as a coordinate axis, x, as is shown in Fig. 3. We will designate the area of both base planes and the height of the cylinder as σ and δx respectively. When the coordinate of one base plane, S_1, on which the concentration of the diffusing substance may be designated as c, is taken as x, then the coordinate and the concentration at the other base plane, S_2, should be $x+\delta x$ and $c+(\partial c/\partial x)\delta x$ respectively. As is well known, the rate of the passage of a diffusing substance through a plane perpendicular to the x axis is proportional to $-\partial c/\partial x$. Thus, the rate of flow in the left-to-right direction through S_1 and S_2 in Fig. 3 should amount to $-D_1\sigma(\partial c/\partial x)$ and $-D_1\sigma[\partial c/\partial x + (\partial^2 c/\partial x^2)\delta x]$ respectively, where D_1 is a constant. On the other hand, the rate of the flow out through the generating surface of the cylinder can be taken as proportinal to the mean concentration in the cylinder, multiplied by a constant, s for instance, chracteristic of the structure of the medium, which can be represented as $sl\delta x\cdot c$, where l represents the length of the border-line of a rectangular cross-section of the cylinder. Consequently, the rate of the total flow out of the cylinder should be $D_1\sigma(\partial c/\partial x) - D_1\sigma[\partial c/\partial x + (\partial^2 c/\partial x^2)\delta x] + sl\delta x\cdot c$. For a stationary or quasi-stationary diffusion, the above quantity must vanish, so that

$$D_1\sigma\frac{\partial^2 c}{\partial x^2} = slc$$

namely:

$$\frac{\partial^2 c}{\partial x^2} = k^2{}_1 c$$

where

$$k^2{}_1 = \frac{sl}{\sigma D_1}$$

In three-dimentional treatments:

$$\nabla^2 c = k^2 c$$

where k is a constant.

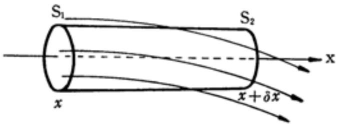

Fig. 3

Comparison with the Hatta Theory.—The above equation takes the same form as that of the well-known Hatta theory, which treats diffusion phenomena accompanied with the consumption of diffusing substances due, for instance, to a chemical reaction of the first order, to absorption or to capillary phenomena. This coincidence seems to us very interesting, for these results, obtained by a different method of computation, may not yet be taken as utterly different in physical meaning. This theory is all the more convincing because we notice that the irregular turn-asides of stationary flow lines can reasonably be replaced with a definite distribution of wells and sinks in dynamical treatments of a turbulent flow of a fluid. For this reason, the present case can be taken as closely analogous to Hatta's case, and so it is not strange that the same hydrodynamic equation is applicable in both cases.