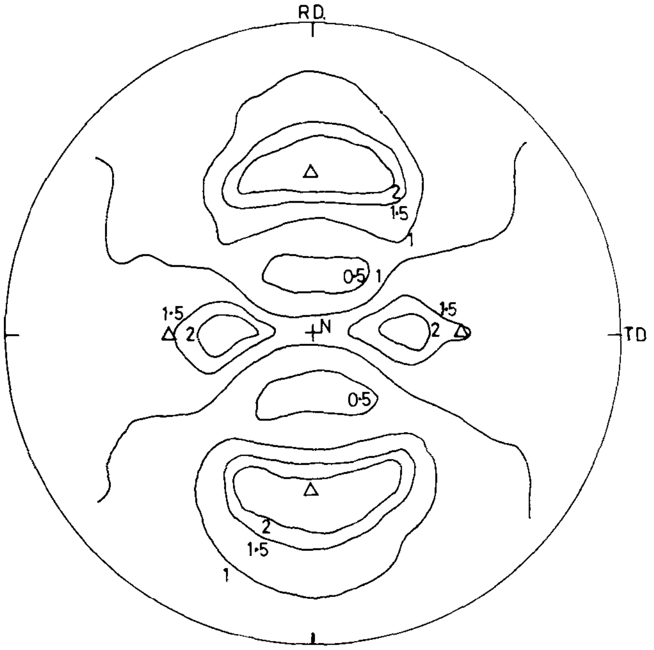

Fig. 2—{111}pole figure from midthickness of sheet aged at 200°C for 3 h. △{100}⟨011⟩.

this earing behavior can be attributed to the presence of planar precipitates of θ' which tend to make the material behave in a more isotropic manner.

Some tests were also made on commercial sheet with the usual specification, HS 15, for age-hardenable aluminum alloy containing 4 pct copper. Although the ears were less distinct in this material, the same trends were observed.

Thanks are due to Professor D. V. Wilson for the provision of laboratory facilities.

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On the Kinetics of Anisothermal Oxidation

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A model for anisothermal oxidation kinetics has been presented by Wolf and Grochowski[1] (WG) based on the assumptions a) that the system under consideration is described by a "parabolic rate law" under isothermal conditions, and b) that its temperature increases linearly with time. This model is summarized below, and certain points pertinent to its development are discussed. Finally, a revised model is developed, based on a fundamentally different assumption compared to that used by WG, and a new expression is derived through which weight-gain is related to time.

Summary of Wolf-Grochowski Model.[1] The WG model is concerned with an oxidizing system which is assumed to satisfy, under isothermal conditions, a parabolic rate law having the form

$$W^2 = K_p t \qquad [1]$$

where W is the specific weight change, t the time over which oxidation has taken place (W being assumed to be zero at $t = 0$), and K_p a rate constant taken to be of the form

$$K_p = A \exp\left(\frac{-Q}{RT}\right) \qquad [2]$$

where A is the preexponential factor (which may be a function of the ambient oxygen pressure[2]), Q the activation energy, R the gas constant, and T the absolute temperature. WG assumed A and Q to be independent of T, and T to increase linearly with time, *i.e.*,

$$T = T_i + rt \qquad [3]$$

where T_i (noting that they used upper case for this subscript) is the temperature at $t = 0$, and r is the rate at which T changes with time. They then combined Eqs. [1], [2], and [3] to obtain

$$W^2 = At \exp\left[-\frac{Q}{R(T_i + rt)}\right]. \qquad [4]$$

Eq. [4] was then used to calculate dW/dt and the result combined with [3] to obtain dW/dT. Then, a new variable Z was defined such that

$$Z \equiv \frac{Q}{RT} \qquad [5]$$

and they found that

$$2WdW = -\left(\frac{AQ}{rR}\right) e^{-Z}(Z^{-2} + Z^{-1} - Z_i^{-1})dZ \qquad [6]$$

where

$$Z_i \equiv \frac{Q}{RT_i}. \qquad [7]$$

Finally, they integrated Eq. [6] to obtain (except for an incorrect sign with one of the terms in the integrand, which is corrected here)

$$W_m^2 = -\frac{AQ}{rR}\int_{Z_i}^{Z_m} e^{-Z}(Z^{-2} + Z^{-1} - Z_i^{-1})dZ \qquad [8]$$

where

$$Z_m \equiv \frac{Q}{RT_m} \qquad [9]$$

and $W_m \equiv W(Z_m)$ with T_m being some maximum temperature (occurring at time $t_m = (T_m - T_i)/r$). They concluded that the integral in Eq. [8] above is "amenable to solution by graphical or computer techniques."[1]

Critique of Wolf-Grochowski Model. A number of points can be made relative to the WG derivation which was summarized above. These are the following:

First, we note that the integral on the right-hand side of Eq. [8] can be obtained in *closed form*, without the need for approximation methods. One approach would be to carry out an appropriate integration by

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parts of the function $e^{-Z}Z^{-2}$ which appears in the integrand on the right-hand side of [8].

Actually, the differentiation and subsequent integration carried out by WG were not necessary. One need only combine Eqs. [1], [2], [3], [7], and [9] taking conditions, in Eqs. [1], [2], and [3], to correspond to the "maximum" values of W, T, and t.

Finally, the most important point relative to the WG model is concerned with the analysis leading to Eq. [4] above, which must be reconsidered. Substitution of the time dependence of temperature (Eq. [3]) was carried out by WG in the *integrated* form of the parabolic rate law (Eq. [1]), rather than in the form expressed as the following differential equation:

$$\frac{dW}{dt} = \frac{K_p}{2W}\ . \qquad [10]$$

However, if oxidation proceeds such that the instantaneous rate of change of W with t is always inversely proportional to the instantaneous value of W, with the proportionality constant itself being time-dependent as described in Eqs. [2] and [3], then it is necessary to begin with Eq. [10] rather than [1]. This procedure is developed below. We note that Kofstad,[3] in his treatment of oxidation occurring with the temperature varying linearly with time, did indeed substitute the time-dependent temperature into the differentiated form of the weight-gain expression (see the analysis leading to his Eq. [7]).

Redevelopment of Weight-Gain Equation. Beginning with Eq. [10] (as contrasted to the WG approach of beginning with [1]), we find, upon appropriate combination of this expression with Eqs. [2], [3], and [5],

$$\frac{dW^2}{dZ} = -\frac{AQ}{rR}Z^{-2}e^{-Z}. \qquad [11]$$

Integrating Eq. [11], again taking $W(t = 0) = 0$,

$$W_m^2 = \frac{AQ}{rR}\int_{Z_m}^{Z_i} Z^{-2}e^{-Z}\,dZ. \qquad [12]$$

The integral in Eq. [12] can be expressed as an exponential integral, the general definition of which is[4]

$$E_n(z) \equiv \int_1^{\infty} t^{-n}e^{-zt}dt \qquad [13]$$

where $n = 0, 1, 2, \ldots\ldots$ and $\Re(z) > 0$. Using Eq. [13], we find that [12] can be written as

$$W_m^2 = \frac{AQ}{rR}[Z_m^{-1}E_2(Z_m) - Z_i^{-1}E_2(Z_i)]. \qquad [14]$$

Now let us change Eq. [14] to one which involves E_1 functions rather than E_2 functions. Toward this end, we note the following relation, which can be readily derived using Eq. [13]:

$$E_{n+1}(z) = n^{-1}[e^{-z} - zE_n(z)] \qquad [15]$$

for $n = 1, 2, 3, \ldots\ldots\ldots$ Setting $n = 1$ in Eq. [15] and using the resultant expression with [14], we obtain

$$W_m^2 = \frac{AQ}{rR}[Z_m^{-1}e^{-Z_m} - Z_i^{-1}e^{-Z_i} + E_1(Z_i) - E_1(Z_m)]. \qquad [16]$$

The E_1 function can be expressed, to a relatively high degree of accuracy, in terms of certain well-known polynomial and rational expansions[4,5] as well as in terms of Padé approximations.[5] (Expansions of this function in infinite series also exist,[4,5] including expansions in terms of Chebyshev polynomials.[5]) Consequently, the time dependence of W_m^2 can be accurately expressed in terms of a sum of elementary functions.

One can show that Eq. [16] is well-behaved in the limit as $r \to 0$. Indeed, evaluation of this limit on the right-hand side of [16] yields

$$\lim_{r \to 0} W_m^2 = At_m e^{-Z_i}, \qquad [17]$$

Eq. [17] being equivalent to Eq. [4] above for the case $r = 0$ (Eq. [4] being correct, of course, for this special case).

The initial condition assumed in the analysis leading to Eq. [16], namely, that $W(t = 0) = 0$ could be generalized by taking $W(t = 0) = W_i$ where W_i is some given initial value for the weight-gain. For this situation, the left-hand side of Eq. [16] would simply be replaced with the quantity $W_m^2 - W_i^2$. In addition, it should be noted that Eq. [16] is also valid if $r < 0$ (in which case $T_m < T_i$).

It should be noted that the analysis presented here is also applicable to other rate-laws (see Ref. 3); for example, Eq. [10] could be generalized to $dW^j/dt = K_j$ where $j = 1$, 2, and 3 for linear, parabolic, and cubic rate-laws, respectively. (In this notation, K_p, as defined above, is equal to K_2.) If the temperature dependence of the K_j's is that expressed in Eq. [2], then Eq. [16] would remain unchanged except that W_m^2 would be replaced with W_m^j. Also, similar analyses could, in principle, be carried out for other types of time-temperature relationships, although numerical-integration methods might be needed, for given cases, to determine the explicit relationship between weight-gain and time.

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