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On the Kinetics of the Aluminum-Water Reaction During Exposure in High-Heat Flux Test Loops

1. A Computer Program for Oxidation Calculations

R. E. Pawel

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Metals and Ceramics Division

ON THE KINETICS OF THE ALUMINUM-WATER REACTION DURING EXPOSURE IN HIGH-HEAT FLUX TEST LOOPS

I. A COMPUTER PROGRAM FOR OXIDATION CALCULATIONS

R. E. Pawel

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I. A COMPUTER PROGRAM FOR OXIDATION CALCULATIONS*

R. E. Pawel

ABSTRACT

The "Griess Correlation," in which the thickness of the corrosion product on aluminum alloy surfaces is expresed as a function of time and temperature for high-flux-reactor conditions, was rewritten in the form of a simple, general rate equation. Based on this equation, a computer program that calculates oxide-layer thickness for any given time-temperature transient was written.

INTRODUCTION

The High Flux Isotope Reactor (HFIR) Project supported aluminum corrosion testing at the Oak Ridge National Laboratory in the early 1960s. A water loop was constructed in which aluminum specimens were exposed under conditions of high heat flux [up to ~6 MW/m^2 (~2 × 10^6 $Btu/h \cdot ft^2$)] and water velocity [up to ~15 m/s (~50 ft/s)]. The advantages of using pH-5 water with aluminum were examined in this loop, and the corrosion behavior of several alloys under consideration for HFIR fuel plates was investigated.[1-4]

Measurements (calculated from temperature changes) of the thickness of the oxide film on the aluminum-alloy specimens as functions of time and temperature at the water-oxide interface were included in the collected data. Within the scatter of the data, there were no observable effects of flow rate from 9 to 15 m/s and of

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heat flux from 3 to 6 MW/m^2 (other than the influence of heat flux on the specimen temperature). On the other hand, it was clear that water brought to pH-5 with nitric acid led to less oxide formation than that found for high-purity water. The three principal alloys tested (1100, 6061, and X8001) showed substantially the same corrosion behavior; less-extensive tests on several other experimental alloys showed similar results.

Preliminary data analyses from short-duration tests indicated that in nearly all cases the rate of oxide growth was approximately constant during a run at constant heat flux, water temperature, and water velocity, although the specimen temperature and average oxide temperature generally increased substantially. The almost-constant rate of oxide thickening was surprising from several standpoints, including the anticipated effect of the observed temperature changes in the oxide and the possible erosion-dissolution of part of the oxide into the water. On the other hand, the temperature of the oxide at the oxide-water interface was presumed constant during an experiment, and the correlation of the oxide growth rate with this temperature was a reasonable one. Later experiments, carried out for longer times and over a wider range of surface temperatures, indicated that the oxide growth rate was not constant but actually decreased with exposure time. Thus, all of the data were reexamined and correlated[4] on the basis of the empirical equation

$$X = 443\ \theta^{0.778}\ \exp(-4600/K)\ , \qquad (1)$$

where

X = thickness of oxide film, mils (SI units were not in use at that time);

θ = time, h;

K = absolute temperature of the oxide at the oxide-water interface, K.

The Griess Correlation [Eq. (1)] is currently used to describe the growth of oxide (boehmite) on several aluminum alloys in pH-5 water under the

previously described conditions. For reaction in high-purity deionized water, the first coefficient in Eq. (1) was 1200 rather than 443.

Griess et al.[4] suggested that in order to calculate the oxide thickness under conditions where the oxide-water interface temperature changed with time, or where a film was present at the start of the experiment, a calculation scheme based on "equivalent times" be used in conjunction with Eq. (1). While somewhat cumbersome, the technique gave acceptable results for several experimental measurements.

COMPUTERIZING THE GRIESS CORRELATION

Primarily to take advantage of computerized computations to describe oxide growth for any known time-temperature excursion based on the previous data set, we chose a slightly different kinetic model and wrote the first version of a computer code to accomplish these calculations.

It is often convenient to express the kinetics of a heterogeneous reaction, such as the growth of an oxide film on a metal, by a simple, general rate equation such as

$$d\phi/dt = k/\phi^n \ , \tag{2}$$

where

ϕ = instantaneous thickness of the film,
t = time,
k = rate constant,
n = a number that depends on the particular mechanism of film growth.

For example, for $n = 0$, the rate of oxide growth is independent of the oxide thickness and, therefore, is constant at a given temperature. Similarly, if $n = 1$, the rate of growth is inversely proportional to the oxide thickness, and integration of the equation leads directly to the parabolic rate law. The mechanistic influence on the exponent is clear, and in many cases where complex reaction mechanisms dominate, n will not be an integer or will change with time as the reaction proceeds.

The rate constant k is commonly described by an Arrhenius relationship:

$$k = A \exp(-Q/RT) \quad , \tag{3}$$

where

A = preexponential term, appropriate units;
Q = activation energy, J/mol;
R = gas constant, 8.314 J/mol·K;
T = absolute temperature, K.

Therefore, if a specimen undergoes isothermal oxidation, the thickness of the reaction product ϕ, as a function of time, is given by the integration of Eq. (2):

$$\phi = [(n + 1)A \exp(-Q/RT)t]^{1/n+1} \quad . \tag{4}$$

It is clear that the form of Eq. (4) is sustantially identical to that of Eq. (1), and the appropriate constants in Eq. (4) can be evaluated. For example, for ϕ in micrometers and t in hours, the constants are n = 0.28535, $A = 1.2538 \times 10^5\ \mu m^{1.28535}/h$ (1.9612×10^3 mils$^{1.28535}$/h), and Q = 49,157 J/mol, so that

$$\phi_{\mu m} = 1.2157[(1.2538 \times 10^5) \exp(-49157/RT)]^{0.778}\ t_h^{0.778} \quad . \tag{5}$$

A convenient way to calculate the oxide thickness for any known time-temperature transient is to divide the transient into small time increments and calculate sequentially the oxide thickness at the end of each time increment. Equation (2) can be integrated to give

$$\phi_2 = [\phi_1^{n+1} + (n + 1)k\Delta t]^{1/n+1} \quad , \tag{6}$$

where

ϕ_1 = oxide thickness at beginning of the time increment,
ϕ_2 = oxide thickness at end of the time increment,
Δt = time increment.

A computer program was written in BASIC language for use with the PDP-10 or a personal computer system. The time-temperature transient is input to the program as end points defining a series of linear segments. Time increments may be specified according to the kind of transient and the sensitivity desired, and the results are tabulated at specified time intervals.

Several tests of the program indicate that it is performing correctly from a mathematical standpoint. In addition, the calculated changes in the specimen temperatures and rate of temperature increases produced by the stepwise changes in cooling water temperature discussed by Griess et al.[4] were essentially reproduced using the present procedure. Various inputs and outputs for this program can be easily modified, including variations in the kinetic model or changes in the parameters of the reaction rate constant, if and when they become necessary. One version of the program and two sample outputs are listed in the Appendix.

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3. J. C. Griess et al., *Effect on Heat Flux on the Corrosion of Aluminum by Water. Part III. Final Report on Tests Relative to the High-Flux Isotope Reactor*, ORNL-3230, December 1961.

4. J. C. Griess, H. C. Savage, and J. L. English, *Effect of Heat Flux on the Corrosion of Aluminum by Water. Part IV. Tests Relative to the Advanced Test Reactor and Correlation with Previous Results*, ORNL-3541, February 1964.

APPENDIX

COMPUTER PRINTOUT

JCGRT6 13:23 30-JUL-87

```
1E1$="........................................"  '     *** HEADLINE***"
2REM
3REM
4REM   THIS PROGRAM ACCEPTS LINEAR SEGMENT INPUT FOR TIME-TEMPERATURE
5REM    EXCURSIONS AND CALCULATES THE CORRESPONDING BEHAVIOR OF TWO
6REM    KINETIC PARAMETERS, EACH HAVING A KNOWN ARRHENIUS (OR OTHER)
7REM    TEMPERATURE DEPENDENCE OF THEIR ISOTHERMAL RATE CONSTANTS
8REM    (PARABOLIC OR OTHERWISE).       INPUT INFO AND RUN .
9REM
10REM                                              **************************
11REM   A1=PREEXPONENTIAL TERM, NO. 1.            *****INPUT HOURS/DEG C*****
12REM   Q1=ACTIVATION ENERGY, NO. 1.
13REM   A2=PREEXPONENTIAL TERM, NO. 2.            *****OUTPUT MICRONS*****
14REM   Q2=ACTIVATION ENERGY, NO. 2.
15REM                                              **************************
16REM    ARRHENIUS TEMPERATURE DEPENDENCES FOR **TWO** KINETIC
17REM     PARAMETERS ARE INPUT IN LINES  26 -  29  IN FORM SHOWN THERE.
18REM
19REM
20REM  DATA BELOW INPUTS RATE CONSTANT DATA FOR JC GRIESS IV DATA FOR ALUMINUM
21REM   CORROSION FOR PH 5 AND PH 5.7-7.0.  NON PARABOLIC RATES USED.
22REM   ------------------------------------------------------------------
23REM
24REM
25REM             ****  RATE CONSTANT PARAMETERS  ****
26 A1=1.2538E5       '   MICRONS^(1+N)/HR
27 Q1=49157      '     J/MOL
28 A2=4.5133E5    '    MICRONS^(1+N)/HR
29 Q2=49157      '     J/MOL
30 N9=0.28535      '   REACTION PARAMETER: RATE=K/(O^N)
31REM
32REM
33REM
34REM
100 DATA 1,226.85,0,226.85,400,226.85    '   SAMPLE DATA.
101REM   LINEAR SEGMENT DATA INPUT HERE IN FORM :
102REM    100 DATA Z1, Z2, T(1),F(1), ... T(Z1+1),F(Z1+1)
103REM     WHERE  Z1= NO. OF SEGMENTS
104REM            Z2=MAX TEMP OF TRANSIENT, (DEG. C)
105REM        T( ),F( ),= TIME, TEMP PTS( INTERCEPTS OF LINEAR'SEGMENTS)
106REM                      [HRS., DEG. C]
107REM
108REM
109REM
110REM
```

```
110REM
190REM    DON'T FORGET TO INPUT INTEGRATION AND PRINTOUT TIME STEPS:
191REM     200 Z3=1/4       INTEGRATION STEP TIME, HRS.
192REM     202 Z4=100        PRINTOUT TIME INCREMENT, HRS.
193REM
194REM
200 Z3=1/4    '  HOURS
201REM  Z3 IS THE TIME INCREMENT FOR INTEGRATION (HOURS)
202 Z4=50
203REM  Z4 IS THE TIME INCREMENT FOR PRINTOUT (HOURS).
204REM
205 DIM T(50),F(50),R(50)
210 READ Z1,Z2
220 FOR N1=1 TO Z1+1
230 READ T(N1),F(N1)
240 NEXT N1
250 FOR N2 = 1 TO Z1
260 R(N2)=(F(N2+1)-F(N2))/(T(N2+1)-T(N2))
261REM    R( )= SLOPE OF LINEAR SEGMENTS, C/HR
262REM
270 NEXT N2
300 X1=0
310 X2=0
320REM  X1=X2=INITIAL XI VALUE AT START OF EXCURSION.
321REM
330 PRINT" EXCURSION NO. "E1$
340 PRINT" ----------------------"
345 PRINT"                                                  ----------------"
350 PRINT "      RATE EQ:  X = [(N+1)(K1)(T1)]^(1/(N+1))     X IN MICRONS"
355 PRINT"                                                  ----------------"
360 PRINT
370PRINT"   PEAK TEMP. = "Z2" DEG. C."
380PRINT"   TIME INC. FOR INTEGRATION = "Z3" HRS."
390PRINT"   EXCURSION DIVIDED INTO "Z1" SEGMENTS."
400PRINT
405 N8=(INT((1/(N9+1))*1E3+.5))/1E3
410PRINT"                  N = "N9"     1/(1+N) = "N8
420PRINT"    RATE CONST 1. = "A1"*EXP(-"Q1"/RT)    [PH=5]"
430PRINT"    RATE CONST 2. = "A2"*EXP(-"Q2"/RT)    [PH=5.4-7]"
440PRINT"           RATE CONSTANT UNITS = [(MICRONS)^("1+N9")]/[HOUR]"
450PRINT
460PRINT,,"**KINETIC PARAMETER INTEGRATIONS**"
470PRINT,,"     SPECIFIED RATE CONSTANTS"
475PRINT"TIME","TEMP                        **MICRONS**"
480PRINT"HRS.","DEG. C       RATE CONST 1.          RATE CONST 2."
490PRINT"*********","*********      ***************      ***************"
500:#####.##      #####.#         ###.###              ###.###
510PRINT USING 500, T(1),F(1),X1,X2
520 C2=1
521'       SET COUNTER FOR PRINTOUT STATEMENT, SEE LINES 670,690,720
530 FOR N2 = 1 TO Z1
531'       FOR EACH LINEAR SEGMENT .....
540 C1=1
541'       SET COUNTER FOR THERMOMETER RAMP: SEE LINE 570
```

```
550 FOR H1= T(N2) + Z3 TO T(N2+1) STEP Z3
551'        CLOCK MECHANISM
560REM   H1 IS TIME AT END OF EACH INCREMENT
561REM
570 Z9=F(N2) + R(N2)*C1*Z3 - Z3*R(N2)/2
571'        THERMOMETER MECHANISM
580REM   Z9 IS AVG TEMP OF EACH INCREMENT
581REM
590 Z8=Z9+273.15
600K1=A1*EXP(-Q1/(8.314*Z8))
610 K2=A2*EXP(-Q2/(8.314*Z8))
620 X1=(X1^(N9+1)+(N9+1)*K1*Z3)^(1/(N9+1))
630 X2=(X2^(N9+1)+(N9+1)*K2*Z3)^(1/(N9+1))
640 IF C2<>Z4/Z3 THEN 680
650REM  NUMERATOR IN 712 IS TIME INTERVAL FOR PRINT-OUT.
651REM
660PRINT USING 500, H1,Z9+Z3*R(N2)/2,X1,X2
670 C2=0
680 C1=C1+1
690 C2=C2+1
700 NEXT H1
710 NEXT N2
720 IF C2=1 THEN 740
730PRINT USING 500, H1,Z9+Z3*R(N2)/2,X1,X2
740 END

READY
```

JCGRT6 13:35 30-JUL-87

EXCURSION NO. DEMO #2 : 350 HOUR RAMP, 165 TO 185 DEG C.

RATE EQ: X = [(N+1)(K1)(T1)]^(1/(N+1)) X IN MICRONS

PEAK TEMP. = 185 DEG. C.
TIME INC. FOR INTEGRATION = 0.25 HRS.
EXCURSION DIVIDED INTO 1 SEGMENTS.

N = 0.28535 1/(1+N) = 0.778
RATE CONST 1. = 125380 *EXP(- 49157 /RT) [PH=5]
RATE CONST 2. = 451330 *EXP(- 49157 /RT) [PH=5.4-7]
RATE CONSTANT UNITS = [(MICRONS)^(1.28535)]/[HOUR]

KINETIC PARAMETER INTEGRATIONS
SPECIFIED RATE CONSTANTS
MICRONS

TIME HRS.	TEMP DEG. C	RATE CONST 1.	RATE CONST 2.
0.00	165.0	0.000	0.000
50.00	167.9	6.737	18.248
100.00	170.7	11.958	32.390
150.00	173.6	16.971	45.970
200.00	176.4	21.981	59.541
250.00	179.3	27.079	73.351
300.00	182.1	32.321	87.550
350.00	185.0	37.746	102.245

TIME: 1.11 SECS.

READY

```
JCGRT6          13:32          30-JUL-87


 EXCURSION NO.   DEMO #1 :  350 HOUR ISOTHERMAL AT 175 DEG C.
 ----------------------
                                                   ----------------
     RATE EQ:  X = [(N+1)(K1)(T1)]^(1/(N+1))        X IN MICRONS
                                                   ----------------

   PEAK TEMP. =  175  DEG. C.
   TIME INC. FOR INTEGRATION =  0.25  HRS.
   EXCURSION DIVIDED INTO  1  SEGMENTS.

                N =  0.28535       1/(1+N) =  0.778
    RATE CONST 1. =  125380 *EXP(- 49157 /RT)     [PH=5]
    RATE CONST 2. =  451330 *EXP(- 49157 /RT)     [PH=5.4-7]
           RATE CONSTANT UNITS = [(MICRONS)^( 1.28535 )]/[HOUR]

                              **KINETIC PARAMETER INTEGRATIONS**
                                   SPECIFIED RATE CONSTANTS
TIME            TEMP                        **MICRONS**
HRS.            DEG. C        RATE CONST 1.          RATE CONST 2.
*********       *********       ***************       ***************
    0.00          175.0            0.000                 0.000
   50.00          175.0            8.228                22.287
  100.00          175.0           14.109                38.217
  150.00          175.0           19.341                52.390
  200.00          175.0           24.192                65.531
  250.00          175.0           28.779                77.954
  300.00          175.0           33.164                89.833
  350.00          175.0           37.390               101.279


TIME:  1.12 SECS.

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