

# The linear solution for hydriding of uranium

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## Abstract

A set of equations describing the hydriding of solid pieces of uranium is presented, together with an approximate solution of the equations. The solution predicts a constant velocity of the spall front in the solid piece, which leads to a constant value of weight gain rate (or other measure of the extent of the hydriding reaction) for a portion of the duration of the measurement. The solution allows calculation of the spall front velocity, and thus of the constant reaction rate, from expressions that are closed-form with the exception of one simple numerical integration. Expressions are given for all the parameters needed to calculate reaction rates for well annealed samples of uranium. Calculated reaction rates are compared with published data taken at a hydrogen pressure of 1.0 atm. The calculated results match the data quite well.

## 1. Introduction

The reaction between uranium and hydrogen has been of interest to the nuclear industry for many years. The papers cited in ref. 1 reach back more than 40 years to the declassification of research performed during World War II. We are particularly interested in the reaction of hydrogen with solid pieces of uranium. The evolution of our model for this process and our solution of the equations may be traced in refs. 1–4.

One of the characteristics of the hydriding of solid pieces of uranium is that, for part of the duration of the process, the reaction rate is a constant. Much of the published experimental data contains values for this constant reaction rate. Condon [2] proposed a mathematical model for the hydriding process and showed that finite-difference solutions of his equations exhibited the characteristic constant reaction rate. Kirkpatrick [3] found a closed-form approximate solution of Condon's equations. Kirkpatrick's solution included three other stages in the hydriding process besides the constant rate stage. The shapes of the weight gain and rate curves in Kirkpatrick's stages are similar to some experimental observations. We refer to Kirkpatrick's closed-form solution and the generalizations that we have made to it in succeeding years as the "linear solution" for uranium hydriding. One of the principal virtues that we claim for our model and its solution is that it predicts many

of the results of hydriding experiments as phases of a process described by the solution of a single set of equations.

For a specified hydrogen pressure, the results of ref. 3 give a plot of the logarithm of the constant reaction rate *vs.* the reciprocal of the absolute temperature which is a straight line. However, experimental data show that the curve begins to bend down at high temperatures and eventually goes through a maximum. For a specified temperature, the curve of the logarithm of the reaction rate *vs.* the logarithm of the hydrogen pressure from ref. 3 shows the reaction rate to be proportional to the square root of the pressure. Experiment, however, shows rates falling below the line at both high and low pressures. In ref. 4, we proposed corrections to Condon's equations that would account for the measured deviations from simple straight lines that we mentioned in this paragraph.

Reference 4 contains a detailed discussion of our current understanding of the dynamics of the uranium hydriding problem, including explanations of the terms in our model. Our study of uranium hydriding encompasses two separate but related tasks. The first is the development of differential equations to model the reaction. The second is solving these equations.

One of our goals is to determine as many of the parameters in our model as possible, using measurements of phenomena other than the reaction rates of solid pieces of uranium in hydrogen. Our reasons for this goal are twofold. The first is obvious: the values of constants of the model of any phenomenon are more credible if they can be estimated using more than one type of measurement. The second is that we have often found it difficult, and sometimes impossible, to separate accurately the effects of changes in particular parameters on the hydriding rates of solid uranium pieces. The reason for this is that hydriding of a solid piece is an integral experiment so that the hydriding rate is the result of several different rates. Thanks to a combination of the published work of many other investigators and to some of our own earlier work, we have determined values for most of the parameters or expressions for their values as functions of the experimental variables (hydrogen pressure and sample temperature). However, there remain a few that we are forced to determine using only data on the hydriding of solid pieces. In the paper presented here, we summarize our model for the hydriding of pieces of uranium and our linear solution for uranium hydriding and propose a set of parameter values and models that yield the best fit to the available experimental data.

## 2. The model of the hydrogen-uranium reaction

The differential equations for hydrogen and uranium concentrations are as follows:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( \frac{DN}{N-C} \frac{\partial C}{\partial x} \right) + s \frac{\partial U}{\partial t} \quad (1)$$

and

$$\frac{\partial U}{\partial t} = -k_1(C - C_{eq})U + k_2(1 - U)^{1/3} \quad (2)$$

where the meanings for the symbols for the independent variables  $t$  and  $x$ , the dependent variables  $C$  and  $U$ , and the parameters are given in Appendix A. Equation (1) is a one-dimensional time-dependent diffusion equation with a source (sink) term given by the second term on the right-hand side of eqn. (1) and by eqn. (2). The first term on the right-hand side of eqn. (2) represents the hydriding reaction while the second term represents the reverse or dehydriding reaction. Equations (1) and (2) are modifications of expressions originally published in ref. 2. The initial conditions are as follows:

$$C(x, 0) = 0 \quad (3)$$

$$U(x, 0) = 1 \quad (4)$$

The boundary conditions are as follows:

$$C(x \leq x_C, t) = C_0 \quad (5)$$

$$U(x = x_C, t) = U_C \quad (6)$$

where the meanings of the symbols are given in Appendix A. Equation (6) defines the spall front location as that depth such that  $U = U_C$ . Equations (5) and (6) contain one of the key features of our model of uranium hydriding. It is well known that after a portion of a solid piece of uranium has been partially hydrided, some of the hydrided material breaks away from the unhydrided metal. We model this process by assuming that any portion of the problem domain for which  $U < U_C$  has broken away from the solid piece. We further assume that the broken (spalled) material is so finely divided that its hydrogen concentration is  $C_0$ . This is the meaning of eqn. (5). From eqn. (6), one sees that the condition  $U \leq U_C$  applies in the region  $0 \leq x \leq x_C$ . In this region, the diffusion as described by eqn. (1) no longer occurs. Instead, the hydrogen concentration is  $C_0$  as shown in eqn. (5) and the hydriding as described by eqn. (2) continues with  $C$  replaced by  $C_0$ . For the region  $x_C < x$ , both diffusion and hydriding continue. Because the location of the spall front is constantly moving, eqns. (1)–(6) represent a moving boundary problem.

The constants for eqns. (1)–(6) are given by the following, with units shown in parentheses:

$$k_1 = 10.4 \exp(1592/T) (\text{s}^{-1}) \quad (7)$$

$$k_2 = 137.5 \exp(-4900/T) \text{ (molar fraction U s}^{-1}\text{)} \quad (8)$$

$$D = 1.9 \times 10^{-6} \exp(-5820/T) \text{ (m}^2 \text{s}^{-1}\text{)} \quad (9)$$

$$C_0 = N 4.183 \times 10^{-6} \exp(-894/T) P^{1/2} / [N + 4.183 \times 10^{-6} \exp(-894/T) P^{1/2}] \text{ (mf)} \quad (10)$$

where mf is an abbreviation for molar fraction and the meanings of the other symbols are given in Appendix A. Equations (7) and (9) were published in ref. 2. Equation (10) is a revised version of an expression from ref. 2 modified to account for matrix saturation. (A value for the first constant ( $4.183 \times 10^{-6}$  mf Pa<sup>-1/2</sup>) in eqn. (10) was given incorrectly in ref. 2 as the result of an error in the conversion from Torr to Pa.) Equation (8) represents a new evaluation of the dehydriding data by the authors which is being published in ref. 4.

Some parameters that are needed to determine the reaction rates have not yet been given. The parameter  $C_{eq}$  from eqn. (2) is a threshold value of concentration. When  $C < C_{eq}$ , we replace the hydriding reaction term in eqn. (2) with zero. We assume that  $C_{eq}$  should be related to the plateau pressure of hydrogen over hydride powder, an expression for which was published in ref. 5 (in ref. 4, we refer to the plateau pressure as an "equilibrium" pressure with the symbol  $P_{eq}$ ). However, we also presume that the plateau pressure should represent some equilibrium between hydriding and dehydriding. For some time we have suspected that use of both a non-zero value of  $C_{eq}$  and a dehydriding term (the second term on the right-hand side of eqn. (2)) might be redundant. As we were doing the work that is presented in the present paper, we concluded that our suspicion is correct. For calculating reaction rates, we believe that our model works best for a zero value of  $C_{eq}$ :

$$C_{eq} = 0 \text{ (mf)} \quad (11)$$

Our specifying a zero value of  $C_{eq}$  does not mean we believe that the plateau pressure is zero, but rather that  $P_{eq}$  is a direct consequence of the dehydriding reaction as given in the last term of eqn. (2). In effect, by including both  $C_{eq}$  and the dehydriding reaction term in our model, we have two different terms to account for one phenomenon. Thus, for the purpose of matching reaction rates with our model, use of a non-zero  $C_{eq}$  term is redundant provided that the dehydriding reaction is included.

The parameter  $N$  is the maximum concentration of free (*i.e.* not bound into hydride) hydrogen atoms in the metal lattice. We use this term to model the effect of saturating the uranium matrix with free hydrogen. We expect that  $N$  should rise with increasing temperature. Our proposed fit for this parameter is as follows:

$$N = \exp(-2.362 - 2305/T) \text{ (mf)} \quad (12)$$

This expression represents values estimated from attempts to match the data of Bloch and Mintz [6] with our model. Our match with that particular set of data was not very satisfactory, so eqn. (12) should be considered no better than a very approximate estimate.

The parameter  $U_C$  is the value of  $U$  for which spall will occur. Attempts to match data using  $U_C$  as a free parameter have yielded values ranging from 0.989 to 0.95. Like most other metals, uranium becomes more ductile with increasing temperature. It is probable that this increase in ductility will lead to a corresponding increase in the percentage of the metal that must be

reacted before the metal will spall. At some sufficiently high temperature, it is probable that the ductility will be great enough that the metal will no longer spall. However, this does not rule out the possibility that the resulting hydride will be so porous that the transport of hydrogen through the hydride will be quite rapid compared with diffusion through intact material. For most of the available data, we estimate that  $U_C$  (molar fraction U) is given by the following expression:

$$U_C = \begin{cases} 1 - (1 - 0.989)^{**}\{0.5 - 0.5 \cdot \tanh[-2950(1/T - 0.00146)]\} & (T < 835.5 \text{ K}) \\ 0.54534 + 1745 \cdot (1/T - 0.0011969) & (835.5 \text{ K} \leq T) \end{cases} \quad (13)$$

where the double asterisk (\*\*) represents the customary FORTRAN symbol for exponentiation. Equation (13) represents an exercise in curve fitting designed to match the data we have at a hydrogen pressure of 1.0 atm. A portion of the curve of  $U_C$  vs.  $1/T$  is shown by the chain-dashed line in Fig. 2. The hyperbolic tangent shape was picked because it is extremely smooth (*i.e.* has an infinite number of non-singular derivatives) and thus did not cause any sudden breaks in the curves of spall front velocity vs. reciprocal temperature. The expression for  $T > 835.5$  K represents a simple extrapolation from the inflection point on the curve of  $U_C$  vs.  $1/T$  (*i.e.* the point at which the second derivative of  $U_C$  with respect to  $1/T$  is zero). This extrapolation leads to  $U_C = 0$  at 1130.8 K (857.6 °C). Our presumption has been [1] that  $U_C$  is related to the tensile strength of the metal. Vandermeer's [7] plots of tensile strength vs. temperature can be approximated by a straight line from about 0 °C to about 300 °C and a second line with a somewhat steeper slope that reaches a nearly zero value of tensile strength by about 650 °C (the  $\alpha$ - $\beta$  phase transition at 668 °C complicates the shape of the stress curve at high temperatures). A plot of  $U_C$  as given in eqn. (13) vs. temperature in degrees celsius has a much more rounded shape than Vandermeer's tensile strength curves. However, the value of  $U_C$  given by eqn. (13) begins to diverge from its asymptotic value of 0.989 at a temperature of about 250 to 300 °C. This divergence may be significant because Vandermeer found a ductility minimum at 300 °C, with rapid increases in ductility for temperatures above that value. We speculate that  $U_C$  is not affected appreciably by changes in strength and ductility until the strength begins to fall rapidly and the ductility begins to rise rapidly, both of which happen after about 300 °C.

In ref. 2, it was shown that the reaction rate depends on such details as the residual stress in the solid piece. Our attempts to match the data of Bloch and Mintz [6] have required a consistently smaller value of  $U_C$  for any given combination of temperature and pressure than most of the other data that we have found. We believe that eqn. (13) should be reasonably accurate for well annealed uranium samples. However, matching some experimental results may require considerably lower values of  $U_C$ .

### 3. The linear solution

In ref. 3, an approximate analytical solution for the uranium hydriding moving boundary problem was developed. One of the results from this solution is that the spall front  $x_C$  moves with a constant velocity  $V_S$ . As our model has become more complex, we have relied on finite-difference calculations to study the hydriding rates. We have found that the linear solution of ref. 3 may be generalized and that almost all of the significant results from that approximate solution have generalized equivalents. The generalized spall front velocity is as follows:

$$V_S = \frac{1}{t_1} \left[ \frac{D_E}{s k_1 U_E} \right]^{1/2} \text{ (m s}^{-1}\text{)} \quad (14)$$

where  $t_1$  is the time at which the surface of the metal first spalls (*i.e.* when the value of  $U$  on the surface first reaches  $U_C$ ). If the dehydriding term (the second term on the right-hand side of eqn. (2)) can be neglected, then the solution for  $t_1$  is as follows:

$$t_1 = -\ln(U_C)/[k_1(C_0 - C_{eq})] \text{ (s)} \quad (15)$$

The increase in  $t_1$  that comes with non-negligible dehydriding will be discussed later. The generalized effective diffusivity  $D_E$  is as follows:

$$D_E = D[N/(N - C_0)]^{1/2} \text{ (m}^2 \text{ s}^{-1}\text{)} \quad (16)$$

The generalized effective uranium concentration  $U_E$  is as follows:

$$U_E = (U_0 U_C)^{1/2} \text{ (molar fraction U)} \quad (17)$$

where  $U_0$  is the concentration of uranium in the unreacted metal (if concentrations are given in molar fractions as is the case here, then by definition  $U_0 = 1.0$ ).

In eqns. (14)–(17), there are some slight changes in notation compared with the original versions in ref. 3, specifically in the symbols for the stoichiometric ratio and the hydriding reaction rate constant. The term raised to the  $1/2$  power in eqn. (14) is a distance scale factor that represents the e-folding distance for the curve of  $C$  *vs.*  $x - x_C$  in the approximate solution of ref. 3. The values of this parameter are usually quite small ( $4 \times 10^{-7}$  m at  $300^\circ\text{C}$ ), which indicates that the hydrogen atoms do not penetrate very deeply into the unspalled metal before they are captured by the hydriding reaction.

Equation (2) indicates that both the threshold and dehydriding terms will lead to a lengthening of the time scale for the hydriding reaction. One result is that  $t_1$ , the time taken from the beginning of the exposure to hydrogen to the first spall, is raised. At the surface of the metal ( $x = 0$ ), eqn. (2) may be converted into an ordinary differential equation for  $U$  as a function of time by replacing  $C$  with  $C_0$ . The result is

$$\frac{\partial U}{\partial t} = -k_1(C_0 - C_{eq})U + k_2(1 - U)^{1/3} \quad (18)$$

The first spall time  $t_1$  is the time for which  $U$  equals  $U_C$ . Unfortunately, we have not found a closed-form solution of eqn. (18) for a case with non-zero dehydriding. The only way to be sure of the new value of  $t_1$  is to integrate eqn. (18) numerically. The time  $t_1$  is not a linear function of either  $U_{\text{stop}}$  or the dehydriding rate constant. Trials with numerically integrating eqn. (18) showed that the increase in  $t_1$  above the value given by eqn. (15) is minor for  $U_{\text{stop}} \ll U_C$ . However,  $t_1$  shows large increases as  $U_{\text{stop}}$  approaches  $U_C$ . In the limit,  $t_1$  becomes infinite for  $U_{\text{stop}} = U_C$ .

The threshold and dehydriding terms lower the spall velocity by lessening the uranium depletion rate. Our finite-difference calculations yield spall velocities that are very close to those given by eqn. (14), provided that the spall time used is the value that is given by integrating eqn. (18) until  $U = U_C$ . For values of  $U_{\text{stop}}$  greater than about  $0.9 U_C$ , the spall velocity began to fall below this simple result. However, the spall velocity from the finite-difference calculation was only 10% below the value produced by the simple approximation when  $U_{\text{stop}}$  was  $0.98 U_C$ .

The presence of a dehydriding term,  $k_2(1 - U)^{1/3}$ , in eqn. (2) limits the fraction of uranium that can be converted to hydride to less than 100%. The minimum value of uranium concentration  $U$  (for a given pressure and temperature) occurs when the hydriding and dehydriding terms of eqn. (2) are exactly equal. Obviously, this minimum value is a function of  $C$ ,  $C_{\text{eq}}$ , and the hydriding and dehydriding reaction constants. The maximum value for the hydrogen concentration is  $C_0$ . Thus, the minimum value that  $U$  may attain anywhere in the sample for a given hydrogen pressure is that given by setting  $\partial U / \partial t = 0$  in eqn. (18). Let this minimum value of  $U$  be called  $U_{\text{stop}}$ .  $U_{\text{stop}}$  is an important parameter for analyzing the results of uranium hydriding measurements. The equation for  $U_{\text{stop}}$  is

$$k_1(C_0 - C_{\text{eq}})U_{\text{stop}} = k_2(1 - U_{\text{stop}})^{1/3} \quad (19)$$

A significant effect of the dehydriding term is in the total weight gain that is expected as the sample (and the hydride powder produced by the breakup of the sample) approaches its maximum degree of hydriding. As was described in the previous paragraph, the minimum value of uranium concentration for a reaction that includes the dehydriding term is  $U_{\text{stop}}$ . The maximum weight gain is the weight gain that could be found in the absence of any dehydriding multiplied by  $(1 - U_{\text{stop}})$ .

The dehydriding term will have a similar effect on the weight gain rate for a sample. In the previous paragraph, it was pointed out that the portion of the total weight gain that represents hydrogen fixed as hydride must be multiplied  $(1 - U_{\text{stop}})$ . In general, the weight gain rate will also be reduced by the same factor. Equation (13) of ref. 3 gives the weight gain rate (wg) for the linear solution as a function of time. This equation is

$$\text{wg} = sU_0 V_S \{1 - (U_C/U_0) \exp[-k_1 C_0(t - t_1)]\} + C_0 V_S (\text{mf m s}^{-1}) \quad (20)$$

Weight gain rates in  $\text{mf m s}^{-1}$  may be converted to more customary units ( $(\text{mole H})\text{m}^{-2} \text{s}^{-1}$ ) by multiplying by the molar density of uranium,  $7.846 \times 10^7$

(mole U)  $\text{m}^{-3}$ . In eqn. (20), the weight gain rate asymptotically approaches a constant at large values of time. This asymptote is

$$\dot{w}_\infty = sU_0 V_S + C_0 V_S (\text{mf m s}^{-1}) \quad (21)$$

For a case with dehydriding, the asymptotic weight gain rate is the same as eqn. (21) provided that the spall velocity used is correct for the case with dehydriding and that the term containing  $sU_0$  is multiplied by  $(1 - U_{\text{stop}})$ . The resulting equation for asymptotic weight gain rate with dehydriding is

$$\dot{w}_\infty = sU_0 V_S(1 - U_{\text{stop}}) + C_0 V_S (\text{mf m s}^{-1}) \quad (22)$$

It should be noted that the term of eqn. (22) that represents weight gain from the uptake of free hydrogen contains  $C_0$ , not  $(C_0 - C_{\text{eq}})$ . The reason is that the weight gain for the ordinary diffusion asymptotically approaches  $C_{\text{eq}}$  times the spall velocity. An equation that describes the shape of the weight gain rate curve for a case with dehydriding before it reaches its asymptote has not been found. Plots of weight gain rate *vs.* time for cases with dehydriding do not have the simple decaying exponential approach to an asymptote that is given by eqn. (20). Part of the reason for this difference is that the cases with dehydriding take some time for the spall velocity itself to reach a steady-state value. This effect becomes noticeable for values of  $U_{\text{stop}}$  greater than about  $0.25 U_C$ .

Most experiments do not measure the progress of the spall front, but rather the extent of the hydriding reaction (through such quantities as the weight gain or the consumption of hydrogen). As we noted in the introduction, many of the published sets of data report the characteristic constant hydriding rate. These constant rates are converted to reaction front velocities using an expression such as eqn. (21). However, for cases in which  $U_{\text{stop}}$  is significant, the constant value would be that given by eqn. (22). Thus, the apparent spall velocity inferred from an experimentally measured reaction rate would not be the true spall velocity  $V_S$ , but rather  $V_S(1 - U_{\text{stop}})$ . The difference between the true velocity of the spall front and the apparent spall velocity that comes from the weight gain rate should be considered when comparing experimental measurements with results from our model. As we shall show in Figs. 1 and 2, the difference can be significant.

#### 4. Comparison of calculated results with data

Figure 1 shows a comparison of data from three sources with spall front velocities calculated using the equations given in the present paper. As we have explained, we consider the comparison between the spall velocity multiplied by  $1 - U_{\text{stop}}$  to be the most relevant. We believe that our model matches the data quite well except for the last three of the high-temperature data points from Galkin *et al.* [8]. For a hydrogen pressure of 1.0 atm, the curve of  $U_{\text{stop}}$  *vs.*  $1/T$  crosses our proposed curve for  $U_C$  at a temperature of about  $384^\circ\text{C}$ . Thus, for temperatures greater than  $384^\circ\text{C}$ , the spall velocity



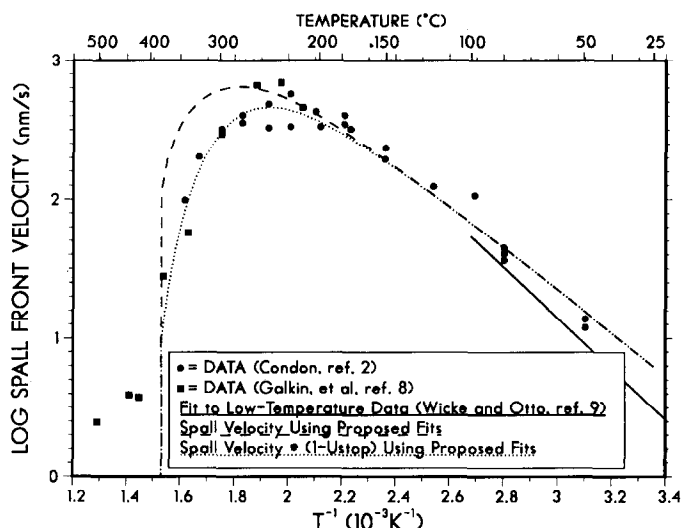


Fig. 1. Apparent spall front velocity for a hydrogen pressure of 1.0 atm showing comparison of data with calculations: ● data [2]; ■ data [8]; — fit to low-temperature data [9]; - - - spall velocity using proposed fits; ..... spall velocity multiplied by  $(1 - U_{\text{stop}})$  using proposed fits.

according to our model is zero. Further, the value of  $P_{\text{eq}}$  is 1 atm at about 430.5 °C. Although the spall velocities in our model do not depend on  $P_{\text{eq}}$  (as long as  $C_{\text{eq}} = 0$ ), the point where  $P_{\text{eq}}$  reaches the hydrogen pressure is at least near the point where the spall velocity becomes zero. The data of Galkin *et al.* show some low velocities for temperatures as large as 500 °C. Thus, we conclude that our model is not adequate for temperatures large enough to yield a value of  $P_{\text{eq}}$  that is of comparable magnitude to (or greater than) the hydrogen pressure. The fact that Galkin *et al.* measured spall front velocities for temperatures larger than 384 °C indicates that the reaction process at high temperatures is more complicated than the assumptions in our relatively simple model.

In Fig. 2, we show a repeat of some of the data and of the calculated spall velocity curves for a hydrogen pressure of 1.0 atm. On the secondary axis, we show the curves of  $U_C$ ,  $N$  (multiplied by 100), and  $U_{\text{stop}}$  vs.  $1/T$ . These additional curves are shown to give a clearer idea of the shapes of the curves of those quantities. The data and calculated spall velocities are shown in Fig. 2 so that we may make some observations about the effect of  $U_C$  and  $U_{\text{stop}}$  on the calculated spall velocities. First, we note that the maximum in the apparent spall velocity (the dotted line) occurs before  $U_C$  has significantly deviated from its asymptotic value of 0.989. Thus, the location of the maximum in the apparent spall velocity is mostly due to the dehydriding reaction rather than to changes in  $U_C$ . Also, the temperature at which the spall velocity becomes zero in our model is that for which  $U_C = U_{\text{stop}}$ . This is a direct consequence of eqns. (6) and (19). If, as specified in eqn. (6), the spall does not occur until  $U = U_C$ , and if, as specified in eqn. (19),  $U$  may never be

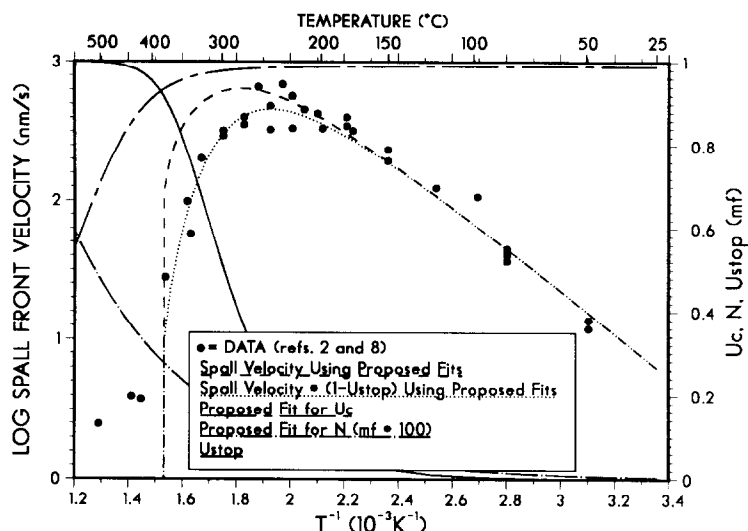


Fig. 2. Apparent spall front velocity for a hydrogen pressure of 1.0 atm. showing proposed fits for  $U_C$  and  $N$ , together with the resulting curve of  $U_{stop}$ : ● data [2, 8]; - - - spall velocity using proposed fits; .... spall velocity multiplied by  $(1 - U_{stop})$  using proposed fits; - - - - proposed fit for  $U_C$ ; - · - · - proposed fit for  $N$  (in mf  $\times 100$ ); - - - -  $U_{stop}$ .

less than  $U_{stop}$ , then for  $U_C \leq U_{stop}$ , no spall can occur. As we stated in the previous paragraph, we are well aware that our model needs further work if it is to match the data of Galkin *et al.* [8] at the highest temperatures.

In ref. 4, we reported that we attempted to match the extensive data of Bloch and Mintz [6] with our model. The values of  $N$  that we inferred from that work did not show any obvious physically unrealistic behavior and thus were used as the basis for our proposed fit for  $N$ , eqn. (12). However, the values of  $U_C$  that were necessary to make our model match their data did not make sense to us. First, the values of  $U_C$  were considerably different from the values given by our proposed fit for  $U_C$ , eqn. (13). In addition, the values did not reveal a consistent trend (*i.e.* values of  $U_C$  did not decline monotonically with increasing temperature). We are dissatisfied with the match of our model to the data of Bloch and Mintz and have no good explanation for the differences. We refer those who wish further details to ref. 4.

## 5. Conclusions

We have presented a summary of our model for the hydriding of well annealed pieces of uranium. Our model provides an inexpensive way to calculate reaction rates. Results from our model have been compared with data taken at a hydrogen pressure of 1.0 atm. We have adjusted the parameters of our model to provide a good match between these data and our model, except at temperatures large enough that the equilibrium pressure of

hydrogen over the hydrided powder is nearly as large as the pressure of the hydrogen in the atmosphere.

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## References

- 1 J. B. Condon and E. A. Larson, *J. Chem. Phys.*, **59** (1973) 855.
- 2 J. B. Condon, *J. Phys. Chem.*, **79** (1975) 392.
- 3 J. R. Kirkpatrick, *J. Phys. Chem.*, **85** (1981) 3444.
- 4 J. R. Kirkpatrick and J. B. Condon, *Modeling the Reaction Between Uranium and Hydrogen, K/CSD/TM-87*, (Martin Marietta Energy Systems, Inc., Oak Ridge, TN) in the press (available from Office of Scientific and Technical Information, U.S. Department of Energy, P.O. Box 62, Oak Ridge, Tn 37831, U.S.A.).
- 5 J. B. Condon, Standard Gibbs energy and standard enthalpy of formation of  $\text{UH}_3$  from 450 to 750 K, *J. Chem. Thermodyn.*, **1980** (1980) 1069.
- 6 J. Bloch and M. H. Mintz, *J. Less-Common Met.*, **81** (1981) 301.
- 7 R. A. Vandermeer, An overview—constitution, structure, and transformation in uranium and uranium alloys. In *Metallurgical Technology of Uranium and Uranium Alloys*, Vol. 1, *Physical Metallurgy of Uranium and Uranium Alloys*, American Society for Metals, Metals Park, OH, 1982.
- 8 N. P. Galkin, B. N. Sudarikov, Iu. D. Shishkov and V. I. Tarasov, *Mosk. Khim-Tekhnol. Inst.*, **43** (1963) 67.
- 9 E. Wicke and Kl. Otto, The uranium–hydrogen system and the kinetics of uranium hydride formation, *Z. Phys. Chem., N.F.*, **31** (1962) 222 (in German); English translation, *ORNL-tr-4979* (Oak Ridge National Laboratory, Oak Ridge, TN).

## Appendix A: Nomenclature

$C$	molar fraction of diffusing free hydrogen in the uranium phase
$C_{\text{eq}}$	equilibrium (threshold) hydrogen molar fraction, eqn. (11)
$C_0$	solubility molar fraction for free hydrogen in uranium, eqn. (10)
$D$	diffusivity of free hydrogen in uranium, eqn. (9) ( $\text{m}^2 \text{s}^{-1}$ )
$D_E$	generalized effective diffusivity, eqn. (16) ( $\text{m}^2 \text{s}^{-1}$ )
$k_1$	hydriding rate constant, eqn. (7) ( $\text{s}^{-1}$ )

$k_2$	dehydriding rate constant, eqn. (8) ((molar fraction uranium) $s^{-1}$ )
$N$	maximum amount of free diffusing hydrogen that the uranium matrix can hold, eqn. (12) (mf, molar fraction of hydrogen).
$P$	hydrogen gas pressure (Pa)
$s$	stoichiometric constant for hydriding reaction ( $s = 3$ for $UH_3$ )
$t$	time (s)
$t_1$	time for first spall, eqn. (15) (s)
$T$	absolute temperature (K)
$U$	uranium molar fraction
$U_0$	uranium molar fraction for unreacted material (molar fraction uranium)
$U_C$	uranium molar fraction for spall, eqn. (13) (molar fraction uranium)
$U_E$	generalized effective uranium molar fraction for spall velocity, eqn. (17) (molar fraction uranium)
$U_{stop}$	uranium molar fraction for which hydriding reaction rate becomes zero because hydriding and dehydriding rates are in balance, eqn. (19) (molar fraction uranium)
$V_S$	spall front velocity, eqn. (14) ( $m\ s^{-1}$ )
$w\dot{g}$	weight gain rate, eqn. (20) ( $mf\ m\ s^{-1}$ )
$w\dot{g}_\infty$	asymptotic weight gain rate for large time, eqns. (21), (22) ( $mf\ m\ s^{-1}$ )
$x$	depth from original surface of uranium metal (m)
$x_C$	depth at which spall front is located (m)