Prediction of Low Temperature Sensitization
of Austenitic Stainless Steels

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satisfactorily, although the uncertainty in the results will be large. There are in existence models of two phase flow (two dimensional) and other theoretical information which suggest that the problem is not completely intractable. Because this modeling effort has not been initiated, although some preliminary study of the problem has been carried out, it seems prudent to assume that ground water is present at the time sensitization has occurred. This is a conservative approach. If the modeling of groundwater flow indicates that it will play a significant role in determining the time predicted for failure of the container to occur, it would be a simple matter to use the convolution approach to include the effect.

Modeling of the processes that occur during welding and predicting the stress conditions that could occur would appear to involve even greater uncertainty. Thus it is proposed that the initial model make the assumption that once sensitization has occurred, failure will occur rapidly thereafter. Again this is a very conservative assumption. If it can be shown that a zone of no tensile stress or compression occurs in the container then the process of intergranular stress corrosion cracking will not proceed and the container can fail by corrosion only if other modes of corrosion are invoked, such as crevice, pitting or galvanic corrosion.

IGSCC Model and Data

As has been described previously the process of IGSCC is facilitated by the loss of chromium at grain boundaries through the process of precipitation of chromium carbide. When the chromium concentration has been reduced to about 13 wt% it no longer protects the material from corrosion. The process that occurs is governed by the diffusion of carbon and chromium to the grain boundary, carbon diffusion being rapid compared to the diffusion of chromium, and by the kinetics of the reaction that results in the precipitation of the carbide $Cr_{23}C_6$. Both of these processes are temperature dependent and because the temperature of the container declines with time, the processes are time dependent.

The theoretical is based on the assumption that the concentration of chromium at the grain boundary depends on both the effective concentration of carbon and the equilibrium reaction kinetics that form the carbide. It is futher assumed that the concentration of chromium is controlled by the slow rate of diffusion of chromium from the bulk alloy into the grain boundary region. A straightforward application of linear diffusion theory then leads to an expression for the time necessary for the thickness of the chromium depleted region at the boundary to increase to a value that permits intergranular corrosion to occur (Fullman[2]).

By definition, the time needed to reduce the concentration of chromium at the grain boundary sufficiently for corrosion to

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occur is the time for sensitization. It is temperature dependent and a simple closed form expression is possible only if the temperature is constant. For a container in a repository the temperature declines with time so that a more complex expression is necessary. The time for sensitization to occur is given by the following integral expression;

$$t = \frac{1}{2D_{Cr}} \frac{(X_{Cr}^* - X_{Cr}^i)^2}{(0.13 - X_{Cr}^i)^2} \int^{W=20nm} W dW \qquad \text{(see note}^1) \qquad (1)$$

Where; W   = the width of the chromium depleted grain boundary layer,

D_{Cr} = the temperature dependent bulk diffusion coefficient of chromium,

X_{Cr}^* = the equivalent concentration of chromium in the alloy (mole fraction),

X_{Cr}^i = the temperature dependent chromium concentration in the depletion zone as determined by its equilibrium with the carbide (mole fraction).

Each of these parameters has an uncertainty associated with it. For W and X_{Cr}°, which have no temperature dependence, the uncertainties are simply described. For purposes of this report the following is suggested;

$$W = (2 \pm 0.2) \times 10^{-6} \text{ cm},$$
$$X_{Cr}^* = (0.18 \pm 0.01) \text{ mole fraction},$$

where the uncertainties are the standard deviations.

The value of 20 nm for W is based on the fact that when the depletion zone has become this thick, sensitization has begun (Mozhi[3] et al). On the other hand Fullman[4] has used 300 nm as the width when sensitization is complete.

The region of depletion is not sharply defined because it is controlled by both a diffusion mechanism and a chemical equilibrium. As temperature declines the equilibrium between chromium and the carbide favors the carbide. This changes the location of the 0.13 mole fraction chromium concentration

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[1] In principal it would be possible to integrate all the relevant temperature dependent functions and write out equation (1) in detail. In practice this would be difficult and it is much more reasonable to integrate equation (1) numerically as is done for the pitting corrosion function in CONVO. The basic form is simply;

dW = f(t)/(W + W*)dt,

where f(t) represents everything to the left of the integral sign in equation (1) and W* is an appropriately small value of the initial thickness of the depleted layer. The integration ceases at the value of time for which W = 20 nm.

relative to the minimum and maximum concentrations along the gradient of chromium concentration. Thus the meaning of W is somewhat ambiguous compared to the analogous situation of the tarnishing reaction in copper where the width of the region controlled by diffusion of copper is well defined, being the region defined by a copper concentration of zero (the oxide surface) and one (the metal surface). In this case the equilibrium between copper and copper oxide results in a copper concentration of approximately zero.

The concentration of chromium in the alloy X_{Cr}° is not a completely satisfactory measure of the effective chromium concentration. As pointed out by Cihal[5] and extended by Fullman[2] and Mozhi[3] et al, some adjustments should be made for certain alloying elements, particularly molybdenum and nitrogen. The effect of molybdenum depends on the nature of the corrosive environment to some extent, but the small concentrations usually encountered probably make this refinement unnecessary. Titanium acts in a manner similar to molybdenum and its concentration can be treated as equivalent to molybdenum. Thus the following approximation for the effective concentration of chromium should be used;

$$X_{Cr}^{*} = X_{Cr}^{\circ} + (1.4 \pm 0.2)(X_{Mo} + X_{Ti}) + 12X_{N}, \qquad (2)$$

where all concentrations are in mole fraction. According to Mozhi[3] et al, above a concentration of 0.0016 mole fraction, the effect of nitrogen declines rapidly. For analysis purposes, the nitrogen term is set to zero if $X_{N} \geq 0.0016$.

The diffusion coefficient, D_{Cr}, has been measured by a number of researchers and its value evaluated by Fullman[4]. There are two contributions to diffusion, bulk lattice diffusion and grain boundary plus pipe diffusion. At temperatures below about 500°C the latter is expected to be the rate determining process. The temperature dependence follows a simple Arrhenius rate relationship of the form;

$$D_{Cr} = a \exp(b/RT). \qquad (3)$$

Careful analysis makes it very unlikely that some other form of diffusion with an activation energy ("b" in the above expression) lower than 40 kcal will occur.

There is considerable uncertainty in the values of the coefficients "a" and "b" in the above expression for the temperature dependence of the diffusion coefficient. Evaluation of the available data leads to the following values;

$$a = (2.7 \pm 1.3) \times 10^{-7} \text{ cm}^2/s,$$
$$b = (40.7 \pm 2.2) \text{ kcal/mole,}$$

where the errors are expressed as the standard deviation.

The concentration of chromium in the depleted layer is found by evaluating the chemical reaction that precipitates chromium carbide at the grain boundary. This reaction is assumed to be at equilibrium.

The chemical reaction that occurs is;

$$23Cr + 6C \underset{\longleftarrow}{\overset{K}{\longrightarrow}} Cr_{23}C_6 \ , \qquad (4)$$

where K is the equilibrium constant for the reaction.

For a reaction at equilibrium, the equilibrium constant is described by the free energy of formation of the carbide (or alternatively, the activation energy, not quite the same thing, but formulated in the same way), that is;

$$°G_f = -RTlnK, \qquad (5)$$

where; $\quad R = 1.9 \ Cal/°K.$

This is simply an alternative way of expressing the Arrhenius relationship used above for the diffusion process. The temperature dependence of the change in free energy of formation of the carbide has been measured and the data evaluated by Hultgren[6] and is expressed by a cubic dependence on temperature over the temperature range $300°K \le T \le 1000°K$, that is,

$$°G_f (Cr_{23}C_6) = -RTlnK = a + bT + cT^3 . \qquad (6)$$

The coefficients in this expression are given by;

$$a = -(1.36 \pm 0.15) \times 10^5 \ cal,$$
$$b = -(8.26 \pm 0.75) \ cal/°K,$$
$$c = -(5.19 \pm 0.65) \times 10^{-6} \ cal \ °K^{-3} .$$

For a chemical reaction at equilibrium, the equilibrium constant is a function of the activities of the reactants and products in the normal formulation. Hence for this reaction the equilibrium constant is given by:

$$K = \frac{1}{(Y_{Cr} \ X_{Cr}^{\frac{1}{23}} \ Y_C \ X_C)^6} \qquad (7)$$

Where; $\quad Y_x \quad$ = the activity coefficient of carbon or chromium,

$\quad\quad\quad\quad X_c$ = the concentration of carbon (mole fraction).

The activity of $Cr_{23}C_6$ is assumed to be one and is subsumed in the measurement of K. The activities of chromium and carbon are

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just the product of their activity coefficients and concentrations as indicated in equation (7).

There are now two new unknowns, the activity coefficients of chromium and carbon, whose values must be found in order to use equation (7) to calculate the value of X_{Cr}^i. As might be anticipated, both of these coefficients are temperature dependent.

Of the two, the activity coefficient of carbon presents the lesser difficulty. The data of Natesan and Kassner[7] has been analyzed in detail to develop the activity of carbon.

The result is the following expression for the carbon activity as a function of temperature, carbon concentration and nickel concentration:

$$\ln a_c = \ln(\frac{X_c}{1 - X_c}) + (-0.176 + \frac{0.608}{T}) \, \delta X_{Ni} + (a* + \frac{b*}{T}) \tag{8}$$

where
$$a* = -0.469 \pm 0.439,$$
$$b* = 2.312 \pm 0.555,$$
$$\delta X_{Ni} = 0.01 \text{ mole fraction,}$$
$$X_c = (2.0 - 0.1) \times 10^{-4} \text{ mole fraction.}$$

The value of δX_{Ni} should be derived from the variation in the concentration of nickel in different batches of alloy as determined by experiment. The nominal concentration of nickel in AISI 304 stainless steel is approximately 0.09 mole fraction with a desired maximum variation of about ± 0.01 mole fraction which is a reasonable estimate for δX_{Ni}. The concentration of carbon is specified as an upper limit, consequently the use of a standard deviation for the expected variation in this quantity is inappropriate. The approach suggested is to use a one-sided standard deviation, although this could result in an underestimate of the true average carbon concentration, which would lead to an overestimate of the time for sensitization to occur. Experimental data from different batches of alloy should clarify the issue.

Note that in this formulation the activity is calculated directly, rather than calculating the activity coefficient and then combining it with the selected value of carbon concentration.

The procedure used to estimate the activity coefficient for chromium is much more complex than the calculation of carbon activity. It is based on the procedure developed by Kaufman and Nesor[8]. The alternative formulations of Hasebe and Nishizawa[9] and of Hillert and Waldenström[10] would give similar results. These procedures are based on combining the experimentally determined temperature dependent thermodynamic data for the three binary alloys. Mozhi[3] and his co-workers give an explicit

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description of this process for AISI 304 stainless steel using the procedure developed by Kaufman and Nesor.

The activity coefficient for chromium is estimated assuming that the activity has a temperature coefficient of a regular solid solution. The activity coefficient is estimated using equation (7) below. The quantities in equation are defined as follows:

$^{\circ}G_{Cr}$ = The free energy difference between chromium in the face centered cubic lattice of austenite and in its free state.

g_{ij} = temperature dependent constants.

The subscripts 1,2, and 3 refer to Fe, Cr, and Ni respectively.

$$E\overline{G}_{Cr} = \overline{G}_{kn}^{*} + {}^{\circ}G_{Cr} + \frac{X_1}{(X_1 + X_2)^2} [X_2(X_2 + 2X_1)g_{21} + X_1^{2}g_{12}]$$

$$+ \frac{X_3}{(X_2 + X_3)^2} [X_2(X_2 + 2X_3)g_{23}] + X_3^{2}g_{32} = RT\ln Y_{Cr} \qquad (9)$$

Where

$$\overline{G}_{kn}^{*} = -\sum_{ij}^{3} \frac{X_i X_j}{X_i + X_j} (X_j g_{ji} + X_j g_{ij}) \qquad \text{for } i < j. \qquad (10)$$

From these equation and the known values of the various constants and coefficients the activity coefficient of chromium can be determined.

The coefficients g_{ij} are temperature dependent. They have been developed by evaluating the results of measurements made on the three binary alloys. These coefficients are given below.

For the iron chromium binary alloy;

$$g_{12} = 1770 - 2.5 \ T, \qquad (12)$$
$$g_{21} = 1770 - 2.5 \ T. \qquad (13)$$

For the iron nickel binary alloy;

$$g_{13} = 500 - 0.91573 \times 10^{-2}T^2 + 0.39029 \times 10^{-6}T^3, \qquad (14)$$
$$g_{31} = -8320 + 0.58327 \times 10^{-2}T^2 - 0.24859 \times 10^{-5}T^3. \qquad (15)$$

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For the nickel chromium binary alloy;

$$g_{23} = -2000 + 0.11202 \times 10^{-2} T^2 - 0.18649 \times 10^{-5} T^3, \qquad (16)$$
$$g_{32} = -6000 + 0.22651 \times 10^{-2} T^2 - 0.6231 \times 10^{-6} T^3. \qquad (17)$$

The other important variable involved in equation (1) is $^\circ G_{Cr}$. Chromium exists as a body centered cubic lattice at the temperatures of interest. What is required is the free energy difference between chromium in its reference state and in the face centered cubic lattice of austenite. This is the difference between the free energy of mixing of FeCr in the BCC and FCC lattices which is given by;

$$^\circ G_{Cr} = 4730 - 1.0\ T \qquad (18)$$

These equations have been used by Fullman[2] to calculate the chromium activity coefficient at temperatures of 500°K, 600°K and 700°K. Both the formulations of Kauffman and Nesor[8] and of Hasebe and Nishisawa[9] were used. The value of $E_{\overline{G}_{Cr}}$ as a function of T for the two formulations is shown in figure 1. It is worth noting that although the sign of the slope of these two formulations is different they do not yield very different results for Y_{Cr}. Futhermore the variations in the results based on variations in the coefficients of the g_{ij} equations are small, so that it is model variations that are most important. Thus it seems reasonable to use these results without invoking any further uncertainties other than the rather large model uncertainties.

The results can be described in the following formulae:

Hasebe and Nishizawa;

$$E_{\overline{G}_{Cr}} = 2048 - 0.6T, \qquad (19)$$

Kaufman and Nesor;

$$E_{\overline{G}_{Cr}} = 1671 + 0.165\ T^{-2} \times 10^{-5} T^2. \qquad (20)$$

In both cases an extrapolation to a temperature of 400°K is likely to result in only modest inaccuracy. It appears reasonable to use this result or a somewhat more precise one developed by direct calculation of the $E_{\overline{G}_{Cr}}$ as a function of temperature for a larger range of temperature. This approach greatly simplifies the calculation of the activity coefficient of chromium.

Sensitivity

The most important first order sensitivities come about from the variables in equation (1). It is clear from examination of this equation that the variation in the effective concentration of

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Figure 1. Chromium Excess Free Energy
Activity Coefficients for 12 % Chromium
Are Shown for Each Temperature

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EXCESS FREE ENERGY (Cal/Mole)

TEMPERATURE (Kelvin)

KAUFMAN AND NESOR

HASEBE AND NISHIZAWA
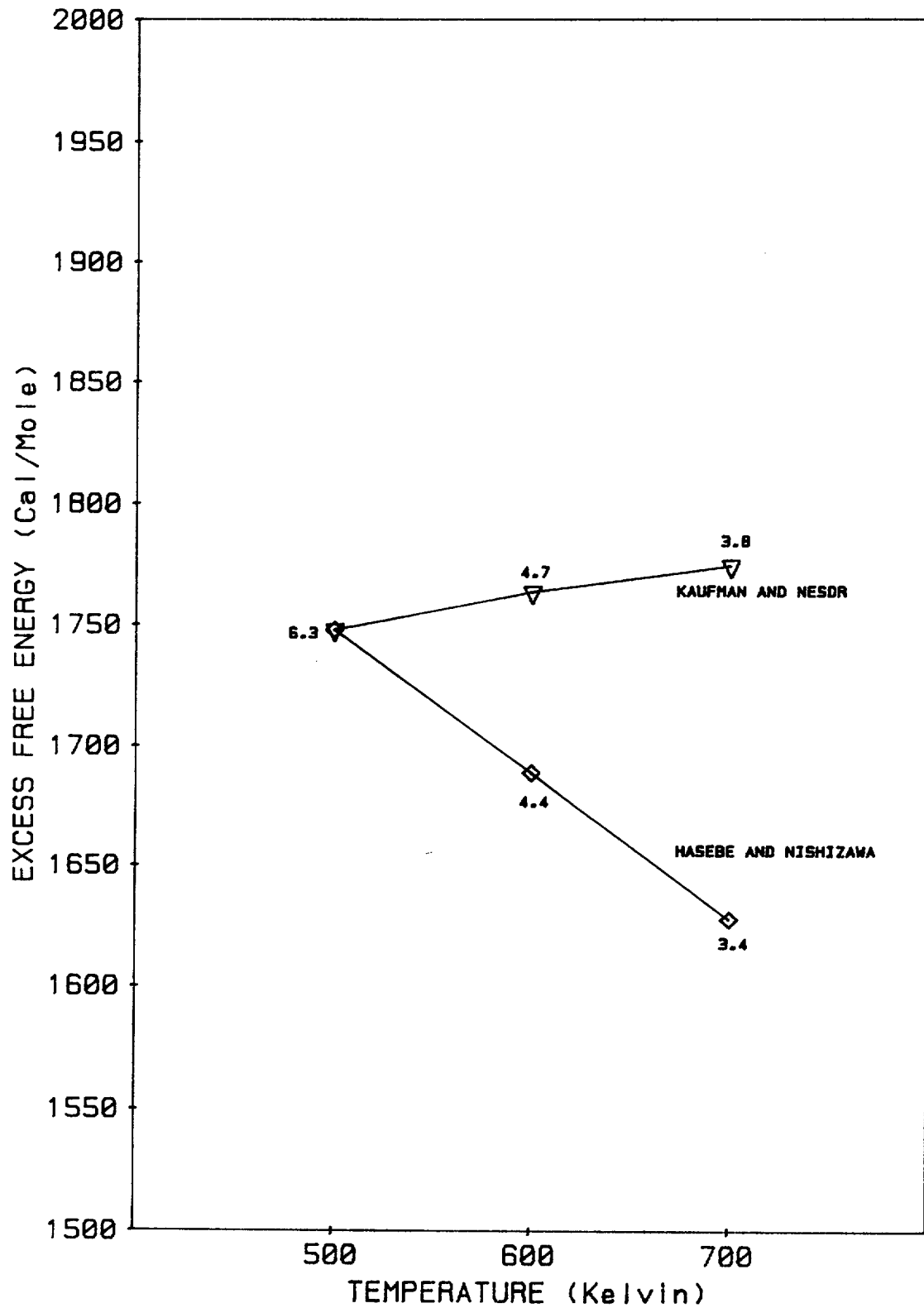
chromium X^*_{Cr} will have a large effect on the time t, particularly in light of the fact that this term is squared. Assuming that X^i_{Cr} is small compared to X^*_{Cr}, the relative sensitivity is $\delta t/t = 2\delta X^*_{Cr}/X^*_{Cr}$. If X^i_{Cr} is reasonably large, then the effect on $\delta t/t$ is more complex because the two variances and their covariance must be combined; however, the net effect will be a larger impact on $\delta t/t$.

The other major effect on t is the result on the uncertainty in the value of D_{Cr}. As is apparent from the uncertainties of the coefficients in equation (3), this effect can be quite large. If the uncertain constants "a" and "b" in the diffusion coefficient are assumed to be independent, it is appropriate to write;

$$\delta t/t = [(\delta a/a)^2 + (\delta b/a)^2]^{0.5}.$$

For the values of "a" and "b" and their uncertainties given for equation (3), the calculated value of $\delta t/t$ is 0.95, a very large value. This means that for nominal variations in these "constants" the relative variation in time is nearly 100%. Thus it is certain that the diffusion coefficient of chromium dominates the uncertainty in the time to achieve sensitization. In the above equation it is the value δb that has the greatest impact. This is the uncertainty in the exponential coefficient, that is, the activation energy for diffusion. This value was determined from an evaluation of the slope of the logarithmic form of equation (3) based on experimental data. There may be available additional data that would improve on this uncertainty. In any case it is worthwhile to note that more precise knowledge of its value would reduce the uncertainly in time to sensitization markedly.

Although the value of X^i_{Cr} has a substantial uncertainty, it enters into equation (1) in such a way that it is partially offset. Rewriting equation (8) to solve for X^i_{Cr};

$$X^i_{Cr} = Y_{Cr}^{-1} (K\, a_c^6)^{-1/23},$$

it is apparent that the activity coefficient must be the dominant uncertainty unless the constants for K have very large uncertainties, which they do not. Putting in the appropriate quantities shows that the effect of carbon activity is only about 5% on the chromium concentration while the variations in the chromium activity coefficient contribute more than 10%. The contribution of the uncertainties in the value of K are negligible.

Conclusions

All the necessary data are available to calculate the time to sensitization as a function of temperature. There are several simplifications that can be employed that greatly reduce the calculational burden without introducing any significant bias into the results. The calculation of the activity coefficient of

chromium can be done using an empirical fit to the results of more detailed calculations without any loss of generality, gaining a very large reduction in complexity thereby.

The time to achieve sensitization could be calculated with surprisingly good precision if it were not for the large uncertainty in the data for the diffusion coefficient of chromium. This result strongly suggests that experimental studies be directed toward improving this quantity and its temperature dependence.

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