August 3, 1971

To: H. E. McCoy

Subject: Formation of Grain-Boundary Cracks in Ni-Base Alloys

You have described a corrosion problem with a Ni-base alloy in a steam generator to me and inquired whether the kinetics are such that the process might be diffusion controlled. I will attempt to put the kinetics problem in some perspective in this note. As I understand the problem, the alloy in question sees virtually no neutrons, and separates the primary coolant (LiF + BeF\(_2\) + ZrF\(_4\) + UF\(_4\) + dissolved fission products) from the secondary coolant (LiF + BeF\(_2\)). In preliminary testing, the alloy proved to be compatible with both salts (although the primary "test salt" contained no fission products): a rare grain boundary or two, perhaps of a special orientation, might have been attacked. However, in reactor service the primary coolant attacked the alloy along grain boundaries. You have convinced yourself that cracks not visible in the optical microscope extend along the boundaries which intersect the surface for an average distance of one grain diameter (about 2.5 \times 10^{-2} \text{ cm}) after a service period of about 10^8 \text{ sec}. The alloy is under a slight compressive load during service, and you state that of the three major elements present, Fe, Cr, and Ni, that only Cr has an appreciable "solubility" in the salt, by the reaction:

\[
\text{UF}_4 + \text{Cr} \rightleftharpoons \text{CrF}_2 + \text{UF}_3
\]

Let us postulate the most probable rate-limiting steps for the process according to the model of Fig. 1. A 1 cm length of boundary has had material removed to a depth \(\Delta y\) creating a uniformly wide channel of thickness \(h\). We will assume that \(h\) is sufficiently narrow that no convection or normal liquid flow can occur, and that all transport must be by diffusion through the liquid. Then our first possible rate-limiting mechanism is:

(1) Material transport through the liquid, of element \(n\), because of a concentration gradient between points A and B. The flux of material \(J\) at any time (when \(\Delta y\) has any value instantaneously) will be assumed to follow steady-state kinetics, and:

\[
J_n = -\frac{D_n}{n} \frac{\partial}{\Delta y} (c_n^B - c_n^A)
\]

where \(J\) has units \(\frac{\text{mass}}{\text{cm}^2\text{sec}}\), the diffusivity of \(n\) in the liquid is \(D_n\), and the concentration point B is \(c_n^B\). We can check the feasibility of the diffusion of any element in the liquid roughly by assuming \(D_n \approx 10^{-5} \text{ cm}^2/\text{sec}\). There are
two likely diffusing species of importance: (a) the dissolved fission products, because in the absence of fission products the attack did not occur; thus getting fission products to the grain boundary area may be important, and (b) getting elements of the alloy out of the crack is a reasonable part of enlarging the crack. We first check on whether a diffusing species can go far in the liquid by calculating the RMS diffusion distance as

\[(4 \bar{D} \Delta t)^{1/2} = (4 \cdot 10^{-5} \text{cm}^2 \cdot \text{sec} \cdot 10^8 \text{sec})^{1/2} = 63 \text{ cm}.\]  

(2)

Since this is very large compared to \(\Delta y\), we feel that liquid diffusion is feasible as a transport mechanism.

We now consider whether diffusion of alloy elements through the liquid out of the crack is occurring under reasonable rate. The total mass of element \(n\) removed from a 1 cm long crack is

\[Q_n = 1 \text{cm} \times \Delta y \times h \times \rho_n\]  

(3)

where \(\rho_n\) is the mass of \(n\)/cm\(^3\) of the alloy. By removing the subscripts, we obtain an equation which applies to all the elements. For any species to diffuse out of a crack of time-averaged length \(\Delta y = \Delta y/2\) with a mean concentration gradient \(\Delta C_n = C_{n,0} - C_{n,0}^\Delta\),

\[Q_n = J \times 1 \text{cm} \times h \times \Delta t\]  

(4)

where \(\Delta t \sim 10^8 \text{ sec}\). Then we readily combine Eq. (3) and Eq. (4) and obtain:

\[\Delta C_n = \frac{\Delta y^2 \cdot \rho_n}{2 \bar{D}_n \Delta t}\]  

(5)

and substituting our typical values \(\Delta y = 2.5 \times 10^{-2} \text{ cm}^2\), \(\rho_n = 4 \text{ gr/cm}^3\) (for an element which constitutes half of an 8 gr/cm\(^3\) alloy), \(\bar{D}_n = 10^{-6} \text{ cm}^2/\text{sec}\) and \(\Delta t = 10^8 \text{ sec}\), \(\Delta C_n \approx 1.25 \times 10^{-6} \text{ gr/cm}^3\). Translated into words, this means that for our assumptions a concentration difference on the order of parts per million is required to drive all the material we need to transport into or out of the crack by liquid diffusion. The result says three things:
(i) If transport of Cr out of the crack is the major transport item, we can get all the Cr required out through the liquid.

(ii) If transport of minute quantities of fission product in the crack to the grain boundary is important, we can get all the fission product required into the crack. Very little dissolved fission product is required.

(iii) If transport of Fe or Ni out is considered, and ppm quantities of Fe and Ni can dissolve in the liquid, then diffusion of Fe or Ni can be rate-limiting. The latter two steps may be rate-limiting, the first is probably just one that proceeds as rapidly as required by the rest of the situation.

A second step which may limit the rate of the reaction must be considered as a consequence of the fact that no grain boundary attack occurs until fission products are added to the salt. This suggests that they may be necessary to make the dissolution process occur. It seems unlikely that fission products would significantly increase in chemical potential in the crack much above their level in the surrounding salt; should this occur, liquid diffusion should rapidly remove the excess fission products from the crack. Hence, the attacking liquid is likely of nearly the same composition in the crack as elsewhere, and we cannot blame a gross change in liquid composition for the accelerated attack. But if the fission products dissolved in the liquid diffuse into the solid from Point A to Point C, at least two things can happen.

(i) As you suggest, the solid composition may be changed by the addition of fission products, and local melting might occur.

(ii) Another possibility is that the rate of dissolution of the solid may be affected by one or more species of dissolved fission product. In Fig. 2, the activation energies for various dissolution processes for the alloy species are considered. In the absence of dissolved fission product, because of the presence of the boundary,

\[ Q_d > Q_{ab} \]  \hspace{1cm} (6)

and dissolution occurs more readily at the boundary than on a nearly flat surface. Dissolved fission product may increase the rate of dissolution at both sites by making
Regardless of the precise mechanism by which the solution of Fe, Cr, or Ni is affected, then the second choice of rate-limiting mechanism may be:

(2) Transfer of fission products from the salt into the alloy. This step may be limited at the liquid-solid interface, which is a situation that we cannot easily treat. This is equivalent to saying \( Q_t^* \) is large, in Fig. 2. It may also be limited by the rate of diffusion of the fission product into the solid, to build up a concentration of fission product in the solid near the surface. Let us assume that the fission products diffuse about as fast as a normal matrix atom, or \( D_{fp,s} \sim 10^{-17} \text{ cm}^2/\text{sec} \). Then the RMS diffusion distance is

\[
\tilde{x} = (4 D_{fp,s} \tau t)^{1/2} = 6.3 \times 10^{-4} \text{ cm}
\]

which gives an estimate of both the maximum penetration distance of fission product atoms into the solid, and the maximum distance that matrix atoms can be transported during the service life of the element. We ignore here the effects of local curvature on the equilibrium concentration of vacancies, to be discussed below.

A third rate-limiting step might be the diffusion of some matrix element which is insoluble in the liquid away from the liquid-solid interface, or the diffusion of the fission products in the solid to regions where they might affect the rate of dissolution of the alloy. We note in passing that diffusion of fission products into the alloy and diffusion of excess matrix elements may be speeded up along the grain boundary, where a Fisher-Whipple analysis might be appropriate. Thus, our third possibly rate-limiting event is:

(3) Diffusion in the solid. Any atom sitting on the bottom surface of the crack has a mean lifetime on that surface of \( \bar{t} \) (assuming that it does not jump back into the solid),

\[
\bar{t} \approx \frac{a_o \Delta t}{\Delta y} = \frac{3 \times 10^{-8} \text{ cm} \cdot 10^8 \text{ sec}}{2.5 \times 10^{-2} \text{ cm}} \approx 10^7 \text{ sec}
\]
where a₀ is a lattice parameter, \( \sim 3 \times 10^{-8} \) cm. The average jump frequency of an atom is given in terms of the diffusivity of the \( n^{th} \) matrix species by \( \tau \),

\[ \tau = \frac{2 D_n}{a_0^2} = \frac{2 \times 10^{-17}}{9 \times 10^{-16}} = 0.2 \text{ /sec} \quad (10) \]

Thus, the mean number of volume-diffusion type jumps for an atom just on or just below the surface without considering curvature appears to be very small. Our estimate may be too low because the local radius of curvature near the bottom of the crack should increase the equilibrium number of vacancies present in that region. Since vacancies move quickly relative to atoms, the local equilibrium assumption is reasonable, and the nearby grain boundary or surface itself may be a good vacancy source. The exact increase in number present depends on \( p \sim h/2 \), and is simply given as:

\[ \frac{C_v}{C_{v0}} = (1 + \frac{\gamma a}{\rho kT}) \quad (11) \]

where \( \gamma \) is surface tension, \( \Omega \) is atomic volume, \( k \) is Boltzmann's constant, \( T \) is temperature, and \( C_{v0} \) is the equilibrium vacancy concentration under a flat surface, and \( C_v \) exists under a surface of curvature \( \gamma \). (Typically, \( \gamma \sim 10^3 \) ergs/cm², \( \Omega \sim 10^{-23} \) cm³, \( k = 1.38 \times 10^{-16} \) erg/deg, and \( T = 923^\circ \text{K} \); then:

\[ \frac{C_v}{C_{v0}} \approx (1 + \frac{8 \times 10^{-9}}{\rho (cm)}) \quad (12) \]

For \( \rho \) of about \( 10^{-6} \) cm, then the local lattice diffusivity must increase by nearly a factor of 1000 just under the crack bottom. The effect is 90% reduced a distance of about \( \rho \) from the bottom.) The image that this conjures up in my mind is that of a peaceful matrix atom, sitting a little distance away from a grain boundary, jumping 2 times/100 sec. The first indication he sees of his impending disaster is a few ominous strangers (fission product atoms) who wander down main street (grain boundary) and sidle off into the matrix. Meanwhile he gets itchy feet and begins to jump a little faster as the vacancy concentrations steadily increases. All this time, the tornado (crack tip) is roaring down on the town at the rate of \( \bar{v} = \) one atom layer/100 sec. Our little guy gets more and more nervous, and jumps faster; perhaps he sees a few guys running away from the storm (the matrix atoms which dissolve less readily). From the time that he is \( \rho \) away from the storm front until it advances by \( \rho \), he is jumping an average of perhaps 10 times/sec, and he has
about 30,000 fast jumps which can carry him about $5 \times 10^{-6}$ cm$^2$ (the RMS diffusion distance computed as $n a_0^2$ where $n$ is number of jumps). Thus, he has plenty of time to avoid the storm — as an individual — but someone is going to get caught and dissolved out with the help of the ominous stranger atoms. If we regard the diffusivities of all the atoms near the bottom of the crack as being nearly alike, then we see that there is ample time for concentration redistribution near the crack bottom because of the excess vacancies which are present. Interestingly enough, with the small distances involved make it likely that there is a net vacancy flux from point A to point B in Fig. 2; this is analogous to sintering by volume diffusion. The crack width may thus be increased as one goes away from the bottom by vacancy diffusion to the flat surface, assuming that the sources are strong enough.

If this approach to the problem seems to be worth further pursuit, I would be glad to discuss it with you.

R. T. King

RTK: smp
Fig. 1. Model of grain boundary attached by salt.