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SODIUM MASS TRANSFER: XVI

THE

SELECTIVE CORROSION COMPONENT

OF STEEL EXPOSED TO

FLOWING SODIUM

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E.G. BRUSH

U.S. ATOMIC ENERGY COMMISSION
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VALLECITOS ATOMIC LABORATORY

GENERAL ELECTRIC

ATOMIC POWER EQUIPMENT DEPARTMENT
SAN JOSE, CALIFORNIA

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SODIUM MASS TRANSFER: XVI
THE SELECTIVE CORROSION COMPONENT OF
STEEL EXPOSED TO FLOWING SODIUM

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VALLECITOS ATOMIC LABORATORY
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SAN JOSE, CALIFORNIA

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I. SUMMARY

The corrosion of Type-316 stainless steel in 1100 and 1200 F isothermal sections of sodium heat transfer systems, contaminated with 12 parts per million of oxygen, is a partially selective process. That is: all alloying elements enter the sodium phase in a transport process whose first step is oxidation (which is not accompanied by visible oxide film formation) and whose primary driving force is the degree of unsaturation of alloying element (reduced or oxidized) solutes in the sodium solvent. Initially the alloying elements enter the sodium phase at rates different than the stoichiometric rates that are dictated by the bulk alloy composition.

The partially selective process has been postulated to be composed of selective, $j_{(s)}$, and of non-selective, $j_{(ns)}$ corrosion rate components. The behavior of these components in specimens exposed to sodium at 1100 F and at 1200 F has been examined by the electron microprobe and the resulting analysis indicates the following behavior characteristics:

1. At points along the sodium flow path where the degree of unsaturation of the alloying elements dissolved in sodium is different than zero iron behaves nobly, molybdenum is neutral (i. e., it corrodes in stoichiometric proportions during the entire specimen exposure time) and chromium, nickel, and manganese behave actively. The noble nature of iron demands that during initial exposure periods, when alloy corrosion rates are under nonlinear rate control, less iron than that dictated by stoichiometric corrosion behavior enters the sodium phase. Conversely, the active elements enter the sodium phase at rates greater than those dictated by stoichiometric rate considerations.* This behavior results in an increase in the iron concentration in the alloy phase near the sodium-alloy interface and in a decrease in the chromium, nickel and manganese concentrations. The compositional change produces a face-to-body centered cubic transformation, occurring at some concentration ΣC_d of the active elements and at some distance x_d from the sodium alloy interface.
2. Selective and nonselective corrosion rate components are such that:

$$J_{Fe} = j_{Fe(ns)} = C_{Fe(0)} \frac{d\Delta W}{dt} - \Sigma j_{i \text{ active}(s)}$$

$$j_{i \text{ active}(ns)} = C_{i \text{ active}(0)} \frac{d\Delta W}{dt}$$

$$J_{i \text{ active}} = j_{i \text{ active}(s)} + j_{i \text{ active}(ns)}$$

*It should be noted that the terms "active" and "noble" when used in this context do not have the same meaning as they do in thermodynamic considerations.

where J_i is the total corrosion rate of any element, $d \Delta W/dt$ is the alloy corrosion rate and $C_{i(0)}$ is the alloy phase concentration of any element at the reaction product-alloy interface and where by definition of partially selective corrosion processes the noble selective component, in this case $j_{Fe(s)}$, returns to the alloy phase rather than entering the sodium phase.

3. Alloy rate control is exerted in a nonturbulent liquid sodium boundary layer whose effective thickness depends upon the sodium flow velocity. Following a nonlinear transient, the alloy rate control becomes linear, that is, $d \Delta W/dt = \text{some constant, } R$. When this occurs, the alloy phase active element concentration profiles may be described by the following expressions which are based upon the postulate that when $d \Delta W/dt$ is constant the active element selective components $j_{(s)}$ are constant and upon the postulate that the excess iron constitutes a continuous diffusion source depositing in the plane of the moving (from its original position at $t = 0$) sodium - alloy interface

(i) in the region $0 \leq x \leq x_d$

$$C_\infty - C_1 = (j_{(s)}/R) + I_1 \left\{ \operatorname{erf}(u_{x1}, t) + \exp(-Rx/\rho_a D_1) \operatorname{erf}(v_{x1}, t) \right\}$$

(ii) in the region $x \geq x_d$

$$C_\infty - C_2 = I_2 \left\{ \operatorname{erfc}(u_{x2}, t) + \exp(-Rx/\rho_a D_2) \operatorname{erfc}(v_{x2}, t) \right\}$$

where I_1 and I_2 are integration constants to be determined at $x = x_d$ from:

$$C_1 = C_2 = C_d$$

$$D_1 \partial C_1 / \partial x = D_2 \partial C_2 / \partial x$$

and where:

$$(u_{x1}, t) = (x/2\sqrt{D_1 t}) + R\sqrt{t}/2\rho_a\sqrt{D_1}$$

$$(v_{x1}, t) = (x/2\sqrt{D_1 t}) - R\sqrt{t}/2\rho_a\sqrt{D_1}$$

D_1 = diffusion coefficient in the b. c. c. (body-centered cubic) region,
 $0 \leq x \leq x_d$, dm^2/mo

$U_2, V_2 =$ same as U_1, V_1 except that they contain D_2 instead of D_1

$D_2 =$ diffusion coefficient in the f. c. c. (face-centered cubic) region,
 $x > x_d, \text{ dm}^2/\text{mo}$

$\rho_a =$ alloy density, mg/dm^3

4. At $x = 0$, the reaction product - alloy interface, the profile descriptive expression for the $0 \leq x \leq x_d$ region shows that:

$$j_{(s)}/R = C_\infty - C_{(0)}$$

when this is coupled with the previous expressions describing the partially selective process it will be seen that:

$$J_{\text{Fe}} = C_{\text{Fe}\infty} R$$

$$J_{i \text{ active}} = C_{i \text{ active}\infty} R$$

That is: upon transformation to linear rate law control, the partially selective corrosion process transforms to full stoichiometric alloy corrosion behavior just as if no compositional disturbance had ever taken place, since by definition of stoichiometric alloy corrosion:

$$J_i = C_{i\infty} R$$

where $C_{i\infty}$ is the bulk alloy composition of a given element i , in weight fraction (w.f.) units.

5. The interplay between error function, error function complement, and exponential terms in the profile descriptive expressions forces a limiting extent of compositional disturbance at a time defined approximately by:

$$\sqrt{t_e} = 3.644 \rho_a \sqrt{D_2/R}$$

when this happens the concentration profile description expressions become:

(i) in the $0 \leq x \leq x_d$ region

$$C_\infty - C_1 - (j_{(s)}/R) + I_1 \left[1 - \exp(-Rx/\rho_a D_1) \right]$$

(ii) in the $x > x_d$ region

$$C_\infty - C_2 - 2I_2 \exp(-Rx/\rho_a D_2)$$

When I_1 and I_2 are evaluated the slopes of these expressions, noting that since D_1 has large expected magnitude, yield;

$$dC_1/dx = (C_d - C_{(0)})/x_d, \text{ at all } x \text{ in the region } 0 \leq x \leq x_d$$

$$dC_2/dx = (C_\infty - C_d)R/\rho_a D_2, \text{ at } x = x_d$$

These slopes can be measured, with proper care, from the concentration profiles, as can x_d , C_d , and $C_{(0)}$. Assuming equilibrium, D_2 can be calculated from the exposure time after the onset of linear rate control by:

$$\sqrt{D_2} = R\sqrt{t}/3.644 \rho_a$$

Most of the local specimen regions chosen for examination indicated that equilibrium had been attained. Evidence was primarily optical and indicated rather extensive compositional changes of as much as 15 microns. Therefore, the expression for $\sqrt{D_2}$ and for R allowed both of these quantities to be estimated. Then the relationship:

$$D_1 dC_1/dx = D_2 dC_2/dx \quad \text{at } x = x_d$$

allowed D_1 to be evaluated. Once done the ratio, $j_{(s)}/R = C_\infty - C_{(0)}$ was established indicating that $C_{(0)}$ was decreasing with increasing sodium flow velocity; providing evidence that oxygen transport to the sodium-alloy interface was increased by velocity, and therefore formed the basis for postulating the presence of a rate-controlling liquid-sodium boundary layer.

6. The point alloy rates, R , calculated from the concentration profiles, were in good agreement with the observed length average rates, $\bar{R}$, calculated from specimen weight losses.
7. The diffusion coefficient, D_2 , in the face-centered cubic region, $x > x_d$, was found to be, for a summed active element C_d concentration, ΣC_d , of 0.082 weight fraction:

$$D_2 = 38.4 \exp(-51,757/RT)$$

where D_2 is expressed in dm^2/mo , R is the gas constant and T is in $^\circ\text{K}$. This gives a D_2 about sixty times greater (at 1200 F) than the self-diffusion coefficients of chromium, nickel, and manganese. Diffusivities in dilute solutions would normally be about 10 times greater than the self-diffusion coefficient, which they are in this instance in the ΣC_d range that is greater than 0.15 w.f. The diffusivity, D_1 , in the body-centered cube region, $0 \leq x \leq x_d$ was found to be about 2 orders of magnitude greater than that in the face centered cubic region. This was to be expected.

8. At planes where the sodium becomes saturated with metallic alloying elements, a new mechanism takes over and chromium behaves nobly, nickel and molybdenum are neutral, and iron and manganese are active. Oxide films form and are accompanied by alloy weight gains.
9. The length average time to reach equilibrium and the extent of the length average equilibrium depth of composition change are given by:

$$(i) \Sigma \bar{C}_{(0)} < 0.1 \text{ w.f.}$$

$$\bar{t}_e = 3.26 \times 10^{+16} \exp(26,140/T) / (\bar{R})^2$$

$$\bar{x}_e = -\frac{7.07 \times 10^{+8}}{\bar{R}} \left[5.45(1.46)^{-\frac{922-T}{56}} + 1 \right] \exp(-26,140/T) \log_{10} \left[\frac{0.005}{0.309 - \Sigma \bar{C}_{(0)}} \right]$$

$$(ii) 0.1 < \Sigma \bar{C}_{(0)} < 0.15$$

$$\bar{t}_e = 0.82 \times 10^{+16} \exp(-26140/T) / (\bar{R})^2$$

$$\bar{x}_e = -\frac{1.77 \times 10^{+8}}{\bar{R}} \left[8.52(1.46)^{-\frac{922-T}{56}} + 1 \right] \exp(-26140/T) \log_{10} \left[\frac{0.005}{0.309 - \Sigma \bar{C}_{(0)}} \right]$$

$$(iii) \Sigma \bar{C}_{(0)} > 0.15 \text{ w.f.}$$

$$\bar{t}_e = 0.41 \times 10^{+16} \exp(-26140/T) (\bar{R})^2$$

$$\bar{x}_e = -\frac{0.88 \times 10^{+8}}{\bar{R}} \left[14.78(1.46)^{-\frac{922-T}{56}} + 1 \right] \exp(-26140/T) \log_{10} \left[\frac{0.005}{0.309 - \Sigma \bar{C}_{(0)}} \right]$$

In which $\Sigma \bar{C}_{(0)}$ is the alloy phase summed length average active element reaction product - alloy interfacial concentration, w.f., T is in °K, $\bar{t}_e$ is in months and $\bar{x}_e$ is in dm. The total immersion time for equilibrium is $\bar{t}_e + 1.25$.

10. The impact of the partially selective corrosion process is not as important to the future design of sodium cooled reactor systems as are the control features that arise in the sodium phase. A rational analytical model that relates corrosion rate with sodium heat transfer system parameters (geometry of flow channel, flow rate, local temperatures, and over-all temperature differentials, oxygen content or other impurities) is lacking for systems in which saturation is not achieved and for systems where boundary layers play significant transport roles, particularly where transport is under activity rather than concentration gradient control.

The development of an appropriate descriptive model embodying these concepts should be given a high priority. The development must rely primarily upon observed corrosion rates as functions of sodium system parameters and upon boundary layer transport concepts. The electron microprobe may be of corollary assistance in such model development. In particular alloy phase response to varying oxygen levels and to saturation effects are needed. These are currently being examined in a few additional specimens.

II. INTRODUCTION

The corrosion behavior of several structural alloys in liquid sodium heat transfer test loops is being evaluated by the General Electric Company's Atomic Power Equipment Department (APED) in a program sponsored by the United States Atomic Energy Commission under Contract AT(04-3)-189, Project Agreement 15.

The scope of the over-all test program has been described elsewhere⁽¹⁾. Comprehensive analysis of the test results from the nonisothermal, pumped test loops supports the conclusion that the corrosion of iron-base structural alloys, in isothermal regions of the ascending temperature zones at least, is a partially selective process⁽²⁾. That is: all metallic elements, principally iron, chromium, nickel, manganese and molybdenum, enter the sodium phase but they may do so in amounts different than those dictated by a given bulk alloy composition. The result is experimentally detectable by x-ray fluorescence and diffraction measurements, by optical microscopy, by magnetic susceptibility and by electron microprobe traverses.

Such behavior results in a compositionally changed layer, extending into the alloy phase from the interface between the sodium-alloy reaction product and the alloy phase. The alloying element concentration profiles in this layer are intimately related to the kinetic behavior of the corrosion process. In particular, the profiles contain direct information bearing on the total alloy corrosion rate, on diffusivities, and on corrosion rates of the individual alloying elements.

The concentration profiles in the layer can be precisely established by the electron microprobe. The following discussion examines their value in the kinetic interpretation of the partially selective corrosion behavior of Type-316 stainless steel specimens exposed to isothermal, flowing sodium, contaminated with 12 ppm oxygen, at 1100 F and at 1200 F in regions of the ascending sodium temperature cycle (hot leg) in bimetallic sodium test loops.

III. THEORY

Quantitative kinetic studies of partially selective corrosion processes are not widely documented. In fact the only formal treatment of the general subject with which the author is familiar is Wagner's dissertation⁽³⁾ on fully selective processes (where one or more elements do not corrode at all) in high temperature oxygen and it is restricted to parabolic rate laws. Some background considerations are therefore necessary to set the stage for the analysis of partially selective corrosion processes in liquid sodium.

1. GENERAL DRIVING FORCE CONCEPTS.

Historically, the primary driving force that promotes hot-zone corrosion of structural metallic materials in sodium heat transfer systems containing small* amounts of dissolved sodium oxide (say 10 to 50 ppm as oxygen in systems whose maximum temperature does not exceed 1200 F) has been attributed to thermal gradient mass transport, assisted by an oxidation step at the sodium - alloy interface as discussed in Epstein's classic paper.⁽⁴⁾ Thus for a system composed of a pure metal, iron for instance, the corrosion rate at a given plane along the sodium flow path of ascending temperatures (the hot leg) is proportional to the degree of unsaturation of dissolved iron in sodium at the plane. That is, providing that there are no intermediate transport phases between the turbulent sodium stream and the structural wall:

$$d\Delta W/dt = \alpha_{Fe}^{\theta} (S_{Fe}^O - S_{Fe}) \quad (1)$$

where, at a given plane:

ΔW^{θ} = the alloy (in this case all iron) weight loss after any time t, mg/dm²,

α_{Fe}^{θ} = the specific wall solution rate constant of iron, mg/dm² mo.

S_{Fe}^O = the saturated solubility of iron in sodium at the given temperature in question, weight fraction (1w.f. = 100%).

S_{Fe} = the actual concentration of iron in sodium at the given plane in question, weight fraction.

The rate constant, α_{Fe}^{θ} , is a function of the wall temperature at the sodium wall interface and it is also a function of the sodium oxide concentration in the sodium stream. This latter dependency arises from the oxidation step by which a metal atom first leaves the metal lattice. This reaction

* The definition of "small" as used here, depends upon the temperature. At temperatures above 1400 F, for instance, 50 ppm is not "small" and at temperatures above 1600 F, as witnessed by the British work with refractory metals, (5) 10 ppm is disastrously large.

can involve subsequent reduction, as explored by Horsey⁽⁶⁾, in which case the final form of the corroding species is elemental iron dissolved in sodium. Thus:

in which the oxidation-reduction couple involved between steps 1 and 3 occurs as a result of thermodynamic energy differences between the metal lattice surface and dissolved iron phases. Conversely the reaction may involve only the first two steps, in which case, as proposed by Mottley⁽⁷⁾, the final form of the corroding species would be the structural metal oxide. For the kinetic content, insofar as this report is concerned, the nature of the final form is of no consequence except as discussed in Section VII, Future Work.

2. STOICHIOMETRIC CORROSION RATE CONTROL IN ISOTHERMAL, FLOWING SYSTEMS.

Consider an iron-chromium-nickel alloy structural carrier of circular geometry with radius r (dm) and length L (dm) in which sodium is flowing isothermally at a temperature T ($^{\circ}\text{K}$) and at a volume flow rate G (dm^3/mo). (See Figure 1.) At some plane y , along the length L , $0 \leq y \leq L$, iron, chromium and nickel will be corroding respectively at rates of J_{Fe}^{θ} , J_{Cr}^{θ} , and J_{Ni}^{θ} , such that the alloy corrosion rate is:

$$\frac{\theta}{d\Delta W/dt} = J_{\text{Fe}}^{\theta} + J_{\text{Cr}}^{\theta} + J_{\text{Ni}}^{\theta}$$

If stoichiometric corrosion is imposed it must follow:

first that:

$$J_{\text{Fe}}^{\theta} = C_{\text{Fe}\infty} \frac{\theta}{d\Delta W/dt}$$

$$J_{\text{Cr}}^{\theta} = C_{\text{Cr}\infty} \frac{\theta}{d\Delta W/dt}$$

$$J_{\text{Ni}}^{\theta} = C_{\text{Ni}\infty} \frac{\theta}{d\Delta W/dt}$$

where the $C_{i\infty}$ represent the bulk alloy concentrations of the three alloying elements, weight fractions (w.f.), and second that: the corrosion couple $\text{Na}, \text{Na}_2\text{O} + \text{Alloy}_{\text{FeCrNi}}$ is energetically more favorable than the couple $\text{Na}, \text{Na}_2\text{O} + \text{Fe}_{\text{FeCrNi}} + \text{Cr}_{\text{FeCrNi}} + \text{Ni}_{\text{FeCrNi}}$. It is therefore a fair approximation to write:

$$\frac{\theta}{d\Delta W/dt} = \alpha_{\text{alloy}}^{\theta} (S_{\text{alloy}}^{\theta} - S_{\text{alloy}})$$

Except for 1) the transient influence of any structural member surface oxidation prior to its sodium exposure, or 2) the influence of any secondary phases* between the bulk sodium stream and the alloy wall, linear rate laws will prevail from essentially time zero and the linear alloy rate constant, R , will be given (Appendix I) by:

$$d\Delta W/dt = R = \alpha_a^\theta (S_a^0 - S_{a(0)}) \exp(-2\pi r \alpha_a^\theta y / G \rho_{Na}) \quad (2)$$

where:

α_a^θ = The specific wall solution rate constant of the alloy, mg/dm² mo.

S_a^0 = The saturated solubility of the specific alloy in sodium at the temperature T in question, weight fraction.

$S_{a(0)}$ = The concentration of the alloy in the bulk, turbulent stream at the plane $y = 0$, weight fraction.

ρ_{Na} = The sodium density, mg/dm³.

At this point definition of terminology is necessary. The carrier, just described, is schematically illustrated in Figure 1.

This report deals primarily with electron microprobe analyses taken at some point p on a plane at some distance y (see Figure 1). It will be shown that $d\Delta W/dt$ at p can be calculated from the microprobe concentration profiles. All values inherent to behavior at any point, such as p which is only one micron in cross section, will be identified by the absence of any mark over the symbol chosen to represent a particular parameter at that point. Of most interest to a designer are (a) average general corrosion behavior patterns and (b) the presence of any severe localized attack. This latter does not normally occur under sodium exposure conditions in regions along isothermal flow paths where the data points under discussion were collected. The discussion is, therefore, oriented toward average general corrosion behavior patterns. Among these, the pattern of greatest interest is corrosion behavior at some plane located at a distance y from some reference position. For instance, the corrosion rate of a reactor fuel element at an anticipated plane of maximum temperature. By experience, it is to be expected that the plane rate is not equal to the rate $d\Delta W/dt$ at some point on the plane, but is some local average, $d\Delta W/dt$, around the plane. The parameters reflecting this local or plane average bear the identifying mark θ above symbols that identify them as in expression (2) except that, structural metal concentrations in any sodium phase, turbulent main stream, or laminar boundary layer will be assumed uniform in any plane, and their symbol, S, will bear no capping mark.

*Two such phases in the direction indicated could be a stagnant liquid sodium boundary layer in which transient control could either be concentration gradient controlled or activity gradient controlled, as discussed by Weeks⁽⁸⁾; and an oxide layer composed of the complex oxides of iron chromium and nickel with sodium, in which transient control might occur from competition of steps 2 and 3, previously discussed.

FIGURE 1 STRUCTURAL CARRIER

Finally, the most common physical measure of general corrosion behavior is the weight change of a specimen immersed at a given position. The specimen will have a finite length and the recorded weight change will be the summation of the weight changes at all planes y . This measure, therefore, provides a length average corrosion rate of all $d\Delta W/dt$ and the parameters pertaining to such length average measurements are designated by a capping bar, such as a $d\overline{\Delta W}/dt$.

3. PARTIALLY SELECTIVE CORROSION RATE CONTROL IN ISOTHERMAL, FLOWING SYSTEMS.

a. General.

In the case of selective corrosion, either full or partial, the alloy, instead of corroding homogeneously with respect to its bulk composition, corrodes with respect to each one of its alloying elements. Thus, the energy favor is reversed so that first, the dominant corrosion couple is: $\text{Na}, \text{Na}_2\text{O} + \text{Fe}_{\text{FeCrNi}} + \text{Cr}_{\text{FeCrNi}} + \text{Ni}_{\text{FeCrNi}}$ and second, a given elemental rate, J_i , is such that, initially at $t = 0$:

$$J_i \neq C_i \cdot d\Delta W/dt.$$

If:

$$J_1^{\theta} < C_{1\infty}^{\theta} d\Delta W/dt$$

then that element is initially corroding at rates less than those dictated by its bulk alloy composition and it is termed a "noble" element for that particular corrosion couple. If on the other hand:

$$J_1^{\theta} > C_{1\infty}^{\theta} d\Delta W/dt$$

then the element is considered "active" for the particular corrosion couple in which this event occurs. The alloy corrosion rate is again:

$$d\Delta W/dt = \sum J_1^{\theta}$$

but now the contribution, and the consequent rate influence, of elemental transport in the alloy phase must be taken into account.*

In the case of an active element the mass initially corroding above stoichiometric amounts must come from within the alloy phase by diffusion toward the interface between the Na, Na₂O - alloying element reaction products and the alloy, hereafter referred to as the "reaction product - alloy interface." One of two possible mechanisms, or a combination of both, can accompany such movement. First, as noted by Manly⁽⁹⁾, the vacancies caused by active-element forward diffusion can coalesce to form voids. This phenomenon is known as "subsurface voiding", and when it is present there may be no movement of the noble element within the alloy phase lattice. In the absence of subsurface voiding, however, the alloy phase vacancies, created by forward diffusion of the active elements, must be filled by the back diffusion of the excess noble elemental mass left by the less than stoichiometric noble element corrosion, on the further assumption that this mass does not become physically detached from the alloy phase. This process will cause an upward shift in the noble element concentrations in the alloy near the "reaction product - alloy interface", and a corresponding downward shift of the active elemental alloy phase concentrations, Figure 2.

b. The Corrosion - Diffusion Couple

A dominant feature of partially selective corrosion is the coexistence of nondiffusive and of diffusive components. Previously defined as nonselective and selective fractions, their interdependence has been examined in iron and in nickel base alloys exposed to high temperature steam⁽¹⁰⁾. The fundamental relationships, in the absence of subsurface voiding and of noble element physical detachment, for an alloy composed of iron, chromium and nickel exposed so that iron acts nobly, for instance are:

$$J_{Fe}^{\theta} + J_{Cr}^{\theta} + J_{Ni}^{\theta} = d\Delta W/dt \quad (3)$$

*It should be noted that the above definitions "active" and "noble", do not have the same meaning as they do when used in thermodynamic terminology.

FIGURE 2 ELECTRON MICROPROBE TRACES TAKEN ON SPECIMEN 3402. EXPOSURE IN THE H3 INLET POSITION FOR 1446 HOURS; SODIUM VELOCITY: 7.6 fps; TEMPERATURE: 1200°F; O₂ LEVEL 12 ppm.

NOTE: HERE AS IN ALL OTHER FIGURES OF ELECTRON MICROPROBE TRACES THE '0' DISTANCE POSITION IS THE SODIUM-ALLOY INTERFACE AND THE DISTANCE IS DISTANCE INTO THE ALLOY FROM THIS INTERFACE.

$$j_{Fe(ns)}^{\theta} = C_{Fe(0)}^{\theta} d\Delta W/dt - j_{Cr(s)}^{\theta} - j_{Ni(s)}^{\theta} \quad (4)$$

$$j_{Cr(ns)}^{\theta} = C_{Cr(0)}^{\theta} d\Delta W/dt \quad (5a)$$

$$j_{Ni(ns)}^{\theta} = C_{Ni(0)}^{\theta} d\Delta W/dt \quad (5b)$$

$$J_{Cr}^{\theta} = j_{Cr(ns)}^{\theta} + j_{Cr(s)}^{\theta} \quad (6a)$$

$$J_{Ni}^{\theta} = j_{Ni(ns)}^{\theta} + j_{Ni(s)}^{\theta} \quad (6b)$$

$$J_{Fe}^{\theta} = j_{Fe(ns)}^{\theta} \quad (7)$$

where, in units of mg/dm^2 mo, except as noted:

$d\Delta W/dt^{\theta}$ = plane average alloy corrosion rate

J_i^{θ} = total plane average corrosion rate of an element i

$j_{i(ns)}^{\theta}$ = nonselective plane average corrosion rate of an element i

$j_{i(s)}^{\theta}$ = selective plane average corrosion rate of an element i

$C_{i(0)}^{\theta}$ = alloy phase interfacial concentration of an element i at the reaction product - alloy interface

and where, by definition of partial selectivity, no noble element, iron in this case, enters the reaction product by noble-element forward diffusion. Its entry into the reaction product is therefore associated only with the nonselective corrosion component as indicated by expression(7).

In the previous discussion it was also argued that the following identities must prevail everywhere in the alloy phase:

$$\Sigma C_i = 1 \quad (8)$$

$$\left| \Sigma D_{iN} \partial C_{iN} / \partial x \right| = \left| \Sigma D_{iA} \partial C_{iA} / \partial x \right| \quad (9)$$

in which D_i is the alloy phase diffusivity of an element i. That is: the elemental concentrations must sum to unity and the elemental diffusion fluxes, in satisfaction of mass conservation, must

balance. A further argument was, that if the elemental alloy phase diffusion processes can be assumed to be linearly additive then separate fractions of the noble element can be assigned to each active element, so that in the iron-chromium-nickel alloy of the above example, for instance:

$$\left| D_{\text{Fe}} \partial C_{(\text{Fe-Cr})} / \partial x \right| = \left| D_{\text{Cr}} \partial C_{\text{Cr}} / \partial x \right| \quad (10a)$$

$$\left| D_{\text{Fe}} \partial C_{(\text{Fe-Ni})} / \partial x \right| = \left| D_{\text{Ni}} \partial C_{\text{Ni}} / \partial x \right| \quad (10b)$$

The sum of expressions (10a and b) leads back to expression (9). The concept leads to two iron fractions, Fe-Cr and Fe-Ni, each a mirror image of its corresponding active element, and both summing to the total iron concentration profile, as illustrated in Figure 3. The concept is vital to the successful kinetic interpretation of concentration profiles furnished by electron microprobe scans of specimens exposed to partially selective corrosion environments.

The development of analytical expressions for concentration profile description in the discussion of partially selective corrosion in high temperature steam treated the excess noble mass as an instantaneous source and explicitly ignored any influence that the moving reaction product-alloy interface might exert analytically⁽¹⁰⁾. A more general approach would treat the excess noble mass as a continuous source and would explicitly recognize the interface movement.

The latter recognition is based on the probability that, contrary to the sequential occurrence of the nonselective corrosion component followed by the selective, or diffusion component that was postulated in the steam exposure analysis⁽¹⁰⁾, these components occur simultaneously. Under these circumstances diffusion transport is occurring across a phase separation boundary that is moving with respect to the movement of the diffusing species. In the absence of such movement Fick's second law would apply everywhere in the alloy phase with its distance coordinate referenced to the interface. In the presence of such movement it applies everywhere in the alloy phase only when the distance coordinate of the alloy phase is referenced to the initial alloy - environment position at $t = 0$. When referenced to the moving interface the basic diffusion law, Appendix II, for the concentration change, w. f., of any element i with respect to time, months, and distance, dm , from the interface, is given by:

$$\partial C_i / \partial t = D_i \partial^2 C_i / \partial x^2 + (d\Delta W / \rho_a dt) \partial C_i / \partial x \quad (11)$$

assuming a constant alloy phase diffusion coefficient, D_i , dm^2/mo , for any element i .

Specific solutions of expression (11), applicable for continuous source concepts, can be found for two important total corrosion rate laws. The first is when $d\Delta W/dt$ is parabolic. The second, and the one of greatest interest to those concerned with APED's sodium corrosion program, is when $d\Delta W/dt$ is constant. That is, when linear rate laws control the partially selective corrosion

CONSIDER NOBLE ELEMENT N TO HAVE A FRACTION (NA1) ASSIGNED TO ACTIVE ELEMENT A1 AND A FRACTION (NA2) ASSIGNED TO ACTIVE ELEMENT A2. THEN $C_{(NA1)\infty} = 0.6 \times 3/4 = 0.45$ AND $C_{(NA2)\infty} = 0.6 \times 1/4 = 0.15$. $C_{(NA1)}$ PROFILE ON LEFT IS A MIRROR IMAGE OF C_{A1} ABOVE AND $C_{(NA2)}$ IS A MIRROR IMAGE OF C_{A2} ABOVE.

FIGURE 3 SCHEMATIC REPRESENTATION OF NOBLE ELEMENT FRACTION ASSIGNMENT TO TWO ACTIVE ELEMENTS

process. When $d\Delta W/dt = \text{constant} = R$, for instance, a particular solution of expression (11), (as the proper differentiation will show), valid for diffusive description of an instantaneous source deposited initially against the moving interface ($x = 0$), and diffusing across the interface in the direction of its movement, is:

$$C_{i(N)} = A_{i(N)} x \left[2\rho_a (R/\rho_a) t \sqrt{\pi D_{i(N)} t} \right]^{-1} \exp \left[-(x^2/4D_{i(N)} t + R^2 t/4\rho_a^2 D_{i(N)} + Rx/2\rho_a D_{i(N)}) \right] \quad (12)$$

in which:

$A_{i(N)}$ = an amount (of a noble element), mg/dm^2 , originally deposited at $t = 0$, in the plane $x = 0$, which moves with velocity R/ρ_a in the direction of the diffusion of the element

$C_{i(N)}$ = the concentration, w.f., of the noble element, as a function of distance $x(\text{dm})$ measured inward from the moving interface ($x = 0$), and of time t , months.

ρ_a = alloy phase density, mg/dm^3

$D_{i(N)}$ = alloy phase diffusion coefficient of noble element $i(N)$, dm^2/mo

R = linear rate law constant for alloy phase mass conversion (alloy phase corrosion rate), $\text{mg/dm}^2 \text{mo}$

Consider now the partially selective corrosion process that produced the profiles of Figure 2, and the principles that allow the profiles to be represented as in Figure 3. The excess iron generated per unit time by the sweep of $d\Delta W/dt = R$ cannot accumulate at the reaction product - alloy phase interface, but must be absorbed by the alloy phase as fast as it is formed. It therefore constitutes a continuous source⁽¹¹⁾, which may be divided, through expressions (10a and b), into an iron-chromium fraction and an iron-nickel fraction, respectively of strengths $j_{\text{Cr}(s)}$ and $j_{\text{Ni}(s)}$. When $d\Delta W/dt$ is constant, ($= R$), the latter two rates will generally also be constant and the noble fraction profiles, which are the mirror images of each active element profile, can be described, for the iron chromium profile, for instance, by:

$$C_{(\text{Fe-Cr})} = \int_0^t j_{\text{Cr}(s)} x \left[2Rt \sqrt{\pi D_{\text{Cr}} t} \right]^{-1} \exp \left[-(x^2/4D_{\text{Cr}} t + R^2 t/4\rho_a^2 D_{\text{Cr}} + Rx/2\rho_a D_{\text{Cr}}) \right] dt + I \quad (13)$$

in which I is an integration constant and in which all other terms and their units have previously been defined.

Once $D_1(A)$ is known, expressions similar to (13) will provide estimates of the alloy corrosion rate, R , and of the individual active alloying element rates, $J_1(A)(s)$, for the selective component of any given active element, $i(A)$, whose concentration profile is known. The noble element non-selective rate is then available from expression (4), and the nonselective components of the active elements are available from expressions (5a, b, etc for as many active elements as the system has, and for which concentration profiles are obtainable). From these rates expressions such as (2) can be written which will give the specific wall corrosion rate constants of the individual alloying elements for a partially selective corrosion process.

c. Alloy Corrosion Rate Considerations

Any diffusion controlled process in a semi-infinite medium will normally obey parabolic rate laws. Were diffusion in the alloy phase the rate controlling step therefore, one would expect alloy weight losses to be proportional to the square root of time. In most high-temperature oxidizing environments, however, metal weight losses tend, after some short-lived nonlinear transient, to become linear with respect to time⁽¹²⁾. Such is the case of the weight-loss time response in APED's sodium mass transfer test loops⁽¹³⁾, indicating that rate control is exerted elsewhere than within the alloy phase.

The existence of two intermediate transport phases, in one of which eventual rate control will be provided, can readily be imagined between the alloy and the turbulent, bulk sodium stream. The first, Figure 4, is an essentially stagnant, liquid sodium boundary layer (bl), and the second is an oxide film, adjacent to the alloy phase. Assuming perfect mixing at the bulk sodium-bl interface, and recalling that there can be no accumulation in the bulk stream at a given plane along an isothermal sodium flow path, then transient nonlinear corrosion rates can result while diffusive accumulation is occurring in the bl until either its dissolved alloying element concentration, or activity, gradients become linear. If these are very rapid steps, a nonlinear transient could be imposed at the bl-oxide interface if some resistive mechanism were operative to prevent immediate achievement of the saturated concentration, S_1^0 , of a given alloying element i , in the bl at this interface.

The liquid sodium boundary layer thickness is velocity dependent. As such, if it is too thin to provide the observed nonlinear transient time magnitude (between 700 to 1400 hours), control can be exercised in the oxidation product. If this phase contains the rate controlling step, that step is most probably associated with the oxide phase boundaries. This probability results from a corollary probability that transport in the oxide is steric-defect dependent and therefore has a constant gradient (either concentration or activity) through the oxide film. If oxide reduction (step 3, Section III-1), is rate controlling, then alloy corrosion linear rate control will be achieved when the oxide film thickness becomes constant, that is: when the reduction rate at the lsbl interface equals the oxidation rate at the oxide-alloy interface. If the rate of oxidation is the rate-controlling step then linear rate laws will be imposed when thermodynamic equilibrium is

FIGURE 4 SCHEMATIC REPRESENTATION OF TRANSPORT PATHS

established between the oxidant (Na_2O) and the alloy phase interfacial concentrations as dictated by the free energy concepts of reactions such as:

If this mechanism exerts control the partially selective corrosion process must be such that the elemental alloy phase surface concentrations vary in time, at least during the nonlinear transient period.

Such is the theoretical picture.

IV. EXPERIMENTAL

1. SPECIMENS.

The discussion involves only the behavior of Type-316 stainless steel (nominal composition in weight fractions: iron 0.668, chromium 0.168, nickel 0.125, manganese 0.0159, molybdenum 0.0192, carbon 0.0005, others -principally silicon and phosphorus- 0.0034) immersed in the hot legs of the Projects sodium mass transfer test loops in sodium containing 12 ppm oxygen. The design and operation of these loops has been detailed elsewhere.⁽¹⁴⁾ For purposes of orientation the design is schematically shown in Figure 5, primarily for geometry considerations required in Section V, paragraphs 6a and 6b, for determination of wall corrosion constants in conjunction with the loop dimensions given in Appendix III.

Microprobe traces were taken on "hockey stick"⁽²⁾ samples (inserted in the sample holders labeled H2, H3, H3R, in the hot leg) and on "in-pipe" samples (inserted in the pipes connecting the H3-H3R sample holders). The exposure conditions for the specimens, on which traces were obtained, are given in Table I. As noted in column 2 (Table I) traces were taken only on specimens immersed in loops 2, 3 and 4. The hot legs of all three loops were constructed entirely of Type-316 stainless steel; the cold legs of loops 2 and 3 were constructed from $2\frac{1}{4}$ Cr-1 Mo alloy steel, and the cold leg of loop 4 was constructed from 5 Cr- $\frac{1}{2}$ Mo- $\frac{1}{2}$ Ti alloy steel. The Type-316 stainless steel components of loops 2 and 3 picked up significant amounts of carbon,⁽¹⁵⁾ but it is assumed that carbon migration does not seriously affect either the driving forces nor the trace forms in partially selective corrosion in this instance. The run conditions indicated by the roman numerals in column 2, Table I, are given in Table II.

Following the indicated exposure (Table II) the specimens were removed from the test loop position, cleaned and weighed in a standard sequence.⁽²⁾ Metallographic sections were then prepared, generally in a bakelite mount with epoxy resin protection for the specimen - mount edge. These sections were used in obtaining the microprobe traces. It should be noted that metallographic sections have been taken on all of the specimens exposed in the broad general test program (some two thousand specimens). Only a small fraction of the specimens exposed were deemed necessary to be examined by the electron microprobe.

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FIGURE 5 LOOP ARRANGEMENT

TABLE I

Type-316 Stainless Steel Specimens Exposed to Flowing Sodium (Containing 12 ppm O₂)
and Subsequently Examined by the Electron Microprobe

Specimen Number	Loop and Run Number ⁽¹⁾ and Run Type	Exposure					Weight Loss mg/dm ²	Photo Micrographs Ref. Figure No.
		Flow Rate Gallons/Minute	Total Time, Hours	Temp. °F	Velocity feet/sec	Position ⁽²⁾		
3312 ⁽³⁾	3-7-II	0.70	2964	1200	1	in pipe ⁽⁴⁾	39.2 ⁽⁵⁾	A-1, A-2
3303 ⁽³⁾	3-7-II	0.70	8208	1200	1	in pipe ⁽⁴⁾	140.5 ⁽⁵⁾	A-3, A-4
4113 ⁽³⁾	4-4-IIB	0.35	2809	1200	3.6	H1I	139.4	A4-5, A4-6
4211 ⁽³⁾	4-4-IIB	0.35	2809	1200	3.6	H2I	43.9	A4-7, A4-8
4513 ⁽³⁾	4-4-IIB	0.35	2809	1200	3.6	H3I	Gain	A4-9, A4-10
2507	2-5-II	0.70	14101	1200	7.6	H3RI	154.3	A4-11
3402 ⁽³⁾	3-7-II	0.70	1446	1200	7.6	H3I	107.7	A4-12, A4-13
2401 ⁽³⁾	2-4-II	0.24	2800	1200	2.6	H3I	80.0	A4-14, A4-15
3403 ⁽³⁾	3-7-II	0.70	2813	1200	7.6	H3I	170.4	A4-16, A4-17
3408 ⁽³⁾	3-8-IV	0.70	5629	1200	7.6	H3I	358.7	A4-18
2481	2-5-II	0.70	2805	1200	23	H3O	183.2	A4-19
3485 ⁽³⁾	3-8-IV	0.70	5629	1200	23	H3O	524.7	A4-20
2485	2-5-II	0.70	5704	1200	23	H3O	398.0	A4-21
2486	2-5-II	0.70	5704	1200	23	H3I	552.5	A4-22
2482 ⁽³⁾	2-5-II	0.70	6971	1200		H3I	612.1	A4-23, A4-24
2206 ⁽³⁾	2-5-II	0.70	14101	1100	7.6	H2I	217.9	A4-25
2207 ⁽³⁾	2-5-II	0.70	14101	1100	7.6	H2I	219.6	A4-26

(1) During or after which specimens were removed.

(2) Last letters I and O refer to inlet and outlet of sample holder.

(3) Duplicate traces, see Appendix IV.

(4) Between H3 and H3R specimen holders

(5) Corrected for carbon pickup. Not done for others since carbon gain is small fraction of the weight loss.

TABLE II
Test Plan Parameters

Run Type	T max °F	ΔT °F	Oxygen Level ppm
I	1200	500	~50
II	1200	500	~12
III	1100	500	~12
IV	1200	250	~12
V	1100	250	~50

ΔT = temperature differential between hottest (H3 sample section) and coldest (C3 sample section) in the loop.

Run Type IIB = all four hot leg sample holders run at 1200 F (ordinarily H1 at 1000 F, H2 at 1100 F and H3 and H3R at 1200 F, except in types III and V where they operate at 100° F lower temperature).

2. MICROPROBES.

Trace data obtained on the specimens listed in Table I, are contained in Appendix IV. These data were furnished by the following laboratories.

1. Materials Analysis Company (MAC)
81 Encina Avenue
Palo Alto, California
2. Advanced Metals Research Corporation (AMR)
625 McGrath Highway
Somerville, Massachusetts
3. Materials Testing Laboratories (MTL)
6800 East Washington Blvd.
Los Angeles 22, California

It is not within the scope of this report to discuss the relative merits of each of the three instruments used to obtain the trace data. Therefore only general principles, applicable to all three, involved in electron probe microanalysis will be summarized. More detailed descriptions of these principles have been presented in other publications^(10, 16). The value of the instrument lies in its microanalytical capacity which enables it to provide composition measurements at approximately one micron (μ), $1\mu = 10^{-5}$ dm, intervals. This is achieved by the excitation of characteristic elemental x-rays under the energy of a narrow electron beam, generally one micron or less in diameter, falling after appropriate magnetic focusing, on the surface of the specimen. The beam energy is generally provided by acceleration in fields of approximately 30 kilovolts; and of the

resulting elemental x-rays, those characteristic of $K\alpha$ radiation are generally monitored in the iron-chromium-nickel system. The monitoring process is accomplished using spectrometers set at the appropriate Bragg angle for a desired element. The spectrometer "collects" the characteristic x-radiation and "prints" its intensity, which is proportional to the amount of a given element in the region excited by the primary electron beam. The analyst then reduces the x-ray intensity data to weight percent, using the proper corrections for secondary fluorescence and for adsorption. The emission of x-radiation is a fluorescing process, and x-rays can be stimulated by both the incident electron beam and by other x-rays so produced. Also some elements will adsorb the x-radiation of other elements. It is for these reasons that corrections of the x-ray intensity data must be made. Corrections depend upon the relative amounts of the major elements present and in the iron-chromium-nickel system, where compositions are similar to those of the specimens under discussion, these correction factors provide weight fraction measurements (Appendix IV) accurate to about $\pm 5\%$ of the value recorded. Thus to establish a concentration profile the analyst "scans" his specimen by moving it through the electron beam and recording the elemental x-radiation intensity. The analyst may move the specimen step by step, a process called "point by point" counting, or he may drive it at a given speed through the beam, a process known as "motor-driven scanning". The number of spectrometers and the number of elements dictate how many times a path must be traversed. The MAC scans were performed manually point by point, with one spectrometer, the AMR scans were motor-driven at a rate of one micron every twelve seconds, using one spectrometer, and the MTL scans were point by point, automated, with three spectrometers.

Trace appearances, after reduction to weight fractions, do not generally suggest anomalous behavior. In the case of iron which behaves nobly in an alloy of stainless steel exposed to sodium (containing 12 ppm of oxygen) which is unsaturated with respect to chromium and nickel, one would expect to find progressing from the interior to the surface of a specimen, a steady increase in the iron concentration. Occasionally there may be slight disturbances at grain boundaries, and in the case of Type-316 stainless steel other disturbances which have been attributed to molybdenum. In general, however, the iron (and active element) concentration profiles behave monotonically throughout the alloy phase until nearing the alloy - mounting material interface. Here there is a consistent drop, consistent from specimen to specimen, within the alloy phase of all major elements. The drop is attributable to x-ray source area effects. They have been explored to some extent⁽¹⁰⁾ where their behavior was pertinent to an oxide-alloy interface. The effects are of sufficient importance in trace interpretation to warrant a brief discussion of their behavior at an alloy-metallographic mount interface. This behavior is one that is of primary concern in this report, since any oxide that may have been present on the majority of the specimens during sodium exposure is never detectable after cleaning and mounting.

The origin of the x-ray source area effects is explained in Appendix V. Because of these effects it is difficult to get a true concentration reading within one and one half microns from the mount-alloy interface. As discussed in this report this may make both slope and concentration

measurements at the interface doubtful. Ideally, when concentration drops occur near the mount-alloy interface, established by the microprobe analyst, the true interface should be located 1.5 microns from the point where the drop begins, see Figure 6, for a beam diameter of one micron. The analyst ordinarily will allow his customer, in this case APED, to factor the effect of the x-ray source area into the customer's trace interpretation approach. The interface that the analyst lists is where specimen current and back-scattered electron intensity change abruptly. These two quantities are highly dependent upon the nature of the surface that the electron beam strikes and upon changing from metal to plastic they exhibit a drastic change. However the trace data in Appendix IV show a sufficient number of cases where there is no concentration drop before the interface, fixed by the analyst, so that it has been assumed in all cases that the interface imposed by the analyst (MAC, AMR or MTL) is essentially the true interface, $x=0$.

FIGURE 6 X-RAY SOURCE AREA EFFECT ON NOBLE ELEMENT (IRON IN THIS INSTANCE) TRACE BEHAVIOR NEAR THE INTERFACE

V. DISCUSSION

1. GENERAL.

Examination of the trace data listed in Appendix IV shows that chromium, nickel and manganese behave actively in ascending sodium temperature regions of 1100°F and 1200°F provided that the sodium stream that bathes Type-316 stainless steel surfaces is unsaturated with respect to these elements. Under identical conditions in the same regions iron behaves nobly. Molybdenum seems to have no clearly defined pattern and is therefore assumed to behave neutrally.* As the isothermal flow distance is increased and the flowing sodium becomes saturated the chromium and nickel profiles cease to show the characteristic active-element-concentration drop and begin to show a characteristic** noble-element-concentration increase. Under the same circumstances, the formerly noble iron now behaves actively (Figure 7) while manganese remains active.

Trace examination also reveals that the partially selective corrosion process that preferentially removes chromium and especially nickel, results in a massive diffusivity change where the corresponding face-centered to body-centered cubic phase transformation occurs in the alloy phase. The phase transformation does not always occur at the same chromium and nickel concentration. (See Figure 8.) It is postulated (Figure 9) that this concentration discrepancy depends upon the relative selective corrosion rates of chromium and of nickel. When the initial selective chromium rate is substantially higher than the initial selective rate of nickel the alloy composition shift will occur along line 1 (Figure 9) and will be accompanied by a face-to-body centered transformation at a low concentration of the active elements. On the other hand, as shown by line 2 (Figure 9) if the initial selective nickel rate is higher than its chromium counterpart the crystallographic transformation will occur at a higher concentration of the active elements.

The curves in Figure 8 are typical of a well ordered active element profiles in the presence of a sharp change in diffusivity. It is noteworthy that in the body-centered cubic region, that defined in Figure 8 as $0 \leq x < x_d$, the expected increase in diffusion coefficient magnitude (which can be several orders) provides an essentially linear profile. In several instances the length of this linear run is not very great, but the active element profile behavior is sufficiently well ordered, as in Figure 10 for example, to permit concentration drops to be ignored that occur near the interface, $x = 0$ as a result of x-ray source area effects. There are some cases,

*Neutral behavior is defined as that exhibited by an element that corrodes in stoichiometric proportions at all times of immersion.

**The definition "characteristic" is sensitive to oxygen contamination level. The active - noble combination noted above is characteristic of sodium contaminated with 12 ppm oxygen in the temperature ranges given. It is known that higher oxygen contamination levels alter this combination.

FIGURE 7 SELECTIVITY SHIFT WITH LOOP POSITION. SPECIMENS AS NOTED AT 1200°F, FOR 2809 HOURS, AT 3.6fps, O₂: 12 ppm.

FIGURE 8 EVIDENCE FOR FCC SHIFT AT DIFFERENT CHROMIUM AND NICKEL CONCENTRATIONS

FIGURE 9 SCHEMATIC ILLUSTRATION OF SHIFT FROM FCC TO BCC PHASE. 1200°F ISOTHERM OF Fe-Cr-Ni SYSTEM.

FIGURE 10 ELECTRON MICROPROBE TRACE OF CHROMIUM IN SPECIMEN 2486. AN EXAMPLE OF EXCELLENT ORDER IN THE PRESENCE OF A DIFFUSIVITY SHIFT.

however, as identified in Table III, where a diffusivity shift has occurred but where the profiles are not sufficiently well ordered, especially with respect to x-ray source area effects, to characterize it. Examples of such behavior are illustrated in Figure 11. In Figure 11a the profile could be extrapolated by the analyst to the interface $x = 0$ to give a positive value of the alloy phase interfacial concentration, thereby allowing the process to be treated as though no diffusivity shift had occurred. The designation "undefined 1" (UND 1) has been given to such profiles. In Figure 11b the profile cannot be extrapolated to a positive concentration at $x = 0$. Such profiles have been labeled "undefined 2" (UND 2).

There is one more profile category which can not be characterized for either the case for which no diffusivity change occurs (Figure 12 is an example of a fairly well ordered trace that does not involve a diffusivity change), or for those in which diffusivity changes do occur. The origin of the trace disturbance is not well understood, and such traces, of which Figure 13 is an example, have been labeled "disordered" (DIS).

2. DATA ANALYSIS.

a. Methods

All traces, except possibly those of specimen 3402 (Table I) taken after a total exposure of approximately 2 months, were taken after the onset of linear rate control for the alloy corrosion behavior. That is: when $d\Delta W/dt = \text{constant} = R$. The time for this onset has been established elsewhere as occurring at from 1 to 1.5 months. Therefore the proper trace descriptive expressions are (Appendix II):

(i) Diffusivity change absent

$$C_i - C_{i\infty} = (j_{i(s)}/2R) \left\{ \text{erfc}(u_{x,t}) + \exp(-Rx/\rho_a D_i) \text{erfc}(v_{x,t}) \right\} \quad (14)$$

(ii) Diffusivity change present

in the region $0 \leq x < x_d$

$$C_{i1} - C_{i\infty} = (j_{i(s)}/R) + I_1 \left\{ \text{erf}(u_{x,t}) + \exp(-Rx/\rho_a D_{i1}) \text{erf}(v_{x,t}) \right\} \quad (15)$$

in the region $x \geq x_d$

$$C_{i2} - C_{i\infty} = I_2 \left\{ \text{erfc}(u_{x,t}) + \exp(-Rx/\rho_a D_{i2}) \text{erfc}(v_{x,t}) \right\} \quad (16)$$

NOTE: Symbols described on page 40.

FIGURE 11 EXAMPLES OF POORLY ORDERED TRACES. SPECIMEN 3408-2. EXPOSED AT 1200°F FOR 5629 HOURS, H3 INLET, 7.6 fps, 12 ppm O₂

**FIGURE 12 ELECTRON MICROPROBE TRACE OF CHROMIUM IN SPECIMEN 3312-2.
 AN EXAMPLE OF GOOD ORDER IN THE ABSENCE OF A DIFFUSIVITY SHIFT.**

**FIGURE 13 ELECTRON MICROPROBE TRACE OF NICKEL IN SPECIMEN 3485-2.
AN EXAMPLE OF EXTREME DISORDER IN THE BCC REGION**

in which:

C_i = the concentration of an active element i in the alloy phase compositionally changed region weight fraction (w.f.)

$C_{i\infty}$ = the bulk alloy phase concentration of an active element i , w.f.

$j_{i(s)}$ = the selective corrosion rate constant of an active element i , $\text{mg}/\text{dm}^2 \text{ mo.}$

R = the alloy corrosion rate, $\text{mg}/\text{dm}^2 \text{ mo.}$

$$u_{x,t} = x/2\sqrt{D_{i.}t} + R\sqrt{t}/2\rho_a\sqrt{D_{i.}}$$

$$v_{x,t} = x/2\sqrt{D_{i.}t} - R\sqrt{t}/2\rho_a\sqrt{D_{i.}}, \text{ and where, in}$$

$u_{x,t}$ and $v_{x,t}$, $D_{i.}$ signifies the diffusion coefficient for the appropriate region.

x = distance into the alloy phase, dm

D_i or $D_{i.}$ = diffusion coefficient of an active element i , $\text{dm}^2/\text{mo.}$

t = exposure time, after the onset of linear rate
rate control, months.

ρ_a = alloy phase density, mg/dm^3 .

I_1 and I_2 = integration constants, having concentration units, w.f.

In applying expressions (14), (15) and (16) to microprobe trace analysis the extent of the compositional change that occurred during the 1 to 1-1/2 month nonlinear transient period must be accounted for. If it is assumed that the transient rate control is parabolic the composition change^[17] during the transient period will be given by:

$$C_i - C_{i\infty} = \left(k_i / k_p \sqrt{\pi} \right) \exp \left(+k_p^2 / \rho_a^2 D_i \right) \int_{f(x,t)}^{\infty} \sum_0^{\infty} (-1)^n \left(\rho_a \sqrt{D_i} / k_p \right)^n (\lambda)^n \exp(-\lambda^2) d\lambda \quad (17)$$

Expression (17) applies to the case where there is no diffusivity change. Similar expressions can be derived for cases where there is a diffusivity change. In expression (17):

k_i = the transient period rate constant of an active element i , $\text{mg}/\text{dm}^2 \text{ mo.}$

k_p = the transient period parabolic rate constant for the alloy corrosion,
 $\text{mg}/\text{dm}^2 \text{ mo.}$

$$f(x, t) = x/2\sqrt{D_i t_{n1}} + k_p/\rho_a \sqrt{D_i}$$

and where the other parameters are defined as before, except that t_{n1} is the time during the nonlinear transient, mo.

Expression (17), or its equivalent in the presence of diffusivity changes, will establish the extent of composition change at the onset of linear rate control. To a first approximation such changes could be treated as instantaneous sources and would vanish in time according to expression (12), in which, now, the source strength A_i would be replaced by:

$$A_i = \int_0^\infty (C_i - C_{i\infty}) dx$$

where the integrand is given by expression (17) with $t_{n1} = t_{nlc}$, t_{nlc} being the time span required for the onset of linear rate control. For the purposes of this report t_{nlc} shall be taken as being equal to 1-1/4 months. Since most of the traces herein involved were taken after fairly long exposure periods compared to t_{nlc} of 1-1/4 months of nonlinear weight-change-time behavior it is probable that the effect of the nonlinear transient source is small. It is assumed for the purposes of this discussion that it has a particularly small effect upon the trace slopes.

There need be no concern over the behavior of the alloy phase interfacial concentrations at the oxide (or mount) alloy interface. These constant surface concentrations at $x = 0$ in expressions (14), (15) and (16) will be those dictated by setting $x = 0$ in expression (17). Thus:

$$C_{i(0)} - C_{i\infty} = \left(k_i / k_p \sqrt{\pi} \right) \exp \left(k_p^2 / \rho_a^2 D_i \right) \int_{k_p / \rho_a \sqrt{D_i}}^\infty \sum_0^\infty (-1)^n \left(\rho_a \sqrt{D_i} / k_p \right)^n (\lambda)^n \exp(-\lambda^2) d\lambda$$

Slope and critical concentration (at $x = 0$ and at $x = x_d$) will therefore be used in the following trace analysis. Before starting it, however, it should be noted that there is an additional analytical technique that might have occasional merit since it does not require the iteration required to pull the corrosion constants from expressions (14), (15) and (16) were they to be used with each concentration value in a given profile. The trace disturbances previously

discussed, that is those that are undefined or disordered, make it difficult to assess accurate slope and critical concentration values for those profiles where such disturbances occur. This alternate technique would use the areas under each elemental profile, since these areas are proportional to the selective mass having been corroded in a given exposure time. However, as illustrated in Figure 14, such areas may be far more affected by the nonlinear transient than are the slopes and therefore are not used in this discussion.

FIGURE 14 SCHEMATIC ARGUMENT AGAINST USING PROFILE AREA (EXTENT OF NON-LINEAR TRANSIENT MAY HAVE A SIGNIFICANT EFFECT ON AREA BUT SMALL EFFECT ON SLOPES)

b. Equilibrium Concepts

Note that the interplay between error function (erf), error function complement (erfc) and the exponential terms in expressions (14), (15) and (16) will render these expressions independent of time when the term $R\sqrt{t}/2\rho_a\sqrt{D_i}$ is approximately numerically equal to 1.822. For

$\text{erf}(1.822) = 0.99$, essentially one, and $\text{erfc}(1.822) = 0.01$, essentially zero. Under these circumstances expressions (14), (15) and (16) reduce to:

(i) Diffusivity Change Absent

$$C_i - C_{i\infty} = (j_{i(s)}/R)\exp(-Rx/\rho_a D_i) \quad (18)$$

(ii) Diffusivity Change Present

in the region $0 \leq x < x_d$

$$C_{i1} - C_{i\infty} = (j_{i(s)}/R) + I_1 \left[1 - \exp(-Rx/\rho_a D_{i1}) \right] \quad (19)$$

in the region $x \geq x_d$

$$C_{i2} - C_{i\infty} = 2I_2 \exp(-Rx/\rho_a D_{i2}) \quad (20)$$

In the case of expressions (19) and (20) the integration constants may be evaluated at $x = x_d$ where the concentration $C_i = C_{id}$, that concentration at which the diffusivity changes from D_{i1} in the body-centered cubic region to D_{i2} in the face-centered cubic region. Once the integration constants are determined and remembering that the D_{i1} region profiles are essentially linear, so that the term $[1 - \exp(-Rx/\rho_a D_{i1})]$ is approximately equal to $Rx/\rho_a D_{i1}$, the pertinent slope and critical concentration relationships are:

(i) Diffusivity Changes Absent

$$\left. \frac{dC_i}{dx} \right|_{x=0} = -j_{i(s)}/\rho_a D_i \quad (21)$$

$$C_{i(0)} - C_{i\infty} = j_{i(s)}/R \quad (22)$$

(ii) Diffusivity Changes Present

in the region $0 \leq x \leq x_d$

$$\left. \frac{dC_{i1}}{dx} \right|_{\text{all } x, 0 \leq x \leq x_d} = -(C_{i1(0)} - C_{id})/x_d \quad (23)$$

$$C_{i1(0)} - C_{i\infty} = j_{i(s)}/R \quad (24)$$

in the region $x \geq x_d$

$$dC_{12}/dx = -(C_{1d} - C_{1\infty})R/\rho_a D_{12} \quad (25)$$

That the slope expressions bear a negative sign reflects the fact that we are working with the mirror image iron fractions of the active elements 1.

The large number of metallographic sections taken in the over-all program offer strong experimental evidence that the composition changes brought on in annealed Type 316 stainless steel by partially selective corrosion processes in the Projects sodium test loops reach an average equilibrium value of about 12 microns (1/2 mil or 0.0005 in.) thick. In particular the test loop exposure conditions of specimens 2507 (H3R inlet, 1200 F, 7.6 ft/sec sodium flow velocity, 12 ppm contaminating oxygen, loop ΔT of 500 F) and 2482, 2486 (H3 inlet, 1200 F, 23 feet per second sodium flow velocity, 12 ppm oxygen, 500 F ΔT) provided a family of specimens of varying times of exposure that produced Figure 15 ⁽¹⁹⁾. It shows that the high-velocity family reaches equilibrium in 9.33 months and the low-velocity family reaches equilibrium in 28 months. Table III, listing the slope and critical concentration values for the microprobe profiles taken on the specimens in Table I, shows that several of the traces, in the column labeled x_0 (where x_0 equals the observed metallographic extent of composition change available from the photomicrographs in Appendix IV) were taken in regions where the change depth is approximately 12 microns. In particular this is apparent for specimens 2206, 2207, 2507, 2482, 2485 and 2486. This is important for reasons discussed in the following paragraph. Remembering that Figure 15 is based on averages, and that the extent of compositional change varies from spot-to-spot on a given specimen, all the trace data in Table III will be analysed as though the particular composition change for that trace were at equilibrium. Independent checks, as shown later, will test the validity of this assumption for each profile.

c. Slope Adjustment Considerations

In expressions (21) through (25) there are always three unknowns and but two independent expressions. The third expression is provided by

$$R\sqrt{t_e}/2\rho_a\sqrt{D_{1e}} = 1.822 \quad (26)$$

the equilibrium condition previously examined (paragraph V-2b). Expression (26) in conjunction with either expression (21) or (25), as the case may be, allow R to be determined, from which expressions (22) or (24) allow evaluation of $J_1(s)$. There is, however, one additional factor that

FIGURE 15 GROWTH OF BCC LAYER ON TYPE 316 SPECIMENS EXPOSED DURING RUN 2-5. METALLOGRAPHIC AVERAGE OF MANY SPECIMENS. H3 INCLUDES BOTH INLET AND OUTLET, WHICH WERE BOTH AT 23 fps. H3R IS INLET ONLY, 7.6 fps. ALL 1200° F, 12 ppm O₂. MEASUREMENTS ARE SIMILAR TO THOSE LABELED X₀, THIS REPORT.

TABLE III-1

Critical Microprobe Trace Values (as measured) for
Manganese after Isothermal Exposure to Flowing Sodium
(containing 12 ppm oxygen) at 1100 F and 1200 F.

Specimen Number	Exposure Time mo ⁽¹⁾	$C_{(o)}$ w. f.	$C_{(d)}$ w. f.	X_d dm $\times 10^{-5}$	X_o dm $\times 10^{-5}$	(2) dC_1/dx_1 w. f./dm $\times 10^{-3}$	(3) dC_2/dx_1 w. f./dm $\times 10^{-3}$
<u>1100 F</u>							
2206-1	18.33	0.0004	0.0013	1.8	10.0	0.04	0.68
2207-1	18.33	0.0008	0.0016	3.8	6.0	0.02	0.86
<u>1200 F</u>							
4113	2.65	0.0010	----	---	9.3	0.08 ⁽⁴⁾	---
4211	2.65				UND-2		
2507	18.33	0.0016	0.0064	8.8	10.0	0.07	0.52
3402	0.76	0.0024	0.0095	4.4	5.2	0.16	0.30
2401	2.65	0.0022	0.0064	3.4	6.6	0.12	0.50
2481	2.65	0.0002	0.0022	2.8	8.0	0.03	0.56
2485	6.67				UND-2		
2486	6.67	0.0002	0.0022	3.6	10.0	0.06	0.70

(1) after onset of linear rate law control (times listed = total immersion time - 1.25 mo). One month taken as 720 hours.

(2) at all x , $0 \leq x \leq x_d$ except as noted in (4) below.

(3) at $x = x_d$.

(4) in absence of diffusivity change, slope at $x = 0$ reported here.

TABLE III-2
Critical Microprobe Trace Values for Chromium
(exposure as in Table III-1)

Specimen Number	Exposure Time mo ⁽¹⁾	C ₍₀₎ w.f.	C _d w.f.	X _d dm x 10 ^{7/5}	X ₀ dm x 10 ^{7/5}	(2) dC ₁ /dx w.f./dm x 10 ⁻³	(3) dC ₂ /dx w.f./dm x 10 ⁻³
<u>1100 F</u>							
2206-1	18.33	0.051	0.058	3.8	10.0	0.20	4.3
2206-2	18.33	0.048	0.055	3.7	10.0	0.20	6.6
2207-1	18.33	0.042	0.051	2.4	6.0	0.30	4.0
2207-2	18.33	0.046	0.067	2.3	6.0	0.80	4.5
<u>1200 F</u>							
3312-1	2.87	0.118	----	----	8.0	1.5 ⁽⁴⁾	---
3312-2	2.87	0.10	----	----	8.0	1.9	---
3303-1	10.15	0.072	0.084	9.8	16.0	0.15	4.5
3303-2	10.15	0.070	0.082	9.8	12.8	0.15	4.3
4113	2.65	0.087	----	----	9.3	0.45	---
4211	2.65	0.101	----	----	7.9	0.60	---
4513					WEIGHT GAIN		
2507	18.33	0.088	0.107	7.9	10	0.23	2.4
3402	0.76	0.083	0.106	4.2	5.2	0.60	2.1
2401	2.65	0.104	0.121	5.4	6.6	0.40	3.3
3403-1	2.65	0.048	0.054	3.0	5.0	0.20	5.9
3403-2	2.65				UND-1		
3408-1	6.57	0.054	0.072	4.0	3.7	0.40	2.9
3408-2	6.57				UND-1		
2481	2.65	0.053	0.064	3.0	8.0	0.40	4.1
3485-1	6.57	0.076	0.113	11.5	11.8	0.35	2.4
3485-2	6.57				DIS		
2485	6.67	0.048	0.055	3.9	8	0.25	3.8
2486	6.67	0.042	0.056	4.8	10.0	0.30	6.4
2482-1	8.43	0.035	0.058	11.2	13.1	0.20	4.4
2482-2	8.43	0.023	0.067	9.6	13.1	0.45	2.1

- (1) after onset of linear rate law control (times listed = total immersion time - 1.25 mo). 1 month taken as 720 hours.
- (2) at all x, $0 \leq x \leq x_d$ except as noted in (4) below.
- (3) at $x = x_d$
- (4) in absence of diffusivity change, slope at $x = 0$ reported here.

TABLE III-3

Critical Microprobe Trace Values for Nickel
(exposure as in Table III-1)

Specimen Number	Exposure Time mo ⁽¹⁾	C ₀ w.f.	C _d w.f.	X _d dm x 10 ^{7/5}	X ₀ dm x 10 ^{7/5}	(2) dC ₁ /dx w.f./dm x 10 ⁻³	(3) dC ₂ /dx w.f./dm x 10 ⁻³
<u>1100 F</u>							
2206-1	18.33	0.022	0.028	4.0	10.0	0.18	5.2
2206-2	18.33	0.025	0.027	3.8	10.0	0.10	5.7
2207-1	18.33	0.017	0.029	2.8	6.0	0.40	2.7
2207-2	18.33	0.021	0.029	2.6	6.0	0.30	5.0
<u>1200 F</u>							
3312-1	2.87	0.11	----	---	8.0	0.4 ⁽⁴⁾	---
3312-2	2.87			DIS			
3303-1	10.15			DIS			
3303-2	10.15			DIS			
4113	2.65	0.068	----	---	9.3	0.25	---
4211	2.65	0.064	----	---	7.9	1.00	---
4513	2.65			WEIGHT GAIN			
2507	18.33	0.076	0.091	7.2	10.0	0.20	1.5
3402	0.76	0.075	0.091	4.3	5.2	0.40	1.4
2401	2.65			DIS			
3403-1	2.65	0.01	0.016	2.6	5.0	0.20	5.9
3403-2	2.65			UND-1			
3408-1	6.57	0.007	0.023	3.3	3.7	0.55	1.8
3408-2	6.57			UND-2			
2481	2.65	0.018	0.023	3.0	8.0	0.20	5.3
3485-1	6.57			DIS			
3485-2	6.57			DIS			
2485	6.67	0.014	0.019	3.7	8.0	0.20	4.1
2486	6.67	0.014	0.024	4.8	10.0	0.20	5.6
2482-1	8.43	0.012	0.020	11.4	13.1	0.10	3.0
2482-2	8.43			UND-2			

(1) after onset of linear rate law control (times listed = total immersion time - 1.25 mo). 1 month taken as 720 hours.

(2) at all x, 0 ≤ x ≤ x_d except as noted in (4) below.

(3) at x = x_d

(4) in absence of diffusivity change, slope at x = 0 reported here.

must be assessed before the preceding 6 expressions (21 through 26) can be applied to the data in Table III. This factor arises from the fact that although the large values expected of D_{i1} accurately permit the D_{i1} region concentration profiles to be approximated by a straight line (thus making the slope measurements, dC_{i1}/dx , precise) the dC_{i2}/dx slopes at $x = x_d$ are at the front end of a steeply dropping exponential curve. The recorded values of dC_{i2}/dx in Table III were measured as shown in Figure 10. It is highly probable that these measured slopes are too small. Figure 16 illustrates the difficulty, as compounded by x-ray source area effects. Their adjustment can be provided by the trace data of specimens 2206, 2207, 2482, 2485 and 2486 as follows:*

First note that equilibrium is established, or better, controlled, by behavior in the D_{i2} region, since from expression (26) the time in which equilibrium is reached is given by:

$$\sqrt{t_e} = 3.644 \rho_a \sqrt{D_{i.}} / R$$

and therefore, the smaller the magnitude of $D_{i.}$ the shorter the time to achieve equilibrium. Since it has already been established (paragraph V-1) that $D_{i2} \ll D_{i1}$, the magnitude of the diffusion coefficient in the region $x > x_d$, that is the magnitude of D_{i2} will dictate when equilibrium composition changes occur.**

*Specimen 3485 is also at equilibrium. However its traces were taken in a portion of the specimen known to have been cold worked. As discussed in previous reports⁽¹⁸⁾ these regions produce, again on the average, deeper compositional changes than annealed surfaces, on which all other traces were taken. The inference is that cold work increases the magnitude of the diffusion coefficients. Regardless of the effect, it is quite obvious that specimen number 3485 is not of the same family as the balance of the specimens.

**The arrest of the compositional change in the $0 \leq x \leq x_d$ region where D_{i1} prevails is forced by the flux mass conservation of expression (27). For when C_{i2} no longer is a function of time the slope dC_{i2}/dx at $x = x_d$ becomes constant. Therefore the slope dC_{i1}/dx must be constant. Since the concentration $C_{i(0)}$ at $x = 0$ is always constant the only way in which dC_{i1}/dx can remain constant is to force x_d to be constant, that is: no further change in time of C_{i1} must accompany the time independence of C_{i2} .

FIGURE 16 SLOPE MEASUREMENT DIFFICULTIES. VALUES OF $\bar{r}$, D_1 AND D_2 TAKEN FROM SPECIMEN 2486. NOTE CONSTRUCTED TRACE SIMILARITY TO MEASURED CHROMIUM TRACE IN FIGURE 10

Second note that if accurate values of R and of t_e , the time to reach equilibrium exist, then the magnitude of D_{i2} can be established from expression (26). Such is the case for specimens 2206, 2207, 2507, 2482, 2485 and 2486. The equilibrium times for these specimens can be taken as those in Table I, and accurate values of their respective $\bar{R}$'s (note that these are average alloy rates) have been made available⁽¹⁹⁾. These are in the order listed, in $\text{mg/dm}^2 \text{ mo}$ 11.32, 11.23, 7.66, 62.26, 38.14 and 68.25

Third note that mass conservation principles at $x = x_d$ require that:

$$D_{i1} dC_{i1}/dx = D_{i2} dC_{i2}/dx \quad \text{at } x = x_d \quad (27)$$

With this relationship, and with the measured values of x_d , $C_{i1(0)}$, and C_{id} , expressions (23) and (25) will allow the determination of D_{i1} . Thus:

$$(C_{id} - C_{i\infty})\bar{R}/\rho_a = (C_{i1(0)} - C_{id})D_{i1}/x_d \quad (28)$$

Now recalling that dC_{i1}/dx can be accurately measured, and equipped with known values of $\bar{R}$ and of t_e , we get D_{i1} from expression (28), and D_{i2} from expression (26). Now refer back to expression (27) to obtain the correct value of dC_{i2}/dx at $x = x_d$. For example, based upon summed active element behavior for reasons shortly explained, the slope and critical concentration behavior values for specimen 2507 are:

$$\Sigma C_{\infty} = C_{Cr\infty} + C_{Ni\infty} + C_{Mn\infty} = 0.309 \text{ w.f.}$$

$$\Sigma C_{(0)} = C_{Cr(0)} + C_{Ni(0)} + C_{Mn(0)} = 0.166 \text{ w.f.}$$

$$\Sigma C_d = C_{Crd} + C_{Nid} + C_{Mnd} = 0.204 \text{ w.f.}$$

$$\text{at } x = x_d:$$

$$\Sigma dC_1/dx = 500 \text{ w.f./dm}$$

$$\Sigma dC_2/dx = 4400 \text{ w.f./dm}$$

Then:

$$\sqrt{D_2} = \bar{R} \sqrt{t} / 2\rho_a (1.822) \quad \text{and with } \rho_a \text{ taken equal to } 8 \times 10^6 \text{ mg/dm}^3,$$

$$= 7.66 \times 4.28 / 16 \times 1.822 \times 10^6 = 1.13 \times 10^{-6} \text{ dm}^2/\text{mo}$$

and:

$$D_1 = (\Sigma C_d - \Sigma C_\infty) R x_d / \rho_a (\Sigma C_{(0)} - \Sigma C_d)$$

$$= 0.105 \times 7.66 \times 7.9 \times 10^{-5} / 8 \times 0.038 \times 10^6 = 20.90 \times 10^{-11} \text{ dm}^2/\text{mo}$$

Also:

$$\left. \Sigma dC_2/dx_{(\text{true})} \right|_{x=x_d} = D_1 (\Sigma dC_1/dx) / D_2 \left|_{x=x_d} \right.$$

$$= 500 \times 20.90 \times 10^{-11} / 1.28 \times 10^{-12} = 81900 \text{ w.f./dm}$$

Thus the required measured $\Sigma dC_2/dx$ correction factor at $x = x_d$ is

$$81900/4420 = 18.52$$

Note that if diffusivity changes are absent the correction factor is required for $\Sigma dC/dx$ at $x = 0$.

When similar calculations were performed for specimens 2206, 2207, 2482, 2485 and 2486 Figure 17 resulted. The correction curves were derived by standard regression techniques. Figure 17 gives the value of the correction factor to convert measured $\Sigma dC_2/dx$ (or $\Sigma dC/dx$ at $x=0$ in the absence of diffusivity changes), values for the active elements at x_d to true $\Sigma dC_2/dx$ values. Summation of active element slopes and critical concentration values is employed here and in the following sections as a normalizing procedure to obtain a mean point rate R directly, rather than by calculating it from individual active element behavior and then averaging these latter results.

FIGURE 17 CORRECTION FACTOR PLOT TO OBTAIN TRUE SLOPE AT THE APPROPRIATE BOUNDARY, $x=0$ OR $x=x_d$, GIVEN THE MEASURED SLOPE

d. Analytical Results.(i) Diffusivity Changes Absent

Specimens 3312-1, 3312-2, 4113 and 4211 are assumed to be in this category. Using expressions (21), (22) and (26) with the data in Table III, and correcting the measured slope $\Sigma dC/dx$ at $x = 0$ through use of Figure 17, calculated values of R and of the selective corrosion component, $j_{i(s)}$ are obtained and are listed in Table IV. Here and in Section V-3, it is assumed that the diffusivities of chromium, of nickel and of manganese are equal. It is further assumed that molybdenum behaves as a neutral element and therefore has no selective component. Thus:

$$J_{Mo} = RC_{Mo}, \text{ at all times}$$

The active element nonselective corrosion component values, $j_{i(ns)}$, are obtained from expression (5) using the measured values of $C_{i(0)}$ and the calculated values of R . The iron corrosion component could then be obtained from expression (4), which of course must be extended to include manganese and molybdenum. However, as discussed later, there is over-all stoichiometric corrosion (imposed as soon as $d\Delta W/dt = \text{constant} = R$, with the noble element fractions behaving as instantaneous diffusion sources) so that, quite simply:

$$J_{Fe} = RC_{Fe}$$

and of course, for any element under these circumstances:

$$J_i = RC_i$$

Here, and in Section V2dii, when no traces exist for manganese it has been treated as though it were a neutral element; and, when one active element trace is listed as "DIS", "UND-1" or "UND-2", values of R and of D can be obtained from estimates of the critical concentration values $C_{Ni(0)}^*$, $C_{Mn(0)}^*$, $\Sigma C_{(0)}$ and ΣC_d and of the measured slopes $\Sigma dC/dx$ at appropriate boundaries, see Figures 18, 19, 20, 21 and 22. These estimates are constructed from the appropriate parameters when there are no trace disturbances.

*Chromium generally always gives the most satisfactory (that is: well ordered) trace when trace disturbances exist elsewhere.

TABLE IV

Corrosion Components Determined from Electron Microprobe Traces
of Type-316 Specimens Exposed Isothermally to Flowing Sodium
(Containing 12 ppm oxygen) at 1100 and at 1200 F.
R Calculated by Expressions (31) or (33)

Specimen Number	Point Alloy Rate R mg/dm ² mo	Selective Components, j _(s) , mg/dm ² -mo			D ₁ dm ² /mo x 10 ⁺¹⁰	D ₂ dm ² /mo x 10 ⁺¹²
		Cr	Ni	Mn		
<u>1100 F</u>						
2206-1	11.85	1.39	1.22	0.19	5.3	3.02
2206-2	10.90	1.31	1.09	----	6.9	2.56
2207-1	13.69	1.72	1.48	0.21	5.4	4.04
2207-2	10.76	1.31	1.12	----	2.3	2.50
<u>1200 F</u>						
3312-1	49.00		(1)		(2)	8.05
3312-2	52.30		(1)		(2)	9.12
4113	250.40		(1)		(2)	196.00
4211	157.90		(1)		(2)	77.50
3303-1	20.40	1.96	1.57	----	15.9	4.95
3303-2	20.90	2.05	1.65	----	16.9	5.20
2507	8.04	0.64	0.39	0.15	2.1	1.39
3402	199.00		(1)		35.4	22.10
2401	33.80	2.16	1.15	0.47	3.6	3.56
3403-1	145.00		(1)		98.0	66.30
3408-1	41.10	4.69	4.85	----	10.7	13.10
2481	150.80		(1)		78.6	69.00
3485-1	17.76		(3)		35.7	27.50
2485	47.00	5.64	5.23	0.71	30.4	17.20
2486	65.31	8.23	7.25	1.04	33.1	33.40
2482-1	34.58	4.60	3.91	----	30.9	11.80
2482-2	30.26	4.39	3.48	----	7.5	9.10

(1) Not at equilibrium since trace point rate R much higher than known length average rate, $\bar{R}$.

(2) No apparent diffusivity change, hence no D₁.

(3) Different family because of cold work. May not be at equilibrium.

FIGURE 18 METHOD OF OBTAINING $C_{(0)}$ OR C_d FOR NICKEL WHEN THE NICKEL TRACE IS DISTURBED

FIGURE 19 METHOD OF OBTAINING $C_{(0)}$ OR C_d FOR MANGANESE WHEN THE MANGANESE TRACE IS DISTURBED

FIGURE 20 METHOD OF GETTING $\Sigma C_{(0)}$ OR ΣC_d FROM $C_{Cr(0)}$ OR $C_{Cr d}$ WHEN NICKEL, OR MANGANESE, OR BOTH TRACES ARE DISTURBED

FIGURE 21 METHOD OF APPROXIMATING $\sum dC_1/dx$ WHEN ACTIVE TRACES FOR dC_1/dx FOR NICKEL, FOR MANGANESE, OR FOR BOTH ARE MISSING

FIGURE 22 METHOD OF APPROXIMATING $\Sigma dC_2/dx_{x=x_d}$ WHEN TRACES FOR NICKEL OR FOR MANGANESE OR FOR BOTH ARE DISTURBED.

An example of how the descriptive corrosion parameters are calculated in the absence of diffusivity changes (for specimen 3312 - 1) is as follows:

Elimination of $j_{1(s)}$ in expressions (21) and (22) leads to

$$R = -(\rho_a D \Sigma dC/dx_{x=0}) / (\Sigma C_{(0)} - \Sigma C_{\infty}) \quad (29)$$

When expression (29) is used in combination with expression (26) the following working relationships are obtained:

$$\sqrt{D} = 3.644 (\Sigma C_{(0)} - \Sigma C_{\infty}) / (\Sigma dC/dx_{x=0}) \sqrt{t} \quad (30)$$

$$R = 29.152 \sqrt{D} \times 10^{+6} / \sqrt{t} \quad (31)$$

again with $\rho_a = 8 \times 10^{+6} \text{ mg/dm}^3$. The negative sign denoting slope direction has been abandoned, since it is a physical, rather than an arithmetic symbol. For specimen 3312-1 Table III yields.

$$\Sigma C_{(0)} = 0.228 \text{ w.f.}$$

$$\Sigma C_{\infty} = 0.293, \text{ since the only active element traces taken were chromium and nickel, w.f.}$$

$$\Sigma dC/dx_{x=0} = 1900 \text{ w.f./dm}$$

$$\sqrt{t} = 1.69 \text{ mo}^{1/2}$$

Figure 17 indicates a correction factor of 26.00 for the slope. Therefore:

$$\sqrt{D} = 3.644 \times 0.065 / 1.9 \times 2.6 \times 1.69 \times 10^{+4} = 2.84 \times 10^{-6} \text{ dm}^2/\text{mo}$$

and:

$$R = 29.152 \times 2.84 / 1.69 = 49.0 \text{ mg/dm}^2 \text{ mo.}$$

In this instance the selective corrosion components $j_{i(s)}$ are not calculated, for as explained later in this report the calculated rate, 49 mg/dm²mo is more than three times the observed rate for this specimen.

(ii) Diffusivity Changes Present

The remainder of the specimens in Table III show strong evidence of a diffusivity change. Their point alloy corrosion rate, R , will be determined from concentration profile behavior in the $x > x_d$ region for here there is probably more order, certainly with respect to the diffusion coefficient D_2 , than there is in the $0 \leq x \leq x_d$ region where severe morphological changes have occurred. However, as a test point of model merit, R will also be calculated from its related quantities in this latter region, for with exception of D_2 , these quantities are not correlated from a data treatment viewpoint with the corrosion-determining trace characteristics of the $x \geq x_d$ region.

The primary working relationships to obtain R are obtained from expressions (25) and (26):

$$\sqrt{D_2} = 3.644 (\Sigma C_d - \Sigma C_\infty) / (\Sigma dC_2 / dx_{x=x_d}) \sqrt{t} \quad (32)$$

$$R = 29.152 \sqrt{D_2} \times 10^{+6} / \sqrt{t} \quad (33)$$

The check working relationships are, from expressions (27) and (28), using D_2 as determined in expression (32):

$$D_1 = (D_2 \Sigma dC_2 / dx_{x=x_d}) / \Sigma dC_1 / dx_{x=x_d} \quad (34)$$

$$R = D_1 (\Sigma C_{(0)} - \Sigma C_d) \rho_a / (\Sigma C_d - \Sigma C_\infty) x_d \quad (35)$$

An example of how the four expressions (32, 33, 34, 35) are used is as follows for specimen 2401. (This specimen was chosen since it will also show how disturbed traces are handled.)

Table III provides the following values:

$$C_{Cr(0)} = 0.104 \text{ w.f.}$$

$$C_{Mn(0)} = 0.0022 \text{ w.f.}$$

$$C_{Cr d} = 0.121 \text{ w.f.}$$

$$C_{Mn d} = 0.0064 \text{ w.f.}$$

$$dC_{Cr1}/dx = 400 \text{ w.f./dm}$$

$$dC_{Mn1}/dx = 120 \text{ w.f./dm}$$

$$dC_{Cr2}/dx = 3300 \text{ w.f./dm}$$

$$dC_{Mn2}/dx = 500 \text{ w.f./dm}$$

$$\sqrt{t} = 1.63 \text{ mo}^{1/2}$$

The nickel trace, however is disturbed. In expression (32) $\Sigma dC_2/dx$ is obtained from Figure 22, and ΣC_d is obtained from Figure 20. These values are:

$$\Sigma dC_2/dx_{(calc)} = 6850 \text{ w.f./dm}$$

$$\Sigma C_{d(calc)} = 0.242 \text{ w.f.}$$

Figure 17 now provides a slope correction factor of 11.6 and $\sqrt{D_2}$ is given by, noting that since all three active elements are being considered, $\Sigma C_\infty = 0.309$:

$$\sqrt{D_2} = 3.644 \times 0.067 / 6.85 \times 1.16 \times 1.63 \times 10^{+4} = 1.89 \times 10^{-6} \text{ dm}^2/\text{mo}$$

and:

$$R = 29.152 \times 1.89 / 1.63 = 33.8 \text{ mg/dm}^2 \text{ mo}$$

The selective corrosion components are obtained from expression (24), having used Figure 18 to obtain $C_{Ni(0)}$. Thus:

$$j_{Cr(s)} = (0.168 - 0.104) \times 33.8 = 2.16 \text{ mg/dm}^2 \text{ mo}$$

$$j_{Ni(s)} = (0.125 - 0.091_{(calc)}) \times 33.8 = 1.15 \text{ mg/dm}^2 \text{ mo}$$

$$j_{Mn(s)} = (0.0161 - 0.0022) \times 33.8 = 0.47 \text{ mg/dm}^2 \text{ mo}$$

These values are calculated because the R value of $33.8 \text{ mg/dm}^2 \text{ mo}$ is similar to the calculated value from known weight changes for the family (of which specimen 2401 is a member) and therefore the equilibrium trace concepts are assumed to be correct. On the check $\Sigma dC_1/dx$ and $\Sigma C_{(0)}$ are obtained from Figures 21 and 20, which give:

$$\Sigma dC_1/dx_{(calc)} = 795 \text{ w.f./dm}$$

$$\Sigma C_{(0)} (calc) = 0.200 \text{ w.f.}$$

Therefore:

$$D_1 = (1.89)^2 \times 6.85 \times 11.6 \times 10^{-9} / 795 = 0.357 \times 10^{-9} \text{ dm}^2/\text{mo}$$

and:

$$R = 0.357 \times 0.042 \times 8 \times 10^{-3} / 0.067 \times 5.4 \times 10^{-5} = 33.14 \text{ mg/dm}^2 \text{ mo}$$

(iii) Evidence of Non Equilibrium

Table V provides primary trace point corrosion rate determination, with either expression (31) or (33) being used, depending upon diffusivity behavior, and the check trace point corrosion rate determination, expression (35), using behavior in the $0 \leq x \leq x_d$ region when diffusivity changes exist. Table V also provides the observed average length rate for a given specimen, and the plane rate at a specimen midplane, for the family of which the specimen is a member, as

determined by regression analysis of several hundred specimens from APED's sodium mass transfer study⁽¹³⁾.

When more than one time point exists for a given specimen the observed linear length average rate constant may be readily determined. In the case of Table V, column 3, such values were obtained by averaging the observed length average rates for periods beyond the nonlinear transient, as illustrated in Figure 23.

When only one time point exists for a given specimen, those identified by an asterisk, in Table V, column 3 use was made of a general observation⁽²⁰⁾ that the intercept in:

$$\Delta \bar{W} = \Delta \bar{W}_0 + \bar{R}t$$

is equal to R , (Figure 23).

FIGURE 23 METHOD OF DETERMINING OBSERVED LINEAR RATE CONSTANTS

TABLE V
Rate Analysis of Type-316 Stainless Steel in Isothermal
Flowing Sodium Based on Electron Microprobe Studies

Specimen Number	Alloy Corrosion Rate in mg/dm ² - mo				j _(s) /R ₍₁₎			Velocity dm/mo x 10 ⁻⁷
	R Trace (1) Analysis	R Trace (2) Analysis	$\bar{R}_{obs}$ (3)	d $\Delta\bar{W}$ /dt Calculated by Regression (4)				
					Cr	Ni	Mn	
<u>1100 F</u>								
2206-1	11.9	6.9	11.3	7.4	0.117	0.103	0.016	6.0
2206-2	10.9	6.2	11.3	7.4	0.120	0.100	---	6.0
2207-1	13.7	16.1	11.2	7.4	0.126	0.108	0.015	6.0
2207-2	10.8	10.9	11.2	7.4	0.122	0.104	---	6.0
<u>1200 F</u>								
3312-1	49.0	----(5)	7.7*	2.2	---	---	---	0.79
3312-2	52.3	----(5)	7.7*	2.2	---	---	---	0.79
4113	250.4	----(5)	28.5*	13.5	---	---	---	2.8
4211	157.9	----(5)	8.9*	3.4	---	---	---	2.8
3303-1	20.4	27.8	11.4*	1.7	0.096	0.077	---	0.79
3303-2	20.9	27.4	11.4*	1.7	0.098	0.079	---	0.79
2507	8.0	7.8	7.7	4.1	0.080	0.049	0.015	6.0
3402	199.0	191.9	35.8*	35.0	---	---	---	6.0
2401	33.8	33.1	16.3*	10.2	0.064	0.034	0.014	2.0
3403-1	145.0	151.0	34.8*	26.0	---	---	---	6.0
3408-1	41.1	36.7	40.7*	21.4	0.114	0.118	---	6.0
2481	150.8	209.6	37.4*	41.0	---	---	---	18.0
3485-1	17.8	16.9	59.5*	33.0	---	---	---	18.0
2485	47.0	49.7	38.1	33.0	0.120	0.111	0.015	18.0
2486	65.3	63.2	68.3	57.0	0.126	0.111	0.015	18.0
2482-1	34.6	31.8	62.3	55.0	0.133	0.113	---	18.0
2482-2	30.3	27.4	62.3	55.0	0.145	0.115	---	18.0

(1) Calculated by expressions (31) or (33), point rate

(2) Check rate, calculated by expression (35), point rate

(3) Based on listed specimen weight changes, length average rate

(3*) Calculated from $\Delta W = \Delta W_0 + \bar{R}t$, with $\Delta W_0 \approx \bar{R}$, length average rate

(4) Calculated by expression (36), length average rate

(5) Check expressions for R (point) from traces do not exist since there is no diffusivity change

The over-all regression analysis corrosion rate equation⁽¹³⁾ for hot leg weight losses is:

$$d\Delta w^{\theta}/dt = V^{0.884} \text{Ox}^{1.156} \exp \left\{ +12.845 - \left[23,827/(T+460) \right] - 0.676d + \frac{2.26}{t+1} \right\}$$

$$\cong d\Delta \bar{w}/dt, \text{ when calculated for a } d \text{ taken at a specimen midpoint.} \quad (36)$$

where:

ΔT temperature differential between loop maximum and minimum temperatures, °F

V local sodium flow velocity, feet/sec.

Ox contaminating oxygen content, ppm

T temperature (°F) of sodium in which the specimen of interest was exposed.

d a downstream factor, * as described in reference (20), dimensionless.

t exposure time, months.

*Starting at the exit of a heater for a given isothermal section, where L is defined as $L = 0$, the downstream factor is given by $d = (L/d_h) \times 10^{-2}$; L being the distance to the center of a given test specimen, measured along the isothermal flow path in inches, and where d_h is the hydraulic diameter given by $d_h = 4\pi r^2 / 2\pi r$, the ratio of 4 times the flow area to the wetted perimeter, $= 2r$, inches, r being an effective flow path radius.

For the specimens herein listed the downstream factors are:

<u>Position</u>	<u>Loop Runs</u>		
	2-4	2-5, 3-7 and 3-8	4-4
H1 inlet		0.515	0.523
H1 outlet		1.32	
H2 inlet		0.515	2.540
crossover, inlet to outlet H1, H2, H3*		0.917	
H2 outlet*		1.320	
H3 inlet	0.673	0.515	4.370
H3 outlet		1.320	
In pipe**		1.500	
H3R inlet		2.74	

These, with the data in Tables I and II, provide, through expression (36), the values listed in column 5 of Table V.

Although, as examination of the photomicrographs in Appendix IV will show, that compositional disturbance which is revealed by the lightly etching surface layer, is nonuniform, thus indicating the presence of locally differing point corrosion rates, it seems improbable that these local point rates would differ by factors greater than three. The primary-trace-point rate calculations for specimens 3312-1, 3312-2, 4113, 4211, 3402, 3403-1, 2481 and 3485-1 indicate that these point rates differ from the observed length-average rates by a factor of three, or more. Such traces are interpreted as not being at equilibrium. Therefore, in these instances, the use of the equilibrium expressions is not justified. Note that in the case of specimen 3485-1 the trace point rate is too small. In view of the thick extent of compositional disturbance in this specimen it is probable that it reached equilibrium in a shorter time than its exposure time. Its trace point rate would have been larger if a shorter time had been used in its calculation. Conversely all other nonequilibrium specimens have trace point rates that are too high. In view of the relatively small extent of compositional disturbance in these specimens it is probable that several additional months would have been required to bring their particular trace regions to equilibrium. Under such circumstances, i.e., using longer times, the trace point rates would be smaller.

*Required for $\bar{R}$ calculations for this position for use in discussion in Section VII - future work. No traces were taken in this position, nor were corrosion specimens inserted in this position.

**estimated.

Specimens 4113 and 2411 have the largest rate discrepancies. There is some slight evidence from their trace appearance (Figure 7) that a diffusivity change might have occurred. If so, they should have been treated by expressions (32) and (33) instead of by expressions (30) and (31).

3. DIFFUSIVITIES.

Consider now the diffusion coefficients of those specimens that are properly analyzed by the equilibrium expressions. First note that the coefficient magnitude in the $0 \leq x \leq x_d$ region, where the body-centered-cubic phase exists, that is the magnitude of the D_1 coefficients, is, on the average, two orders of magnitude greater than in the $x \geq x_d$ region, where the coefficients D_2 are those for the face-centered-cubic phase. Such a difference is quite common.

If the D_2 coefficients are plotted as a function of ΣC_d , using Figure 20 to get ΣC_d in those cases where trace disturbance exists, Figure 24 is obtained. Taking the ΣC_d region between 0.077 and 0.096, the values of D_2 at 1100 and at 1200 F can be examined. Their average values are:

$$D_{2(1100)} = 3.03 \times 10^{-12} \text{ dm}^2/\text{mo}$$

$$D_{2(1200)} = 18.9 \times 10^{-12} \text{ dm}^2/\text{mo}$$

For the concentration range in question these values give:

$$D_2 = 38.4 \exp(-51,757/RT), \text{ dm}^2/\text{mo} \quad (37)$$

where R is the gas constant and T is the temperature in °K.

Taking the activation energy for combined element self diffusion in an alloy of iron, chromium, nickel and manganese to be 70 kilocalories^(22, 23, 24) with a frequency factor of $0.5 \text{ cm}^2/\text{sec}$, D_2 at 1200 F is $1.16 \times 10^{-17} \text{ cm}^2/\text{sec}$ or $3 \times 10^{-13} \text{ dm}^2/\text{mo}$, whereas from expression (37) it is $18.9 \times 10^{-12} \text{ dm}^2/\text{mo}$. An order of magnitude difference for self and for dilute diffusion is common⁽²⁵⁾ and exists here for concentration changes in the D_2 region that are in the higher concentration range, that is $\Sigma C \geq 0.15 \text{ w.f.}$, Figure 24. For the lower ranges, $\Sigma C_d < 0.1 \text{ w.f.}$, a factor of sixty is the average recorded difference in comparative magnitude. It is not considered unrealistic because the diffusion activation energy, 70 kilocalories, used to make the comparison, is a figure estimated from self diffusion studies. To the author's knowledge accurate measured values of ternary diffusion behavior in the iron, chromium, nickel system have not been widely publicized, particularly for a system subject to the severe distortion that exists at the boundary $x = 0$, and at the phase transformation boundary common to these particular partially selective corrosion phenomena.

FIGURE 24 VARIATION IN DIFFUSIVITY IN $x \geq x_d$ REGION, D_2 WITH ΣC_d

4. TRANSFORMATION TO STOICHIOMETRIC CORROSION.

An important feature of the postulated partially selective corrosion process, in particular the stated concepts that involve selective and nonselective corrosion components in the presence of a moving boundary upon which the selective corrosion component is viewed as a continuous diffusion source, is that, coincident with the onset of alloy linear corrosion rate control, each element reacts in stoichiometric proportions, just as though it had never been subjected to partial selectivity. This is the result of expressions (14) or (15), as the case may be, and of expressions (4), (5) and (6). The first two expressions yield:

$$j_{i(s)} = R(C_{i\infty} - C_{i(0)}), \text{ when written for an active element rather than for its iron}$$

mirror image. Expression (5) states that:

$$j_{i(ns)} = RC_{i(0)}$$

Expression (6), the total element rate, gives:

$$J_i = j_{i(s)} + j_{i(ns)}$$

and expression (4) for iron, the noble element states that:

$$J_{Fe} = j_{Fe(ns)} = RC_{Fe(0)} - \sum j_{i(s)}$$

Therefore for any active element, chromium for instance:

$$J_{Cr} = R(C_{Cr\infty} - C_{Cr(0)}) + RC_{Cr(0)} = RC_{Cr\infty}$$

and for iron, noting that $\sum C_{i(active)} = 1 - C_{Fe}$,

$$J_{Fe} = RC_{Fe(0)} - R(\sum C_{i(act)\infty} - \sum C_{i(act)(0)})$$

$$= RC_{Fe(0)} - R(1 - C_{Fe\infty}) + R(1 - C_{Fe(0)})$$

$$= RC_{Fe\infty}$$

This behavior is of significant aid for corrosion studies in the presence of surface compositional changes for it indicates, that once linear rate control is exerted, weight changes and corrosion products may be analysed as though no compositional changes were occurring from that point on.

Such behavior explains why the cold, and deposition regions of the sodium mass transfer loops continue, over long periods of time to show relatively high chromium and nickel gains, as measured by x-ray fluorescence techniques⁽¹⁵⁾.

5. EVIDENCE FOR A HYDRAULIC VELOCITY EFFECT.

Sodium flow velocity for a given system is a measure of volume flow rate, G , and vice versa, Appendix I. For equal flow geometry the larger G the larger will be v , the velocity, dm/mo. The larger G , the larger will be R , expression (2).

In a system in which there is no appreciable oxygen consumption, one would expect if oxygen had the same access rate to the structural carrier wall that the alloy phase concentration, $C_{i(0)}$ of an element i at the reaction product - alloy interface would be relatively constant. General oxidation theory would dictate that the surface changes in partially-selective corrosion processes would be greater with increasing oxidizing power; provided, that such increase does not effect alloy phase diffusivities, nor alter those oxide characteristics that are related to dissociation concepts.⁽³⁾ At a given temperature both of the latter should remain unchanged with position along the isothermal sodium flow path. In the 1200 F range (from columns 6, 7 and 9 of Table V) it may be seen that $C_{i(0)}$, since $j_{i(s)}/R = C_i - C_{i(0)}$, is decreasing with increasing velocity. This is interpreted to mean that the oxidizing power increases with increasing velocity, and it can only do so if its rate of supply to the alloy wall is controlled by a velocity dependent effect. Quite clearly this must be a liquid-sodium boundary layer through which transport is diffusion controlled, transport rates at the steady state being inversely proportional to its thickness, among other things. This thickness decreases with increasing velocity, and is discussed later. Thus higher corrosion rates are to be expected with increasing velocity, not only because higher velocities signify higher volume flow rates which tend to minimize saturation effects, but they are also accompanied by thinner liquid-sodium boundary layers which favor greater rates of both oxygen supply and of solute dispersal.

6. LOCAL TRANSPORT RATE COEFFICIENTS.

a. At 1200 F.

Within the derivation framework of expression (2), the rate constant α is a solution-rate constant. As such, its inclusion in the basic rate expression:

$$R = \alpha (S^0 - S) \quad (1)$$

explicitly ignores the presence of diffusional processes.

In other words, the rate dependence implied in expression (1) assumes that the slow step, in the transport of alloying elements, from a structural wall into a flowing-sodium stream is some form of interfacial solution rather than diffusion, as explained in detail by Epstein. (4)

If the observation that a stagnant boundary layer exerts rate control is indeed true, then expression (1) must be revised to reflect the diffusional influence. The system under study, namely the projects sodium mass transfer loops, is turbulent in all isothermal test section regions from the H1 heater inlet to the C3 cooler outlet (heaters and coolers themselves may be borderline cases between laminar and turbulent flow). In isothermal sections under such circumstances boundary layer, or better "film," theory recognizes the presence of a momentum film thickness, δ_{vel} , and a transport film thickness, δ_{mass} . (See Figure 25) In the absence of chemical reaction they both depend primarily upon velocity and upon sodium phase diffusivities. In the presence of chemical reaction, oxidation and reduction in this instance, the two films also depend upon reaction magnitude and therefore upon distance along the flow path.

FIGURE 25 SCHEMATIC REPRESENTATION OF SODIUM PHASE TRANSPORT REGIONS

The transport rate, taken equal to the corrosion rate, R , in unsaturated regions will still be proportional to the degree of unsaturation. However, the proportionality expressed as a local transport rate constant k_{loc} , will be a function of the film thicknesses (δ_{vel} and δ_{mass}), and may be a function of the transport rate if this rate is large enough to distort the film thickness profiles. In the absence of chemical reaction, expressions for film thicknesses in terms of uncorrected local transport coefficients (k_{loc}), have been developed. (26) To a first approximation they give:

$$R(y) = k_{loc} (S^0 - S_y)$$

Using the principles of Appendix I, and ignoring, to a second approximation, the dependence of k_{loc} upon distance y , $R(y)$ will be given by:

$$R(y) = k_{loc} (S^0 - S_{(0)}) \exp(-2\pi r k_{loc} y / \rho_{Na} G) \quad (38)$$

Since $(S^0 - S_y)$ is given by:

$$(S^0 - S_y) = (S^0 - S_{(0)}) \exp(-2\pi r k_{loc} y / \rho_{Na} G) \quad (39)$$

Expressions (38) and (39) could be applied to the point rates established, Table V, for specimens 2486, 2485, and 2507, assuming that the point rates are representative of the plane rates $R(y)$. However, the large difference between the rates of specimens 2485, 2486 and the rate of specimen 2507 demands that the fact that k_{loc} for 2507 may be different than the k_{loc} for specimens 2486 and 2485 be taken into account. However, if the difference in the local transport coefficients, k_{loc} , for the H3 inlet (specimen 2486, $R = 65.3 \text{ mg/dm}^2 - \text{mo}$) and H3 outlet positions (specimen 2485, $R = 47 \text{ mg/dm}^2 - \text{mo}$) is assumed to be small, and if it is further assumed that the local transport coefficient in the crossover between H3 inlet and H3 outlet is the same as that of the two specimen slot positions, then, Appendix III,

$$R_{H3I(2486)} = k_{loc} \Delta S_{(04)} \exp(-0.254 \Sigma P_4 k_{loc} / \rho_{Na} G)$$

$$\begin{aligned}
 R_{H30(2485)}^{\theta} &= k_{loc}^{\theta} \Delta S_{(06)} \exp(-0.254 \Sigma P_6 k_{loc}^{\theta} / \rho_{Na} G) \\
 &= k_{loc}^{\theta} \Delta S_{(04)} \exp \left[- (k_{loc}^{\theta} / \rho_{Na} G) (L_4 \Sigma P_4 + 2 \pi r_5 L_5) \right] \times \\
 &\quad \times \exp(-0.254 \Sigma P_6 k_{loc}^{\theta} / \rho_{Na} G)
 \end{aligned}$$

in which the first exponential term in $R_{H30(2485)}$ is the factor necessary to reference this specimen to $\Delta S_{(04)}$. In both expressions, the specimen distance term 0.254 reflects the fact that the microprobe trace for that specimen was taken approximately one inch from the specimen holder inlet end of that specimen. ΣP_i , Appendix III, is the wetted perimeter of a test specimen test slot. It includes both the holder perimeter and the specimen perimeter, with the assumption that the corrosion rates of both holder and specimen are identical. Then:

$$\begin{aligned}
 R_{H3I(2486)}^{\theta} &= 65.3 = k_{loc}^{\theta} \Delta S_{(04)} \exp(-0.076 \times 10^{-11} k_{loc}^{\theta}) \\
 R_{H30(2485)}^{\theta} &= 47.0 = k_{loc}^{\theta} \Delta S_{(04)} \exp(-0.487 \times 10^{-11} k_{loc}^{\theta})
 \end{aligned}$$

for which $G = 0.7$ gallons per minute $= 1.14 \times 10^5 \text{ dm}^3/\text{mo}$ and in which ρ_{Na} , the sodium density at 1200 F, is $0.795 \times 10^6 \text{ mg/dm}^3$. The expressions give:

$$\begin{aligned}
 k_{loc, 1200(H3I, H30)}^{\theta} &= 8 \times 10^{+10} \text{ mg/dm}^2 \text{ mo} \\
 \Delta S_{(04)1200(H3I)} &= 8.65 \times 10^{-10} \text{ w. f.}
 \end{aligned}$$

b. Temperature Dependence.

The same procedure just followed cannot be adopted for the 1100 F region since only one position, H2 inlet (specimens 2206 and 2207), was examined. However, since stoichiometric corrosion is involved length average specimen rates may be used. The length average rate from $y = 0$ to $y = L$ is given by the equation on the following page.

$$\bar{R} = (1/L) \int_0^L k_{loc}^{\theta} \Delta S_{(0)} \exp(-2\pi r k_{loc}^{\theta} / \rho_{Na} G) dy \quad (40)$$

Again, ignoring the dependence of k_{loc}^{θ} upon distance y , expression (4) leads to:

$$\bar{R} = (\rho_{Na} G \Delta S_{(0)} / 2\pi r L) \left[1 - \exp(-2\pi r k_{loc}^{\theta} L / \rho_{Na} G) \right] \quad (41)$$

Expression (41) can be applied to observed total average rates at 1000 F, 1100 F, and 1200 F, provided that the relative loop geometries at the three temperatures is the same (flow rate G , wetted perimeter ΣP , and distance L) and provided that the observed rates for two given test positions at a given temperature are not widely different. In run 2-5 for instance, the observed total average rates are⁽¹⁹⁾:

TABLE VI
Corrosion Rate Data From Run 2-5

	Position	$\bar{R}$, mg/dm ² - mo
1000 F	H1 inlet _(1/3 flow)	2.25
	H1 outlet _(full flow)	3.15
1100 F	H2 inlet _(1/3 flow)	10.8
	H2 outlet _(full flow)	18.00
1200 F	H3 inlet _(full flow)	60.1
	H3 outlet _(full flow)	41.4

or if it is assumed that had full flow existed in the H1 and H2 inlet positions their rates would have been 3 times that of 1/3 flow then, in mg/dm² mo, these rates would have been:

	1000 F	1100 F	1200 F
inlet	6.75	32.4	60.1
outlet	3.15	18.0	41.4

When referenced to $y = 0$ of the inlet sample holders, the 3 temperature test geometries are the same. Thus, if a factor of 2 difference in rates is assumed to have but a slight effect upon k_{loc}^{θ} , the following ratio can be formed.

$$\frac{\bar{R}_O}{\bar{R}_I} = \frac{\int_0^\theta S_{(0)I} \left\{ 1 - \exp \left[-(\Sigma PL)_{slot} \frac{\theta}{k/\rho_{Na} G} \right] \right\} \exp \left\{ -(k/\rho_{Na} G) \left[(\Sigma PL)_{slot} + (\Sigma PL)_{cross over} \right] \right\} d\theta}{\int_0^\theta S_{(0)I} \left\{ 1 - \exp \left[-(\Sigma PL)_{slot} \frac{\theta}{k/\rho_{Na} G} \right] \right\} d\theta}$$

or:

$$\frac{\bar{R}_O}{\bar{R}_I} = \exp \left\{ - (k/\rho_{Na} G) \left[(\Sigma PL)_{slot} + (\Sigma PL)_{crossover} \right] \right\} \quad (42)$$

in which k signifies k_{loc}^θ .

Taking ρ_{Na} at 1000, 1100, and 1200 F to be, respectively, 0.825×10^6 , 0.807×10^6 and 0.795×10^6 mg/dm³, the previous rates give, for the loop 2 inlet and outlet positions of the first sample holder after the heaters, using expression (42):

$$\exp (-0.396 \times 10^{-11} k_{1000}^\theta) = .467$$

$$\exp (-0.405 \times 10^{-11} k_{1100}^\theta) = .556$$

$$\exp (0.411 \times 10^{-11} k_{1200}^\theta) = .689$$

Therefore:

$$k_{loc 1000}^\theta, H1I-H10 = 19.2 \times 10^{+10} \quad \text{mg/dm}^2 \text{ mo}$$

$$k_{loc 1100}^\theta, H2I-H20 = 14.5 \times 10^{+10} \quad \text{mg/dm}^2 \text{ mo}$$

$$k_{loc 1200}^\theta, H3I-H30 = 9.3 \times 10^{+10} \quad \text{mg/dm}^2 \text{ mo}$$

Note that k_{loc} decreases with increasing temperature, that is, with increasing transport rate $\bar{R}$. This behavior is to be expected when two conditions are satisfied: (1) the process involves transport into the stream, and (2) transport rates are sufficiently large to distort the film profiles. Since alloying elements are being transported from the structural wall to the bulk sodium stream, the first condition is satisfied. However, the transport rates fall, within film theory concepts, into the low rate category in which film distortion is minimal. Under these circumstances, as

discussed under future work, film theory indicates that k_{loc}^{θ} should increase with increasing temperature. The discrepancy is attributed to the fact that activity, rather than concentration, gradients exert control in the boundary layer as proposed by Weeks.⁽⁸⁾

c. Shift in Selective Direction

(i) With Increasing Length of Travel in the Direction of Isothermal Flow.

Saturation with respect to alloying elements occurs in sodium with increasing length of travel in the direction of isothermal flow, that is, in "downstream" positions. When saturation is approached, there is a shift in the direction of partially selective behavior, such that chromium becomes noble, nickel becomes neutral, while iron becomes active, with molybdenum and manganese remaining neutral and active, respectively, Figure 7. This process is also accompanied by the formation of oxide films and resulting specimen weight gains. The primary driving force is no longer the degree of metallic structural element unsaturation, but rather is imposed by an oxidation mechanism in the presence of relatively stable oxide film formation. As such, rate control may no longer be so firmly established in the boundary layer - even though this layer continues to provide a gradient for oxygen supply - and the principles governing the observed selectivity behavior will be strongly influenced by oxide film morphology.

(ii) As a Function of Bulk Sodium Oxygen Content.

No microprobe traces were taken on specimens exposed to other than sodium containing 12 ppm of contaminating oxygen. However, in a companion report⁽¹⁵⁾ evidence is presented for a shift in selective direction in unsaturated positions along the sodium flow path. It can be inferred from x-ray fluorescence measurements of surfaces exposed to sodium containing 50 ppm oxygen that specimens located in H1, H2, H3 and H3R positions in run types I and V, Table II, have the following elemental selective directions; the behavior of the lower oxygen runs, types II, III and IV, applicable to all of the specimens examined in this report are shown for comparative purposes.

	Iron		Chromium		Nickel	
Oxygen, ppm	10	50	10	50	10	50
H1						
900	N	A	A	N	A	N
1000	N	A	A	N	A	N
H2						
1000	N	A	A	N	A	N
1100	N	A	A	N	A	N
H3						
1100	N	A	A	N	A	N
1200	N	N	A	A	A	N
H3R						
1100	N	A	A	N	A	N
1200	N	N	A	A	A	N

Of particular interest is the secondary reversal of iron and of chromium at 1200F in the higher oxygen runs. It is suggested that the explanation lies in the relative selective corrosion component energies of the couple:

as a function of temperature and of oxygen content. Figure 26 shows such energy. Where a particular selective energy is zero, there will be no selective component and that element will behave nobly.

d. Non Selective Component Rate Considerations

A very interesting observation, discussed in the companion report⁽¹⁵⁾, is that within the test variable framework of the sodium-mass-transfer test program, alloy specimens of 2-1/4Cr-1Mo and of 5Cr-1/2Mo-1/2Ti have essentially the same linear corrosion rate constants as does Type-316 stainless steel. This observation strongly suggests that, at the steady state, 1) elemental transport characteristics in the liquid-sodium boundary layer are similar, and 2) that total alloy

FIGURE 26 SCHEMATIC DEPENDENCE OF SELECTIVE COMPONENT UPON TEMPERATURE AND UPON OXYGEN CONTENT.

**FIGURE 27 ELECTRON MICROPROBE TRACE
BEHAVIOR OF MOLYBDENUM AT 1200F**

performance is governed by an interaction between the compositionally-changed surface region and the bulk alloy, with significant influence being exerted by the nonselective corrosion component. Its summed rate is essentially proportional to $\Sigma C_{(0)}R$ and in the specimens under consideration $\Sigma C_{(0)}$ is essentially all iron. Therefore if the nonselective corrosion component figures prominently in establishing over-all rate behavior, it is reasonable to expect that the three alloys, each presenting an iron rich surface to the Na - Na₂O environment, would have the same alloy corrosion rate.

7. MOLYBDENUM BEHAVIOR.

Typical molybdenum profiles are shown in Figure 27. The random behavior thus shown is common to all the molybdenum traces that were taken and the lack of a clear cut pattern is interpreted to mean, that, on the average, molybdenum behaves as a neutral element, that is: it corrodes stoichiometrically at all times, under all of the exposure conditions listed for the specimens examined in this report. The only explanation, and one that is quite tentative, for the large increases and decreases in molybdenum content within the body of the surface region is that some type of complex Mo-Fe carbides may form.

8. APPLICATION TO CORROSION RATE STUDIES.

Three significant factors emerge if stoichiometric corrosion behavior does indeed accompany the transformation to linear rate law control.

a. No correction of measured length average corrosion rates, $\bar{R}$, need be made to account for the extent of the accompanying compositional change. In particular these length average rates may be used directly in calculations involving the sodium system parameters of distance, volumetric flow, temperature, velocity, contamination and degree of unsaturation with respect to structural alloy solutes.

b. The length average time to reach the equilibrium extent of compositional change, after the onset of linear rate control, may be determined from:

$$\sqrt{t_e} = 3.644 \rho_a f(\bar{D}_2) \sqrt{\bar{D}_2/\bar{R}}$$

where, in keeping with the following paragraphs $f(\bar{D}_2) = 1$ when $\Sigma \bar{C}_{(0)}$, the length average active element interfacial (at $x = 0$) concentration sum is < 0.10 w.f., $f(\bar{D}_2) = 0.25$ in the range $0.10 < \Sigma \bar{C}_{(0)} < 0.15$, $f(\bar{D}_2) = 0.125$ when $\Sigma \bar{C}_{(0)} > 0.15$ w.f. and where $\sqrt{\bar{D}_2}$ can be obtained from expression (37). Thus taking $\rho_a = 8 \times 10^{-6}$ mg/dm³:

$$(i) \Sigma \bar{C}_{(0)} \sim 0.10 \text{ w. f.}$$

$$\bar{t}_e = 3.26 \times 10^{+16} \exp(-26,140/T)/(\bar{R})^2$$

$$(ii) 0.10 < \Sigma \bar{C}_{(0)} < 0.15$$

$$\bar{t}_e = 0.82 \times 10^{+16} \exp(-26,140/T)/(\bar{R})^2$$

$$(iii) \Sigma \bar{C}_{(0)} > 0.15 \text{ w. f.}$$

$$\bar{t}_e = 0.41 \times 10^{+16} \exp(-26,140/T)/(\bar{R})^2$$

c. A potentially significant characteristic of a partially selective corroding surface is the plane average depth of composition change. As has been noted the partially selective corrosion of Type 316 stainless steel in unsaturated, isothermal regions of flowing sodium (at 1100 and at 1200 F) contaminated with 12 ppm of oxygen results in the formation of a body-centered cubic, or ferritic, surface layer within the alloy phase. It has been assumed that the point ferritic layer thickness is identifiable with the depth " x_d ". However, if such a layer is associated with detrimental mechanical properties it is more proper to assign the extent of such damage to the entire compositionally changed depth, that is, the entire region in which a given elemental concentration C is different than C_∞ . And if detrimental behavior accompanies the composition change, then its equilibrium depth is an important quantity for design purposes, particularly in thin walled structures. The method by which this depth, $\bar{x}_e$, is determined follows: the calculation is for a total average depth, $\bar{x}_e$. The expressions obtained, however, are numerically applicable for plane average equilibrium depths, providing that the appropriate plane average corrosion rates and interfacial values, assumed to be known, are used.

Note from Figure 28, that at equilibrium the length average summed active element profile in the region $x \leq \bar{x}_{de}$ is given by

$$\Sigma C_\infty - \Sigma \bar{C}_2 - (\Sigma C_\infty - \Sigma C_d) \exp \left[-\bar{R}(x - \bar{x}_{de})/\rho_a \bar{D}_2 \right]$$

If it is assumed that a length average summed concentration change of 0.5 weight percent (0.005 w.f.), or less from the bulk composition will produce insignificant changes in mechanical properties, then the length average layer depth, $\bar{x}_e$, of concern is given by

$$\bar{x}_e = \bar{x}_{de} + \bar{x}'_e \quad (43)$$

FIGURE 28 PARAMETERS INVOLVED IN DETERMINING EQUILIBRIUM DEPTH, X_e , OF COMPOSITIONAL CHANGE

where $\bar{x}_e$ is such that:

$$0.005 = (\Sigma C_\infty - \Sigma \bar{C}_d) \exp \left[-\bar{R} (\bar{x}_e - \bar{x}_{de}) / \rho_a \bar{D}_2 \right]$$

or:

$$0.005 = (\Sigma C_\infty - \Sigma \bar{C}_d) \exp (-\bar{R} \bar{x}'_e / \rho_a \bar{D}_2)$$

from which:

$$\bar{x}'_e = - \left[2.3 \rho_a f(\bar{D}_2) \bar{D}_2 / \bar{R} \right] \log_{10} \left[0.005 / (\Sigma C_\infty - \Sigma \bar{C}_d) \right] \quad (44)$$

The factor $f(\bar{D}_2)$ is required because of the $\bar{D}_2$ dependence upon the summed value of $\Sigma \bar{C}_d$. Figure 24, equally applicable for point, or for plane or length averages. The nature of the concentration dependence has not been explored since there is only one concentration range common to both 1100 and 1200 F in the observations in this report, and this is the range upon which expression (37) was founded. This range, and its diffusivity, must therefore be taken as a base for diffusivity behavior at other concentrations in order to use expression (37). There are essentially three concentration ranges in Figure 24, and these are listed in Table VII with other values pertinent to the determination of $\bar{x}'_e$, expression (44). As an approximation it is assumed that $f(\bar{D}_2)$ is given by:

$$(i) \quad \Sigma \bar{C}_d < 0.10 \text{ w.f.}$$

$$f(\bar{D}_2) = 18.9/18.9 = 1$$

$$(ii) \quad 0.10 < \Sigma \bar{C}_d < 0.15$$

$$f(\bar{D}_2) = 5.08/18.9 \approx 0.25$$

$$(iii) \quad \Sigma \bar{C}_d > 0.15 \text{ w.f.}$$

$$f(\bar{D}_2) = 2.48/18.9 \approx 0.125$$

With these approximations, and noting that, essentially, $\Sigma \bar{C}_d = \Sigma \bar{C}_{(0)}$, the length average equilibrium depth could be determined, provided that estimates of $\bar{x}'_e$ existed, from the observed values of $\bar{R}$, expression (37) and values of $\Sigma \bar{C}_{(0)}$. This last quantity can be readily estimated by standard, and inexpensive compared to microprobe tracing, x-ray fluorescence

TABLE VII
Corrosion Data Pertinent to the Establishment of
Equilibrium Depths of Compositional Disturbance

Specimen Number	Observed Length Average Alloy Corrosion Rate $\bar{R}$ mg/dm ² mo	ΣC_d w. f.	D_2 dm ² /mo $\times 10^{+12}$	x_d dm $\times 10^{+5}$
1100 F				
2206-1	11.3	0.087	3.02	3.8
2206-2	11.3	0.082	2.56	3.7
2207-1	11.2	0.083	4.04	2.4
2207-2	11.2	0.096	2.50	2.3
Mean	11.25	0.087	3.03	3.05
1200 F				
3408-1	40.7	0.095	13.1	4.0
2485	38.1	0.083	17.2	3.9
2486	68.3	0.082	33.4	4.8
2482-1	62.3	0.077	11.8	11.2
Mean	52.4	0.084	18.9	5.98
3303-1	11.4	0.152	4.95	9.8
3303-2	11.4	0.147	5.20	9.8
Mean	11.4	0.150	5.08	9.8
2507	7.7	0.204	1.39	7.9
2401	16.3	0.242	3.56	5.4
Mean	12.0	0.223	2.48	6.7

surface concentration measurements. However, the point x_d , and consequently the x_{de} , dependence upon the partially selective corrosion process parameters has not been explicitly sought in this report. The absence of its description can be overcome by examining the point relationship between x'_e and x_{de} in those specimens assumed to be at equilibrium from the foregoing analysis, under the assumption that these point values are representative of the length average values of $\bar{x}'_e$ and $\bar{x}_{de}$. The pertinent specimens and their corrosion characteristics are given in Table VII. $\bar{x}'_e$ has been calculated for each concentration range, using expression (44). These $\bar{x}'_e$ values have then been used to establish a relationship of the type:

$$\bar{x}_{de} = f(\bar{x}_{de}) \bar{x}'_e$$

Once $f(\bar{x}_{de})$ is known, expression (43) becomes:

$$\bar{x}_e = \left[f(\bar{x}_{de}) + 1 \right] \bar{x}'_e$$

in which the value of $\bar{x}'_e$ is given by expression (44), as modified by the $\Sigma \bar{C}_d \cong \Sigma \bar{C}_{(0)}$ approximation. Thus:

$$\bar{x}_e = - \left[f(\bar{x}_{de}) + 1 \right] \left[2.3 \rho_a f(\bar{D}_2) \bar{D}_2 / \bar{R} \right] \log_{10} \left[0.005 / (0.309 - \Sigma \bar{C}_{(0)}) \right] \quad (45)$$

An illustration of how Table VII and expression (44) are used to obtain $f(\bar{x}_{de})$ is given below for the 1100 F and 1200 F low $\Sigma \bar{C}_d$ ranges, that is $\Sigma \bar{C}_d < 0.10$ w.f.

1100 F

$$\bar{D}_2 = 3.03 \times 10^{-12} \text{ dm}^2/\text{mo}$$

$$f(\bar{D}_2) = 1.00$$

$$\Sigma \bar{C}_d = 0.087 \text{ w.f.}$$

$$\bar{R} = 11.25 \text{ mg/dm}^2\text{mo}$$

$$\rho_a = 8 \times 10^{-6} \text{ mg/dm}^3$$

Then:

$$\bar{x}'_e = 2.3 \times 8 \times 3.03 \times 1.648 \times 10^{-6} / 11.25 = 0.817 \times 10^{-5} \text{ dm}$$

Also:

$$\bar{x}_{de} = 3.05 \times 10^{-5} \text{ dm}$$

Therefore:

$$f(\bar{x}_{de}) = 3.05/0.817 = 3.73$$

1200 F

$$\bar{D}_2 = 18.9 \times 10^{-12} \text{ dm}^2/\text{mo}$$

$$f(\bar{D}_2) = 1.00$$

$$\Sigma \bar{C}_d = 0.084 \text{ w. f.}$$

$$\bar{R} = 52.4 \text{ mg/dm}^2\text{mo}$$

Then:

$$\bar{x}'_e = 2.3 \times 8 \times 18.9 \times 1.653 \times 10^{-6} / 52.4 = 1.097 \times 10^{-5} \text{ dm}$$

and since $\bar{x}_{de} = 5.98 \times 10^{-5} \text{ dm}$,

$$f(\bar{x}_{de}) = 5.98/1.097 = 5.45$$

The ratio between $f(\bar{x}_{de})_{1100}$ and $f(\bar{x}_{de})_{1200}$ in the low $\Sigma \bar{C}_d$

range is 1.46. Assuming no interaction between temperature and the concentration dependence of $\bar{D}_2$, $f(\bar{x}_{de})$ at all temperatures will be given by:

$$f(\bar{x}_{de})_T = (1.46)^{-\frac{922 - T}{56}}$$

where T is in °K, and noting again that the operational base is in the low range, the only range where comparable data exist for 1100 F and 1200 F behavior.

When the values of $\bar{x}'_e$ and of $\bar{x}_{de}$ for the other two concentration ranges at 1200 F are examined the following are obtained:

$$f(\bar{x}_{de})_{1200} = 8.52 \quad 0.10 < \Sigma \bar{C}_d < 0.15$$

$$f(\bar{x}_{de})_{1200} = 14.78 \quad \Sigma \bar{C}_d > 0.15 \text{ w. f.}$$

Use of the temperature approximation gives:

$$f(\bar{x}_{de})_T = 8.52(1.46)^{-\frac{922-T}{56}} \quad 0.10 < \Sigma \bar{C}_d < 0.15$$

$$f(\bar{x}_{de})_T = 14.78(1.46)^{-\frac{922-T}{56}} \quad \Sigma \bar{C}_d > 0.15 \text{ w. f.}$$

And finally the expressions for $\bar{x}_e$ are, using: $f(\bar{x}_{de})_T$ values, $f(\bar{D}_2)$ approximations, $\Sigma \bar{C}_d \cong \Sigma \bar{C}_{(0)}$ approximation, and expression (37):

$$(i) \quad \Sigma \bar{C}_{(0)} < 0.10 \text{ w. f.}$$

$$\bar{x}_e = -\frac{7.07 \times 10^8}{\bar{R}} \left[5.45(1.46)^{-\frac{922-T}{56}} + 1 \right] \exp(-26140/T) \log_{10} \left[\frac{0.005}{0.309 - \Sigma \bar{C}_{(0)}} \right]$$

$$(ii) \quad 0.10 < \Sigma \bar{C}_{(0)} < 0.15$$

$$\bar{x}_e = -\frac{1.77 \times 10^8}{\bar{R}} \left[8.52(1.46)^{-\frac{922-T}{56}} + 1 \right] \exp(-26140/T) \log_{10} \left[\frac{0.005}{0.309 - \Sigma \bar{C}_{(0)}} \right]$$

$$(iii) \quad \Sigma \bar{C}_{(0)} > 0.15 \text{ w. f.}$$

$$\bar{x}_e = -\frac{0.88 \times 10^8}{\bar{R}} \left[14.78(1.46)^{-\frac{922-T}{56}} + 1 \right] \exp(-26140/T) \log_{10} \left[\frac{0.005}{0.309 - \Sigma \bar{C}_{(0)}} \right]$$

where T is in °K, $\Sigma \bar{C}_{(0)}$ is in w. f., and $\bar{x}_e$ is in dm.

VI. CONCLUSIONS

Evaluation of the Electron Microprobe Analyses of Specimens exposed in the Sodium Mass Transfer test loops indicate that:

1. The partially selective corrosion of Type 316-stainless steel in sodium at 1100 F and 1200 F contaminated with 12 ppm oxygen is such that iron behaves nobly, that molybdenum is neutral, and that chromium, nickel, and manganese behave actively. This results in a compositionally-changed surface layer that is rich in iron, unchanged in molybdenum and impoverished in chromium, nickel, and manganese in positions along isothermal flow paths where the sodium solvent is unsaturated with respect to the alloying elements. In such regions no oxide film formation is observed and specimen corrosion behavior is characterized by weight losses. The compositional change results in a face-centered to body-centered cubic transformation at some distance x_d from the interface at an average concentration, of a given active element, $\bar{C}_d$, whose magnitude depends upon the nonlinear transient corrosion rates of chromium and of nickel.
2. Alloy rate control is exerted in a sodium boundary layer when the degree of alloying element unsaturation in sodium is other than zero. Upon the onset of linear rate control, with length average rate constant $\bar{R}$, mg/dm²-mo, the average alloy phase concentration profile of a given active element is:

(i) in the region $0 \leq x \leq x_d$

$$C_\infty - \bar{C}_1 = (\bar{j}_s / \bar{R}) + I_1 \left\{ \text{erf}(u_{x1}, t) + \exp(-\bar{R}x / \rho D_1) \text{erf}(v_{x1}, t) \right\}$$

(ii) in the region $x > x_d$

$$C_\infty - \bar{C}_2 = I_2 \left\{ \text{erfc}(u_{x2}, t) + \exp(-\bar{R}x / \rho D_2) \text{erfc}(v_{x2}, t) \right\}$$

where:

C_∞	=	bulk alloy composition of a given active element, w. f.
$\bar{j}_s$	=	length average selective corrosion component of a given active element,
mg/dm ² mo
u_{x1}, t	=	$(x/2 \sqrt{D_1 t}) + \bar{R} \sqrt{t} / 2 \rho \sqrt{D_1}$
v_{x1}, t	=	$(x/2 \sqrt{D_1 t}) - \bar{R} \sqrt{t} / 2 \rho \sqrt{D_1}$
ρ	=	alloy phase density, mg/dm ³
t	=	time in months after onset of linear rate control = total exposure time,
months, minus 1.25

and where $(u_{x2,t})$ and $(v_{x2,t})$ are as above except contain D_2 instead of D_1 and where D_1 and D_2 are the diffusion coefficients in the body centered cubic and face centered cubic regions respectively. I_1 and I_2 are integration constants to be evaluated at x_d where $\bar{C}_1 = \bar{C}_2 = C_d$, $D_1 \partial \bar{C}_1 / \partial x = D_2 \partial \bar{C}_2 / \partial x$. The concentration profile data give:

$$D_2 = 38.4 \exp(-26,140/T)$$

with D_2 in dm^2/mo and T in $^\circ\text{K}$. The data show that D_1 is roughly equal to $100 D_2$.

3. The transformation to linear rate control is accompanied by a transformation from partially selective to full-stoichiometric corrosion behavior. That is, each element corrodes in direct proportion to its bulk alloy composition:

$$\bar{J}_{\text{Fe}} = C_{\text{Fe}\infty} \bar{R}$$

$$\bar{J}_{\text{Cr}} = C_{\text{Cr}\infty} \bar{R}, \text{ etc}$$

This is the result of the fact that for an active element

$$\bar{J}_{\text{element}} = \bar{j}_{\text{el(s)}} + \bar{j}_{\text{el(ns)}}$$

$$\bar{j}_{\text{el(ns)}} = \bar{C}_{\text{el(0)}} \bar{R}$$

and from the C_1 profile description

$$\bar{j}_{\text{el(s)}} = \bar{R} (C_{\text{el}\infty} - \bar{C}_{\text{el(0)}})$$

This behavior is significant since it means that the compositional change can be ignored in corrosion rate studies, provided that linear rate control exists.

4. The extent of average compositional change reaches a limit in a time given by:

$$\sqrt{t_e} = 3.644 \rho \sqrt{D_2} / \bar{R}$$

when this occurs the error function terms go to their upper limit and the profile descriptions become:

$$C_\infty - \bar{C}_1 = (\bar{j}_{\text{(s)}} / \bar{R}) + I_1 \left[1 - \exp(-\bar{R}x / \rho D_1) \right]$$

$$C_\infty - \bar{C}_2 = 2I_2 \exp(-\bar{R}x / \rho D_2)$$

Once equilibrium is established, locally, it is a simple task to calculate the local alloy corrosion rate from the C_2 concentration profile furnished by the electron microprobe at x_d , where $C_2 = C_d$. It is given by:

$$R = (\rho D_2 dC_2/dx) / (C_\infty - C_d)$$

When dC_2/dx is properly measured, the local R 's thus calculated agreed well (within a factor of 2) with the observed length average alloy corrosion rates $\bar{R}$, for the specimens examined.

5. At points along the flow path where sodium, contaminated with 12 ppm oxygen, becomes saturated with the metallic alloying elements, a mechanism change is observed. Chromium now behaves nobly, nickel and molybdenum are neutral, and iron and manganese behave actively. The mechanism is accompanied by oxide film formation and accompanying weight gains.
6. The length average time to reach equilibrium and the extent of the total average equilibrium depth of compositional change are given by:

$$(i) \Sigma \bar{C}_{(0)} < 0.1 \text{ w.f.}$$

$$\bar{t}_e = 3.26 \times 10^{+16} \exp(-26140/T) / (\bar{R})^2$$

$$\bar{x}_e = \frac{7.07 \times 10^{+8}}{\bar{R}} \left[5.45(1.46)^{-\frac{922-T}{56}} + 1 \right] \exp(-26140/T) \log_{10} \left[\frac{0.005}{0.309 - \Sigma \bar{C}_{(0)}} \right]$$

$$(ii) 0.1 < \Sigma \bar{C}_{(0)} < 0.15$$

$$\bar{t}_e = 0.82 \times 10^{+16} \exp(-26140/T) / (\bar{R})^2$$

$$\bar{x}_e = \frac{1.77 \times 10^{+8}}{\bar{R}} \left[8.52(1.46)^{-\frac{922-T}{56}} + 1 \right] \exp(-26140/T) \log_{10} \left[\frac{0.005}{0.309 - \Sigma \bar{C}_{(0)}} \right]$$

$$(iii) \Sigma \bar{C}_{(0)} > 0.15$$

$$\bar{t}_e = 0.41 \times 10^{+16} \exp(-26140/T) / (\bar{R})^2$$

$$\bar{x}_e = \frac{0.88 \times 10^{+8}}{\bar{R}} \left[14.78(1.46)^{-\frac{922-T}{56}} + 1 \right] \exp(-26140/T) \log_{10} \left[\frac{0.005}{0.309 - \Sigma \bar{C}_{(0)}} \right]$$

In which $\Sigma \bar{C}_{(0)}$ is the alloy phase summed length average active element reaction product-alloy interfacial concentration, w.f., T is in $^{\circ}\text{K}$, $\bar{t}_e$ is in months and $\bar{x}_e$ is in dm. The total length average immersion time for equilibrium is $\bar{t}_e + 1.25$.

VII. FUTURE WORK

1. INFLUENCE OF ALLOY PHASE ON CORROSION RATE BEHAVIOR.

The model adopted in the discussion (Section V) will impose over-all stoichiometric corrosion behavior upon the onset of linear rate law control. This is an important concept and, hopefully, may someday be directly tested in partially selective corrosion processes. Its impact upon sodium corrosion technology, however, is not as important to the future design of sodium-cooled reactor systems as are the control features that arise in the sodium phase. Alternate boundary conditions can be chosen for:

$$\partial C / \partial t = D \partial^2 C / \partial x^2 + (d\Delta W / \rho dt) \partial C / \partial x$$

which do not employ the principle of continuous diffusion sources. One in particular, related to the familiar "radiation" boundary condition in heat transfer studies, is that, at $x = 0$,

$$J_i = D_i \partial C_i / \partial x = h_i C_{(0)i} / \rho$$

When $d\Delta w / dt = R = \text{constant}$, this condition will lead to a solution that contains the terms $\text{erfc}(u)$, $\text{erfc}(v)$ and $\exp(-Rx / \rho D)$ and will, as $R\sqrt{t} / 2\rho \sqrt{D}$ approaches 1.822, result in an expression similar to expression (18) (in the absence of diffusivity changes) and which will contain the constant h_i , whose magnitude will determine the equilibrium value of $C_{(0)i}$. $C_{(0)i}$ will change continuously until equilibrium is established, and although J_{Cr} , J_{Ni} , J_{Fe} , J_{Mn} , J_{Mo} must sum to the rate constant R , they vary individually, such that if chromium, nickel and manganese are active and iron is noble, J_{Cr} , J_{Ni} and J_{Mn} decrease while J_{Fe} increases. As in the text model, equilibrium extents of surface compositional change will eventually be reached as will constant corrosion rates of each element. However, the total rate will be other than stoichiometric. Note, however, that in the alternate alloy phase model, transition to linear rate control must also be exerted in the sodium phase, and that the alloy rates will, of course, be those that were measured. When these rates are used in an effort to characterize the sodium parameters of volume flow rate, of velocity, of position, and of temperature, the same difficulties are present as were discussed in Section V-6-b, and the effects of these parameters are those that a reactor designer must know!

Therefore, future emphasis is strongly needed on the development of rate models that reflect the influence of the sodium parameters on structural material corrosion behavior.

2. SODIUM PHASE RATE CONTROL CONSIDERATIONS.

a. Nature of the Sodium Phase Corrosion Product.

It has been proposed^(7, 27, 28) that oxides of the structural alloying elements, which may or may not be complexed with sodium, are the major transporting species in the sodium test loops. There is experimental evidence, from cold leg deposition analyses,⁽¹⁵⁾ that reduced species are also present in, and frequently dominate, the cold leg deposition

product. There is also evidence that oxide films form and adhere to the structural walls in positions of increasing distance along the sodium flow path (high downstream). Thus it would seem, forgiving the license that may accompany the application of thermodynamic concepts in this particular instance, that the transport process could involve the following chemical reactions:

- (i) in the hot zone - oxidation at the wall followed by dissolution of the oxides to an extent that satisfies the equilibrium inherent in:

for which, if ΔF^0 is the free energy change in the standard state, and ΔF that for a given Na_2O concentration, $[\text{Na}_2\text{O}]$, the concentration of alloy oxides, $[\text{AO}]$, will be given by:

$$[\text{AO}] = [\text{Na}_2\text{O}] \exp [-(\Delta F - \Delta F^0)/RT] \quad (46)$$

- (ii) in the cold zone - reduction in satisfaction of the temperature dependence of expression (46). Some part or all of the excess alloy thus formed will be transported by convection to the alloy wall.

b. Transport Paths.

The existence of a low-velocity boundary layer in which hot-zone rate control is exerted was suggested by the results of the microprobe analyses. Treatment of transport through it by film theory, in which the saturated solubility S^θ , where $S^\theta = [\text{AO}]^\theta$ as dictated by expression (46) was taken to exist at the sodium - sodium alloy reaction product interface, indicated that the local rate constant $k_{1\text{loc}}^\theta$ is decreasing with increasing temperature. As previously explained, such cannot be the case with low mass transfer rates. The difficulty can be empirically resolved by examining the natures of $k_{1\text{loc}}^\theta$ and of the corrosion product solution process. $k_{1\text{loc}}^\theta$ is given by⁽³⁰⁾:

$$k_{1\text{loc}}^\theta = 0.0395 \rho_{\text{Na}} v (Sc)^{-2/3} (Re)^{-1/4} \quad (47)$$

where Sc , the Schmidt number, is given by:

$$Sc = \mu_{\text{Na}} / \rho_{\text{Na}} D_{\text{AO}}^{\text{Na}}$$

and where Re is the length Reynolds number, given by:

$$Re = v y \rho_{\text{Na}} / \mu_{\text{Na}}$$

and in which:

$$\begin{aligned}
 v &= \text{turbulent stream velocity, dm/mo} \\
 \rho_{\text{Na}} &= \text{sodium density, mg/dm}^3 \\
 \mu_{\text{Na}} &= \text{sodium viscosity, mg/dm-mo} \\
 y &= \text{distance, from some reference point, in the direction of flow, dm} \\
 D_{\text{AO}}^{\text{Na}} &= \text{diffusivity of alloy oxides in sodium, dm}^2/\text{mo.}
 \end{aligned}$$

The failure of the analyses in Section V-6-b is attributed to the fact transport was considered through the boundary layer as concentration gradient controlled. If, as suggested by Weeks, (8) the transport is through an activity gradient, then the flux will be proportional to the partial molal free energy which in turn will be a function of the degree of unsaturation. This situation can be approximated by treating the diffusion coefficient $D_{\text{AO}}^{\text{Na}}$ in expression (47) as a function of the degree of unsaturation. Thus:

$$(D_{\text{AO}}^{\text{Na}})_{\text{eff.}} = k(S^0 - S)$$

When this is done, and when the resulting value of k_{10c}^{θ} in expression (47) is used in:

$$R_{(y)}^{\theta} = k_{10c}^{\theta} (S^0 - S)$$

the corrosion rate $R_{(y)}^{\theta}$ at a plane y is given by:

$$R_{(y)}^{\theta} = 0.0395 \rho_{\text{Na}}^{1.42} k_v^{0.75} (S^0 - S)^{1.67} / \mu_{\text{Na}}^{0.42} y^{0.25}$$

Using techniques similar to those of Appendix I and Section V-6-b:

$$(S^0 - S)^{-2/3} = (16\pi r A y^{3/4} / 9 \rho_{\text{Na}} G) + (S^0 - S_{(0)})^{-2/3} \quad (48)$$

and:

$$\bar{R} = (\rho_{\text{Na}} G / 2\pi r L) \left\{ \Delta S_0 - \left[(16\pi r L^{3/4} A / 9 \rho_{\text{Na}} G) + \Delta S_0^{-2/3} \right]^{-3/2} \right\} \quad (49)$$

in which all symbols are as previously given, and in which:

$$A = 0.0395 \rho_{\text{Na}}^{1.42} v^{3/4} k^{2/3} / \mu_{\text{Na}}^{0.42}$$

Treatment of the corrosion rate data from run 2 - 5 in Table VI, and using values for $d\Delta\bar{w}/dt$ the crossover as calculated from expression (36) in which $\frac{2.26}{t+1}$ is assumed $\ll 1$ so that $d\Delta\bar{w}/dt \simeq \bar{R}$, gives the following parameters:

	SO-S ppb*	$\frac{\theta}{k}$ $\text{dm}^2/\text{mo} \times 10^{-10}$	$(\bar{D})_{\text{eff}}^{\theta} = k(S^0 - S)$ dm^2/mo
1000F	0.082	14.47	11.79
1100F	0.274	10.52	28.82
1200F	0.565	7.2	40.68

* At the entrance of H1, H2, H3 inlet specimen slots.

In the context in which used, $\frac{\theta}{k}$ has no physical significance. The term of interest is $(\bar{D})_{\text{eff}}^{\theta}$. In essence, it is a transport rate constant in a system under activity gradient control. Its activation energy is 16.67 kcal, as compared to 10.8 kcal reported by Epstein⁽⁴⁾ for the specific solution rate constant, α , for iron in low flow systems. Since the transport process is associated with a balanced consumption of oxygen, 16.67 kcal also represents an oxidation activation energy. It should be noted that $(\bar{D})_{\text{eff}}^{\theta}$ as used above is a function of position as well as temperature. $\frac{\theta}{k}$, however, is independent of distance, and its activation energy, if it is proper to use the Arrhenius temperature dependence, is 9.3 kcal.

Expressions (46) to (49) are empirical and as such are but the first step in the development to a rational description of the rate control exerted in the sodium phase. The reduction of the degree of empiricism, using a more refined approach to both boundary layer theory and activity gradient concepts coupled with additional experimental data on the nature of the corrosion product is most worthy of future serious effort.

APPENDIX I

THE ROLE OF POSITION AND OF VOLUME FLOW
IN SODIUM CORROSION PROCESSES

The major driving force in the mass transfer of structural alloys that constitute the containment system for liquid sodium heat transfer systems is the degree of unsaturation of the individual alloying elements in sodium. Heavy metal solubility in sodium has been characterized^(1, 2), and though there may be some question as to magnitude there is little question as to effect. Thus, with a structural carrier consisting, for the sake of simplification of nomenclature, of a single heavy metal, this metal will enter the sodium phase that bathes it at a rate:

$$d \frac{\theta}{\Delta W} / dt = \frac{\theta}{\alpha} (S^0 - S) \quad (I-1)$$

where:

- $d \frac{\theta}{\Delta W} / dt$ = the corrosion rate, $\text{mg}/\text{dm}^2 \text{mo}$
- $\frac{\theta}{\alpha}$ = the specific wall solution rate constant of the particular metal in question, $\text{mg}/\text{dm}^2 \text{mo}$
- S^0 = the saturated solubility of the metal carrier in sodium, weight fraction (w.f.).
- S = the local concentration of the structural carrier in sodium (local in the sense that such locality exists where $d \frac{\theta}{\Delta W} / dt$ is operative), w.f.

Now consider a single metal structural carrier of circular geometry, radius r , dm , in which sodium is flowing at a volume rate of G , dm^3/mo . If an incremental slice, Δy , is chosen (Figure 29), and assuming that there are no intermediate rate controlling steps, and that linear

FIGURE I-1 STRUCTURAL CARRIER

rate control holds, then there can be no accumulation of solute carrier metal in the sodium in Δy provided that the velocity values associated with G for given values of r are sufficiently greater than the solute diffusivity in liquid sodium. Such is generally the case in most sodium heat transfer systems where the sodium velocity associated with average values of G and of r are greater than one foot per second ($7.9 \times 10^{+6}$ dm/mo) and where solute diffusivities are on the order of 10^{-5} cm²/sec (0.26 dm²/mo).

If S is the solute concentration, w.f., then the total solute flux, f , mg/mo, at a point y along the flow path is:

$$f_y = GS\rho_{Na} \quad (I-2)$$

If the plane average corrosion rate of the carrier wall along the slice Δy is R , mg/dm²mo, then, since there is no solute mass accumulation within Δy , the total solute flux at a plane $y + \Delta y$ must be:

$$f_{y+\Delta y} = f_y + 2\pi r \Delta y R \quad (I-3)$$

This latter relationship can also be expressed as:

$$f_{y+\Delta y} = f_y + (df/dy) \Delta y \quad (I-4)$$

where the total differential reflects the fact that there is no accumulation and that R is chosen constant. Expressions (I-2), (I-3) and (I-4) lead to:

$$dS/dy = 2\pi R/G\rho_{Na} \quad (I-5)$$

or, upon using the value of R in expression (I-1):

$$dS/(S^0 - S) = 2\alpha\pi r (G\rho_{Na})^{-1} dy \quad (I-6)$$

Expression (I-6) describes the rate of solute change as a function of distance along the sodium flow path. It will be solved for isothermal and nonisothermal flow in the following paragraphs.

1. ISOTHERMAL FLOW

In this instance both α and S^0 are constant at all y , and expression (I-6) is readily integrated to provide:

$$S^0 - S = I \exp(-2\alpha \pi r y / G \rho_{Na})$$

The constant I is evaluated at $y = 0$, by noting that at this point S must have some value $S_{(0)}$. Therefore:

$$S^0 - S = (S^0 - S_{(0)}) \exp(-2\pi \alpha r y / G \rho_{Na}) \quad (I-7)$$

Using expression (I-1) with (I-7) R is given by:

$$R = \alpha (S^0 - S_{(0)}) \exp(-2\pi \alpha r y / G \rho_{Na}) \quad (I-8)$$

2. VARIABLE TEMPERATURE

Here it will be assumed that the sodium temperature increases linearly along the flow path y , that the bulk sodium and wall temperatures at any given point are the same, and that for the variable temperature length of interest sodium density changes are insignificant compared to other changes. In particular these latter changes encompass two quantities, and S^0 , whose temperature dependencies will be assumed to be:

$$\alpha = \alpha_0 \exp(-\alpha_1 / T) \quad (I-9)$$

$$S^0 = \beta_0 + \beta_1 T \quad (I-10)$$

It is further assumed that the linear temperature increase along the flow path y is given by:

$$T = \gamma_0 + \gamma_1 y \quad (I-11)$$

where in expressions (I-9), (I-10) and (I-11):

α = the specific wall solution rate constant, $\text{mg}/\text{dm}^2\text{mo}$

α_0 = wall solution rate frequency factor, $\text{mg}/\text{dm}^2\text{mo}$.

α_1 = a factor related to the activation energy, here that energy required for solution, and here expressed in reciprocal temperature units, $(^\circ\text{K})^{-1}$, on the Kelvin scale.

- T = temperature, degrees Kelvin
 S^0 = the saturated solubility of the metal in question in sodium at a temperature T , w. f.
 β_0 = the saturated solubility at zero temperature, w. f.
 β_1 = the rate of solubility increase with temperature, w. f. / °K
 γ_0 = the temperature at the inlet of the variable temperature length in question, °K
 γ_1 = the rate of temperature increase as a function of distance, °K/dm
 y = distance along the variable temperature length in question, dm.

Using expressions (I-9), (I-10) and (I-11) expression (I-6) can be written:

$$dS/dy = A \alpha_0^{\theta} \left[\beta_0 + \beta_1 (\gamma_0 + \gamma_1 y) - S \right] \exp \left[-\frac{\theta}{\alpha_1} / (\gamma_0 + \gamma_1 y) \right] \quad (I-12)$$

If a variable u is chosen so that:

$$u = \beta_0 + \beta_1 (\gamma_0 + \gamma_1 y) - S \quad (I-13)$$

expression (I-12) can be reduced to:

$$du/dy + A \alpha_0^{\theta} u \exp \left[-\frac{\theta}{\alpha_1} / (\gamma_0 + \gamma_1 y) \right] = \beta_1 \gamma_1 \quad (I-14)$$

where:

$$A = 2 \pi r / G \rho_{Na}$$

Expression (I-14) is a first order linear differential equation and has the solution:

$$u = \exp(-g_y) \int_0^y \beta_1 \gamma_1 \exp(+g_y) dy + I \exp(-g_y) \quad (I-15)$$

where:

$$g_y = A \alpha_0^{\theta} \int \exp \left[-(\alpha_1 / (\gamma_0 + \gamma_1 y)) dy \right] \quad (I-16)$$

If a variable x is now chosen so that:

$$x = \frac{\theta}{\alpha_1} / (\gamma_0 + \gamma_1 y) \quad (I-17)$$

expression (I-15) becomes:

$$u = -\exp(+q_x) \int_{\frac{\theta}{\alpha_1} / \gamma_0}^{\frac{\theta}{\alpha_1} / (\gamma_0 + \gamma_1 y)} \frac{\theta}{\alpha_1} \beta_1 x^{-2} \exp(-q_x) dx + I \exp(+q_x) \quad (\text{I-18})$$

where:

$$q_x = A \frac{\theta}{\alpha_0} \frac{\theta}{\alpha_1} \gamma_1^{-1} \int x^{-2} \exp(-x) dx \quad (\text{I-19})$$

Expression (I-19) can be integrated by parts setting:

$$x^{-n} = u' \quad , \quad n=2, 3, 4, \dots \infty$$

$$\exp(-x) dx = dv'$$

Successive integrations by parts establish that:

$$q_x = A \frac{\theta}{\alpha_0} \frac{\theta}{\alpha_1} \gamma_1^{-1} (-x^{-2} + 2x^{-3} - 2 \cdot 3x^{-4} + \dots) \exp(-x) \quad (\text{I-20})$$

For the expected magnitude of $\frac{\theta}{\alpha_1}$ (probably around 5000, since the activation energies are about 10 kilocalories ⁽¹⁾, and $\alpha_1 = Q/1.98$) and for temperature variations in the range of 700 F (644°K) to 1200 F (922°K) the terms of negative exponent smaller than -2 in expression (I-20) can be dropped and expression (I-18) becomes:

$$u = -\exp(-q'_x) \int_{\frac{\theta}{\alpha_1} / \gamma_0}^{\frac{\theta}{\alpha_1} / (\gamma_0 + \gamma_1 y)} \frac{\theta}{\alpha_1} \beta_1 \exp(+q'_x) dx + I \exp(-q'_x) \quad (\text{I-21})$$

where:

$$q'_x = A \frac{\theta}{\alpha_0} \frac{\theta}{\alpha_1} \gamma_1^{-1} x^{-2} \exp(-x) \quad (\text{I-22})$$

Since $x^{-2} \exp(-x)$ will be quite small:

$$\exp(+q'_x) = 1 + q'_x$$

$$\exp(-q'_x) = 1 - q'_x$$

and expression (I-21) becomes:

$$u = -(1-q'_x) \int_{\frac{\theta}{\alpha_1/\gamma_0}}^{\frac{\theta}{\alpha_1/(\gamma_0 + \gamma_1 y)}} \beta_1 x^{-2} (1+q'_x) dx + I(1-q'_x)$$

Or, having previously dropped terms smaller than x^{-2} :

$$u = -(1-q'_x) \int_{\frac{\theta}{\alpha_1/\gamma_0}}^{\frac{\theta}{\alpha_1/(\gamma_0 + \gamma_1 y)}} \beta_1 x^{-2} dx + I(1-q'_x) \quad (I-23)$$

From expression (I-17):

$$-x^{-2} dx = \gamma_1 \alpha_1^{-1} dy$$

so that expression (I-23) becomes:

$$u = (1-q'_x) \int_0^y \beta_1 \gamma_1 dy + I(1-q'_x)$$

and finally, replacing u by its value in expression (I-13), which is equal to $S^0 - S$:

$$S^0 - S = (\beta_1 \gamma_1 y + I) \left\{ 1 - \left[2\pi r \alpha_0 (\gamma_0 + \gamma_1 y)^2 / \rho_{Na} G \alpha_1^\theta \gamma_1 \right] \exp \left[-\frac{\theta}{\alpha_1/(\gamma_0 + \gamma_1 y)} \right] \right\} \quad (I-24)$$

in which all quantities are as previously defined and in which the integration constant, I , must be determined from the value of $S_{(0)}$ at $y = 0$.

APPENDIX II

THE MATHEMATICS OF CONTINUOUS DIFFUSION SOURCES
IN THE PRESENCE OF MOVING BOUNDARIES

1. MODIFICATION OF FICK'S SECOND LAW TO ACCOUNT FOR A MOVING DISTANCE COORDINATE.

Consider a semi infinite solvent medium lattice, a defect alloy lattice, for instance, through which some solute i is diffusing, with constant diffusion coefficient D_i , in the direction of increasing distance, x' , Figure II-1. Fick's second law applies everywhere in the distance coordinate system x' , referenced to a fixed space position, $x' = 0$. Thus:

$$\partial C_i / \partial t = D_i \partial^2 C_i / \partial x'^2 \quad (\text{II-1})$$

Now consider a plane moving in the direction of increasing x' at a rate $d\Delta W / \rho_a dt$, where ΔW is the solvent medium mass traversed by the plane in time t , where ρ_a is the density of the solvent medium, and where at $t = 0$, the moving plane position corresponds to $x' = 0$. A distance coordinate, x , can be specified which is referenced, $x = 0$, to the moving plane. At any point P , in the x' , x coordinates, it is obvious that, at any time t :

$$\partial C_i / \partial x' = \partial C_i / \partial x \quad (\text{II-2})$$

and that:

$$P(x) = P(x') - \Delta W / \rho_a$$

or:

$$x = x' - \Delta w / \rho_a \quad (\text{II-3})$$

Noting that, generally:

$$dC_i = \left(\partial C_i / \partial x' \right)_t dx' + \left(\partial C_i / \partial t \right)_{x'} dt = \left(\partial C_i / \partial x \right)_t dx + \left(\partial C_i / \partial t \right)_x dt$$

it follows from expressions (II-1) and (II-2) that:

$$\partial C_i / \partial t = D_i \partial^2 C_i / \partial x^2 - (dx/dt) \partial C_i / \partial x$$

FIGURE II-1 SCHEMATIC REPRESENTATION OF CONCENTRATION PROFILES AND OF DISTANCE COORDINATES IN A DIFFUSION SYSTEM POSSESSING A MOVING DISTANCE COORDINATE REFERENCE POINT, $x=0$

or, using expression (II-3)

$$\partial C_i / \partial t = D_i \partial^2 C_i / \partial x^2 + (d\Delta W / \rho_a dt) \partial C_i / \partial x \quad (\text{II-4})$$

Expression (II-4) is the modification of Fick's second law to account for the presence of a moving distance coordinate.

2. SOLUTIONS OF CONTINUOUS SOURCE DIFFUSION EQUATIONS IN THE PRESENCE OF A MOVING DISTANCE COORDINATE.

There are two solutions of interest. The first is for a system in which the diffusion coefficient, D_i , is constant throughout the alloy phase. The second is that required for a system in which there is a sudden shift in the value of D_i , as would occur, for instance, when an alloy phase undergoes a face-centered to body-centered cubic crystallographic transformation at some constant concentration, C_{id} , occurring at a plane $x = x_d$.

Both solutions will be sought for $d\Delta W/dt = \text{constant}$, say $= R$, $\text{mg/dm}^2 \text{ mo}$, and both will assume that very little composition change occurred during any initial nonlinear transient, involving the boundary, $x = 0$, movement as a function of time. This assumption establishes that at $t_{\text{linear}} = 0$, $C_i \cong C_i^\infty$. The profile form at the onset of linear rate control can be ignored if a judicious choice of the analytical characteristics of the concentration profiles is made in their application to partially selective corrosion phenomena.

a. Constant D_i , all x

The concentration profile of a noble element i involved in a partially selective corrosion process of alloy corrosion rate R , $\text{mg/dm}^2 \text{ mo}$, such that the element is continuously deposited in the plane $x = 0$, at a constant rate j_i , $\text{mg/dm}^2 \text{ mo}$, will be given by:

$$C_i(x, t) = \int_0^t j_i x (2Rt \sqrt{\pi D_i t})^{-1} \exp \left[-(x^2/4D_i t + R^2 t/4\rho_a^2 D_i + Rx/2\rho_a D_i) \right] dt + I \quad (\text{II-5})$$

in which R/ρ_a is the rate at which the plane $x = 0$ moves, dm/mo , away from the original interface $x = 0$ at $t = 0$, and in which C_i is expressed in weight fraction units. Expression (II-5) may be written as:

$$(C_i - C_{i\infty}) \exp(+Rx/2\rho_a D_i) - (j_i - R) \int_0^t x (2t \sqrt{\pi D_i t})^{-1} \exp \left[-(x^2/4D_i t + R^2 t/4\rho_a^2 D_i) \right] dt \quad (\text{II-6})$$

where $C_{i\infty}$ is the bulk alloy concentration of C_i . If two variables λ_1 and λ_2 are chosen so that:

$$\lambda_1 = x/2 \sqrt{D_i t} + (R/2\rho_a) \sqrt{t/D_i} \quad (\text{II-7a})$$

$$\lambda_2 = x/2 \sqrt{D_i t} - (R/2\rho_a) \sqrt{t/D_i} \quad (\text{II-7b})$$

and then if these two expressions are differentiated with respect to time, the term $x(2t \sqrt{D_i t})^{-1} dt$ in the integral will be given by:

$$x(2t \sqrt{D_i t})^{-1} dt = -(d\lambda_1 + d\lambda_2) \quad (\text{II-8})$$

Now note that the exponent in the integral may be written:

$$\begin{aligned} \exp \left[-(x^2/4D_i t + R^2 t/4\rho_a^2 D_i) \right] &= \exp \left\{ - \left[x/2 \sqrt{D_i t} + (R/2\rho_a) \sqrt{t/D_i} \right]^2 \right\} \exp(+Rx/2\rho_a D_i) \\ &= \exp(+Rx/2\rho_a D_i) \exp(-\lambda_1^2) \end{aligned} \quad (\text{II-9a})$$

and may also be written:

$$\begin{aligned} \exp \left[-(x^2/4D_i t + R^2 t/4\rho_a^2 D_i) \right] &= \exp \left\{ - \left[x/2 \sqrt{D_i t} - (R/2\rho_a) \sqrt{t/D_i} \right]^2 \right\} \exp(-Rx/2\rho_a D_i) \\ &= \exp(-Rx/2\rho_a D_i) \exp(-\lambda_2^2) \end{aligned} \quad (\text{II-9b})$$

Using first expression (II-8) and then expressions (II-9a and II-9b), expression (II-6) becomes, upon multiplying through by $\exp(-Rx/2\rho_a D_i)$:

$$\sqrt{\pi} (C_i - C_{i\infty}) = -(j_i/R) \int_{\infty}^{\left[x + (R/\rho_a)t \right] / 2 \sqrt{D_i t}} \exp(-\lambda_1^2) d\lambda_1 - (j_i/R) \exp(-Rx/\rho_a D_i) \int_{\infty}^{\left[x - (R/\rho_a)t \right] / 2 \sqrt{D_i t}} \exp(-\lambda_2^2) d\lambda_2 \quad (\text{II-10})$$

Noting further that:

$$-\int_{\infty}^u e^{-\lambda^2} d\lambda = + \int_u^{\infty} e^{-\lambda^2} d\lambda = \int_0^{\infty} e^{-\lambda^2} d\lambda - \int_0^u e^{-\lambda^2} d\lambda$$

and that:

$$(2/\sqrt{\pi}) \int_0^{\infty} e^{-\lambda^2} d\lambda = 1$$

$$(2/\sqrt{\pi}) \int_0^u e^{-\lambda^2} d\lambda = \text{erf}(u)$$

$$1 - \text{erf}(u) = \text{erfc}(u)$$

it follows that expression (II-10) becomes:

$$C_i - C_{i\infty} = (j_i/2R) \left\{ \text{erfc} \left(\left[x + (R/\rho_a)t \right] / 2\sqrt{D_i t} \right) + \exp(-Rx/\rho_a D_i) \times \right. \\ \left. \times \text{erfc} \left(\left[x - (R/\rho_a)t \right] / 2\sqrt{D_i t} \right) \right\} \quad (\text{II-11})$$

- b. Shift from D_{i1} to D_{i2} at a Concentration C_d Occurring at a Distance $x = x_d$ (Variable) from the Interface $x = 0$.

In this instance D_{i1} is operative in the region $0 \leq x \leq x_d$, and D_{i2} is operative in the region $x \geq x_d$. Designating the concentrations in the two regions respectively by C_{i1} and C_{i2} then:

$$\partial C_{i1} / \partial t = D_{i1} \partial^2 C_{i1} / \partial x^2 + R \partial C_{i1} / \partial x, \quad 0 \leq x < x_d \quad (\text{II-12a})$$

$$\partial C_{i2} / \partial t = D_{i2} \partial^2 C_{i2} / \partial x^2 + R \partial C_{i2} / \partial x, \quad x \geq x_d \quad (\text{II-12b})$$

$$C_{i1} = C_{i2} = C_{id}, \quad x = x_d \quad (\text{II-12c})$$

and for mass conservation:

$$D_{i1} \partial C_{i1} / \partial x - D_{i2} \partial C_{i2} / \partial x, \quad x = x_d \quad (\text{II-12d})$$

Also, at large x :

$$C_{i2} = C_{i\infty} \quad (\text{II-12e})$$

Complete definition of the problem requires a knowledge of the behavior of C_{i1} at $x = 0$. This is obtained from expression (II-11) of the previous paragraph. For it will be noticed that at $x = 0$, for all t , the alloy phase interfacial concentration is constant and is given by:

$$C_{i1(0)} = C_{i\infty} + j_i/R \quad (\text{II-12f})$$

Under the circumstances imposed by equations (II 12a) through (II 12f), a technique discussed by Crank⁽¹⁾ for diffusion coefficient changes in the absence of a moving reference ($x = 0$) boundary may be adapted to the current problem in which the boundary $x = 0$ moves, as a known function, of time, with respect to the initial interface at $t = 0$. Differentiation will show that the function:

$$C_{i1} - C_{i\infty} = (j_{i1}/R) + I_1 \left\{ \text{erf} \left(\left[x + (R/\rho_a)t \right] / 2\sqrt{D_{i1}t} \right) + \exp(-Rx/\rho_a D_{i1}) \right. \\ \left. \times \text{erf} \left(\left[x - (R/\rho_a)t \right] / 2\sqrt{D_{i1}t} \right) \right\} \quad (\text{II-13})$$

satisfies

expressions (II-12a) and (II-12f), and that the function:

$$C_{i2} - C_{i\infty} = I_2 \left\{ \text{erfc} \left(\left[x + (R/\rho_a)t \right] / 2\sqrt{D_{i2}t} \right) + \exp(-Rx/\rho_a D_{i2}) \right. \\ \left. \times \text{erfc} \left(\left[x - (R/\rho_a)t \right] / 2\sqrt{D_{i2}t} \right) \right\} \quad (\text{II-14})$$

satisfies expressions (II-12b) and (II-12e). Determination of the constants I_1 and I_2 that is explicitly independent of x_d requires knowledge of how x_d varies in time. The time dependence of x_d is such that, using expression (II-12c) the large bracketed terms, $\left\{ \right\}$, must be constant when x is set equal to x_d in their error function, error function complement and exponential terms. As yet an analytical description of some function $x_d = f(t)$ has not been determined. However, this need be of no concern provided that actual measurements of x_d exist when applying expressions (II-13) and (II-14).

APPENDIX III

COMMON DEGREE OF UNSATURATION PRINCIPLES

1. TEST LOOP DIMENSIONS.

The test loop hot leg dimensions of interest are shown in Figures III-1 and III-2. Note that except for the number of specimen slots per specimen holder, Figure III-1 applies to the H1, H2 and H3 sections, unless otherwise indicated.

2. CALCULATIONS

In run 2-5, plane corrosion rates, $R_{(y)}^{\theta}$, are available from the microprobe traces of specimens 2486, H3 inlet, and 2485, H3 outlet. These traces were taken one inch from the inlet end of the respective specimens. Therefore in $R_{(y)}^{\theta}$, as given by:

$$R_{(y)}^{\theta} = k_{loc}^{\theta} (S^0 - S) \exp(-2\pi r y \quad k_{loc}^{\theta} / \rho_{Na} G)$$

, in both cases is 0.254 dm.

The factor $(S^0 - S)$ is given by:

$$(S^0 - S) = (S^0 - S_{(0)}) \exp(-2\pi r y \quad k_{loc}^{\theta} / \rho_{Na} G)$$

where $(S^0 - S_{(0)})$ is the degree of unsaturation at the beginning of a section of constant r and G (volumetric sodium flow, dm^3/mo , ρ_{Na} being the sodium density, mg/dm^3). Note that $2r$ is the wetted perimeter. Therefore, from Figures III-1, and III-2:

$$R_{2486} = k_{loc}^{\theta} \Delta S_{(04)} \exp(-0.254 \times \Sigma P_4 \quad k_{loc}^{\theta} / \rho_{Na} G)$$

$$R_{2485} = k_{loc}^{\theta} \Delta S_{(06)} \exp(-0.254 \times \Sigma P_6 \quad k_{loc}^{\theta} / \rho_{Na} G)$$

where:

$$\Delta S_{(04)} = S^0 - S_4$$

$$\Delta S_{(06)} = S^0 - S_6$$

$$\Sigma P_4 = \Sigma P_6 = 0.27 \text{ dm, the sample holder wetted perimeter.}$$

The quantity $\Delta S_{(06)}$ can be referenced to $\Delta S_{(04)}$ by noting that:

$$(S^0 - S_6) = (S^0 - S_5) \exp(-2\pi r_5 L_5 \quad k_{loc}^{\theta} / \rho_{Na} G)$$

and that:

$$(S^0 - S_5) = (S^0 - S_4) \exp(-2\pi r_4 L_4 \quad k_{loc}^{\theta} / \rho_{Na} G)$$

(1) SEE FIGURE III-2

(2) REFERENCE 14

(3) SPECIMEN (HOCKEY STICK) LENGTH IS THE SAME REGARDLESS OF THE NUMBER OF SLOTS.

(4) IN RUN 2-5 { H1, H2 AND H3R INLETS HAD THREE SPECIMENS IN PARALLEL - EACH 1/3 FLOW } AND THE VELOCITIES ARE GIVEN IN TABLE V.
 { H3 INLET, H1, H2 AND H3 OUTLETS HAD ONE SPECIMEN ONLY - FULL FLOW }

(5) BASED ON A VOLUME FLOW OF 0.7 GPM.

FIGURE III-1 TYPICAL HOT LEG GEOMETRY

FIGURE III-2 SPECIMEN (HOCKEY STICK) AND SLOT CROSS SECTION

in which:

r_5 , L_5 are respectively the radius (0.085 dm) and length (0.320 dm) of the crossover and $2\pi r_4$, L_4 are the perimeter ($\Sigma P_4 = 0.27$ dm) and length (0.747 dm) of the inlet sample holder.

Thus:

$$(S^0 - S_6) = (S^0 - S_4) \exp \left[- \frac{k_{loc}^{\theta}}{\rho_{Na} G} (2 \pi r_5 L_5 + \Sigma P L_4) \right]$$

and:

$$R_{2485}^{\theta} = k_{loc}^{\theta} \Delta S_{04} \exp \left\{ - \frac{k_{loc}^{\theta}}{\rho_{Na} G} [0.27(0.254 + 0.747) + 6.284 \times 0.085 \times 0.320] \right\} \quad (III-2)$$

Expressions (III-1) and (III-2) are simultaneous equations for k_{loc}^{θ} and ΔS_{04} .

APPENDIX IV

TRACE DATA

The tables in this Appendix list element concentrations in weight fractions as a function of distance with "zero" distance taken as the specimen - sodium (actually metallographic mounting material) interface.

In those cases where no readings are given at the zero, or first few micron ($\text{dm} \times 10^{-5}$) steps, the analyst had estimated the surface to be at the zero step. X-ray source area effects are responsible for those cases where the readings at the zero step are significantly different than their adjacent readings.

In several instances duplicate traverses were run in areas that appeared to be essentially similar as viewed by light optics. If the x-ray intensity data were similar, such data of one traverse only were reduced to concentration (except in the case of 4113 A and B where only A is reported, since B was in a grain boundary. Although there are cases where grain boundary compositional changes occur due to selective corrosion they are not under discussion in this report). In those instances where the numerals 1 and 2 follow a specimen number they signify that two traces were taken along the same traverse path with iron as the common element, nickel and chromium being gotten on one traverse, manganese and molybdenum on the next.

TABLE AIV-1

IRON, w.f. as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken Normal to Surface.

Distance dm x 10 ⁺⁵	Specimen Number					
	3312-A	3312-B	3303-A	3303-B	4113-A	2507
0	-	-	-	-	-	0.805
1	0.765	0.769	-	-	-	0.817
2	0.720	0.750	0.772	0.743	-	0.821
3	0.676	0.669	0.787	0.747	0.792	0.813
4	0.675	0.669	0.776	0.758	0.780	0.810
5	0.658	0.676	0.799	0.769	0.770	0.807
6	0.643	0.675	0.761	0.750	0.763	0.792
7	0.655	0.675	0.774	0.773	0.752	0.790
8	0.679	0.675	0.771	0.767	0.738	0.725
9	0.655	0.666	0.782	0.770	0.724	0.692
10	0.660	0.665	0.807	0.764	0.688	0.682
11	0.663	0.667	0.772	0.687	0.666	0.665
12	-	0.666	0.740	0.661	-	-
13	-	-	0.709	0.645	-	-
14	-	-	0.675	0.665	-	-
15	-	-	0.677	-	-	-
16	-	-	0.667	-	-	-
17	-	-	0.665	-	-	-

TABLE AIV-2

IRON, w. f., as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken Normal to Surface.

Distance dm x 10 ⁺⁵	Specimen Number					
	3403-A	3403-B	2481	2485	2486	2206-1
0	0.766	0.904	0.656	0.298	0.743	0.678
1	0.834	0.864	0.892	0.846	0.925	0.858
2	0.862	0.730	0.918	0.883	0.923	0.925
3	0.818	0.674	0.906	0.868	0.904	0.928
4	0.694	0.676	0.794	0.832	0.859	0.914
5	0.654	0.716	0.672	0.722	0.730	0.799
6	0.674	0.668	0.666	0.681	0.665	0.665
7	0.663	0.666	-	0.708	0.663	0.662
8	0.668	0.660	-	0.715	0.665	0.666
9	-	-	-	0.719	-	-
10	-	-	-	0.696	-	-
11	-	-	-	0.670	-	-
12	-	-	-	0.667	-	-
	-	-	-	-	-	-

	2206-2	2207-1	2207-2
0	0.808	0.127	-
1	0.867	0.837	0.842
2	0.932	0.930	0.855
3	0.942	0.896	0.770
4	0.901	0.808	0.652
5	0.732	0.751	0.645
6	0.664	0.678	0.657
7	0.660	0.667	0.655
8	0.660	0.664	0.658
9	0.664	0.666	0.665
10	-	-	0.673
11	-	-	0.660

TABLE AIV-3

IRON, w. f. , as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken at 45° to the Surface.

Distance dm x 10 ⁺⁵	Specimen Number					
	4211-B	4513-B	3402-A	2401-A	3408-A	3408-B
0	-	-	-	-	-	-
0.71	-	-	-	-	-	-
1.42	-	-	-	-	-	0.842
2.13	0.729	0.634	0.791	0.765	0.853	0.800
2.84	0.741	0.648	0.791	0.755	0.858	0.767
3.55	0.744	0.656	0.777	0.733	0.884	0.729
4.26	0.739	0.661	0.766	0.712	0.872	0.700
4.97	0.729	0.661	0.740	0.699	0.841	0.685
5.68	0.725	0.660	0.714	0.684	0.797	0.685
6.39	0.722	0.662	0.698	0.675	0.766	0.685
7.10	0.714	0.664	0.686	0.667	0.738	0.692
7.81	0.706	0.664	0.667	0.665	0.713	0.697
8.52	0.704	0.666	0.665	-	0.703	0.703
9.23	0.696	-	-	-	0.692	0.703
9.94	0.690	-	-	-	0.686	0.703
10.65	0.684	-	-	-	0.682	0.692
11.36	0.676	-	-	-	0.678	0.685
12.07	0.672	-	-	-	0.675	0.677
12.78	0.668	-	-	-	0.667	0.665
13.49	0.666	-	-	-	0.665	-
14.20	-	-	-	-	-	-
14.91	-	-	-	-	-	-
15.62	-	-	-	-	-	-

TABLE AIV-4

IRON, w. f. , as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken at 45° to the Surface.

Distance dm x 10 ⁺⁵	Specimen Number			
	3485-A	3485-B	2482-A	2482-B
0				
0.71	-	-	-	-
1.42	-	-	-	-
2.13	-	-	-	-
2.84	0.805	0.805	0.947	0.966
3.55	0.801	0.816	0.936	0.960
4.26	0.792	0.824	0.939	0.950
4.97	0.796	0.804	0.940	0.942
5.68	0.800	0.801	0.946	0.935
6.39	0.801	0.800	0.938	0.931
7.10	0.806	0.801	0.936	0.923
7.81	0.799	0.801	0.934	0.916
8.52	0.790	0.794	0.926	0.908
9.23	0.755	0.787	0.910	0.885
9.94	0.717	0.775	0.906	0.845
10.65	0.684	0.756	0.922	0.788
11.36	0.673	0.759	0.915	0.742
12.07	0.667	0.725	0.889	0.712
12.78	0.666	0.722	0.852	0.688
13.49	0.665	0.705	0.777	0.674
14.20	-	0.692	0.745	0.695
14.91	-	0.682	0.750	0.676
15.62	-	0.674	0.725	0.674
16.33	-	0.672	0.714	0.666
17.04	-	0.669	0.695	-
17.75	-	0.667	0.654	-
18.46	-	0.666	0.665	-
19.17	-	0.665	0.665	-

TABLE AIV-5

CHROMIUM, w. f. , as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken Normal to the Surface

Distance dm x 10 ⁺⁵	Specimen Number					
	3312-A	3312-B	3303-A	3303-B	4113-A	2507
0	-	-	-	-	-	-
1	0.133	0.119	0.062	-	-	0.090
2	0.145	0.141	0.070	0.070	-	0.093
3	0.155	0.159	0.071	0.074	0.099	0.095
4	0.156	0.161	0.076	0.076	0.103	0.097
5	0.161	0.158	0.077	0.076	0.107	0.100
6	0.164	0.165	0.080	0.079	0.113	0.101
7	0.167	0.166	0.081	0.078	0.118	0.107
8	0.168	0.167	0.081	0.079	0.124	0.109
9		-	0.084	0.080	0.134	0.134
10	-	-	0.092	0.090	0.143	0.152
11	-	-	0.137	0.129	0.154	0.159
12	-	-	0.147	0.152	0.161	0.167
13	-	-	0.156	0.159	0.165	0.168
14	-	-	0.160	0.163	0.166	-
15	-	-	0.164	0.165	0.167	-
16	-	-	0.168	0.170	0.168	-
17	-	-	-	0.165	-	-

TABLE AIV-6

CHROMIUM, w. f. , as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken Normal to the Surface.

Distance dm x 10 ⁺⁵	Specimen Number					
	3403-A	3403-B	2481	2485	2486	2206-1
0	0.026	0.041	0.052	0.017	0.017	0.040
1	0.034	0.058	0.056	0.049	0.038	0.044
2	0.052	0.083	0.060	0.052	0.048	0.055
3	0.054	0.135	0.064	0.055	0.051	0.057
4	0.114	0.154	0.105	0.063	0.055	0.065
5	0.142	0.155	0.156	0.098	0.067	0.109
6	0.159	0.155	0.165	0.138	0.131	0.160
7	0.160	0.161	0.168	0.158	0.159	0.165
8	0.163	0.160	-	0.156	0.165	0.168
9	0.162	0.168	-	0.158	0.164	
10	0.160	-	-	0.159	0.165	
11	0.170	-	-	0.162	0.168	
12	-	-	-	0.149	-	
	-	-	-	0.130	-	
	-	-	-	0.123	-	
	-	-	-	0.126	-	
	-	-	-	0.157	-	
	-	-	-	0.168	-	

	2206-2	2207-1	2207-2
0	0.048	0.008	-
1	0.050	0.046	0.055
2	0.052	0.049	0.063
3	0.055	0.070	0.097
4	0.074	0.110	0.142
5	0.140	0.137	0.144
6	0.166	0.160	0.160
7	0.168	0.164	0.161
		0.166	0.166
		0.165	0.166
		0.166	0.168
		0.168	

TABLE AIV-7

CHROMIUM, w. f. , as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken at 45° to Surface.

Distance dm x 10 ⁺⁵	Specimen Number					
	4211-B	4513-B	3402-A	2401-A	3408-A	3408-B
0	-	-	-	-	-	-
0.71	-	-	-	-	-	-
1.42	-	-	-	-	-	0.076
2.13	0.114	0.199	0.091	0.111	0.064	0.088
2.84	0.118	0.185	0.100	0.113	0.067	0.108
3.55	0.125	0.179	0.104	0.115	0.072	0.132
4.26	0.128	0.168	0.111	0.118	0.080	0.141
4.97	0.133	-	0.125	0.124	0.101	0.149
5.68	0.135	-	0.138	0.137	0.119	0.155
6.39	0.138	-	0.149	0.155	0.140	0.153
7.10	0.141	-	0.160	0.159	0.147	0.158
7.81	0.145	-	0.160	0.160	0.155	0.151
8.52	0.150	-	0.162	0.161	0.164	0.148
9.23	0.153	-	0.163	0.163	0.160	0.146
9.94	0.157	-	0.166	0.163	0.163	0.147
10.65	0.163	-	0.168	0.164	0.164	0.151
11.36	0.164	-	-	0.164	0.165	0.160
12.07	0.166	-	-	0.165	0.164	0.166
12.78	0.168	-	-	0.166	0.163	0.168
13.49	-	-	-	0.166	0.168	-
14.20	-	-	-	0.168	-	-
14.91						
15.62						

TABLE AIV-8

CHROMIUM, w. f. , as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken at 45' to Surface.

Distance dm x 10 ⁺⁵	Specimen Number			
	3485-A	3485-B	2482-A	2482-B
0	-	-	-	-
0.71	-	-	-	-
1.42	-	-	-	-
2.13	-	-	0.039	-
2.84	0.082	0.075	0.044	0.028
3.55	0.088	0.098	0.045	0.039
4.26	0.090	0.089	0.045	0.043
4.97	0.099	0.094	0.047	0.045
5.68	0.103	0.099	0.046	0.047
6.39	0.103	0.099	0.048	0.053
7.10	0.100	0.099	0.049	0.057
7.81	0.101	0.100	0.051	0.059
8.52	0.104	0.104	0.052	0.068
9.23	0.106	0.114	0.054	0.072
9.94	0.109	0.123	0.058	0.078
10.65	0.111	0.132	0.062	0.089
11.36	0.119	0.147	0.074	0.107
12.07	0.129	0.158	0.086	0.118
12.78	0.146	0.161	0.116	0.134
13.49	0.156	0.163	0.142	0.144
14.20	0.165	0.165	0.157	0.156
14.91	0.168	0.164	0.161	0.162
15.62	-	0.161	0.159	0.161
16.33	-	0.163	0.163	0.162
17.04	-	0.166	0.162	0.162
17.75	-	0.167	0.166	0.165
18.46	-	0.168	0.164	0.166
19.17	-	-	0.166	0.168
19.88	-	-	0.167	-
20.59	-	-	0.168	-

TABLE AIV-9

NICKEL, w.f., as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken Normal to the Surface.

Distance dm x 10 ⁺⁵	Specimen Number					
	3312-A	3312-B	3303-A	3303-B	4113-A	2507
0	-	-	-	-	-	-
1	0.114	0.106	0.083	-	-	0.078
2	0.119	0.104	0.082	0.131	-	0.080
3	0.122	0.115	0.098	0.134	0.076	0.082
4	0.122	0.121	0.104	0.124	0.080	0.083
5	0.122	0.118	0.113	0.122	0.084	0.088
6	0.130	0.123	0.106	0.131	0.086	0.089
7	0.127	0.129	0.108	0.129	0.088	0.092
8	0.120	0.124	0.101	0.127	0.091	0.103
9	0.120	0.125	0.105	0.116	0.099	0.118
10	0.122	-	0.100	0.109	0.101	0.125
11	0.123	-	0.096	0.113	0.108	-
12	0.123	-	0.099	0.114	0.111	-
13	0.119	-	0.108	0.125	0.117	-
14	0.125	-	0.116	-	0.119	-
15	-	-	0.122	-	0.121	-
16	-	-	0.122	-	0.123	-
17	-	-	0.120	-	0.125	-
18	-	-	0.127	-	-	-
19	-	-	0.127	-	-	-
20	-	-	0.123	-	-	-
21	-	-	0.124	-	-	-

TABLE AIV-10

NICKEL, w. f. , as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken Normal to the Surface.

Distance dm x 10 ⁺⁵	Specimen Number					
	3403-A	3403-B	2481	2485	2486	2206-1
0	0.004	0.023	0.013	0.004	-	0.014
1	0.012	0.053	0.021	0.019	0.013	0.021
2	0.014	0.078	0.021	0.018	0.017	0.025
3	0.036	0.113	0.025	0.018	0.020	0.029
4	0.099	0.121	0.078	0.029	0.021	0.029
5	0.119	0.125	0.119	0.070	0.034	0.067
6	0.119	-	0.123	0.111	0.100	0.118
7	0.126	-	0.125	0.118	0.120	0.120
8	0.118	-	-	0.122	0.124	0.123
9	0.125	-	-	0.122	0.125	0.125
10	-	-	-	0.123	-	
11	-	-	-	0.121	-	
12	-	-	-	0.118	-	
13	-	-	-	0.100	-	
14	-	-	-	0.095	-	
15	-	-	-	0.098	-	
16	-	-	-	0.114	-	
17	-	-	-	0.125	-	

	2206-2	2207-1	2207-2
0	0.023	0.001	-
1	0.026	0.021	0.024
2	0.026	0.025	0.027
3	0.026	0.033	0.050
4	0.039	0.060	0.102
5	0.099	0.082	0.123
6	0.121	0.117	0.125
7	0.123	0.125	-
8	0.125	-	-

TABLE AIV-11

NICKEL, w. f. , as a Function of
Distance From the Mount-Alloy
Interface. Traces Taken at 45° to the Surface.

Distance dm x 10 ⁺⁵	Specimen Number					
	4211-B	4513-B	3402-A	2401-A	3408-A	3408-B
0	-	NO CHANGE	-	-	-	-
0.71	-		-	-	-	-
1.42	-		-	-	-	0.032
2.13	0.084		0.083	0.106	0.018	0.058
2.84	0.092		0.086	0.106	0.022	0.085
3.55	0.098		0.089	0.111	0.029	0.102
4.26	0.101		0.091	0.113	0.044	0.103
4.97	0.103		0.101	0.115	0.059	0.106
5.68	0.107		0.111	0.117	0.075	0.110
6.39	0.110		0.116	0.117	0.094	0.115
7.10	0.112		0.122	0.112	0.108	0.120
7.81	0.113		0.122	0.113	0.115	0.122
8.52	0.114		0.123	0.115	0.120	0.122
9.23	0.116		0.125	0.118	0.122	0.121
9.94	0.116		-	0.116	0.123	0.123
10.65	0.118		-	0.116	0.125	0.124
11.36	0.119		-	0.121	-	0.125
12.07	0.121		-	0.124	-	-
12.78	0.123		-	-	-	-
13.49	0.124	0.125	-	-	-	-

TABLE AIV-12

NICKEL, w.f., as a Function of Distance
 From the Mount-Alloy Interface.
 Traces Taken at 45° to the Surface

Distance dm x 10 ⁺⁵	Specimen Number			
	3485-A	3485-B	2482-A	2482-B
0	-	-	-	-
0.71	-	-	-	-
1.42	-	-	-	-
2.13	-	-	0.014	-
2.84	0.102	0.098	0.014	0.004
3.55	0.101	0.081	0.014	0.004
4.26	0.099	0.010	0.015	0.009
4.97	0.098	0.098	0.014	0.013
5.68	0.096	0.098	0.015	0.015
6.39	0.092	0.098	0.015	0.015
7.10	0.095	0.096	0.015	0.020
7.81	0.097	0.095	0.016	0.022
8.52	0.099	0.097	0.016	0.026
9.23	0.100	0.096	0.016	0.037
9.94	0.106	0.100	0.018	0.055
10.65	0.112	0.109	0.019	0.083
11.36	0.123	0.114	0.020	0.111
12.07	0.124	0.115	0.035	0.123
12.78	0.125	0.116	0.040	0.125
13.49	-	0.118	0.060	-
14.20	-	0.119	0.080	-
14.91	-	0.120	0.092	-
15.62	-	0.119	0.113	-
16.33	-	0.120	0.113	-
17.04	-	0.121	0.115	-
17.75	-	0.123	0.118	-
18.46	-	0.124	0.120	-
19.17	-	0.124	0.123	-
20.59	-	-	0.125	-

TABLE AIV-13

MANGANESE, w. f., as a Function of Distance
 From the Mount-Alloy Interface.
 Traces Taken Normal to Surface

Distance dm x 10 ⁺⁵	Specimen Number						
	4113-A	2507	2481	2485	2486	2206-1	2207-1
0	-	0.0028	-	-	-	0.0004	-
1	-	0.0016	0.0008	-	0.0008	0.0009	0.0005
2	-	0.0028	0.0016	0.0018	0.0014	0.0022	0.0012
3	0.0032	0.0033	0.0038	0.0070	0.0018	0.0088	0.0014
4	0.0042	0.0032	0.0089	0.0128	0.0048	0.0098	0.0034
5	0.0052	0.0032	0.0148	0.0110	0.0116	0.0150	0.0118
6	0.0058	0.0038	0.0158	0.0082	0.0152	0.0156	0.0158
7	0.0066	0.0055	0.0160	0.0065	0.0162	0.0158	0.0158
8	0.0072	0.0062	-	0.0080	-	0.0162	0.0162
9	0.0086	0.0072	-	0.0116	-	-	-
10	0.0088	0.0124	-	0.0146	-	-	-
11	0.0098	0.0146	-	0.0156	-	-	-
12	0.0110	0.0154	-	0.0160	-	-	-
13	0.0124	0.0160	-	-	-	-	-
14	0.0144	-	-	-	-	-	-
15	0.0152	-	-	-	-	-	-
16	0.0160	-	-	-	-	-	-

TABLE AIV-14

MANGANESE, w.f., as a Function of Distance
 From the Mount-Alloy Interface.
 Traces Taken at 45° to Surface

Distance dm x 10 ⁺⁵	Specimen Number			
	4211-B	3402-A	2401-A	4513-B
0	-	-	-	-
0.71	-	-	-	-
1.42	-	-	-	-
2.13	-	0.0030	0.0048	0.0308
2.84	-	0.0050	0.0056	0.0117
3.55	0.0002	0.0080	0.0070	0.0128
4.26	0.0016	0.0093	0.0108	0.0136
4.97	0.0022	0.0110	0.0124	0.0142
5.60	0.0034	0.0130	0.0138	0.0150
6.39	0.0063	0.0142	0.0144	0.0152
7.10	0.0096	0.0148	0.0148	0.0156
7.81	0.0124	0.0148	0.0154	0.0159
8.52	0.0130	0.0150	0.0156	0.0162
9.23	0.0140	0.0152	0.0158	-
9.94	0.0142	0.0156	0.0160	-
10.65	0.0146	0.0160	-	-
11.36	0.0150	-	-	-
12.07	0.0153	-	-	-
12.78	0.0156	-	-	-
13.49	0.0158	-	-	-
14.20	0.0160	-	-	-
14.91	-	-	-	-

TABLE AIV-15

MOLYBDENUM, w. f. , as a Function of Distance
 From the Mount-Alloy Interface.
 Trace Taken Normal to the Surface.

Distance dm x 10 ⁺⁵	Specimen Number					
	4113-A	2507	2481	2485	2486	2206-1
0	-	-	0.0156	-		0.0002
1	-	0.0058	0.0165	0.0100	0.1900	0.0060
2	-	0.0120	0.0274	0.0160	0.0186	0.0150
3	0.0106	0.0125	0.0394	0.0160	0.0202	0.0164
4	0.0130	0.0153	0.0244	0.0200	0.0282	0.0144
5	0.0158	0.0142	0.0204	0.0160	0.0226	0.0212
6	0.0166	0.0142	0.0212	0.0250	0.0218	0.0180
7	0.0172	0.0153	0.0156	0.0270	0.0168	0.0176
8	0.0245	0.0124	0.0196	0.0830	0.0226	0.0188
9	0.0304	0.0200	-	0.0700	0.0242	0.0162
10	0.0289	0.0160	-	0.0240	0.0202	0.0188
11	0.0230	0.0200	-	0.0198	0.0218	0.0192
12	0.0172	-	-	-	0.0160	0.0170
13	0.0158	-	-	-	0.0234	0.0192
14	0.0166	-	-	-	0.0168	0.0202
15	0.0174	-	-	-	-	0.0180
16	0.0177	-	-	-	-	-
17	0.0180	-	-	-	-	-
18	0.0185	-	-	-	-	-
19	0.0190	-	-	-	-	-

	2207-1		2207-1 (cont)
0	-	9	0.0188
1	0.0094	10	0.0194
2	0.0065	11	0.0214
3	0.0065	12	0.0188
4	0.0088	13	0.0188
5	0.0146	14	0.0220
6	0.0184		0.0176
7	0.0175		-
8	0.0175		-

TABLE AIV-16

MOLYBDENUM, w.f., as a Function of Distance
 From the Mount-Alloy Interface.
 Trace Taken at 45° to Surface

Distance dm x 10 ⁺⁵	Specimen Number			
	4211-B	4513-B	3402-A	2401-A
0	-	-	-	-
0.71	-	-	-	-
1.42	-	-	-	-
2.13	0.0450	0.0248	0.0126	0.0308
2.84	0.0302	0.0224	0.0134	0.0220
3.55	0.0224	0.0204	0.0142	0.0214
4.26	0.0200	0.0194	0.0148	0.0170
4.97	0.0200	-	0.0156	0.0163
5.68	0.0198	-	0.0162	0.0170
6.39	0.0194	-	0.0174	0.0189
7.10	-	-	0.0188	0.0201
7.81	-	-	0.0188	0.0208
8.52	-	-	0.0196	0.0214
9.23	-	-	-	0.0214
9.94	-	-	-	0.0218
10.65	-	-	-	0.0220
11.36	-	-	-	0.0220
12.07	-	-	-	0.0220
12.78	-	-	-	0.0218
13.49	-	-	-	0.0214
14.20	-	-	-	0.0207
14.91	-	-	-	0.0195

EXPOSURE POSITION - IN-PIPE BETWEEN SAMPLE HOLDERS H3 AND H3R

**FIGURE IV-1 SPECIMEN No. 3312 (EXPOSED 2964 HOURS TO
1200F SODIUM FLOWING AT 1 fps)**

AREA A

625X

10% OXALIC ACID

EXPOSURE POSITION - IN-PIPE BETWEEN SPECIMEN HOLDERS H3 AND H3R

AREA B

625X

10% OXALIC ACID

FIGURE IV-2 SPECIMEN No. 3303 (EXPOSED 8208 HOURS
TO 1200 F SODIUM FLOWING AT 1 fps)

AREA A

540X

10% OXALIC ACID

EXPOSURE POSITION - H1 INLET

AREA B

540X

10% OXALIC ACID

FIGURE IV-3 SPECIMEN No. 4113 (EXPOSED 2809 HOURS
TO 1200 F SODIUM FLOWING AT 3.6 fps)

EXPOSURE POSITION - H₂ INLET

FIGURE IV-4 SPECIMEN No. 4211 (EXPOSED 2809 HOURS
TO 1200 F SODIUM FLOWING AT 3.6 fps)

AREA A

EXPOSURE POSITION - H3 INLET

AREA B

FIGURE IV-5 SPECIMEN No. 4513 (EXPOSED 2809 HOURS
TO 1200 F SODIUM FLOWING AT 3.6 fps)

500X

GLYCEREGIA

EXPOSURE POSITION - H3R INLET

FIGURE IV-6 SPECIMEN No. 2507 (EXPOSED 14,101 HOURS
TO 1200 F SODIUM FLOWING AT 7.6 fps)

EXPOSURE POSITION - H3 INLET

FIGURE IV-7 SPECIMEN No. 3402 (EXPOSED 1446 HOURS
TO 1200 F SODIUM FLOWING AT 7.6 fps)

AREA A

540X

10% OXALIC ACID

EXPOSURE POSITION - H3 INLET

AREA B

540X

10% OXALIC ACID

FIGURE IV-8 SPECIMEN No. 2401 EXPOSED 2800 HOURS
TO 1200 F SODIUM FLOWING AT 2.6 fps)

AREA A

600X

10% OXALIC ACID

EXPOSURE POSITION - H3 INLET

AREA B

600X

10% OXALIC ACID

FIGURE IV-9 SPECIMEN No. 3403 (EXPOSED 2813 HOURS
TO 1200 F SODIUM FLOWING AT 7.6 fps)

EXPOSURE POSITION - H3 INLET

540X

10% OXALIC ACID

FIGURE IV-10 SPECIMEN No. 3408 (EXPOSED 5629 HOURS
TO 1200 F SODIUM FLOWING AT 7.6 fps)

EXPOSURE POSITION - H3 OUTLET

500X

GLYCEREGIA

FIGURE IV-11 SPECIMEN No. 2481 (EXPOSED 2805 HOURS
TO 1200 F SODIUM FLOWING AT 23 fps)

EXPOSURE POSITION - H3 OUTLET

540X

10% OXALIC ACID

FIGURE IV-12 SPECIMEN No. 3485 (EXPOSED 5629 HOURS
TO 1200 F SODIUM FLOWING AT 23 fps)

500X

EXPOSURE POSITION - H3 OUTLET

GLYCEREGIA

FIGURE IV-13 SPECIMEN No. 2485 (EXPOSED 5704 HOURS
TO 1200 F SODIUM FLOWING AT 23 fps)

500X

GLYCEREGIA

EXPOSURE POSITION - H3 INLET

FIGURE IV-14 SPECIMEN No. 2486 (EXPOSED 5704 HOURS
TO 1200F SODIUM FLOWING AT 23 fps)

EXPOSURE POSITION - H3 INLET

FIGURE IV-15 SPECIMEN No. 2482 (EXPOSED 6971 HOURS
TO 1200 F SODIUM FLOWING AT 23 fps)

EXPOSURE POSITION - H2 INLET

500X

GLYCEREGIA

**FIGURE IV-16 SPECIMEN No. 2206 (EXPOSED 14,101 HOURS
TO 1100 F SODIUM FLOWING AT 7.6 fps)**

500X

EXPOSURE POSITION -
H3 INLET

10% OXALIC ACID

**FIGURE IV-17 SPECIMEN No. 2207 (EXPOSED 14,101 HOURS
TO 1100 F SODIUM FLOWING AT 7.6 fps)**

APPENDIX V

X-RAY SOURCE AREA EFFECTS

In the traces under discussion the beam diameter was approximately one micron (1μ). For the atomic numbers of the elements considered (Fe-26, Cr-24, Ni-28) under a beam acceleration of 30 kv, the X-ray source volume corresponding to a 1μ beam diameter is roughly proportional to a hemisphere of 3μ diameter; that is: the source area is a 3μ diameter circle, Figure V-1a. Therefore, when the beam is centered at 1.5μ in from the reaction produce-alloy interface, the X-ray source area is entirely in the alloy phase and the trace for a given element should give the true alloy phase concentration of that element, Figure V-1b. But, when the beam is advanced to within 1μ of the surface, Figure V-1c, only 89 per cent of the source area is within the alloy phase, which at this point, for the specimens under discussion is enriched in iron and impoverished in chromium, nickel, and manganese.

The remaining 11 percent, however, is in the metallographic mount which contains insignificant amounts of the alloying elements in question. The result is that the alloy phase iron concentration as measured by the electron microprobe ceases to rise and appears to fall, while the alloy phase chromium, nickel, and manganese concentrations appear to drop even more rapidly near the mount-alloy phase interface. The type of calculation that describes this behavior in the case of iron for instance is given below.

The concentration readout in the vicinity of the mount-alloy interface provided by the electron microprobe is given by:

$$\text{w. f.} = \frac{\text{Weight of Fe in X-ray source volume}}{\text{Total weight of X-ray source volume}}$$

or essentially, ignoring, to a first approximation, the effect of spherical geometry:

$$\text{w. f.} = \rho_a F \bar{P}_{\text{Fe}} / \left[\rho_a F + \rho_{\text{mo}}(1-F) \right]$$

where:

$$\rho_a = \text{alloy phase density, } 8 \times 10^6 \text{ mg/dm}^3$$

$$F = \text{fraction of source area in alloy phase}$$

$$\bar{P}_{\text{Fe}} = \text{average weight fraction of iron across the iron gradient in the alloy phase region occupied by the X-ray source area.}$$

$$\rho_{\text{mo}} = \text{mounting material density } \approx . 2 \times 10^6 \text{ mg/dm}^3.$$

For example, in the case of points A, B, and C on Figures V-1b and V-1c, the iron readout will be:

$$w. f. Fe(A) = \frac{8 \times 10^{+6}}{8 \times 10^{+6}} \left(\frac{1 + 0.895}{2} \right) = 0.9475$$

$$w. f. Fe(B) = \frac{8 \times 0.89 \left(\frac{1 + 0.91}{2} \right)}{8 \times 0.89 + 2 \times 0.11} = 0.9264$$

$$w. f. Fe(C) = \frac{8 \times 0.5 \left(\frac{1 + 0.9475}{2} \right)}{8 \times 0.5 + 2 \times 0.5} = 0.779$$

FIGURE V-1 SCHEMATIC REPRESENTATION OF X-RAY SOURCE AREA EFFECT.

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$$\partial C / \partial t = D \partial^2 C / \partial x^2 + (d\Delta W / \rho dt) \partial C / \partial x$$

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