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ELECTRON BEAM MICROPROBE STUDIES OF
THE OXIDATION BEHAVIOR OF THE IRON-
CHROMIUM-NICKEL SYSTEM IN HIGH-
TEMPERATURE STEAM. I. TRACE
INTERPRETATION TECHNIQUES

By
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March 1964

General Electric Company
Vallecitos Atomic Laboratory
San Jose, California

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ELECTRON BEAM MICROPROBE STUDIES
OF THE OXIDATION BEHAVIOR
OF THE IRON-CHROMIUM-NICKEL SYSTEM
IN HIGH-TEMPERATURE STEAM

I. TRACE INTERPRETATION TECHNIQUES

E. G. Brush

U.S. Atomic Energy Commission
Contract No. AT(04-3)-189
Project Agreement No. 13

March 1964

VALLECITOS ATOMIC LABORATORY
GENERAL ELECTRIC
ATOMIC POWER EQUIPMENT DEPARTMENT
SAN JOSE, CALIFORNIA

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INTRODUCTION

The United States Atomic Energy Commission is sponsoring an extensive nuclear superheat development program by contractual arrangements with several laboratories throughout the Nation. One major task is a comprehensive corrosion study of commercially-available materials that might be suitable for nuclear superheat fuel cladding application. This development is being conducted by the Atomic Power Equipment Department of the General Electric Company under Contract AT(04-3)-189, Project Agreement No. 13.

Fuel cladding materials are exposed under heat transfer conditions to superheat steam containing oxygen and hydrogen representative of a typical boiling water reactor (BWR) steam source.⁽¹⁾

Early testing of Type-304 stainless steel at metal temperatures up to 1300 F indicated the development of a layer of different composition from the base metal at the metal surface.⁽²⁾ At a metal temperature of 1300 F the layer increased in depth with time of exposure, averaging about 0.0002 inch in 1000 hours as compared to 0.0005 inch after 2465 hours of exposure. Similar development of a compositionally-disturbed layer was noted on exposure of Incoloy-800, Inconel-600, and Hastelloy-X to high-temperature steam⁽³⁾ both with and without heat transfer. The composition disturbance results from selective oxidation: a phenomenon that occurs when alloying elements enter the oxide phase in amounts different than those of the bulk alloy stoichiometry.

Although the absolute magnitude of the compositionally-disturbed metallic layer was small, two potentially significant problems became obvious: (1) the effect of a possible change in mechanical properties on a thin-walled fuel cladding, and (2) the resulting selective loss of metallic oxides to the system with potential downstream contamination.

An electron beam microprobe (MP), capable of measuring metallic concentration over 1 to 2 micron (μ) intervals, gave an indication of the relative concentrations of iron, chromium, and nickel present in the base metal, disturbed metallic layer, and adjacent oxide.^(2,3) It was found that this approach had the promise of establishing the morphology and kinetics of the oxidation process.

No previous study was available as a guide for the kinetic interpretation of the data from the MP analyses for the resolution of the basic considerations applicable to corrosion in superheated steam. It is the purpose of this report to document a technique developed for the interpretation of MP data and to point out its salient features as it relates to the oxidation process of iron-chromium-nickel (Fe-Cr-Ni) alloys. In a companion report⁽⁴⁾ the principles herein developed are applied specifically to Incoloy-800 for verification of long-term corrosion rates and establishment of the selective release of metallic oxides into transport.

CONCLUSIONS

1. Electron beam microprobe (MP) traces can play a key role in studying and interpreting the oxidation behavior of the iron-chromium-nickel alloys in high-temperature steam.
 2. MP traces alone cannot be applied to oxidation phenomena. For proper interpretation, the following are desirable in combination with optical microscopy:
 - a. The x-ray source area size to permit proper corrections for MP readings across an interface (e.g., oxide-metal).
 - b. Exact locations of interfaces on MP traces, especially when major changes in elemental composition occurs.
 - c. Standard oxide phase morphological models to permit mass balancing with proper amount of metal (e.g., FeO contains 77 percent iron, while Fe_2O_3 contains only 69 percent iron).
 3. A mathematical model based on displacement reaction postulates was developed to fit the mechanistic concepts of mixed selective-nonselective oxidation phenomena. The major implications of the model are:
 - a. The extent of the compositional disturbance will reach a maximum, equilibrium value.
 - b. When such equilibrium is established, the alloying elements enter the oxide phase in direct proportion to the bulk alloy composition.
- The model may be used for the quantitative analysis of MP concentration profiles and it may also provide a method of mass balancing under the MP profiles across oxidation reaction zones. This will permit a quantitative measure of the alloy selectivity in the metal-to-system lost in transport.
4. The MP alone may not provide sufficient measurements for the evaluation of steady-state oxidation (corrosion) rates. Classical methods for determining total oxidation rates will continue to be needed.
 5. The principles developed can be applied quantitatively to MP traces of Fe-Cr-Ni alloys exposed at several temperatures to high-temperature steam for various time periods. The results will serve as an independent check of the descaled weight loss measurements as a measure of metal attrition resulting from oxide formation. In addition, it will provide an estimate of the magnitude and composition of oxide loss to the steam environment.
 6. The experience of applying MP traces to the definition of the performance of the Fe-Cr-Ni alloys should be factored into a continuous refinement of the mathematical model for improved and future data interpretation.

EXPERIMENTAL

1. Materials and Steam Exposure History

The MP traces considered herein were taken from only four of the many specimens examined. Their composition is listed in Table I, and their steam exposure history and weight change data are listed in Table II. The unit $\mu\text{g}/\mu^2$ is used throughout this report to reflect the fact that measurements are carried out at the micron level. The unit is easily convertible to more common units, $1 \mu\text{g}/\mu^2 = 1 \times 10^{-7} \text{ mg}/\text{dm}^2$. The 1300 F 304 stainless steel specimen was a heat-transfer sheath (transferring heat at a rate of 175,000 Btu/ft²-h into steam flowing at 200 ft/sec). The 1050 F specimens were non-heat-transfer (isothermal) coupons, exposed to superheated steam flowing at 20 ft/sec. Both types of specimens were exposed in the facility schematically illustrated in Figure 1. The bulk steam temperature in the case of the 304 specimen (whose metal temperature was 1300 F) was also 1050 F. The steam was generated from demineralized water containing $< 0.1 \text{ ppm Cl}^-$. A nominal level of 20 ppm oxygen and 2.5 ppm hydrogen was maintained in the steam, a condition representative of the oxygen and hydrogen formed in a boiling water reactor from radiolytic water decomposition.

2. Electron Beam Microprobe Analyses

The traces herein discussed, chosen to illustrate the interpretative features which are the subject of this report, were obtained by motor-driven scanning (12 sec/micron) on a Philips Microprobe Analyzer, Model AMR/3, operated by the Advanced Materials Research Corporation, Somerville, Massachusetts.

An electron beam microprobe is an analytical tool that monitors characteristic elemental X radiation in extremely small regions, thus allowing chemical analyses to be made in one to two micron increments of length across a given alloy region. A beam of electrons, accelerated under high potentials ($\sim 30 \text{ kv}$ in this instance) is focused by electromagnetic lenses to a diameter of one to two microns on the specimen surface, which acts as a primary source of x-rays that are excited by the electron beam.

The induced X radiation is composed of a continuous spectrum, as well as fluorescent x-rays characteristic of each element that the electron beam "sees". The fluorescent X radiation, Fe K α , Cr K α , and Ni K α , is collected in one or more spectrometers (in this instance, equipped with curved LiF focusing crystals), each adjusted to the angle which corresponds to the desired elemental K α radiation wavelength (through Bragg's law considerations) to be monitored.

The chemical composition studies are made by amplifying and recording the intensity of the characteristic X radiation which, when adjusted for absorption and secondary fluorescence effects, will be proportional to the concentration of its element in the volume under the electron beam.

TABLE I

SUPERHEAT TEST PROGRAM
ALLOY COMPOSITIONS
PERCENT OF ELEMENT

	C	Fe	Cr	Ni	Mn	Co
304 S.S.	0.04	70.3	18.4	9.5	---	---
Incoloy-800	0.05	45.1	20.6	32.6	---	---
Inconel-600	0.05	6.9	15.9	76.2	---	---
Hastelloy-X	0.10	18.7	21.7	46.6	9.2	1.9

TABLE II

STEAM EXPOSURE HISTORY AND ACCOMPANYING WEIGHT CHANGES
OF FOUR Fe-Cr-Ni ALLOYS

Alloy	Exposure		Weight Change $\mu\text{g}/\mu^2 \times 10^{-6}$ *		
	Temp (°F)	Time (hrs)	Oxide Weight Remaining on Specimen Before Descaling	Descaled Metal Loss	Metal Lost to Steam (Based on 72% Metal in Oxide)
304 S.S.	<u>1300</u>	2465	38.9	35.4	7.4
Incoloy-800	<u>1050</u>	5116	16.8	14.0	1.9
Hastelloy-X	1050	5116	17.5	13.4	0.8
Inconel-600	1050	5116	5.4	4.6	0.7

* $1 \text{ mg}/\text{dm}^2 = 1 \times 10^{-7} \mu\text{g}/\mu^2$

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Figure 1. Superheat Corrosion Facility

DISCUSSION

1. General

Cursory examination of all traces taken to date has revealed three apparently reproducible observations that would require serious consideration if physically related to the oxidation process, for they have not been noted in previous dissertations of selective oxidation. The first and second observations, schematically illustrated in Figure 2, are that the profiles have maxima and minima (non-monotonicity) in the alloy phase, also noted by Wood and Melford,⁽⁵⁾ and that the concentration, $C_{\Sigma x}$, in the alloy phase at the oxide-alloy interface varies in time. The third observation (Figure 3) is that the depth of the compositionally-disturbed metallic layer is significantly affected by the thickness of the overlying oxide film.

The discussion that follows will explore the origin and nature of these three observations in order that they may be factored into quantitative mass balancing under electron microprobe traces of oxidation reaction zones.

In particular, it will establish that trace non-monotonicity is caused by x-ray source area effects. These effects can also account for the apparent changes in time of exposure of the alloy phase alloying element interfacial concentrations. However, arguments will be advanced in support of a postulate that such changes may be real, and not merely artifacts due to x-ray source area behavior. The discussion treats the third observation by considering oxidation modes; it will show that the depth dependence of the compositionally disturbed metallic layer upon the overlying oxide film thickness is real and results from local (and secondary) oxidation phenomena.

Finally, the discussion will incorporate these three features in the quantitative interpretation of electron microprobe traces with the use of suggested analytical models for chemical reaction coupled with diffusion in the presence of a moving boundary.

2. Significance of the X-Ray Source Area

A logical first step in interpreting MP trace data is to examine expected concentration changes in both oxide and alloy phases of a hypothetical alloy undergoing selective oxidation. Assume that an 85 weight percent Fe, 15 weight percent Cr alloy is subject to oxidation such that the oxide consists of 75 percent Fe_2O_3 and 25 percent Cr_2O_3 . It is further assumed that the oxides are distributed in a $10\ \mu$ layer such that, as expected from a consideration of their dissociation pressures, Cr_2O_3 is concentrated near the oxide-alloy interface, and Fe_2O_3 near the oxidant-oxide interface as shown in Figure 4. The non-stoichiometric constituent oxide fractions dictate that, in the absence of subsurface voiding, the excess iron that does not enter the oxide phase must diffuse back into the interior of the alloy, while the excess chromium that does enter the oxide phase must diffuse from within the interior of the alloy to the oxide-alloy interface. The counter diffusion establishes the concentration profiles in the alloy phase.

Figure 2. Deviations from Theoretical Selective Oxidation

Figure 3. Apparent Effect of Oxide Thickness on Chromium Behavior in Alloy. The Thin Oxide Produces a Greater Disturbance Depth.

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Figure 4. Hypothetical Fe-Cr Oxidation, Cr₂O₃ and Fe₂O₃
Assumed 100% of Theoretical Density. That is:
both $5.2 \times 10^{-6} \mu\text{g}/\mu^3$

If this specimen is now examined by MP analysis, at $1\ \mu$ intervals, starting well within the interior of the alloy, the resulting MP traces should follow the Figure 4 alloy concentration profiles exactly, until the beam is within $\sim 2\ \mu$ of the oxide-alloy surface. At this point, the magnitude of the x-ray source area (excited by the electron beam) which provides the K_{α} x radiation (more generally used than L_{α} in Fe-Cr-Ni systems) that will eventually be reduced to metallic concentrations, must be taken into account.

In the traces under discussion, the beam diameter was $\sim 1\ \mu$. 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 $1\ \mu$ beam diameter is roughly proportional to a hemisphere of $3\ \mu$ diameter; that is, the source area is a $3\ \mu$ diameter circle (Figure 5a). Therefore, when the beam is centered at $1.5\ \mu$ in from the oxide-alloy interface, the x-ray source area is entirely in the alloy phase and the MP traces should follow the hypothetical profiles (Figure 5b). But, when the beam is advanced to within $1\ \mu$ of the surface (Figure 5c), only 89 percent of the source area is within the alloy phase, which at this point is enriched in iron and impoverished in chromium.

The remaining 11 percent, however, is in the oxide phase, which is very poor in iron and is highly enriched in chromium. The result is that the Cr concentration in the alloy phase appears to rise and that of Fe to fall. The type of calculation used in establishing the true concentration is detailed in the note below.

NOTE

The concentration readout in the vicinity of the oxide-alloy interface provided by the microprobe is given, in the case of iron for instance, by:

$$\text{Percent} = \frac{\text{Weight of iron in x-ray source volume}}{\text{Total weight of x-ray source volume}} \times 100$$

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

$$\text{Percent} = \frac{\rho_a f \bar{P}_a + \rho_{ox} (1-f) \bar{P}_{ox}}{\rho_a f + \rho_{ox} (1-f)}$$

where:

- ρ_a = Alloy density = $8 \times 10^{-6}\ \mu\text{g}/\mu^3$
- f = Fraction of source area in alloy phase
- $\bar{P}_a$ = Average weight percent of iron across the iron gradient in the alloy phase region occupied by the x-ray source area.

Figure 5. X-Ray Source Area Effects on Microprobe Readout of Alloy Phase Concentration

$$\begin{aligned}\rho_{\text{ox}} &= \text{Oxide density} = 5.2 \times 10^{-6} \text{ } \mu\text{g}/\mu^3 \\ \bar{P}_{\text{ox}} &= \text{Average weight percent of iron across the} \\ &\quad \text{iron gradient in the oxide phase region occupied} \\ &\quad \text{by the x-ray source area.}\end{aligned}$$

In the case of points A, B, and C, Figure 5b and 5c, the iron readout will be:

$$\begin{aligned}P(A) &= \frac{8 \times 10^{-6}}{8 \times 10^{-6}} \left(\frac{100 + 89.5}{2} \right) = 94.75\% \\ P(B) &= \frac{8 \times 0.09 \left(\frac{100 + 91}{2} \right) + 5.2 \times 0.11 \left(\frac{0 + 2.5 \times 0.69}{2} \right)}{8 \times 0.89 + 5.2 \times 0.11} = 88.5\% \\ P(C) &= \frac{8 \times 0.5 \left(\frac{100 + 94.75}{2} \right) + 5.2 \times 0.5 \left(\frac{0 + 7.5 \times 0.69}{2} \right)}{8 \times 0.5 + 5.2 \times 0.5} = 60\%\end{aligned}$$

where 0.69 is the weight fraction of Fe in Fe_2O_3 .

The result is (Figure 5b) that the iron concentration between the oxide-alloy interface and a point of 1.5μ within the alloy appears to drop. Correspondingly, by the same reasoning the chromium concentration in this region will appear to rise.

If the MP tracing is continued on into the oxide phase, traces similar to those in Figure 6 are obtained. Here, as on the x-ray intensity readout chart of the instrument, no interfaces yet appear. These must be imposed by the analyst. The instrument gives him but one definitive space point on his charts: that where the beam enters the non-metallic specimen mount, whose high resistance causes a sharp drop in the specimen current induced by the electron beam. Generally, the characteristics of the light optical system, chart movement, and analyst motion-visual reflexes make this current drop-off point location accurate to within $\pm 2\mu$ of the true oxide-oxidant interface. The point of this sharp drop off is referred to as the "advertised edge." Taking this into account along with the sharp directional changes at $\pm 1.5\mu$ of the oxide-alloy interface and with light optical measurements of oxide thickness across the trace path, the interfaces may be rather precisely located, as in Figure 7. The profile non-monotonicity in the alloy phase is therefore nothing more than an artifact due to x-ray source area effects.

Note that beyond the 1.5μ depth toward the interior of the alloy, the constituent alloying element fractions as measured by the MP trace must sum to one; but between the oxide-alloy interface and 1.5μ within the alloy, the MP trace reflects mixed oxide and alloy metallic concentration. Here, the MP trace concentrations do not necessarily sum to one, and indeed are

Figure 6. Iron-Chromium Traces Before Interface Location

Figure 7. Iron Chromium Traces After Interface Location

meaningless in terms of actual concentrations in each phase. This is particularly true of the MP trace interface concentrations. The dashed lines are true concentrations in this mixed region. However, MP trace profiles in the mixed region are important for comparative purposes with standard models.

3. Constituent Oxide Form and the Role of Standard Trace Models

Figure 7 suggests the use of an important aid in the interpretation of MP traces. The aid is one that could be available in a card index file of standard traces, constructed in the manner of Figure 7 with a variety of non-stoichiometric fractions and constituent oxide forms and distributions. For instance, the reader can visualize how the hypothetical Fe-Cr trace would appear if the constituent oxide forms were FeCr_2O_4 and FeO , noting that the metallic content of this last oxide is near 77 percent rather than 69 percent, as in Fe_2O_3 .

The constituent oxide forms that can exist in the Fe-Cr-Ni system consist of various spinel and rhombohedral combinations. Theoretically, during thermodynamically equilibrated oxidation, if all three elements enter the oxide phase, the constituent oxides would appear from oxide-alloy to oxide-oxidant surface such that those with the lowest dissociation pressure were closest to the oxide-alloy interface (Figure 8), see note below. The transport paths for the p-type semiconductors, presumably all but Fe_2O_3 ,⁽⁶⁾ are shown in Figure 9, for which the boundary reactions are listed in Figure 10. The transport paths and boundary reactions would normally be an important factor in multiphase moving boundary diffusion (in this case coupled with chemical - therefore oxidation - reaction) problems. However, the steric, as opposed to mechanical, defect structure (site vacancies and electron deviations) that is responsible for mass and charge transport in oxide films is sufficiently uniform to justify the adoption of a linear concentration gradient in any given oxide structure.⁽⁷⁾

NOTE

The dissociation pressures of the pure oxides were determined from the thermochemical data of Coughlin according to the principles adopted by Dushman⁽⁸⁾ who uses the relationship

$$\log P_{\text{atm}}(\text{O}_2) = \frac{1}{n} \frac{\Delta F^\circ}{4.575 T}$$

for the reaction:

for the pure oxides of non-volatile metals. In the case of the spinels of iron and nickel with chromium, Schmalzried⁽⁹⁾ gives the free energies of the reactions:

OXIDANT	OXIDE	METAL
	Fe_2O_3 - NiFe_2O_4	
	NiO - NiCr_2O_4	
	Fe_3O_4 - FeO	
	FeO - FeCr_2O_4	
	Cr_2O_3	

DISSOCIATION PRESSURES.	
$\pi_{\text{ox}}, (1000\text{K})$	
OXIDE	$\pi_{\text{ox}}, \text{ATM}$
Cr_2O_3	3.30×10^{-31}
FeCr_2O_4	3.17×10^{-25}
FeO	1.21×10^{-21}
Fe_3O_4	5.48×10^{-21}
NiCr_2O_4	1.12×10^{-18}
NiO	4.62×10^{-16}
NiFe_2O_4	3.15×10^{-13}
Fe_2O_3	4.35×10^{-11}

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Figure 8. Theoretical Equilibrium Oxide Distribution

Figure 9. Theoretical Transport Paths

BOUNDARIES IN FIGURE 9.

AT BOUNDARY 1

AT BOUNDARY 3

(n-p) SWITCH

AT BOUNDARY 4

1683-11

Figure 10. Boundary Reactions

as -8.2 kcal and -6.0 kcal respectively at 1300K. The entropies are sufficiently small so that these values are but slightly different at 1000K. With them and with Coughlin's data for the pure oxides, ΔF° for the two spinels may be determined. With these latter values, the dissociation pressure for the reactions:

may be calculated by the method of Dushman.

Similar principles are applicable to the iron-nickel spinel where the free energy for the reaction:

was estimated according to the methods outlined by Kubaschewski.⁽¹⁰⁾

Therefore, the rate control - except where FeO is involved - suggested in Figures 9 and 10 is not as pertinent to this discussion as is the fact that full n-p switches (boundary 3) and quasi n-p switches create rather large internal stresses that promote gross mechanical defects, either spallation or voiding, spherical or crack-like.⁽¹¹⁾ Quasi n-p switches occur from O_2 dissociation to create p defects, as shown at boundaries 2 and 3 (Figures 9 and 10). The mechanical damage will tend to increase the oxidant pressure over the alloy at the oxide-alloy interface, which will favor the formation of the rhombohedral oxides, Fe_2O_3 , Cr_2O_3 (NiO has the NaCl crystal form) rather than the spinel oxide forms.⁽¹²⁾ Therefore, whenever oxidation is accompanied by mechanical defection of the oxide, the constituent oxide forms would logically consist of Fe_2O_3 , Cr_2O_3 , and NiO mixtures but not of any spinel involving FeO. Under these circumstances, it would be expected that the oxidation rate, and hence the degree of metallic layer disturbance that accompanies selective oxidation, would be increased over that where neither spallation nor voiding occurs. Such expectancy assumes the rate to be proportional to film barrier strength; that is, inversely proportional to its steric or non-mechanically-defected thickness. It would also be expected that mechanical defection should occur randomly over the oxide-oxidant surface, resulting in a wavy, compositionally-disturbed, metallic layer depth, roughly constant, at a given time, as measured from the oxide-alloy interface inward toward the bulk alloy composition.

This is not entirely the case in the Fe-Cr-Ni exposed to high-temperature steam, where weight change measurements and light optical examination indicate that spalling and voiding in the oxide phase are both occurring. In the majority of the Fe-Cr-Ni specimens examined by APED after steam exposure, regardless of time or of temperature, there is apparent wavy constancy of the distance between the original steam-alloy interface (its location is inferrible) at $t = 0$, and the point within the alloy where compositional disturbance begins (optically detectable) (Figures 11 and 12). However, in the majority of specimens examined to date (~150) the following was observed:

Figure 11. Hastelloy-X After Isothermal Exposure to Steam at 1050 F for 5116 Hours.
Photomicrograph 540X, 10% Oxalic Acid Electrolytic Etch

Figure 12. Inconel-600 After Isothermal Exposure to Steam at 1050 F for 5116 Hours. Photomicrograph 540X, 10% Oxalic Acid Electrolytic Etch. Area A Scans.

- a. The depth of the compositional disturbance is greatest where the oxide film is thinnest.
- b. The total amount of oxidation (with reference to the $t = 0$ steam-alloy interface) is least where the oxide film is thinnest, and is also least where no spalling has occurred (Figure 13 is a good example of this latter observation) but where the oxide is voided.
- c. Massive oxidation occurs into the compositionally-disturbed metallic layer where the oxide film is thick and apparently free of mechanical defects.

These observations are schematically summarized in Figure 14.

In view of the previous remarks concerning expected constituent oxide forms with mechanically-defected oxide films, these experimental observations suggest that the normal mode of oxidation of the Fe-Cr-Ni system by high temperature steam is one of random oxide defection resulting in the formation of rhombohedral oxide forms. Should defection cease, the oxidant pressure at the oxide-alloy interface will not support the presence of Fe_2O_3 at this interface and it will dissociate according to:

FeO is a highly cation-deficient oxide whose rate of formation is generally greater than that of Fe_2O_3 .⁽¹³⁾ Its cation deficiency is much greater than that of either NiO ⁽¹⁴⁾ or Cr_2O_3 ,⁽¹⁵⁾ and as suggested in the phase boundary reactions of Figure 10, it is probably responsible for initiating the p-type defects required to bring Cr^{+3} and Ni^{+2} ions into the oxide phase in those instances where low oxidant pressures at the alloy surface allow Fe-Cr spinel formation. It should be noted that this situation also promotes internal oxidation.⁽¹²⁾⁽¹⁶⁾

However, in our light-optical examination of scaled and descaled specimens, such internal oxidation appears to be essentially absent. In its presence, MP trace models would have to account for the fact that the metallic content is $1 \geq \Sigma \text{ metal} \geq 0.79$, where 0.79 is the metallic fraction of pure NiO , the greatest fraction of any combination of the three oxides.

When oxide film defection ceases and FeO becomes stable, deep oxide pits will grow into the compositionally-disturbed metallic layer at rates in excess of those at which diffusion in alloy can maintain the former degree of selective oxidation in these pit regions, with the result that the compositionally-disturbed metallic layer is consumed. In cases where alloy surface iron enrichment and chromium impoverishment exist, the normally high transport rates in FeO will be increased due to Cr^{+3} dissolution, because Cr^{+3} will reduce the electron defects $\oplus$, and thereby increase the cation defects $\square''\text{Fe}^{++}$.

Figure 13. 304 Stainless Steel Microprobe Traces After 2465 Hours in Steam at a Metal Temperature of 1300°F. Photomicrograph 540X, 10% Oxalic Acid Electrolytic Etch.

1643-14

Figure 14. Schematic Oxide Morphology

Thus, the general observations in the cursory examination of MP traces of Fe-Cr-Ni alloys exposed to steam have been explained:

- a. The non-monotonicity is an artifact of the MP itself.
- b. The varying surface concentrations may be artifacts, but if displacement reactions are important, these variations in time are to be expected.
- c. The changes in the depth of compositional disturbance with changing oxide film thickness are the result of a secondary oxidation process which occurs when the normal mechanical defection of the oxide film is interrupted.

With this information and with the information available from light microscopy on film morphology, standard models of constituent oxide forms and distribution can be constructed and used in the interpretation of actual MP traces at a given time of exposure.

4. Mass Balance Principles

How such information is used in establishing a mass balance of MP trace data across a given reaction zone is best illustrated by considering the features of an actual trace across a region of thick oxide in an Incoloy specimen exposed to 1050 F steam for 5116 hours (see Figure 15). Light optics suggest that the oxide film is mechanically defected by voiding and that, therefore, the constituent oxides should be Fe_2O_3 , Cr_2O_3 and NiO. Considering source area effects, advertised oxide edges, and optically-detectable oxide and compositionally-disturbed metallic layer thicknesses, interfaces may be imposed as shown. The elemental distribution in oxide and in alloy phase is shown by heavy solid lines outside of the source area affected zone that is at $\pm 1.5\mu$ of the oxide-alloy interface. The dashed lines in the oxide phase indicate actual concentrations in the affected oxide zone, and the dashed lines in the alloy phase, starting at the limit of optical detection, are the actual concentrations in the alloy phase. These have been adjusted to satisfy the following:

The assumptions concerning selective oxidation under solid-state diffusion control, as discussed further in this section.

Alloying fraction summing to one in light of the probable error of the MP trace concentration (about ± 5 percent of the true concentration in these systems), taking into account attenuation and magnification effects due to absorption and secondary fluorescence. For instance, NiK_α will fluoresce Fe, and FeK_α will fluoresce Cr. However, Ni absorbs CrK_α radiation. So in an alloy of 74 percent Fe, 8 percent Ni, and 18 percent Cr, chromium will appear as 20 percent, where in an alloy of 74 percent Ni, 8 percent Fe, and 18 percent Cr, it will appear as 16 percent.

a. Metallic Mass in the Oxide Phase

The oxide film (see Figure 15) is 8.5μ thick. Consider a composition grid whose ordinate is in weight fractions from 0 to 1.0 and whose abscissa is in μ length units. If the average oxide

Figure 15. Incoloy-800 After Isothermal Exposure to Steam at 1050 F for 5116 Hours. Photomicrograph 540X, 10% Oxalic Acid Electrolytic Etch.

density (that of the mixture of constituent oxides in the 8.5μ film where no striation is detectable) is $\bar{\rho}$, $\mu\text{g}/\mu^3$, then the oxide mass is, per unit area: $8.5\bar{\rho}$, $\mu\text{g}/\mu^2$. It must all be contained in the composition grid so that each grid unit contains $8.5\bar{\rho}/85 = 0.1 \times \bar{\rho}$ $\mu\text{g}/\mu^2$ of oxide. The areas (that is, number of grid units easily obtainable from the trace with a precision planimeter) for Fe, Cr and Ni under their respective MP traces in Figure 15, in the oxide phase, are 28.6, 16.9, and 11.7 grid units. These correspond to:

$$28.6/0.69 = 42.9 \text{ grid units Fe}_2\text{O}_3$$

$$16.9/0.68 = 24.8 \text{ grid units Cr}_2\text{O}_3$$

$$11.7/0.79 = 14.8 \text{ grid units NiO}$$

The mean oxide density $\bar{\rho}$ is given by:

$$\begin{aligned}\bar{\rho} &= \frac{82.5}{85.5} \left(\frac{42.9}{82.5} \times 5.2 + \frac{24.8}{82.5} \times 5.2 + \frac{14.8}{82.5} \times 7.45 \right) \times 10^{-6} \\ &= 5.37 \times 10^{-6} \mu\text{g}/\mu^3\end{aligned}$$

where 5.2×10^{-6} is the 100 percent theoretical density of Fe_2O_3 and of Cr_2O_3 and 7.45×10^{-6} $\mu\text{g}/\mu^3$ is that of NiO. The mass of Fe, Cr and Ni in the oxide are therefore, per unit area:

$$\text{Fe: } 42.9 \times 0.69 \times 0.537 \times 10^{-6} = 15.85 \times 10^{-6} \mu\text{g}/\mu^2$$

$$\text{Cr: } 24.8 \times 0.68 \times 0.537 \times 10^{-6} = 9.10 \times 10^{-6} \mu\text{g}/\mu^2$$

$$\text{Ni: } 14.8 \times 0.79 \times 0.537 \times 10^{-6} = 6.25 \times 10^{-6} \mu\text{g}/\mu^2$$

The total alloy mass oxidized, as measured by the oxide that remains on the specimen, is therefore 31.20×10^{-6} $\mu\text{g}/\mu^2$.

b. Metallic Mass Disturbance in the Alloy Phase

Since all major alloying elements have entered the oxide phase, the oxidation process is only partially selective. The difference between the stoichiometric amounts involved in 31.20×10^{-6} $\mu\text{g}/\mu^2$ and the actual amounts will measure the degree of selectivity. To a first approximation, the non-selective amounts are:

$$\text{Fe: } 31.20 \times 10^{-6} \times 0.46 = 14.35 \times 10^{-6} \mu\text{g}/\mu^2$$

$$\text{Cr: } 31.20 \times 10^{-6} \times 0.21 = 6.55 \times 10^{-6} \mu\text{g}/\mu^2$$

$$\text{Ni: } 31.20 \times 10^{-6} \times 0.33 = 10.30 \times 10^{-6} \mu\text{g}/\mu^2$$

The selective metal masses are:

$$\text{Fe: } (15.85 - 14.35) \times 10^{-6} = +1.50 \times 10^{-6} \mu\text{g}/\mu^2$$

$$\text{Cr: } (9.10 - 6.55) \times 10^{-6} = +2.55 \times 10^{-6} \mu\text{g}/\mu^2$$

$$\text{Ni: } (6.25 - 10.30) \times 10^{-6} = -4.05 \times 10^{-6} \mu\text{g}/\mu^2$$

These values are determined from the metal mass in the oxide film. If no oxide were lost to the steam environment, these values should be measurable by the excess Ni not entering the oxide phase and which is stored under the Ni profile in the composition grid $\left[\int_{\Sigma x}^{\infty} (C - C_{\infty})_{\text{Ni}} dx \right]$, and by the amounts of Fe and Cr that entered the oxide in excess of their bulk alloy fraction, and which are stored above the Fe and Cr profiles $\left[\int_{\Sigma x}^{\infty} (C_{\infty} - C)_{\text{Fe}} dx, \int_{\Sigma x}^{\infty} (C_{\infty} - C)_{\text{Cr}} dx \right]$.

Note that in the case of pure non-selective oxidation, MP traces alone will not indicate any oxide fraction that is lost. Supporting data are required in order to establish the original ($t = 0$) alloy steam oxide interface. In the case of partially selective oxidation, however, mass balance will certainly give an idea of how much of the active constituents (Fe and Cr with respect to Ni) should appear in the oxide, and therefore if any, how much of these were lost. For instance, the thin solid lines in the alloy phase (see Figure 15) represent the stored mass over a 6μ depth of Fe, Cr, and Ni, given roughly by:

$$\text{Fe: } \frac{(C_{\infty} - C_{\Sigma x}) \times 6}{2} \times 8 \times 10^{-6} = 1.50 \times 10^{-6}$$

$$\text{Cr: } \frac{(C_{\infty} - C_{\Sigma x}) \times 6}{2} \times 8 \times 10^{-6} = 2.55 \times 10^{-6}$$

$$\text{Ni: } \frac{(C_{\Sigma x} - C_{\infty}) \times 6}{2} \times 8 \times 10^{-6} = 4.05 \times 10^{-6}$$

where $C_{\Sigma x}$ represents the interfacial concentrations (weight fractions) and $8 \times 10^{-6} \mu\text{g}/\mu^3$ is the alloy density, assuming no mechanical defecting in this phase. Compared to the actual storage traces, it is quite obvious that $1.50 \times 10^{-6} \mu\text{g}/\mu^2$ is too little Fe and that $2.55 \times 10^{-6} \mu\text{g}/\mu^2$ is too much Cr to have been involved in the selective process. The obvious remedy is to increase the amount of Fe in the oxide to shift the stored amounts so that they match the MP alloy phase traces. The amounts of Fe and Cr necessary in this adjustment are simply those that were lost by spallation.

c. Selective Oxidation with a Moving Boundary

Before the alloy phase profile storage areas can be used in a mass balance, the problem of the moving boundary (that is, the oxide-alloy interface) must be considered. Note that its movement due to the non-selective fraction oxidized does not influence considerations of diffusion within the alloy phase because, by definition, non-selective oxidation is not accompanied by diffusion in the alloy phase.

Therefore, in this initial analysis the two oxidation modes, selective and non-selective, will be considered to be orthogonal and their oxidation product masses will be assumed to be linearly additive, without interaction. In later stages of the investigation of Fe-Cr-Ni steam oxidation behavior as evaluated by MP tracing, these assumptions may well have to be altered. For the time being, however, they will provide a valuable numerical tool to help quantify the MP trace data in terms of mass transported.

The specific problem that the moving boundary creates is the effect it might have on the proportionality between $\bar{Q}$, the actual selective fraction of any active element, and $\hat{Q}$, the fraction that is measurable by composition grid techniques, under the MP traces in the alloy phase; $\hat{Q}$ being given by:

$$\hat{Q} = \int_{\Sigma x}^{\infty} [C_{\infty} - C_{(x,t)}] dx$$

The first step in determining $C_{(x,t)}$ is a consideration of any interaction between the diffusion phenomena in the oxide and in the alloy phases. Diffusion in an oxide phase occurs through oxide steric defect structures; that is, cation vacancies and electron holes for p-type oxides, and anion vacancies and quasi free electrons for n-type oxides. It is assumed, in keeping with generally acceptable observations, that diffusion in the oxide phase occurs on an essentially linear gradient; which is established by steric defect considerations at the oxide-alloy and oxidant-oxide interfaces. These may vary in time but the linear gradient will, as a simplifying approximation, make diffusion in the alloy phase independent of diffusion in the oxide phase and vice-versa.

The second step involves the over-all growth rate of the total oxidation product, which is proportional to the rate at which metallic alloy enters the oxide phase. This latter, in the case of Hastelloy-X, Incoloy, and Inconel, exposed to 1050 F steam, is essentially parabolic (see Figure 16) during the steam exposure time span of specimens that have been examined by MP traces. The $\sqrt{t}$ dependence will be considered further in the discussion of alternate selective oxidation models later in the report, but in view of Figure 16, it is at least temporarily acceptable. Therefore, if $X(S)$ is defined as the volume per unit area of a given active element, entering the oxide phase selectively:

$$\sum X(S) = \sum k'_{(s)} \sqrt{t}$$

The third step concerns the mechanistic features of mixed selective and non-selective (MSNS) oxidation. Consider, for instance, an Incoloy surface exposed to an oxidizing environment such that $100/\sqrt{\Delta t}$ incremental volume units of alloy enter the oxide phase per $\sqrt{\Delta t}$ incremental time unit, and consist of 60 volume units of iron, 30 volume units of chromium, and 10 volume units of nickel. Initially (at $t \cong 0$), the elemental non-selective fractions would be 0.46 Fe, 0.21 Cr and 0.33 Ni. The non-selective fraction entering the oxide phase is $46 + 21 + 10 = 77$. As the oxide is generated, it leaves behind $33 - 10 = 23$ volume units of nickel. At its alloy front, it accepts

Figure 16. Descaled Weight Loss of Coupons Exposed to 1050 F Superheated Steam

60 - 46 = 14 volume units of iron and 30 - 21 = 9 volume units of chromium by diffusion from the interior of the alloy. The lattice site vacancies created by this alloy phase diffusion can be destroyed either by coalescing to form sub-surface voids (in which case there would be no selective oxidation boundary movement) or they can be filled by the back diffusion of the 23 volume units of nickel that did not enter the oxide phase. No visual evidence of massive sub-surface voiding exists, and therefore is assumed to be absent.

Under this assumption, the selective oxidation boundary movement is precisely equal to the volume $X_{Ni}(S)$ that moves into the alloy lattice which, in turn, is equal to the sum of the selective iron and chromium volumes $X_{Fe}(S)$ and $X_{Cr}(S)$ that do enter the oxide phase. This assumption implies that there is no net flow of diffusant across any plane of constant x , the distance from the non-selectively created oxide-alloy interface, $\Sigma x(NS)$, at any time $t > 0$. That is, $D_{Ni} \nabla C_{Ni} = D_{Fe} \nabla C_{Fe} + D_{Cr} \nabla C_{Cr}$ where D = alloy phase diffusion constants. The previous assumption of orthogonality allows the elemental $X_{Fe}(S)$ and $X_{Cr}(S)$ to be split, such that, where $\nabla \equiv \partial/\partial x$,

$$(D_{Ni} \nabla C_{Ni})_{Fe} = D_{Fe} \nabla C_{Fe}$$

$$(D_{Ni} \nabla C_{Ni})_{Cr} = D_{Cr} \nabla C_{Cr}$$

where the notation () $\equiv$ fraction attributable to each active element. Zero net flow of diffusant across any plane of constant x is still maintained, where x is now measured in the case of iron from the $X_{Fe}(NS)$ interface, and in the case of chromium from the $X_{Cr}(NS)$ interface at any time $t > 0$.

If k'_s , in $X(S) = k'_s \sqrt{t}$, is set equal to $2k_s \sqrt{D}$, then

$$X(S) = 2k_s \sqrt{Dt} \quad (1)$$

With this condition, the concentration of either iron or chromium in the alloy phase as a function of time and distance is given by Danckwerts⁽¹⁷⁾ in his treatment of diffusion with a moving boundary as:

$$C(x, t) = C_\infty - \frac{(C_\infty - C_{\Sigma x})}{\text{erfc}(k_s)} \text{erfc}(x/2\sqrt{Dt}) \quad (2)^*$$

*This is equivalent to Wagner's⁽¹⁸⁾ expression for selective oxidation alloy phase active element concentration changes, when his term $(\alpha/2\gamma)^{1/2}$ is equated to k_s . Wagner's constant α is given by $\Delta X_m = \sqrt{2\alpha Dt}$, and γ is given by $\gamma = D/k_c^0$ where ΔX_m is equivalent to X_S and k_c^0 is the specific oxidation rate constant of pure active element.

in which

C_{∞} = the bulk weight fraction of active element

k_s = a function of the specific oxidation rate constant of active element

$C_{\Sigma X}$ = the alloy phase oxide-alloy interfacial concentration of active element

D = alloy phase diffusivity of active element assumed to be constant

and where, generally

$$\operatorname{erfc}(u) = 1 - \frac{2}{\sqrt{\pi}} \int_0^u e^{-\lambda^2} d\lambda$$

Also from Danckwerts' discussion:

$$f(k_s) = k_s \sqrt{\pi} \exp(k_s^2) \operatorname{erfc}(k_s) \quad (3)$$

from which

$$C_{\Sigma X} = [C_{\infty} - f(k_s)] / [1 - f(k_s)] \quad (4)$$

or

$$f(k_s) = (C_{\infty} - C_{\Sigma X}) / (1 - C_{\Sigma X}) \quad (5)$$

Furthermore:

$$dX(S)/dt = D \nabla C \Big|_{x=\Sigma X} + C_{\Sigma X} dX(S)/dt \quad (6)$$

where (6) expresses the necessary conservation of diffusant at the interface, and the condition inherent to the absence of subsurface voiding, that the quantity of diffusant crossing the interface $x = \Sigma X$ is at all times proportional to the displacement $X(S)$.

The area in question, for composition grid manipulation, is (see Figure 17):

$$\bar{Q} = \int_{\Sigma X}^{\infty} [C_{\infty} - C_{(X,t)}] dx$$

That is,

$$\begin{aligned} \bar{Q} &= \int_{\Sigma X}^{\infty} [(C_{\infty} - C_{\Sigma X}) / \operatorname{erfc} k_s] \operatorname{erfc}(x/2\sqrt{Dt}) dx \\ &= (C_{\infty} - C_{\Sigma X}) / \operatorname{erfc} k_s \int_{\Sigma X}^{\infty} \left(1 - \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-\lambda^2} d\lambda\right) dx \end{aligned}$$

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Figure 17. Schematic Representation of a Given Active Element Alloy Phase Concentration Profile in MSNS Oxidation

The double integral is easily evaluated by parts,

setting $dv = dx, u = \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-\lambda^2} d\lambda,$

noting that $d/dx(u) = \frac{1}{\sqrt{\pi Dt}} \exp(-x^2/4Dt),$

and by setting $x^2/4Dt$ equal to η to evaluate $\int vdu$ in $\bar{Q} = \int u dv = uv - \int vdu.$

The result is that

$$\bar{Q} = \left\{ (C_\infty - C_{\Sigma X}) / \operatorname{erfc}(k_s) \right\} \left\{ \frac{2}{\sqrt{\pi}} \sqrt{Dt} \exp[-X^2(S)/4Dt] - X(S) \operatorname{erfc}[X(S)/2\sqrt{Dt}] \right\},$$

which becomes with the use of (1) and (3),

$$\bar{Q} = [C_\infty - C_{\Sigma X}] [1 - f(k_s)] X(S) / f(k_s).$$

But from (4)

$$[C_\infty - C_{\Sigma X}] [1 - f(k_s)] / f(k_s) = 1 - C_\infty.$$

Therefore

$$\bar{Q} = X(S) (1 - C_\infty),$$

and since the total amount having entered the oxide phase selectively is $X(S)$,

$$\bar{Q}/Q = 1/(1 - C_\infty).$$

That is, the desired proportionality between $\bar{Q}$ measured and $\bar{Q}$ having actually entered the oxide phase selectively is

$$\bar{Q} = X(S) = \bar{Q}/(1 - C_\infty). \quad (7)$$

d. Mass Balancing

For a given element, say iron, a mass balance can be written across the reaction zone as follows:

$$\bar{X}_{Fe} = X_{Fe}(NS) + X_{Fe}(S) = X_{Fe,r} + X_{Fe,l} \quad (8)$$

	<u>Total Converted to Oxide</u>	<u>Remaining in Scale</u>	<u>Lost to Environment</u>
Fe	294	158	136
Cr	118	91	27
Ni	<u>94</u>	<u>62</u>	<u>32</u>
Total	506	311	195

The total metal converted to oxide as measured by descaling techniques was 140 mg/dm^2 . The amount lost to the oxidizing environment was found by similar techniques to be 19 mg/dm^2 .

The discrepancy between these latter values and those calculated from the MP profiles can arise from several factors:

- The MP trace calculations are made for an extremely small region, whereas the descaled calculations are averages for the entire exposed surface.
- The oxidation morphology assumptions (mixture of Fe_2O_3 , Cr_2O_3 , and NiO) may be in error since the trace was taken along a 45-degree line to the surface. Since areas of oxide pitting (where no loss is postulated) and defect areas occur in close proximity, a 45-degree trace might traverse the oxide phase for one and the alloy phase for the other (Figure 15). This fact points up the desirability of scanning normal to the surface.
- Both internal oxidation and sub-surface voiding may occur to some degree, which, along with the difficulties involved with a 45-degree trace, could affect oxide alloy interface locations upon the MP traces.
- Finally, as discussed in the following subsection, the mixed selective, non-selective oxidation analytical model may be in error.

5. Alternate Models for Mixed Selective and Non-Selective Oxidation Processes

The treatment in the preceding paragraphs demands that the rate of metal selectively converted to oxide be proportional to $\sqrt{t}$, and that the alloy phase oxide-alloy interfacial alloying element concentrations be constant in time. The fact that these conditions may be too restrictive is explored below.

In spite of Figure 16, there is strong experimental evidence in both high-temperature steam and in high-temperature water that the rate of metal conversion to oxide after exposure periods ranging from 500 to 1000 hours can be approximated by a constant as well as by another time dependence. The transition from non-linear response, say parabolic, to a linear response

is consistent with, and in fact may necessarily accompany, the concept of mechanical defecting in the oxide phase that was discussed previously. That concept implies the presence of a barrier film which transforms to a non-barrier film by becoming defect at p-n junction points. Expressed quantitatively:

$$dW_1/dt = (k_1/W_1) - k_2, \quad (11)$$

$$dW_2/dt = k_2, \quad (12)$$

where

W_1 = weight of non-defect, or barrier oxide,
 W_2 = weight of defect oxide,
 k_1 = non-defect film growth rate constant, and
 k_2 = defect film growth rate constant.

Expression (11) readily integrates to give

$$W_1 + (k_1/k_2) \log_e [1 - (k_2/k_1)W_1] = -k_2 t, \quad (13)$$

while

$$W_2 = k_2 t. \quad (14)$$

From (13) it is apparent that as $k_2 t$ becomes $\gg 1$, W_1 must tend toward the limit k_1/k_2 (curve W_1 , Figure 18) and W_2 grows linearly according to (14) as shown in Figure 18, curve W_2 . The total oxide weight W_{ox} is

$$W_{ox} = W_1 + W_2,$$

and its response is shown in curve W_{ox} , which asymptotically approaches linearity (its asymptote having intercept k_1/k_2 and slope k_2). This behavior explains the transition to linear weight gains, and a corresponding transition to linear kinetics for the metal mass entering the oxide phase. Curves of the type W_{ox} are those that are so prevalent in high-temperature aqueous oxidation, and when they approach the linear region, expression (2) and its corollary expressions, particularly expression (1), may no longer apply.

The derivation of an alternate model that will circumvent these difficulties is based upon a more detailed, differential examination of the MSNS oxidation process than that previously discussed.

Figure 18. Schematic Representation of Oxide Film Growth Involving a Barrier Film w_1 That Grows to a Limiting Thickness

Consider an alloy composed of a noble element, N, and an active element, A. After some time, t , the oxide-alloy interface will be at $\Sigma\bar{x}$ where $\Sigma\bar{x}$ = total alloy volume (per unit area) that has entered the oxide phase. In a time increment Δt , the alloy-oxide interface recedes by an amount $\Delta\Sigma x$ containing $p_N \Delta\Sigma\bar{x}$ units of N and $p_A \Delta\Sigma\bar{x}$ units of A. All $p_A \Delta\Sigma\bar{x}$ will enter the oxide phase $[= \Delta X_A(NS)]$, but only some of $p_N \Delta\Sigma\bar{x}$ will enter the oxide phase. The balance of N, $\Delta X_N(S)$, will eventually enter the alloy phase to replace, sub-surface voiding still assumed absent, the excess (over bulk composition) of A, $\Delta X_A(S)$, that enters the oxide phase by diffusion from the alloy lattice. It is postulated that the movement of $\Delta\Sigma\bar{x}$ into the oxide phase is a step-wise process, as explained in the following sequence.

- a. The entire volume, $\Delta\Sigma\bar{x}$, is activated to enter the oxide phase. The new location of the oxide-alloy interface $\Sigma x + \Delta\Sigma x$ is thus fixed, but is not yet in contact with the oxide phase.

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- b. Atom layers of $\Delta\Sigma\bar{x}$ enter the oxide phase by successive conversion of all their A and N content to oxide, by either p or n type reactions without alloy phase diffusion participation.

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- c. As the first atom layer (3), containing atoms of N that are not going to enter the oxide phase, enters this phase, its A content does enter the oxide phase but its N content remains anchored to the alloy atom layer immediately behind it.

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- d. As the second atom layer (4), containing atoms of N that are not going to enter the oxide phase, enters this phase, its N atoms remain anchored to the layer behind it and the N atoms in the previous layer move backward.

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- e. This process is repeated; layers of activated alloy entering the oxide phase carry their entire A content to this phase, leaving behind atoms of N which coalesce in a backward movement until the $\Sigma x + \Delta \Sigma x$ interface is reached.

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- f. At this point, atoms of A in the alloy lattice equal in volume to $X_A(S)$ [$= X_N(S)$] become activated.

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- g. By alloy phase diffusion, the activated N atoms $X_N(S)$ enter the alloy phase to replace the activated alloy phase A atoms $X_A(S)$ which enter the oxide phase, also by alloy phase diffusional processes. Note that the $\Sigma x(t)$ interface has already been fixed and is not influenced by alloy phase diffusion. The problem of the moving boundary in the alloy phase diffusion participation in the oxidation process is thus eliminated by this postulate of the MSNS mechanism.

The physical quantities of interest are the selective and non-selective fractions $X(S)$ and $X(NS)$ that have entered the oxide phase. They are related by:

$$dX_A(NS)/dt = p_A d\Sigma\bar{X}/dt$$

$$dX_N(NS)/dt = p_N d\Sigma\bar{X}/dt - dX_N(S)/dt$$

$$X_N(S) = X_A(S)$$

where, from Figure 18, $\Sigma\bar{X}$ can be estimated by:

$$\Sigma\bar{X} = \frac{k_1 \sqrt{t}}{1 + k_2 \sqrt{t}} + k_2 t \quad (15)$$

$$d\Sigma\bar{X}/dt = \frac{k_2}{2\sqrt{t}(k_0 + k_2\sqrt{t})^2} + k_2$$

or more simply

$$\cong \frac{k_1}{2\sqrt{t}} + k_2$$

and where: p = the average, instantaneous weight fraction in an activated volume increment $\Delta\Sigma\bar{X}$, and is essentially (as $\Delta\Sigma\bar{X} \rightarrow 0$) equal to $C_{\Sigma X}$, where $C_{\Sigma X}$ = the alloy phase oxide-alloy interfacial weight fraction of any given element.

The interfacial weight fractions, $C_{\Sigma X}$, and the alloy diffusional components $X(S)$ need to be determined. The absence of sub-surface voiding imposes, at all X within the alloy lattice, the condition:

$$|D_A \nabla C_A| = |D_N \nabla C_N|$$

Therefore, the diffusional component $X(S)$ could be examined for either N or A. $X_N(S)$ will be examined since the presence of MSNS oxidation in alloys consisting of an element (nickel with respect to iron and chromium, for instance) of high comparative nobility is probably related to the rate that the noble element can enter the alloy phase lattice. (18)

It is a logical assumption that this rate is governed by oxide displacement reactions (19) that occur in alloy systems composed of active and of noble constituent elements, and which operate as follows. The noble elements tend to enter the oxide phase through a reaction such as,

at a rate that can be taken to be proportional to the thermodynamic free energy change in the above reaction. That is:

$$J_{N \rightarrow NO} \cong \frac{\Delta F^\circ}{RT} + \log_e \left(C_{N_{\Sigma X}} p_{O_2}^{1/2} \right)^{-1} / W_1$$

where W_1 is the barrier film weight.

In the presence of active element A, however, the displacement reaction,

takes place, at a rate given by:

This reaction proceeds so long as the right-hand term is negative. $\bar{\Delta F}^0$ being negative, the reaction will cease when:

$$\log_e (C_{N_{\Sigma x}}) (C_{A_{\Sigma x}})^{-1} = \bar{\Delta F}/RT$$

or when:

$$\log_e C_{N_{\Sigma x}} / (1 - C_{N_{\Sigma x}}) = \bar{\Delta F}^0/RT \quad (17)$$

At this point $C_{N_{\Sigma x}}$ will remain constant, for if it further increased, N would become active with respect to A and a new displacement reaction would tend to lower $C_{N_{\Sigma x}}$ to its value $C_{N_{\Sigma x}(e)}$ where (17) holds. Thus $C_{N_{\Sigma x}}$ will vibrate, with low amplitude, at equilibrium about $C_{N_{\Sigma x}(e)}$, given by (17). The rate of entry of N into the alloy phase will therefore be proportional to $\text{NO} \xrightarrow{J} \text{N}$.

However, when $C_{N_{\Sigma x}(e)}$ is reached, the displacement reaction cannot cease entirely, for if this were the case, as $\Sigma \bar{X}$ proceeds, without further selective oxidation, $C_{N_{\Sigma x}(e)}$ would drop as its concentration gradient in the alloy phase is consumed. This, in turn, would initiate the displacement reaction $\text{NO} \rightarrow \text{N}$. What happens to avoid this is that when $C_{N_{\Sigma x}(e)}$ is reached, the

volume of N removed from the excess N in the alloy, $\int_{\Sigma x}^{\Sigma x + \Delta \Sigma x} (C_{N_{\Sigma xe}} - C_{N_{\infty}}) dx$, as sketched, in each subsequent $\Delta \Sigma \bar{X}$ will re-enter into the alloy phase. The result is that when $C_{N_{\Sigma x}(e)}$ is reached, in the MSNS oxidation postulate, the excess (selective) N stored in the lattice, $\bar{X}_{N(3)}$

$$= \int_{\Sigma x}^{\infty} [C_{N(x,t)} - C_{N_{\infty}}] dx \quad \text{approaches a constant value.}$$

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This condition is analytically described by examining the net rate of accumulation of selective N, $\widehat{dX}_N(S)/dt$, that is stored in excess in the alloy lattice. It will be given by:

$$\text{net rate of acc.} = \text{rate of dynamic gain} - \text{rate of dynamic loss}$$

The rate of loss is immediately given, from the preceding paragraph, as:

$$(C_{N_{\Sigma x}} - C_{N_{\infty}}) d\Sigma\bar{X}/dt$$

The rate of gain will be some fraction of the rate of alloy activation by the inward sweep of $\Delta\Sigma\bar{X}$.

The rate of activation of N is $C_{N_{\Sigma x}} d\Sigma\bar{X}/dt$ and unless some unoxidized N is left in the oxide phase:

$$C_{N_{\Sigma x}} d\Sigma\bar{X}/dt = dX_N(NS)/dt + dX_N(S)/dt$$

in which $dX_N(S)/dt$ is now defined as the rate of dynamic gain of N stored in excess in the alloy lattice. That is:

$$dX_N(S)/dt = r_N C_{N_{\Sigma x}} d\Sigma\bar{X}/dt$$

and:

$$\begin{aligned} \widehat{dX}_N(S)/dt &= r_N C_{N_{\Sigma x}} d\Sigma\bar{X}/dt - (C_{N_{\Sigma x}} - C_{N_{\infty}}) d\Sigma\bar{X}/dt \\ &= \left[(r_N - 1) C_{N_{\Sigma x}} + C_{N_{\infty}} \right] d\Sigma\bar{X}/dt \end{aligned}$$

When

$$d\widehat{X}_N(S)/dt = 0 ;$$

$$r_N = 1 - C_{N_\infty}/C_{N_{\Sigma x}}$$

It is postulated that initially r_N is essentially 1; that is, in the early stages of oxidation no N enters the oxide phase. It is further postulated that r_N approaches $1 - C_{N_\infty}/C_{N_{\Sigma x}}$ as $C_{N_{\Sigma x}}$ approaches its equilibrium value, $C_{N_{\Sigma x}(e)}$. That is, the rate of excess storage, $d\widehat{X}_N(S)/dt$, goes to zero as $C_{N_{\Sigma x}(e)}$ is approached. The behavior of $C_{N_{\Sigma x}}$ in time can be approximated by:

$$C_{N_{\Sigma x}} = C_{N_{\Sigma x}(e)} + [C_{N_\infty} - C_{N_{\Sigma x}(e)}] \exp(-\alpha_N t) \quad (18)$$

The behavior of r_N in time can be expressed by:

$$r_N = \left\{ 1 - \frac{C_{N_\infty}}{C_{N_{\Sigma x}(e)}} [1 - \exp(-\alpha_N t)] \right\}$$

Thus:

$$d\widehat{X}_N(S)/dt = C_{N_\infty} \left\{ 1 - \frac{C_{N_{\Sigma x}}}{C_{N_{\Sigma x}(e)}} [1 - \exp(-\alpha_N t)] \right\} d\overline{\Sigma X}/dt \quad (19)$$

in which $C_{N_{\Sigma x}}$ is given by expression (18).

Note that in MP tracing $\widehat{X}_N(S)$, or $\widehat{X}_A(S)$, is the only measurement of the selective oxidation that is actually available. Note also that when $d\widehat{X}_N(S)/dt = 0$, a condition tantamount to pure non-selective oxidation is achieved in which the alloy phase concentration gradients must necessarily be maintained as $\overline{\Sigma X}$ progresses. Therefore, all MP measurements made beyond $d\widehat{X}_N(S)/dt = 0$ will reveal nothing about the kinetics of the oxidation process, unless the entire oxidation product remains on the surface, as previously mentioned.

Among the possible approaches to describe the diffusion processes involved in MSNS oxidation, one has particular merit. It is based upon the concept that $\widehat{X}_N(S)$ constitutes an instantaneous plane source, which at any time $t > 0$ is wholly contained within the alloy lattice. The concentration - distance profile at any time t will then be given by:⁽²⁰⁾

$$C_{N(x,t)} - C_{N\infty} = \frac{\widehat{X}_N(S)}{2\sqrt{\pi Dt}} \exp -\left(\frac{x^2}{4Dt}\right) \quad (20)$$

in which D is the alloy phase diffusivity of N and in which $x = 0$ coincides with the observed oxide-alloy interface, Σx . The values $\widehat{X}_N(S)$ and D may be estimated from expression (20) when applied to a given microprobe concentration profile which, of course, furnishes values of C_N as a function of x at any t . The value of $C_{N\Sigma x}$ (that is, the value of C_N at the oxide-alloy interface) may be obtained from (20) by setting $x = 0$. The equilibrium value of $C_{N\Sigma x}$, $C_{N\Sigma x(e)}$, and the value of the rate constant α may then be calculated from expression (18), providing that microprobe profiles exist for at least two time periods. If an expression is adopted for $d\Sigma\bar{X}/dt$, expression (19) may be integrated to give

$$\widehat{X}_N(S) = f \left(C_{N\infty}, C_{N\Sigma x(e)}, \alpha, k_1, k_2, t \right)$$

where k_1 and k_2 are the oxidation rate constants. With $\widehat{X}_N(S)$, $C_{N\infty}$, $C_{N\Sigma x(e)}$, and α known, the oxidation rate constants may be evaluated from the integral of expression (19). For instance, if $d\Sigma\bar{X}/dt$ is approximated by expression (16), $\widehat{X}_N(S)$ is found to be at first approximation:

$$\begin{aligned} \widehat{X}_N(S) = \frac{C_{N\infty}}{C_{N\Sigma x(e)}} & \left\{ \frac{k_1}{\sqrt{\alpha}} \left[\left(2C_{N\Sigma x(e)} - C_{N\infty} \right) \operatorname{erf} \sqrt{\alpha t} \right. \right. \\ & \left. \left. - \left(C_{N\Sigma x(e)} - C_{N\infty} \right) \operatorname{erf} \sqrt{2\alpha t} \right] \right. \\ & + \frac{k_2}{\alpha} \left[\left(2C_{N\Sigma x(e)} - C_{N\infty} \right) \left(1 - e^{-\alpha t} \right) \right. \\ & \left. \left. - \left(C_{N\Sigma x(e)} - C_{N\infty} \right) \left(1 - e^{-2\alpha t} \right) \right] \right\} . \end{aligned}$$

It follows that for oxidation kinetics corresponding to expression (16), the equilibrium value of $\widehat{X}_N(S)$, $\widehat{X}_{N(e)}(S)$ is given by:

$$\widehat{X}_{N(e)}(S) = C_{N\infty} \left(\frac{k_1}{\sqrt{\alpha}} + \frac{k_2}{\alpha} \right) .$$

As discussed, Expressions (2) and (20) will provide estimates of the diffusion coefficients, D . These latter can be compared, in view of possible phase shifts, as suggested in Figure 19, for the Incoloy specimen (Figure 15) with values predictable from self-diffusion behavior of the iron, (21) chromium, (22) and nickel (23) systems, keeping in mind that diffusivities increase about two orders of magnitude should a shift from fcc to bcc structure occur, and that diffusion in dilute solutions may increase greater than an order of magnitude.

Figure 19. Fe-Ni-Cr Phase Diagram

NOMENCLATURE

α_N	Specific rate constant for the climb of the alloy phase oxide-alloy interfacial weight fraction $C_{\Sigma x_N}$ to its equilibrium value $C_{N_{\Sigma x(e)}}$, appropriate reciprocal time units.
C_∞	Bulk alloy phase concentration of any given element, weight fraction.
$C_{\Sigma x}$	Alloy phase oxide-alloy interfacial concentration of any given element, weight fraction.
$C_{N_{\Sigma x}}$	Alloy phase oxide-alloy interfacial concentration of a noble element, weight fraction.
$C_{N_{\Sigma x(e)}}$	Alloy phase oxide-alloy interfacial equilibrium concentration of a noble element, weight fraction.
$\epsilon_{(ox)}$	Ratio of weight fractions between any two elements in the oxide phase at the oxidant-oxide interface.
$\text{erf}(u)$	$\frac{2}{\sqrt{\pi}} \int_0^u e^{-\lambda^2} d\lambda$
μ	Micron, 10^{-4} cm.
μg	Microgram, 10^{-6} g.
P_N, P_A	Average concentration of a noble and of an active element in the alloy phase near the oxide alloy interface, weight fraction.
π_{ox}	Dissociation pressure, atm.
$\bar{Q}$	$X(S), \mu^3/\mu^2$.
$\widehat{Q}$	$X(S)$ measurable under MP profiles in alloy phase, μ^3/μ^2 .
r_N	Fraction of noble element involved in the displacement reaction that must re-enter the oxide phase, dimensionless.

ρ	Average density, $\mu\text{g}/\mu^3$ (unless otherwise specified).
Σx	Oxide-alloy interface position.
ΣX	Total alloy volume entering the oxide phase, μ^3/μ^2 .
$X(S)$	Metallic volume of any given element involved in the selective fractions of the oxidation process, μ^3/μ^2 .
$X(NS)$	Metallic volume of any given element involved in the non-selective fraction of the oxidation process, μ^3/μ^2 .
$\widehat{X}_N(S)$	The excess stored selective volume of noble element in the alloy phase, μ^3/μ^2 .
$\widehat{X}_{N(e)}(S)$	Equilibrium value of the excess stored selective volume of noble element in the alloy phase, μ^3/μ^2 .
$\bar{X}$	$X(S) + X(NS)$ = total metallic volume of any given element entering the oxide phase.
X_r	Metallic volume of any given element in oxide remaining on surface, μ^3/μ^2 .
X_ℓ	Metallic volume of any given element in oxide lost to environment, μ^3/μ^2 .
k_1	Non-defect film growth rate constant, $(\mu\text{g}/\mu^2 - \text{sec})^2$.
k_2	Defect film growth rate constant $\mu\text{g}/\mu^2 - \text{sec}$.
w_1	Non-defect film weight, $\mu\text{g}/\mu^2$
w_2	Defect film weight, $\mu\text{g}/\mu^2$
w_{ox}	Total film weight, $\mu\text{g}/\mu^2$

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