LETTERS TO THE EDITOR

SURFACE ANALYSIS

Dear Sir:

In the article on the corrosion of Incoloy-800 in superheated steam on pp 235-245 of the June 1965 issue of *Nuclear Applications,* the use of electron microprobe measurements was discussed as a method to study the compositionally changed region in the alloy phase near the oxide/alloy interface resulting from the partial selective oxidation of Incoloy-800. The value of this technique was limited by the 1 to 2 micron (μ) width of the span measured. In order to circumvent the problem of seeing only a line analysis by microprobe techniques, an inexpensive method was developed to obtain an average surface analysis on a spot of about 3 cm^2 on the compositionally disturbed metallic layer next to the oxide scale. A controlled anodic dissolution of a few microns at a time followed by an x-ray fluorescence analysis permits the definition of the disturbed layer as well as an integrated measure of the composition of metal reacted.

The method was successfully demonstrated on a descaled Incoloy-800 heat-transfer test sheath that had been operated at a calculated metal temperature of 1500°F for 1044 h. The sheath had a 14 mg/dm^2 weight gain, 244 mg/dm^2 descaled weight loss with a calculated 68 mg/dm^2 (28%) metal loss to system. Steps of 10μ each were taken through the compositionally disturbed layer. Concentration gradients of the alloy components were found up to a depth of 50μ (metallographically only 25μ was seen) with a depletion in Cr, Cu, and Mn and enrichment in Fe and Ni.

By use of a planimeter the average metal composition in the disturbed layer was found graphically to compare with the base metal as shown in Table I.

A mass balance over all the depleted and enriched metals in the compositionally disturbed layer was set up and found to be correct resulting in the change column listed in Table I. As preferential diffusion and selective oxidation of Cr, Mn, and Cu ions are causing enrichment in the oxide scale and depletion in the compositionally disturbed layer, the divergence of average alloy composition of the oxide scale from the base metal can be calculated also. Using the descaled metal weight loss after the oxidation reaction, the integrated metal content of adherent and nonadherent oxide is shown in the final column of Table I. By analysis of the composition of the

TABLE I

Incoloy-800 Disturbed Layer Composition

Original Material % (= $100C\infty_i$)	Average Layer Disturbed %	Change %	Total Oxide Formed	
			mg/dm^2	%
Fe	47.0	47.8	+ 0.8	81.8	33.5
Cr	19.1	17.7	- 1.4	104.2	42.7
Ni	32.3	33.2	+ 0.9	42.6	17.4
Mn	1.05	0.78	- 0.27	13.6	5.6
Cu	0.40	0.38	- 0.02	1.8	0.8

adherent oxide (not carried out on the sample cited), the composition of the nonadherent oxide lost to the system can be calculated by difference.

The compositionally disturbed (CD) area data yield another significant piece of information, based upon the diffusional characteristics of the selective corrosion process. The application of Fick's second law to a diffusion system in which the boundary $X = 0$ moves at a constant rate (equal to the alloy corrosion rate when under linear rate law control) gives the compositionally disturbed areas as

Area of CD
of element i $= \pm (C_{oi} - C_{\infty i})\Big[(1/a)\ \exp\ (-\Phi_1)\ \mathrm{erfc}\ (\Phi_2)$
$\qquad + (Dt/\pi)^{1/2}\ \exp\ (-\Phi_3^2) - \alpha Dt\ \mathrm{erfc}\ (\Phi_3)$
$\qquad + (1/2\alpha)\ \mathrm{erf}\ (\Phi_3)\Big].$ (1)

The positive values of the right side of Eq. (1) apply to an enriched element; the negative values, to an impoverished element, where C_{oi} is the alloy-phase oxide-alloy interfacial composition and where

$2\alpha DP =$ Total Alloy Linear Corrosion Rate, mg/dm^2-month

$D =$ alloy phase diffusivity, dm^2/month

$\alpha =$ a rate constant, 1/dm

$a = k_{np}\ /(Dt_c)^{1/2}$,1/dm

$t =$ time of linear rate-control exposure, months;

a is a factor related to the nonlinear transient, k_{nl} being a dimensionless nonlinear rate constant and t_c the nonlinear transient duration period. The functions Φ are given by

$$\Phi_1 = 2\,a\,\alpha Dt - Da^2 t$$

$$\Phi_2 = (a - \alpha)\,(Dt)^{1/2}$$

$$\Phi_3 = \alpha\,(Dt)^{1/2}. \tag{2}$$

When Φ_3 becomes numerically equal to 2, the time dependence vanishes, and the compositionally disturbed layer approaches a limit, given by

$$\text{Area of CD} = \pm\,(C_{oi} - C_{\infty i})/2\,\alpha. \tag{3}$$

The additional significant factor is the limiting extent of composition disturbance given by Eq. (3). For the sheath specimen in question, $t_c \ll 1$, so that the nonlinear transient terms involving Φ_1 and Φ_2 vanish, and the linear corrosion rate $(2\,\alpha D\rho)$ measures 167 mg/dm^2-mo. Using this value with Eq. (1), the calculated value of α is 447, and the limiting disturbed mass of Cr, for instance, is given as

$$\rho\,(\text{Area Cr CD}) = \frac{\rho\,(0.191 - 0.148)}{2 \times 447} = 385 \text{ mg/dm}^2,$$

where $\rho =$ alloy phase density, 8×10^6 mg/dm^3, and 0.148 $= C_{oi}$ for Cr, as compared with the value of 100 mg/dm^2 (Table I) obtained in the first 1044 h.

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BURNUP UNITS

Dear Sir:

Various units are used to express the amount of energy extracted from a given amount of reactor fuel. The useful unit for this, however, depends on the particular property in question. Traditionally, units of fission/cm^3, MWD/T, and % burnup have been used. A volumetric unit (e.g., f/cm^3) is frequently used, in that volumetric retention of volatile fission products is thought to be related to fuel swelling phenomena. Such a

TABLE I

Burnup Units Equivalent to 1 gf/cm^3 [a]

	Oxides [b]	Carbides [c]	Solid Metals [d]	Liquid Metals [e]
gf/cm^3	1.0	1.0	1.0	1.0
gf/cm^3 smeared [f]	0.90	0.95	0.80	0.95
% BU of heavy atoms	12.17	9.09	6.54	25.0
MWD/metric ton heavy atoms	114 100	85 200	61 200	234 200
MWD/long ton heavy atoms	115 900	86 600	62 200	238 000
MWD/short ton heavy atoms	103 500	77 300	55 500	212 500
MWD/metric ton fuel	100 600	81 100	55 100	100 500
MWD/long ton fuel	102 200	83 000	56 000	102 100
MWD/short ton fuel	91 300	73 600	50 000	91 200
f/cm^3	25.3×10^{20}	25.3×10^{20}	25.3×10^{20}	25.3×10^{20}
f/cm^3 smeared	22.8×10^{20}	24.0×10^{20}	20.2×10^{20}	24.0×10^{20}

[a]Based on 199 MeV/fission = 3.2×10^{-17} MWsec/fission.

$= 8.1 \times 10^4$ MWsec/gf = 0.937 MWD/gf.

[b]Oxides are taken to have a density of 9.316 g/cm^3 (85% of theoretical) smeared density of 8.384 g/cm^3 (90 vol %)

[c]Carbides are taken to have a density of 11.56 g/cm^3 (85% of theoretical) smeared density of 10.98 g/cm^3 (95 vol %)

[d]Solid metals are taken to have a density of 17 g/cm^3 (90 wt % heavy atoms) smeared density of 13.6 g/cm^3 (80 vol %)

[e]Liquid metals are taken to have a density of 9.32 (4 g Pu/cm^3 fuel)

[f]The "smeared density" is the ratio of fuel mass-to-total internal volume of the fuel element, including bond volume. The smeared densities used are illustrative and are not associated with specific designs.