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ELECTRON MICROPROBE ANALYSIS OF IRRADIATED S8ER CLADDING

AUTHOR

W. E. Krupp, L. Cooper

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		ABSTRACT <p>Extensive precipitation was observed in S8ER cladding following irradiation. Electron microprobe analysis was proposed as a means to identify these precipitates. Subsequently, the electron microprobe was successfully used for qualitative analysis of unirradiated and irradiated S8ER cladding.</p> <p>The unirradiated, thermally aged control specimen analyzed showed two major precipitates. One, a randomly distributed intergranular phase, contained Ti, Mo, Fe, Cr and Ni and a second, a randomly distributed intragranular phase, contained Si, Mo, Fe, Cr and Ni.</p> <p>The irradiated specimen analyzed showed the same precipitates. The phase containing Ti, Mo, Fe, Cr and Ni was also randomly distributed intergranularly. The phase containing Si, Mo, Fe, Cr and Ni was in the grain boundaries, and preferentially segregated to the outer and inner diameter.</p> <p>Analysis of the irradiated specimen did not result in excessive personnel exposures or contamination of the electron microprobe.</p>	

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I. INTRODUCTION

Extreme precipitation, both intra- and intergranular, was observed during the post-irradiation metallographic examination of S8ER cladding¹. Electron microprobe analysis was proposed as an approach for identification of these precipitates.

The electron microprobe analyzer is capable of both qualitative and quantitative analysis of a micron-sized region². In this method of analysis, a high energy focused electron beam strikes a pre-selected region on the metallographic cross-section of a specimen, causing emission of characteristic x-rays of elements present in the impacted region. These x-rays are converted to electrical signals in an x-ray spectrometer that is set to select the characteristic x-rays of a particular element, and counted for a fixed time interval. After subtracting background, a net positive count indicates the presence of the selected element in the impacted region. If quantitative analysis is desired, a first approximation of the element weight fraction is obtained by comparing the counts obtained for the element present in the specimen to the counts obtained from a standard specimen of the pure element, with both counted for the same time interval. After application of corrections for absorption, fluorescence, electron back-scatter, dead time and dark current, it is possible to obtain element concentrations accurate to a few percent.

In an unshielded electron microprobe analyzer³, the examination of an irradiated specimen can be limited by several factors: (1) because of the need to avoid excessive personnel radiation doses, there may be a limit on the amount of time available for performing a particular analysis; (2) because of the gamma rays emitted by the irradiated specimen, there will be an increase of the background level in the x-ray detection equipment, resulting in a loss of sensitivity that affects analysis for minor constituents and low atomic numbered elements; (3) care must be taken to avoid transfer of radioactive contamination from the surface of the specimen to the inside of the electron microprobe.

To minimize the time spent analyzing the irradiated specimen, and

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at the same time retain normal x-ray sensitivity, it was proposed that an unirradiated, thermally aged control specimen be examined prior to placing the radioactive specimen in the electron microprobe for examination. Thus, the major objective of this electron microprobe study would be the detection of differences between precipitate phases observed in the unirradiated and irradiated specimens.

The control specimen was taken from the center of a section 9-13 in. from the top of a SNAK IV loop test element⁴. This section was exposed to static NaK at 1150°F for 10,000 hours. The irradiated specimen was taken from the center of a section 9-13 in. from the top of S8ER element 188. This section was exposed to flowing NaK at 1150°F for 12,000 hours, while accumulating a neutron dose of 9.9×10^{19} nvt thermal, 2.1×10^{21} nvt fast ($E > 0.3$ mev). Vacuum-melted Hastelloy-N heat Y-8437 was used for both specimens. An analysis of this material is given in Table 1.

TABLE 1

Chemical Composition of Hastelloy-N Heat Y-8437

Element	Weight Percent
Nickel	71.22
Molybdenum	16.00
Chromium	7.70
Iron	4.08
Manganese	0.27
Aluminum + Titanium	0.25
Silicon	0.21
Cobalt	0.10
Copper	0.05
Tungsten	0.05
Carbon	0.04
Sulfur	0.008
Phosphorus	0.005
Boron	0.005

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II. PROCEDURE

An abrasive cutoff wheel was used to remove 0.250 x 0.250 x 0.010 in. specimens from the unirradiated and irradiated cladding sections. Both specimens were mounted in epoxy resin so as to reveal a transverse section. The irradiated specimen had a 0.125 in. thick lead ring around the outside of the mount.

Both specimens were prepared in a cold laboratory, using the same processing methods. Specimens were ground flat on 240, 320, and 600 grit SiC abrasive papers, using water as the lubricant. Polishing steps involved use of a water slurry of six micron diamond on cotton cloth and a water slurry of 0.3 micron Linde-B on rayon cloth. Specimens were etched by dipping into a solution of three parts HCl, two parts H₂O, and one part 10% chromic acid. After microscopic examination and marking of the areas to be analyzed with hardness indentations, repeating the polishing steps removed etching effects on the sample surface.

Transfer operations and electron microprobe analyses involving the irradiated specimen were monitored by a health physics representative to control personnel exposure and spread of radioactive contamination. Table 2 presents the levels of activity present in the irradiated specimen prior to microprobe analysis.

TABLE 2
Activity of Irradiated S8ER Cladding Specimen Prior
to Electron Microprobe Analysis

Type of Activity	Level at Contact	Level at 12 in.
gamma activity, mR/hr	300	10
beta + gamma activity, mrad/hr	600	15
surface contamination, dpm	750	--

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The electron microprobe equipment used was an Applied Research Laboratories Model EMX⁵. The unit was equipped with a 3-50 kv power supply and could produce an electron beam continuously adjustable from 1 to 300 microns in diameter. Light optics provided a magnification of 280 X, and electron optics were capable of magnifications up to 7120 X (at 30 kv). The recording system included three x-ray spectrometers, oscilloscopes, x-y plotter, x-ray pulse counters, and typewriter printout system.

Analysis of the unirradiated specimen centered on typical precipitates as revealed by the optical metallographic examination. These precipitates were examined to determine what elements were present. Precipitate results were compared to the analysis of a matrix region relatively free of precipitation. Elements studied in this manner were Ni, Mo, Cr, Fe, Mn, Al, Ti, Si, Co, Cu and W. Microprobe methods included specimen current illumination, x-ray area scans, and x-ray line profiles. The specimen current method employed the small fraction of the impinging electrons that are not reflected by the target material, but conducted through it to ground. The area scan involved holding the specimen stationary, and performing a raster scan* for elements of interest, displaying the results on an oscilloscope. In the line profile method, the electron beam was traversed linearly over a pre-selected path, providing an oscilloscope trace of element distribution. All three methods were recorded by taking time-exposure photographs of the oscilloscope.

Analysis of the irradiated specimen was governed by results of the examination of the unirradiated specimen. Analysis of precipitate phases for the elements examined in the unirradiated specimen was successful. The analysis of the irradiated specimen did not result in excessive personnel exposure, or transfer of radioactive contamination to the microprobe.

* Raster scanning involves motion from left to right and top to bottom, and is the type employed in television tubes.

III. RESULTS AND DISCUSSION

Metallographic examination of the unirradiated control specimen revealed two major precipitate phases, as shown in Figure 1. The intergranular phase was evenly distributed throughout the specimen. This phase was clear in the as-polished condition, but dark in the as-etched condition, due to preferential attack of the etchant. The intragranular phase, clear in both processing conditions, was also evenly distributed throughout the specimen. A summary of the electron microprobe results is presented in Table 3. These results indicate the intergranular phase contained Ti, Mo, Fe, Cr, and Ni; while the intragranular phase contained Si, Mo, Fe, Cr and Ni.

TABLE 3

Results of Electron Microprobe Analysis of the
Unirradiated Hastelloy-N Cladding Specimen

Precipitate	Observations
Intergranular	Ti level in precipitate > matrix. Mo, Fe, Cr, Ni levels in precipitate < matrix, but significant.* Mn, Al, Si, Co, Cu, W levels in precipitate $\approx$ matrix, not significant.
Intragranular	Mo, Si levels in precipitate > matrix. Fe, Ni, Cr levels in precipitate < matrix, but significant. Mn, Al, Co, Cu, Ti, W levels in precipitate $\approx$ matrix, not significant

* Significant and not significant are used here in a broad sense, namely, if the element was considered to be present in amounts greater than 1% then its presence was considered significant, less than 1%, insignificant.

Figure 1. Photo 1770-1, 500X,
as-etched. Microstructure of
unirradiated Hastelloy-N
cladding specimen.

Metallographic examination of the irradiated specimen also revealed two major precipitates, as shown in Figure 2. The precipitate located by the hardness indentations was evenly distributed throughout the specimen. Also, an intergranular precipitate network was preferentially segregated to the inner and outer diameter of the specimen.

The electron microprobe examination of the precipitate located by hardness indentations in Figure 2 indicated a random, intergranular distribution of a Ti bearing precipitate, as shown in Figures 3a, 3b. Further work indicated Mo, Fe, Cr and Ni were also present, as shown in Figures 4a - 4d. Thus, this precipitate was identical to the intergranular precipitate observed in the unirradiated specimen.

The electron microprobe examination of the precipitate network at the inner diameter in Figure 2 indicated a Mo and Si bearing precipitate, as shown in Figures 3c - 3e. Line profiles, such as those in Figures 5a and 5b, indicated Fe, Cr and Ni were also present. Therefore, this precipitate, which was identical to the intragranular phase in the unirradiated specimen, was preferentially segregated to the grain boundaries at the inner and outer diameters of the irradiated specimen.

The results of other investigations with Hastelloy-N^(6,7,8) have indicated grain boundary and intragranular precipitation. Future microprobe examination of the precipitates should be performed to determine approximate element concentrations and whether either or both of the precipitates are carbides.

IV. SUMMARY

The electron microprobe was used for qualitative analysis of the elements Ni, Mo, Cr, Fe, Mn, Al, Ti, Si, Co, Cu and W in irradiated and unirradiated S8ER cladding. Analysis of the irradiated specimen did not result in excessive personnel exposures or radioactive contamination of the electron microprobe.

The unirradiated, thermally aged control specimen showed two major precipitates. One phase, randomly distributed intergranularly, contained Ti, Mo, Fe, Cr, and Ni. A second phase, randomly distributed intragranularly, contained Si, Mo, Fe, Cr and Ni.

Figure 2. Photo 7036-1, 250X, as-polished. Microstructure of irradiated Hastelloy-N cladding specimen at inner diameter.

Figure 3. Area scans of the irradiated Hastelloy-N specimen.

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3a. Photo S8EMP-1, 400X or 22.5 microns per division, using specimen current. Bright areas correspond to elements with atomic numbers less than the matrix, while dark areas represent elements with atomic numbers higher than the matrix, which is mainly nickel.

3b. Photo S8EMP-1a, 400X or 22.5 microns per division, using 41 Ti x-rays. Light areas indicate presence of Ti in bright areas shown in Figure 3a.

Ceramic Layer

3c. Photo S8EMP-5b, 1600X or 5.38 microns per division, using specimen current. Enlargement of region showing dark areas in Figure 3a.

3d. Photo S8EMP-5c, 1600X or 5.38 microns per division, using Si Ka x-rays. Light areas indicate presence of Si in areas appearing dark in Figure 3a.

3e. Photo S8EMP-5d, 1600X or 5.38 microns per division, using Mo La x-rays. Light areas indicate presence of Mo in areas appearing dark in Figure 3a. Also note the Mo rich layer at the cladding/ceramic interface.

Figure 4. Line profiles across the precipitate evenly distributed throughout the irradiated specimen.

4a. Photo S8EMP-A5, 3200X or 2.75 microns per division, Ni/Ti x-rays. Ti content up at precipitate; Ni depressed, but present in the precipitate.

4b. Photo S8EMP-A2, 3200x or 2.75 microns per division, Mo/Fe x-rays. Mo and Fe content depressed in precipitate, but present.

4c. Photo S8EMP-A1, 3200X or 2.75 microns per division, Mo/Cr x-rays. Mo and Cr content depressed in precipitate, but present.

4d. Photo S8EMP-A4, 3200X or 2.75 microns per division, Si/Ni x-rays. Ni depressed in precipitate but present, Si unchanged.

Figure 5. Line profiles across the precipitate network at the inner diameter of the irradiated Hastelloy-N specimen.

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5a. Photo S8EMP-B1, 3200X or 2.75 microns per division, Cr/Mo x-rays. Cr content rises from matrix level in chromized layer, drops in the ceramic. Mo content same in matrix and chromized layer, up in the precipitate.

5b. Photo S8EMP-B2, 3200X or 2.75 microns per division, Cr/Si x-rays. Cr content rises from matrix level in chromized layer, drops in the ceramic. Si content same in the matrix and chromized layer, up in the precipitate and ceramic layer.

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The irradiated specimen showed the same phases as the unirradiated control specimen. The phase containing Ti, Mo, Fe, Cr and Ni was also randomly distributed intergranularly in the irradiated specimen. The phase containing Si, Mo, Fe, Cr and Ni was in the grain boundaries, preferentially segregated to the inner and outer diameter of the irradiated specimen.

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