SEGREGATION BEHAVIOR OF SULFUR AND OTHER IMPURITIES ONTO THE FREE SURFACES OF ED-NI DEPOSITS

by

Binayak Panda
IIT Research Institute
Building 4628, Marshall Space Flight Center
George C. Marshall Space Flight Center, AL 35812
(256) 544-6349 (bpanda@iitri.org)

and

Gregory Jerman
National Aeronautics and Space Administration
Building 4612, Marshall Space Flight Center
George C. Marshall Space Flight Center, AL 35812
(256) 544-5346 (gregory.a.jerman@msfc.nasa.gov)

ABSTRACT

Most researchers attribute grain boundary embrittlement in electro-deposited Nickel (ED-Ni) to the presence of small quantities of Sulfur as an impurity. It occurs in a highly mobile form that segregates to the grain boundaries. Evaluation of Sulfur segregation requires that a sample be fractured through the grain boundaries. However, this action may not always be possible. ED-Ni is inherently tough at ambient temperature, especially if a low level of Sulfur was intentionally maintained.

A new method was developed to study Sulfur and other migrant species to the grain boundaries, which also migrate to free surfaces. A test specimen is heated by a quartz lamp within the sample preparation chamber, allowing the mobile species to migrate to polished free surfaces. There the mobile species are analyzed using X-ray photoelectron spectroscopy (XPS) also known as Electron Spectroscopy for Chemical Analysis (ESCA).

INTRODUCTION

ED-Ni is one of the structural materials used in the main combustion chamber (MCC) of the Space Shuttle Main Engine (SSME). During manufacture, a Nickel sulfamate bath is used to obtain a deposit of high-purity Nickel. Table 1 shows impurity levels commonly seen in the composition of ED-Ni, given in parts per million (ppm).[1]

Table 1 – Impurity levels in ED-Ni (ppm)[1]

Carbon	Copper	Iron	Manganese	Silicon	Cobalt	Hydrogen	Oxygen	Nitrogen	Sulfur
50	<100	<100	<5	<10	1000	8	20	6	10

Functional characteristics can be seriously impaired by some impurities, even at very low levels, especially in material exposed to elevated temperatures during annealing or welding. High-temperature exposure promotes diffusion of some impurities to grain boundaries, which may result in grain boundary embrittlement characterized by loss of ductility at high temperature. Most researchers[1-3] associate such degraded mechanical properties with Sulfur segregation, while others attribute them to Carbon reacting with Oxygen to form Carbon Monoxide at grain boundaries.[4] Both groups consider Sulfur (in the absence of Oxygen) to be the most important cause of grain boundary embrittlement.

Sulfur has very low solubility in Nickel, with strong segregation tendencies toward grain boundaries. Even at the small ppm level, Sulfur present in a bulk composition can segregate up to several atomic percentages at the grain boundaries.[3] Sulfur is gettered by other elements such as manganese, magnesium, and calcium, which prevent its migration to the grain boundaries.

Measurement of grain boundary Sulfur is an important means of predicting embrittlement. All previous work has made such measurements using Auger electron spectroscopic analysis,[1,3] requiring exposure of the grain boundaries. This action is usually accomplished by introducing large quantities of Sulfur that induce the sample to break easily within the Auger sample preparation chamber.

EXPERIMENTAL PROCEDURE

This paper describes a new method to measure the amount of diffusing species onto a free surface. This phenomenon is considered to be directly related to the amount of diffusing species present on the grain boundaries. XPS was used to identify and quantitatively measure segregating species on a polished surface. This technique allowed the analysts to use a large diameter monochromatic X-ray beam (800 micrometers) for better sensitivity. They were also able to use X-rays as the excitation source in order to prevent heating effects and evaluate polished samples instead of fractured samples.

Both mounted and unmounted samples were analyzed using an SSX-100 ESCA instrument. Mounted and polished ED-Ni samples were introduced into the sample preparation chamber and allowed to outgas. The samples were then introduced into the main analytical chamber. Selected areas of each polished surface were then cleaned using an argon ion sputter gun. After cleaning, the samples were removed from the analytical chamber, reintroduced into the sample preparation chamber, and heated by a quartz lamp for 2 hours. See Figure 1 for heating and cooling curves. After about 4 hours, the cooled samples were reintroduced into the analytical chamber where the cleaned regions were analyzed for possible migration of species.

RESULTS

The limits of elemental sensitivity for XPS are generally in the same range as that of Auger. An element must be present as at least a fraction of a percent in order to be detected. Elements detected on the clean surface are assumed to be species segregating from inside the material. Several runs were made to confirm this phenomenon, as well as to eliminate spurious deposits from the vacuum atmosphere. Therefore two groups of results were obtained. The first was to ascertain the origin of various species found on the sample surface, the second to provide quantitative determination of these species.

To establish this method's effectiveness, analysis was conducted on a sample taken from an MCC (S/N 6014). It was mounted in Bakelite and then polished for microstructural and elemental analysis. Combustion analysis was used to determine that it contained 3 ppm bulk Sulfur. This low amount permitted the XPS method of detection to be effective if Sulfur segregation occurs to the free surface of the sample.

A quartz lamp was used to heat the mounted and polished sample in the XPS sample preparation chamber for 2 hours to remove volatile matter. After cooling, the sample was introduced into the main analytical chamber for analysis. Regional scans were taken between the 150 and 350 eV binding energy range at two locations for an iteration of 10 times each. These scans included positions for Carbon and Sulfur peaks. Table 2 indicates that these locations produced nearly identical scans showing both Carbon and Sulfur on the sample surface. Then the second location was sputtered with argon ions for 2 minutes to remove adsorbed contaminants. After sputtering, the Sulfur peak was eliminated and the Carbon peak reduced. The sample was removed to the sample preparation chamber again, heated with a quartz lamp for 1 hour and then reintroduced into the analytical chamber. Analysts noted a small Sulfur peak and a significant Carbon peak, although not as large as the one seen after heating for 2 hours. Both peaks were removed by 2 minutes of sputter with the argon gun.

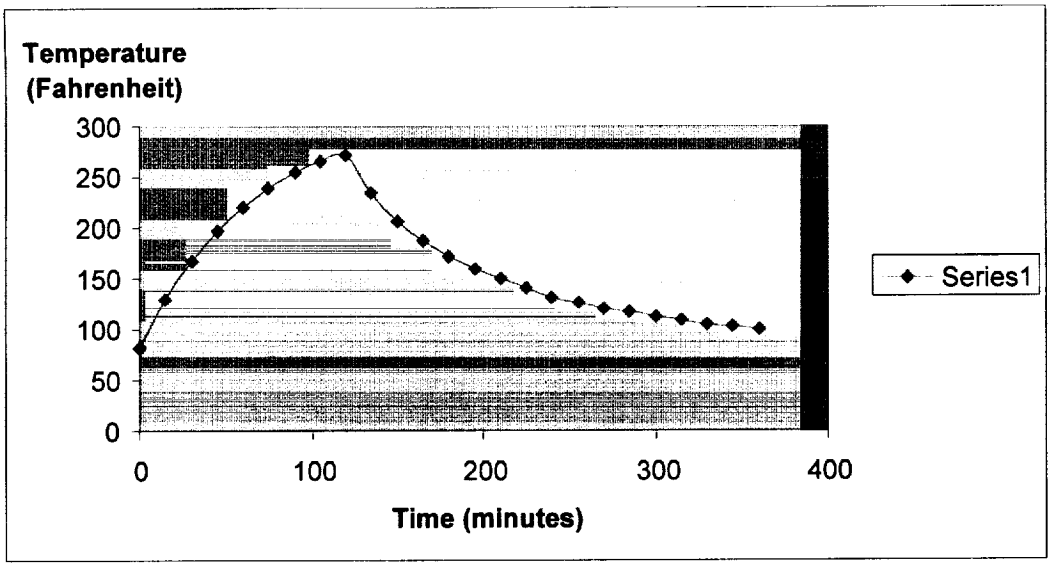

Figure 1 – Sample heating/cooling cycle

Due to sample outgassing, the pressure was elevated to 2 x 10^{-8} torr inside the analytical chamber. An attempt was made to determine whether the appearance of Carbon and Sulfur lines was due to adsorption of gaseous species from the chamber atmosphere. The sample surface was cleaned by sputter with the argon gun, left inside the analytical chamber for 4 hours, and then scanned for Carbon and Sulfur. No evidence of Sulfur was seen, although the Carbon peak had grown somewhat. It was inferred that, for the Bakelite-mounted samples, surface Carbon content could increase either from the atmosphere or through diffusion from inside the sample. In another attempt, the sample was cleaned and then placed in the preparation chamber. It was heated for 2 hours while shielded from direct radiation from the quartz lamp. No Sulfur was observed. Analysts noted the presence of a Carbon peak as large as the one produced by direct heating.

Analysis was conducted on Bakelite-mounted material, as well as on silver paste applied to the mounted samples to improve conductivity during electron microprobe evaluations. Each was analyzed twice. Both showed broader Carbon peaks, but no Sulfur. Upon cleaning, reheating, and analysis, Sulfur was again detected on the same sample.

Table 2 – Peak Areas for Carbon and Sulfur
(Preliminary Studies)

Run	Description	Carbon (1s) Counts	Sulfur (2p) Counts	Comments
13	After heating for 2 hr	68,546	10,312	First location
14	After heating for 2 hr	56,787	5,900	Second location
15	After sputter for 2 min.	5,851	-	Second location
16	After sputter, heating for 1 hr	46,200	4,299	Second location
17	Clean surface exposed to analysis chamber vacuum for 4 hr	21,524	-	Second location
18	After heating for 2 hr without direct radiation	67,347	-	Second location (Carbon pickup only)
24	As in Run #13, but at another location	52,061	7,989	Third location

After Sulfur was observed migrating to the clean surface, overall scans were performed between 0 and 1100 eV to determine whether other species were migrating. During Run #24, regional scans were performed between 150 and 350 eV. They showed evidence of Bromine, which was identified from the position of three peaks (182, 189, and 256 eV) and their relative heights. During Run #25, an overall scan was performed from 0 to 550 eV, as shown in part in Figure 2. Bromine and Cadmium species were seen with Carbon, Oxygen, Nitrogen, and Sulfur.

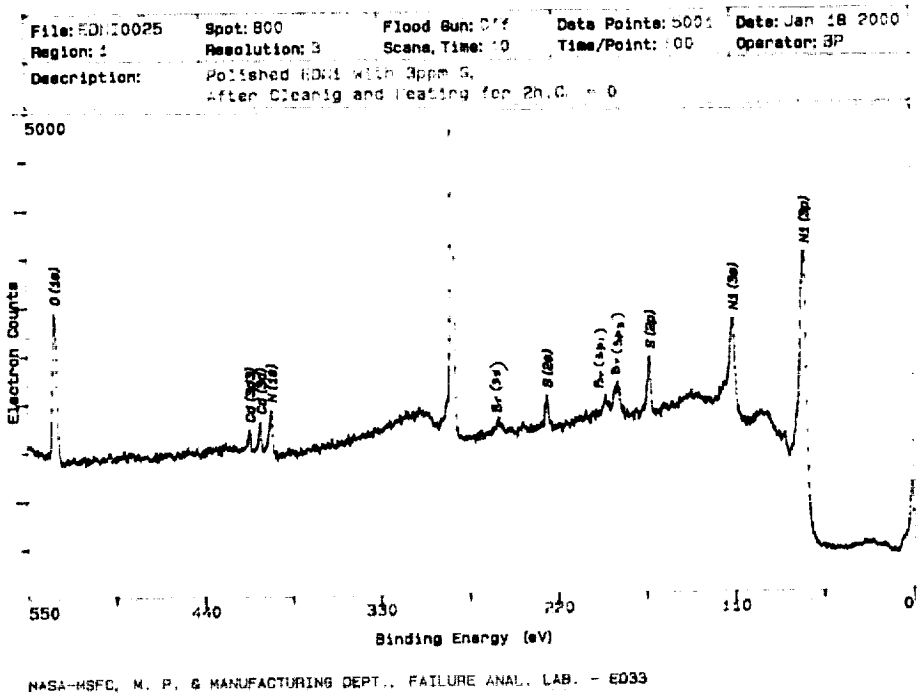

Figure 2 – Scan which shows several elements segregating to surface of Sample 6014

In Table 3, surface analysis is shown in atomic percentages. Carbon and Oxygen covered most of the Nickel surface. A sputtered surface shows about 75% Nickel, 10% Nitrogen, 10% Oxygen, and 5% Carbon. These percentages are approximate. Their accuracy depends upon degree of surface cleanliness, peak-to-background ratio of the peak being evaluated, and the test instrument's inherent machine characteristics. Here, the standard deviation should be around 0.8% for strong lines such as Nickel (10 iterations) and close to 1.8% for Carbon and other light elements (11 iterations).

Table 3 – Quantitative Surface Analysis for Sample 6014 (Atomic Percentages)

Nickel	Oxygen	Cadmium	Nitrogen	Carbon	Sulfur	Bromine
17.93	10.52	0.17	4.24	59.68	4.71	2.75

Systemic analysis was then conducted on several samples from actual MCC liners, using the methodology discussed above. Analysis was conducted on a sample taken from an MCC liner (S/N 6021), which contained more bulk Sulfur than was seen in Sample 6014. Sample 6021 was longitudinally sectioned, polished, and then removed from the mount to eliminate any elemental interference of species emanating from mounting materials. Combustion analysis indicated that it contained 6 to 7 ppm of bulk Sulfur, while the microprobe analysis indicated that it contained 3.5-ppm Sulfur. Combustion analysis gives data for the bulk material, whereas the microprobe gives data for a region of only a few micrometers on the surface.

Table 4 shows that the sample showed Sulfur, Bromine, and Cadmium, as well as small amounts of Chlorine on the surface. Despite higher levels of Sulfur in combustion analysis seen between the two samples, the migrating quantity was less than that seen in the 3 ppm material. Several readings were taken on the same sample, in order to find out whether segregation might be dependent upon location, previous exposure, or polishing. The sample was also repolished and reexamined. Run #36 showed about 11.6% Sulfur on the surface. Afterwards, a depth profiling evaluation indicated that Sulfur was present on the surface to a depth of around 0.7 nm. Thus nearly two monolayers of Sulfur were present on the sample surface.

Table 4 - Surface Analysis Results for Sample 6021
(Atomic Percentages)

Run	Nickel	Oxygen	Cadmium	Nitrogen	Carbon	Sulfur	Bromine	Chlorine	Comments
36	41.00	5.14	0.00	0.00	42.27	11.60	0.00	0.00	First location, first attempt
42	31.08	6.11	1.16	3.54	50.78	3.71	1.28	2.33	Second location, first attempt
48	37.08	7.06	0.72	2.77	43.88	6.32	2.15	0.00	First location, second attempt
49	34.69	7.01	0.42	2.88	46.76	6.41	1.82	Trace	Second location, second attempt
76	34.22	4.21	0.23	3.73	51.04	1.87	2.47	2.23	Third location after grinding

Table 5 shows results for a sample taken from the aft area of an MCC liner (S/N 6005) analyzed at two locations. Both microprobe and combustion analysis showed very small amounts of Sulfur (~1.2 ppm).

Table 5 – Surface Analysis Results for Sample 6005
(Atomic Percentages)

Nickel	Oxygen	Cadmium	Nitrogen	Carbon	Sulfur	Bromine	Chlorine
26.90	10.04	0.23	-	58.03	2.67	2.09	-
28.79	9.80	0.20	1.71	54.28	1.84	3.35	-

Another high-Sulfur sample taken from an MCC liner (S/N 6018) was analyzed at two locations. Sample 6018 contained around 5 to 6 ppm of bulk Sulfur, as confirmed by both combustion and microprobe analyses. Table 6 reports XPS analysis results indicating the presence of traces of Cadmium and Nitrogen on the surface, in addition to Sulfur.

Table 6 – Surface Analysis Results for Sample 6018
(Atomic Percentages)

Nickel	Oxygen	Cadmium	Nitrogen	Carbon	Sulfur	Bromine	Chlorine
26.98	9.33	Trace	Trace	58.36	2.96	2.38	-
25.88	8.93	-	Trace	58.89	3.66	2.65	-

Analysis was also conducted on a sample taken from an MCC liner (S/N 6016). It contained an intermediate amount of Sulfur, with a bulk analysis of approximately 4 ppm. Table 7 shows negligible amounts of Cadmium, with Tin seen as one of the species seen migrating onto the surface.

Table 7 – Surface Analysis for Sample 6016 (Atomic Percentages)

Nickel	Oxygen	Cadmium	Nitrogen	Carbon	Sulfur	Bromine	Chlorine	Tin
23.96	10.44	Trace	3.04	57.80	2.78	1.68	-	0.28
22.28	10.13	Trace	3.89	57.63	3.39	2.23	-	0.43

DISCUSSIONS

Impurities are common in Nickel sulfamate baths. The common impurities in Nickel deposits are Oxygen, Carbon, Sulfur, and Chlorine.[5] These impurities occur in amounts that vary largely depending upon the operating parameters. Metallic impurities generally originate as contamination and additives. Such impurities are generally present in very small concentrations. Their presence and origins are generally not apparent unless the species are specifically sought out. Earlier publications[6] discussed possible sources of these species. Here, the XPS used a residual gas analyzer in the sample preparation chamber to identify species present in the vacuum chamber. During heating, the sample preparation chamber contained Oxygen, Nitrogen, moisture, Carbon dioxide, and Hydrogen gases. No additional species were found after heating for 2 hours using gold samples, unlike results for the ED-Ni material.

Several studies have found Sulfur in Nickel, which is known to segregate to grain boundaries, as well as to free surfaces. That phenomenon occurred here after heating to 275 °F. Segregation effects will be faster for high-temperature exposure. The amount migrating to grain boundaries will depend upon how much free Sulfur remains after compounding with other elements (e.g., calcium and/or manganese) that may be present in ED-Ni. Several readings for Sample 6021 showed scatter in surface Sulfur compositions. However, average analyses at different locations for different liners correspond well with the findings of total Sulfur by combustion and microprobe analysis. Table 8 compares average results for surface analysis and combustion analysis.

While the origin of Cadmium and Bromine is unclear, they may be present in very small quantities in ED-Ni. However, additional study is needed as to their segregation propensity, in addition to that of Sulfur. Investigation is also required to determine whether synergistic effects exist among such segregating species.

Table 8 – Comparison of Average Results for Sulfur During Surface Analysis and Combustion Analysis

MCC Liner Serial Number	Sulfur by Combustion Analysis (ppm)	Average Sulfur on Surface (Atomic Percent)
6021	6.5	5.98
6005	1.2	2.25
6018	5.5	3.31
6016	4.0	3.08

CONCLUSIONS:

1. A viable experimental method using XPS has been shown to conduct a quantitative assessment of migrating species in ED-Ni.

2. This method can be used to evaluate small amounts of segregating species as they accumulate on the free surface.

3. Elements other than Sulfur (such as Cadmium, Tin, and Bromine) were also seen segregating onto the free surface.

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