High Temperature Heat Treatment Of Electroless Nickel Deposits For Improved Corrosion Resistance and Abrasion Properties

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Introduction

Electroless nickel (EN) technology has been utilized for nearly fifty years in various coating applications. Surface preparation, nickel-phosphorus ratio and heat treatment have been used to modify corrosion resistance, hardness and deposit adhesion. Most literature and ASTM specifications discuss a typical heat treatment cycle of 400°C for one hour, as a standard technique to improve microhardness of EN deposits from about 500 to 900 Knoop. In some cases this treatment has been reported to lower corrosion resistance. In applications where hardness is the major performance criteria, the lowering of corrosion resistance, may not be significant. But there are applications were both wear and corrosion are required by the end user. The following reflects a study done by an end user, a plater and a supplier of sodium hypophosphite, to aid the industry with this problem.

Discussion

Earlier work by C.F. Beer set the stage for this study by relating structural changes that take place in the deposit after various heat treatment cycles. The Beer study mentions a heating cycle used for hydrogen embrittlement relief at 200°C. At this temperature, improved nitric acid corrosion resistance was observed, but hardness was not substantially increased. At 400°C, similar corrosion tests showed poor results in the oxidizing acid, but improved hardness was observed. The question was, can both properties be improved with one post deposit heat treatment (HT) cycle?

The present study comprises of two types of steel substrates (SAE 4130 & 1018), two heat treatment cycles (400 and 600°C, at 1 and 10 hours respectively) and two baking atmospheres (air and nitrogen). An oil field application, using high temperature (600°C) bake technology in an experimental test program, will also be reviewed.

Test panel conditions (substrate, deposit, heat treatment), SEM-EDS (scanning electron microscopy/energy dispersive spectrometry) photomicrograph analysis and Knoop hardness, at various areas within the coating /substrate, will be reviewed. Because of a high number of potential corrosive environments, we choose to investigate corrosion resistance in aggressive chemicals, such as, hydrochloric acid, sodium hydroxide and boiling sodium chloride in laboratory controlled studies.

Results and Observations

Two photographs, following this text, show the appearance of both types of plated panels, before and after treatment cycles. At 400°C, a typical bluish tinge is seen on both air and nitrogen samples. When heat treatment cycles are increased to 600°C, the color changes to an olive drab.

Table I lists the 24 coupon test conditions of this study.

Table II offers references to the SEM-EDS analysis and photomicrograph views. Figures A-I, from this Table, reviews the work done over the 4130 steel, while J-O details conditions over 1018 steel. Figure A (Coupon 5) is a cross section photomicrograph of the “as plated” EN/steel panel. Figure B (Coupon 13) is of a similar view, but the panel has been subjected to a 400°C, one hour heat treatment. Figure C (Coupon 21) is the same coating after a 600°C, ten hour heat treatment. The visual difference in these views can been categorized as where the 600°C heat treated sample developed at least a third metallic layer at the EN/substrate interface, thus indicating the development of a diffusion zone. Figure D (Coupon 5) shows ESD scans of the non heat treated specimen, where four spot analysis were taken horizontally across its viewable area. What is seen at Spot 1 is the very high iron substrate. Spot 2 on the substrate side of the steel/EN interface, still shows very high iron content with a very low level of nickel present. The iron to nickel ratio was 29:1. Spot 3 is on the EN side of the interface and records nickel and phosphorus plus a low level of iron at the site. In this case, the nickel to iron ratio was 9:1. Spot 4 is similar to 3, but the ratio of nickel to iron has grown to 15:1. Figure F (Coupon 13), the 400°C test panel, reveals metal ratios at Spots 1, 2, 3 and 4, as being iron to nickel 126:1 and 29:1 and nickel to iron ratios of 10:1 and 17:1, respectively.

Figures H and I (Coupon 21), the 600°C treatment, were analyzed at seven spots across the SEM viewing area. In this instance two readings were taken in the substrate and five in the diffusion zone. In each case as you moved across from deep within the substrate to within the deposit, the metallic content variations indicated a diffusion zone. Metal ratios across this cross section were 70:1 and 5:1 iron to nickel at Spots 1 and 2. Spots 3, 4 and 5, in a two micron zone, revealed nickel to iron metal ratios of 1.1:1, 2:1 and 4:1. Spots 6 and 7 were analyzed at 5:1 and 9:1 nickel to iron, respectively. After viewing the photomicrograph more closely, it was felt that this series of spot analysis may never ventured out of the diffusion zone.

A second SEM analysis series also yielded interesting results for two deposits over 1018 steel. The control deposit without heat treatment, as seen in Figure J photomicrograph, (top) reveals no diffusion zone at the EN / substrate interface of the non heat treat, Coupon 7. The lower half of Figure J shows a photomicrograph of the 600°C HT, Coupon 19. Here can be seen a separate layer or diffusion area at the deposit/substrate interface. An artists drawing (Figure K) and actual EDS scans in Figures L-O reviews SEM spot analysis for these samples. Figure L (Coupon 7), EDS scans 1-4, on the non HT sample, show that away from the interface at Spot 1, 100% iron was found. Spot 2, on the iron side of the EN/substrate interface analysis found 91.3 % iron, 7.3% nickel and 1% phosphorus . On the EN side of the interface, analysis reveals 4% iron, 84.9% nickel and 11% phosphorus. As you move a distance away from the interface, readings of 89.5% nickel and 10.5% phosphorus were observed. The second sample (Coupon 19) tested was heat treated at 600°C for ten hours. These results can be found on Figures M-O. On this sample ten spot analyses were taken after it was observed that there was a diffusion area at the interface. Three distinct shading differences on the photomicrographs indicated this diffusion phenomena. Spot 1 was in the substrate, a good distance from the interface. Spot 2 was just to the iron side of what appeared to be the diffusion zone. Spot 3, several Spot 4 areas and Spot 5 were examined within the diffusion zone. The last two, Spots 6 and 7, were analyzed on the EN side of the diffusion zone. Results indicated from 0 to 88.75% nickel, 0-11.25% phosphorus and iron from 100 to 0% across this entire cross section. These results, as seen in Figure J are another indication that elemental diffusion has taken place.

The hardness of deposits and substrates can be found in Table III. The high phosphorus EN (HP-EN) deposit was found to be three mils in thickness on all panels tested. Shimadzu microhardness (100 gram wt) testing of EN over 4130 and 1018 steel, revealed the “as plated” deposit was 480-530 Knoop hardness. Values recorded after 400°C

HT showed an increase, to 790-890 Knoop. At 600°C, deposits were in 718-755 Knoop range.

Corrosion tests results can be seen in Table IV. Standard ASTM G-31 and G-123 corrosion tests were selected to show the wide range of protection provided by HP-EN coatings and the added benefits that may be derived from heat treatment. These environments included boiling acidified sodium chloride, 10% hydrochloric acid at 25°C and 50% sodium hydroxide at 145°C. Society of Automotive Engineers (SAE) 1018 steel is a relatively low carbon commercial product used primarily in consumer goods. This material is serviceable under a variety of conditions and adaptable to low cost techniques of mass production. It provides ease of fabrication, predetermined strength, ductility and a relatively attractive appearance after fabrication. SAE 4130 steel contains higher carbon (0.30%) than that of 1018 (0.18 %) steel and is normally used in hardened and tempered condition. Chromium, manganese, silicon and molybdenum, found in 4130 provides improved ductility and reduced stresses because of higher tempering temperature requirements. While SAE 4130 is more susceptible to stress-corrosion cracking and hydrogen embrittlement than is 1018 steel, both substrates stress crack in hot strong sodium hydroxide environments and are severely attacked by the environments selected.

An uncoated 1018 coupon in 10% HCl corroded at greater than 1000 mils per year (mil/yr.). Three mils of HP-EN deposit over the 1018, exhibited a corrosion rate of 9.49 mil/yr. Heat treating the deposit at 400°C resulted in increased corrosion to almost 14 mil/yr., while the 600°C heat treatment brought the rate down to 9.15 mil/yr., which was lower than the unheated deposit.

It was a similar scenario in the caustic environment. The 1018 steel stress cracked and corroded at a rate >250 mil/yr. The EN deposit corroded at 7.06 mil/yr., while the heat treated (400 and 600°C) deposits exhibited 22.65 and 6.17 mil/yr. corrosion respectively.

The final test, in boiling NaCl, showed the uncoated substrate to pit and corrode at 56.9 mil/yr. The as plated, 400° and 600°C heat treated deposits, exhibited corrosion rates of 15.05, 23.62 and 6.71 mil/yr. respectively.

In the same NaCl test a 4130 steel coupon corroded at 45.22 m/yr. and stress cracked in seven days. The EN coated 600°C coupon corroded at 5.87 mil/yr and did not stress crack. These result over 4130 and 1018 steel revealed heat treatment at 400°C reduced deposit corrosion protection, while 600°C brought protection to levels better even than the “as plated” deposit. A note with this testing is that all heat treated deposits were conditioned in HCl or NaOH to remove an oxide layer that developed during heating cycles.

End User Tests and Field Application

A manufacturer of oil related production equipment began to look toward high temperature heat treatment as a way of solving one of their corrosion/abrasion resistance problems. Test panels of 4130 low alloy steel were coated with three mils of HP-EN and heat treated at 600°C for 10 hours in a nitrogen atmosphere. Tests, such as ones found in ASTM B733, as well as other industry standards were used to determine deposit and substrate integrity. The heat treated panel visually had a mottled olive drab appearance, which appeared to be an oxide scale. A cross section of the panel was mounted in epoxy, ground, polished to a mirror image and etched. A SEM evaluation clearly revealed a diffusion layer. The outer most layer was categorized as a 5 micron thick nickel oxide. A second layer, 50 microns thickness, appeared to be nickel from an EN deposit. A third zone, near the substrate, was a 15 micron austenite structure. The final deposit layer was a nickel-iron solid solution that transitioned into the base metal. Data from this test program concluded that elemental changes had occurred at and away from the EN/substrate interface. Vickers hardness (100 gr) resulted in deposit values before heat treatment of 606 and after heat of 772. The ASTM B733 bend tests was successful after a 180° mandrel bend and impact tests also proved satisfactory, as 10x magnification revealed no blistering or flaking. An immersion test in 30% nitric acid for thirty seconds at 25-35°C showed no deposit discoloration to the unaided eye.

Porosity was measured by a ferroxyl test, which provided data as to the lack of deposit pores. And an ASTM B 117 salt fog test found no corrosion after 1500 hours in the chamber.
Field tests of high heat treatment 4130 couplings for flexible hoses have been ongoing since March, 1999 off the east coast of Brazil.

Conclusion

The results of several test programs done at three facilities, coupled with earlier Beer work, confirms that high temperature (600°C for 10 hours) heat treatment is a viable option for improving deposit corrosion resistance and hardness properties. SEM/EDS analysis of the deposits over both 4130 and 1018 steel substrate found elemental mixing in the interfacial areas. This supports the theory that a diffusion zone is produced when heat treatment (HT) is sufficiently high enough to cause such intermetallic diffusion.
This diffusion zone produces a deposit where the corrosion resistant layer, in the tests run, is superior to non-heat or 400°C treatment.
This information should always be coupled with the understanding that one must have a substrate that will not be adversely effected by such post treatment either by alteration of mechanical properties or distortion of the part. Other specific corrosion environments should be checked individually, to assure this trend will be correct for the application environment of concern.

Table I

Test Panel Reference

Test Coupon #	Substrate	Coating	Heat Treatment		
			Temp	Time	Atmosphere
1	4130	none	none		
2	4130	none	none		
3	1018	none	none		
4	1018	none	none		
5	4130	HP-EN	none		
6	4130	HP-EN	none		
7	1018	HP-EN	none		
8	1018	HP-EN	none		
9	4130	HP-EN	400°C	1 hr	air
10	4130	HP-EN	400°C	1 hr	air
11	1018	HP-EN	400°C	1 hr	air
12	1018	HP-EN	400°C	1 hr	air
13	4130	HP-EN	400°C	1 hr	nitrogen
14	4130	HP-EN	400°C	1 hr	nitrogen
15	1018	HP-EN	400°C	1 hr	nitrogen
16	1018	HP-EN	400°C	1 hr	nitrogen
17	4130	HP-EN	600°C	10 hr	air
18	4130	HP-EN	600°C	10 hr	air
19	1018	HP-EN	600°C	10 hr	air
20	1018	HP-EN	600°C	10 hr	air
21	4130	HP-EN	600°C	10 hr	nitrogen
22	4130	HP-EN	600°C	10 hr	nitrogen
23	1018	HP-EN	600°C	10 hr	nitrogen
24	1018	HP-EN	600°C	10 hr	nitrogen

Table II

SEM-EDS Photomicrographs and Scan Analysis

Figure	Substrate	Coupon#	Process History	Magnification
A	4130	5	none	600x
B	4130	13	400°C, 1 hr, N_2	600x
C	4130	21	600°C, 10 hr, N_2	2000x
D	4130	5	none	-----
E	4130	9	400°C, 1 hr, air	-----
F	4130	13	400°C, 1 hr, N_2	-----
G	4130	17	600°C, 10 hr, air	-----
H	4130	21	600°C, 10 hr, N_2	-----
I	4130	21	600°C, 10 hr, N_2	-----
J	1018	7, 19	none & 600°C, 10 hr	1000x
K	1018	7, 19	none & 600°C, 10 hr	drawing
L	1018	7	none	-----
M	1018	19	600°C, 10 hr	-----
N	1018	19	600°C, 10 hr	-----
O	1018	19	600°C, 10 hr	-----

Table III

Shimadzu Knoop (100 gr) Microhardness

Coupon #	Substrate	Process History	Microhardness, Knoop Substrate	Microhardness, Knoop EN Coating
1	4130	No EN	209	-----
5	4130	As plated	233	480 - 536
9	4130	400°C, 1 hr, air	241	889
13	4130	400°C, 1 hr N_2	241	889
17	4130	600°C, 10 hr, air	233	735 - 755
21	4130	600°C, 10 hr N_2	261	725 - 735
3	1018	No EN	134	-----
7	1018	As plated	126	525 - 536
11	1018	400°C, 1 hr, air	142	791 - 846
15	1018	400°C, 1 hr N_2	142	769 - 782
19	1018	600°C, 10 hr, air	142	718 - 721
23	1018	600°C, 10 hr, N_2	124	735 - 742

Table IV

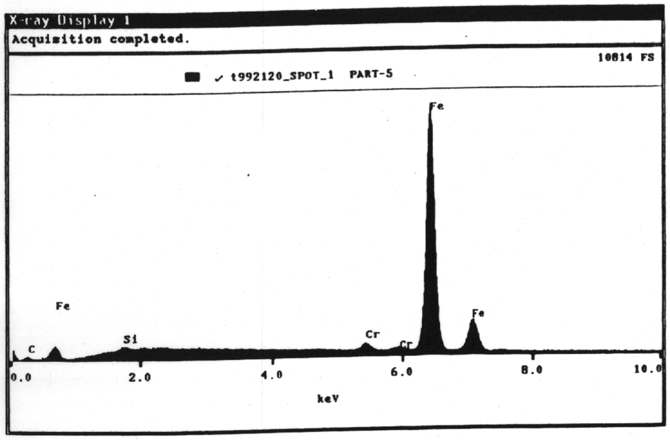
Effect of Heat Treatment on Corrosion Rate of 3.0 mils HPEN

Substrate SAE Steel	Deposit	ASTM G-31 10% HCl @25^{0}C	ASTM G-31 50% Caustic @145^{0}C	ASTM G-123 Acidified NaCl Boiling
1018	None	>1000	>250 SCC	56.90 Pits
1018	As Plated	9.49	7.06	15.05 6000 Hours No cracks
1018	400^{0}C 1 hour	13.97[1]	22.65[2]	23.62[2]
1018	600^{0}C 10 hours	9.15[1]	6.17[2]	6.71[2]
4130	None	>1000	~250 SCC	45.22 Pits SCC, 7 Days
4130	600^{0}C 10 hours	-----	-----	5.87[2]

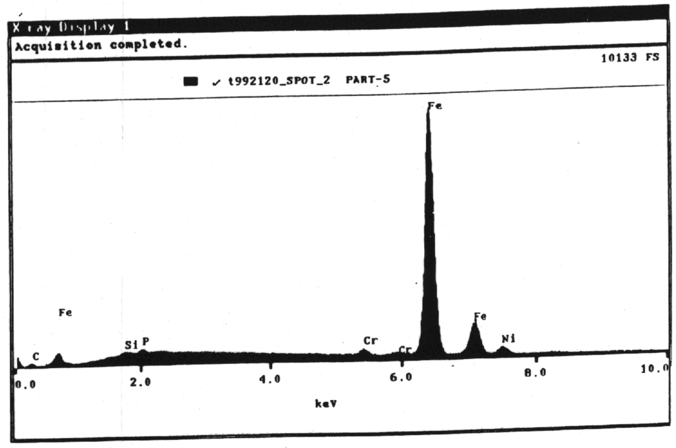
1= Corrosion rate based on steady state after conditioning by exposure for one-hour in HCl to remove oxide produced during heat treatment.
2= Corrosion rate based on steady state after conditioning by exposure for 24 hours in caustic or NaCl to remove oxide produced during heat treatment.
SCC= Stress-Corrosion-Cracking.

FIGURE D

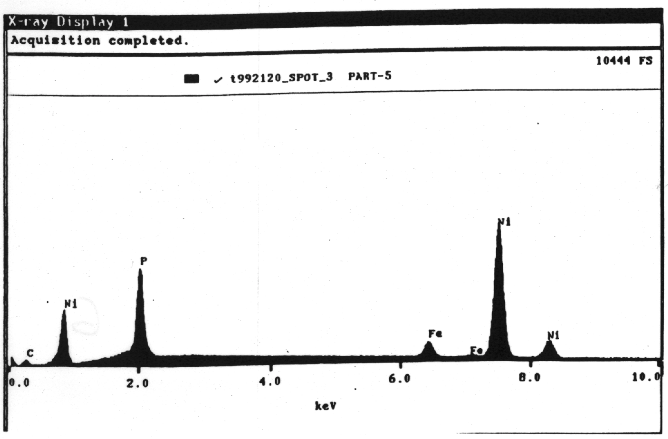
PART-5 SPOT-1



PART-5 SPOT-2



PART-5 SPOT-3



PART-5 SPOT-4

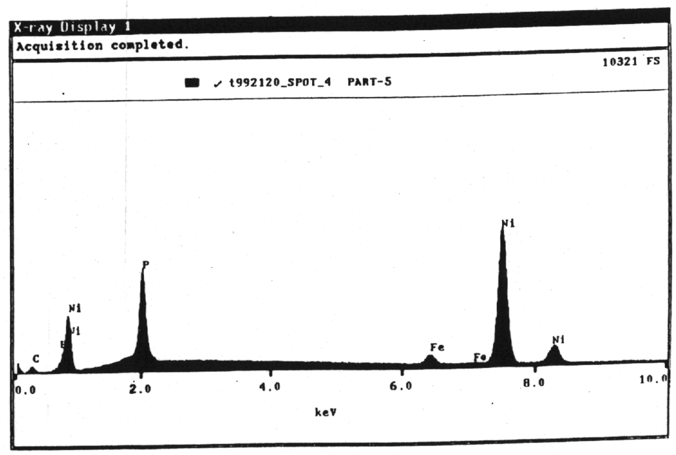
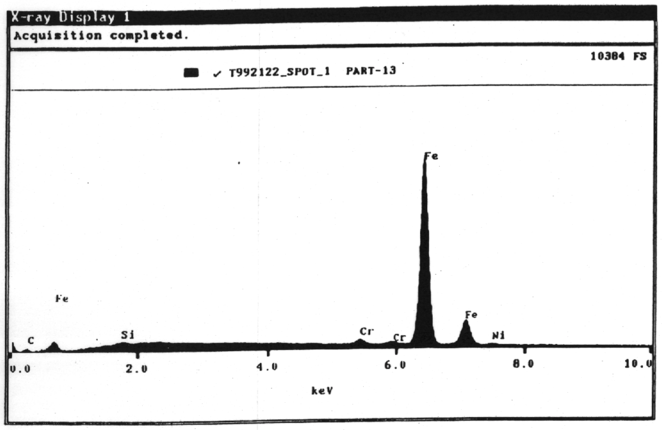
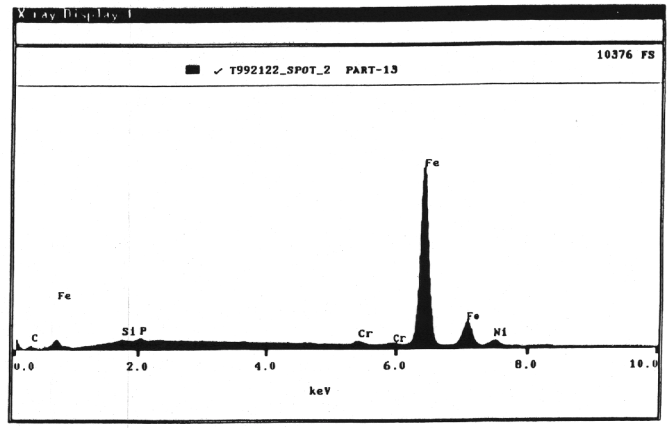


FIGURE F

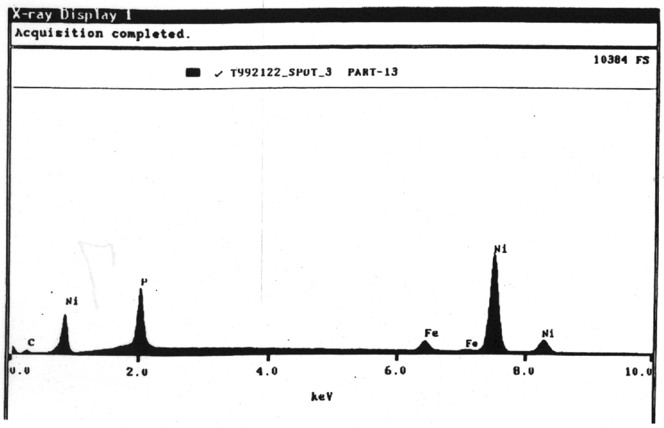
PART-13 SPOT-1



PART-13 SPOT-2



PART-13 SPOT-3



PART-13 SPOT-4

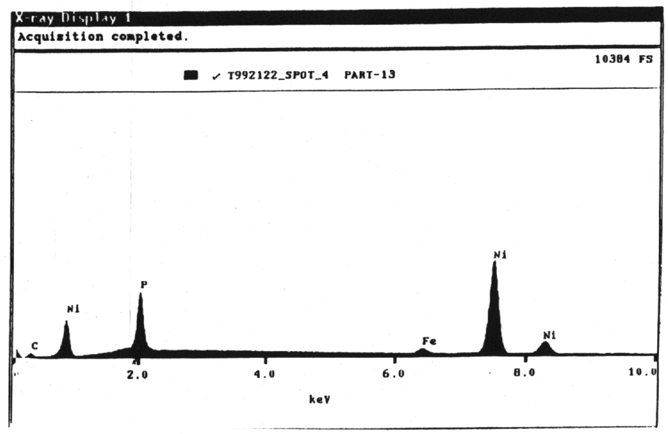
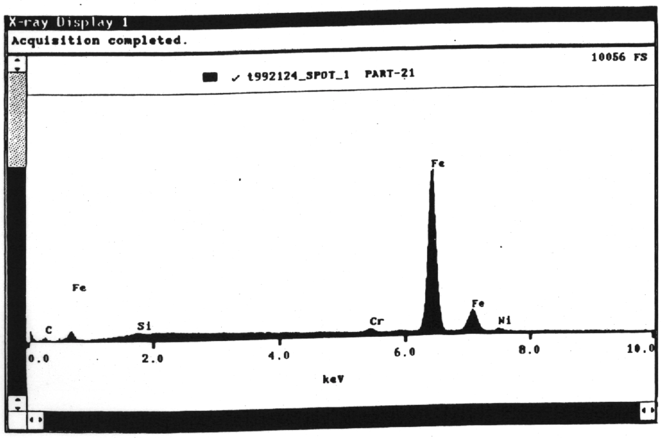
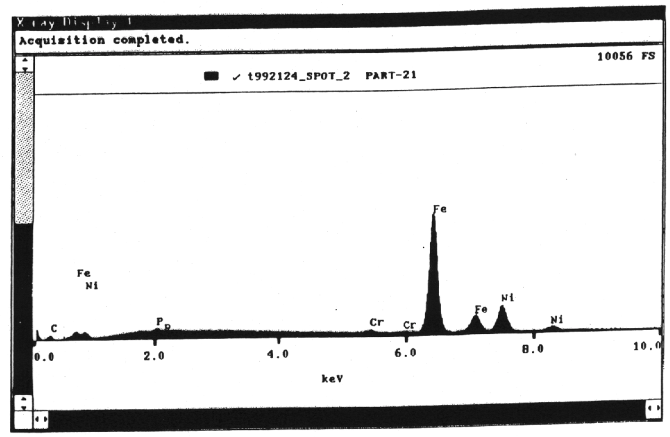


FIGURE H

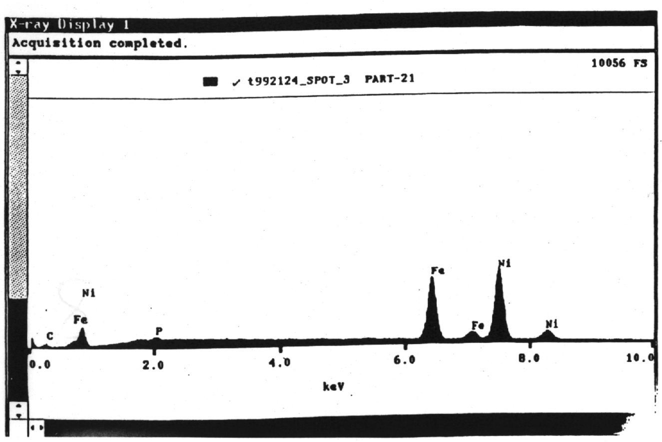
PART-21 SPOT-1



PART-21 SPOT-2



PART-21 SPOT-3



PART-21 SPOT-4

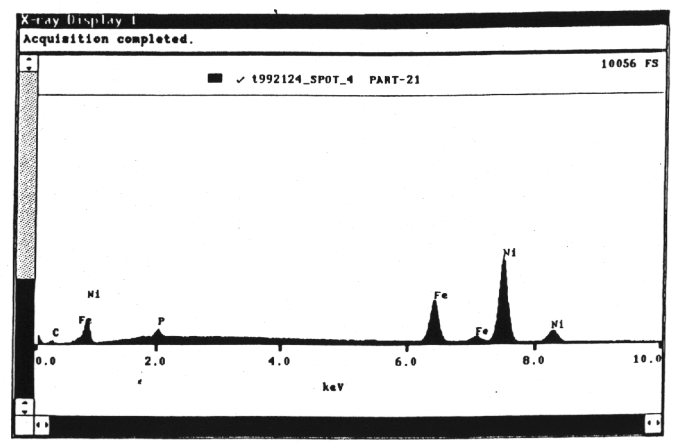
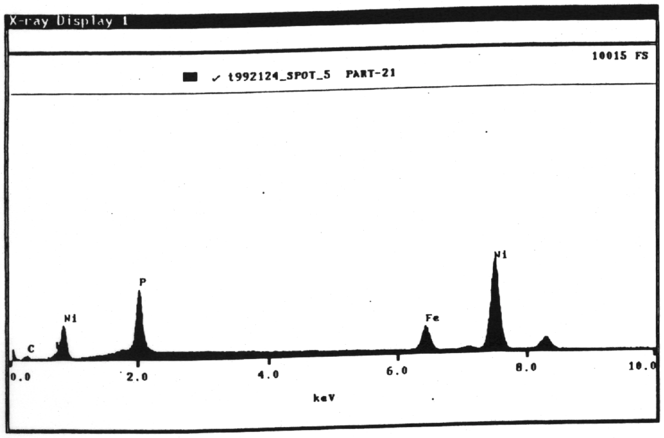
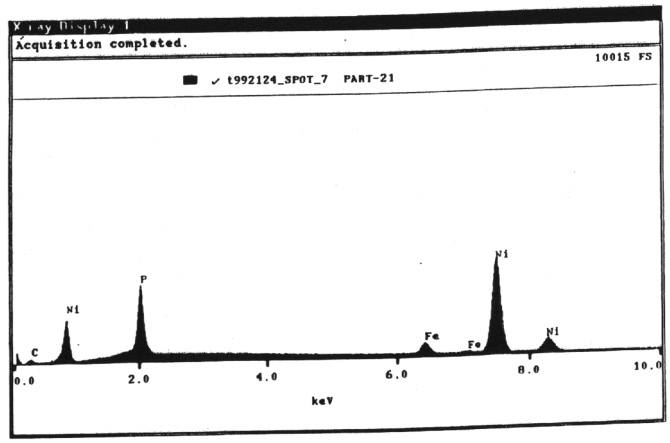


FIGURE I

PART-21 SPOT-5



PART-21 SPOT-7



PART-21 SPOT-6

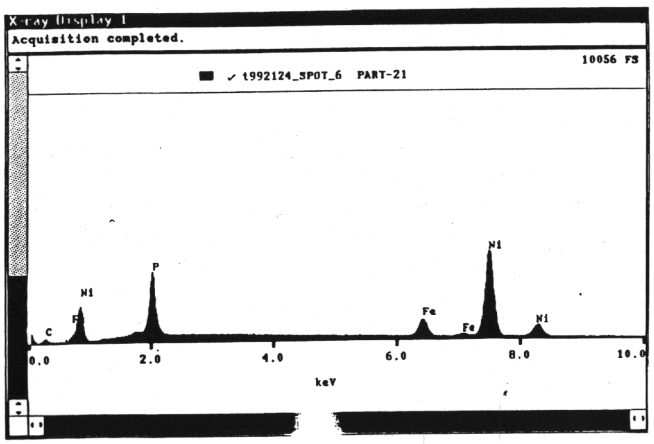
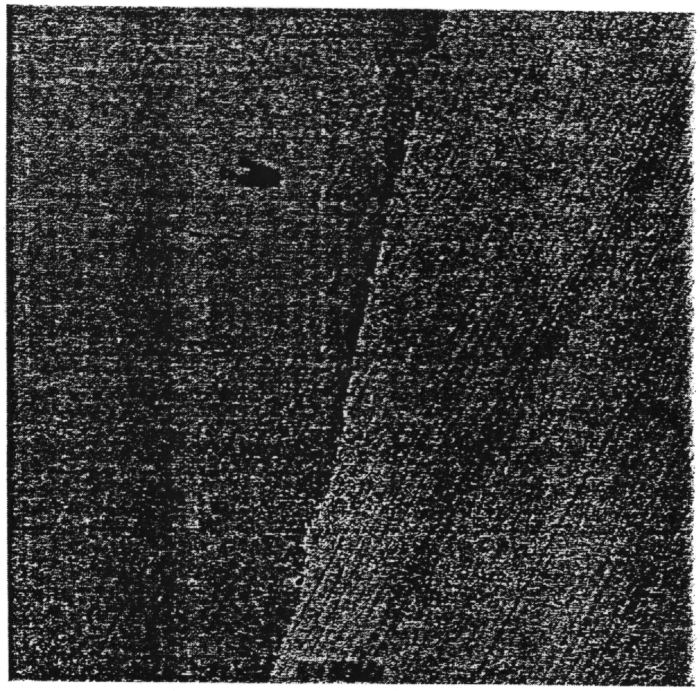


FIGURE J

Part 7 "As Plated"



Part 19 10 Hr @ 600°C

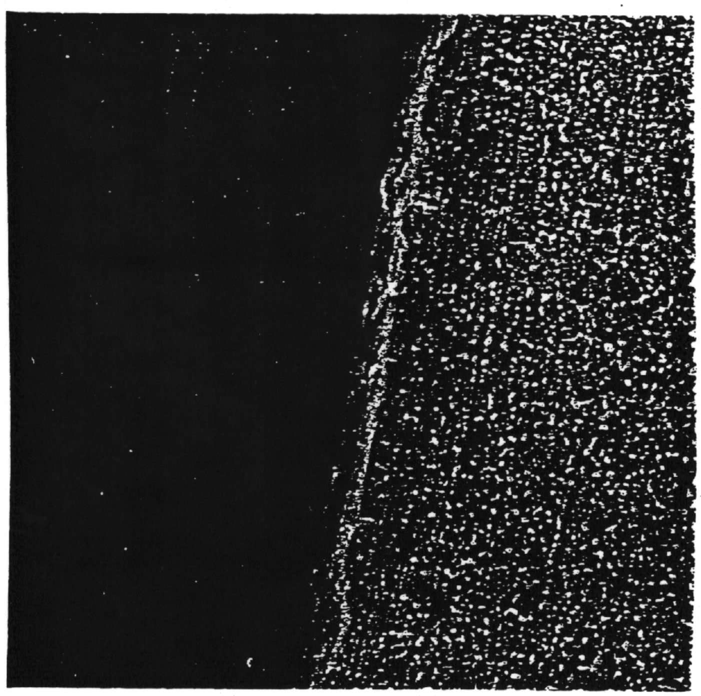
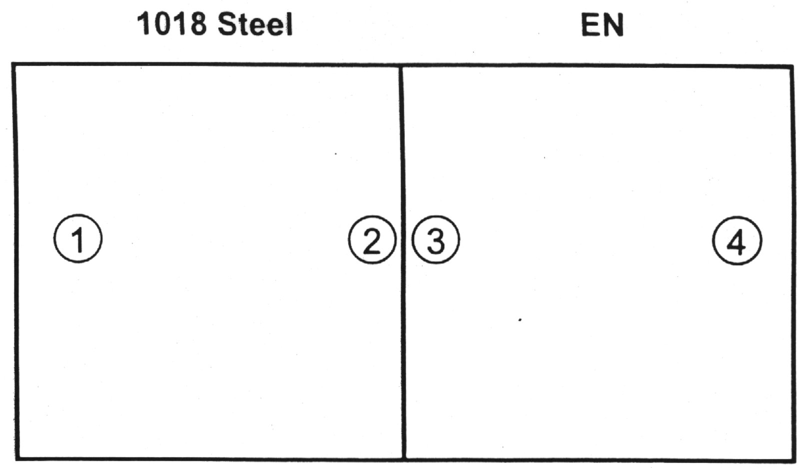


FIGURE K

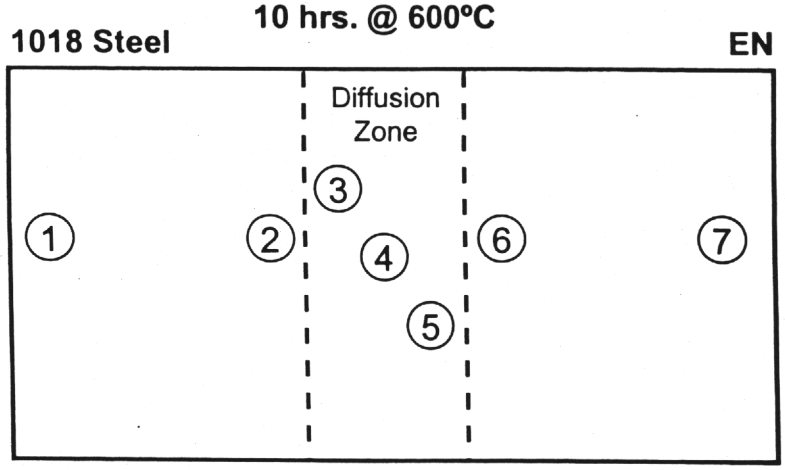
As Plated



	1	2	3	4
Ni	–	7.6	84.9	89.5
P	–	1.0	11.0	10.5
Fe	100	91.3	4.0	–

Heat Treatment

10 hrs. @ 600ºC



	1	2	3	4	5	6	7
Ni	–	.4-.5	15.1	47.7-64.8	73.5-74.1	81.40	88.75
P	–	0.-.13	.23	0-.4	.23-.29	4.57	11.25
Fe	100	99.4	84.6	34.7-52.3	25.7-26.2	14.02	–

FIGURE L

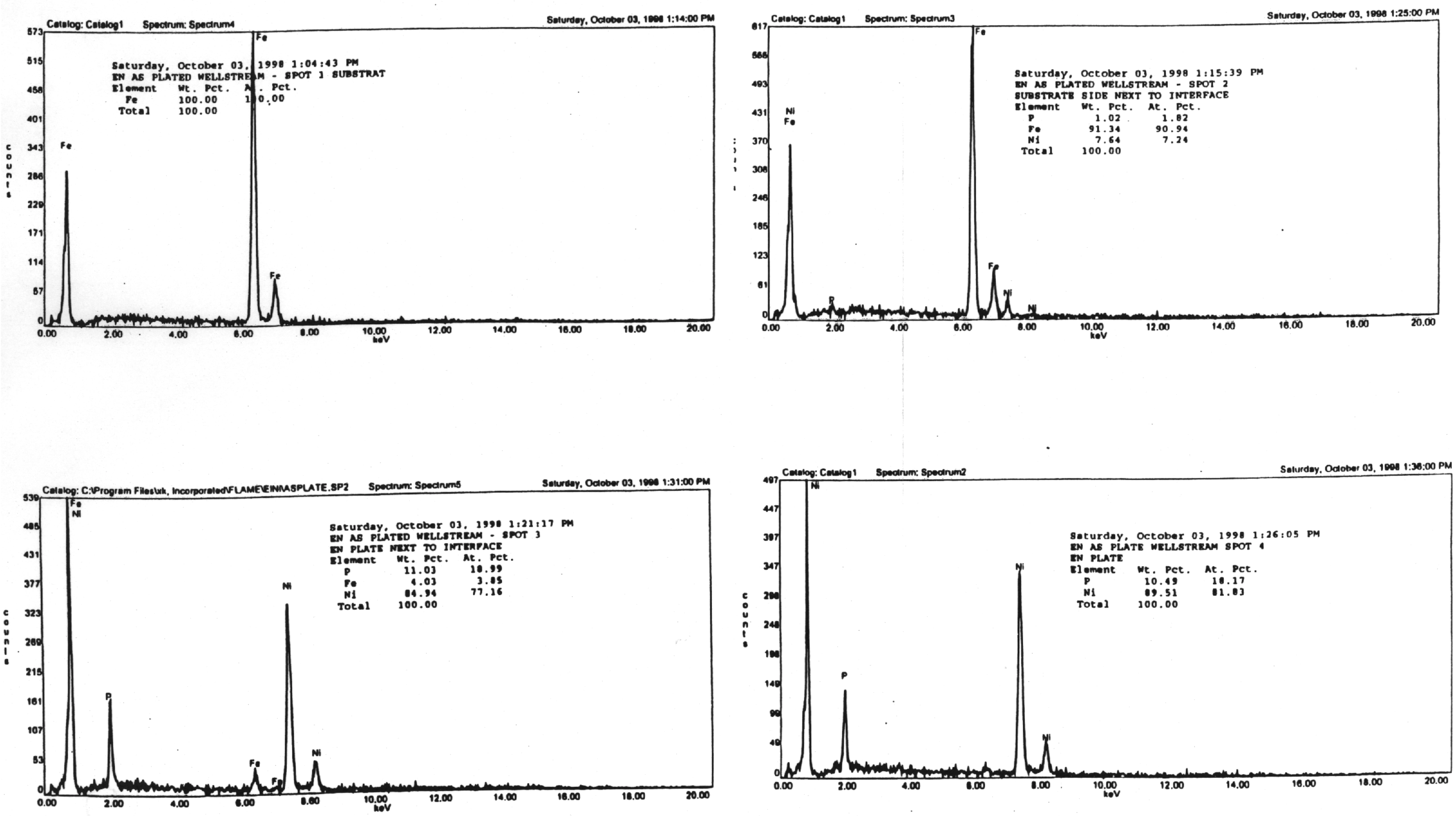


FIGURE M

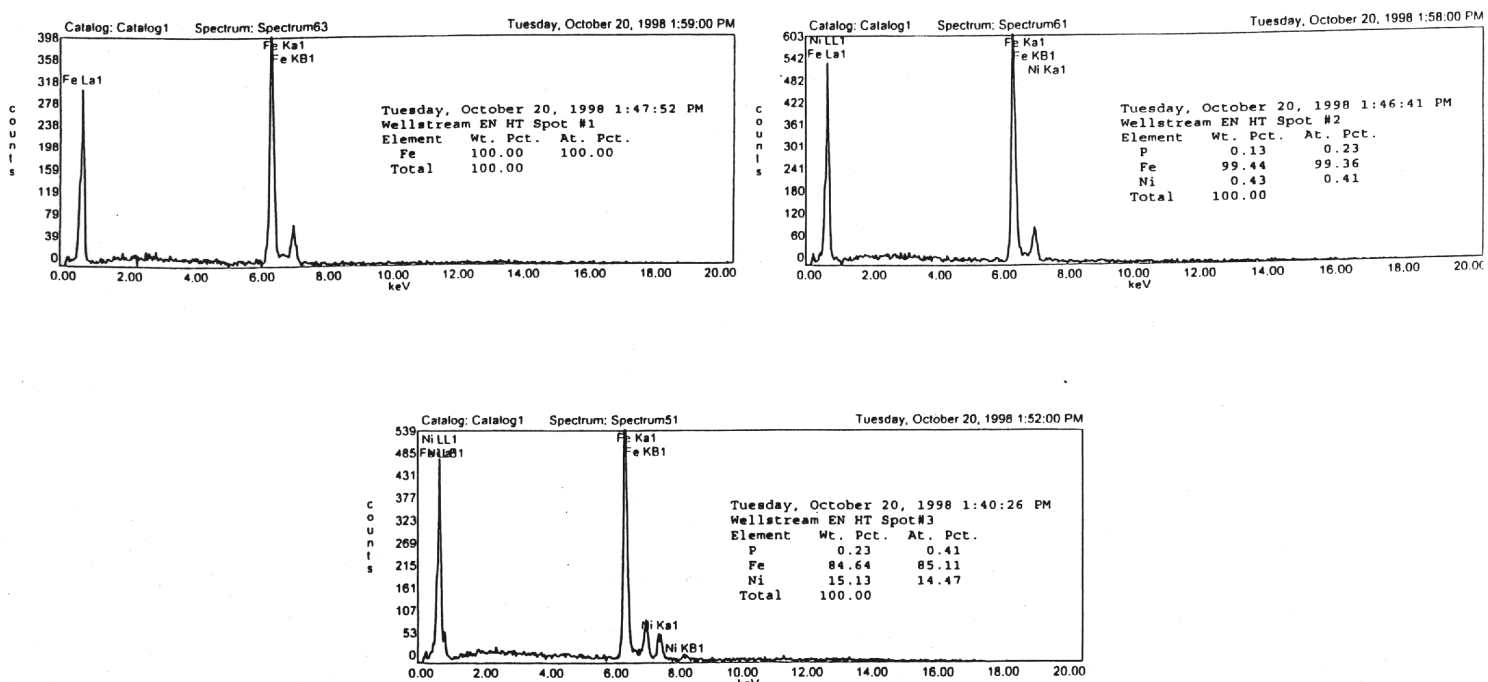


FIGURE N

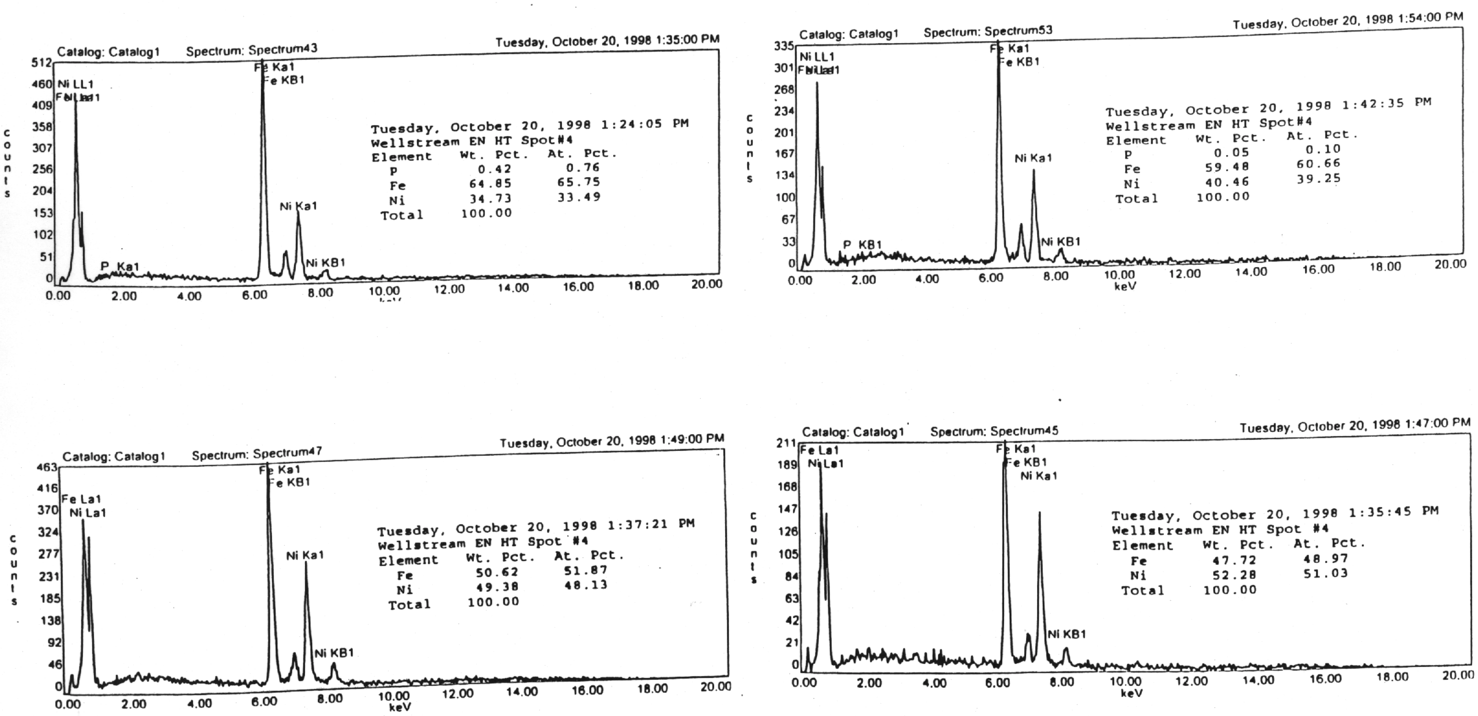


FIGURE O