FINAL REPORT

Phase Measurement of Galvanneal Task

**JPL Task Order #: RF-152
Amendment #: 543**

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March 1, 1995

JET PROPULSION LABORATORY

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I INTRODUCTION

The objective of this task was to demonstrate an x-ray fluorescence (XRF) technique which would measure the phase composition of galvanneal coatings of sheet steel rapidly and non-destructively with an accuracy of $\pm 0.5\%$. This data acquisition and analysis method would be implemented as an on-line process control input.

The AISI sample matrix evaluated for this study is shown in Appendix I. The Jet Propulsion Laboratory (JPL) and Data Measurement Corporation (DMC) measured iron and zinc XRF responses from these samples. In addition, JPL performed metallography, x-ray diffraction (XRD), and transmission electron microscopy (TEM) to characterize the samples' galvanneal phase morphology. This data was correlated with the XRF experimental results and then compared to phase composition models, which were generated using a Fundamental Parameters Method (FPM) approach.

II. EXPERIMENTAL PROCEDURES

A. JPL X-ray Fluorescence

1. Experimental Set-up

Optimum Conditions

The XRF experimental set-up was optimized to maximize the signal from the galvanneal coating in minimum data collection time. The spectral response of zinc and iron was measured by a silicon-lithium detector and recorded on a multi-channel analyzer. The x-ray beam was generated using a molybdenum target at a filament current of 25 mA and tube voltage of 35 mV. Optimum incident and take-off angles were each determined to be 25° . The working distances from the x-ray tube to the sample and from the sample to the detector were both approximately 13.35 cm. Two collimators were placed in front of the detector. Figure 1 shows a diagram of the XRF experimental set-up.

Figure 1: XRF Experimental Set-up

Incident and Take-off Angles

X-ray penetration depth, a function of the incident angle, is defined as the angle that the x-ray source makes with the sample surface. For the purpose of this experiment, it is desirable to minimize the penetration of the incident beam into the steel substrate but maintain complete penetration through the coating. Figure 2 shows the zinc/iron XRF response ratios of multiple incident and take-off angles for an unalloyed and alloyed interstitial-free sample. The take-off angle is defined as the angle which the detector makes with the sample surface. The unalloyed sample responses clearly showed the influence of the iron from the substrate at incident angles of 35° or higher. The alloyed case is less dramatic but also shows increasing iron response at the higher incident angles.

(2a) Unalloyed

(2b) Alloyed

Figure 2: Zinc/Iron XRF Response Dependence on Incident and Take-off Angles for IF Samples

It was on this basis that the 25° incident angle was selected for the fluorescence experiments. Penetration depth approximations concluded that this incident angle would penetrate all the AISI sample coating weights (Appendix I), whereas a 15° incident angle was only marginal. The influence of take-off angle on the fluorescence response is summarized by the zinc response decreasing with increasing take-off angle and the iron response increasing with increasing take-off angle. The take-off angle of 25° was selected because it provided an acceptable data collection time for both the zinc and iron responses.

Tube Current and Voltage

The optimum tube current and voltage of 15 mA and 35 kV were determined by the limitations of the detector signal processing (i.e. dead-time) [1], the physical experimental set-up and safety precautions. Empirical data intended to optimize signal-to-noise ratios and maximize count rates for the zinc and iron fluorescence responses was also used to optimize current and voltage settings.

2. Data Collection

Fixed Counts

XRF zinc and iron response data was taken at fixed total counts to determine optimum incident and take-off angles and optimum data collection times. A statistical basis for calculating precision and sensitivity was used to determine optimum fixed total counts of 100,000 for zinc and 10,000 for iron. 10,000 counts achieves a relative standard deviation of 1.0% and 100,000 counts achieves a relative standard deviation between 0.2% - 0.4% [2].

Fixed Time

The optimum data collection times of 20 seconds for zinc and 30 seconds for iron were determined from the fixed total counts analysis described above. These times ensured satisfactory counting statistics for all samples.

Sample Area and Sample Volume

Sample area and volume during optimum XRF experimental conditions were approximately 1.87 cm² and 3.07E-3 cm³. Sample area was determined using known experimental set-up dimensions and applying them to basic trigonometric and geometric principles. Sample volume was calculated by multiplying sample area by an approximated penetration depth of 16.37 μm. Penetration depth was calculated using an average percent iron of 8.40% in the coating at 95% total fluoresced intensity. The equation used for penetration depth was:

$$G_x = [1 - e^{-mx(1/\sin\gamma + 1/\sin\beta)}]$$

where G_x = fraction of total fluoresced intensity, x = surface layer depth, m = mass absorption coefficient, γ = incident angle, and β = take-off angle [3]. Results show that the variation in penetration depth, as a function of percent iron in the coating (from 0%-14% iron), is minimal.

B. Metallography

1. Sample Handling

Specimens were cut from all the AISI samples (Appendix I) for metallographic evaluation with an abrasive cut-off machine and water. Index cards were used to protect sample surfaces from damage. In order to minimize moisture effects, samples were ultrasonically cleaned with ethyl alcohol after cutting, followed by immediate drying with high pressure air.

2. Polishing Procedures

The AISI samples (Appendix I) were embedded in Struers Epofix Epoxy for cross-sectional microscopic evaluation. The sample mounts were ground and polished using a Struers Rotopol-2 polisher equipped with a Pedemat automatic polishing head. The specific grinding and polishing parameters are described below:

1. *Initial Grinding:*

Abrasive:	SiC
Grit size:	320, 500, 1200
Speed (RPM):	300
Load (N):	25
Lubricant:	Water
Time:	As needed for 320 grit. 1 minute for 500 and 1200 grit.

2. *Coarse Polishing:*

Disc/Cloth:	DP-PAN
Abrasive:	Diamond
Grain size:	6 μ m aerosol spray
Abrasive Dosing:	Manual
Speed (RPM):	150
Load (N):	25
Lubricant:	DP-Green
Time:	3 minutes.

3. *Coarse Polishing:*

Disc/Cloth:	DP-DAC
Abrasive:	Diamond
Grain size:	3 μ m aerosol spray
Abrasive Dosing:	Manual

Speed (RPM):	150
Load (N):	20
Lubricant:	DP-Green
Time:	3 minutes

4. *Coarse Polishing:*

Disc/Cloth:	DP-MOL
Abrasive:	Diamond
Grain size:	1 μm aerosol spray
Abrasive Dosing:	Manual
Speed (RPM):	150
Load (N):	20
Lubricant:	DP-Green
Time:	5 minutes

5. *Final Polishing:*

Disc/Cloth:	OP-CHEM
Abrasive:	OP-S (diluted 1:1 with ethyl alcohol)
Grain size:	0.04 μm colloidal SiO_2
Abrasive Dosing:	Manual
Speed (RPM):	150
Load (N):	15
Lubricant:	Ethyl Alcohol as needed
Time:	1 minute

*Samples were then hand-lapped for about 30 seconds with wheel rotation parallel to the galvanneal coating.

Sample cleaning between successive polishing steps consisted of swabbing with an ethyl alcohol saturated cotton swab, followed by flushing with ethyl alcohol and drying with nitrogen gas or Dust-Off®.

Samples evaluated under scanning electron microscope were repolished using the same procedure above, however, final polishing was stopped at 1 μm diamond in order to eliminate discrepancies caused by OP-S chemical/mechanical polishing compound.

3. Etching Procedures

Upon completion of the sample polishing phase, each sample was stain etched to reveal the various phases in the galvanneal coating. Two etchants were evaluated for this examination. The first etchant, developed by J.R. Kilpatrick at Bethlehem Steel [4], consisted of adding 2 ml of zephryn chloride to a stock solution of 25 ml of 4% picral, 25 ml nitric acid and 150 ml of ethyl alcohol. This etchant was further diluted with ethyl alcohol at a ratio of 5:1. The samples were immersed in this etchant for 5 seconds, rinsed with ethyl alcohol and dried with nitrogen gas or Dust-Off®.

The second etching technique, developed by C.E. Jordan at Lehigh University [5], consisted of immersing the samples in a stock solution of 1% picric acid + 1% nitric acid + amyl alcohol for 20 seconds followed by immersion in ethyl alcohol and flushing with ethyl alcohol. Immediately after flushing, the samples were immersed for 10 seconds in the stock solution with 4 drops HF added, flushed with ethyl alcohol, and blown dry.

4. Microscopy

All sample cross-sections were examined optically at 1000x magnification using a Zeiss Axiovert-450M metallograph, and photographed with Polaroid type 59 color film. Representative samples, which had been flash-coated with gold, were examined at 1000x and 6000x magnification with a Cambridge Stereoscan 360 scanning electron microscope in order to validate optical photomicrographs of etched sample cross-sections.

C. X-ray Diffraction Analysis

1. Experimental Set-up of Preliminary Analysis

Zeta and Delta Phase Analysis

Rectangular pieces were cut from the original samples, using tin snips, for zeta and delta phase XRD analysis. The diffraction from these samples was measured by a silicon-lithium detector and recorded on a multi-channel analyzer. The x-ray beam was generated using a copper target at a filament current of 20 mA and tube voltage of 40 kV. An incident beam collimator was used and the sample was placed on a rotating stage. Data was taken for the 2-theta range of 73.5° to 76° from AISI samples (Appendix I) having lab coating weights between 34-77 gsm. Samples were chosen from all three substrate types.

Gamma Phase Analysis

Peeled galvaneal coatings from selected AISI samples were used for gamma phase XRD analysis. Long, thin pieces were cut, using an abrasive cut-off machine (Please refer to Section II.B.1.), from the original samples. The sample surfaces were cleaned with ethyl alcohol and coated with Epoxi-patch epoxy. After curing at 60°C for 2 hours, samples were bent ~90° to peel-off the coating from the steel substrate. XRD data was taken from the coating adhering to the epoxy, which revealed the coating/substrate interface.

The same XRD experimental set-up mentioned in the previous section was used, however, data was taken for the 2-theta range of 70° to 79°. The epoxy was also scanned in this range to ensure the integrity of the reflections from the coating.

2. Experimental Set-up of Primary Analysis

An attempt was made to remove the coatings from all the AISI samples (Appendix I) using the same peeling procedure as described above in Section II.C.1.. Peeling the coatings from the unalloyed samples and samples annealed at relatively low galvanneal temperatures was unsuccessful. The optical photomicrographs taken of these samples showed them to have minimal interfacial gamma phase.

A grazing angle x-ray diffractometer with an Inel position-sensitive detector was used to obtain the diffraction spectra of the peeled and unpeeled samples. The x-ray beam was generated using a cobalt target at a filament current of 26 mA and tube voltage of 40 kV. Scans were taken from a 2-theta range of 20°-120° with relatively constant counting statistics. This experimental set-up was different from the one used for the preliminary XRD analysis because, by using the Inel position-sensitive detector, data collection time was shorter and angular scan range was larger.

D. Transmission Electron Microscopy

Specimens were cut with tin snips from AISI samples, 2-15-d and 3-5-b, and prepared for TEM using conventional cross-sectional methods (e.g. thinning, polishing, dimpling, and ion-milling). Table 1 shows the average phase thicknesses determined from metallography, substrate type, coating weight and iron content for these two samples.

TEM micrographs and selected area electron diffraction (SAD) patterns were taken at several magnifications from various areas within the coating. A camera length of 1485 mm and beam wavelength of 0.00197 nm for 300 keV were used.

Table 1: Samples Used for TEM Analysis

Sample ID #	Substrate Type	Average Thickness [μm]				Lab CW [gsm]	Lab Fe [%]
		Zeta	Delta	Gamma	Total		
2-15-D	IF	2.5	4	0.5	7	57	8.7
3-5-B	Rephos	0.5	6	0.5	7	55	11.2

III. RESULTS AND DISCUSSION

A. X-ray Fluorescence

1. JPL XRF Experimental Data Analysis

Figure 3 shows JPL's experimental zinc and iron fluorescence response data versus iron content in the coating for the AISI samples (Appendix I). The error bars were determined from the inter-sample variation analysis described below in Section III.A.3.. The data plotted in Figure 3 generally showed good linear correlation. Table 2 gives the linear regression equations for each coating weight set of each substrate type for the separate iron and zinc responses. **Evaluation of these equations show the slopes to have substrate dependence and the y-intercept values to have coating weight dependence.** Figure 4 shows a representation of XRF response dependence on substrate type and coating weight for the AISI samples (Appendix I). Lighter coating weights resulted in greater penetration of the x-ray beam into the substrate. Consequently, the iron response was enhanced. Ideally, the experimental set-up would have the x-ray beam penetration limit at the coating/substrate interface. Based on our experimental results, the iron response enhancement is reproducible for a given coating weight.

Note: The AISI samples were received for evaluation in two batches. Batch one corresponds to sample IDs beginning with 1, 2 and 3. Batch two corresponds to sample IDs beginning with 4, 5 and 6.

(3a) ELC : Iron Response

(3b) ELC : Zinc Response

(3c) IF : Iron Response

(3d) IF : Zinc Response

(3e) Rephos : Iron Response

(3f) Rephos : Zinc Response

Figure 3: JPL Iron and Zinc XRF Responses versus Iron Content

Table 2: JPL XRF Iron and Zinc Response Linear Regression Data

Fe Response				
Substrate Type	Batch	Ave. CW [gsm]	F(x)	R ²
ELC	1	59-73	16724+1676.8x	0.997
ELC	1	88-101	6583.7+1627.4x	0.802
IF	1	69-74	8110.1+2358.7x	0.991
IF	1	93-102	1129.6+2420.6x	0.975
IF	1	52-59	34150+618.24x	0.425
Rephos	1	48-56	32555+1180.3x	0.977
Rephos	1	34-39	52931+1028.4x	0.903
Rephos	1	69-77	17099+1364x	0.886
Rephos	1	81-94	15581+858.26x	0.775
ELC	2	66-73	17525+1632.5x	0.945
ELC	2	90-96	4963.3+1929x	0.883
IF	2	86-92	3928.5+2676.3x	0.943
IF	2	116-120	1017.5+1957.8x	0.801
IF	2	47-58	31816+1075.8x	0.863
IF	2	40-52	44482+721.67x	0.862
Rephos	2	36-40	51677+1064.6x	0.825
Rephos	2	61-72	30217+397.22x	0.324
Zn Response				
Substrate Type	Batch	Ave. CW [gsm]	F(x)	R ²
ELC	1	59-73	249300-3977.3x	0.99
ELC	1	88-101	256780-2617.7x	0.673
IF	1	69-74	269360-5496.9x	0.878
IF	1	93-102	285700-6386.7x	0.948
IF	1	52-59	222080-2246.2x	0.618
Rephos	1	48-56	196290-1431x	0.75
Rephos	1	34-39	173130-1472.9x	0.888
Rephos	1	69-77	222440-1421.8x	0.483
Rephos	1	81-94	239010-2540.5x	0.85
ELC	2	66-73	257980-4974.2x	0.95
ELC	2	90-96	282340-5612.5x	0.951
IF	2	86-92	276440-5937x	0.964
IF	2	116-120	296710-6067.9x	0.861
IF	2	47-58	222790-2479.4x	0.87
IF	2	40-52	202040-1812.4x	0.863
Rephos	2	36-40	180890-1802.2x	0.789
Rephos	2	61-72	211010-442.4x	0.482

Figure 4: XRF Dependence on Coating Weight and Substrate type

2. Comparison of JPL and DMC's Experimental Data

DMC also performed XRF on the AISI samples (Appendix I). Details on the DMC zinc/iron gauge set-up can be found in Appendix II. Figure 5 shows DMC's experimental normalized zinc and iron XRF response data versus iron content in the coating for the AISI samples. Table 3 gives the linear regression equations for each coating weight set of each substrate type (Please see "Note" in section III.A.1.). In general, excellent correlation was seen between the DMC data and the JPL data. Several exceptions were seen in the low coating weight samples (34-39 gsm) and in samples with very low iron coating content(<1%). An examination of the data suggested that the DMC gauge retained linearity in response at very low iron contents and was more sensitive than the JPL detector to small variations in iron content. In summary, the analysis of both the JPL and DMC XRF data indicated that the DMC gauge could achieve an accuracy of 0.5% for iron detection under DMC laboratory conditions.

(5a) ELC : Iron Response

(5b) ELC : Zinc Response

(5c) IF : Iron Response

(5d) IF : Zinc Response

(5e) Rephos : Iron Response

(5f) Rephos : Zinc Response

Figure 5: DMC Normalized Iron and Zinc XRF Responses versus Iron Content

Table 3: DMC XRF Iron and Zinc Response Linear Regression Data

Fe Response				
Substrate Type	Batch	Ave. CW [gsm]	F(x)	R ²
ELC	1	59-73	0.091353+0.014398x	0.995
ELC	1	88-101	0.031369+0.016409x	0.773
IF	1	69-74	0.024300+0.020163x	0.994
IF	1	93-102	(-0.003713)+0.021070x	0.99
IF	1	52-59	0.115202+0.014212x	0.8
Rephos	1	48-56	0.18591+0.010176x	0.986
Rephos	1	34-39	0.296779+0.00656x	0.99
Rephos	1	69-77	0.102435+0.011637x	0.987
Rephos	1	81-94	0.077006+0.011697x	0.953
ELC	2	66-73	0.076279+0.015594x	0.995
ELC	2	90-96	0.005885+0.018371x	0.928
IF	2	86-92	0.002339+0.020481x	0.979
IF	2	116-120	(-0.02577)+0.018448x	0.774
IF	2	47-58	0.157877+0.010221x	0.946
IF	2	40-52	0.226381+0.007713x	0.97
Rephos	2	36-40	0.271882+0.007839x	0.977
Rephos	2	61-72	0.139778+0.008271x	0.639
Zn Response				
Substrate Type	Batch	Ave. CW [gsm]	F(x)	R ²
ELC	1	59-73	0.758743-0.007793x	0.961
ELC	1	88-101	0.853105-0.009667x	0.752
IF	1	69-74	0.813710-0.011883x	0.985
IF	1	93-102	0.882852-0.013300x	0.979
IF	1	52-59	0.695851-0.00599x	0.468
Rephos	1	48-56	0.656743-0.00557x	0.922
Rephos	1	34-39	0.530701-0.0034x	0.775
Rephos	1	69-77	0.773525-0.00745x	0.919
Rephos	1	81-94	0.81613-0.00696x	0.897
ELC	2	66-73	0.767457-0.00839x	0.927
ELC	2	90-96	0.877391-0.01184x	0.906
IF	2	86-92	0.872047-0.0145x	0.925
IF	2	116-120	0.925539-0.01276x	0.709
IF	2	47-58	0.669435-0.00502x	0.846
IF	2	40-52	0.594246-0.00264x	0.744
Rephos	2	36-40	0.553128-0.0047x	0.864
Rephos	2	61-72	0.710001-0.00354x	0.22

3. JPL XRF Response Variation

Reproducibility

Two XRF zinc and iron response measurements were taken for approximately the same sample area from each of thirty-one samples chosen from Appendix I. The thirty-one samples consisted of unalloyed and alloyed samples from each of the three substrate types. Percent variation between the two measurements was calculated for each sample. Table 4 shows the percent variation values. The following equation was used to calculate percent variation:

$$\% \text{ variation} = \frac{\text{ABS}(\text{first} - \text{second})}{(\text{first} + \text{second})} * 100$$

where first = first XRF response, second = second XRF response, and ABS = absolute value. (Note: The XRF data for this analysis was taken prior to determining the optimum incident and take-off angles. Consequently, the incident and take-off angles used were each 30° as opposed to the optimum angles of 25° and 25°.)

Sample Inhomogeneity

In order to evaluate XRF response variation, as a function of measurement location, XRF zinc and iron response data was taken at five different locations from each of the thirty-one samples described in the previous section. The five measured areas may have had some overlap, however all stayed within the boundaries of the sample edges. Percent variation between the highest and lowest counts per second of the five XRF responses was calculated for each sample. Table 4 shows the percent variation values. The following equation was used to calculate percent variation:

$$\% \text{ variation} = \frac{\text{ABS}(\text{high} + \text{low})}{(\text{high} + \text{low})} * 100$$

where high = highest XRF response, low = lowest XRF response and ABS = absolute value. (Note: These measurements were taken at incident and take-off angles of 30°).

Table 4: JPL XRF Response Percent Variation

Substrate Type	Sample ID#	% Variation of Response from Same Sample Area		% Variation between Highest and Lowest XRF Response	
		Fe	Zn	Fe	Zn
ELC	1-1d	0.88	0.28	8.89	1.66
	1-3-d	0.30	0.13	3.76	2.49
	1-6-c	0.52	0.05	10.26	1.67
	1-7-c	1.20	0.66	8.92	4.08
	4-1-a	0.59	0.06	4.21	2.80
	4-4-a	0.63	0.01	2.55	2.70
	4-8-d	1.22	0.15	6.80	1.14
	IF	2-1-b	1.24	0.01	2.71
2-3-a		0.10	0.04	2.72	3.67
2-7-b		1.94	0.15	5.04	4.33
2-11-c		0.22	0.16	4.73	5.16
2-14-b		1.08	0.21	2.60	3.09
5-1-d		2.38	0.01	31.40	9.19
5-4-c		0.76	0.63	5.83	4.94
5-6-a		0.89	0.02	35.68	3.88
	5-7-b	1.52	0.64	6.80	4.81

	6-1-c	1.12	0.18	3.90	3.19
	6-4-a	0.25	0.07	1.87	3.25
	6-10-a	0.48	0.49	1.29	3.67
	6-11-a	0.11	0.19	1.98	2.40
Rephos	3-1-x	0.80	0.18	7.32	5.26
	3-3-a	0.43	0.29	4.44	1.97
	3-10-a	0.36	0.31	4.55	4.81
	3-13-b	0.64	0.57	1.84	1.77
	3-22-d	0.42	0.12	3.45	2.29
	3-28-d	2.37	0.06	10.77	10.78
	3-32-b	0.31	0.13	4.01	2.37
	3-36-b	1.26	0.14	18.82	5.18
	6-17-b	0.04	0.40	3.36	3.68
	6-24-c	0.83	0.41	9.99	7.07
	6-26-a	1.02	0.27	8.38	4.44

Dust/Oil Experiment

An experiment was conducted to test the effects of dust and oil on the zinc and iron XRF responses. XRF measurements of zinc and iron were taken under three different conditions from approximately the sample location of a galvanneal steel sample. First, the sample was measured as received from Inland Steel. Second, the sample was measured after being blown with high pressure air. Lastly, the sample was measured after a thin layer of Vaseline and coarse air cleaner test dust was smeared on its surface. The results showed virtually no difference in XRF response between the three cases.

4. DMC XRF Response Variation

In order to evaluate their XRF response variation, as a function of measurement location, DMC generated XRF data from two sets of AISI samples. The samples from each set were processed under the same conditions, however taken from different areas of the steel coil. Table 5 shows the percent variation between the normalized iron/zinc ratios for the two sample sets. Samples having percent variations >20% were re-measured by DMC. The results of these re-evaluations have not been received by JPL. The following equation was used to calculate the percent variation:

$$\% \text{ variation} = \frac{\text{ABS}(\text{first} - \text{second})}{(\text{first} + \text{second})} * 100$$

where first = first set Fe/Zn XRF ratio, second = second set Fe/Zn XRF ratio and ABS = absolute value.

Table 5: DMC XRF Percent Variation

Sample ID	% Variation	Sample ID	% Variation
1-1-d,b	7.1	3-32-b,c	0.1
1-2-d,a	1.1	3-33-c,x	4.8
1-3-d,a	0.6	3-34-c,b	3.5
1-4-a,d	0.1	3-35-c,x	3.0
1-5-d,a	47.4	3-36-b,x	1.6
1-6-c,a	0.8	4-1-a,c	1.7
1-7-c,a	0.3	4-2-c,b	0.9
1-8-b,c	6.7	4-3-d,b	1.5
1-9-b,c	4.1	4-4-a,c	0.3
2-1-b,a	3.2	4-5-b,a	0.9
2-2-c,b	0.3	4-6-a,b	1.1
2-3-a,d	0.1	4-7-d,a	53.1
2-4-b,c	0.9	4-8-d,b	1.6
2-5-a,c	0.3	4-9-b,a	3.6
2-6-a,b	1.8	4-10-c,a	1.7
2-7-b,c	58.1	4-11-d,c	36.8
2-9-c,b	0.9	5-1-d,b	1.0
2-10-b,c	1.9	5-2-a,b	5.8
2-11-c,d	4.8	5-3-a,c	3.5
2-12-a,c	3.6	5-4-c,b	1.1
2-13-a,c	0.9	5-5-a,d	83.7
2-14-b,d	0.8	5-6-a,c	15.4
2-15-d,c	1.1	5-7-b,a	42.6
2-16-c,b	1.3	5-8-c,a	5.5
2-17-c,d	0.6	5-9-c,a	63.8
2-18-b,c	0.6	6-1-c,d	0.3
2-19-d,b	2.2	6-2-b,c	0.4
2-20-c,a	0.4	6-3-b,d	1.1
3-1-x,a	1.3	6-4-a,b	0.1
3-2-a,b	1.9	6-5-d,c	0.4
3-3-a,c	0.8	6-6-b,a	1.2
3-4-b,a	1.3	6-7-c,b	0.5
3-5-b,d	2.8	6-8-b,d	0.5
3-6-x,x	2.7	6-9-b,a	2.1
3-8-d,c	2.1	6-10-a,b	0.1
3-10-a,c	1.2	6-11-a,c	0.5
3-11-c,a	0.5	6-12-c,b	0.7
3-12-b,x	1.6	6-13-b,c	2.0
3-13-a,d	0.3	6-14-b,d	0.5
3-14-c,b	0.5	6-15-d,a	2.2
3-15-b,c	0.6	6-16-c,b	1.2
3-16-c,b	0.8	6-17-b,a	1.4
3-17-a,c	1.4	6-18-b,d	3.0
3-20-c,a	5.8	6-19-a,c	0.1
3-22-d,c	3.0	6-20-d,a	0.2
3-23-b,c	3.2	6-21-c,a	0.8
3-24-d,c	1.6	6-22-b,a	0.3
3-25-c,a	5.0	6-23-c,d	1.8
3-26-d,c	3.2	6-24-c,b	1.0
3-27-b,d	0.7	6-25-d,b	8.8

3-28-d,a	1.9	6-26-a,b	5.4
3-30-b,c	7.4	6-27-c,d	0.3
3-31-c,x	0.9	6-28-c,a	20.8

B. Galvanneal Morphology

1. Metallography

- Average Phase Thickness Measurements

The appearance of eta, zeta, delta and gamma phases were identified from the optical photomicrographs using a technique developed by Kilpatrick at Bethlehem Steel [6]. Table 6 gives the average phase thicknesses measured, with a metric ruler, directly from optical photomicrographs of etched sample cross-sections taken at 1000x magnification. The volume percents of eta, zeta, delta and gamma phases were calculated by dividing the measured phase thickness values by their total measured coating thicknesses. **Figure 6 shows how volume percent of iron-zinc phases determined by metallography relates to iron content in the coating (Appendix I).** Phase determination based on metallographic procedures will be discussed further in Section V.

Table 6: Measured Average Phase Thicknesses and Volume Percents

Sample ID #	eta [μm]	zeta [μm]	delta [μm]	gamma [μm]	Total Thickness	%eta	%zeta	%delta	%gamma
1-1-d	5	5	0	0	10	50	50	0	0
1-2-d	0	3	6	1	10	0	30	60	10
1-3-d	0	0	9	1	10	0	0	90	10
1-4-a	0	0	9	1	10	0	0	90	10
1-5-d	0	4	4.25	0.75	9	0	44	47	8
1-6-c	9	3	3.75	0.25	16	56	19	23	2
1-7-c	0	3	11.5	0.5	15	0	20	77	3
1-8-b	-	-	-	-	-	-	-	-	-
1-9-b	0	1	11	1	13	0	8	85	8
2-1-b	4	3	3.5	0.5	11	36	27	32	5
2-2-c	0	5	4.5	0.5	10	0	50	45	5
2-3-a	0	0.5	8.5	1	10	0	5	85	10
2-4-b	0	0.5	8.5	1	10	0	5	85	10
2-5-a	0	3	6.5	0.5	10	0	30	65	5
2-6-a	0	4	5.5	0.5	10	0	40	55	5
2-7-b	5	3	3.5	0.5	12	42	25	29	4
2-9-c	0	5	9.5	0.5	15	0	33	63	3
2-10-b	0	0	11.5	1.5	13	0	0	88	12
2-11-c	0	2	10	1	13	0	15	77	8
2-12-a	0	6	6.5	0.5	13	0	46	50	4
2-13-a	0	3	9.5	0.5	13	0	23	73	4
2-14-b	1	2.5	3	0.5	7	14	36	43	7
2-15-d	0	2.5	4	0.5	7	0	36	57	7
2-16-c	0	1	6	1	8	0	13	75	13
2-17-c	0	2	5	1	8	0	25	63	13

2-18-b	0	2	5	1	8	0	25	63	13
2-19-d	0	2	5	1	8	0	25	63	13
2-20-c	0	1	6	1	8	0	13	75	13
3-1-x	6	2	0	0	8	75	25	0	0
3-2-a	0	3	4.5	0.5	8	0	38	56	6
3-3-a	0	0.5	5.5	1	7	0	7	79	14
3-4-b	0	0.5	5.5	1	7	0	7	79	14
3-5-b	0	0.5	6	0.5	7	0	7	86	7
3-6-x	0	2	5.5	0.5	8	0	25	69	6
3-7-b	-	-	-	-	-	-	-	-	-
3-8-d	0	6	0	0	6	0	100	0	0
3-10-a	6	3	0	0	9	67	33	0	0
3-11-c	0	4	2	0	6	0	67	33	0
3-12-b	0	0.5	3.5	1	5	0	10	70	20
3-13-a	0	0.5	4	0.5	5	0	10	80	10
3-14-c	0	1	4.5	0.5	6	0	17	75	8
3-15-b	0	0.5	4	0.5	5	0	10	80	10
3-16-c	0	2	3.5	0.5	6	0	33	58	8
3-17-a	0	6	0	0	6	0	100	0	0
3-20-c	0	5	5.5	0.5	11	0	45	50	5
3-22-d	0	3	8.5	0.5	12	0	25	71	4
3-23-b	0	3	8.5	0.5	12	0	25	71	4
3-24-d	0	7	5.5	0.5	13	0	54	42	4
3-25-c	0	7	4.5	0.5	12	0	58	38	4
3-26-d	5	5	0	0	10	50	50	0	0
3-27-b	0	2	8.5	0.5	11	0	18	77	5
3-28-d	8	3	0	0	11	73	27	0	0
3-30-b	0	5	7.5	0.5	13	0	38	58	4
3-31-c	0	5	8.5	0.5	14	0	36	61	4
3-32-b	0	6	6.5	0.5	13	0	46	50	4
3-33-c	0	5	7.5	0.5	13	0	38	58	4
3-34-c	0	5	7.5	0.5	13	0	38	58	4
3-35-c	0	5	7.5	0.5	13	0	38	58	4
3-36-b	9	2	0	0	11	82	18	0	0
4-1-a	4	3	2.5	0.5	10	40	30	25	5
4-2-c	0	3	6	1	10	0	30	60	10
4-3-d	0	0.5	8.5	1	10	0	5	85	10
4-4-a	0	0.5	8.5	1	10	0	5	85	10
4-5-b	0	0.5	8.5	1	10	0	5	85	10
4-6-a	0	1	9	1	11	0	9	82	9
4-7-d	2	3.5	5	0.5	11	18	32	45	5
4-8-d	9	3	1.5	0.5	14	64	21	11	4
4-9-b	2	4	6	1	13	15	31	46	8
4-10-c	0	3	9	1	13	0	23	69	8
4-11-d	0	3	10	1	14	0	21	71	7
5-1-d	7	3.5	3	0.5	14	50	25	21	4
5-2-a	0	5	7.5	0.5	13	0	38	58	4
5-3-a	0	2	9.5	0.5	12	0	17	79	4
5-4-c	0	1	10	1	12	0	8	83	8
5-5-a	0	0.5	10.5	1	12	0	4	88	8
5-6-a	14	3	1.5	0.5	19	74	16	8	3
5-7-b	0	1	16	1	18	0	6	89	6
5-8-c	0	5	11.5	0.5	17	0	29	68	3

5-9-c	6	2	11	1	20	30	10	55	5
6-1-c	2	6	0	0	8	25	75	0	0
6-2-b	1	4.5	3	0.5	9	11	50	33	6
6-3-b	0	1	6.5	0.5	8	0	13	81	6
6-4-a	0	0.5	6.5	1	8	0	6	81	13
6-5-d	0	0.5	5	1.5	7	0	7	71	21
6-6-b	0	0	6.5	1.5	8	0	0	81	19
6-7-c	0	1	6	1	8	0	13	75	13
6-8-b	0	2	6	1	9	0	22	67	11
6-9-b	1.5	4	2	0.5	8	19	50	25	6
6-10-a	3	4	0	0	7	43	57	0	0
6-11-a	1	5	2	0	8	13	63	25	0
6-12-c	0	8	0	0	8	0	100	0	0
6-13-b	0	0	5	1	6	0	0	83	17
6-14-b	0	0	5.5	1.5	7	0	0	79	21
6-15-d	0	0	5.5	1.5	7	0	0	79	21
6-16-c	0	0	6	1	7	0	0	86	14
6-17-b	2.5	2.5	0	0	5	50	50	0	0
6-18-b	0	5	0	0	5	0	100	0	0
6-19-a	0	1	3.5	0.5	5	0	20	70	10
6-20-d	0	1	3.5	0.5	5	0	20	70	10
6-21-c	0	0.5	4	0.5	5	0	10	80	10
6-22-b	0	5	0	0	5	0	100	0	0
6-23-c	0	5	0	0	5	0	100	0	0
6-24-c	7	3	0	0	10	70	30	0	0
6-25-d	0	4	7.5	0.5	12	0	33	63	4
6-26-a	0	3	8.5	0.5	12	0	25	71	4
6-27-c	0	3	7	0	10	0	30	70	0
6-28-c	7	5	0	0	12	58	42	0	0

(6a) ELC/IF

(6b) Rephosphorized

Figure 6: Iron-Zinc Intermetallic Compounds versus Iron Content

Experimental Error

Causes of experimental error in determining the average phase thicknesses included ruler measurement inaccuracy, sample preparation, etching techniques and scattered distribution of phases (non-distinct phase layers).

- **Microscopy**

Etchant and Film Selection

The etchant prescribed by Kilpatrick at Bethlehem Steel [7] was used first to highlight the different phases in the galvaneal coatings. It was anticipated that the gamma phase would appear dark brown, the delta as light blue/brown, the zeta as blue/bronze, and the zinc as white. However, the prepared samples did not show these phase distinctions very clearly, therefore the formulation of the stain etch was varied. An etchant formulated by Jordan at Lehigh University [8] was evaluated. It was determined that this etchant revealed the interfacial layer and made the various phases more distinct. Therefore, all AISI samples (Appendix I) were etched with this solution. Additionally, it was found that the lighting was critical for optical examination. The Zeiss Axiovert metallograph uses a tungsten light source which can result in a red tinting of the micrographs. In order to improve the blue compensation, several types of Polaroid film were tested. Polacolor ER 4x5 instant sheet film (Polaroid 59) gave the best results.

Interfacial Etching

Scanning electron microscopy (SEM) examination of several AISI samples (Appendix I) revealed discontinuities at the substrate/coating interface. After examining samples with various anneal temperatures in both the polished and unpolished conditions, it was determined that the interfacial region was being preferentially attacked by the OP-S final polishing compound. This compound was designed to act as a chemical/mechanical polish and, although the compound was diluted with 50% ethyl alcohol, the pH(7) was caustic enough to preferentially etch the interface. The interfacial etching was only predominant when the gamma phase was present in the sample.

Surface Irregularities

Reddish areas were observed on both fronts and backs of sample surfaces after samples were cut for metallographic evaluation. SEM examination was used to determine the elemental composition of these areas. Results showed them to consist primarily of phosphorus, oxygen and iron. Cause of surface irregularities is still unknown. Possible sources are cleaning agents and handling procedures. SEM examination also revealed uncoated microscopic areas on galvanealed surfaces.

2. X-ray Diffraction Analysis

- Preliminary Analysis

Due to the difficulty of phase identification using Inland Steel's XRD data, JPL conducted a preliminary XRD analysis, covering a wider angular scan range than Inland Steel, on selected unalloyed and alloyed samples in the 34-77 gsm coating weight range. Samples were chosen from all three substrate types. The success of JPL's preliminary analysis led to the primary XRD evaluation.

Inland Steel XRD Data

Inland Steel XRD data was taken in the 2-theta scan range of 30°-60°. JCPDS file data (Appendix III) was used to identify the presence of eta, zeta, delta, and gamma phases. Overlapping of the reflections from the different phases made this analysis difficult. Delta and gamma phase reflections were the most difficult to evaluate from Inland Steel's data. Consequently, JPL XRD data was used in conjunction with Inland Steel's XRD data for percent phase evaluation.

JPL XRD Data

An XRD analysis method developed by Dofasco Inc. [9] was used to analyze the galvanneal phase compositions of peeled and unpeeled samples. Unalloyed samples exhibited better adhesion than alloyed samples. Consequently, obtaining an unalloyed peeled sample was not feasible. Zeta, delta and gamma phase compositions determined by XRD assumed that the intensity of the XRD response was proportional to the volume fraction of the phase present in the sample. These results were compared with the optical photomicrographs. Changes in the diffraction intensity correlated with changes in the observed phase thicknesses, however, the presence of preferred crystallographic orientation could present serious difficulties in interpreting the XRD data.

- Primary Analysis

Objective

The objective of the XRD analysis was to use an alternative method of percent phase determination to validate the measured metallographic percent phases and to further investigate the gamma phase and other possible interfacial phases.

Percent Phase Analysis

Both JPL and Inland Steel's XRD data sets were used to calculate the percent phases of zeta, delta and gamma assuming that the intensity of the XRD response was proportional to the volume fraction of the phase present in the sample. Unfortunately, phase analysis was extremely difficult due to overlapping of diffraction reflections. Table 7 shows the calculated percent

phase values. Percent eta phase was not determined because preferred orientation was observed. Also, the percent phases for samples containing a significant amount of eta phase (i.e. unalloyed samples and samples annealed at relatively low alloying temperatures) were not determined because their diffraction patterns showed mainly eta reflections. Lastly, sample set six was not evaluated because Inland Steel's XRD data was unavailable for comparison. The following equation was used to calculate the percent phases:

$$\begin{aligned}\% \zeta + \% \delta + \% \Gamma &= 100\% \\ \% \zeta &= (\% \Gamma) * (\zeta / \Gamma) \\ \% \Gamma &= \frac{1}{(\zeta / \Gamma)(1/100) + (\delta / \Gamma)(1/60) + (1/80)}\end{aligned}$$

where ζ/Γ = measured zeta/gamma ratio, δ/Γ = measured delta/gamma ratio, and Γ is used as the internal standard.

The d-spacing values of the reflections used to determine the percent phases of zeta, delta and gamma were 2.174Å, 2.366Å and 2.592Å, respectively. The zeta reflection chosen for phase analysis was the [131] reflection reported in the JCPDS files (Appendix III). No unique delta reflections were found within Inland Steel's 2-theta scan range of 30°-60°. Therefore, in order to use Inland's XRD data, a delta reflection was chosen by comparing trends of unknown reflections in the 30°-60° scan range with trends of the [210] and [004] reflections reported in the JCPDS files. Also, XRD data from samples of primarily zeta and primarily delta were used to verify the chosen zeta and delta reflections. Lastly, the gamma reflection chosen for phase analysis was the [222] reflection reported in the JCPDS files. Trends of the [444] and [750] reflections were used to validate the chosen gamma reflection.

Experimental Error

Cause of experimental error in determining the percent phases from the XRD data included counting statistics, background estimation, use of peak heights to determine percent phase ratios, preferred orientation, and approximations used for determining the delta reflection.

Comparison of XRD and Metallographic Phase Data

Comparison of the XRD phase analysis and the metallographic phase analysis showed decent correlation when the average zeta phase was less than 30%. For both XRD and metallography, the gamma phase varied between approximately 5-15%.

Table 7: XRD Percent Phase Analysis

Sample				Sample			
ID#	%zeta	%delta	%gamma	ID#	%zeta	%delta	%gamma
1-1-d	-	-	-	3-14-c	10	81	8
1-2-d	54	42	4	3-15-b	0	88	12
1-3-d	16	76	8	3-16-c	14	72	13
1-4-a	15	77	8	3-17-a	-	-	-
1-5-d	84	15	2	3-20-c	21	68	11
1-6-c	-	-	-	3-22-d	21	73	6
1-7-c	13	77	10	3-23-b	23	67	9
1-8-b	0	89	11	3-24-d	21	72	7
1-9-b	19	74	7	3-25-c	22	69	9
2-1-b	-	-	-	3-26-d	84	11	5
2-2-c	21	71	8	3-27-b	0	85	15
2-3-a	16	75	9	3-28-d	-	-	-
2-4-b	14	79	7	3-30-b	22	65	12
2-5-a	74	24	1	3-31-c	18	73	9
2-6-a	71	23	6	3-32-b	23	69	8
2-7-b	-	-	-	3-33-c	25	68	8
2-9-c	21	72	7	3-34-c	21	69	10
2-10-b	0	85	15	3-35-c	20	70	10
2-11-c	24	68	8	3-36-b	-	-	-
2-12-a	18	74	8	4-1-d	-	-	-
2-13-a	22	72	6	4-2-c	73	24	2
2-14-b	-	-	-	4-3-d	13	78	9
2-15-d	65	29	5	4-4-a	17	75	8
2-16-c	16	75	9	4-5-b	13	79	8
2-17-c	32	60	8	4-6-a	19	73	7
2-18-b	62	34	4	4-7-d	-	-	-
2-19-d	73	24	4	4-8-d	-	-	-
2-20-c	17	76	7	4-9-b	69	27	3
3-1-x	-	-	-	4-10-c	21	70	9
3-2-a	24	67	9	4-11-d	20	72	8
3-3-a	12	79	9	5-1-d	-	-	-
3-4-b	16	76	8	5-2-a	21	71	8
3-5-b	15	74	11	5-3-a	21	73	6
3-6-x	12	80	8	5-4-c	13	76	11
3-7-b	14	77	9	5-5-a	15	78	6
3-8-d	82	13	5	5-6-a	-	-	-
3-10-a	-	-	-	5-7-b	0	85	15
3-11-c	66	31	4	5-8-c	0	84	16
3-12-b	5	84	11	5-9-c	21	72	7
3-13-a	11	81	9				

- Zeta Phase XRD Re-evaluation

Objective

AISI samples (Appendix I), having an average coating percent iron $\geq 8\%$ and an average lab coating weight between 30-70 gsm, and Stelco round-robin samples, 21T1-15D and 26H1-27FF, were chosen for re-evaluation by top-down XRD in order to verify the presence of the zeta phase, as seen in metallography. The $d \approx 2.174 \text{ \AA}$ reflection was used to identify zeta from the diffraction patterns. Inland Steel's XRD data was used to evaluate the AISI samples, and XRD data obtained using the technique described in Section II.C.2 was used to evaluate the Stelco samples. Evaluating the $d \approx 2.174 \text{ \AA}$ zeta reflection from the bottom-up (peeled samples) XRD patterns was not helpful in verifying the presence of zeta phase. Therefore, set six samples were not re-evaluated because only bottom-up data was available.

Analysis

Table 8 shows the results of this analysis. Disagreement was found between the x-ray diffraction and JPL metallographic results in the following cases:

- Diffraction patterns from samples 3-6-x, 3-15-b and 3-27-b (all rephosphorized samples) did not show the zeta reflection, even though JPL metallography indicated an average zeta phase thickness for these samples.
- Sample 1-4-a did show a zeta reflection, even though JPL metallography indicated an average zeta phase thickness of zero for this sample.

The x-ray diffraction patterns of the samples containing $>11\%$ average coating iron content, with the exception of sample 3-27-b, showed the presence of zeta reflections. This disagreed with Stelco's observation that zeta phase should not exist above 11% average coating iron content. Consequently, the JPL cross-sectional photomicrographs taken at $1000\times$ were re-examined. Table 8 indicates samples having a less distinct zeta phase (column I). All these samples, with the exception of sample 3-6-x, contain $>11\%$ average coating iron content. Additionally, Table 8 shows the relative intensities of the $d \approx 2.174 \text{ \AA}$ zeta reflection, measured using a millimeter ruler. Samples with $>11\%$ average coating iron content had relative zeta intensities $\leq 21\%$. LTV Steel also performed this analysis reporting the presence/no presence of the $d \approx 2.174 \text{ \AA}$ zeta reflection. Their results were essentially the same as JPL's results.

Table 8: Zeta Phase XRD Re-evaluation Results

A	B	C	D	E	F	G	H	I
Sample ID	Producer	Substrate Type	JPL Zeta [μm]	Inland Ave. Lab CW [gsm]	Inland Ave. Lab %Fe	Top Down Zeta Peak	%Rel. Intensity of Zeta	Less Distinct Zeta at 1000x
1-2-d	Inland	ELC	3	67	9.55	Y	81	
1-4-a	Inland	ELC	0	65	11.55	Y	15	Y
4-2-c	Inland	ELC	3	65	8.5	Y	100	
2-5-a	Inland	IF	3	70	8.35	Y	83	
2-15-d	Inland	IF	2.5	57	8.65	Y	50	
2-16-c	Inland	IF	1	56	11.75	Y	16	Y
2-17-c	Inland	IF	2	56	10	Y	41	
2-18-b	Inland	IF	2	55	9.3	Y	68	
2-19-d	Inland	IF	2	54	9.15	Y	60	
2-20-c	Inland	IF	1	59	11.65	Y	21	Y
3-2-a	Inland	Rephos	3	51	8.1	Y	23	
3-3-a	Inland	Rephos	0.5	54	12.15	Y	12	Y
3-4-b	Inland	Rephos	0.5	56	13.3	Y	19	Y
3-5-b	Inland	Rephos	0.5	55	11.15	Y	15	Y
3-6-x	Inland	Rephos	2	55	10.45	N	0	Y
3-7-b	Inland	Rephos	-	53	9.85	Y	13	
3-12-b	Inland	Rephos	0.5	38	14.15	Y	5	Y
3-13-a	Inland	Rephos	0.5	38	12.25	Y	10	Y
3-14-c	Inland	Rephos	1	39	11.55	Y	10	Y
3-15-b	Inland	Rephos	0.5	38	11	N	0	
3-16-c	Inland	Rephos	2	38	9.85	Y	14	
3-27-b	Inland	Rephos	2	69	12.4	N	0	Y
21T1-15E	Stelco	IF	1	55.1	11	Y	-	Y
26H1-27JJ	Stelco	Rephos	2	59.7	12.8	Y	-	Y

3. Transmission Electron Microscopy

Objectives

- Profile the iron and zinc ratios throughout the thickness of the coating using energy dispersive analysis of x-rays (EDAX).
- Phase identification through the coating using SAD.
- Study electron micrographs taken of the different phases through the coating and analyze the differences between their microstructures.

Sample Preparation Difficulties

The wedge technique was the preferred sample preparation method for the TEM specimens, however, due to the porosity of the coating, poor adhesion between the coating and substrate, and slight buckling of the samples from the tin snipping, it was not feasible. Therefore, the conventional sample preparation methods discussed in Section II.D. were used.

EDAX Analysis

EDAX Fe-Zn depth profiles were not feasible due to difficulties in sample preparation described above.

Analysis of SAD Patterns

SAD patterns taken from the top, middle and bottom of the coatings from sample 2-15-d and 3-5-b were analyzed for phase identification. JCPDS files (Appendix III) were used to index the SAD rings and spots. Overlapping of reflections from the different phases and secondary effects (e.g. twin spots, double diffraction spots and multiple diffraction effects) made phase analysis difficult. Table 9 gives a summary of the TEM phase analysis results and Figure 7 shows representative SAD patterns of zeta, delta and gamma reflections from samples 2-15-D and 3-5-B.

Microstructure Analysis

The phases within the coating did not appear as distinct, uniform layers in the electron micrographs. Figure 8 shows electron micrographs and their corresponding SAD patterns of a crack and inclusion found in the coating of sample 3-5-b. Analysis of the SAD patterns of the crack and inclusion showed that both zeta and delta existed in these regions. However, the SAD pattern of the area just outside of the inclusion indicated having only delta phase. Cracks and inclusions were also found in sample 2-15-d.

Table 9: TEM Phase Analysis Results

	Fe-Zn Phase(s) Identified from SAD Patterns
SAMPLE 2-15-D	
top of coating	zeta and delta
middle of coating	zeta and delta
bottom of coating	delta and gamma
SAMPLE 3-5-B	
top of coating	zeta and delta
middle of coating	delta
bottom of coating	delta

(a) Zeta and Delta Reflections

(b) Delta Reflections

(c) Delta and Gamma Reflections

Figure 7: Representative SAD Patterns From Samples 2-15-D and 3-5-B

(a) Representative Crack in Coating

(b) Representative Inclusion in Coating

Figure 8: Electron Micrographs taken at 42.5 kX Magnification and their Corresponding SAD Patterns from Sample 3-5-B.

4. Critical Process Variables

A review of the XRF, metallography and XRD experimental data showed that, in a critical annealing temperature range, multiple combinations of phases could result in having either the same normalized iron XRF response or zinc XRF response. Therefore, it was concluded that unique phase composition predictions would be difficult to deduce from using the XRF results alone. Consequently, the project team agreed that it was necessary to investigate other possible variables that could be used to help predict coating phase compositions.

Substrate Composition and Zinc Bath Chemistry

Critical process parameters which influence phase development include substrate composition and zinc bath chemistry. Substrate and zinc bath chemical compositions have been shown in literature to influence the substrate/coating interfacial phase formation, which, in turn, influences the subsequent phase formation in the coating [10]. For the AISI samples (Appendix I), the zinc bath compositions remain fairly constant. However, the substrate compositions for each of the substrate types were significantly different. In agreement with research done by Jordan and Marder at Lehigh University [11], the rephosphorized samples contained significantly more aluminum in their substrates than the extra-low carbon and interstitial-free samples. Table 10 lists Inland Steel's reported substrate chemical composition values.

Table 10: Substrate Chemical Compositions

ELC					
C %	0.05	V %	0.002	O %	-
Mn %	0.33	Ti %	0.001	H %	-
P %	0.003	B %	0.0001	Sa %	-
S %	0.02	Al %	0.002	La %	-
Si %	0.007	Pb %	-	Se %	-
Cu %	0.02	Te %	-	Mg %	-
Sn %	0.001	Bi %	-	Ta %	-
Ni %	0.01	Ca %	-	Fe %	-
Mo %	0.01	Zr %	-	Cd %	-
Cr %	0.01	Sb %	0.002	Zn %	-
Ag %	0.003	Ce %	-		
Cb %	0.002	N %	0.0027		
IF					
C %	0.0035	V %	0.002	O %	-
Mn %	0.24	Ti %	0.07	H %	-
P %	0.015	B %	0.0001	Sa %	-
S %	0.011	Al %	0.068	La %	-
Si %	0.029	Pb %	-	Se %	-
Cu %	0.01	Te %	-	Mg %	-
Sn %	0.001	Bi %	-	Ta %	-
Ni %	0.02	Ca %	-	Fe %	-
Mo %	0.01	Zr %	-	Cd %	-
Cr %	0.02	Sb %	0.002	Zn %	-
Ag %	0.002	Ce %	-		
Cb %	0.002	N %	0.0021		
Rephos					
C %	0.017	V %	0.003	O %	-
Mn %	0.71	Ti %	0.002	H %	-
P %	0.077	B %	0.0007	Sa %	-
S %	0.012	Al %	0.283	La %	-
Si %	0.28	Pb %	-	Se %	-
Cu %	0.02	Te %	-	Mg %	-
Sn %	0.001	Bi %	-	Ta %	-
Ni %	0.01	Ca %	-	Fe %	-
Mo %	0.01	Zr %	-	Cd %	-
Cr %	0.02	Sb %	0.003	Zn %	-
Ag %	0.003	Ce %	-		
Cb %	0.002	N %	0.0051		

Furthermore, optical photomicrographs, XRD, TEM and atomic composition dot map results showed that phase formation was inhibited in the rephosphorized samples, as compared to the extra-low carbon and interstitial-free samples. Figure 9 shows a schematic representation of galvanneal morphology development for the interstitial-free and rephosphorized substrate types, as seen from optical photomicrographs shown in Figure 10. The extra-low carbon substrate samples behaved similarly to the interstitial-free substrate samples.

Figure 9: Schematic of Phase Morphology Development

UNALLOYED

~400°C

~490°C

REPHOSPHORIZED

INTERSTITIAL-FREE

**Figure 10: Galvanneal Morphology Development
(photos taken at 1000x magnification)**

XRD analysis indicated that the zeta to delta phase transformation occurred at a higher galvanneal temperature for the rephosphorized samples than for the extra-low carbon and interstitial-free samples. Additionally, Figure 11 shows x-ray spectra of peeled coatings from three alloyed samples, one from each substrate type. The rephosphorized sample showed no gamma phase response at a galvanneal temperature of 474°C, whereas the extra-low carbon and interstitial-free samples indicated the formation of gamma at a temperature as low as 363°C. The influence of substrate type on phase formation was also seen in the TEM analysis discussed in Section III.B.3.

Lastly, atomic composition dot maps taken of unalloyed extra-low carbon, interstitial-free and rephosphorized samples showed the presence of aluminum at the substrate/coating interface of the rephosphorized sample only.

Figure 11: Preliminary XRD Results of Peeled Samples

Process Time and Temperature Profiles

The aluminum "diffusion barrier" discussed above could be the result of either the formation of an iron/aluminum or an iron/zinc/aluminum compound, or, more likely, by the presence of the aluminum in the grain boundaries. As alloying time and temperature increased, the "diffusion barrier" was observed to break down. Consequently, it was concluded that in order to more accurately study phase formation, accurate alloying time and temperature profiles were necessary. Unfortunately, literature on diffusion kinetics of the galvanneal iron/zinc system was limited and inconclusive. Figure 12 shows a schematic diagram of Inland Steel's experimental galvanneal coating line. Figure 13 gives an example temperature profile for the coating.

Figure 12: Inland Steel's Galvanneal Coating Line

Figure 13: Example Temperature Profile for Galvanneal Coating

Iron/Zinc XRF Ratios

In addition to limited diffusion kinetics information, the proprietary nature of the galvanneal on-line process conditions made it difficult to base any XRF model predictions on these parameters. Thus, using on-line process parameters, as a means of predicting phase compositions, was abandoned. However, by implementing DMC's successful demonstration of using both the

normalized iron and normalized zinc XRF responses to obtain unique sample solutions for a given substrate type, the decision was made to use the normalized iron/zinc XRF response ratio as a major input parameter for predicting phase compositions.

C. Mechanical Property Data Analysis

Inland Steel performed mechanical property tests on most of the AISI samples (Appendix I). The results of Inland Steel's reverse Olsen Mass Loss and 60° Reverse Bend Rating (i.e., Tape Test) tests, as a function of Inland Steel's average iron content values and percent zeta, delta and gamma phases determined from JPL's metallography, are documented in the JPL viewgraph package presented at the 8/23/94 program review held in Pittsburgh, PA. In general, Inland Steel rated an Olsen Mass Loss greater than 10 mg as a "poor" coating, and a Bend Rating less than 4 mm as "good" and one greater than 6 mm as "poor".

The following is a summary of the results:

Extra-Low Carbon/Interstitial-Free

•Reverse Olsen Mass Loss

<u>Condition</u>	<u>Rating</u>
>8% Fe	>10 mg
<30% zeta	>10 mg
>70% delta	>10 mg
>5% gamma	>10 mg

•60° Reverse Bend Rating

<u>Function</u>	<u>Rating</u>
10-12% Fe	some >6 mm
<20% zeta	>6 mm
>80% delta	>6 mm
5-15% gamma	some >6 mm
>15% gamma	>6 mm

Rephosphorized

•Reverse Olsen Mass Loss

<u>Function</u>	<u>Rating</u>
14% Fe	<10 mg
0% zeta	<10 mg
100% delta	< 10mg
>10% gamma	<10 mg

•60° Reverse Bend Rating

<u>Function</u>	<u>Rating</u>
14% Fe	none >6 mm
0% zeta	none >6 mm
100% delta	none >6 mm
20% gamma	none >6 mm

Overall, the rephosphorized substrate samples showed better coating ductility ratings than the extra-low carbon and interstitial-free substrate samples for the same coating weight range and iron content in the coating. Generally, samples with less than 8% iron have "good" coatings. Also, the relationship between the coating ductility rating and iron content in the coating correlated more closely with the amount of zeta and delta phases, as opposed to the amount of gamma phase, present in the coating. However, the data did show that "poor" coatings are more likely to occur in samples containing greater than 10% gamma phase.

IV. PHASE COMPOSITION MODELING

A. Fundamental Parameters Method Model

1. Description

The Fundamental Parameters Method (FPM) model is based on a mathematical model which corrects for x-ray absorption/enhancement effects in a multi-element/multi-layer material system. The mathematical model assumes that the intensity corrected for matrix effect ($P_{(i)}C_i$) is equal to the emitted intensity *plus* a correction for the decrease in intensity due to absorption and *minus* an intensity due to secondary enhancement [12]:

$$P_{(i)}C_i = P_i + S_i + \sum X_j C_j - \sum X_k C_k$$

The FPM model predicts the distribution of the zeta and delta phases. Necessary inputs to the FPM model are substrate type, coating weight, coating iron content, and normalized iron and zinc XRF response.

The FPM model for predicting phase compositions was created using a software program [13] that generates iron and zinc fluorescence values based on actual on-line conditions and user-defined values. These inputs were as follows:

•X-ray source:	Molybdenum
•Incident/Take-Off Angles:	Zinc = 90°/50° Iron = 15°/85°
•X-ray Tube Energy:	20 kV
•Filter	Aluminum
•Phase Layers Compositions:	Zeta = 7.5%Fe:92.5%Zn Delta = 10.5%Fe:89.5%Zn Gamma = 20%Fe:80%Zn
•Phase Layer Thicknesses	User-Defined
•XRF Normalization Factors:	Iron = 1/5000 Zinc = 1/4420

Figures 14-15 show input/output flow charts for the FPM percent phase determination model.

Figure 14: Input/Output Flow Chart for the FPM Model

Figure 15: Input/Output Flow Chart for Determining FPM Curve-fit Equations

2. Model Application

Assumptions

Due to the inaccurate calculation of pure elemental zinc on the surface of the coating, the model assumes that no eta phase is present. Also, in order to have no more than two unknowns, the FPM model must assume a fixed fraction of either zeta, delta or gamma. **Since the variation of the volume percent of the gamma phase is minimal within the commercial percent iron content range (9%-12% iron) for galvanneal, the model assumes a fixed fraction of gamma.** Lastly, the FPM model is coating thickness dependent.

FPM Model Curves

Percent phase versus normalized iron/zinc XRF ratio curves, for the zeta and delta phases (assuming a fixed 10% gamma phase), were plotted using the data generated from the aforementioned software program simulations. Figure 16 shows the results of the 7, 8, 9 and 10 μm coating thickness curves and representative 0.2 μm increment curves (dotted lines). Separate curve-fit equations were calculated for the zeta and delta phase curves and are shown in Table 11.

Table 11: Curve-fit Equations for FPM Model Curves

Coating Thickness [μm]	Zeta Phase	R ²	Delta Phase	R ²
7	783.25-1625.64x	0.993	-693.25+1625.64x	0.993
8	703.25-1699.24x	0.992	-613.25+1699.24x	0.992
9	644.27-1776.67x	0.989	-554.27+1776.67x	0.989
10	586.36-1813.46x	0.985	-496.36+1813.46x	0.985

(16a) Zeta Phase

(16b) Delta Phase

Figure 16: FPM Model Curves (assuming 10% gamma phase)

Selecting FPM Model Form

Analysis of DMC's normalized iron/zinc XRF ratios and the iron content in the coating of the AISI samples (Appendix I) showed that their relationship to one another could be used as a filter for selecting the most appropriate FPM model form to predict phase compositions. Figure 17 shows examples, based on the AISI samples, of how iron content and DMC's normalized iron/zinc XRF ratios relate to the presence of eta and the amount of gamma in the coating, as determined from metallography. These plots determine allowable ranges of iron/zinc XRF values for given iron contents, percent phases and coating weight ranges. **Therefore, only samples having iron/zinc XRF ratios which fall within the ranges of the chosen FPM model form should be applied to that specific model. This selection method is also substrate type dependent, as exemplified in Figure 17.**

(17a) ELC/IF : 65-75 gsm≈10 μm Coating Thickness

(17b) Rephosphorized : 65-75 gsm≈11μm Coating Thickness

Figure 17: Examples of how Iron Content and DMC's Normalized Iron/Zinc XRF Ratios Relate to the Presence of Eta and the Amount of Gamma in the Coating

FPM Model Validation

The following analysis was performed with DMC during the Technology Transfer meeting held on July 20-21, 1994, at JPL.

In order to validate the FPM model, a comparison was made between data that was plotted using percent phase data determined from metallography and DMC's normalized iron and zinc XRF data for extra-low carbon and interstitial-free samples with 7, 8, 10 and 13 μm coating thicknesses and iron contents ranging from 7%-14%. First, normalized iron and zinc XRF data was generated using metallographic percent phase data and the FPM software (no fixed fraction of gamma phase assumed). These results are represented as the black symbols in Figure 18. Second, metallographic percent phases were plotted against DMC's normalized iron/zinc XRF ratios. These results are represented as the white symbols in Figure 18.

Comparison of the black and white symbols showed that the general slopes of the data generated using the FPM software (black symbols) were inconsistent with the slopes of the experimental data (white symbols). Varying the inputs to the FPM program (i.e. incident/take-off angles, phase composition, and filtering) was insufficient in bringing the slopes of the FPM model data and the slopes of the experimental data to agreement. Figure 19 shows the effects of varying the Fe-Zn phase layer compositions within the coating, assuming 10% gamma phase and an 8 μm coating thickness. The results showed that the slope of the generated curves were dependent on the compositions of the zeta and delta phases and not the gamma phase.

Identified Limitations

Accurate experimental phase analysis was difficult, therefore it was difficult to validate FPM simulations. Also, significant error in predicting percent phase composition could arise from errors in coating thickness determination. In addition, the FPM model will have to be modified if the presence of pure elemental zinc (eta phase) on the coating surface and large variations in percent gamma phase are expected.

(18a) Zeta Phase

(18b) Delta Phase

(18c) Gamma Phase

Figure 18: FPM Model Validation Comparison

Varying Zeta Layer Fe-Zn Compositions

(19a) Delta Layer 9% Fe - Gamma Layer 20% Fe

(19c) Delta Layer 12% Fe - Gamma Layer 20% Fe

(19b) Delta Layer 9% Fe - Gamma Layer 20% Fe

(19d) Delta Layer 12% Fe - Gamma Layer 20% Fe

Varying Delta Layer Fe-Zn Compositions

(19e) Zeta Layer 6%Fe - Gamma Layer 20%Fe

(19g) Zeta Layer 9%Fe - Gamma Layer 20%Fe

(19f) Zeta Layer 6%Fe - Gamma Layer 20%Fe

(19h) Zeta Layer 9%Fe - Gamma Layer 20%Fe

Varying Gamma Layer Fe-Zn Compositions

(19i) Zeta Layer 6% Fe - Delta Layer 12% Fe

(19j) Zeta Layer 6% Fe - Delta Layer 12% Fe

Figure 19: Effect of Varying Iron-Zinc Phase Layer Composition on FPM Model Curves (assuming 10% gamma and 8 μm coating thickness)

V. ADDITIONAL STUDIES

A. Inland Steel and Stelco Sample Comparison

1. Objective

In order to verify that the results of the phase composition evaluation done on the AISI samples (Appendix I) could also apply to Stelco's on-line process, a metallographic comparison was done between ten Stelco samples and nine AISI (Inland Steel) samples. Both JPL and Stelco separately prepared and analyzed these samples using their own prescribed metallographic techniques.

2. JPL's Assessment

Nineteen Study Samples

Cross-sections of the nineteen study samples were polished, etched and photographed using the techniques described in Section II.B. Average phase thicknesses were measured using the method described in Section III.B.1. Table 12 shows a summary of the JPL results. Differences between JPL and Stelco's preparation and analysis techniques made comparing the results from average phase thicknesses measurements difficult and inconclusive. Therefore, the project team agreed to redo two of the Inland Steel samples and two of the Stelco samples in a round-robin experiment.

Four Round-Robin Samples

In order to clarify the confusion between the metallographic phase thickness measurements between JPL and Stelco, two Inland Steel samples and two Stelco samples were analyzed by JPL, Stelco, LTV Steel Company and Bethlehem Steel. The same four samples were passed around to each team member for metallographic phase thickness evaluation. The samples were etched using both the JPL method [14] and the one prescribed by Stelco (Appendix IV). JPL measured the average phase thicknesses of the four samples using the method described in Section III.B.1. Table 13 shows a summary of the JPL results for both etchant techniques. The two etchants highlighted certain areas of the zeta and delta phases differently, however, the differences were not significant enough to affect the average phase thickness measurement values.

The results of the round-robin experiment showed that confusion and disagreement existed among all team members in optically identifying the coating phases and that there was no conventional method to metallographically measure phase thicknesses.

Table 1: JPL Study Sample Results

Comparison of IF Steel vs. ELC Steel								
Sample ID#	Grade	Producer	Average Thickness [μm]				Lab CW [gsm]	Lab Fe [%]
			Zeta	Delta	Gamma	Total		
2-15-D	IF	Inland	2.5	4	0.5	7	57	8.7
1-2-D	ELC	Inland	3	6	1	10	67	9.6
2-20-C	IF	Inland	1	6	1	8	59	11.7
4-3-D	ELC	Inland	0.5	8.5	1	10	71	11.4
2-4-B	IF	Inland	0.5	8.5	1	10	73	11.2
1-3-D	ELC	Inland	0	9	1	10	73	12
Comparison of IF Steel vs. Rephosphorized Steel								
Sample ID#	Grade	Producer	Average Thickness [μm]				Lab CW [gsm]	Lab Fe [%]
			Zeta	Delta	Gamma	Total		
24H1-15A	IF	Stelco	1.5	5.5	1	8	49.2	11.2
20T1-27C	Rephos	Stelco	1	6.5	0.5	8	48.9	12
2-16-C	IF	Inland	1	6	1	8	56	11.8
3-4-B	Rephos	Inland	0.5	5.5	1	7	56	13.3
2-17-C	IF	Inland	2	5	1	8	56	10
3-6-X	Rephos	Inland	2	5.5	0.5	8	55	10.5
21T1-15D	IF	Stelco	1	7	1	9	55.1	11
R30	Rephos	Stelco	3.5	4	0.5	8	51.1	8.2
Comparison of Inland Samples vs. Stelco Samples								
Sample ID#	Grade	Producer	Average Thickness [μm]				Lab CW [gsm]	Lab Fe [%]
			Zeta	Delta	Gamma	Total		
3-6-X	Rephos	Inland	2	5.5	0.5	8	55	10.5
65J5	Rephos	Stelco	1	6	1	8	76.6	13.1
6-13-B	IF	Inland	0	5	1	6	46	11.2
24H1-15H	IF	Stelco	2	5	1	8	52.6	11.4
3-5-B	Rephos	Inland	0.5	6	0.5	7	55	11.2
26H1-27FF	Rephos	Stelco	2	5.5	0.5	8	59.7	12.8

Table 13: JPL Round-Robin Results for Both JPL/Stelco Etchant Techniques

Sample ID#	Grade	Producer	Average Thickness [μm]				Lab CW [gsm]	Lab Fe [%]
			Zeta	Delta	Gamma	Total		
2-15-D	IF	Inland	2.5	4	0.5	7	57	8.7
3-5-B	Rephos	Inland	0.5	6	0.5	7	55	11.2
21T1-15D	IF	Stelco	1	7	1	9	55.1	11
26H1-27FF	Rephos	Stelco	2	5.5	0.5	8	59.7	12.8

VI. SAMPLE OMISSIONS

A. Sample set 1-6-c to 1-9-b

Sample IDs 1-6-c to 1-9-b were taken out of the JPL XRF analysis because of their unusual zinc XRF responses. The XRD pattern on sample 1-8-b revealed a large amount of pure zinc in the galvaneal coating, however, the AISI data matrix (Appendix I) indicated a galvaneal temperature of 502°C. Pure zinc is very unlikely to exist at this temperature. Optical microscopy examination supported the XRD results, however, the chemical analysis indicated a moderate (9%) iron content in the coating. DMC fluorescence data also appears to show unusual response. Due to the apparent discrepancies in these sample the decision was made to not consider this set of data in the JPL XRF analysis.

B. Sample 6-28-c

Sample 6-28-c was taken out of the JPL XRF analysis because unusual zinc and iron XRF responses were noted and no galvaneal temperature data was recorded in the AISI data matrix (Appendix I).

VII. CONCLUSION

The analysis of both the JPL and DMC XRF experimental data indicated that the DMC Zn/Fe gauge could achieve an accuracy of $\pm 0.5\%$ for iron and zinc detection under DMC laboratory conditions. In order to correlate the XRF data to galvanneal phase morphology, metallography, XRD and TEM were performed. The results showed that, within a critical annealing temperature range, multiple combinations of phases could result in having either the same normalized iron XRF response or the same normalized zinc XRF response. Therefore, it was concluded that predicting unique phase compositions with the XRF data would require using the normalized iron/zinc XRF ratios.

In order to predict phase compositions using XRF, a FPM approach was used to generate theoretical models. For this study, due to unavailable process parameter and diffusion kinetics information, only the normalized iron/zinc XRF ratios, substrate type, coating weight and iron content were used as inputs for the phase composition prediction model. Disagreement was shown to exist between the FPM model and experimental data. Limitations in the FPM software program are being investigated by DMC in order to correct the inconsistencies.

VIII. ACKNOWLEDGEMENTS

The authors thank AISI for providing the funding for this study, and Elzbieta Kolawa, Paul Jacoy and Jim Kulleck of the Jet Propulsion Laboratory and Carol Garlund of the California Institute of Technology for their technical support.

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X. APPENDICES

APPENDIX I: AISI Data Matrix

	Sample	Substrate	Pot Chem	Line Speed	Entry	Pot	Galvanneal	NDS CW	Lab CW	Lab CW	Lab Fe	Lab Fe
	ID #	Type	Al/Fe [%]	[ft/min]	Temp [°C]	Temp [°C]	Temp [°C]	[gsm]	#1 [gsm]	#2 [gsm]	#1 [%]	#2 [%]
1	1-1-d	ELC	.112/.046	50	477	463	U/A	73	55	62	3	3.5
2	1-2-d	ELC	.112/.046	50	477	463	382	73	68	67	9.6	9.5
3	1-3-d	ELC	.112/.046	50	477	463	477	67	73	74	12.1	11.9
4	1-4-a	ELC	.112/.046	50	477	463	421	70	63	67	11.7	11.4
5	1-5-d	ELC	.112/.046	50	477	463	329	73	67	66	5.6	5.7
6	1-6-c	ELC	.112/.046	50	477	463	U/A	104	90	87	2.7	2.9
7	1-7-c	ELC	.112/.046	50	477	463	466	98	98	101	9.9	9.7
8	1-8-b	ELC	.112/.046	50	477	463	502	101	97	104	9.5	9
9	1-9-b	ELC	.112/.046	50	477	463	413	104	99	97	8.7	8.5
10	2-1-b	IF	.083/.029	50	469	471	U/A	67	70	70	5.2	5.1
11	2-2-c	IF	.083/.029	50	471	471	399	64	73	74	10.4	10.1
12	2-3-a	IF	.083/.029	50	472	471	471	61	75	73	11.6	11.8
13	2-4-b	IF	.083/.029	50	468	471	441	61	74	71	11	11.3
14	2-5-a	IF	.083/.029	50	472	471	363	64	69	70	8.4	8.3
15	2-6-a	IF	.083/.029	50	469	471	354	67	68	70	7	7
16	2-7-b	IF	.083/.029	50	473	471	U/A	92	96	91	3.7	3.9
17	2-9-c	IF	.083/.029	50	467	471	443	85	99	104	9.2	8.9
18	2-10-b	IF	.083/.029	50	472	470	491	79	100	98	11.5	11.5
19	2-11-c	IF	.083/.029	50	471	472	477	82	101	97	9.9	10.1
20	2-12-a	IF	.083/.029	50	472	472	457	82	100	99	9.5	9.4
21	2-13-a	IF	.083/.029	50	479	472	421	82	98	93	8.7	9.1
22	2-14-b	IF	.083/.029	70	476	471	U/A	49	52	52	7	7.1
23	2-15-d	IF	.083/.029	70	477	471	354	49	53	60	8.7	8.6
24	2-16-c	IF	.083/.029	70	476	472	399	52	56	56	11.2	12.3
25	2-17-c	IF	.083/.029	70	476	472	374	49	56	56	9.9	10.1
26	2-18-b	IF	.083/.029	70	473	472	360	49	55	55	9.3	9.3
27	2-19-d	IF	.083/.029	70	474	472	338	49	52	56	8.9	9.4
28	2-20-c	IF	.083/.029	70	472	472	427	52	62	56	11.4	11.9
29	3-1-x	Rephos	.117/.038	50	474	474	U/A	61	49	48	1.2	1.2
30	3-2-a	Rephos	.117/.038	50	487	474	388	58	52	50	8.2	8
31	3-3-a	Rephos	.117/.038	50	477	474	477	55	54	55	12.1	12.2
32	3-4-b	Rephos	.117/.038	50	477	474	432	55	56	56	13.3	13.3
33	3-5-b	Rephos	.117/.038	50	479	474	454	55	56	54	11	11.3
34	3-6-x	Rephos	.117/.038	50	477	474	438	55	55	56	10.5	10.4
35	3-7-b	Rephos	.117/.038	50	476	474	413	55	51	54	9.9	9.8
36	3-8-d	Rephos	.117/.038	50	480	474	377	55	51	47	3.4	3.3
37	3-10-a	Rephos	.117/.038	50	481	474	U/A	40	35	34	1.6	1.6
38	3-11-c	Rephos	.117/.038	50	478	474	385	40	37	35	7.6	7
39	3-12-b	Rephos	.117/.038	50	487	474	527	37	39	38	14.1	14.2
40	3-13-a	Rephos	.117/.038	50	481	474	488	37	38	38	12.1	12.4
41	3-14-c	Rephos	.117/.038	50	482	474	454	37	39	38	11.5	11.6

42	3-15-b	Rephos	.117/.038	50	481	474	416	37	38	39	11	11
43	3-16-c	Rephos	.117/.038	50	488	474	399	37	38	38	9.9	9.8
44	3-17-a	Rephos	.117/.038	50	479	474	371	40	34	35	3.4	3.4
45	3-20-c	Rephos	.117/.038	50	482	474	393	73	72	70	6.7	6.6
46	3-22-d	Rephos	.117/.038	50	482	474	474	76	74	75	10.1	10.2
47	3-23-b	Rephos	.117/.038	50	482	474	454	76	77	76	9.5	9.7
48	3-24-d	Rephos	.117/.038	50	479	474	438	76	77	74	8.9	9.2
49	3-25-c	Rephos	.117/.038	50	479	474	410	79	73	74	7.9	7.7
50	3-26-d	Rephos	.117/.038	50	485	474	379	82	74	69	3	2.6
51	3-27-b	Rephos	.117/.038	50	484	474	493	73	69	68	12.5	12.3
52	3-28-d	Rephos	.117/.038	50	484	474	U/A	82	74	70	1	1
53	3-30-b	Rephos	.117/.038	50	485	474	443	95	93	94	7.3	7.7
54	3-31-c	Rephos	.117/.038	50	491	474	488	92	95	91	9.5	9.8
55	3-32-b	Rephos	.117/.038	50	489	474	474	92	86	92	9.5	9.8
56	3-33-c	Rephos	.117/.038	50	485	474	463	95	93	88	8.3	8.9
57	3-34-c	Rephos	.117/.038	50	484	474	452	92	93	90	8.1	8.2
58	3-35-c	Rephos	.117/.038	50	486	474	421	95	88	88	6.6	7
59	3-36-b	Rephos	.117/.038	50	483	474	U/A	101	81	80	0.8	0.8
60	4-1-d	ELC	.126/.037	50	477	474	U/A	76	65	66	3.6	3.6
61	4-2-c	ELC	.126/.037	50	479	474	371	73	64	66	8.5	8.5
62	4-3-d	ELC	.126/.037	50	476	474	446	70	71	70	11.4	11.4
63	4-4-a	ELC	.126/.037	50	476	474	482	73	73	73	12.3	12.5
64	4-5-b	ELC	.126/.037	50	473	474	468	73	73	70	11.8	12.1
65	4-6-a	ELC	.126/.037	50	473	474	399	73	71	71	10.2	10.1
66	4-7-d	ELC	.126/.037	50	478	474	332	76	66	65	5.9	5.8
67	4-8-d	ELC	.126/.037	50	474	474	U/A	107	93	89	2.3	2.3
68	4-9-b	ELC	.126/.037	50	475	474	366	101	88	91	6.3	6.1
69	4-10-c	ELC	.126/.037	50	473	474	435	92	92	96	9.2	9.2
70	4-11-d	ELC	.126/.037	50	471	474	532	92	96	96	10.2	9.9
71	5-1-d	IF	.158/.033	50	478	468	U/A	92	88	84	3.7	3.9
72	5-2-a	IF	.158/.033	50	477	468	382	88	86	85	8	8
73	5-3-a	IF	.158/.033	50	479	468	449	82	87	90	10.3	10.1
74	5-4-c	IF	.158/.033	50	480	468	488	82	92	92	11.8	11.9
75	5-5-a	IF	.158/.033	50	474	468	516	85	88	88	11	11.1
76	5-6-a	IF	.158/.033	50	482	466	U/A	116	106	107	2.3	2.4
77	5-7-b	IF	.158/.033	50	487	465	488	107	117	123	10.6	10.3
78	5-8-c	IF	.158/.033	50	472	465	504	113	116	119	8.5	8.5
79	5-9-c	IF	.158/.033	50	477	466	466	107	117	114	8.4	8.6
80	6-1-c	IF	.143/.035	50	485	463	U/A	46	51	50	2.9	2.7
81	6-2-b	IF	.143/.035	50	478	463	341	46	53	53	6.3	6.7
82	6-3-b	IF	.143/.035	50	482	463	388	43	56	54	10.7	10.9
83	6-4-a	IF	.143/.035	50	481	463	488	43	58	57	14.8	14.1
84	6-5-d	IF	.143/.035	50	484	463	493	40	56	56	13.5	13.5

85	6-6-b	IF	.143/.035	50	484	463	499	40	57	57	14.5	15
86	6-7-c	IF	.143/.035	50	479	463	454	43	56	55	12.1	12.1
87	6-8-b	IF	.143/.035	50	487	463	366	43	53	52	8.9	8.9
88	6-9-b	IF	.143/.035	50	478	463	332	43	51	52	5.4	5.7
89	6-10-a	IF	.143/.035	50	479	463	U/A	46	47	46	2.3	2.5
90	6-11-a	IF	.143/.035	50	447	463	U/A	37	40	41	1.3	1.4
91	6-12-c	IF	.143/.035	50	455	463	349	37	43	43	6.8	7
92	6-13-b	IF	.143/.035	50	457	463	421	37	46	45	11.2	11.2
93	6-14-b	IF	.143/.035	50	457	463	516	37	46	47	13.5	13.6
94	6-15-d	IF	.143/.035	50	465	463	532	37	52	51	13.3	13.7
95	6-16-c	IF	.143/.035	50	469	463	454	37	51	52	12.7	12.5
96	6-17-b	Rephos	.143/.035	50	431	466	U/A	34	36	36	1.7	1.5
97	6-18-b	Rephos	.143/.035	50	433	467	377	34	36	36	3.9	4
98	6-19-a	Rephos	.143/.035	50	428	467	416	34	40	39	10.5	11
99	6-20-d	Rephos	.143/.035	50	432	467	421	34	40	39	12.1	12.5
100	6-21-c	Rephos	.143/.035	50	437	467	438	31	39	40	11.4	11.6
101	6-22-b	Rephos	.143/.035	50	434	467	?	34	37	38	6.8	6.5
102	6-23-c	Rephos	.143/.035	50	432	465	371	34	36	35	2.9	3.4
103	6-24-c	Rephos	.143/.035	50	434	463	U/A	61	63	58	0.8	0.8
104	6-25-d	Rephos	.143/.035	50	443	462	449	58	68	66	9.5	9.8
105	6-26-a	Rephos	.143/.035	50	459	462	471	61	70	74	10.6	10.6
106	6-27-c	Rephos	.143/.035	50	455	462	432	61	67	71	8.4	7.7
107	6-28-c	Rephos	.143/.035	50	457	462	?	64	64	60	3.2	3.8

APPENDIX III

JCPDS Files for Galvanneal Phase Analysis

APPENDIX II

Description of DMC Zn/Fe Gauge Set-up

The AISI samples (Appendix I) were measured on a Data Measurement Corporation Zn/Fe laboratory gauge. This gauge is capable of measuring coating weight and total percent iron. The measurements are calculated from the fluorescence of zinc and iron atoms in the galvanneal coating.

The details of each measurement are described as follows:

Zinc Fluorescence: The incident beam of radiation is generated by an x-ray tube operated at an energy of 20 keV. The beam is directed through an annular ion chamber and strikes the sample perpendicular to its surface. The vertical depth of penetration is approximately 150 μm . The incident beam excites both the zinc in the coating and the iron in the coating and the substrate. The annular ion chamber is filtered in such a manner to output a voltage proportional to the amount of zinc fluorescence.

Iron Fluorescence: In order to reduce the iron fluorescence from the substrate, the incident beam (20 keV) is directed at a sharp angle to the surface of the sample. The vertical depth of penetration is reduced to less than 40 μm . A cylindrical detector placed approximately 50 mm above the intersection of the incident beam and sample surface is filtered to output a voltage proportional to the iron fluorescence.

On the face of the sample, both beam sizes are 40 mm in diameter. For the AISI samples, the voltages from each chamber were averaged for 15 seconds. The voltages were averaged and recorded automatically by the DMC 800 electronics.

The voltages were normalized with respect to a piece of bare zinc and a piece of bare low carbon steel. The normalization was as follows:

	<u>Zinc Detector</u>	<u>Iron Detector</u>
Bare Zinc Sample:	Maximum Signal	Minimum Signal
Bare Iron:	Minimum Signal	Maximum Signal
Normalization:	$\frac{(V_{\text{sample}} - V_{\text{iron}})}{(V_{\text{zinc}} - V_{\text{iron}})}$	$\frac{(V_{\text{sample}} - V_{\text{zinc}})}{(V_{\text{iron}} - V_{\text{zinc}})}$

				d Å	Int.	h k l
Fe				2.0268	100	1 1 0
Iron				1.4332	20	2 0 0
				1.1702	30	2 1 1
Iron, syn				1.0134	10	2 2 0
				0.9064	12	3 1 0
Rad: CuKα	Lambda: 1.5405	Filter: Ni	d-sp:	0.8275	6	2 2 2
Cutoff:	Int: Diffractometer	I/Icor:				
Ref: Swanson et al., Natl. Bur. Stand. (U.S.), Circ. 539, 4 3 (1955)						
Sys: Cubic						
S.G.: Im3m (229)						
a: 2.8664	b:	c:	A:	C:		
A:	B:	C:	Z: 2	mp:		
Ref: Ibid.						
Dx: 7.88	Dm:	SS/FOM: F6=225(.004,6)				
ea:	nwB:	ey:	Sign:	2V:		
Ref:						
Color: Gray or silvery white						
X-ray pattern at 25 C. CAS no.: 7439-89-6. The iron used was an exceptionally pure rolled sheet prepared at the NBS [Moore, G.A., J. Met., 5 1443 (1953)]. It was annealed in an H ₂ atmosphere for 3 days at 1100 C and slowly cooled in a He atmosphere. Total impurities of sample <0.0013% each metals and non-metals. Occurs as terrestrial "iron" and in meteorites as "Kamacite".						
a=2.8587 at -194 C to 2.8993 at 800 C. alpha-Fe (bcc)=(-910 C) gamma-Fe (fcc)=(1390 C) delta-Fe (bcc). Opaque mineral optical data on specimen from Meteorite: RR2Re= 57.7, Disp.=16, VHN=158 (mean at 100, 200, 300), Color values=.311, .316, 57.9, Ref.: IMA Commission on Ore Microscopy QDF. W type.						
Iron group. Also called: pearlite. Also called: sorbite. Also called:						

‡ Strong lines: 2.03/X 1.17/3 1.43/2 0.91/1 1.01/1 0.83/1 0.00/1 0.00/1

				d Å	Int.	h k l
Zn				2.473	53	0 0 2
Zinc				2.308	40	1 0 0
inc, syn				2.091	100	1 0 1
				1.687	28	1 0 2
				1.342	25	1 0 3
Rad: CuKα1	Lambda: 1.5405	Filter: Ni	d-sp:	1.332	21	1 1 0
Cutoff:	Int: Diffractometer	I/I _{cor} : 3.80		1.237	2	0 0 4
Ref: Swanson, Tatge, Natl. Bur. Stand. (U.S.), Circ. 539, 1 16 (1953)				1.1729	23	1 1 2
				1.1538	5	2 0 0
				1.1236	17	2 0 1
sys: Hexagonal		S.G.: P6 ₃ /mmc (194)		1.0901	3	1 0 4
a: 2.665	b:	c: 4.947	λ:	1.0456	5	2 0 2
λ:	B:	C:	Z: 2	0.9454	8	2 0 3
Ref: Ibid.		mp: 420 deg.		0.9093	6	1 0 5
				0.9064	11	1 1 4
Dx: 7.14	Dm: 7.05	SS/FOM: F20=55(.018,20)		0.8722	5	2 1 0
αa:	n _w B: 2.58	ey:	Sign:	0.8589	9	2 1 1
Ref: Winchell, Elements of Optical Mineralogy, 1 (1927)				0.8437	2	2 0 4
				0.8245	1	0 0 6
				0.8225	9	2 1 2
Color: Bluish white						
Pattern at 26 C. Sample from New Jersey Zinc Company, Sterling Hill, New Jersey, USA. CAS no.: 7440-66-6. Spectroscopic analysis shows faint traces of Pb, Cu, Mg, Si. Merck Index, 8th Ed., p. 1127. Mg type. Zinc group. PSC: hP2. Mwt: 65.38. Volume[CD]: 30.43.						

† Strong lines: 2.09/X 2.47/5 2.31/4 1.69/3 1.34/3 1.17/2 1.33/2 1.12/2

					d Å	Int.	h k l
FeZn 7					2.23	90	0 0 2
Iron Zinc					2.14	100	1 0 1
					1.634	50	1 0 2
					1.390	60	1 1 0
					1.270	90	1 0 3
Rad: FeKα Lambda: 1.9373 Filter: d-sp:					1.180	90	1 1 2
Cutoff: Int: I/Icor:					1.165	90	2 0 1
Ref: Osawa, Ogawa, Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem., 68					1.120	60	0 0 4
186 (1928); Bablick, H. et al., Z. Metallkd., 30 122 (1938)					1.063	50	2 0 2
Sys: Hexagonal S.G.: P6/**c							
a: 2.788 b: c: 4.480 A: C: 1.6069							
A: B: C: Z: 0.22 mp:							
Ref: Ibid.							
Dx: 6.220 Dm: 7.250 SS/POW: F9=4(.227,11)							
ea: nwB: ey: Sign: 2V:							
Ref:							
O assigned because of insufficient range of intensities. 89.27% Zn. Bablick, H. et al. Z. Metallk., 30 122 (1938) report: FeZn10. Reference reports: a=12.83, c=57.72 based on single-crystal data with Z=555 atoms ±8. PSC: hP1.76. Mwt: 513.51. Volume[CD]: 30.16.							

† Strong lines: 2.14/X 2.23/9 1.39/6 1.27/9 1.18/9 1.17/9 1.12/6 1.63/5

					d Å	Int.	h k l					
Zeta-FeZn					6.21	4	1 1 0					
Iron Zinc					4.117	3	-1 1 1					
					3.693	3	1 1 1					
					3.025	4	0 2 1					
					2.769	10	-2 2 1					
Rad: CuKα	Lambda: 1.54178	Filter:	d-sp:		2.558	2	-4 0 1					
Cutoff:	Int:	I/Icor:		2.511	11	2 2 1						
Ref: Gellings, P. et al., Z. Metallkd., 70 315 (1979)					2.442	27	-3 2 1					
Sys: Monoclinic S.G.:					2.248	14	-1 3 1					
					2.228	8	1 1 2					
					a: 10.862	b: 7.608	c: 5.061	A: 1.4277	C: 0.6652	2.188	60	3 2 1
					A:	B: 100.53	C:	Z:	mp:	2.174	100	1 3 1
Ref: Ibid.					2.160	50	-3 1 2					
dx:	Dm:	SS/FOM: F21=5(.043,101)			2.123	88	-4 2 1					
sa: nwB: ey: Sign: 2V:					2.113	40	2 0 2					
					2.085	49	0 2 2					
					2.057	71	5 1 0					
					1.986	15	1 2 2					
Synthesized by using the liquids-hot-pressing methods. Mwt: 121.23.					1.900	44	4 2 1					
Volume[CD]: 411.19.					1.787	18	-1 3 2					
					1.721	9	-2 4 1					

† Strong lines: 2.17/X 2.12/9 2.06/7 2.19/6 2.16/5 2.09/5 1.90/4 2.11/4

				d Å	Int.	h k l
Fe Zn						
11 40						
Iron Zinc						
				2.998	10	6 0 0
				2.845	10	6 2 0
				2.742	10	5 3 3
				2.598	30	4 4 4
				2.519	30	5 5 1
Rad:	Lambda:	Filter:	d-sp:			
Cutoff:	Int: Visual	I/Icor:		2.493	10	6 4 0
Ref: Bastin et al., Z. Metallkd., 65 656 (1974)				2.404	60	6 4 2
				2.343	60	7 3 1
				2.197	60	7 3 3
				2.183	80	8 2 0
Sys: Cubic	S.G.: F-43m (216)					
a: 17.98	b:	c:	A:	2.120	100	6 6 0
A:	B:	C:	Z: 8	2.078	80	7 5 1
Ref: Ibid.				2.064	40	6 6 2
				1.974	40	9 1 1
				1.962	30	8 4 2
Dx: 7.381	Dm:	SS/FOM: F30=15(.039,52)				
ea:	nwB:	ey:	Sign:	2V:		
Ref:				1.918	30	6 6 4
				1.887	30	9 3 1
				1.836	30	8 4 4
Prepared from Zn-18% Fe melt, by heating pressed powder 380 C for 180 hours then 500 C for 139 hours. <u>Termed 'SVG' phase by authors.</u> Approximate range of composition 75.5 to 81 atomic % Zn at 300 C. Fe ₁₁ Zn ₄₀ type. PSC: cF408. Mwt: 3229.52. Volume[CD]: 5812.58.				1.808	10	9 3 3
				1.764	20	10 2 0
				1.731	20	10 2 2
				1.671	5	10 4 0
				1.644	5	10 4 2
				1.624	5	11 1 1
				1.590	5	8 8 0

d Å	Int.	h k l	d Å	Int.	h k l	d Å	Int.	h k l
1.572	5	11 3 1	1.298	20	8 8 8	1.106	10	16 2 2
1.527	5	9 7 3	1.285	10	14 0 0	1.091	20	16 4 0
1.500	5	12 0 0	1.272	40	10 10 0	1.0847	20	15 5 5
1.479	5	12 2 0	1.262	30	13 5 3			
1.460	5	12 2 2	1.238	5	11 9 3			
1.377	10	11 7 1	1.224	40	14 4 2			
1.356	10	12 4 4	1.215	10	13 5 5			
1.344	10	13 3 1	1.191	30	14 4 4			
1.326	10	12 6 2	1.153	30	15 3 3			
1.315	20	13 3 3	1.141	5	12 10 2			

† Strong lines: 2.12/X 2.18/8 2.08/8 2.40/6 2.34/6 2.20/6 2.06/4 1.97/4

					d Å	Int.	h k l
Fe Zn							
4 9							
Iron Zinc					2.841	20	3 1 0
					2.592	80	2 2 2
					2.402	60	3 2 1
					2.116	100	3 3 0
					1.915	80	3 3 2
Rad:	Lambda:	Filter:	d-sp:		1.833	40	4 2 2
Cutoff:	Int: Visual	I/Icor:			1.762	20	4 3 1
Ref: Bastin et al., Z. Metallkd., 65 656 (1974)					1.540	10	5 3 0
					1.497	40	6 0 0
					1.456	10	6 1 1
Sys: Cubic		S.G.: I-43m (217)					
a: 8.95	b:	c:	A:	C:			
A:	B:	C:	Z: 4	mp:	1.349	10	6 2 2
Ref: Ibid.					1.325	20	6 3 1
					1.295	60	4 4 4
Dx: 7.521	Dm:	SS/FOM: F20=3(.219,35)			1.269	40	7 1 0
					1.222	60	7 2 1
ea:	nWB:	ey:	Sign:	2V:			
Ref:					1.140	20	7 3 2
					1.105	40	8 1 1
					1.089	10	6 4 4
					1.050	80	
					1.040	80	[7 5 0]
					1.030	80	6 6 2
Sample taken from iron-zinc diffusion couples prepared by welding carefully ground and cleaned iron (99.9%) and zinc (99.99%) rods in argon and annealing at 380 C approximate range of composition 69-72 atomic % Zn at 300 C. Termed gamma phase by reference, and epsilon phase elsewhere. Cu5Zn8 type. PSC: ci52. To replace 2-1203. Mwt: 811.81. Volume[CD]: 716.92.							

Sample taken from iron-zinc diffusion couples prepared by welding carefully ground and cleaned iron (99.9%) and zinc (99.99%) rods in argon and annealing at 380 C approximate range of composition 69-72 atomic % Zn at 300 C. Termed gamma phase by reference, and epsilon phase elsewhere. Cu5Zn8 type. PSC: CI52. To replace 2-1203. Wwt: 811.81. Volume[CD]: 716.92.

Strong lines: 2.12/X 2.59/8 1.92/8 1.05/8 1.04/8 1.03/8 2.40/6 1.30/6

APPENDIX IV

Stelco Galvanneal Metallographic Preparation: "Individual Specimen" Technique

1	Section Long. & Trans. Specimens			
	1) Obtain ~3 x 5" Sample 2) Clean in Acetone 3) Section a Longitudinal and Transverse specimen			
2	Mounting Media & Rough Polishing			
	1) Mount Long. & Trans. Samples in Epoxy Resin (High Edge Retention Epoxy) 3) Rough polish on Abrapol-2 - SIC papers 120, 240, 320, 400, 600 - Speed: 300 rpm, Force: 150 N - Water Rinse and Blow Dry After Each Stage - Time: 45 sec. per paper - Immediately Swab & Rinse with Ethanol (SDA) after 600 grit, Blow Dry			
3	Fine Polishing			
	<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;"> 1) PAN-W Cloth - 6 micron diamond - Speed: 150 rpm - Force: 200 N - Red Lubricant @5 - Time : 120 sec. - Ethanol Swab & Rinse </td> <td style="width: 50%; vertical-align: top;"> 2) Imperial Polishing Cloth - 1 micron diamond - Speed: 150 rpm - Force: 200 N - Red Lubricant @5 - Time : 120 secs. - Ethanol Swab & Rinse </td> </tr> </table> Note: Do not use water to rinse specimen	1) PAN-W Cloth - 6 micron diamond - Speed: 150 rpm - Force: 200 N - Red Lubricant @5 - Time : 120 sec. - Ethanol Swab & Rinse	2) Imperial Polishing Cloth - 1 micron diamond - Speed: 150 rpm - Force: 200 N - Red Lubricant @5 - Time : 120 secs. - Ethanol Swab & Rinse	
1) PAN-W Cloth - 6 micron diamond - Speed: 150 rpm - Force: 200 N - Red Lubricant @5 - Time : 120 sec. - Ethanol Swab & Rinse	2) Imperial Polishing Cloth - 1 micron diamond - Speed: 150 rpm - Force: 200 N - Red Lubricant @5 - Time : 120 secs. - Ethanol Swab & Rinse			
4	Etching			
	Etch by immersion in the following solution with gentle agitation for 30 seconds, increasing in 5 second intervals, if required. - 300ml SDA #32 (Ethynal) - 50ml de-ionized water - 0.8g picric acid The specimen may then be prepared for the SEM by Gold Sputter Coating the specimen surface or dissolving the epoxy in Methylene Chloride (cut away excessive epoxy)			