Chapter V

5 Mixed oxide deposition by spray pyrolysis

Zinc ferrate (III) ($ZnFe_2O_4$) a mixed oxide of ZnO and Fe_2O_3 was synthesized as a thin film on the mild steel substrate by the spray pyrolysis technique. The coatings were obtained at three different temperatures (300°, 400° and 500°C) and were analyzed for their changes in their crystallinity, morphology and corrosion resistance, with the processing temperature. The experimental details are given in section 2. The results of the experimental studies on the coatings of zinc ferrate (III) thus obtained on mild steel substrate as a possible protective coating against corrosion are presented in this chapter.

5.1 XRD Analysis

X-ray diffractograms of the coating obtained at three different temperatures were analyzed for the structural changes. Figure 5.1, 5.2 and 5.3 shows the diffractogram of the coating obtained at a substrate temperature of 300°C, 400°C and 500°C respectively. The degree of crystallinity of the coating obtained at 300°C is very poor when compared to the coatings obtained at other substrate temperatures. The peak with high reflection intensity for the coating obtained at 300°C appears at 82.43°.

increase in the intensity of the peaks indicates the increase in crystallinity. Comparing the X-ray diffraction of these coatings it can be understood that with increase in the substrate temperature the coating becomes more crystalline. This also gives an insight into the reaction, which might have occurred at the surface while the crystals were grown. Increase in the substrate temperature results in near completion of the reaction.

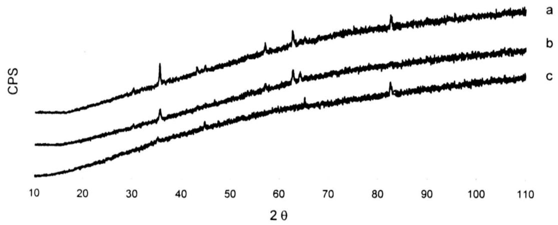

Figure 5.4 Comparison of X-ray diffractogram of the coatings obtained at various temperaturs

a=500°C
b=400°C
c=300°C

Figure 5.4

Since the starting materials where $Zn(NO_3)_2$ and $FeCl_3$, and the expected product is a mixture of these two oxides. The diffractograms were compared with that of the zinc oxide and ferric oxide. Also since the average thickness is 4μm the appearance of the mild steel in the diffractogram can be anticipated and so the diffractograms were compared with the standard. Figures 5.5, 5.6, and 5.7 are the comparison of X-ray diffractogram of the coating obtained at 300, 400, 500°C respectively and the diffractogram of the substrate with out coating.

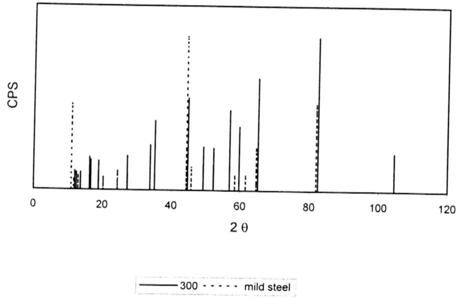

Figure 5.5 Comparison of the X-ray diffractograms of the coating obtained at 300°C and the mild steel substrate

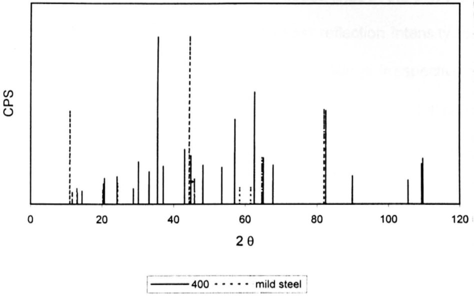

Figure 5.6 Comparison of the X-ray diffractograms of the coating obtained at 400°C and the mild steel substrate

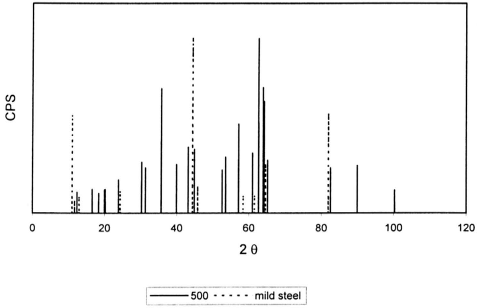

Figure 5.7 Comparison of the X-ray diffractograms of the coating obtained at 500°C and the mild steel substrate

The 2 θ values from the peak search were used to plot the graph in order to facilitate the comparison. The dotted lines in the plot are those of the mild substrate. The peak with highest reflection intensity for mild steel (substrate) appears at 44.31°. All the coatings irrespective of the temperature of deposition show a peak with a shift in the position to that of the standard, the 2θ being 44.71°, 44.75°, 44.81° for the coatings obtained at 300, 400, 500°C respectively. The second highest peak for mild steel appears at 81.92°, third highest peak at 64.62°. Coatings obtained at all the three temperatures do not have any peak at these 2θ values. This confirms that the substrate signature is not registered along the coatings diffractograms. This analysis also highlights the continuity of the coating.

The anticipated product is the coating of zinc ferrate (III), a mixed oxide of ZnO and Fe_2O_3, which is a black, octahedral crystal with a hardness value of 7.2. Table 5.1 gives the 2θ value of the peak with highest reflection intensity and peaks significantly close to this peak for the ZnO powder sample, which is used as an internal standard.

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Table 5.1 Comparison of the peak positions of the standard zinc oxide and the peak positions of the coatings obtained at 300°, 400° and 500°C.

ZnO		300°C		400°C		500°C	
2θ	Relative Intensity (%)	2θ	Relative Intensity (%)	2θ	Relative Intensity (%)	2θ	Relative Intensity (%)
33.52	100	82.43	100	35.44	100	35.66	100
58.21	77.10	65.09	73.31	62.51	66.83	62.66	71.76
32.86	73.57	44.71	30.21	82.41	55.88	82.53	71.22
44.83	58.40	35.12	45.19	57.03	50.77	64.22	63.90
31.09	57.78	59.68	41.67	43.03	32.78	57.11	50.89

The 2θ value of the first peak with maximum intensity of ZnO does not coincide with those peaks of the coatings, next peak with relative high intensity for ZnO which appears at 58.210° also does not match likewise with the peak of 73.57% relative intensity at 32.856°. But the peak at 44.83° with relative intensity of value 58.90%, is present in the coatings with a slight shift. This does not lead to a conclusion that the coating is of ZnO in a separate phase.

The following figures 5.8, 5.9, 5.10 shows the comparisons of the X-ray diffractograms of ZnO with coatings obtained at 300, 400, 500°C respectively. It should be noticed that the intensity of the peak of the coatings which matches with the standard ZnO decreases with increase in substrate temperature.

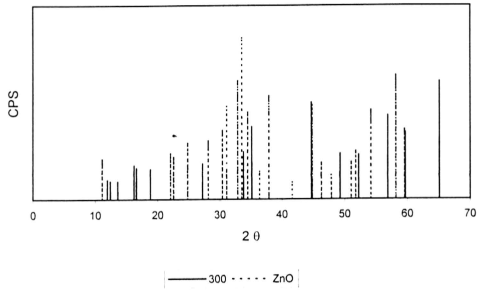

Figure 5.8 Comparison of X-ray diffractograms of the coating obtained at 300°C with the diffractogram of standard Zinc Oxide

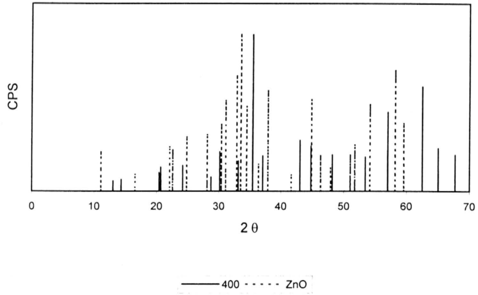

Figure 5.9 Comparison of X-ray diffractograms of the coating obtained at 400°C with the diffractogram of standard Zinc Oxide

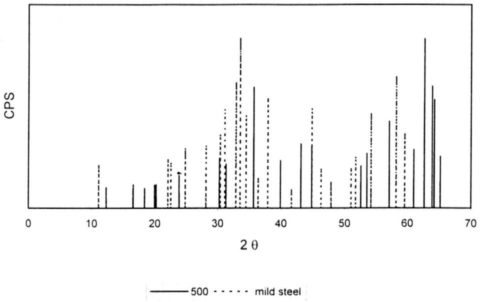

Figure 5.10 Comparison of X-ray diffractograms of the coating obtained at 500°C with the diffractogram of standard Zinc Oxide

In order to distinguish the presence of Fe_2O_3 in the coating the X-ray diffractogram of pure analytical grade Fe_2O_3 was also obtained. Figure 5.11, 5.12, 5.13 shows the comparison of the X-ray diffractograms of the coatings obtained at 300, 400, 500°C respectively with the standard Fe_2O_3.

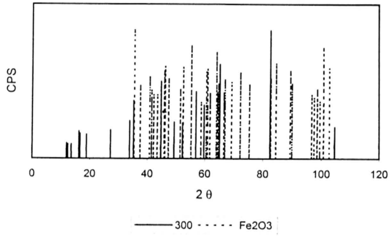

Figure 5.11 Comparison of the X-ray diffraction of the coating obtained at 300°C with standard Fe_2O_3

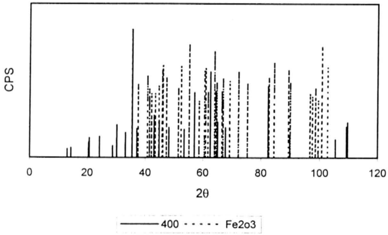

Figure 5.12 Comparison of the X-ray diffraction of the coating obtained at 400°C with standard Fe_2O_3

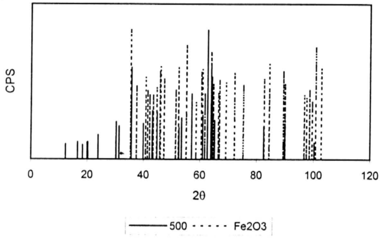

Figure 5.13 Comparison of the X-ray diffraction of the coating obtained at 500°C with standard Fe_2O_3

Table 5.2 shows the intensity values for the two peaks of Fe_2O_3, the 2θ values of Fe_2O_3 where compared with 2θ values of the coatings. Peaks, which appear at 86.34°, 87.84° for Fe_2O_3 do not appear in the diffractogram of the coatings. The peak with 82% relative intensity which appears at 63.94° for Fe_2O_3 is not to be seen with the coatings obtained at 300° and 400°C but appears in the diffractogram of the deposit obtained at 500°C. Likewise the peak at 52.56° of the coating obtained at 500°C is in close agreement with a peak at 51.42° with a relative intensity of 70.84% for Fe_2O_3 this shows the possible inclination of the coating obtained at 500°C to have a separate phase of Fe_2O_3.

Table 5.2 showing the relative intensities of the peaks of the standard Fe2O3 and for the coatings obtained at various temperatures.

Fe_2O_3		300°C		400°C		500°C	
2θ	Relative Intensity (%)	2θ	Relative Intensity (%)	2θ	Relative Intensity (%)	2θ	Relative Intensity (%)
35.35	100	82.43	100	35.44	100	35.66	100
55.20	87.89	65.09	73.31	62.51	66.83	62.66	71.76
100.77	86.34	44.71	30.21	82.41	55.88	82.53	71.22
63.94	82.51	35.12	45.19	57.03	50.77	64.22	63.90
84.45	73.67	59.68	41.67	43.03	32.78	57.11	50.89

As said earlier the objective of this experiment is to get the coating of zinc ferrate (III) on the substrate. From the above discussions it is clear that the coating obtained at various temperatures does not contain ZnO or Fe_2O_3 in a separate phase (except the coating obtained at 500°C). In order to find whether the coating obtained is the expected Ferrite coating or not, the peak positions of the coatings were compared with the peak positions of the zinc ferrate (III). Table 5.3 shows the peak positions of the zinc ferrate (III) and the coatings obtained at various temperatures. The values shaded in light gray indicate the match to the zinc ferrate (III)'s d-value given in the first column.

Table 5.3 showing the relative intensities of the peaks of the standard zinc ferrate (III) and for the coatings obtained at various temperatures.

Zinc Ferrate (III)		Substrate temperature					
		300°C		400°C		500°C	
d-value (Ang)	Relative intensity (%)	d-value (Ang)	Relative intensity (%)	d-value (Ang)	Relative intensity (%)	d-value (Ang)	Relative intensity (%)
2.54	100	1.16	100	2.53	100	1.48	100
1.49	80	1.43	73.31	1.48	66.83	1.45	71.76
1.62	70	2.02	60.21	1.16	55.88	2.51	71.22
2.99	50	1.61	52.19	1.61	50.77	1.44	63.9
1.09	50	2.55	45.19	2.10	32.78	1.61	50.89
2.11	40	1.54	41.67	2.02	28.89	2.09	37.78
1.72	40	2.64	29.36	1.43	27.56	2.02	36.61
1.28	40	1.84	28.28	0.94	27.3	1.51	34.34
0.97	40	1.75	27.57	2.96	25.25	1.71	32.14
1.12	30	0.97	24.5	0.94	24.01	1.43	30.36
1.05	30	3.27	22.24	1.88	23.28	2.95	29.31
0.86	30	5.45	21.3	1.38	23.28	2.25	27.95
4.85	20	5.33	19.49	2.42	22.56	1.09	27.28
1.33	20	4.70	18.9	1.71	21.86	2.85	25.96
0.88	20	7.4	12.33	2.70	19.36	1.16	25.96
0.81	20	7.12	11.41	1.09	16.81	1.73	24.68
2.43	10	6.49	11.41	3.67	16.4	1.00	23.13
1.27	10			4.29	15.41	3.27	19.04
0.83	10			0.96	14.25	5.34	13.65
				4.34	12.08	4.38	13.65
				3.10	9.15	4.44	13.41
				6.16	7.7	7.17	12.05
				6.77	6.76	4.82	11.4

Counting the number of peaks close to the zinc ferrate (III) value show the similarity between the standard and the coatings under investigation. Thus coating obtain at 300° has 4 peaks, 400°C has 8 and 500°C has 9 peaks close to the standard. This quantitative studies show that the coating obtained at 500°C is most likely the Ferrite when the intensities were matched with that of the zinc ferrate (III), the coating obtained at 400°C is found to be close to that of the zinc ferrate (III). When the d-value of the peaks with highest reflection intensity of the standard is compared with the d-value of the coatings, the coating obtained at 400°C is found to be close than the coating obtained at 500°C.

5.2 EDAX analysis

Figures 5.14, 5.15 and 5.16 shows the EDAX results for the coatings obtained at various substrate temperatures. From the plots it is clear that the concentration of zinc decreases with increase in the substrate temperature. The increase in the iron and oxygen in the coating with increase in substrate temperature indicates the possibility of the substrate getting oxidized. Since the concentration of the iron and zinc in the feed is kept constant, the excess iron should have come from the substrate.

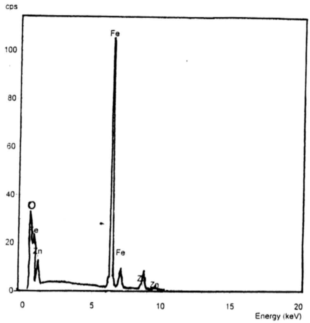

Figure 5.14 EDAX results of mixed oxide coating obtained at 300°C

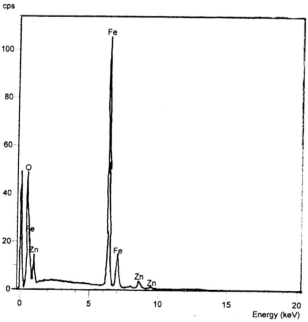

Figure 5.15 EDAX results of mixed oxide coating obtained at 400°C

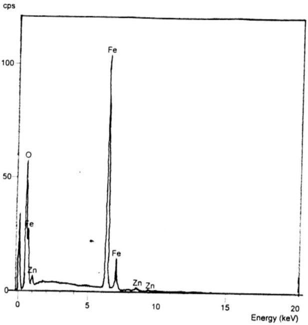

Figure 5.16 EDAX results of mixed oxide coating obtained at 500°C

Table 5.3 gives the atomic percentage of zinc, iron and oxygen in the coating thus obtained at various temperatures.

Table 5.3 Changes in atomic percentage of zinc, iron and oxygen in the coating with increase in temperature.

Element	Substrate temperature		
	300°C Atomic %	400°C Atomic %	500°C Atomic %
Zinc-Nickel	6.02	4.20	0.79
Fe	65.66	60.42	31.18
O	28.32	35.38	68.02

The increase in oxygen concentration with increase in the substrate temperature indicates the increased oxidation of the starting materials. At 500°C the oxygen concentration is very high favoring most probably the process of formation of separate phases of iron oxide either from the substrate or from $FeCl_3$.

5.3 SEM micrograph analysis

Figures 5.17 to 5.19 show the SEM micrograph of the deposit obtained at 300°, 400° and 500°C respectively. From the SEM micrograph the morphological changes with respect to the deposition temperature is very clear. Spheres of uniform dimension could be seen scattered all over the surface of the substrate as shown in Fig. 5.17.

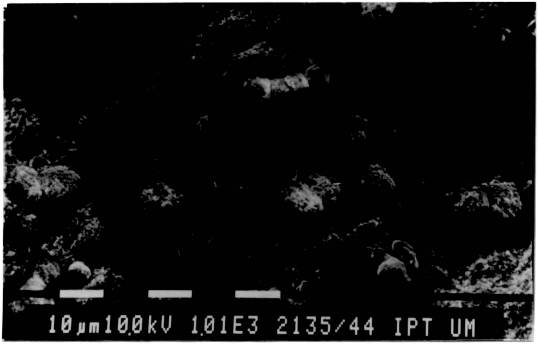

Figure 5.17 SEM micrograph of the mixed oxide coating obtained at 300°C.

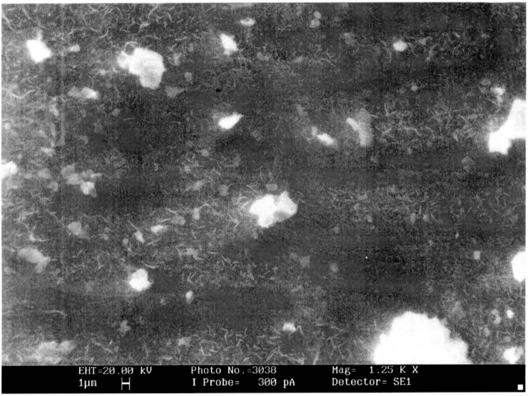

Figure 5.18 SEM micrograph of the mixed oxide coating obtained at 400°C

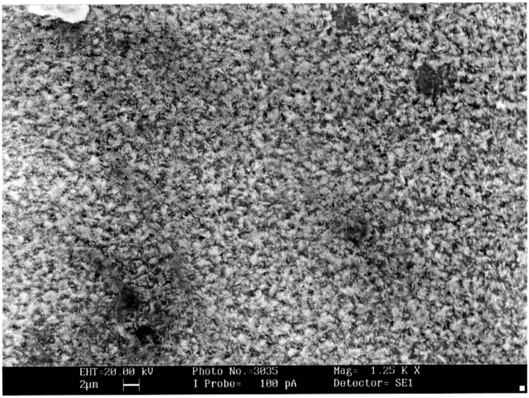

Figure 5.19 SEM micrograph of the mixed oxide coating obtained at 500°C.

Closer examination of the substrate where there is no spherical deposits reveals needle like or long fibrous fine structure, which were again seen on the surface of the sphere at higher magnification (Fig. 5.20). This indicates that the area on the substrate where there is no sphere is still coated with the same material. The surface is not uniformly covered with the spheres due to method of deposition, in order to maintain the substrate temperature at the experimental condition; the feed stock was sprayed in pulses with few seconds interval. At the end of one single pulse the temperature of the substrate will go down resulting in a layer of the oxide rather than a spherical particulate.

Figure 5.20 SEM micrograph at higher magnification of the mixed oxide coating obtained at 300°C

Figure 5.18 and 5.19 show the SEM micrograph of the coating obtained at 400 and 500°C. The coating obtained at 400°C has fewer spheres and it is wide spread, there is reduction in the diameter of the sphere and few clusters of improper shapes could also be seen. SEM micrograph of this coating, at higher magnification (Fig. 5.21) shows the morphology, which is similar to the coating obtained at 300°C.

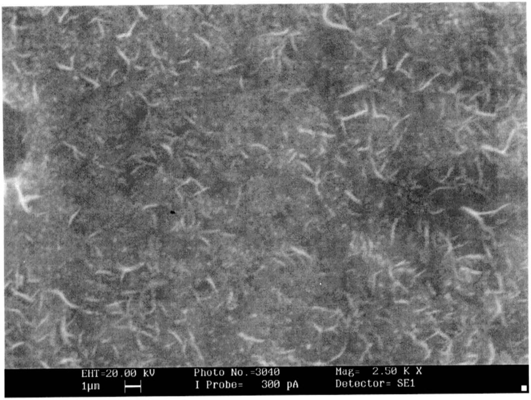

Figure 5.21 SEM micrograph at higher magnification of the coating obtained at 400°C

At low magnification of the coating obtained at 500°C, the coating is continuous and the spheres are of uniform in shape. The uniform shape and even distribution of the spheres is due to the increase in substrate temperature. At this high temperature the droplets were given no time to have a free flow or film formation thus resulting in morphology like this. Fig. 5.22 shows the magnified view of the coating obtained at 500°C.

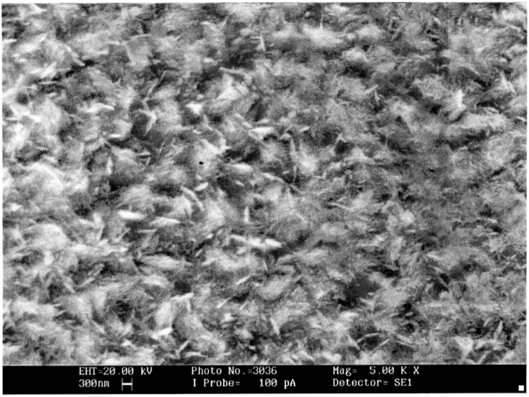

Figure 5.22 SEM micrograph at higher magnification of the coating obtained at 500°C.

5.4 IMPEDANCE ANALYSIS

The protective property of the coatings obtained by spray pyrolysis was evaluated by electrochemical impedance spectroscopy method as discussed in chapter 2. The electrolyte used in the study was 3% NaCl solution. The impedance data were collected periodically until the coating fails. Since the coating obtained by this method acts like a barrier coating the sudden drop in resistance of the system gives an indication that the coating has lost its property.

Figure 5.23 to 5.25 shows the Cole-Cole plot for the coatings obtained at substrate temperature 300, 400 and 500°C respectively, one hour after the addition of electrolyte to the cell which is considered as t=0. The resistance value calculated from the Cole-Cole plot at t=0 are 300°C=2.5 M ohm, 400°C = 1 K ohm and 500°C = 4 K ohm. The low resistance offered by the coating at 400°C is still not understood, since the trend changed after prolonged wetting time. The coating obtained at 300°C gives the better protection is evident from initial resistance itself. After 24 hours of wetting time the data were collected and plotted as shown in Fig. 5.26 to 5.28. The resistance offered by the coating at 300°C still remains higher than the other coatings. The coating obtained at 400°C shows the Warbug impedance-diffusion parameter. After 48 hours of immersion, the coating obtained at 500°C failed which can be noted by the drop in resistance of the system 300 Ω from 4 K Ω (t=0). Where as the coating obtained at 300°C still remains on the higher side, while the coating obtained at 400°C remained at 600 K Ω. Though the SEM micrograph and EDAX results favor more for the increase in the protective property for the coating obtained at 500°C. Since the increase in oxygen concentration with iron leads to increase in formation of iron oxide, whish is a well know for its barrier properties. The failure of the coating could be because, during the process of deposition, when the droplets enters the reaction zone of the furnace the reaction gets accelerated and the material on the surface of the droplet attains completion whilst the material in the core of the droplets experiences a deceleration. This proposed mechanism happens when the temperatures where between 600 to 800°C. Hence the coating at 500°C experience a premature failure despite of the high iron and oxygen content in the coating (iron oxide and zinc oxide are well know passivators).

Figures 5.29 to 5.31 shows the Cole-Cole plot for the deposits obtained at 300, 400 and 500°C respectively after 168 hrs of test. Coating obtained at 500°C has almost reached the solution resistance while the Warbug (diffusion) part of the impedance of the deposit obtained at 400°C disappeared and the diffusion process is complete. Resistance of the system dropped down to 100 Ω reaching close to the metal-solution interfacial resistance. After 192 hours of exposure the coating obtained at 300°C showed a resistance more than 1MΩ but red rust started appearing. Compared with the coatings appeared at other temperatures the coating obtained at 300°C gives better protection. Though the coating obtained at 400°C is zinc ferrate (III) the protective property of the coating is not well exhibited because of the morphological changes. Also it should be noted that the protective property of the coating is decreases with decrease in concentration of zinc. In spite of the increase in concentration of oxygen with increase in temperature indicating the increased concentration of metal oxides in the coating the performance of the coating obtained at higher temperatures is not satisfactory due to the superficial oxidation leaving soft and loose material in the core.

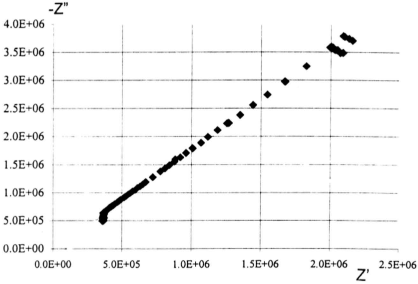

Figure 5.23 Cole-Cole plot for coating obtained at 300°C, one hour after the addition of electrolyte

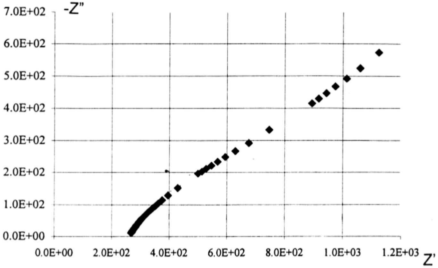

Figure 5.24 Cole-Cole plot for coating obtained at 400°C, one hour after the addition of electrolyte

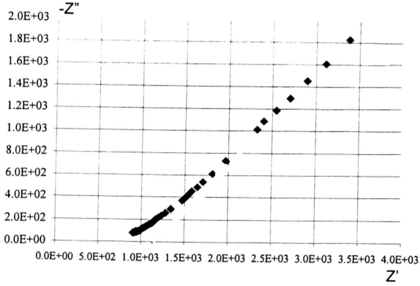

Figure 5.25 Cole-Cole plot for coating obtained at 500°C, one hour after the addition of electrolyte

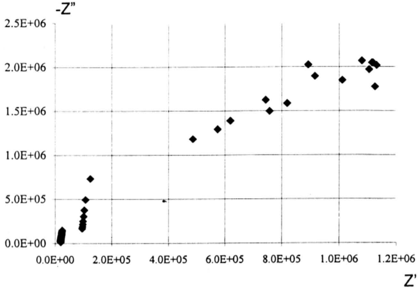

Figure 5.26 Cole-Cole plot for coating obtained at 300°C, after 24 hours

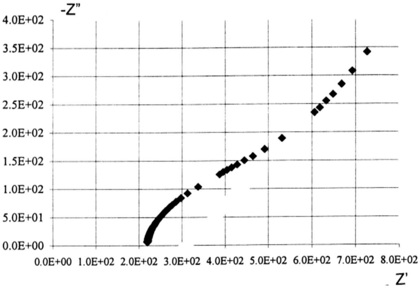

Figure 5.27 Cole-Cole plot for coating obtained at 400°C, after 24 hours

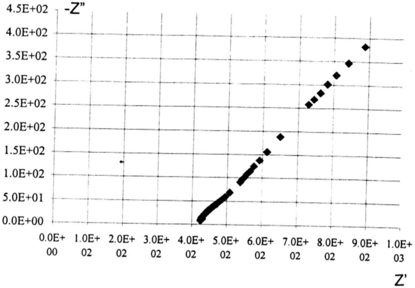

Figure 5.28 Cole-Cole plot for coating obtained at 500°C, after 24 hours

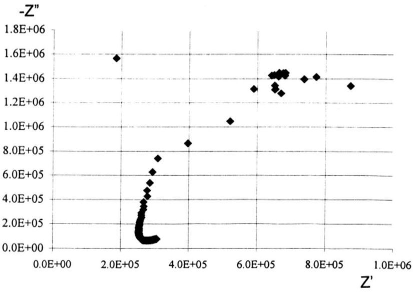

Figure 5.29 Cole-Cole plot for coating obtained at 300°C, after 168 hours

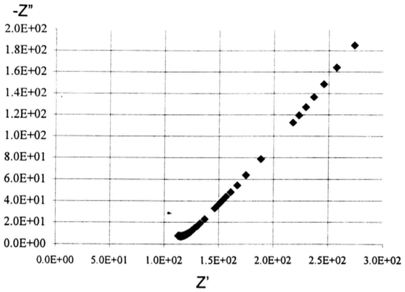

Figure 5.30 Cole-Cole plot for coating obtained at 400°C, after 168 hours

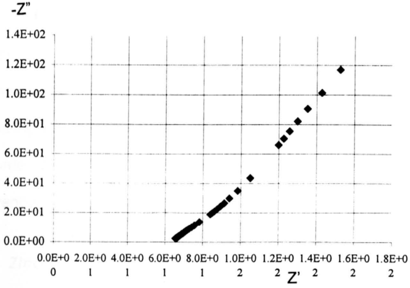

Figure 5.31 Cole-Cole plot for coating obtained at 500°C, after 168 hours