MANAGER'S SUMMARY
ZCO-45-5, "Investigation of Advanced Zinc-Based Coatings"

Progress Report No. 1 - March 2008-November 2008
Issued: December 2008

The objectives of this program is to determine the possible contribution of complex surface or gradient layer coatings, either metallic or compound in form, to improve corrosion resistance of zinc-based automotive coatings. From the initial list of seven alloying elements to combine with zinc, six were chosen and additionally pure zinc, Zn-Al and Zn-Mg alloys were produced to serve as references. Two different compositions of each of these alloys have been produced with the exception of Zn-Ca and Zn-Li, for which one composition was produced. We are grateful to Salzgitter Mannesmann Forschung who donated the steel substrates used in production of these coatings. Simultaneous evaporation from two evaporators was used to produce the alloy coatings together with argon ion beam acceleration.

All coatings smoothed the initial cold rolled surface, which had surface roughness levels between 2 and 4 microns with maximum roughnesses of 8 microns. X-ray photo electron spectroscopy (XPS) was used to characterize the compositions of the produced coatings. For the Zn-10% Mg alloy, a 10.8 wt.% Mg coating was produced. Challenges were realized in analyzing some of the other coatings. The 1% Ti sample was found to contain between 2 and 6 wt.% Ti whereas for the 10% Zr sample, 14.8 wt.% was found. For the 1% Zr sample, no Zr could be detected. For the 2% Li sample, a composition around 4.2% Li was obtained. The composition of other samples has yet to be determined.

We are also grateful to the coaches who have agreed to assist with their expertise on this project. In view of the variable results seen in the compositions obtained, it was correct to use a larger number of panels together with fewer alloys.

The next stage of work is to assess the corrosion resistance of these panels at French Corrosion Institute.

1/09

Investigation of Advanced Zinc-Based Coatings

Project ZCO-45-5

Semi-annual report
March 2008 - November 2008

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Content

1. Summary

This report gives an overview of the work which was done at Limedion Ltd., Mannheim, and at the French Corrosion Institute, Brest in the period between March 2008 and November 2008 within the Project Nr. ZCO-45-5.

The previous program ZCO-45-3 was finished at the beginning of 2008 and its main results were that many of the investigated Zn-PVD coatings combined with eighter interlayers between substrate and main layer or alloying the zinc with different metals or a thin toplayer on the main protection layer bring a substantial gain in corrosion resistance of the applied steel. The interlayers consisted of Ti, the alloying materials were Mg, Ti and Mn and the the top-layers consisted of Mn. All of the three approaches turned out to be beneficial for the cathodic protection of the substrate. Detailed results can be found in previous reports on ZCO-45-3. Based on these results and on the finding, that the conductivity of the protecting layer influences the corrosion resistance, the program ZCO-45-5 was established. It is a joint research project between French Corrosion Institute, Brest, Limedion and industrial partners.

The objective of this program is to determine if improvements in performance of automotive steels with zinc-based protective coatings on them can be obtained with complex surface or gradient layer coatings involving constituents that are in either metallic or compound form. These are expected to be of lower coating mass than presently utilized. These may include combinations of relatively reactive elements such as Li, Ca, and Mg or passivating elements like Ti, Cu, Al, Mn, Zr or Cr. The scope of the project includes fabrication of such coated steels together with assessment of their corrosion and formability properties. Also a mechanistic study on the nature of the improvement in corrosion resistance of these new coatings is included in the scope.

Before the GAP meeting, March 2008 in Brussels coating alloys (task A1) were identified by Limedion and French Corrosion Institute. During discussions at the GAP meeting, it turned out, that it is desirable to have a higher amount of samples per system, for this reason the originally planned number of panels was increased whereas the number of systems to be coated and tested was reduced. Additionally, a group of coaches was assigned to support the project from both scientific and industrial point of view. The coaches will receive short status reports approximately every two months or on demand.

According to the time schedule (task A2) all of the planned coatings were produced. Characterization (A3) such as XPS, confocal and electron microscopy, adhesion tests, conductivity tests are ongoing. By the end of November 2008, samples will be sent to the French Corrosion Institute for corrosion tests and to Corus Ijmuiden for GDOES measurements and for cup drawing of some of the panels. After formation of the panels at Corus, they will be sent to the French Corrosion Institute for further corrosion tests (A4)

2. A1: Identification of promising alloying elements

The following elements to form alloys with Zn were proposed: lithium, zirconium, cerium (or other lanthanides), scandium, manganese, titanium and calcium. In order to reduce the amount of systems originally proposed, finally the elements Li, Zr, Ce, Mn, Ti and Ca in different concentrations were chosen. Additionally a pure Zn layer and ZnAl and ZnMg alloys will be deposited and serve as reference. The number of panels was determined at the GAP meeting in Brussels, March 2008. The following table gives an overview of the alloys, composition and total number of samples.

Alloy	Weight % 1	Weight % 2	Weight % 10	Approx. cost of alloying metal $/kg
ZnMg	–	6	6	3
ZnAl	–	6	6	3
ZnLi	–	6	–	2
ZnZr	6	–	6	25
ZnCe	6	–	6	125
ZnMn	–	6	6	1
ZnTi	6	–	6	21
ZnCa	–	6	–	4

Table 1: Number of samples and alloy composition

2.1 Coaching

The following coaches were assigned to support ZCO-45-5: Raj Singh, U. S. Steel, Gerhard Angeli, Voestalpine, Margot Vlot, CORUS, and Gabriel Cervellini, Ternium. The coaches were informed at the end of July about substrates, cleaning procedure, short information about the deposition process and the coating thickness. The following suggestions were received:

- Defined procedure for cutting panels
- ICP of dissolved coatings
- Rinsing the panels with distilled water in ultrasonic bath after cleaning with basic cleaner
- GDOES depth profiling
- Selection of corrosion tests
- Cross-cut analysis of panels after testing

3. A2: Substrates, samples preparation and coating procedure

Cold-rolled steel, supplied by Salzgitter, was used as substrates. The following table provides the composition. Different sample sizes and additionally silicon substrates were coated for different tests. 100 x 100 mm steel panels were coated for corrosion tests, 10 x 10 mm steel for XPS, SEM, Laser Confocal Microscopy, 30 x 30 mm steel for adhesion tests and Si-substrates for thickness measurements on cross breaks.

Cold Rolled Drawing Qualities (Mild Steel)											
Euronorm	Germany	UK	USA								
EN 10139	DIN 1624	BS 1449	ASTM	%C	%Mn	%Si	%S	%P	%Al	%Cr	% other
DC04	St4	CS1	SAE 1006	.03 - .06	.18 - .40	.02 max	.02 max	.02 max	.02 - .06	-	-

The substrates were pre-cleaned before coating. First they were cleaned in a mixture of acetone/2-propanol (1/10) in an ultrasonic bath for 10 minutes. Then they were put in 10% Hakupur solution (Kluthe Heidelberg, degreasing cleaner, KOH containing) in ultrasonic bath for 30 minutes. After that they were rinsed in dest. water in ultrasonic bath for 5 minutes. This cleaning procedure was followed by the immediate transfer into the IBAD chamber. Before closing chamber the substrates were dust-cleaned with nitrogen. The IBAD system is described in earlier projects e.g. ZCO-45-3. However, a third 10 kW electron beam evaporator was added for the deposition of ternary alloys. When pressure in the chamber

was < $8*10^{-6}$ mbar, the surface of the samples was sputter cleaned with Argon ions for 15 minutes.

Then the metals were evaporated from two electron beam evaporators under simultaneous ion bombardment. So far, Zn is evaporated from the 6 kW evaporator, Mg from the 2 kW evaporator and other alloying elements (Ti, Zr and Li) from the 10 kW evaporator. The coating thickness is aimed to be 5 µm.

The evaporation rates are controlled by oscillating quartz crystals above each evaporator. However, Zink evaporate very easily, even gets to the other quartz crystals and contributes to their measurements. Therefore it is impossible to read an exact deposition rate of the alloying element during deposition. The deposition rate of the alloying element is measured before Zink evaporation. During the co-evaporation this deposition rate is adjusted.

The following table shows the samples and deposition parameters produced so far.

Sample	Pbase [mbar]	Pdep [mbar]	Jion [µA/cm2]	ion energy [eV]	rateZn [Å/s]	rateMe [Å/s]
Zn	6.5*10-6	7.5*10-5	19	1500	40	
ZnMg (10 wt%)	7.5*10-6	7*10-5	15	1500	200	18
ZnTi (10 wt%)	1.5*10-5	9*10-5	20	1500	200	120
ZnTi (1 wt%)	1.3*10-5	9*10-5	12	1300	200	15
ZnZr (10 wt%)	1.3*10-5	9*10-5	12	1200	200	80
ZnZr (1 wt%)	1.5*10-5	9*10-5	12	1450	200	8
ZnLi (2 wt%)	1.5*10-5	9*10-5	12	1450	200	54
ZnMn (1 wt%)	1.5*10-5	9*10-5	12	1450	200	20

Table 2: samples produced so far

4. A3: Initial characterization

So far, XPS and microscopy started. The surface of the pure substrate was imaged with the confocal microscope to get information about surface roughness.

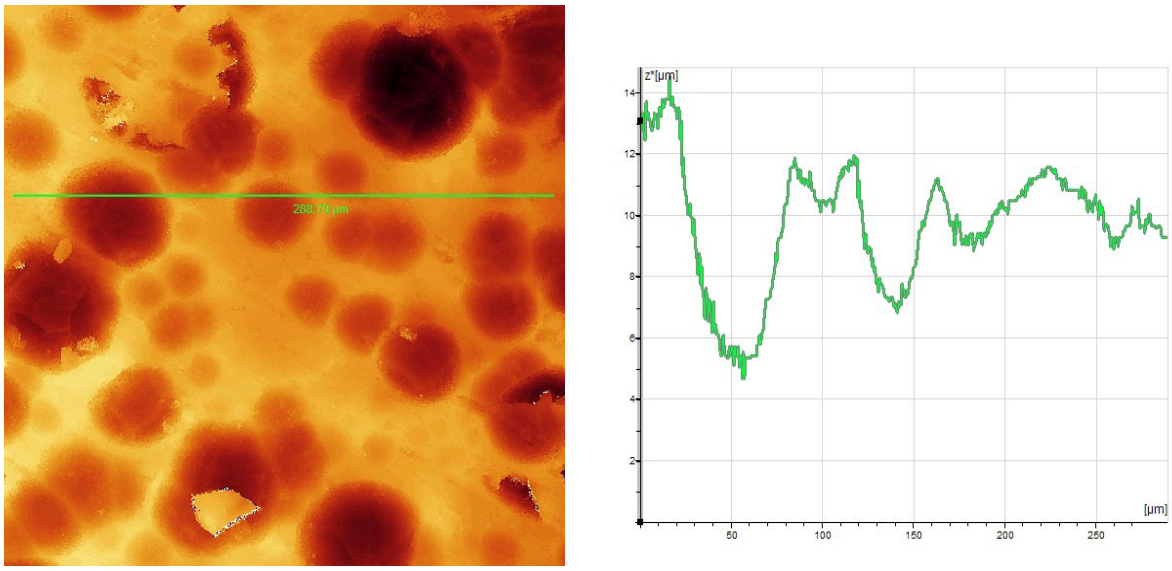


Figure 1: surface roughness of the substrate

The surface roughness seems to be mainly between 2 – 4 µm, however rough areas up to 8 µm were measured as well.

The coated substrates show smoother surfaces

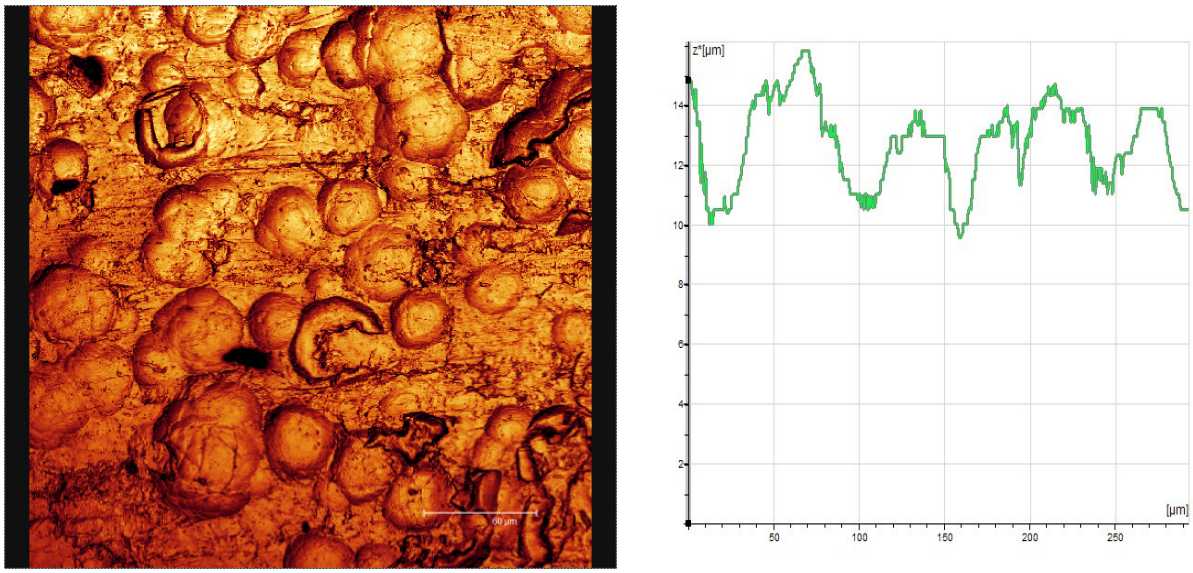


Figure 2: surface roughness of ZnTi coating

XPS results

XP spectra were recorded before and after sputtering. Before sputtering a large amount of carbon and oxygen is present due to adsorbed carbon and oxygen at the surface. Sputtering with argon ions removes the adsorbed carbon and oxygen and gives the coating composition.

This is illustrated in table 4 for the ZnTi 10% system. So far, for almost all coatings Xp-spectra were taken to get information about the composition. For low concentrations 1 and 2 wt % the error bars might as high as 50 %, but this will be discussed later.

For the ZnMg alloy, 10 wt% aimed, the XP spectra show a good agreement, see figure 3. The atomic ratio Zn:Mg 75.5 at% : 24.5 at% corresponds to 89.2 wt% . 10.8 wt%

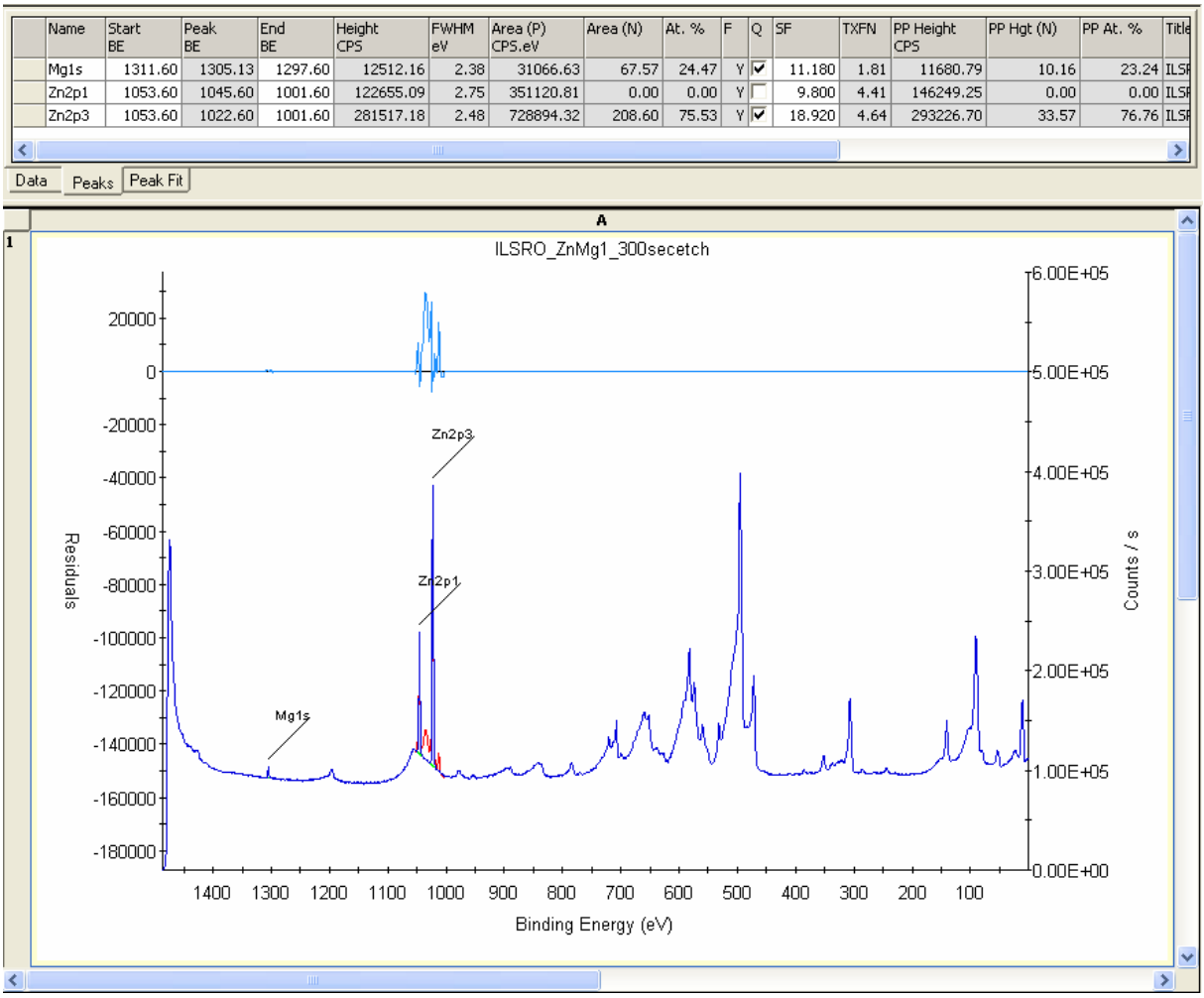
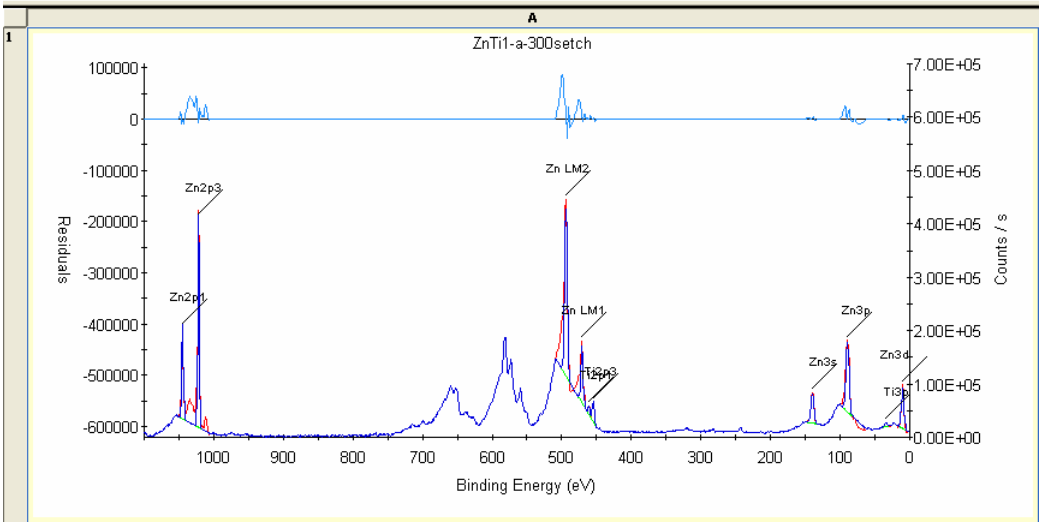


Figure 3: XP spectra and peak table of ZnMg coating, 10 % Mg aimed

In figure 4 the XP spectra of ZnTi coatings are shown: 10% Ti aimed above, 1% Ti aimed below. The peak table above gives the composition in atomic % as well as weight %.
The titanium concentration in the low concentration alloy has to be considered carefully: first the titanium signal rides on a shoulder of much more intense Zn Auger-peaks. Second the signal consists of a duplet, which makes peak fitting more error-prone. Therefore the titanium concentration for this sample can be in the range of 2 to 6 wt%.

	Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N)	At. %	F	Q	SF	TXFN	PP Height CPS	PP Hgt (N)	PP At. %
	Zn2p1	1052.00	1044.81	1004.00	181123.17	2.89	544668.62	0.00	0.00	Y	☐	9.800	4.42	205537.35	0.00	0.0
	Zn2p3	1052.00	1021.82	1004.00	405645.42	2.57	1084426.73	309.52	88.19	Y	☑	18.920	4.65	418841.08	11.95	89.6
	Zn LM2	509.34	494.00	450.23	313454.79	4.51	1472158.24	0.00	0.00	Y	☐	0.580	9.93	426531.21	0.00	0.0
	Zn LM1	509.34	471.00	450.23	105580.22	3.86	425063.85	0.00	0.00	Y	☐	0.170	10.16	161723.74	0.00	0.0
	Ti2p1	509.34	460.69	450.23	16806.69	3.05	53372.86	0.00	0.00	Y	☐	2.690	10.26	40735.27	0.00	0.0
	Ti2p3	509.34	454.71	450.23	38745.59	3.56	143551.28	41.45	11.81	Y	☑	5.220	10.32	47580.90	1.37	10.3
	Zn3s	150.00	139.89	131.00	54113.66	4.98	280744.89	0.00	0.00	Y	☐	1.040	13.47	58961.54	0.00	0.0
	Zn3p	100.00	89.44	62.00	134132.02	5.24	732392.42	0.00	0.00	Y	☐	2.828	13.97	168654.09	0.00	0.0
	Ti3p	46.00	34.35	26.00	7095.35	5.55	41008.27	0.00	0.00	Y	☐	0.813	14.52	11669.09	0.00	0.0
	Zn3d	19.00	10.04	2.00	75116.60	4.27	334209.13	0.00	0.00	Y	☐	0.810	14.77	89543.41	0.00	0.0

Data | Peaks | Peak Fit



	Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N)	At. %	F	Q	SF	TXFN	PP Height CPS	PP Hgt (N)	PP At. %	T
	Zn2p1	1069.00	1045.00	1003.00	143548.84	3.13	467909.56	0.00	0.00	Y	☐	9.800	4.42	153546.39	0.00	0.00	Z
	Zn2p3	1069.00	1022.00	1003.00	300825.72	2.59	811239.61	231.69	94.10	Y	☑	18.920	4.65	305940.94	8.74	94.49	Z
	O1s	548.00	494.63	484.00	271541.56	5.00	1415635.21	0.00	0.00	Y	☐	2.930	9.92	304746.19	0.00	0.00	Z
	C1s	292.00	284.96	278.00	8377.16	4.72	41238.16	0.00	0.00	Y	☐	1.000	12.02	10521.90	0.00	0.00	Z
	Ti2p1	462.00	459.70	452.00	8995.25	2.15	20152.74	0.00	0.00	Y	☐	2.690	10.27	24517.67	0.00	0.00	Z
	Ti2p3	462.00	455.84	452.00	11310.99	4.26	50254.89	14.54	5.90	Y	☑	5.220	10.31	17604.38	0.51	5.51	Z

Data | Peaks | Peak Fit

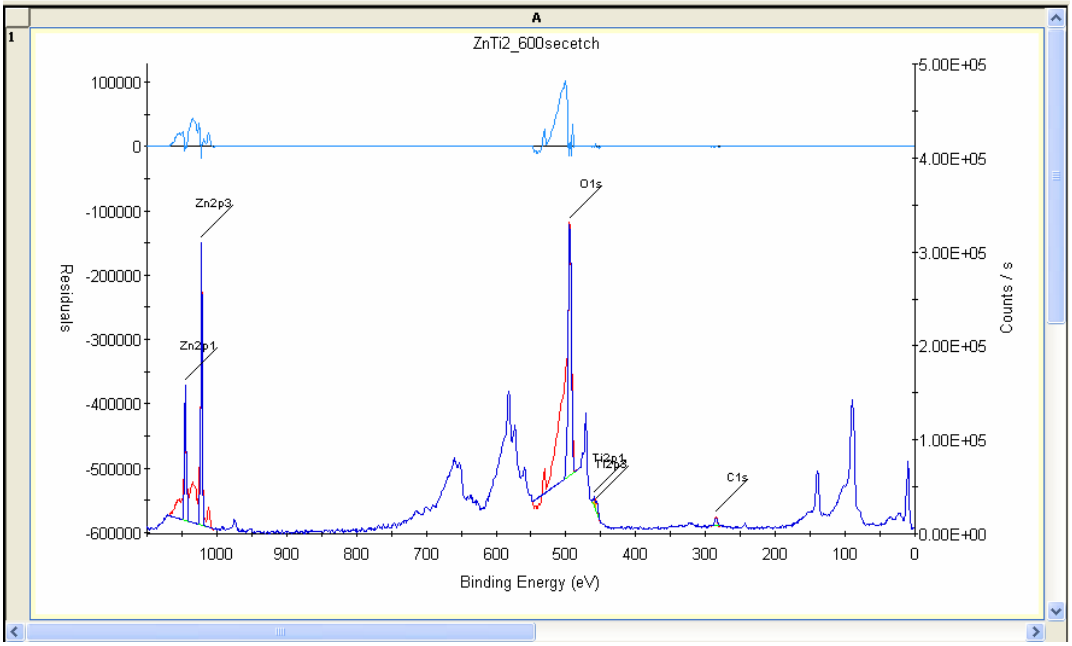


Figure 4: XP spectra and peak table of ZnTi coating 10 % Ti aimed above, 1% aimed below

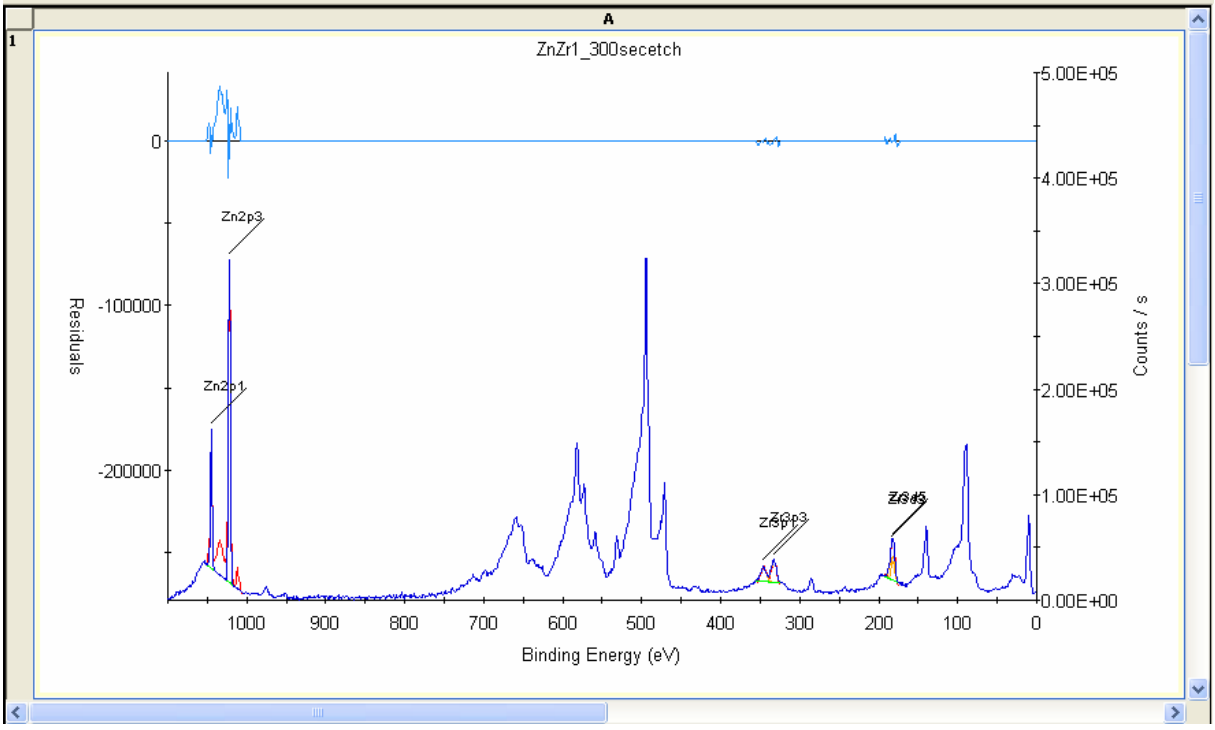
Sample	Zn at. %	Zn wt. %	Ti at. %	Ti wt. %	O at. %	C at. %
ZnTi 10% before sputtering	20.8		2.8		45.8	30.6
ZnTi 10% after 5 min. sputtering	88.2	91.1	11.8	8.9	0	0
ZnTi 10% after 10 min. sputtering	85.5	89	14.5	11	0	0
ZnTi 1% after 10 min. sputtering	94.1	95.6	5.9	4.4		

Table 3: composition of ZnTi coating before and after sputtering

For the the ZnZr alloy 10% aimed an atomic ratio Zn : Zr 88.92% : 11.08% is measured which corresponds to a 85.2 wt% : 14.8 wt%, see figure 5 above. For the low concentration of 1 wt% Zr no zirconium at all could be detected, figure 5 below.

	Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N)	At. %	F	Q	SF	TXFN	PP Height CPS	PP Hgt (N)	PP At. %	Tit
	Zn2p1	1052.00	1045.00	1004.00	131480.94	2.79	382394.85	0.00	0.00	Y	☐	9.800	4.42	155409.89	0.00	0.00	Zn
	Zn2p3	1052.00	1022.00	1004.00	305597.84	2.56	814133.81	232.51	88.92	Y	☑	18.920	4.65	316131.27	9.03	89.38	Zn
	Zr3p1	355.00	346.00	324.00	14191.54	8.16	120606.09	0.00	0.00	Y	☐	2.640	11.41	16644.98	0.00	0.00	Zn
	Zr3p3	355.00	333.00	324.00	21120.54	7.59	167021.35	0.00	0.00	Y	☐	5.140	11.54	22760.13	0.00	0.00	Zn
	Zr3d5	193.00	181.87	173.00	22250.97	5.03	116704.41	28.98	11.08	Y	☑	4.170	13.05	43188.57	1.07	10.62	Zn
	Zr3d3	193.00	183.55	173.00	20034.41	7.10	148187.95	0.00	0.00	Y	☐	2.870	13.03	36654.89	0.00	0.00	Zn

Data | Peaks | Peak Fit



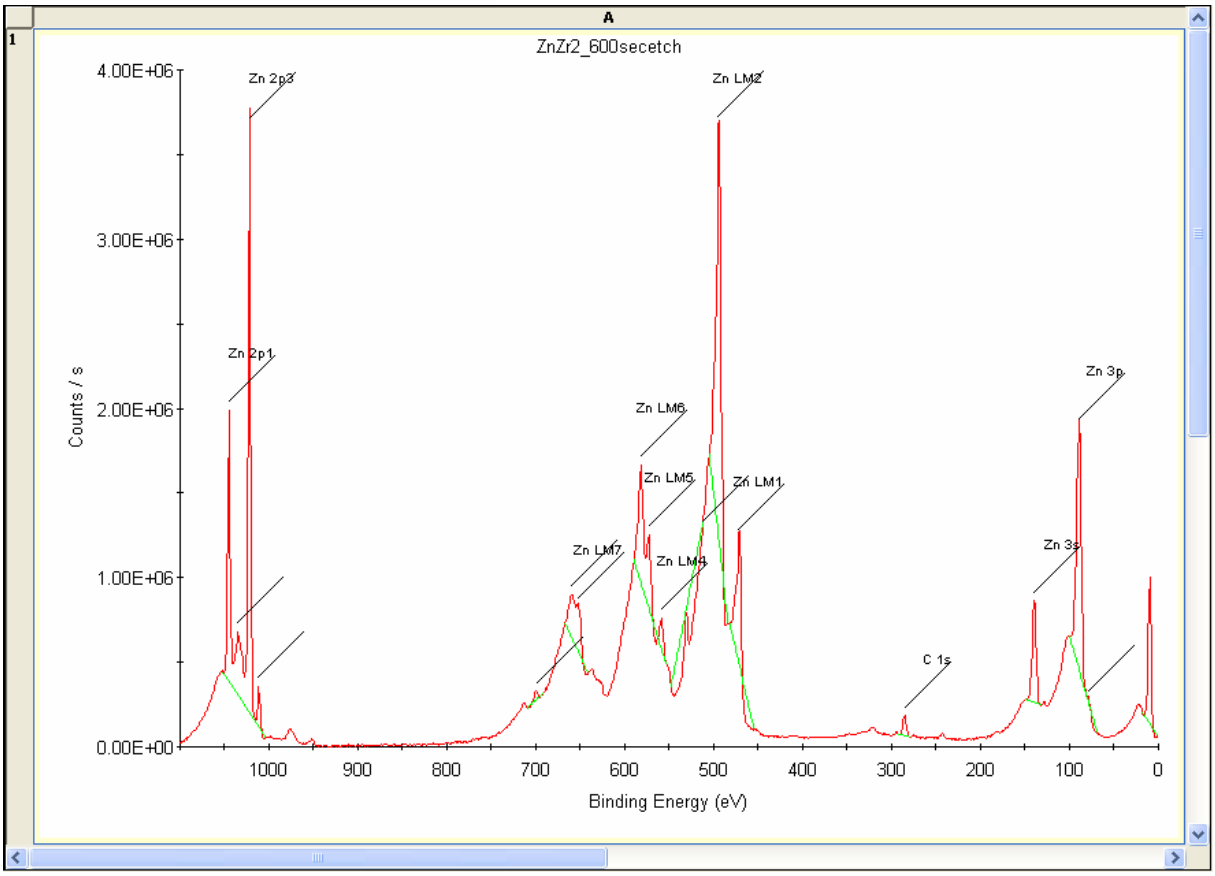


Figure 5: XP spectra and peak table of ZnZr coating 10 % Zr aimed above, 1 % Zr aimed below

Lithium shows only one XP-signal, the 1 s peak, which is located at 55 eV. Since the signal to noise ratio is low (see fig. 6 below) and the sensitivity factor of the Li 1s signal is very small, 0.057 compared to 18.92 of, the error bar for the Li concentration is pretty high. The sample certainly contains lithium, but this system is a candidate for further exploration if the corrosion tests show good results. The atomic ratio of 29.5% to 70.5% (Li to Zn) corresponds to a weight ratio of 4.2% to 95.7%.

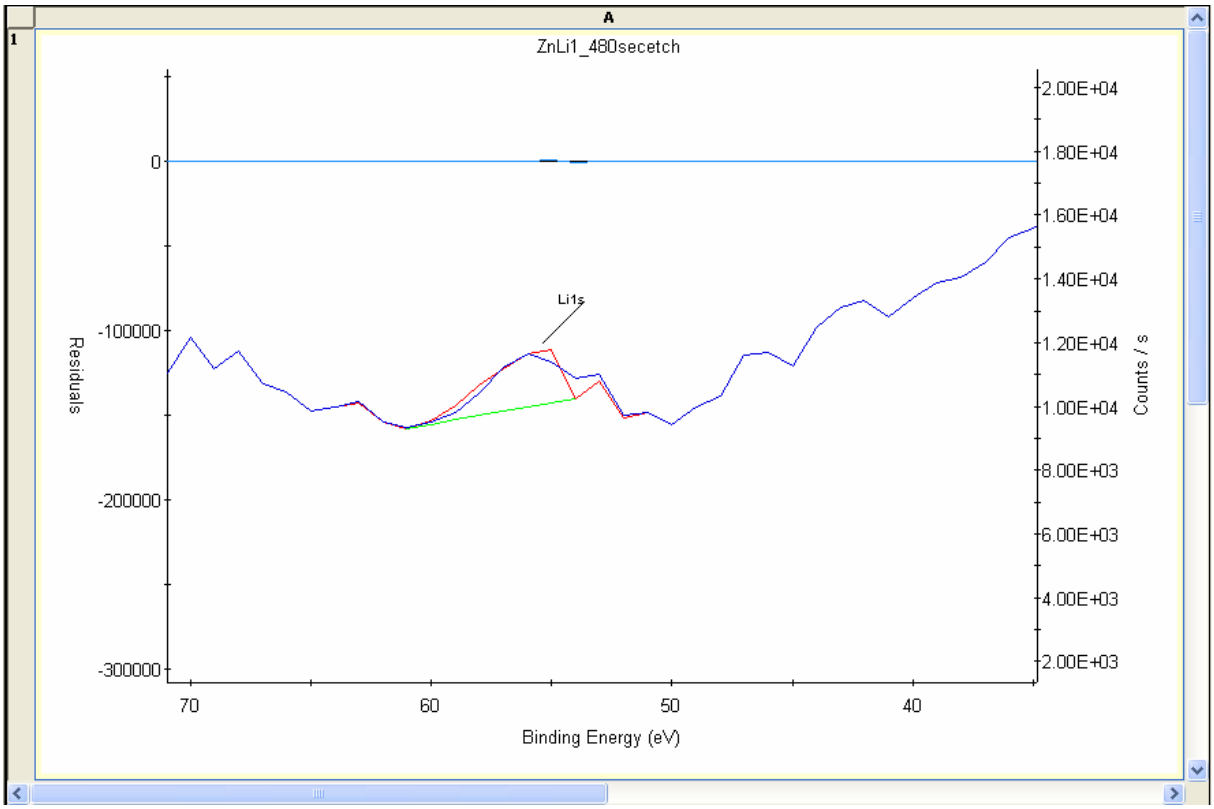


Figure 5: XP spectra and peak table of ZnZr coating 10 % Zr aimed above, 1 % Zr aimed below

So far, for the Zn/Mn system the 1% Mn sample is deposited and a XP spectrum of this sample is taken. For manganese the 2p signals are expected at 638,7 eV (2p3) and 649.7 eV (2p1). On the shoulder of the Zn LM Auger peak there two signals can be observed, see figure 6. However, they are located 2 eV above the energy of the Mn 2p peaks. To clarify the origin of these two peaks, a spectrum of Zn from the evaporator was taken as reference. This reference showed these peaks as well and therefore they cannot be identified as Mn. The coating with a higher Mn concentration should show a clear Mn signal.

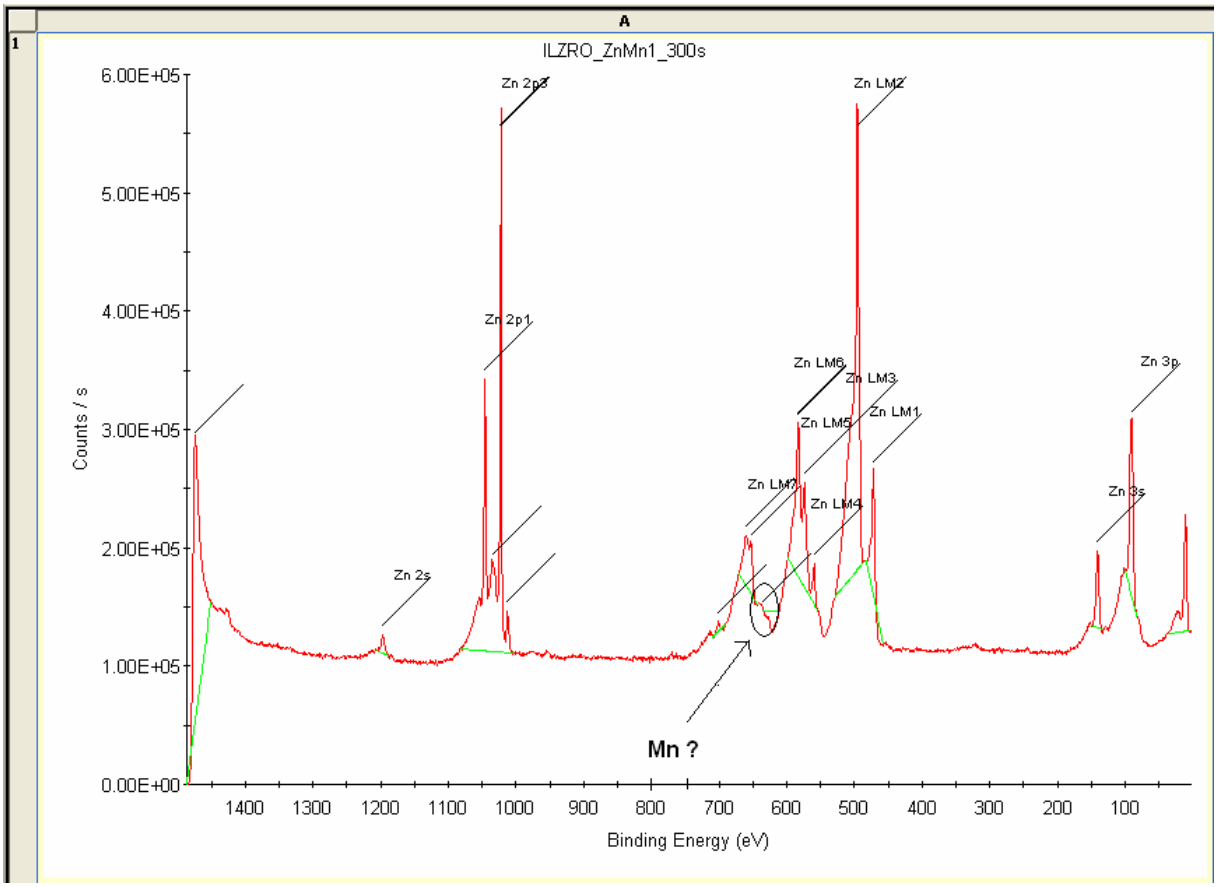


Figure 6: XP spectrum ZnMn coating 1 % Mn aimed

5. Outlook for the next 6 months

By the end of November 2008 all coatings planed in task A2 will be deposited and sent to the French Corrosion Institute and Corus for further corrosion testing. First corrosion tests are planned for December. At Limedion further XPS, SEM, adhesion tests and conductivity tests are ongoing and will be finalized until the next GAP-meeting in Aachen, May 2009. Stage B will start after selecting the most promising systems. Limedion will intensify coating production on the systems that showed the most promising results in corrosion tests and will begin with the production of ternary alloys.