

# Surface properties and protection of magnesium alloys

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## Abstract

Passivity in aqueous solution of Magnesium and its alloys and the possibility of obtaining corrosion resistant coating onto them depend on this element electrokinetic behaviour: Magnesium is much more active than the other light metals Aluminium and Titanium. This general behaviour is related to a parameter of electrochemical electronegativity for metals in aqueous solutions, the Normality-Inertia parameter  $P_{NI}$ . A high value of  $P_{NI}$  corresponds to inertia with high overvoltages for metal ion exchanges and low overvoltages for hydrogen exchange at the electronic surface; low  $P_{NI}$  values correspond to normality with reverse behaviour. The approach is extended to other reactions: oxide, sulphide, fluoride and chloride formation and related to the stability of fluorides at the Magnesium surface. The interpretative scheme is applied to corrosion and protection of the Magnesium alloys.

## Riassunto

La passività in soluzioni acquose del Magnesio e sue leghe e la possibilità di ottenere depositi resistenti a corrosione su di esse dipendono dal comportamento elettrocinetico di questo elemento: il Magnesio è molto più attivo degli altri metalli leggeri Alluminio e Titanio. Questo comportamento è correlato ad un parametro di elettronegatività elettrochimica per i metalli in soluzione acquosa, il parametro di normalità-inerzia  $P_{NI}$ . Un valore elevato di  $P_{NI}$  corrisponde all'inerzia con alte sovratensioni di scambio ionico e basse sovratensioni di scambio di idrogeno alla superficie elettrodica; bassi valori di  $P_{NI}$  corrispondono alla normalità con comportamento inverso. Il parametro è calcolato anche per altre reazioni: la formazione di ossidi, solfuri, fluoruri e cloruri e correlato alla stabilità dei fluoruri alla superficie del Magnesio. Lo schema interpretativo è applicato alla corrosione e protezione delle leghe di Magnesio.

## INTRODUCTION

The surface properties of Magnesium and its alloys in aqueous solution are reviewed, in order to understand the electrochemical passivity and the possibility of obtaining corrosion resistant coating onto them. Magnesium behaves much more actively than the other light metals with high negative electromotive force: Aluminium and Titanium, and this cannot be only related to its very low electromotive force, but also to its electrokinetic behaviour. In the following an electrokinetic parameter for ionisation of elements in aqueous solutions  $P_{NI}$  is presented describing elements Normality-Inertia, and extended to other reactions: oxide, sulphide, fluoride and chloride formation. The application of this interpretative scheme to the corrosion and protection behaviour of the Magnesium alloys permits to gain insight into this field, that is particularly difficult to approach.

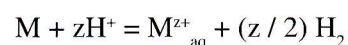
## THE NORMALITY - INERTIA PARAMETER $P_{NI}$

Ionic and lattice properties of the elements determine their electrokinetic behaviour in aqueous solutions. By means of a Born-Haber cycle it is possible to relate the enthalpy change for the metal exchange electrodic reaction to other fundamental physical quantities, independently measured, these are the atomic, ionisation and hydration enthalpies. We refer to an ideal galvanic chain:



of metallic and electrolytic conductors in series, homogeneous, with the only exception of the interphase regions of atomic dimension, with contact phases at equilibrium, chemical modifications arising only from current circulation and electromagnetic field not influenced from distribution of true charges; one part of the chain is the electrodic element and the other the reference Standard Hydrogen Electrode SHE.

The cell chemical reaction is:



and the corresponding electromotive force:

$$E^{\circ} = -(\Delta h^{\circ}_{\text{at}} + \Delta h^{\circ}_{\text{ion}} + \Delta h^{\circ}_{\text{hydr}} - T\Delta s^{\circ}_{\text{cell}}) / zF + K_{\text{SHE}}$$

where the cell enthalpy change is obtained from the three contribution to the Born-Haber cycle.

The standard hydrogen electrode constant  $K_{\text{SHE}}$  is determined from the enthalpy changes for  $\text{H}_2$  discharge,  $\Delta h^{\circ}_{\text{at,H}} = 2.2594\text{V}$ ,  $\Delta h^{\circ}_{\text{ion,H}} = 13.6626\text{V}$  and  $\Delta h^{\circ}_{\text{hydr,H}} = -11.3075\text{V}$ , where the value suggested by Halliwell e Nyburg<sup>1</sup> is assumed for the  $\text{H}^+$  hydration enthalpy and for the other enthalpy changes the values are those reported by Dasent<sup>2</sup>, Latimer<sup>3</sup> and Bard, Parsons e Jordan<sup>4</sup>; we obtain:  $K_{\text{SHE}} = 4.6142\text{V}$ . The cell enthalpy change, expressed in Volts and with reference to SHE, becomes:

$$\frac{\Delta h^{\circ}_{\text{cell}}(M^{z+}_{\text{aq}})}{zF} = \frac{\Delta h^{\circ}_{\text{at}} + \Delta h^{\circ}_{\text{ion}} + \Delta h^{\circ}_{\text{hydr}}}{zF} - 4.61421$$

From the given quantities<sup>2,4</sup> and calculating the entropy change from the isothermal temperature coefficients  $dE^{\circ}/dT_{\text{is}}$ <sup>5</sup>, when known, or estimating it in the Latimer approximation<sup>3</sup> we obtain the results of Table 1, where calculated values of  $E^{\circ}$  are very near to experimental ones.

The atomisation enthalpy change is related to the melting temperature of the element; ionisation and hydration enthalpy changes have high absolute values with opposite signs, increasing with the ion valence; their difference is of the same order of the atomisation term.

Electrochemical behaviour of elements in aqueous solutions can be related to the relative value of the different enthalpy changes, and in particular to the ratio of the enthalpy change for hydration of the gaseous atom  $\Delta h^{\circ}_{\text{ion}} + \Delta h^{\circ}_{\text{hydr}}$  to the whole enthalpy change  $\Delta h^{\circ}_{\text{at}} + \Delta h^{\circ}_{\text{ion}} + \Delta h^{\circ}_{\text{hydr}}$ , corrected by multiplication with a term  $\Delta h^{\circ}_{\text{ion}}/\Delta h^{\circ}_{\text{ion,H}}$ , which takes into account the importance of the ionic charge of the reducing species

**TABLE 1 - Lattice and ionic enthalpies (eV) for ion exchanges at electrodes with cell properties and normality inertia parameter for the elements**

Electrodic Reaction	$\frac{\Delta h^{\circ}_{\text{at}}}{zF}$	$\frac{\Delta h^{\circ}_{\text{ion}}}{zF}$	$\frac{\Delta h^{\circ}_{\text{ion}} + \Delta h^{\circ}_{\text{hydr}}}{zF}$	$\frac{\Delta h^{\circ}_{\text{hydr}}}{zF}$	$\frac{\Delta h^{\circ}_{\text{cell}}}{zF}$	$\frac{T\Delta h^{\circ}_{\text{cell}}}{zF}$	$E^{\circ}$ (V)	$P_{\text{NI}}$
Ca=Ca <sup>2+</sup> +2e	0.9235	9.0568	0.8777	-8.1791	-2.8130	-0.027	-2.84	1.360
Na=Na <sup>+</sup> +e	1.1160	5.2045	1.0143	-4.1903	-2.4839	-0.229	-2.713	0.800
Mg=Mg <sup>2+</sup> +2e	0.7623	11.4018	1.4338	-9.9680	-2.4181	0.062	-2.356	1.278
Al=Al <sup>3+</sup> +3e	1.1390	17.8066	1.6407	-16.1659	-1.8345	0.159	-1.676	2.208
Ti=Ti <sup>3+</sup> +3e	1.3733	16.0882	1.8590	-14.2291	-1.3819	0.172	-1.21	2.047
Mn=Mn <sup>2+</sup> +2e	1.4546	11.5992	2.0156	-9.5836	-1.1440	-0.036	-1.18	1.462
Cr=Cr <sup>2+</sup> +2e	2.0599	11.6951	1.6630	-10.0321	-0.8913	0.0104	-0.9017	1.916
Zn=Zn <sup>2+</sup> +2e	0.6775	13.5408	3.1447	-10.3961	-0.7920	0.029	-0.763	1.205
Cr=Cr <sup>3+</sup> +3e	1.3733	18.1393	2.3738	-15.7655	-0.8671	0.124	-0.743	2.096
Ga=Ga <sup>3+</sup> +3e	0.9570	19.1325	2.9248	-16.2077	-0.7324	0.203	-0.529	1.859
Fe=Fe <sup>2+</sup> +2e	2.1573	12.1050	1.9775	-10.1275	-0.4793	0.009	-0.47	1.853
Cd=Cd <sup>2+</sup> +2e	0.5804	13.0129	3.6405	-9.3724	-0.3933	-0.009	-0.403	1.104
In=In <sup>3+</sup> +3e	0.8405	17.6262	3.4109	-14.2153	-0.3628	0.025	-0.338	1.608
Tl=Tl <sup>+</sup> +e	1.8884	6.1723	2.7814	-3.3909	0.0556	-0.392	-0.336	0.759
Co=Co <sup>2+</sup> +2e	2.2180	12.5222	2.0547	-10.4674	-0.3415	0.065	-0.277	1.906
Ni=Ni <sup>2+</sup> +2e	2.2031	12.9909	2.0794	-10.9115	-0.3317	0.075	-0.257	1.958
Sn=Sn <sup>2+</sup> +2e	1.5598	11.0463	3.0440	-8.0023	-0.0104	-0.127	-0.137	1.223
Pb=Pb <sup>2+</sup> +2e	1.0048	11.2867	3.6178	-7.6689	0.0084	-0.133	-0.125	1.056
H <sub>2</sub> =2H <sup>+</sup> +2e	2.2591	13.6626	2.3551	-11.3075	0.0000	0.000	0.0000	1.959
Sb=Sb <sup>3+</sup> +3e	0.9062	16.8848	3.818	-13.067*	0.11	0.04	0.15	1.529
Ge=Ge <sup>2+</sup> +2e	1.7007	12.1000	3.2305	-8.869*	0.317	-0.07	0.247	1.197
As=As <sup>3+</sup> +3e	1.0451	18.9999	3.749	-15.251*	0.18	0.06	0.24	1.778
Bi=Bi <sup>3+</sup> +3e	0.7155	16.5781	4.1772	-12.4008	0.2785	0.039	0.317	1.421
Cu=Cu <sup>2+</sup> +2e	1.7516	14.0929	3.2035	-10.8893	0.3409	-0.001	0.340	1.595
Ru=Ru <sup>3+</sup> +3e	2.2204	17.5685	2.799	-14.770*	0.405	0.05	0.455	2.342
Cu=Cu <sup>+</sup> +e	3.5031	7.8012	1.8583	-5.9429	0.7473	-0.226	0.521	1.647
Ru=Ru <sup>2+</sup> +2e	3.3306	12.0811	1.832	-10.250*	0.548	0.01	0.558	2.493
Rh=Rh <sup>3+</sup> +3e	1.9240	18.9497	3.408	-15.541*	0.718	0.04	0.758	2.170
2Hg=Hg <sup>++</sup> +2e	0.6355	10.5012	4.8432	-5.6581	0.8645	-0.0685	0.7960	0.869
Ag=Ag <sup>+</sup> +e	2.9506	7.6176	2.7584	-4.8592	1.0948	-0.295	0.799	1.154
Hg=Hg <sup>2+</sup> +2e	0.3178	14.6609	5.1783	-9.4826	0.8818	-0.028	0.8535	1.139
Pd=Pd <sup>2+</sup> +2e	1.9599	13.9462	3.4265	-10.5197	0.7721	0.142	0.915	1.605
Pt=Pt <sup>2+</sup> +2e	2.9295	13.6488	2.823	-10.826*	1.138	0.05	1.188	2.036
Au=Au <sup>3+</sup> +3e	1.2644	19.9813	4.720	-15.262*	1.37	0.15	1.52	1.854
Au=Au <sup>+</sup> +e	3.7933	9.2906	2.881	-6.410*	2.06	-0.23	1.83	1.575

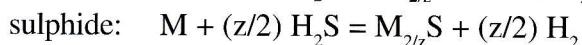
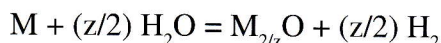
\*Estimated hydration enthalpy

present at the electrode; the normality-inertia parameter results:

$$P_{NI} = \frac{\Delta h_{cell}^{\circ}}{\Delta h_{ion}^{\circ} + \Delta h_{hydr}^{\circ}} \cdot \frac{\Delta h_{ion}^{\circ}}{\Delta h_{ion,H}^{\circ}}$$

a parameter of electrochemical electronegativity, describing the electrokinetic behaviour of metals in aqueous solutions also with respect to metal ion or hydrogen discharge at a cathodic surface<sup>6,7</sup>. A high value of  $P_{NI}$  corresponds to inertia with high overvoltages for metal ion exchanges and low overvoltages for hydrogen exchange at the electrodic surface; the reverse occurs for low  $P_{NI}$  values.

A similar reasoning path is proposed for the reactions of oxide formation in aqueous solutions:



The cell enthalpies become for oxides:

$$\Delta h_{cell}^{\circ}(M_{2/z}O) / (zF) + 1.4812 = (\Delta h_{at}^{\circ} + \Delta h_{ion}^{\circ} + \Delta h_{O}^{\circ}) / (zF) - 4.61421$$

sulphides:

$$\Delta h_{cell}^{\circ}(M_{2/z}S) / (zF) + 0.20572 = (\Delta h_{at}^{\circ} + \Delta h_{ion}^{\circ} + \Delta h_{S}^{\circ}) / (zF) - 4.61421$$

fluorides:

$$\Delta h_{cell}^{\circ}(M_{1/z}F) / (zF) + 3.4475 = (\Delta h_{at}^{\circ} + \Delta h_{ion}^{\circ} + \Delta h_{F}^{\circ}) / (zF) - 4.61421$$

chlorides:

$$\Delta h_{cell}^{\circ}(M_{1/z}Cl) / (zF) + 1.7293 = (\Delta h_{at}^{\circ} + \Delta h_{ion}^{\circ} + \Delta h_{Cl}^{\circ}) / (zF) - 4.61421$$

where  $\Delta h_{cell}^{\circ}$  is the enthalpy change for the formation of oxides, sulphides, fluorides or chlorides from the elements, while  $\Delta h_{O}^{\circ}/(zF)$ ,  $\Delta h_{S}^{\circ}/(zF)$ ,  $\Delta h_{F}^{\circ}/(zF)$  and  $\Delta h_{Cl}^{\circ}/(zF)$  are the enthalpy contributions for oxide, sulphide, fluoride and chloride formation from the ionized gas species in Volts for unit charge.

The values for the elements of major concern related to the electrokinetic behaviour of magnesium alloys are reported in Table 2 and 3.

**Table 2 - Enthalpy and entropy contributions for the formation of oxides and sulphides of elements in aqueous solutions**

Electrodic Reaction	$\Delta h_{O}^{\circ} / zF$	$\Delta h_{cell,0}^{\circ} / zF$	$T\Delta s_{cell,0}^{\circ} / zF$	$E_{O}^{\circ} (V)$	$\Delta h_{S}^{\circ} / zF$	$-\Delta h_{cell,S}^{\circ} / zF$	$T\Delta s_{cell,S}^{\circ} / zF$	$E_{S}^{\circ} (V)$
H <sub>2</sub> /H <sub>2</sub> O, H <sub>2</sub> S	-9.8263	1.4812	-0.252	1.2291	-11.513	0.2057	-0.0615	0.1442
Ca/CaO, CaS	-7.1760	-1.8099	-0.091	-1.9011	-7.6602	-2.2941	-0.035	-2.3295
Mg/MgO, MgS	-9.1660	-1.6161	-0.086	-1.7024	-9.1361	-1.5863	-0.040	-1.6263
Al/Al <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> S <sub>3</sub>	-15.706	-1.3742	-0.045	-1.4190	-15.376	-1.0045		
Ti/Ti <sub>2</sub> O <sub>3</sub> , Ti <sub>2</sub> S <sub>3</sub>	-14.018	-1.1712	-0.074	-1.2449				
Mn/MnO, MnS	-8.9546	-0.5151	-0.136	-0.6515	-9.3439	-0.9043	-0.083	-0.9874
Zn/ZnO, ZnS	-9.9277	-0.3236	-0.097	-0.4205	-10.357	-0.7530	-0.041	-0.7935
Cr/Cr <sub>2</sub> O <sub>3</sub> , Cr <sub>2</sub> S <sub>3</sub>	-15.386	-0.4875	-0.111	-0.5987	-15.321	-0.4231		
Fe/FeO, FeS	-9.5764	0.0717	-0.138	-0.0664	-9.9367	-0.2886	-0.074	-0.3625
Co/CoO, CoS	-9.7398	0.3862	-0.115	0.2712	-10.429	-0.303*		
Ni/NiO, NiS	-10.363	0.2168	-0.107	0.1097	-10.777	-0.1974	-0.249	-0.4463
Sn/SnO, SnS	-7.9928	-0.0009	-0.1018	-0.1027	-8.2526	-0.2607	-0.156	-0.4163
Cu/CuO, CuS	-10.587	0.6433	-0.109	0.5347	-11.298	-0.0679	-0.063	-0.1313
Cu/Cu <sub>2</sub> O, Cu <sub>2</sub> S	-6.0950	0.5951	-0.133	0.4616	-6.9057	-0.2156	-0.094	-0.3095
Ag/Ag <sub>2</sub> O, Ag <sub>2</sub> S	-4.6337	1.3203	-0.149	1.1709	-5.9172	0.0367	-0.103	-0.0664

**Table 3 - Enthalpy and entropy contributions for the formation of fluorides and chlorides of elements in aqueous solutions**

Electrode Reaction	$\Delta h^{\circ}_F / zF$	$\Delta h^{\circ}_{cell,F} / zF$	$T\Delta s^{\circ}_{cell,F} / zF$	$E^{\circ}_0$ (V)	$\Delta h^{\circ}_{Cl} / zF$	$-\Delta h^{\circ}_{cell,Cl} / zF$	$T\Delta s^{\circ}_{cell,Cl} / zF$	$E^{\circ}_{Cl}$ (V)
H <sub>2</sub> /HF <sub>aq</sub> ,HCl <sub>aq</sub>	-7.8600	3.4475	-0.3708	3.0766	-9.5782	1.7293	-0.3710	1.3583
Ca/CaF <sub>2</sub> ,CaCl <sub>2</sub>	-8.1922	-2.8729	-0.0998	-2.9727	-7.7608	-2.3947	-0.1238	-2.5185
Mg/MgF <sub>2</sub> ,MgCl <sub>2</sub>	-9.9283	-2.3783	-0.0884	-2.4667	-9.1439	-1.5940	-0.1129	-1.7069
Al/AlF <sub>3</sub> ,AlCl <sub>3</sub>	-16.102	-1.7706	-0.0966	-1.8672	-15.040	-0.7084	-0.1057	-0.8141
Ti/TiF <sub>3</sub> ,TiCl <sub>3</sub>	-13.953	-1.1059	-0.0223	-1.1282	-13.534	-0.6866	-0.0943	-0.7809
Mn/MnF <sub>2</sub> ,MnCl <sub>2</sub>	-9.1015	-0.6619	-0.1532	-0.8152	-9.2044	-0.7648	-0.1596	-0.9244
Zn/ZnF <sub>2</sub> ,ZnCl <sub>2</sub>	-10.118	-0.5137	-0.1066	-0.6204	-10.026	-0.4218	-0.1343	-0.5561
Cr/CrF <sub>3</sub> ,CrCl <sub>3</sub>	-15.455	-0.5566	-0.1256	-0.6822	-15.092	-0.1933	-0.1281	-0.3214
Fe/FeF <sub>2</sub> ,FeCl <sub>2</sub>	-9.8583	-0.2101	-0.1520	-0.3621	-9.6928	-0.0446	-0.1696	-0.2141
Co/CoF <sub>2</sub> ,CoCl <sub>2</sub>	-10.083	0.0434	-0.1422	-0.0987	-10.0401	0.0858	-0.1477	-0.0619
Ni/NiF <sub>2</sub> ,NiCl <sub>2</sub>	-10.590	-0.01055	-0.1393	-0.1498	-10.488	0.09174	-0.1430	-0.05125
Sn/SnF <sub>2</sub> ,SnCl <sub>2</sub>					-7.9293	-0.08342	-0.1238	-0.2072
Cu/CuF <sub>2</sub> ,CuCl <sub>2</sub>	-10.6096	0.6206	-0.1170	0.50366	-10.6322	0.59804	-0.1409	0.4571
Cu/CuF,CuCl					-6.3808	0.3094	-0.1927	0.1167
Ag/AgF,AgCl	-4.6281	1.3259	-0.1976	1.1283	-5.5423	0.4117	-0.1920	0.2197

Also in these cases it is possible to obtain relative Normality-Inertia Parameters, which are reported in table 4, with com-

parison to other electronegativity parameters and to exchange current densities for hydrogen discharge at metal electrodes.

**Table 4 - Comparison of different P<sub>NI</sub> values for reactions occurring in aqueous solutions with other parameters of electronegativity and cohesion and with i<sup>o</sup><sub>H</sub>**

Electrode Reaction	P <sub>NI,ion</sub>	P <sub>NI,O</sub>	P <sub>NI,S</sub>	P <sub>NI,F</sub>	P <sub>NI,Cl</sub>	EN <sub>PA</sub>	Cohesion Energy	Ion <sub>Mie</sub>	DE <sub>Mie</sub>	Log i <sup>o</sup> <sub>H</sub> mA/cm <sup>2</sup>
H <sub>2</sub> /H(I)	1.959	1.589	1.854	1.389	1.553	2.20	-	5.2	1.50	-
Ca/Ca(II)	1.360	0.988	1.101	1.371	1.135	1.00	1.84	2.55	0.91	-
Mg/Mg(II)	1.278	1.119	1.115	1.266	1.116	1.31	1.51	3.45	1.17	-
Al/Al(III)	2.208	2.010	1.914	2.174	1.840	1.61	3.39	4.20	1.39	-5
Ti/Ti(III)	2.047	1.959	-	1.935	1.811	1.54	4.85	3.80	1.52	-5.3
Mn/Mn(II)	1.462	1.316	1.397	1.343	1.365	1.55	2.92	4.45	1.61	(-7.9)
Zn/Zn(II)	1.205	1.177	1.202	1.187	1.182	1.65	1.35	4.10	1.32	-7.5
Cr/Cr(III)	2.096	1.990	1.975	2.007	1.926	1.66	4.10	4.65	1.73	-3.4
Fe/Fe(II)	1.853	1.642	1.767	1.737	1.678	1.83	4.28	4.93	1.77	-2.6
Co/Co(II)	1.906	1.647	1.888	1.750	1.736	1.88	4.39	5.10	1.75	-2.3
Ni/Ni(II)	1.958	1.748	1.897	1.823	1.788	1.91	4.44	5.20	1.75	-2.25
Sn/Sn(II)	1.223	1.222	1.260		1.244	1.96	3.14	4.15	1.24	-7.0
Cu/Cu(II)	1.595	1.547	1.678	1.550	1.554		3.49	4.45	1.47	-4.8
Cu/Cu(I)	1.647	1.743	2.805		1.979	1.90	3.49	4.45	1.47	-4.8
Ag/Ag(I)	1.154	1.109	1.525	1.108	1.350	1.93	2.95	4.35	1.36	-8.0

Some features from these tables deserve further comments:

1. Magnesium shows an intermediate or quasi-normal electrokinetic behaviour, greatly different from the behaviour of the easily oxidised light metals Aluminium and Titanium
2. Magnesium ionisation and fluoride formation have higher P<sub>NI</sub> than those for oxide, sulphide or chloride formation,

3. A similar behaviour is shown for Aluminium, although much higher values are shown in this case, also in relation to strong inert character of Aluminium surfaces
4. Titanium does not show the same behaviour, correspondingly Titanium Fluorides are easily dissolved.

## CORROSION AND PROTECTION OF MAGNESIUM ALLOYS

The very important role of metal traces, present in Mg alloys, favouring local corrosion, especially in chlorides containing solutions, can be related to their possibility of starting the hydrogen evolution reactions, catalysed by the most dangerous impurities, consisting of inert or intermediate metals, such as Ni, Co, Fe and Cu in the order of decreasing influence. This sequence is the same of these metals  $P_{Ni}$  values.

Metals without deleterious effect on corrosion resistance are: Al, Mn, Na, Si, Sn and Pb; Na, Sn and Pb are normal metals, Mn is quasi-normal, Si and Al have  $P_{Ni}$  values higher than the value for H.

This behaviour is not so crucial for the other light metals, Aluminium and Titanium, because these metals have low  $P_{Ni}$  values, and their interaction and ionisation in water solutions is not so strongly influenced by the presence of inert, or also intermediate, metal impurities.  $P_{Ni}$  value of Magnesium is lower than that of Ni, Co, Fe and even Cu; this is not the case for Aluminium and Titanium.

Magnesium is mainly alloyed with the following metals:

- Aluminium, with a threshold value of 4% for corrosion resistance and a further increase at Al>10%
- Zinc, normally added with Aluminium in small amounts,
- Rare earths

Zinc and rare earths reduce the level of hydration in the oxide, this can be related to their normal or quasi normal behaviour and their  $P_{Ni}$  value lower than that of Magnesium.

The electrokinetic parameters for reactions, such as metal ion exchanges or hydrogen exchanges at the metal electrodic surface, show an anticorrelation easily interpreted according to the reported  $P_{Ni}$  values. The behaviour of the other oxidation reactions, with  $H_2O$ ,  $H_2S$  or halogen acids, can be compared in the same approach with the relative  $P_{Ni}$  reported values, obtaining a general interpretative scheme.

Protection of magnesium with metallic coatings or with paints must take into account the active behaviour of magnesium, if we want to protect it with adherent coatings.

Pretreatment of the magnesium alloy in an etching solution containing fluorides is suggested, because of the possibility to stabilise the surface with fluorides, and this can be related to the reported  $P_{Ni}$  values for Mg fluoride formation.

A typical sequence to obtain adherent coatings (fig.1) on Magnesium and Mg-Al alloys, with solution without chromates, is (with rinsing between the steps):

- degreasing  $Na_3PO_4$  0.1M  $Na_2CO_3$  0.1M; pH 12 90°C 5-10 min
- etching  $Na_4P_2O_7$  0.3M KF 0.15M; pH 12 80°C 5-10 min
- activation  $Na_4P_2O_7$  0.2M  $Na_2B_4O_7$  0.4M KF 0.5M; pH 10 75°C 5 min
- zincating  $ZnSO_4$  0.2M  $Na_4P_2O_7$  0.5M KF 0.15M; pH 10.5 with  $Na_2CO_3$  85°C 3 min

- ACD Ni-P plating with fluorides and  $Mg^{2+}$
- ACD Ni-P plating without fluorides

An alternative, after degreasing, etching and activation, could be ECD Cu plating (fig.2) in a cyanide bath or final ECD Sn plating, to avoid Ni that renders recycling of Mg alloys very difficult.

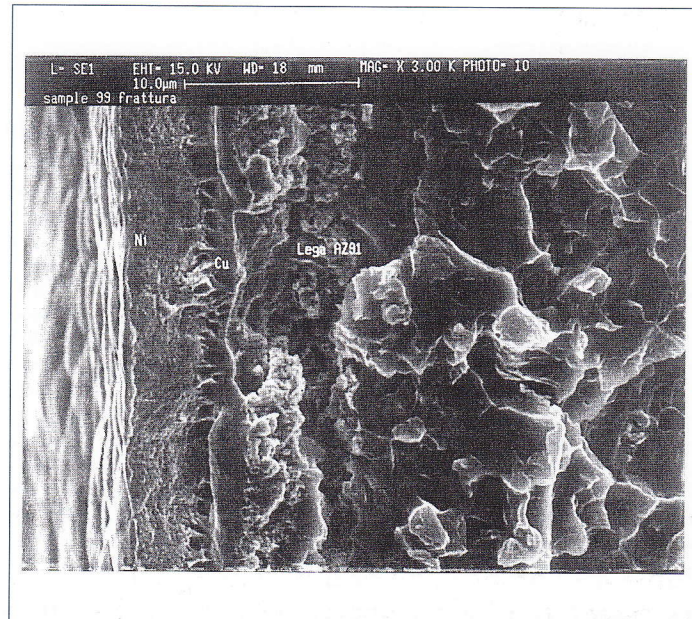


Fig. 1: Magnesium alloy AZ91 coated with two Ni-PACD baths

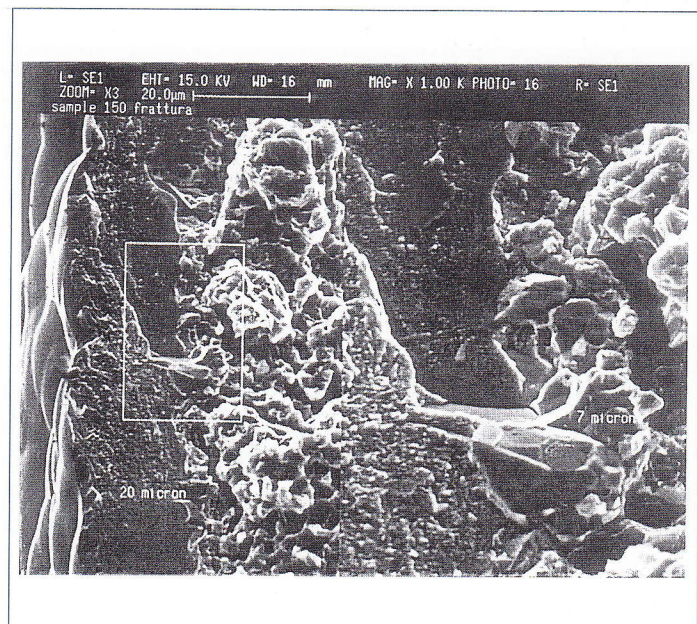


Fig. 2: Magnesium alloy AZ91 coated with Cu from cyanide bath and bright Ni ECD

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