

# **Mg Magnesium Technology 2013**

## **Corrosion I**

# EFFICIENCY OF A NEW HEXAVALENT CHROMIUM-FREE CHEMICAL PICKLING PROCESS BASED ON ORGANIC AND INORGANIC ACIDS ON MAGNESIUM ALLOYS Mg-Y-RE-Zr and Mg-Zn-RE-Zr

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## Abstract

The removal of surface contaminants as result of corrosion attack, inadequate or incorrectly applied surface protection coating (HAE, DOW 19) on Mg-Y-RE-Zr and Mg-Zn-RE-Zr alloys was investigated by a new chemical pickling process based on organic and inorganic acids with addition of anticorrosion compounds and wetting agents. Various combinations of acetic, citric, oxalic, tartaric acids with nitric, sulphuric, phosphoric and hydrofluoric acids were investigated. The influence of the composition, pH and time of pickling, on the surface morphology, roughness, composition (of contaminant film and of alloy surface) were evaluated using Bruker Dektak 150 profilometer, Scanning electron microscopy and X-Ray Photoelectron Spectroscopy.

The experimental results show that the best pickling efficiency was obtained with a combination of tartaric acid, nitric acid and a zirconium fluoride for removal of ~ 20 µm of the contaminated surface. After completely removal of the incorrectly coatings, the alloy surfaces obtained were remarkably cleaned with a low roughness (between 3 and 4 µm) and without any attack at the grain boundaries and surface, and without any surface contaminant. An anti-corrosive effect was obtained by the formation of a protective layer on the surface of the alloy during the pickling. This new tartaric + nitric acids based pickling is an interesting alternative to the environmentally undesirable Cr<sup>6+</sup>- surface pickling.

## Introduction

Magnesium alloys have an interesting future wherever weight saving is essential, including automotive, aerospace and communication fields. However, Mg alloys exhibit low corrosion and wear resistances, which limit their widespread use. Corrosion can be avoided or minimized by the formation of protective layers on the surface. The surface of Mg alloys is supposed to be cleaned prior to surface protection treatments in order to enhance the corrosion resistance and surface appearance. Mechanical and chemical cleaning methods are used depending on the application involved. Mechanical cleaning include grinding and rough polishing, dry and wet abrasive blast cleaning, wet brushing and wet (bowl/ barrel) abrading. Chemical cleaning is achieved by solvent degreasing, alkaline cleaning and acid cleaning. In our study we focus on acid chemical cleaning/ pickling process to remove the incorrectly protective coating (HAE, DOS 19). Nowadays, most of the surface material removal treatments are done with hexavalent chromium compounds. All compounds containing hexavalent chromium radicals are classified as

carcinogenic substances under the current REACH regulation [1] and will be restricted. The search for their substitution is mandatory and prevails against any other risk reduction measures. In this work, we focused upon this major challenge of designing a new hexavalent chromium-free coating removal process based on organic and inorganic acids for magnesium alloys Mg-Y-RE-Zr (WE43) and Mg-Zn-RE-Zr (RZ5). The classically used chemical pickling/ removing process is achieved with chromic acid 180 - 220 g/L at room temperature [2]. Acid pickling is a useful method for the removal of bad or incorrectly applied surface protective layers (obtained by DOW 19 chemical conversion or by HAE anodization), contaminations such as oxide tarnish, heavy metal impurities, embedded sand and burned-in lubricants. Taking into account the chemical composition of the surface layers which are supposed to be removed, we have studied the effects of aqueous solutions of different mineral and organic pure acids: i) separately or ii) in combination, and iii) with addition of anti-corrosion components, wetting agents, on the material removal (etching rate), corrosive attack (surface roughness, appearance, morphology, phases) of Mg alloys. The choice of acids was made according to their potential in pickling by forming soluble salts with the main components of the layers to be removed in agreement with published solubility data [3]. So, we have selected: HNO<sub>3</sub> (nitric acid), H<sub>3</sub>PO<sub>4</sub> (phosphoric acid), H<sub>2</sub>SO<sub>4</sub> (sulphuric acid), HF (hydrofluoric acid) as inorganic acids and C<sub>4</sub>H<sub>6</sub>O<sub>6</sub> (tartaric acid), CH<sub>3</sub>COOH (acetic acid), C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O (oxalic acid), C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> (citric acid) as organic acids. The removal of the bad and heterogeneous coatings with thickness varying between 1 and 24 µm must be done without any attack of the surface alloys. Thus, we have selected inorganic inhibitors such as: ZrO(NO<sub>3</sub>)<sub>3</sub> for the protection against acid attack of the pickled areas during the pickling of the area having higher thickness of the coating. This protective effect is similar to that furnished by the Cr<sub>2</sub>O<sub>3</sub> film formed on the alloy surface during the pickling with chromic acid. The results obtained are reported in this paper.

## Experimental

### Sample preparation

The WE43 and RZ5 magnesium alloys used in this study were commercial alloys with the chemical composition given in Table 1. Some specimens were treated by HAE anodizing (thickness between ~ 5 and 24 µm) or by DOW 19 chemical conversion (thickness between ~ 1 and 5 µm). The HAE coating produced is a mixed MgO-Mg(OH)<sub>2</sub> system with additional compounds. The DOW 19

chemical conversion coating produced contains mainly MgO, Mg(OH)<sub>2</sub> with small amount of Cr<sub>2</sub>O<sub>3</sub>. The specimens were cut into sets of samples of dimensions ~ 50 mm x 50 mm x 3mm using a shear.

**Table 1.**

Chemical composition (wt. %) of the WE43 magnesium alloy.

Alloy	Fe	Zn	Y	RE(Nd)	RE(Ce)	RE(La)	Zr	Mn	Mg
WE43	-	<0.2	4.0	3.0	-	-	0.5	0.15	Bal
RZ5	-	4.4	-	-	0.8	0.3	0.4-1.0	-	Bal

The choice of the composition of the chemical pickling bath is important. We have tested (at medium and higher concentrations, room temperature and pH values between 0.7 and 2.4):

- a set of inorganic acids: HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HF,
- a set of organic acids C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>, CH<sub>3</sub>COOH, C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>,
- additives for the pH correction (NH<sub>4</sub>OH, KOH),
- moderators/ surfactants/ dispersers such as: NH<sub>4</sub>F, HMTA, Dodecylsulphate sodium salt (C<sub>12</sub>H<sub>25</sub>NaO<sub>4</sub>S),
- inorganic inhibitors such as: ZrO(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>.

The coating material removal process was performed by dipping the specimens in the pickling bath. After completely coating removal, the specimens were rinsed in deionized water and then dried in a stream air.

After pickling the specimens were submitted to inhibitive removal pickling rate evaluation and to surface characterization by Profilometry, Scanning electron microscopy and X-Ray Photoelectron Spectroscopy.

A Bruker Dektak 150 profilometer was used to evaluate the surface roughness (RA- parameter) and thickness of the material removed (d – parameter).

Cross-sectional morphology and chemical composition of the WE43 and RZ5 alloys coated (with HAE or DOW 19) and pickled were characterized by SEM analyses using a Hitachi S2500 apparatus operating at 20 keV, coupled with EDS analyses using an EDS-PGT IMIX system.

Chemical composition characterization by X-ray Photoelectron Spectroscopy (XPS), was done with Thermo Electron Escalab 250 spectrometer, using an Al K $\alpha$  X-ray source. The XPS spectra recorded are: Mg 1s, Zr 3d, Cr 3p, Nb 3d, Y 3d, Nd 3d, O 1s, C 1s, F 1s. The reference binding energies are obtained from analyzed reference samples or from published data [4-7].

The inhibitive removal pickling rate - R<sub>ip</sub> was performed by weighing the specimens before and after dipping in the pickling bath using an analytical balance. The weight loss gave the inhibitive removal pickling rate as calculated following Eq. (1).

$$R_{ip} = P \times 10^4 / \rho \times S \times T \quad (1)$$

with R<sub>ip</sub> - the inhibitive removal pickling rate in  $\mu\text{m}/\text{min}$ . P is weight loss in g,  $\rho$  is the coating density in  $\text{g}/\text{cm}^3$  (3), S is the pickled surface in  $\text{cm}^2$ , T is the dipping time in min,  $10^4$  is a unit conversion factor.

## Results

The etching effectiveness of the coating material removal depends on the solubility conditions in aqueous solutions of the reaction products formed between the different inorganic acids and the compounds present in the HAE/ DOW 19 coatings and the addition elements and the impurities present in the coating/ Mg alloy interface. Nitric acid forms soluble nitrates (Mg(NO<sub>3</sub>)<sub>2</sub>, Y(NO<sub>3</sub>)<sub>3</sub>, Nd(NO<sub>3</sub>)<sub>3</sub>, Zr(NO<sub>3</sub>)<sub>4</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>) [3] and hence it has the capability to remove coating/ material. Sulphuric acid forms soluble reaction products [3]. Phosphoric and hydrofluoric acids form insoluble or slightly soluble phosphates and fluorides, respectively [3].

The organic acids tested for this study include: tartaric acid, acetic acid, oxalic acid, citric acid. The tartaric acid forms soluble salts with the compounds present in the surface HAE/ DOW 19 coatings and the addition elements and the impurities present in the substrate. The acetic acid gives rise to soluble salts [3] but the roughness was increased. The pickling in tartaric and acetic acids gives rise to a greyish metallic appearance. Oxalic acid forms insoluble or slightly soluble salts [3] with the HAE/ DOW 19 coating compounds and with Mg, Nd, Zn and Ce elements present in the alloys. A brownish spotted surface appearance was observed on the surface of the pickled alloys. The citric acid forms soluble salts but whitish and dusty deposition precipitates were observed on the pickled surfaces.

The final optimal selected pickling solution was chosen after preliminary tests looking at the surface appearance that is related to the amount of the surface material pickled and the surface roughness. After the completely removal of the coating by pickling in nitric acid, the surface of the alloys has the shiniest metallic appearance. In sulphuric acid the surface had a metallic appearance but the roughness was non uniform. In phosphoric and hydrofluoric acids dark greyish surface films were observed.

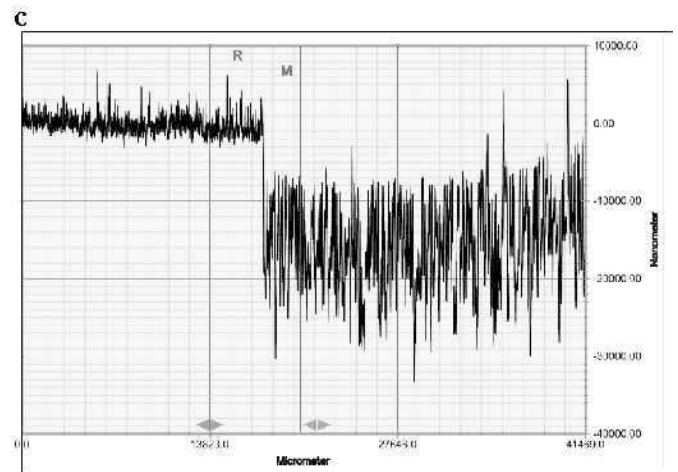
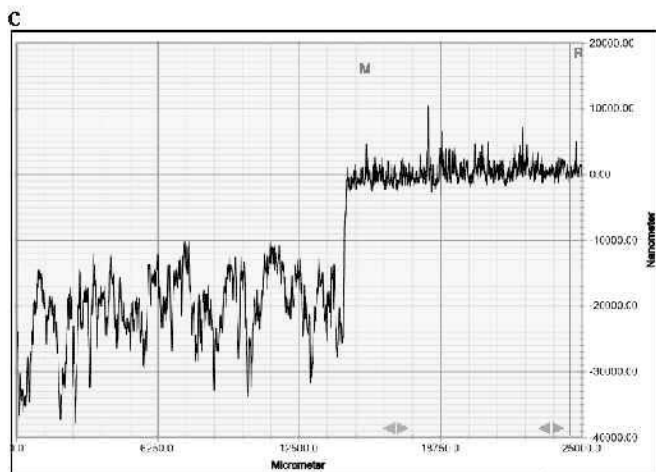
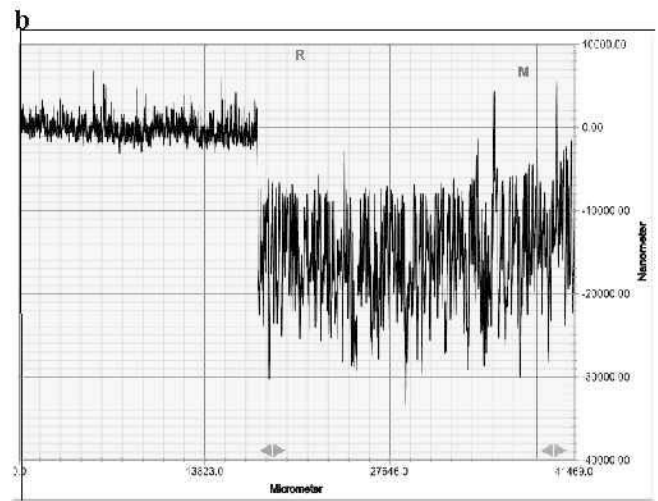
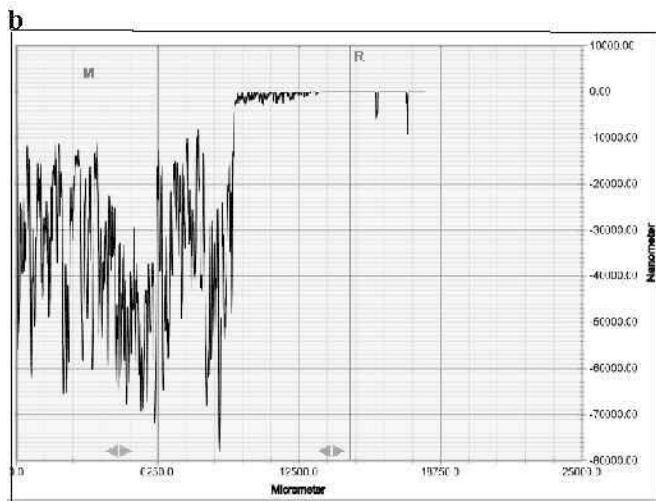
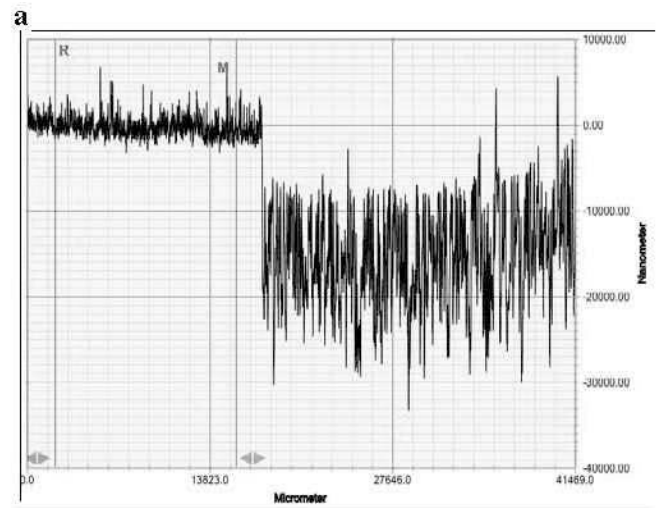
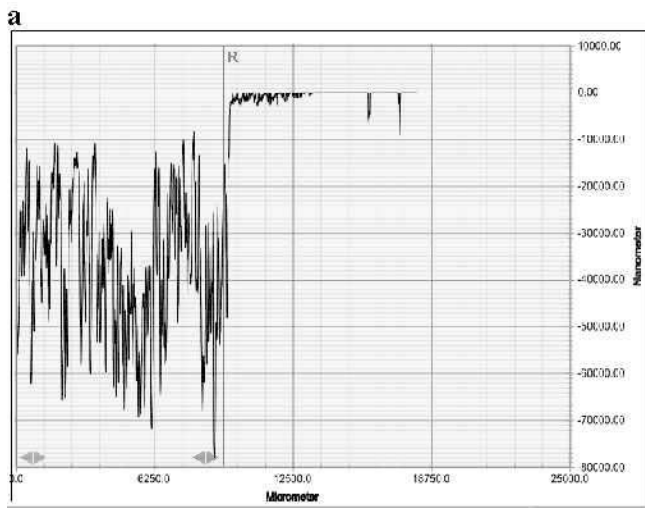
After the completely removal of the coating in tartaric acid, the surface of the alloys has the shiniest metallic appearance.

The mainly compounds of the optimal bath are: tartaric acid, nitric acid and hexamethylene tetramine.

effect on the surface roughness as can be seen in Fig. 1 – 4. It was observed that the roughness increases slightly from  $\approx 1.0 \mu\text{m}$  to  $\approx 4.0 \mu\text{m}$  with  $\sim 20 \mu\text{m}$  of HAE material removal in the optimal bath. Moreover, SEM and EDS analyses carried out after HAE material removal (Fig. 5 and 6) show the absence of any intergranular attack on the pickled alloy surface. After HAE coating removal, we observe the presence in the surface of a thin film mainly containing ZrOx (Fig. 6). So, the absence of any attack on the pickled surface area can be attributed to the protective effect of ZrO(NO<sub>3</sub>)<sub>3</sub> (added). The amount of the material removed varies with the pickling composition bath. The inhibitive removal pickling rates evaluated for the optimal bath with Eq. 1.

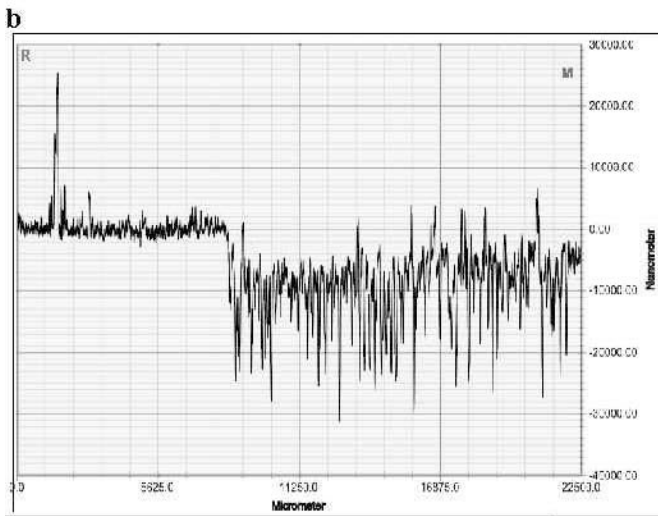
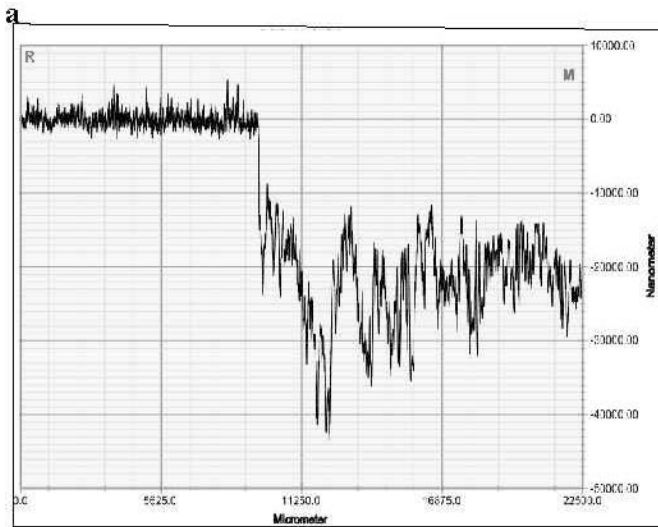
### Surface appearance and roughness after inhibitive removal pickling in optimal bath

The surface appearance is related to the amount of the surface material removed and to the surface roughness. The pickling has an



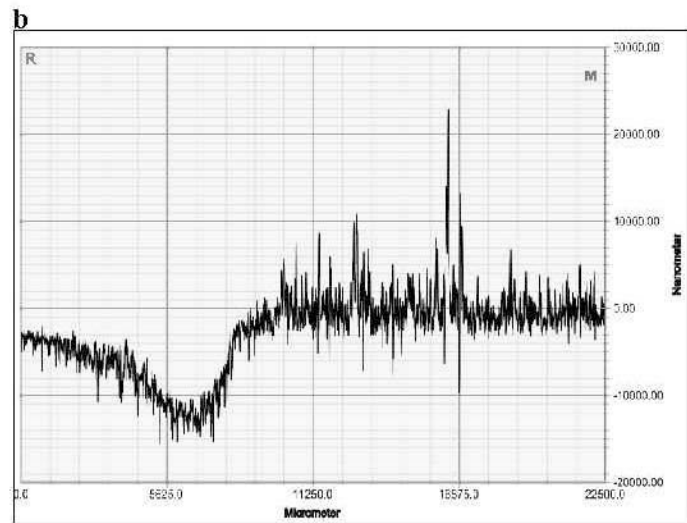
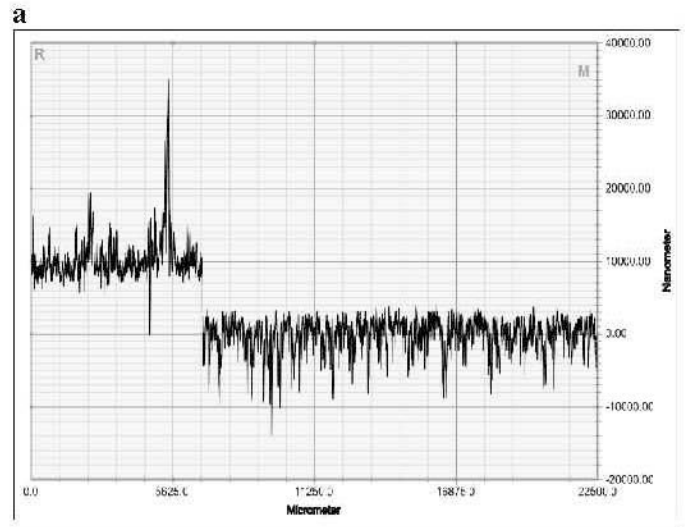
**Fig. 1.** Variation of the surface roughness with HAE coating removal (in OB-optimal pickling bath,) on the WE43 alloy - HAE coated; a) roughness on HAE coating:  $RA \approx 1.0 \mu\text{m}$ . b) roughness on the WE43 alloy after removal of HAE coating:  $RA \approx 4,2 \mu\text{m}$ . c) thickness of the coating removed:  $d \approx 23.0 \mu\text{m}$ .

**Fig. 2.** Variation of the surface roughness with HAE coating removal (OB- optimal pickling bath) on the RZ5 alloy - HAE coated; a) roughness on HAE coating:  $RA \approx 1.0 \mu\text{m}$ . b) roughness on the RZ5 alloy after removal of HAE coating:  $RA \approx 3.2 \mu\text{m}$ . c) thickness of the HAE coating removed:  $d \approx 5.0 \mu\text{m}$ .



**Fig. 3.** Comparison of the variation of the surface roughness with HAE coating removal (in OB optimal pickling bath). a) on the WE43 alloy - HAE coated; roughness on HAE coating:  $RA \approx 1.0 \mu\text{m}$ , roughness on the WE43 alloy after removal of HAE coating:  $RA \approx 4.4 \mu\text{m}$ , thickness of the HAE coating removed  $d \approx 16.5 \mu\text{m}$ . b) on the RZ5 alloy - HAE coated; roughness on HAE coating:  $RA \approx 1.3 \mu\text{m}$ , roughness on the RZ5 alloy after removal of HAE coating:  $RA \approx 4.1 \mu\text{m}$ , thickness of the HAE coating removed:  $d \approx 9.2 \mu\text{m}$ .

effect on the surface roughness as can be seen in Fig. 1. – 4. It was observed that the roughness increases slightly from  $\approx 1.0 \mu\text{m}$  to  $\approx 4.0 \mu\text{m}$  with  $\sim 20 \mu\text{m}$  of HAE material removal in the optimal bath. Moreover, SEM and EDS analyses carried out after HAE material removal (Fig. 5 and 6) show the absence of any intergranular attack on the pickled alloy surface. After HAE coating removal, we observe the presence in the surface of a thin film mainly containing ZrOx (Fig. 6). So, the absence of any attack on the pickled surface area can be attributed to the protective effect of  $\text{ZrO}(\text{NO}_3)_3$  (added in the pickling bath), that forms a thin film of ZrOx on the pickled alloy surface.



**Fig. 4.** Variation of the surface roughness with HAE coating removal (in chromic acid bath) on the WE43 alloy - HAE coated; a) HAE / pickled WE43 interface, roughness on HAE coating:  $RA \approx 2.1 \mu\text{m}$ , roughness on the WE43 alloy after removal of HAE coating:  $RA \approx 1.7 \mu\text{m}$ , thickness of the HAE coating removed:  $d \approx 14.4 \mu\text{m}$ . b) HAE / polished WE43 interface, roughness on the WE43 alloy after mechanical polishing  $RA \approx 1.0 \mu\text{m}$ , thickness of the HAE film at HAE / mechanical polished WE43 interface,  $d = 11.4 \mu\text{m}$ .

### Composition characterization by XPS

The XPS spectra of WE43 after optimal bath (OB) pickling (Fig. 7.) show the presence of metallic Mg, of Mg, Zr and Y oxides and hydroxides, Mg and Zr fluorides and of low amount of addition element Nd oxides. We note the absence of P 2p pick at  $\approx 133 - 134 \text{ eV}$ .

## Surface morphology and elemental composition

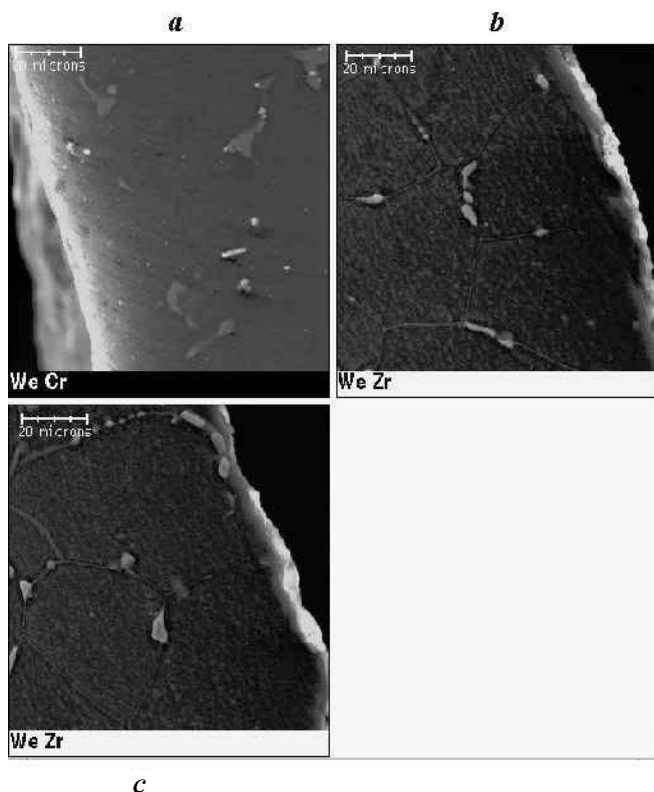


Fig. 5. SEM of WE43 alloy after HAE material removal in: a) chromic acid and b), c) optimal bath.

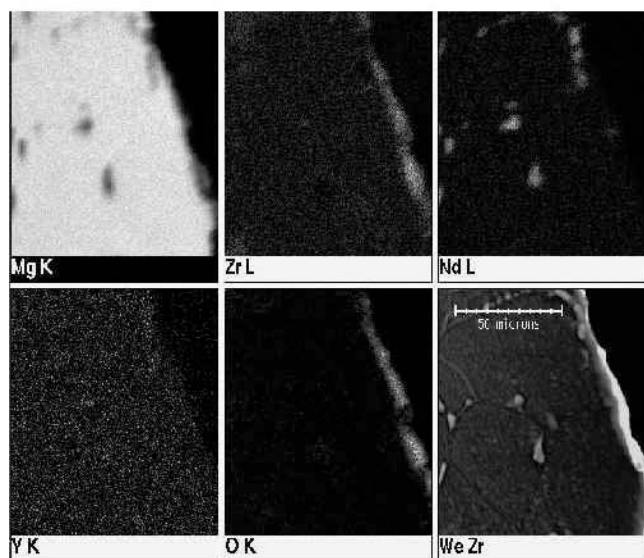


Fig. 6. Elemental composition (Mg, Zr, Nd, Y, O, SEI) by EDS analyses of WE43 alloy after HAE material removal in optimal bath.

The XPS spectra of WE43 after chromic pickling (Fig.8.) show the presence of metallic Mg, of Mg, Cr and Y oxides and hydroxides. We observed also the F 1s peak at  $\approx 687$  eV, of high intensity, attributed to the presence of  $MgF_2$ . We note the peak P 2p localised

at  $\approx 133$  eV, however, its intensity is low. This peak is attributed to the presence of **phosphates** at the surface of the pickled alloy. We observed also small amounts of Nd oxides. We conclude that the removal of the HAE coating was incomplete by chromic acid pickling, contrary to OB pickling (no phosphates at the surface). Moreover, Nd and Zr are observed after removal of HAE coating in OB bath contrary to sample pickled in chromic acid. As previously observed by SEM-EDS, OB bath pickling leads to the formation of a protective layer (containing mainly  $ZrO_xF$  compound) and to a better removal of the HAE coating with reference to the pickling in chromic acid.

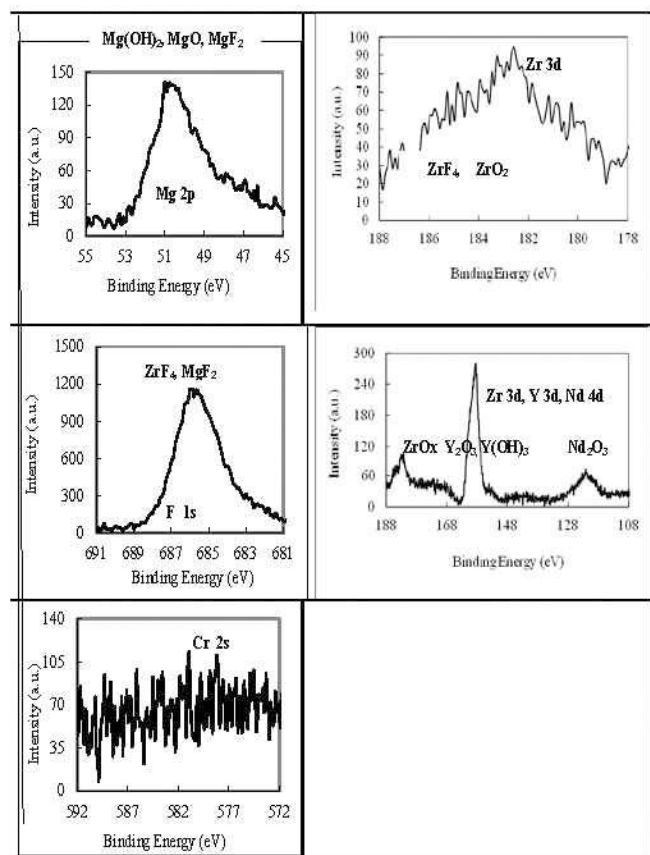


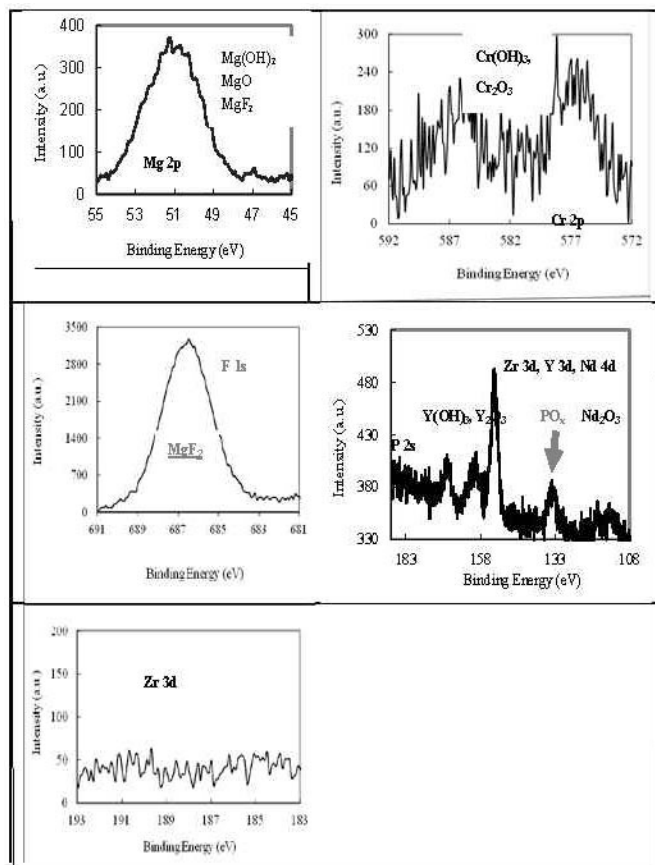
Fig. 7. XPS spectra (Mg 2p, **Zr 3d**, **F 1s**, Y 3d, Nd 4d, Cr 2s) on WE43 surface after OB pickling.

## Conclusion

A new pickling process allowing the removal of HAE and DOW 19 coatings (with the thickness between 1 and 24  $\mu m$ ) and the cleaning of magnesium alloys was designed. The process is based on the chemical dissolution of the coatings into a optimal bath based on tartaric and nitric acids, surfactants (such as sodium lauryl sulphate, moderators (HMTA,  $NH_4F$ ), and an additive (such as KOH) for the pH correction.

The addition of the inorganic inhibitors (such as  $ZrO(NO_3)_3$ ) allows to obtain a good protection against corrosion of the pickled surface area, during the removal of thicker coating area. These inhibitors favor the formation, on the pickled surface, of a thin film containing mainly  $ZrO_xF$  compound which plays a key role in the

anti-corrosion efficiency of the optimal bath. This effect is similar to



**Fig. 8.** XPS spectra (Mg 2p, Cr 2p, F 1s, Zr 3d, Y 3d, P 2p, Nd 4d) on WE43 surface after chromic acid pickling.

that of the ultra-thin film containing  $\text{Cr}_2\text{O}_3$  formed during coatings or contaminants removal in chromic acid. However, the formation and the thickness of this film could be decreased by the decreasing of the inhibitor concentration and of the pH of the pickling bath. The new green treatment provides an alternative to the pickling treatments based on chromic acid, used for Mg alloys (and other alloys).

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